Structural Characterization and Optical Properties
of Group IV Based Semiconductor Alloys
by
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ABSTRACT

This thesis focuses on structural characterizations and optical properties of Si, Ge based semiconductor alloys. Two material systems are characterized: Si-based III-V/IV alloys, which represent a possible pathway to augment the optical performance of elemental silicon as a solar cell absorber layer, and Ge-based Ge_{1-y}Sn_y and Ge_{1-x-y}Si_xSn_y systems which are applicable to long wavelength optoelectronics.

Electron microscopy is the primary tool used to study structural properties. Electron Energy Loss spectroscopy (EELS), Ellipsometry, Photoluminescence and Raman Spectroscopy are combined to investigate electronic band structures and bonding properties. The experiments are closely coupled with structural and property modeling and theory.

A series of (III–V)–(IV) alloys have been synthesized by the reaction of M(SiH_3)_3 (M = P, As) with Al atoms from a Knudsen cell. In the AlPSi_3 system, bonding configurations and elemental distributions are characterized by scanning transmission electron microscopy (STEM)/EELS and correlated with bulk optical behavior. The incorporation of N was achieved by addition of N(SiH_3)_3 into the reaction mixture yielding [Al(As_{1-x}N_x)]_ySi_{5-2y} alloys. A critical point analysis of spectroscopic ellipsometry data reveals the existence of direct optical transitions at energies as low as 2.5 eV, well below the lowest direct absorption edge of Si at 3.3 eV.

The compositional dependence of the lowest direct gap and indirect gap in Ge_{1-y}Sn_y alloys extracted from room temperature photoluminescence indicates a crossover concentration of y_c = 0.073, much lower than virtual crystal approximation but agrees well with large atomic supercells predictions.
A series of Ge-rich Ge$_{1-x}$Si$_x$Sn$_y$ samples with a fixed 3-4% Si content and progressively increasing Sn content in the 4-10% range are grown and characterized by electron microscopy and photoluminescence. The ternary represents an attractive alternative to Ge$_{1-y}$Sn$_y$ for applications in IR optoelectronic technologies.
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CHAPTER 1
INTRODUCTION

1. Background and Motivation

A semiconductor is a material that has an electrical conductivity intermediate between an insulator and a conductor. Most electronic components such as transistors, solar cells, light-emitting diodes (LEDs) and digital and analog integrated circuits are made of semiconductors. Semiconductor electronic devices from computers to cellphones have become a necessity in people’s life.

Silicon is used in most semiconductor devices. Silicon chips are used in integrated circuits, and solar cells based on silicon account for a dominant portion of the photovoltaic market.

In spite of silicon’s current ubiquity, theory and electronics were driven by germanium in the early days of semiconductor technology, and the first transistor was actually based on Ge.\(^1\)\(^2\) Silicon prevailed because of its more stable oxide and better temperature characteristics, but specific applications can be optimized with other materials, and quite often the need arises for semiconductor materials with properties different from those of elemental or binary semiconductors, calling for electronic structure engineering.

One possible route to electronic structure engineering is alloying of semiconductor systems, because the alloy band gaps are functions of composition.\(^3\) Development of Si-Ge based alloys has extended the optoelectronic capabilities of Si and Ge and enabled the tuning of their optoelectronic properties.\(^4\)

Si-based alloys such as \((\text{Si})_{5-2y}(\text{AlP})_y, [\text{Al}(\text{As}_{1-x}\text{N}_x)]_y\text{Si}_{1-2y}\) and Ge based alloys like \(\text{Ge}_{1-x}\text{Sn}_y\) and \(\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y\) with \((0 \leq x \leq 1)(0 \leq y \leq 1)\) have the chance to fill unique
applications in microelectronics, Si photonics and photovoltaics. These new materials based on silicon and germanium are expected to have better absorption and emission capabilities than the current systems, promising a new generation of photovoltaic devices, detectors or even lasers. The ability to integrate the above materials directly on silicon enables their use in Si-photonics.

2. Si-like III-V/IV alloys

Alloys of group IV element and group III-V compounds belong to a specific class of hybrid polar-nonpolar materials. Their electronic structures and optical behavior blend the IV and III-V components, with the possibility of becoming direct gap semiconductors enabling many applications from lasers to photovoltaics.

To date, only a few such IV/III-V compounds have been experimentally explored. Materials such as BNC$_2$, whose hardness rivals that of diamond $^{10}$ and the classic (Ge$_2$)$_x$(GaAs)$_{1-x}$ alloy, which is as candidate material for a 1eV layer in Ge / 1 eV / InGaAs / InGaP 4-junction solar cells $^{11,12,13}$ are good examples. However, phase separation is the issue that hinders the introduction of new families of (III-V)$_{1-x}$(IV)$_x$ materials.

The interplay between the diamond and zincblend symmetry in (III-V)-(IV) alloys may explain the fact that some alloy properties are not smooth functions of compositions, with the possibility of phase transitions.$^{14,15}$

A new approach to synthesize (III-V)-(IV) alloys while avoiding phase segregation problems is described in this thesis. This is achieved by deploying molecular growth precursors such as (H$_3$-IV)$_3$V molecules, which combine group IV and group V elements, as opposed to traditional growth methods, such as Molecular Beam Epitaxy, which
deliver all constituent atoms separately. Thick homogeneous monocrystalline films with AlPSi₃ stoichiometry were grown when (H₃Si)₃P was combined with Al atoms.¹⁶ Later on, Siₓ₋₂y(AlP)ᵧ alloys with tunable Si concentrations were achieved with this method.¹⁷ The growth of films with [Al(As₁₋ₓNx)ᵧ]ₓSi₅₋₂y stoichiometries were enabled by reaction of compounds such as (H₃Si)₃As, (H₃Si)₃N and Al.¹⁸,¹⁹

The pseudomorphic epitaxial growth of the above alloys on Si substrates and the fact that the Si content can be tuned anywhere between 60% and 100% suggests intriguing possibilities in the field of photovoltaics. Over 85% of the photovoltaics market is based on silicon,²⁰ but with commercial Si solar cells delivering efficiencies around 20%, close to the theoretical maximum of 25%, this technology has little room to grow unless Si-based multijunctions become feasible. Before the introduction of these new materials, the options were limited. The best candidate, the GaAsP alloy,²¹ is not even lattice matched to Si. Thus the introduction of AlPSi₃ essentially lattice-matched to Si caught the attention of National Renewable Energy Laboratory (NREL) theorists, who confirmed that this material has two very desirable features for Si-based multijunction solar cells: a higher fundamental band gap than Si and increased absorption of the solar spectrum.²²

The first feature would increase the open circuit voltage, while the stronger absorption would reduce the required film thickness in the absorber layer. It is interesting to note here that in spite of silicon’s dominance of the solar cell market, its photovoltaic properties are actually rather poor, since the direct absorption gap is at 3.4 eV, so that most photons in Si solar cells are absorbed via inefficient indirect transitions. The incorporation of equal amounts of group-III and group-V impurities was recently suggested as a way to improve the optical properties of Si for photovoltaic applications.²³
and the growth method described here accomplishes this goal in an elegant way that makes it possible to reach the maximum concentrations of isolated III-V pairs. Moreover, most of our new materials are based entirely on earth-abundant elements (Al, P, Si, N), which would allow them to contribute to terawatt level deployment of photovoltaics.

3. Ge$_{1-y}$Sn$_y$ system

Germanium, like Si, is an indirect band gap semiconductor, which makes light emission from this material inefficient. However, the direct gap (between the $\Gamma$ valley and the top of the valence band at $\Gamma$, where $\Gamma$ indicates the center of the Brillouin zone) and indirect gap (between the L valleys along the $<111>$ directions of the Brillouin zone and the top of the valence band) separation is only 0.14 eV in Ge (as opposed to 2.3 eV in Si) suggesting that Ge can become a direct band gap material with band-structure engineering.

Tensile strain reduces the separation between the $\Gamma$ and L valleys in the conduction band of Ge, and $n$-type doping shifts the Fermi level toward the higher $\Gamma$-minimum. Tensile strain can be induced in Ge on Si by cooling the sample from high temperature to room temperature due to the thermal expansion mismatch of Ge and Si. The recent optically pumped Ge-on-Si laser uses this tensile strain and heavy $n$-type doping to achieve a “quasi-direct” band gap condition. The direct light emission in Ge was enhanced significantly by tensile strain and $n$-type doping.

Band gap engineering based on thermal expansion mismatch is limited by the maximum tensile strain 0.30% achievable in this approach. An alternative is alloying Ge with Sn to increase direct gap emission. The diamond-structure $\alpha$ phase Sn is a semimetal, with a large “negative” direct gap (-0.4 eV) and vanishingly small indirect
gap. Interpolation of Sn with Ge suggests a strong band gap tunability. It has been estimated that 1% Sn in Ge is approximately equivalent to a tensile strain of 0.35% and corresponds to a sharp reduction in band gap energy.

Ge$_{1-y}$Sn$_y$ alloys (y≤0.04) exhibit photoluminescence (PL) comparable to that of Ge on Si. In addition, Si/Ge$_{1-y}$Sn$_y$ heterostructure pin photodiodes show direct gap electroluminescence. Because of their reduced band gap, Ge$_{1-y}$Sn$_y$ alloys extend the infrared range of Ge-based telecom detectors beyond the wavelength that can be achieved with tensile-strained Ge. Moreover, linear interpolation suggests that at about 20% Sn the alloy should become a direct gap semiconductor, and the accumulation of experimental evidence suggests that this indirect to direct gap transition takes place at more modest Sn amounts, which has contributed to the excitement about these alloys. In addition, the possibility of using relaxed Ge$_{1-y}$Sn$_y$ alloys as tensile stressors for Ge may enable applications not only in Ge emitters/detectors but also in future Ge-based CMOS technology. The careful determination of the direct and indirect edges as a function of composition is crucial for most of these applications, and the observation of distinct direct and indirect gap peaks in photoluminescence (PL) spectra makes this technique a superior alternative to absorption for the determination of the gap energies. However, while in most low-temperature PL studies of semiconductors the identification of the peak maximum with the associated band gap energy is sufficient for practical purposes, a detailed lineshape analysis is needed for room temperature studies. In the case of indirect gap PL, this analysis must include the possibility of phonon emission and absorption. The need for a detailed lineshape analysis that yields accurate band gap energies is very acute for the Ge$_{1-y}$Sn$_y$ system if the purpose of the study is the determination of the crossover
composition $y_c$ at which the material becomes a direct-gap semiconductor, since small systematic changes in the slope of the compositional dependence of either gap translate into significant changes in the predicted value of $y_c$.

4. **Ge$_{1-x}$Si$_x$Sn$_y$ system**

One concern about Ge$_{1-x}$Sn$_y$ system is its thermal stability. Low Sn ($y < 0.02$) concentration samples can withstand rapid thermal annealing (RTA) temperatures as high as 700°C, but the stability deteriorates with increasing Sn concentrations as needed to obtain direct gap materials. For the same amount of Sn, the ternary alloy Ge$_{1-x}$Si$_x$Sn$_y$ is more stable than Ge$_{1-y}$Sn$_y$ due to the larger entropy of mixing in the ternary compound. However, the incorporation of Si also increases the direct band gap, moving the system away from direct band gap conditions. The question then arises as to whether it is possible to compensate for this effect by increasing the Sn even further. The resulting ternary alloy with the same electronic properties as the binary alloy would have a higher Sn concentration, but may still be more stable due to the above-mentioned entropy stabilization. The results confirm that Ge$_{1-y}$Sn$_y$ like conditions, with band gaps lower than that of Ge, can be achieved in the ternary system.

A series of Ge-rich samples with a fixed 3-4% Si content and progressively increasing Sn content in the 4-10% range were grown to explore the possibility of obtaining direct gap materials for the first time in this semiconductor system. The results show that the separation of the direct and indirect edges can be made smaller than in Ge even for the non-negligible 3-4% Si content, confirming that with a suitable choice of Sn compositions the ternary Ge$_{1-x}$Si$_x$Sn$_y$ reproduces all features of the electronic structure of the binary Ge$_{1-y}$Sn$_y$, including the sought after indirect-to-direct gap crossover.
CHAPTER 2

THEORETICAL BACKGROUND OF ELECTRON MICROSCOPY AND OPTICAL
PROPERTIES OF SMEICONDUCTORS

The microscopy part of this chapter is based on the book “Transmission Electron
Microscopy: a Text Book for Materials Science” by David B. Williams, and C. Barry
Carter. The optical part is based on “Handbook of Ellipsometry” by Harland G.
Tompkins and Eugene A. Irene. Raman Spectroscopy part is based on the book “ Raman
Scattering in Materials Science” by José Menéndez.

1. Electron Microscopy

Transmission electron microscopes (TEMs) were developed with the purpose of
obtaining high resolution images compared to optical microscopes. TEM can produce
atomic-resolution images and reveal specimen chemistry and crystallography via electron
beam and sample interaction.

1.1 Lens Aberrations

Aberrations in microscopy include spherical aberration, astigmatism, coma, field
curvature and distortion. Of these five distinct effects, the most important ones are
spherical aberration, astigmatism and coma.

(A) Spherical Aberration. This distortion arises whenever the lens field behaves
differently for rays passing through the edge rather than the center. If the collection angle
of the lens is $\theta$, the diameter of the Gaussian image of a point formed by paraxial rays is
given by

$$ \delta = C_s \times \theta^3 $$

(2.1)
Where $C_s$ is a constant (about focal length of lens) for a particular lens called the spherical aberration coefficient. Magnetic lenses behave like convex lens in optical system which means $C_s$ is positive. A diverging (i.e., concave) lens is applied which spreads out the off-axis beams such that they re-converge to a point rather than a disk in the Gaussian-image plane.

![Figure 1](image-url)

**Figure 1.** Ray diagram showing how the two different commercial systems use (A) multiple quadrupole (Q) and Octupole (O) lenses (Nion) or (B) hexapole and other transfer lens(CEOS) to correct for $C_s$. Reprinted with permission from “Transmission Electron Microscopy: a Text Book for Materials Science” Springer 1999 Figure 6.12

There are two main approaches to the solution of $C_s$ correction. The first is the CEOS commercial system which is installed in JEOL ARM 200F using the hexapoles proposed by Rose and colleagues in Germany.$^{44}$ The second approach to correct aberration is with quadrupoles and octupoles applied by Krivanek et al in Nion system and VG STEMs.$^{45}$ Figure 1 shows schematic ray diagrams for the Nion corrector and the CEOS system.

**(B) Chromatic Aberration.** It consists of radiation with different energies converging at different focal planes. The radius $r_{chr}$ of this disk (referring to the object plane) is given by
\[ r_{\text{chr}} = C_c \frac{\Delta E}{E_0} \beta \]  \hspace{1cm} (2.2)

Where \( C_c \) (about the focal length of the lens) is the chromatic-aberration coefficient of the lens, \( \Delta E \) is the energy loss of the electrons, \( E_0 \) is the initial beam energy, and \( \beta \) is the angle of collection of the lens. While \( \Delta E \) in the incident electron beam is about 1 eV, it is typically 15–25 eV for a good fraction of the electrons coming through a typical 50–100 nm thick foil.\(^\text{46}\)

(C) **Astigmatism.** Astigmatism occurs when the electrons sense a non-uniform magnetic field as they spiral down the optic axis. There are a variety of contributions to astigmatism such as soft-iron pole pieces that are not perfectly cylindrically symmetrical or soft irons that have microstructural inhomogeneities or apertures not precisely centered, which distorts the image by an amount \( r_{\text{ast}} \) where

\[ r_{\text{ast}} = \beta \Delta f \]  \hspace{1cm} (2.3)

and \( \Delta f \) is the maximum difference in focus induced by the astigmatism. Astigmatism is easily corrected using stigmators, which are small octupoles that introduce a compensating field to balance the inhomogeneities causing the astigmatism. Astigmatism should be corrected in both illumination systems and imaging systems in TEM mode and only condenser stigmators are needed in scanning transmission electron microscopy (STEM) mode.

**1.2. Interaction of Electrons with Matter**

The electron-matter interaction produces a wide range of secondary signals from the specimen and some of these are summarized in Figure 2.
Direct beam are electrons penetrating the specimen without any interaction. The rest of the electrons are scattered and the probability increases with sample thickness. Electron scattering caused by the specimen can be classified into two groups: elastic scattering and inelastic scattering. In elastic scattering the momentum of the scattered electrons changes, but their energy does not. Structural information is derived from elastic scattering, which is due to the scattering of electrons through a given angle by a set of planes of atoms. On the other hand, all electrons suffering a change of velocity (or energy) belong to the inelastic scattering. Many of these signals are used in analytical electron microscopy (AEM), giving chemical information and other details about the specimen by X-ray energy dispersive spectrometry (EDS) and electron energy-loss spectrometry (EELS) techniques.

Scanning transmission electron microscopy (STEM), which combines the properties of TEM and scanning electron microscopy (SEM) is used to produce a very small electron
beam used in analytical electron microscopy (AEM) and scanning-imaging microscopy. In addition, Cs correction permits the generation of smaller electron probes with higher current densities, thus significantly improving both the analytical spatial resolution and signal to noise ratio.

Based on the detector used, one can obtain both annular dark field and bright field image which is considered as the reciprocal of TEM although the efficiency is lower. In annular dark field imaging, high angle annular dark field (HAADF) imaging is used most frequently. HAADF images are formed by collecting high-angle scattered electrons. The reasons to choose HAADF are that the contrast is strongly dependent on the average atomic number Z, and it is not strongly affected by dynamical diffraction or defocus, or thickness variations.47,48

Figure 3. Ray diagrams for TEM and STEM to illustrate the reciprocal nature of the bright field images. The BF image in aberration-corrected STEM gives an image optically equivalent to that obtained with aberration-corrected TEM. Reprinted with permission from “Scanning Transmission Electron Microscopy for Nanostructure Characterization” Springer Science+Business Media LLC @2006.

1.3 Elastic Scattering and Diffraction

The electron possesses wave-particle duality. As a particle, it is light and negatively charged making it easily deflected by other electrons or the positive nucleus of an atom.
These Coulomb (electrostatic) interactions cause electron scattering, which is the process that makes TEM feasible. Diffraction theory is used to describe electron scattering on account of the wave nature of the electron.

(A) Scattering. If the specimen thickness is $< 100 \text{ nm}$ or even better $< 50 \text{ nm}$ for EELS analysis, most electrons either undergo a single-scattering event or are not scattered (direct beam). For electrons elastically scattered by nuclei into angles $> \theta$ the cross section is

$$\sigma_{\text{nucleus}} = 1.62 \times 10^{-24} \left( \frac{Z}{E_0} \right)^2 \cot^2 \left( \frac{\theta}{2} \right)$$

(2.4)

We see that the cross section decreases with beam energy ($E_0$) and the angle of scattering ($\theta$), but increases with increasing atomic number ($Z$).

High-angle Rutherford-scattered electrons are incoherent and are used in high angle annular dark field image (HAADF) in which the image contrast is due solely to the value of $Z$. The image is called Z contrast image with a resolution 30% better than that of phase contrast image. Such Z-contrast images provide qualitative atomic-resolution elemental analysis.\(^{47,48}\)

(B) The Atomic Scattering Factor. The classic Rutherford differential cross section Eq.(2.4) works better for high angle scattering. However, to describe the low angle elastic scattering, the concept of the atomic-scattering factor $f(\theta)$ is needed, which is related to the differential elastic cross section by a simple equation

$$f(\theta) = \frac{d\sigma(\theta)}{d\Omega}$$

(2.5)
Usually, \( f(\theta) \) is defined in the following manner

\[
f(\theta) = \left( 1 + \frac{E_0}{m_0 c^2} \right) \left( \frac{\lambda}{\sin(\theta/2)} \right)^2 \times (Z - f_x)
\]  

(2.6)

\( f_x \) is the scattering factor for X-rays. \( E_0 \) is the beam energy, \( a_0 \) is the Bohr radius, \( m_0 \) is the rest mass of electron, \( \theta \) is the scattering angle.

**C. The structure factor** \( F(\theta) \). The structure factor is a function of the type of atom \( f(\theta) \), the position of the atom in the cell (x, y, z), and the specific atomic planes (h k l) that make up the crystal structure.

\[
F(\theta) = \sum f_i e^{2\pi i (hx+ky+lz)}
\]  

(2.7)

The scattering angle \( \theta \) is the angle between the incident and scattered electron beams.

For different type of atoms, the scattering factors are different. The structure factor is a useful tool to determine crystal structures. Take face-centered cubic for example, we have to include four atoms in the unit cell. The coordinates of the atoms are 

\((x,y,z) = (0,0,0), (1/2,1/2,0), (1/2,0,1/2), (0,1/2,1/2)\).  

\[
F = f \left\{ 1 + e^{\pi i (h+k)} + e^{\pi i (h+l)} + e^{\pi i (l+k)} \right\}
\]

From this, we obtain \( F = 4f \) if h, k, l are all even or all odd. \( F = 0 \) if h, k, l are mixed even and odd.

**D. Diffraction.** Electron diffraction in the TEM is used to generate diffraction contrast in image mode and diffraction pattern to identify crystallography. The positions of the diffracted beams of electrons are determined by the size and shape of the unit cell due to the real space and reciprocal space relationship. The intensities of the diffracted beams are governed by the distribution, number, and types of atoms in the specimen, which are related to the structure factor mentioned above.
The diffracted waves are in phase with one another only in certain directions. If the crystal is viewed as a grating, then diffraction creates many electron beams traveling at specific angles relative to the single monochromatic incident beam. We can measure these angles and relate them to the spacing of the scattering planes.

\[ n\lambda = 2d \sin(\theta_B) \]  

(2.8)

We’ll reserve \( \theta_B \) for the Bragg angle, which is the most important scattering angle (where we actually mean semi-angle) in TEM.

1.4 Inelastic Scattering, EDS and EELS

(A) Energy Dispersive Spectroscopy (EDS). X-ray is the most important secondary signal to identify constituent elements and quantify the amount of each element in the specimen in a straightforward way. The high energy electron beam transfers energy higher than that of the binding energy of an inner-shell electron, so that electron can be ejected, leaving a hole in the inner shell. The hole is filled with an electron from an outer shell. This transition is accompanied by the emission of either an X-ray or an Auger electron.

(B) Electron Energy-Loss Spectroscopy (EELS) The EELS technique is based on the analysis of electron energy losses undergone by primary electrons interacting with a sample, revealing information about the nature of the elementary excitations of the crystal. Among the various energy-loss process, the typical ones and their energy ranges are as follows: (1) Lattice vibrations (phonon excitation): less than 0.1eV. (2) Collective excitations of valence electrons (plasmon excitation): less than 30eV. (3) Interband transitions: less than 10eV. (4) Inner-shell electron excitations (core electron excitation): more than 13eV. EELS can identify and quantify the presence of all elements above Li in
the periodic table as EDS. Besides, EELS offer even better spatial resolution and analytical sensitivity. Furthermore, EELS presents several analogies with optical spectroscopy. Both techniques provide information on the density of both filled and empty electronic states in a solid. It would be interesting to combine EELS data with ellipsometry data to explore band structures.

(C) Critical Ionization Energy. The critical ionization energy (E_c) is the threshold energy for electron beam to ionize the atom. It is higher if the electrons are more tightly bound to the nucleus which tracks the atomic number Z. For the same element, the innermost shell (K) has a higher E_c than the next (L) shell, and so on. The X-ray energy and EELS edges increases monotonically with Z, so that we can use the detection of a characteristic X-ray peak or EELS edge with a specific energy as an unambiguous sign of the presence of an element in the specimen.

(D) Inelastic Scattering Cross Section. There are many inelastic scattering processes, as stated above. The cross section is defined for each inelastic scattering process. For inner-shell excitation

\[
\sigma = \frac{\pi e^4 b_s n_s}{(m_0 v^2/2)^2} \left[ \log \left[ \frac{e^2 (m_0 v^2/2)}{E_c} \right] - \log(1 - \beta_r^2) - \beta_r^2 \right],
\]

\[
\beta_r = \left\{ -1 + E/\sqrt{51} \right\}^{2.5}
\]

Where E_c is the energy for ionization; n_s is the number of electrons in the inner shell; m_0 is the rest mass of the electron; and v and e are the velocity of incident electrons and
Figure 4. Cross section for various inelastic scattering processes in Al as a function of the incident energy, assuming a small angle of scattering. Plasmon (P), K and L shell ionization (K,L), secondary electron generation (SE), elastic scattering cross section (E). Reprinted with permission from “Transmission Electron Microscopy: a Text Book for Materials Science” Springer 1999 Figure 4.1

the elementary electric charge, respectively. The \( b_z \) and \( c_z \) values depend on the species of inner shells, such as the K shell, L shell, and so on.\(^{46}\)

(E)Elemental Analysis in EELS. The net signal intensity of an element can be obtained by subtracting background \( I_B \) which is simulated with \( I_B = C \cdot E^{-r} \) where \( E \) is energy loss; and \( C \) and \( r \) are constants. On the other hand, the intensity of the core loss \( I_A \) for element A involved in the area is theoretically given by

\[
I_A = n_A t \sigma_A(\beta, \Delta E, E_0) I_T
\]  

(2.11)

Where \( n_A \) and \( t \) are the number of atoms in a unit volume for element A and specimen thickness, respectively. Here \( \sigma_A(\beta, \Delta E, E_0) \) is the partial cross section of element A for acceptance angle \( \beta \), energy window \( \Delta E \), and incident electron energy \( E_0 \). The partial
cross-sections were calculated from theoretical Hartree-Slater models. Thus the number of atoms in the area can be evaluated as

\[ n_A = \frac{I_A}{I_T \, t \sigma_A (\beta, \Delta E, E_0)} \]

(2.12)

The relative compositions of two different elements such as Ge and Sn can be obtained after background subtraction and removal of Plural scattering by Fourier deconvolution, so that different energy windows \( \Delta Ge, \Delta Sn \) can be used for Ge L edge and Sn M edge to integrate intensity. The Ge L edge, Sn M edge signal can then be integrated over \( \Delta Ge, \Delta Sn \) energy window to obtain \( I_{Ge}^I (\beta, \Delta Ge), I_{Sn}^I (\beta, \Delta Sn) \). The ratio of integrated Sn and Ge EELS signal is then converted to their corresponding atomic ratio using partial cross-sections.

\[ \frac{N_{Ge}}{N_{Sn}} = \frac{I_{Ge}^I (\beta, \Delta Ge) \sigma_{Sn} (\beta, \Delta Sn)}{I_{Sn}^I (\beta, \Delta Sn) \sigma_{Ge} (\beta, \Delta Ge)} \]

(2.13)

where \( \sigma_{Ge} (\beta, \Delta Ge) \) and \( \sigma_{Sn} (\beta, \Delta Sn) \) are “partial” cross-sections for energy loss from Ge L edge and Sn M edge within energy range \( \Delta Ge \) and \( \Delta Sn \) for scattering angles up to \( \beta \) obtained from experiment. 48,49

The EELS collected from a spot in a specimen is called point analysis. While in STEM, the scanned beam can generate two dimensional EELS elemental maps by synchronizing with the position signal.
2. Optical Properties of Semiconductors

2.1 Dielectric Function of Semiconductors

The optical properties of semiconductors are related to their electronic and phonon band structures, which are influenced by crystallographic structure, the type of atoms, and their bonding.

Semiconductor band gaps are mostly in the range of 0-3eV, so photons in the visible range have usually enough energy to excite electrons from the valence band to the conduction band. Optical spectroscopy provides detailed information about semiconductor electronic properties through the light matter interaction. Over the years, classical theory, semi-classical theory and quantum theory have been used to explain the interaction process. In classical theory, we treat light as an electromagnetic wave and atoms as dipole oscillators. The classical theories originate from the work of Lorentz and serve as useful starting points from which one can model the dielectric function of the materials as a collection of oscillating dipoles.\(^{51,52}\) Semi-classical theory treats the electrons in a crystalline material quantum mechanically while light is treated as a classical electromagnetic wave. This approach is sufficient to explain the absorption coefficient of solids but fails to account for spontaneous emission. The latter is obtained from full quantum mechanical treatment of matter and fields.

(A) Classical Theory of Dielectric Function of Semiconductors

The classical theory treats light as electromagnetic wave and the materials with the equation of motion a single electron of charge \(-e\) and mass \(m\), bound to a nucleus of charge \(+e\) fixed in position in the solid. According to Newton’s Second Law

\[
m\ddot{x} = -\beta \dot{x} - k_x x - eEx
\]  

(2.14)
Since the electrical field is harmonic, \( E_x = E_0 e^{-i\omega t} \), we can rewrite the above equation as

\[
\ddot{x} + \gamma \dot{x} + \omega_0^2 x = -\frac{eE_0}{m} x e^{-i\omega t}
\]  

(2.15)

where \( \beta = \gamma m \), and \( k_x = \omega_0^2 m \). \( \omega_0 \) is the natural frequency, and \( \gamma \) is the damping factor.

To find the solution, we assume

\[
x(t) = A e^{-i\omega t}
\]  

(2.16)

Substituting (2.16) into (2.15), and solve for \( A \), we get

\[
A = \frac{-\frac{eE_0}{m}}{\omega^2 - \omega_0^2 - i\gamma\omega}
\]  

(2.17)

\[
x(t) = \frac{-\frac{eE_0}{m} e^{-i\omega t}}{\omega^2 - \omega_0^2 - i\gamma\omega}
\]  

(2.18)

Recall that \( e_x \) is the polarization of one oscillator. If we have \( N_0 \) atoms per unit volume, total polarization is thus

\[
P = N_0 e_x = \frac{-N_0 e^2 E_0 e^{-i\omega t}}{m(\omega^2 - \omega_0^2 - i\gamma\omega)} = \frac{\omega_p^2 e_0 E}{(\omega^2 - \omega_0^2 - i\gamma\omega)}
\]  

(2.19)

\[
\omega_p^2 = \frac{N e^2}{m e_0}
\]  

(2.20)

The polarization is related to the electrical field through the electrical permittivity,

\[
P = \chi e_0 E
\]  

(2.21)
So we have

\[ \chi = \frac{\omega_p^2}{\left(\omega^2 - \omega_0^2 - i\gamma\omega\right)} \]  
(2.22)

The relative dielectric constant \( (\varepsilon = \varepsilon_0\varepsilon_r) \) is

\[ \varepsilon_r = 1 + \chi = 1 + \frac{\omega_p^2}{\left(\omega^2 - \omega_0^2 - i\gamma\omega\right)} = \varepsilon_r' + i\varepsilon_r'' \]  
(2.23)

Where the real and the imaginary parts are

\[ \varepsilon_r = \frac{\omega_p^2(\omega_0^2 - \omega^2)}{\left(\omega^2 - \omega_0^2\right)^2 + \gamma^2\omega^2} \]  
(2.24)

\[ \varepsilon_i = \frac{\omega_p^2\gamma\omega}{\left(\omega^2 - \omega_0^2\right)^2 + \gamma^2\omega^2} \]  
(2.25)

The complex refractive index is calculated from \( \varepsilon_r \) as

\[ N = \sqrt{\varepsilon_r} \]  
(2.26)

\[ n^2 - k^2 = \varepsilon_r' \]  
(2.27)

\[ 2nk = \varepsilon_r'' \]  
(2.28)

\( \omega_0 \) is the resonance frequency of the simple harmonic oscillator. If we have multiple oscillators, the so-called Lorentz model can be written as

\[ \varepsilon_r = 1 + \sum_j \frac{\omega_p^2(\omega_0^2_j - \omega^2)}{\left(\omega^2 - \omega_0^2_j\right)^2 + \gamma_j^2\omega^2} \]  
(2.29)
If the frequency of the electromagnetic wave $\omega$ equals one of the natural frequencies of the atom $\omega_0$, the atom absorbs energy from the light wave.

(B) Quantum Theory of the Dielectric Function of Semiconductors

Assume that the radiation is represented by a vector potential

$$A = \frac{1}{2} A_0 \left[ e^{i(kr-\omega t)} + e^{-i(kr-\omega t)} \right]$$

(2.30)

In terms of this vector potential:

$$E = -\frac{1}{c} \frac{\partial A}{\partial t} = \frac{i\omega}{2c} A_0 \left[ e^{i(kr-\omega t)} - e^{-i(kr-\omega t)} \right]$$

$$B = \nabla \times A = \frac{k \times A_0}{2} \left[ e^{i(kr-\omega t)} - e^{-i(kr-\omega t)} \right]$$

(2.31)

Now we calculate the Poynting vector as

$$S = \frac{c}{4\pi} (E \times B) = \frac{c}{4\pi} \frac{i\omega}{2c} (A_0 \times k \times A_0) \left[ e^{2i(kr-\omega t)} - e^{-2i(kr-\omega t)} - 2 \right]$$

$$= \frac{\omega}{16\pi} (A_0 \times k \times A_0) \left[ 2 + e^{-2i(kr-\omega t)} - e^{2i(kr-\omega t)} \right]$$

(2.32)

The time average of this is

$$S_{av} = \frac{\omega}{8\pi} (A_0 \times k \times A_0)$$

(2.33)

Next we express the cross product in terms of dot products:

$$A_0 \times k \times A_0 = (A_0 \cdot A_0) k - (A_0 \cdot k) A_0 = A_0^2 k$$

(2.34)

where the last step follows from the fact that the field of the electromagnetic wave is transverse, so that $A_0 \cdot k = 0$. Therefore, we finally obtain

$$S_{av} = \frac{\omega A_0^2}{8\pi} k$$

(2.35)
The energy density in the electromagnetic wave is then

\[ \frac{|S_{\omega}|^2}{c^2} = \frac{n\omega_k k A_0^2}{8\pi c} = \frac{n^2 \omega_k^2 A_0^2}{8\pi c^2} = \frac{\hbar \omega_k}{V} \]  

(2.36)

where \( n \) is the index of refraction and \( n_\omega \) is the number of photons with frequency \( \omega_k \).

From this we obtain

\[ A^2 = \frac{8\pi c^2\hbar}{V \omega_k n^2} n_\omega = 4 \left( \frac{4\pi c^2}{n^2 V} \right) \left( \frac{\hbar}{2\omega_k} \right) n_\omega \]  

(2.37)

This form can be used for semi-classical calculations of optical properties. The full quantum mechanical representation follows from introducing a quantization condition for the fields. The step-by-step derivation is found in many textbooks, but Eq. (2.37) already suggests that the vector potential operator, in the occupation number representation, is given by

\[ A = \left( \frac{4\pi c^2}{V n^2} \right)^{1/2} \sum_{k\lambda} \left( \frac{\hbar}{2\omega_k} \right)^{1/2} e_{k\lambda} \left[ a_{k\lambda} e^{ikr} + a_{k\lambda}^* e^{-ikr} \right] \]  

(2.38)

where \( \lambda \) indicates the polarization.

The interaction with matter is given by the term

\[ H_{eR} = \frac{e}{mc} A \cdot p = \left( \frac{4\pi c^2}{V n^2} \right)^{1/2} \left( \frac{e}{mc} \right) \sum_{k\lambda} \left( \frac{\hbar}{2\omega_k} \right)^{1/2} e_{k\lambda} \cdot p \left[ a_{k\lambda} e^{ikr} + a_{k\lambda}^* e^{-ikr} \right] \]  

(2.39)

In the occupation number representation, the one-electron operator can be written as

\[ H_{eR} = \sum_{k\lambda} \langle k' | H_{eR} | k \rangle c_{k'}^+ c_{k} \]  

(2.40)
where the states are Bloch functions and the matrix element is an integral over the entire crystal. Let us compute this matrix element. Using Eq (2.39)

\[
\langle k' | H_{ee} | k \rangle = \left( \frac{4\pi e^2}{\hbar^2} \right)^{\frac{1}{2}} \left( \frac{e}{mc} \right)^2 \sum_{k} \left( \sum_{\lambda, \lambda'} \left( \frac{\hbar}{2\omega_k} \right) \mathbf{e}_{k\lambda} \cdot \mathbf{p} \left[ a_{k\lambda} e^{i k \cdot r} + a_{k\lambda}^* e^{-i k \cdot r} \right] \right) \Psi_k^* (r) \Psi_{k'} (r)
\]

\[
= \left( \frac{4\pi e^2}{V \hbar^2} \right)^{\frac{1}{2}} \left( \frac{e}{mc} \right)^2 \sum_{k} \left( \sum_{\lambda, \lambda'} \left( \frac{\hbar}{2\omega_k} \right) \mathbf{e}_{k\lambda} \cdot \mathbf{p} \left[ a_{k\lambda} e^{i k \cdot r} + a_{k\lambda}^* e^{-i k \cdot r} \right] \right) \Psi_k^* (r) \Psi_{k'} (r)
\]

(2.41)

We will first deal with the photon annihilation part. We have

\[
\left( \frac{4\pi e^2}{V \hbar^2} \right)^{\frac{1}{2}} \left( \frac{e}{mc} \right)^2 \sum_{k} \left( \sum_{\lambda, \lambda'} \left( \frac{\hbar}{2\omega_k} \right) \mathbf{e}_{k\lambda} \cdot \mathbf{p} \left[ a_{k\lambda} e^{i k \cdot r} + a_{k\lambda}^* e^{-i k \cdot r} \right] \right) \Psi_k^* (r) e^{-i k \cdot r} p u_k (r) e^{i (k + k') \cdot r}
\]

(2.42)

Where the u’s are the periodic part of the Bloch functions. Now the gradient operator acts on everything to its right, giving rise to two terms. The first term contains the derivative of u and the second term the derivative of the exponential. In the long wavelength approximation the second term tends to vanish due to the orthogonality of the periodic part of the Bloch function for the same wave vector, so that the integral becomes:

\[
\int dr u_k^* (r) e^{-i k \cdot r} p u_k (r) e^{i (k + k') \cdot r} = \int dr e^{i (k + k') \cdot r} u_k^* (r) e^{i k \cdot r} p u_k (r)
\]

\[
= \sum_R \int_{\text{cell}} dr e^{i (k + k - k') \cdot (r + R)} u_k^* (r + R) p u_k (r + R)
\]

\[
= \sum_R e^{i (k + k - k') \cdot R} \int_{\text{cell}} dr e^{i (k + k - k') \cdot r} u_k^* (r) p u_k (r)
\]

\[
= \sum_R e^{i (k + k - k') \cdot R} \int_{\text{cell}} dr u_k^* (r) p u_k (r)
\]

(2.43)

\[
= \sum R \delta_{k', k + k} \int_{\text{cell}} dr u_k^* (r) p u_k (r) = \delta_{k', k + k} \int dr u_k^* (r) p u_k (r)
\]

\[
= \delta_{k', k + k} P_{k', k}
\]
Introducing this back into Eq. (2.42) and Eq. (2.40):

\[ H^R_e = \left( \frac{4\pi c^2}{n^2V} \right)^{1/2} \left( \frac{e}{mc} \right) \sum_{k,\lambda,k'} \left( \frac{\hbar}{2\omega_k} \right)^{1/2} \mathbf{e}_{k,\lambda} \cdot \mathbf{P}_{k+k',k',\lambda}^+ \mathbf{c}_{k,\alpha} \mathbf{a}_{k,\lambda} \]

(2.44)

Similarly, the component that contains the raising operator for the photons is

\[ H^R_{eR} = \left( \frac{4\pi c^2}{n^2V} \right)^{1/2} \left( \frac{e}{mc} \right) \sum_{k,\lambda,k'} \left( \frac{\hbar}{2\omega_k} \right)^{1/2} \mathbf{e}_{k,\lambda} \cdot \mathbf{P}_{k-k',k',\lambda} \mathbf{c}_{k',\alpha} \mathbf{a}_{k,\lambda}^+ \]

(2.45)

(C) The Transition Rate. Let’s first assume that we are at zero temperature and want to calculate the transition rate for an incident photon of frequency \( \omega \) and linear polarization along the \( x \)-axis. We then have, neglecting the magnitude of the photon’s wavevector:

\[ R_{k,k} = \frac{2\pi}{\hbar} |H^R_{eR}|^2 \delta \left[ E_c(k) - E_e(k) - \hbar\omega \right] \]

(2.46)

where we have dropped the subscript \( e \) for the wavevector because the only wavevector we have now is that of the electrons. The total transition rate is obtained by adding over all \( k \)’s. Thus:

\[ R = \sum_k R_{k,k} = \frac{2\pi}{\hbar} \sum_k |H^R_{eR}|^2 \delta \left[ E_c(k) - E_e(k) - \hbar\omega \right] \]

(2.47)

Converting the sum to an integral:

\[ R = \frac{2\pi}{\hbar} \frac{V}{(2\pi)^3} \left( \frac{4\pi c^2}{n^2V} \right)^{1/2} \left( \frac{e}{mc} \right)^{1/2} \frac{\hbar}{2\omega} \int \frac{d\mathbf{k}}{(P_{k,k})^2} \delta \left[ E_c(k) - E_e(k) - \hbar\omega \right] \]

(2.48)

Because of the integral over \( k \), the momentum matrix element must be averaged over all \( k \) directions.
(D) Direct Gap Absorption. First we specialize the above formulas to the direct gap of a Ge-like material. The conduction band wave function at the $\Gamma$-point of the BZ has s-like symmetry, and we represent these wave functions as $|S \uparrow\rangle$ and $|S \downarrow\rangle$, where the arrows represent the spin. The valence band wavefunctions have p-like symmetry, and a suitable basis can be written as $|X \uparrow\rangle, |X \downarrow\rangle, |Y \uparrow\rangle, |Y \downarrow\rangle, |Z \uparrow\rangle, |Z \downarrow\rangle$. Diagonalizing the spin-orbit interaction within this manifold yields the eigenstates

Heavy holes:

$$
\begin{bmatrix}
\frac{3}{2} \cdot \frac{3}{2} \\
\frac{3}{2} \cdot -\frac{3}{2}
\end{bmatrix} \frac{1}{\sqrt{2}} (X + iY) \uparrow
\begin{bmatrix}
\frac{3}{2} \cdot \frac{3}{2} \\
\frac{3}{2} \cdot -\frac{3}{2}
\end{bmatrix} \frac{1}{\sqrt{2}} (X - iY) \downarrow
$$

(2.49)

Light holes:

$$
\begin{bmatrix}
\frac{3}{2} \cdot \frac{1}{2} \\
\frac{3}{2} \cdot -\frac{1}{2}
\end{bmatrix} \frac{1}{\sqrt{6}} (X + iY) \downarrow - \frac{2}{\sqrt{3}} Z \uparrow
\begin{bmatrix}
\frac{3}{2} \cdot \frac{1}{2} \\
\frac{3}{2} \cdot -\frac{1}{2}
\end{bmatrix} \frac{1}{\sqrt{6}} (X - iY) \uparrow + \frac{2}{\sqrt{3}} Z \downarrow
$$

(2.50)

Split off:

$$
\begin{bmatrix}
\frac{1}{2} \cdot \frac{1}{2} \\
\frac{1}{2} \cdot -\frac{1}{2}
\end{bmatrix} \frac{1}{\sqrt{3}} (X + iY) \downarrow + \frac{1}{\sqrt{3}} Z \uparrow
\begin{bmatrix}
\frac{1}{2} \cdot \frac{1}{2} \\
\frac{1}{2} \cdot -\frac{1}{2}
\end{bmatrix} \frac{1}{\sqrt{3}} (X - iY) \uparrow - \frac{1}{\sqrt{3}} Z \downarrow
$$

(2.51)

We need matrix elements of the momentum operator between these eigenfunctions and the conduction band wave functions. We define

$$
P = -i \langle S \uparrow | p_x | X \uparrow \rangle = -i \langle S \uparrow | p_y | Y \uparrow \rangle = -i \langle S \uparrow | p_z | Z \uparrow \rangle
$$

$$
= -i \langle S \downarrow | p_x | X \downarrow \rangle = -i \langle S \downarrow | p_y | Y \downarrow \rangle = -i \langle S \downarrow | p_z | Z \downarrow \rangle
$$

(2.52)
All other matrix elements of $p$ are zero by symmetry. At the $\Gamma$-point the orientation of the $X, Y, Z$ wave functions is arbitrary, but for $k \neq 0$, the above form in Eq. (2.49) (2.50) (2.51) for the heavy-hole, light-hole, and split-off wavefunctions is valid provided $Z$ is aligned with the wave vector. Thus the integration over $k$ in Eq. (2.48) requires a spatial average of the matrix elements. An elegant way of dealing with this issue is to take advantage of the cubic symmetry of Ge, which makes the $xx, yy$ and $zz$ diagonal components of the dielectric tensor equal to each other, so that one can calculate an average over the three components. The result from the average is $2P^2/3$ after one adds over the two directions of spin, so

$$ R = \frac{2\pi}{h} \left( \frac{V^2}{2\pi} \right)^2 \left( \frac{4\pi e^2}{n^2 V^2} \right)^2 \left( \frac{e}{mc} \right)^2 \left( \frac{\hbar}{2\omega} \right)^2 \frac{2P^2}{3} 4\pi \left[ E_v(k) - E_v(k) - h\omega \right] $$

Next we evaluate the integral over $k$ assuming a parabolic dispersion around the direct gap $E_0$ with a reduced mass $\mu$:

$$ R = \frac{2\pi}{h} \left( \frac{V^2}{2\pi} \right)^2 \left( \frac{4\pi e^2}{Vn^2} \right)^2 \left( \frac{e}{mc} \right)^2 \left( \frac{\hbar}{2\omega} \right)^2 \frac{2P^2}{3} 4\pi \left[ E_0 + \frac{\hbar^2 k^2}{2\mu} - h\omega \right] $$

$$ = \frac{2\pi}{h} \left( \frac{V^2}{2\pi} \right)^2 \left( \frac{4\pi e^2}{Vn^2} \right)^2 \left( \frac{e}{mc} \right)^2 \left( \frac{\hbar}{2\omega} \right)^2 \frac{2P^2}{3} 4\pi \left( \frac{\hbar^2}{2m} \right)^{3/2} \frac{1}{2} \int du u^{1/2} \delta \left[ E_0 + u - h\omega \right] $$

$$ = \frac{2\pi}{h} \left( \frac{V^2}{2\pi} \right)^2 \left( \frac{4\pi e^2}{Vn^2} \right)^2 \left( \frac{e}{mc} \right)^2 \left( \frac{\hbar}{2\omega} \right)^2 \frac{2P^2}{3} 4\pi \left( \frac{\hbar^2}{2m} \right)^{3/2} \frac{1}{2} \left( h\omega - E_0 \right)^{1/2} $$

$$ = \left( \frac{2}{3} \right) \left( \frac{e^2}{mn} \right)^2 \left( \frac{P^2}{\omega} \right) \left( \frac{2\mu}{\hbar^2} \right)^{3/2} \left( h\omega - E_0 \right)^{1/2} $$

$$ = \left( \frac{4\sqrt{2}e^2 P^2}{3m^2 \hbar^2 \omega n^2} \right)^{3/2} \left( h\omega - E_0 \right)^{1/2} $$
Now let’s consider the following geometry:

![Figure 5. Light penetrates an object.](image)

Radiation of intensity $I_0$ (W/cm$^2$) is incident on an infinitesimally thin slab of thickness $\Delta x$ and area $A$. The radiation exiting the slab is, by definition of the absorption coefficient, 

$I = I_0 e^{-\alpha \Delta x}$, therefore, the power lost in the slab is

$$P_{\text{loss}} = A (I_0 - I_0 e^{-\alpha \Delta x}) = I_0 A (1 - e^{-\alpha \Delta x}) = I_0 A \alpha \Delta x$$

(2.55)

Therefore, the power loss per unit volume is

$$\frac{P_{\text{loss}}}{ADx} = \frac{R\hbar \omega}{ADx} = I_0 \alpha$$

(2.56)

Now if only one photon is incident, $I_0 = \hbar \omega / ADt$, which means

$$\alpha = \frac{Rn}{c}$$

$$\varepsilon_2 = \left( \frac{nc}{\omega} \right) \alpha = \frac{Rn^2}{\omega}$$

(2.57)
Combining this with Eq. 2.54, we obtain

\[
\alpha = \left( \frac{4\sqrt{2}e^2 P^2}{3m^2 \hbar^3 \omega c n} \right) \mu^{3/2} \left( \hbar \omega - E_0 \right)^{1/2}
\]

\[
\varepsilon_2 = \left( \frac{4\sqrt{2}e^2 P^2}{3m^2 \hbar^3 \omega c n} \right) \mu^{3/2} \left( \hbar \omega - E_0 \right)^{1/2}
\]

The real absorption/ dielectric function is the sum of two terms like this, one for heavy holes and one for light holes. The only difference between the two terms is the reduced mass \( \mu \).

**(E) Theory of the dielectric function of semiconductors** The dielectric function in Eq. (2.63) in Ref 51 is obtained from a full integration over the BZ. Since \( k \) is conserved in the allowed transitions, then one can convert the summation in Eq. (2.63) to an integral over the \( k_x, k_y \) and \( k_z \) values in the first Brillouin zone of reciprocal space. These integration variables can be converted into energy \( E' \) and two wavevector variables \( k_1 \) and \( k_2 \) that sweep out the points on a constant energy surface \( S \) defined by \( E' = E_{cv}(k) \) in the first zone. (The prime is added to distinguish the integration variable \( E' \) from the photon energy \( E \).) With this transformation one obtains the expression

\[
\varepsilon(E) = 1 + \frac{e^2 \hbar^2}{4\pi^2 \epsilon_0 m^2} \sum_{cv} \int dE' \int dk_x dk_y \frac{|e.p_{cv}(k)|^2}{[E_{cv}(k)]^2 [\nabla_k E_{cv}(k)]^2} \times \left( \frac{1}{E_{cv}(k) - E - i\Gamma} + \frac{1}{E_{cv}(k) + E + i\Gamma} \right)
\]

\[
(2.59)
\]

The following expression for \( \varepsilon_2(E) \) can be derived:

\[
\varepsilon_2(E) = \frac{e^2 \hbar^2}{4\pi^2 \epsilon_0 m^2 E^2} \sum_{cv} \int dk_x dk_y \frac{|e.p_{cv}(k)|^2}{[\nabla_k E_{cv}(k)]^2}
\]

\[
(2.60)
\]
Here the integration is over the surface with an energy difference \( E' = E_{cv}(k) \) given by the specific value of the photon energy \( E \).

**Band structure and critical points in solids.** One can relate the dielectric function more closely to the band structure by noting that the joint density of states \( J_{cv}(E') \), defined as the number of single-spin electronic states per volume per energy interval, separated by energy \( E' \) is given by:

\[
J_{cv}(E') = \frac{1}{8\pi^2} \int \frac{dk_1dk_2}{|\nabla_k E_{cv}(k)|}
\]

If the dependence of the momentum matrix element on \( k_1 \) and \( k_2 \) can be neglected, then Eq. (2.59) can be rewritten as

\[
\varepsilon(E) = 1 + \frac{2e^2\hbar^2}{\varepsilon_0 m^2} \sum_{cv} \int J_{cv}(E') \left| \frac{e \cdot p_{cv}(E')}{E'^2} \right|^2 \left( \frac{1}{E' - E - i\Gamma} + \frac{1}{E' + E + i\Gamma} \right) dE'
\]

And

\[
\varepsilon_2(E) = \frac{2\pi e^2\hbar^2}{\varepsilon_0 m^2 E^2} \sum_{cv} \left| e \cdot p_{cv}(E) \right|^2 J_{cv}(E)
\]

This expression shows clearly the close relationship between the imaginary part of the dielectric function and the joint density of electronic states.

The joint density of states in Eq. (2.61), and hence the dielectric function of Eq.(2.62) and imaginary part of dielectric function (2.63) exhibit sharp structure when \( \nabla_k E_{cv}(k) = 0 \), and the points in \( k \) -space where this condition is met are called critical points or van Hove singularities.
A general form of the dielectric function associated with a critical point can be written as:

\[ \varepsilon(E) = A \Gamma^p \exp(i\varphi)(E - E_g + i\Gamma)^{-p} \]  \hspace{1cm} (2.64)

Where \( A \) is an amplitude factor, \( \varphi \) is the phase projection factor, and \(-p\) is the exponent. The exponent \(-p\) takes on the values of \(-1/2, 0\) (logarithmic), and \(1/2\) for 1D, 2D, and 3D critical points, respectively. With Eq. (2.64) one can also describe the critical point lineshape for discrete excitons, by setting \( p=1 \). In this case, the phase factor is interpreted as a coupling parameter between the exciton and the overlapping interband continuum.

The functional form of Eq. (2.64) is not Kramers-Kronig consistent and is valid only in critical point analyses.

**(G) Kramers-Kronig relations.** The real and imaginary parts of the complex index of refraction are not independent quantities, nor are the real and imaginary parts of the complex dielectric function. The Kramers-Kronig relation connects the real and imaginary parts of the complex index of refraction and complex dielectric function as follows

\[ n(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E'k(E')}{E'^2 - E^2} dE' \]  \hspace{1cm} (2.65)

\[ \varepsilon_1(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E'\varepsilon(E')}{E'^2 - E^2} dE' \]  \hspace{1cm} (2.66)

In other words, if the spectrum of the absorptive part of the optical constants is known, the real part may be evaluated from the equations above. The optical properties of all materials are determined by the types and strengths of the optical absorption processes that occur in the material.
Table 1. The form of the joint density of electronic states $J_{cv}(E)$ versus photon energy $E$ for allowed transitions in the neighborhood of band structure critical points of different types.

<table>
<thead>
<tr>
<th>Type</th>
<th>$D_j(E&lt;E_0)$</th>
<th>$D_j(E&gt;E_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three dimensions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_0$</td>
<td>0</td>
<td>$(E-E_0)^{1/2}$</td>
</tr>
<tr>
<td>$M_1$</td>
<td>$C-(E_0-E)^{1/2}$</td>
<td>$C$</td>
</tr>
<tr>
<td>$M_2$</td>
<td>$C$</td>
<td>$C-(E-E_0)^{1/2}$</td>
</tr>
<tr>
<td>$M_3$</td>
<td>$(E_0-E)^{1/2}$</td>
<td>0</td>
</tr>
<tr>
<td>Two dimensions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_0$</td>
<td>0</td>
<td>$C$</td>
</tr>
<tr>
<td>$M_1$</td>
<td>$-\ln(E_0-E)$</td>
<td>$-\ln(E-E_0)$</td>
</tr>
<tr>
<td>$M_2$</td>
<td>$C$</td>
<td>0</td>
</tr>
<tr>
<td>One dimension</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_0$</td>
<td>0</td>
<td>$(E-E_0)^{1/2}$</td>
</tr>
<tr>
<td>$M_1$</td>
<td>$(E_0-E)^{1/2}$</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 6. Behavior of the joint density of states, as well as the imaginary part of the dielectric function in the absence of broadening, versus optical frequency in the neighborhood of one-, two-, and three-dimensional critical points of different types. Reprinted with permission from “Handbook of Ellipsometry” ELSEVIER.
2.2 Quantum Theory of Photoluminescence

(A). **Absorption Rate at Finite Temperature.** A simple formalism can be used to compute the photoluminescence spectrum. At non-zero temperature the state $E_c(k)$ is occupied with probability $f[E_c(k)]$ and the state $E_v(k)$ is occupied with probability $f[E_v(k)]$. So in this case the absorption rate is

$$R = \frac{2\pi}{\hbar} \sum_k \left[ |H_{or}^-|^2 f[E_v(k)] \{1 - f[E_c(k)]\} \right] \delta\{E_c(k) - E_v(k) - \hbar\omega\}$$

(2.67)

Here the second term represents the possibility of photon emission from the excited carriers in the conduction band. Now the $H^-$ Hamiltonian acts on a state with one photon, whereas the $H^+$ Hamiltonian acts on a state with zero photon. So the matrix elements are identical, and we obtain

$$R = \frac{2\pi}{\hbar} \sum_k \left[ |H_{or}^-|^2 \{ f[E_v(k)] - f[E_c(k)]\} \right] \delta\{E_c(k) - E_v(k) - \hbar\omega\}$$

(2.68)

Near the direct gap where one can assume that the bands are parabolic and isotropic, the Fermi functions in the expression are actually functions of $\omega$ due to the delta function:

$$E_v(k) = E_0 + \frac{\hbar^2 k^2}{2m_e} = E_0 + \left( \frac{\mu}{m_e} \right) (\hbar\omega - E_0)$$

$$E_v(k) = -\frac{\hbar^2 k^2}{2m_h} = -\left( \frac{\mu}{m_h} \right) (\hbar\omega - E_0)$$

(2.69)
Accordingly, we can take the Fermi functions outside the summation over $k$, and therefore, we get

$$
\alpha = \frac{4\sqrt{2} e^2 P^2}{3m^2 \hbar c n c n} \mu \nu^2 (\hbar \omega - E_0)^{1/2} \left[ f_0 (\hbar \omega) - f_0 (\hbar \omega) \right]
$$

(2.70)

where $\alpha_0$ is the zero temperature absorption and we have defined

$$
f_0 (\hbar \omega) \equiv f \left[ E_v (k) \right]
$$

$$
f_0 (\hbar \omega) \equiv f \left[ E_c (k) \right]
$$

(B). Spontaneous Emission. To compute the spontaneous emission, we return to the full expression of the transition rate before going to the limit of zero wavevector.

Thus the corresponding transition rate is

$$
R = \frac{2\pi}{\hbar} \sum_{k, \lambda, k_c} \left[ H_{\lambda \epsilon}^+ \right]^2 f \left[ E_c (k + k_c) \right] \left[ 1 - f \left[ E_v (k) \right] \right] \delta \left[ E_c (k + k_c) - E_v (k) - \hbar \omega \right]
$$

(2.72)

Where the operator acts on an empty photon state. If we convert the sum over $k$ into an integral, and note that the sum over polarizations will give a factor of 2.

$$
R = \left( \frac{2\pi}{\hbar} \right)^2 \frac{V}{(2\pi)^3} \int d\Omega d\omega \sum_{k_c} \left[ H_{\lambda \epsilon}^+ \right]^2 f \left[ E_c (k + k_c) \right] \left[ 1 - f \left[ E_v (k) \right] \right] \delta \left[ E_c (k + k_c) - E_v (k) - \hbar \omega \right]
$$

$$
= \left( \frac{2\pi}{\hbar} \right)^2 \frac{V}{(2\pi)^3} \left( \frac{n}{c} \right)^3 \int d\Omega d\omega \int \sum_{k_c} \left[ H_{\lambda \epsilon}^+ \right]^2 f \left[ E_c (k + k_c) \right] \left[ 1 - f \left[ E_v (k) \right] \right] \delta \left[ E_c (k + k_c) - E_v (k) - \hbar \omega \right]
$$

(2.73)
Now experimentally, we measure the emission into a certain solid angle $d\Omega$, for a certain range of energy $dE$, and we want the emission rate per unit volume, since of course the emission by an infinite solid is infinite. In other words, we are interested in the quantity

$$\frac{1}{V} \frac{dR}{d\Omega d\omega} =$$

$$\frac{2\pi}{\hbar} \left( \frac{2}{(2\pi)^3} \right) \left( \frac{n}{c} \right)^3 \omega^3 \sum_{k} \left[ \left( \frac{E_c(k)}{\hbar} \right)^2 f \left[ E_c(k) \right] \left( 1 - f \left[ E_c(k) \right] \right) \delta \left[ E_c(k) - E_r(k) - \omega \right] \right]$$

We now switch to the limit of vanishing light wave vector, so we can use $k$ again for the electronic wave vectors

$$\frac{1}{V} \frac{dR}{d\Omega d\omega} =$$

$$\frac{2\pi}{\hbar} \left( \frac{2}{(2\pi)^3} \right) \left( \frac{n}{c} \right)^3 \omega^3 \sum_{k} \left[ \left( \frac{E_c(k)}{\hbar} \right)^2 f \left[ E_c(k) \right] \left( 1 - f \left[ E_c(k) \right] \right) \delta \left[ E_c(k) - E_r(k) - \omega \right] \right]$$

(2.74)

(2.75)
Now the Fermi functions can be rewritten as

\[
f(E_v)[1 - f(E_v)] = \frac{1}{\exp\left(\frac{E_v - E_c}{k_BT}\right) + 1}\left[1 - \frac{1}{\exp\left(\frac{E_v - E_c}{k_BT}\right) + 1}\right] = \frac{\exp\left(\frac{E_v - E_c}{k_BT}\right)}{\left[\exp\left(\frac{E_v - E_c}{k_BT}\right) + 1\right]^2}
\]

\[
= \frac{\exp\left(\frac{E_v - E_c}{k_BT}\right) - 1}{\left[\exp\left(\frac{E_v - E_c}{k_BT}\right) + 1\right]^2}
\]

\[
= \left[f(E_v) - f(E_v)\right] \frac{1}{\exp\left(\frac{\hbar\omega - \Delta F}{k_BT}\right) - 1}
\]

(2.76)

Then we can express the differential transition rate as

\[
\frac{1}{V} \frac{dR}{d\Omega d\omega} = \frac{2}{(2\pi)^3} \frac{2 \hbar}{(2\pi)^3} \omega^2 \left[\frac{1}{\exp\left(\frac{\hbar\omega - \Delta F}{k_BT}\right) - 1}\right] \sum_k \left[H^*_{\omega}\int \{f[E_v(k)] - f[E_v(k)]\} \delta[E_v(k) - E_v(k) - \hbar\omega]\right] 
\]

\[
= \frac{2}{(2\pi)^3} \frac{n^2}{c^2} \omega^2 \left[\frac{1}{\exp\left(\frac{\hbar\omega - \Delta F}{k_BT}\right) - 1}\right] \sum_k \left[H^*_{\omega}\int \{f[E_v(k)] - f[E_v(k)]\} \delta[E_v(k) - E_v(k) - \hbar\omega]\right] 
\]

\[
= \frac{2}{(2\pi)^3} \frac{n^2}{c^2} \omega^2 \left[\frac{1}{\exp\left(\frac{\hbar\omega - \Delta F}{k_BT}\right) - 1}\right] \alpha
\]

(2.77)
If we now express the differential transition rate in terms of energy:

$$\frac{1}{V} \frac{d^2R}{d\Omega dE} = \frac{2}{(2\pi \hbar)^3} \left( \frac{nE}{c} \right)^2 \left[ \alpha \exp\left(\frac{E - \Delta F}{k_B T}\right) - 1 \right]$$

(2.78)

This is the so-called Van Rosbroeck-Schockley equation.\(^{54}\)

**Figure 7.** Calculated indirect gap absorption for pure Ge with \(K = \text{constant}\) (dotted line) and with \(K = \text{constant}/(E_0 - E)^2\) (solid line). The inset shows the relevant portion of the electronic band structure and the two-step emission process leading to the resonant denominator.

**C. Indirect gap emission.** The inset in Figure 7 shows schematically the band structure of Ge in the indirect band-gap region. The minimum of the conduction band is at the L point of the BZ. The transition from the maximum of the valence band at the \(\Gamma\) point to the minimum of the conduction band at \(L\) is the indirect gap with energy \(E_{\text{ind}}\), which is the fundamental band gap in Ge. For emission associated with this gap, we must involve the electron-phonon interaction, which we can write.\(^{55}\)
\[ H_{cl} = \sum_{kq} M_{k,k-q} c_k^+ c_{k-q} \left( b_q^+ + b_q \right) \] (2.79)

We assume, following Ridley Eq. 5.116,

\[ M_{k,k-q} = \sqrt{\frac{\hbar}{2 \rho \Omega V}} D \] (2.80)

where \( D \) is the deformation potential.

For later convenience, we also write Eq. (2.45) as

\[ H_{cR}^+ = \sum_{k,\lambda, \lambda'} A_{k-k, \lambda, \lambda'} c_k^+ c_{k-\lambda} a_{\lambda'}^{\lambda} \] (2.81)

with

\[ A_{k-k, \lambda, \lambda'} = \left( \frac{4\pi c^2}{n^2 V} \right)^{1/2} \left( \frac{e}{mc} \right) \left( \frac{\hbar}{2\omega_k} \right)^{1/2} e_{\lambda \lambda'} \cdot p_{k-k, \lambda} \] (2.82)

The perturbation Hamiltonian is thus

\[ H = H_{cR} + H_{cl} \] (2.83)

To obtain emission we need to take this to second order, so the transition rate is

\[ R_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \sum_m \left( f \left| H \right| m \right) \left( m \left| H \right| i \right) \right|^2 \delta \left( E_f - E_i \right) \] (2.84)

Therefore, we obtain

\[ R = \frac{2\pi}{\hbar} \sum_{k, \lambda, \lambda', q} \left[ \sum_m \left( f \left| H_{cl}^+ \right| m \right) \left( m \left| H_{cl} \right| i \right) \right]^2 f_i \left( E_i^a \right) \left[ 1 - f_i \left( E_f^a \right) \right] \delta \left( E_f - E_i \right) \] (2.85)
Where the superscripts “el” mean electronic energy only. Notice that we are only including the $H_{eR}$ and $H_{eL}$ interaction to first order, because our final state has one extra photon. So we ignore “quadratic” terms that arise from Eq. (2.83). In the case of creating a photon, the relevant electron-radiation Hamiltonian is $H^*_e$. Processes in which the electron-phonon interaction move electrons across the band gap are unlikely because the denominator would be large and because we would have intraband matrix elements of the electron-radiation interaction, which are small. So the $eR$ radiation will move the electron from the conduction to the valence band. Notice also that we have taken the $eR/eL$ combination, but there is also in principle $eL/eR$. But the $eR$ operator acting on the initial state with an electron at the indirect gap conduction band can only move vertically at that point. Down to the $L$ point valence band, it is blocked by Pauli principle, and going up leads to large energy denominators. So the dominant contribution will be $eR/eL$. For this combination there are two main channels: (a) $eL$ moves the electron from $L$ to $\Gamma$, and $eR$ recombines the electron and hole at $\Gamma$; and (b) $eL$ moves a hole from $\Gamma$ to $L$, and $eR$ recombines the electron and the hole at $L$ across the $E_1$ gap. Process (a) is indicated in the inset in Figure 7.

We start with an electron close to the $L$ valley minimum, so the initial energy is $E_{\text{ind}}$. If the electron phonon interaction induces a transition to the $E_0$ minimum, the intermediate energy is $E_0 \pm h\Omega$. Therefore, the energy denominator is $E_0 \pm h\Omega - E_{\text{ind}}$. But the delta function in Eq. (2.84) implies $h\omega \pm h\Omega - E_{\text{ind}} = 0$. Combining these two expressions, the energy denominator becomes $E_0 - h\omega$. The alternative route to recombination would be a phonon transition in the valence band moving a hole from the $\Gamma$-point to the $L$ point, followed by an optical transition across the $E_1$ gap. In this case the denominator is
$E_1 - \hbar \omega$. But because the direct and indirect gaps are close in Ge and even more so in
GeSn, the $E_0 - \hbar \omega$ denominator will be very small at the relevant light frequencies, and
therefore this term will be dominant. The energy of $E_1$ is 2.2 eV, so the denominators
would be $2.2 \text{ eV} - 0.7 \text{ eV} = 1.5 \text{ eV}$ and $0.8 \text{ eV} - 0.7 \text{ eV} = 0.1 \text{ eV}$. So in principle the $L$
point transition is suppressed by $(1.5 \text{ eV} / 0.1 \text{ eV})^2 = 225$. Accordingly, we are going to
include only the transition across $E_0$. Interestingly, this means that if the $\Gamma$ valley is
populated, this may suppress the indirect emission.

We will first treat the case of phonon creation. Our initial state is an electron near the $L$
minimum of the conduction band and $n$ phonons with wave vector $-\mathbf{q}$. We call this state
$|1_{Lk}; n_{-q}\rangle$. The final state has one electron recombined near the $\Gamma$ point of the valence band,
one extra phonon, and one photon of wave vector $\mathbf{k}$. We call this state
$|1_{\Gamma k + q + \mathbf{k}}; n_{-q} + 1; 1_k\rangle$. Wave vector conservation is enforced by the matrix elements. So we
can write a typical term in the second-order perturbation theory expression as

$$\frac{\langle n_q + 1; 1_{\Gamma k + q + \mathbf{k}} | A^{cv}_{k + q, k, k, q} c^+_{{\Gamma k + q, k}} c^+_{{\Gamma k, q}} c^+_{{\Gamma k + q, k}} a^+_{{\Gamma k + q, k}} | 1_{Lc, k}; n_{-q} + 1 \rangle \langle n_q + 1; 1_{\Gamma k + q} | M^{cv}_{k + q, k, k, q} c^+_{{\Gamma k + q, k}} c^+_{{\Gamma k, q}} c^+_{{\Gamma k + q, k}} b^+_{{\Gamma k + q, k}} | 1_{Lc, k}; n_{-q} \rangle}{E_{\Gamma k + q} + \hbar \Omega_{-q} - E_{Lc, k}}$$

$$= \frac{A^{cv}_{k + q, k, k, q} M^{cv}_{k + q, k, k, q} \sqrt{n_q + 1}}{E_{\Gamma k + q} + \hbar \Omega_{-q} - E_{Lc, k}}$$

(2.86)

Where we have omitted the obvious quantum numbers for the photons.
Now the energies needed are

\[ E_i = E_{Lc,k} \]
\[ E_f = E_{Tv,k,q} + \hbar \omega_{-q} + \hbar \omega_k \]

But because \( E_i = E_f \) due to the delta function, then the denominator in Eq. (2.86) is

\[ E_{Tv,k,q} + \hbar \omega_{-q} - E_{Lc,k} = E_{Tv,k,q} - E_{Tv,k,q} - \hbar \omega_k \]  
\[ 2.87 \]

So that the expression for the second-order perturbation theory becomes

\[ \frac{A_{k+q-k,k}^c M_{k+q,k}^c \sqrt{n_{-q} + 1}}{E_{Tv,k,q} + \hbar \omega_{-q} - E_{Lc,k}} = \frac{A_{k+q-k,k}^c M_{k+q,k}^c \sqrt{n_{-q} + 1}}{E_{Tv,k,q} - E_{Tv,k,q} - \hbar \omega_k} \]  
\[ 2.88 \]

Therefore, the transition rate is

\[ R = \frac{2\pi}{\hbar} \sum_{k,k_1} \left[ \frac{A_{k+q-k,k}^c M_{k+q,k}^c \sqrt{n_{-q} + 1}}{E_{Tv,k,q} - E_{Tv,k,q} - \hbar \omega_k} f_c \left( E_{Lc,k} \right) \left[ 1 - f_e \left( E_{Tv,k,q} \pm \hbar \omega_k - E_{Lc,k} \right) \right] \right] \]

\[ 2.89 \]

Notice that since the wave vectors \( k \) and \( q \) are fixed for a particular choice of initial and final states, then the intermediate state summation reduces to a single state. We can see this clearly in the limit in which we neglect the wave vector of light, as we do below. So if we have a hole in the valence band, this can only be filled from a conduction band state vertically above it, so there is only one intermediate state.
We first do the summation over the light’s wavevector $\mathbf{k}$,

\[
R = \frac{2\pi}{\hbar} \left[ \frac{2V}{(2\pi)^3} \right] \sum_{k, q} \left[ \frac{A_{k+q, k}^c M_{k+q, k}^c \sqrt{n_q + 1}}{E_{k+q, k} - E_{k, k} - \omega_k} f_c(E_{k+q, k}) \left[ 1 - f_c(E_{k, k}) \right] \right] \delta \left[ E_{k+q, k} + \hbar \Omega_q + \hbar \omega_k - E_{k, k} \right]
\]

\[
= \frac{2\pi}{\hbar} \left[ \frac{2V}{(2\pi)^3} \right] \int \frac{d\Omega d\omega}{c} \sum_{k, q} \left[ \frac{A_{k+q, k, q} M_{k, k, q} \sqrt{n_q + 1}}{E_{k+q, k, q} - E_{k, k, q} - \omega_k} f_c(E_{k+q, k, q}) \left[ 1 - f_c(E_{k, k, q}) \right] \right] \delta \left[ E_{k+q, k, q} + \hbar \Omega_q + \hbar \omega_k - E_{k, k, q} \right]
\]

\hspace{1cm} (2.90)

Therefore, the differential transition rate per unit volume is

\[
\frac{1}{V} \frac{dR}{d\Omega d\omega} = \frac{2\pi}{\hbar} \left[ \frac{2V}{(2\pi)^3} \right] \left( \frac{n}{c} \right)^3 \omega^2 \times
\]

\[
\sum_{k, q} \left[ \frac{A_{k, k, q} M_{k, k, q} \sqrt{n_q + 1}}{E_{k+q, k, q} - E_{k, k, q} - \omega_k} f_c(E_{k+q, k, q}) \left[ 1 - f_c(E_{k, k, q}) \right] \right] \delta \left[ E_{k+q, k, q} + \hbar \Omega_q + \hbar \omega_k - E_{k, k, q} \right]
\]

\hspace{1cm} (2.91)

We can now neglect the $\mathbf{k}$ dependence of everything else. Since we are no longer using the symbol $\mathbf{k}$, we redefine it as $\mathbf{k} = \mathbf{k}_c + \mathbf{q}$. With these changes we can write:

\[
\frac{1}{V} \frac{dR}{d\Omega d\omega} = \frac{2\pi}{\hbar} \left[ \frac{2V}{(2\pi)^3} \right] \left( \frac{n}{c} \right)^3 \omega^2 \times
\]

\[
\sum_{k, q} \left[ \frac{A_{k, k, q} M_{k, k, q} \sqrt{n_q + 1}}{E_{k+q, k, q} - E_{k, k, q} - \omega_k} f_c(E_{k+q, k, q}) \left[ 1 - f_c(E_{k, k, q}) \right] \right] \delta \left[ E_{k+q, k, q} + \hbar \Omega_q + \hbar \omega_k - E_{k, k, q} \right]
\]

\hspace{1cm} (2.92)
Next we can use the manipulation in Eq.(2.76) to obtain

\[
\frac{1}{V} \frac{dR}{d\Omega d\omega} = \left[ \frac{2\pi}{\hbar} \right] \left[ \frac{2}{(2\pi)^3} \right] n^3 \omega^2 \times \left[ \frac{1}{\exp\left(\frac{\hbar \omega - \Delta F}{k_B T}\right) - 1} \right] \delta\left(E_{\Gamma,k} + \hbar \Omega - \hbar \omega - E_{\Gamma,k} - \hbar \omega \right)
\]

\[
= \frac{2\pi}{\hbar} \left[ \frac{2}{(2\pi)^3} \right] n^3 \omega^2 \times \left[ \frac{1}{\exp\left(\frac{\hbar \omega - \Delta F}{k_B T}\right) - 1} \right] \sum_{k,q} A_{k,k}^v M_{k,k-q}^v \sqrt{n_{k-q} + 1} \delta\left(E_{\Gamma,k} - E_{\Gamma,k} - \hbar \omega \right)
\]

To move forward, we assume a constant phonon frequency and we take the average of the momentum matrix element as we did for the direct gap emission. We then obtain

\[
\frac{1}{V} \frac{dR}{d\Omega d\omega} = \left[ \frac{2\pi}{\hbar} \right] \left[ \frac{2}{(2\pi)^3} \right] n^3 \omega^2 \times \left[ \frac{1}{\exp\left(\frac{\hbar \omega - \Delta F}{k_B T}\right) - 1} \right] \sum_{k,q} f_v(E_{\Gamma,k}) - f_c(E_{\Gamma,k}) \delta\left(E_{\Gamma,k} + \hbar \Omega - \hbar \omega - E_{\Gamma,k} - \hbar \omega \right)
\]

(2.94)

We now convert the sum over \( k \) into an integral over the density of states \( g_v \) of the valence band. For this, we notice that if write \( E = E_{vk} \) (where \( E \) is negative for the valence band), then we must have \( E_{c,k} = E_0 - (m_0/m_e) E = E_0 - \beta E \). We then obtain
The first such approximation is to take

Because this integral is difficult, it is customary to make some additional approximations.

Because of the delta function, the integral can be performed immediately, and we obtain

\[
\frac{1}{V} \frac{dR}{d\Omega \omega} = \frac{2\pi}{h} \left( \frac{n^3}{c} \right) \omega^2 \times \left( \frac{4\pi e^2}{n^2 V} \right)^{1/2} \left( \frac{e}{mc} \right) \left( \frac{h}{2\omega} \right)^{1/2} \left( \frac{2p^2}{3} \right) \left( \frac{h}{2\rho \Omega V} \right) D \left( n_\alpha + 1 \right) \left[ \frac{1}{\exp \left( \frac{h\omega - \Delta F}{k_b T} \right) - 1} \right]
\]

\[
(V) \int dE \sum_q f_q(E) - f_q(E_{v,\beta,q}) g_q(E) \delta \left[ E_{v,\alpha} + \hbar \omega + \hbar \omega - E_{v,\beta,q} \right]
\]

(2.95)

Next we convert the sum over \( q \) into an integral over the density of states in the conduction band

\[
\frac{1}{V} \frac{dR}{d\Omega \omega} = \frac{2\pi}{h} \left( \frac{n^3}{c} \right) \omega^2 \times \left( \frac{4\pi e^2}{n^2 V} \right)^{1/2} \left( \frac{e}{mc} \right) \left( \frac{h}{2\omega} \right)^{1/2} \left( \frac{2p^2}{3} \right) \left( \frac{h}{2\rho \Omega V} \right) D \left( n_\alpha + 1 \right) \left[ \frac{1}{\exp \left( \frac{h\omega - \Delta F}{k_b T} \right) - 1} \right]
\]

\[
(V) \sum_q f_q(E_{v,\beta,q} - \hbar \omega - \hbar \Omega) - f_q(E_{v,\beta,q}) g_q(E_{v,\beta,q} - \hbar \Omega - \hbar \omega)
\]

(2.96)

Because this integral is difficult, it is customary to make some additional approximations.

The first such approximation is to take \( 1+\beta = 0 \) in the denominator, which is equivalent to

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taking the denominator in Eq. (2.84) as a constant in the sum over intermediate states.

This is what is usually done, as an excellent approximation, in Si, but it is very questionable in Ge and much less in GeSn, where the denominator actually diverges. Because of this, we are adding a constant broadening. The second approximation is to take the Fermi functions out of the integral by making the Boltzmann approximation.

Thus we write:

\[ f_c(E) \left[ 1 - f_v(E - h\omega - h\Omega) \right] = \exp \left[ \frac{-(E - F_c)}{k_B T} \right] \exp \left[ \frac{-(F_u - E + h\omega + h\Omega)}{k_B T} \right] = \exp \left[ \frac{-(E + (h\omega - h\Omega) + F_u - F_c)}{k_B T} \right] = \exp \left[ \frac{-(h\omega + h\Omega - \Delta F)}{k_B T} \right] \]

Therefore, we obtain:

\[
\frac{1}{V} \frac{dR}{d\Omega d\omega} = \frac{2\pi}{h} \left[ \frac{2}{(2\pi)^3} \right] \left( \frac{n}{e} \right) \omega^2 \times \left[ \left( \frac{4\pi c^3}{n^3} \right)^{1/2} \left( \frac{e}{mc} \right) \left( \frac{h}{2\omega} \right) \right] \left[ \left( \frac{2p^2}{3} \right) \left( \frac{h}{2\rho\Omega V} \right) \right] (n_\Omega + 1) \exp \left[ \frac{-(h\omega + h\Omega - \Delta F)}{k_B T} \right] 
\]

\[
\left( \frac{V}{\omega} \right)^2 \int dE g_c(E) g_v(E - h\Omega - h\omega) 
\]

(2.98)

The limits of integration are \( E_{\text{ind}} \) and \( h\omega + h\Omega \). Now the density of states are given as

\[
g_c(E - h\omega - h\Omega) = \frac{\sqrt{2}}{\pi^2} \left( \frac{m}{\hbar^2} \right)^{3/2} \sqrt{\left( E - h\omega - h\Omega \right)} 
\]

(2.99)

\[
g_c(E) = \frac{\sqrt{2}}{\pi^2 \hbar^2} \left( \frac{m}{2m} \right)^{1/2} \sqrt{E - E_{\text{ind}}} 
\]
So we obtain

\[
\int_{E_{\text{ind}}}^{\hbar \omega + \hbar \Omega} dE g_r(E) g_r(E - \hbar \omega - \hbar \Omega) = \frac{\sqrt{2}}{\pi^2 m^2} \left( \frac{m}{\hbar^2} \right)^{3/2} \frac{1}{\pi^2 \hbar^4 m_\bot (2m_h)^{1/2}} \int_{E_{\text{ind}}}^{\hbar \omega + \hbar \Omega} dE \sqrt{E - E_{\text{ind}}} \sqrt{(E - \hbar \omega - \hbar \Omega)}
\] (2.100)

If we now change variables \( u = E - E_{\text{ind}} \) and call \( E_{\text{max}} = \hbar \omega + \hbar \Omega - E_{\text{ind}} \), we get

\[
\int_{E_{\text{ind}}}^{\hbar \omega + \hbar \Omega} dE \sqrt{E - E_{\text{ind}}} \sqrt{(E - \hbar \omega - \hbar \Omega)} = \int_0^{E_{\text{max}}} du \sqrt{E_{\text{max}} - u} \sqrt{u} = \frac{\pi E_{\text{max}}^2}{8}
\] (2.101)

We then finally obtain:

\[
\frac{1}{V} \frac{dR}{d\Omega d\omega} = \frac{2 \pi}{\hbar} \left( \frac{2}{2 \pi} \right) \left( \frac{n}{c} \right)^{2/3} \left( \frac{4 \pi e^2}{n^2 V} \right)^{1/2} \left( \frac{e}{mc} \right) \left( \frac{\hbar}{2 \omega} \right)^{1/2} \left( \frac{2 \rho^2}{3} \right) \left[ \frac{\hbar}{2 \rho \Omega V} \right] \left( n_\Omega + 1 \right) \exp \left[ \frac{-(\hbar \omega + \hbar \Omega - \Delta F)}{k_B T} \right] \frac{(V)}{(E_0 - \hbar \omega)^2 + \Gamma^2} \pi \left( \frac{2 \hbar^2}{\pi^2} \right)^{1/2} \left( \frac{m}{\hbar^2} \right)^{1/2} \left( \frac{2m_h}{m_\bot} \right)^{1/2} \pi \left( \frac{\hbar \omega + \hbar \Omega - E_{\text{ind}}}{E_{\text{ind}}} \right)
\] (2.102)

This can be simplified:

\[
\frac{1}{V} \frac{dR}{d\Omega d\omega} = \frac{1}{12 \pi^4 \hbar^6 c^3} \left( \frac{eP}{m} \right)^2 \left( \frac{\hbar}{\sqrt{\rho \Omega}} \right) \left[ \frac{m}{\hbar^2} \left( \frac{2m_h}{m_\bot} \right)^{1/2} \right] \times \omega \left( n_\Omega + 1 \right) \exp \left[ \frac{-(\hbar \omega + \hbar \Omega - \Delta F)}{k_B T} \right] \frac{(\hbar \omega + \hbar \Omega - E_{\text{ind}})^2}{(E_0 - \hbar \omega)^2 + \Gamma^2}
\] (2.103)
And if we write the differential expression in terms of energy:

\[
\frac{1}{V} \frac{dR}{d\Omega dE} = \frac{1}{12\pi^4h^5} \frac{n}{c^3} \left( \frac{e^2}{m^2} \right)^2 D^2 \left[ m_{v^2} m_c (2m_h)^{1/2} \right] E(n_\Omega + 1) \exp \left[ \frac{-(\hbar \omega + \hbar \Omega - \Delta F)}{k_B T} \right] \left( \frac{\hbar \omega + \hbar \Omega - E_{ind}}{E_0 - \hbar \omega} \right)^2 + \Gamma^2
\]

(2.104)

Notice that this goes like \( E/h^5 \), the same dependence that we obtain for the direct gap emission after combining Eq. (2.70) and Eq. (2.78). Eq.(2.104) is plotted as a solid line in Figure 7 (with \( \Gamma = 0 \)). In the figure the expression is compared with the energy dependence obtained by assuming \( E_0 - h\omega = \) constant, and we see that the two curves are quite different. This confirms our assertion that the assumption of constant denominator is invalid for Ge-like materials, for which it appears that any realistic treatment of the absorption requires the full integral.

2.3 Vibrational Properties of Semiconductors

Within the harmonic approximation, vibrations are described by

\[
\left( \Phi - \omega_j^2 M \right) \epsilon(f) = 0
\]

(2.105)

Here \( \Phi \) is a force-constant matrix whose elements are given by

\[
\Phi_{ij}(lk,l'k') = \partial^2 V(u)/(\partial u_i(lk)\partial u_j(l'k')) \text{ where } V(u) \text{ is the crystalline potential and the atomic displacements are indicated collectively by } u \text{ and } i, j \text{ means atoms with position at } k^{th} \text{ atom in } l \text{ unit cell and } k^{th} \text{ atom in } l' \text{ unit cell, respectively. The matrix } M \text{ is given by}
\]

\[
M_{ij}(lk,l'k') = M(k) \delta_{k_k,l'k'} \text{ where } M(k) \text{ is the mass of the } k^{th} \text{ atom in the unit cell.}
\]
(A) **Perturbations.** Perturbations like stress or alloying will change the force constant and mass matrices, so that (2.105) becomes

\[
\left[ (\Phi + \Delta \Phi) - \omega_f^2 (M + \Delta M) \right] \epsilon(f) = 0
\]  

(2.106)

Using an unperturbed eigenvectors base,

\[
\sum_f \left( \omega_0^2 - \omega_f^2 \right) \delta_{ff'} + \Delta \Phi_{ff'} - \omega_f^2 \Delta M_{ff'} \epsilon_{ff'} = 0
\]  

(2.107)

Where we have introduced the matrix elements

\[
\Delta M_{ff'} = \delta_0^* (f) \Delta M_0 (f') \quad \Delta \Phi_{ff'} = \delta_0^* (f) \Delta \Phi_0 (f')
\]  

(2.108)

The subscript “0” refers to unperturbed quantities. The \( c_{ff'} \) are the expansion coefficients of the perturbed eigenvectors in terms of the unperturbed ones:

\[
\epsilon_i (l, k | f) = \sum_{f'} c_{ff'} \epsilon_0 (l, k | f')
\]  

(2.109)

(B) **Raman scattering by phonons.** If we consider vibrations in crystals, the optical susceptibility can be written as

\[
\chi_{ij}(u) = \chi_{ij}(0) + \sum_k \chi_{ij,k} Q_k
\]  

(2.110)

Where \( \chi_{ij,k} = \frac{\partial \chi_{ij}(u)}{Q_k} \). In most Raman experiments, polarized light is used, the electric polarization induced by lattice vibration is
Here is the unit polarization vector of the incident light. The scattered light polarization direction is given by \( e^{(s)} \).

Thus the scattered intensity is:

\[
I_s \propto \left| e^{(s)} \frac{\partial \chi}{\partial u} u e^{(i)} \right|^2 \sim \left| e^{(s)} R^k_j e^{(i)} \right|^2
\]  

(2.111)

Here the subscripts i, j, k mean the x, y, z components which are also crystal principal axes, and the superscripts (i) and (s) indicate incident and scattered light, respectively.

\( \chi_{ij,k} \) is a third-rank tensor, and \( \chi_{ij,k} \) multiplied by a displacement vector \( u \) results in the second rank tensor \( R^k_{ji} \) with the equation \( \chi_{ij,k} u = \sum_k \chi_{ij,k} u_k \approx \sum_k R^k_{ji} e_k \). The Raman tensor \( R^k_{ji} \) depends on the incident light polarization \( j \), scattered light polarization \( i \), phonon polarization \( k \) and the crystal symmetry. The symmetry of Raman tensor determines Ramanallowed modes.

The Raman differential cross section is given by

\[
\frac{d^2 \sigma}{d\Omega d\omega} = \frac{\hbar V^2}{2c^3} \sum_j \left\{ n_f + \frac{1}{\omega_j} \right\} \left\{ n_f + 1 \right\} \delta(\omega - \omega_j + n_f \delta(\omega + \omega_j)) \left| \sum_y e_y \chi_{ij,y} e_i \right|^2
\]  

(2.112)

Here \( \omega_j \) is the Raman shift and \( n_f \) is the Bose-Einstein phonon occupation number for mode \( f \). The first term in the curly bracket gives Stokes scattering and the second term give anti-Stokes scattering.
To eliminate the dependence on volume, the “scattering efficiency” \( \frac{dS}{d\Omega d\omega} \) which is

Raman cross section per unit volume is introduced

\[
\frac{dS}{d\Omega d\omega} = \frac{\hbar}{2 \mu \omega} \sum_{\omega_k} \left( \omega_k - \omega \right)^4 \left\{ (n_k + 1) \delta(\omega - \omega_k) + n_k \delta(\omega + \omega_k) \right\} \sum_{ij} e_{di} R^k_{ij} e_{Lj} \tag{2.113}
\]

(C) **Raman tensor.** Since the intensity of Raman scattering is proportional to the
derivative of electronic susceptibility, the bond polarizability model is developed to
describe the electronic susceptibility. This model assigns to each bond a polarizability
which is axially symmetric, and the system’s polarizability is the sum of each bond.

\[
\Pi_{\alpha,\beta}(R) = \frac{R_{\alpha} R_{\beta}}{R^2} \alpha_{||}(R) + \left( \delta_{\alpha\beta} - \frac{R_{\alpha} R_{\beta}}{R^2} \right) \alpha_{\perp}(R) \tag{2.114}
\]

The coefficient \( \alpha_{||} \) and \( \alpha_{\perp} \) are assumed to be functions of the bond length only. Starting
from (2.112), one finds that the susceptibility derivative defined in (2.106) is given by

\[
\chi_{\alpha,\beta}(\omega) = -\frac{1}{V} \sum_{\sigma} \left[ \left\{ \alpha_{\sigma} [R(n)] + 2 \alpha_{\sigma} [R(nb)] \right\} \hat{R}_{x(n)} \hat{F}_{f} \right] + \left[ \left\{ \alpha_{\sigma} [R(n)] - \alpha_{\sigma} [R(nb)] - \frac{2}{3} \alpha_{\sigma} [R(nb)] \right\} \hat{R}_{(nb)} \hat{F}_{f} \right] \times \left\{ \hat{R}_{(nb)} \hat{F}_{f} \right\} \tag{2.115}
\]

Where prime means derivative with regard to bond length; \( R(nb) \) is the bond connecting
atoms \( n \) and \( b \) in equilibrium configuration with the direction \( \hat{R}(nb) \). For the specific
case of zone center phonons in diamond and zincblende semiconductors, the only independent component of the Raman tensor is given by

\[
a = \frac{4}{3\sqrt{3}} \left[ \alpha''_\parallel(R) - \alpha'_\perp(R) - \frac{2(\alpha''_\parallel(R) - \alpha'_\perp(R))}{R} \right]
\]

(2.116)

The Raman tensor for the three optical phonons which are degenerate at \( \Gamma \) in diamond-structure semiconductor is

\[
R_{ij,x} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & a \\ 0 & a & 0 \end{pmatrix}, \quad R_{ij,y} = \begin{pmatrix} 0 & 0 & a \\ 0 & 0 & 0 \\ a & 0 & 0 \end{pmatrix}, \quad R_{ij,z} = \begin{pmatrix} 0 & a & 0 \\ a & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}
\]

(D). Stress measurement. The application of stress alters the interatomic potential via the anharmonic part. The resulting changes in Raman frequencies is a sensitive tool to monitor the stress. For a cubic film epitaxially grown on a cubic substrate and pseudomorphically matched, the off-diagonal components of the strain are zero and the \( xx \) and \( yy \) diagonal components are given by \( e_{xx} = e_{yy} = (a_{\text{substrate}} - a_{\text{film}})/a_{\text{film}} \). The stress splits the three fold degenerate mode into a singlet and a doublet with Raman frequency shifts given by:

\[
\Delta \omega^2_{\text{singlet}} = \frac{2}{3} (p + 2q)(1 - \frac{C_{12}}{C_{11}})e_{xx} + \frac{2}{3} (q - p)(1 + \frac{2C_{12}}{C_{11}})e_{xx}
\]

(2.117)

\[
\Delta \omega^2_{\text{doublet}} = \frac{2}{3} (p + 2q)(1 - \frac{C_{12}}{C_{11}})e_{xx} - \frac{1}{3} (q - p)(1 + \frac{2C_{12}}{C_{11}})e_{xx}
\]

(2.118)

Here \( C \)'s are elastic constants. The strain perturbation has been discussed in Ref 58 and it is given in terms of the phonon deformation potentials \( p, q \) and \( r \).
CHAPTER 3

EXPERIMENT PROCEDURE

1. Electron Microscopy

The work in this thesis is done mainly on the four microscopes JEOL JEM 4000EX, JEOL JEM 2010F, JEOL ARM 200F and NION UltraSTEM100.

The TEM micrographs are acquired at 400kV acceleration voltage on the JEOL JEM 4000EX with LaB$_6$ source. The spherical aberration coefficient in this instrument is $C_s = 1\text{mm}$, the point-to-point resolution is $0.17\text{nm}$. It is installed with top entry double tilt holder, the tilt range is $\pm 25^\circ$.

The JEOL JEM 2010F can be operated in both TEM and STEM modes with its Schottky Field Emission gun operating at 200 kV. Its point-to-point resolution is $0.19\text{nm}$ in TEM mode and $0.14\text{nm}$ in annular dark field STEM mode. The beam diameter is $0.2\text{nm}$ for imaging in STEM mode and $1\text{nm}$ for EELS/EDS analysis for the work reported in this thesis. It accepts both a double-tilt holder and single-tilt holder with a tilt range $\pm 15^\circ$. This instrument is equipped with X-ray detector and energy-loss spectrometer for high spatial resolution microanalysis.

The ARM 200F is an aberration-corrected STEM equipped with a 50 square millimeter windowless light-element-sensitive X-ray detector and electron spectrometer with ultrafast EELS, which allows atomic level mapping covering a range of over $3,500\text{ eV}$ in dual EELS mode. The Schottky field emission gun and a CEOS CESCOR hexapole aberration corrector enables an image resolution of $0.095\text{ nm}$ and an EELS analysis resolution of $0.13\text{nm}$ for the experiments reported in this thesis. The spherical aberration
coefficient is submicron in STEM mode and $C_s = 0.5$ mm in TEM mode. The tilt range of the holder is ±15°.

The Nion UltraSTEM™ 100 is an aberration-corrected STEM that offers sub-angstrom resolution at both 100 keV and 60 keV with a high-brightness cold field emission electron gun (CFEG). The work presented in this thesis was performed at 100 keV. The system is equipped with a high-performance 3rd generation C3/C5 aberration corrector. A special monochromator offers ultra-fast EELS spectra at an energy resolution better than 20 meV (0.02 eV) which makes band gap measurements meaningful. The image resolution is < 1 Å, and the current can be > 0.5 nA with an atom-sized electron probe. Six sample cartridges are supplied with 3 fixed and 3 tilting ultra-stable sample stages using detachable sample cartridges with the tilt range of the tilting cartridge being ±25° (on 2 axes). The objective lens (OL) aberration coefficients (with 4 mm gap polepiece, at 100 keV) are $C_s = 1.1$ mm and $C_c = 1.1$ mm. Complete remote control is available, including sample exchange.

2. Review of Ellipsometry Theory

Ellipsometry is a sensitive technique that can be used to determine film thickness and optical constants. It is an indirect measurement technique, in the sense that the desired optical constants are the adjustable parameters of a model fit of the raw data. Ellipsometry measures the change of polarization state of the light, which is characterized by the ratio of the complex Fresnel reflection coefficient $R_p$ (p polarized light) and $R_s$ (s polarized light). Since the ratio itself is a complex number, it can be written as
The optical constants N and K can be derived from $\Psi$ and $\Delta$.

\[
\frac{R_p}{R_s} = \tan \psi e^{i\Delta} \tag{3.1}
\]

1. *linearly polarized light* ...

2. *reflect off sample* ...

3. *elliptically polarized light* !

Figure 8. Geometry of an ellipsometric experiment

The ellipsometer used in this thesis is a rotating analyzer ellipsometer (RAE) with adjustable retarder. The primary drawback of the RAE system is that it is not accurate if $\Delta$ is close to 0° or 180°. Besides, the range of $\Delta$ is 0°-360°, but the RAE system is limited to 0°-180°. By placing an adjustable compensating element after the polarizer and before the sample, we can generate any polarized state.

The optical elements are arranged so that the detector signal varies with polarization state of light, which makes it possible to determine the polarization state experimentally. Since the complex reflection coefficients in Eq. (3.1) are functions of the optical constants of the material, the latter can be obtained from a fit to adjust the experimental $\Psi$ and $\Delta$. The process is schematically described in Fig. 9
3. **Raman Instrument Setting**

Our Raman scattering setup is shown schematically in Figure 10. It consists of a single stage Acton Spectra Pro 275 monochromator equipped with 600, 1200 and 2400 grooves/mm gratings. It is generally operated in the backscattering geometry. The excitation source is a continuous wave laser (CW) operating in single line mode with typical wavelengths of 532nm and 364nm. The incident beam is polarized by a polarizer. An optical microscope is used to focus the beam onto the sample as well as to collect the scattered light. A beam splitter is needed to deflect the scattered light to the Acton spectrometer. The scattered light passes through the notch filters which reject Rayleigh scattered light and reflected light and an analyzer. The light dispersed by the spectrometer
is then collected by a liquid nitrogen cooled charge-coupled device (CCD) manufactured by Princeton Instruments. This Raman setup has a resolution of about 2 cm$^{-1}$.

**Figure 10.** Schematic diagram of back-scattering Raman setup.

### 4. Photoluminescence Instrument Setup

A 980nm solid-state laser with a dedicated power supply that supplies constant current is used as the excitation source. The output power is 400mW for the work reported in this thesis. The beam is bounced off a gold-coated mirror, and then focused on the sample by a spherical plano-convex lens with antireflection coating for the near-IR range. An optical chopper is placed in the beam path to provide modulation of the light with 190HZ frequency. The light is collected and focused into an $f=320$mm grating spectrometer for wavelength selection. The detector puts out a voltage that is proportional to the light intensity incident on the photodiode. By sweeping through a range of wavelengths and recording the voltage produced by the lock-in amplifier at each step with a time constant
of 3s and 15s integration time, a luminescence spectrum is produced. All the spectra are collected with LN$_2$ cooled InGaAs detector with the detection range 1.3-2.3 um. The luminescence spectra are acquired and manipulated using the Fluorescence software.

Figure 11. Schematic diagram of photoluminescence setup.
CHAPTER 4
NANOSTRUCTURE-PROPERTY CONTROL IN AlPSi₃/Si(100)
SEMICONDUCTORS USING DIRECT MOLECULAR ASSEMBLY: THEORY
MEETS EXPERIMENT AT THE ATOMIC LEVEL


1. Introduction

The synthesis of AlPSi₃ involves low temperature interactions of P(SiH₃)₃ designer hydrides and Al atomic beams, as illustrated schematically in Fig. 12.

Figure 12: Schematic model illustrating a plausible reaction pathway leading to the formation of AlPSi₃ films on Si(100) starting from the molecular and atomic sources (top left), forming an intermediate complex (center) and ultimately adsorbing intact on the Si surface via H₂ elimination (right). The latter configuration illustrates that adsorbed Al-P-Si₃ cores bond to the surface through the Si atoms (in this example) without significant strain penalty due to their structural and chemical compatibility with elemental Si.
It was suggested initially that these interactions lead to the formation of AlP(SiH₃)₃ intermediate complexes. The electron-rich P functionality has the required reactivity to readily combine with the acidic Al atoms to form Al-P bonds without any additional activation. The structure of the intermediate complex is shown in more detail in Fig. 13, and we see that it incorporates tetrahedral (III-V)-(IV)₃ units. Upon elimination of the terminal Si-H bonds, these units can condense intact as a solid with an average diamond structure.

**Figure 13.** Comparison of the simulated structures of the Al-P-Si₃ tetrahedral units in the hypothetical molecule AlH₃:P(SiH₃)₃ and the corresponding core as incorporated within the crystalline environment to form the extended solid network. Si, P, and Al are represented by gold, orange, and pink spheres, respectively. Note that the bond lengths and tetrahedral edge dimensions within an Al-P-Si₃ unit become more regular as the molecular adduct is incorporated into the solid via elimination of the terminal H atoms.

Similar pathways lead to the formation of AlNSiC quaternaries via reaction of molecular SiH₃CN and Al atoms at 700 °C. Under the low-temperature conditions employed in the current deposition experiments (475-500°C), the terminal Si-H bonds can be readily eliminated as H₂.
Note that only two distinct Al-P-Si₃ and P-Al-Si₃ conformations possess the structural motif and chemical makeup of the target solid. However, only the Al-P-Si₃ cluster in which the central P atom is bonded to 3 Si and 1 Al terminal species is a thermodynamically plausible bonding arrangement when viewed as an isolated molecule terminated by hydrogen atoms (Figure 13). The use of such molecular building blocks with preformed bonding arrangements should minimize or even completely avoid the formation of antiphase domains, atomic segregation, or energetically unfavorable bonds in the solid phase.

Figure 14. Polyhedral representation of the SiₓAlP crystal structure corresponding to two distinct arrangements of the AlPSi₃ units. The black arrows indicate the direction of the P-Al bonds. Because the tetrahedral contains 3 Si and 1 Al vertices, the formation of Al-Al bonds can also be avoided by properly orienting neighboring tetrahedra in such a way that only Si-Al bonds are formed. The resulting extended lattice contains a perfectly ordered P sublattice, where each P atom is at a third-neighbor distance from the next one.

The proposed growth mechanism requires that the tetrahedra be interconnected without inducing energetically costly bond strains. The encapsulation of P within a 4-fold coordination sphere of three Si and one Al atoms precludes the formation of undesirable P-P bonds and limits the donor-acceptor interactions to single Al-P functionalities within the structure. Because the tetrahedra contain 3 Si and 1 Al vertices, the formation of Al-Al bonds can also be avoided by properly orienting neighboring tetrahedra in such a way that only Si-Al bonds are formed. The resulting extended lattice contains a perfectly
ordered P sublattice, where each P atom is at a third-neighbor distance from the next one. When viewed from the (001) diamond-structure direction, the P atoms are arranged in columns that form a square lattice, with each column separated by a chess Knight move from its neighbors. The arrangement of the P atoms in Si₃AlP is therefore identical to the arrangement of the C atoms in the Si₄C structure proposed by Rücke et al.⁶¹ and related group IV analogues proposed by Crespi et al.⁶² If the Al atoms are also oriented in a regular fashion, it is possible to envision several simple crystalline structures, as shown in Figure 14, where a polyhedral scheme is used to emphasize the structural relationship between building blocks. Here, the terminal Al and Si atoms are shown as blue and gold spheres respectively, while the black arrows indicate the orientation of the {P,Al} pairs within each Al-P-Si₃ tetrahedron. The simplest ordered structure, shown in Figure 14(a), consists of {P,Al} pairs oriented along a common axis. In this case, the Al atoms also form a square columnar lattice, when viewed from the (001) direction, where each column is at a Knight’s move from the next one. Al atoms are at a third-neighbor distance from each other, so that the environment “seen” by Al atoms is symmetric to that seen by the P atoms. This is shown more clearly in Figure 15a. A more complex structure can be obtained by alternating the orientation of Al-P units within the rows of tetrahedra parallel to the viewing direction, as shown in Figure 14b. In this case, the P sublattice remains the same as in the first structure, whereas the columns of Al atoms, when viewed from the (001) direction, form an oblique lattice with two columns per unit cell. In this structure, some Al-Al pairs are second-neighbors, some are third-neighbors, and some are fourth-neighbors.
The relationship between the structures of Si$_3$AlP and the Si diamond lattice can be understood as follows. Figure 15a shows the conventional 8-atom diamond cubic cell (edge length $a$) and the unit cell for the Si$_3$AlP structure in Figure 14a. Because equivalent P or Al atoms are separated by two Knight steps, the dimensions of the Si$_3$AlP unit cell are \( \left( \frac{\sqrt{2}}{2} \right)^{1/2} a \times \left( \frac{\sqrt{2}}{2} \right)^{1/2} a \times a \), so that it contains 20 atoms. This implies that each unit cell contains 4 atom-centered tetrahedra (5 atoms each), as seen in Figure 15b.

**Figure 15.** (a) View along the cubic (001) direction in a Si$_3$AlP lattice indicating the conventional crystallographic cubic cell (red) and the 20-atom Si$_3$AlP cell (green), with $a \times a$ and $(5/2)^{1/2} a \times (5/2)^{1/2} a$ basal dimensions, respectively. The bottom part of the image corresponds to pure Si and suggests how full Si$_3$AlP tetrahedra could be deposited on a Si (001) surface. (b) Primitive 20-atom cell of a hypothetical ordered phase of Si$_3$AlP showing the placement of Al-P-Si$_3$ tetrahedral units, (c) view along a direction normal to the [110] planes of a conventional diamond lattice, and (d) extended view for the latter orientation using a ball-and-stick representation. In (b)-(d), the 20-atom cell is outlined using a thin black line. Legend: Si, yellow; Al, blue; P, violet.

Reorienting the latter cell along the conventional 110 normal of a diamond lattice shows the stacking order of the polyhedral units, as shown in Figure 15c. The resulting lattice can also be drawn using a simple ball and stick representation along a direction normal to
the [110] planes, revealing the familiar “dimer row” projection of a diamond lattice (see Figure 15d). Finally, disordered variants of the structure can be generated by randomizing the Al-atom distribution, which can be accomplished while still avoiding formation of direct Al-Al bonds and preserving the perfectly ordered nature of the P sublattice. The resulting disorder of the Si and Al sublattice in actual films has implications for the Raman spectra of the solid, as discussed in subsequent sections.

Aside from theoretical simulations described below, the experimental evidence for the proposed reaction path and resulting AlPSi$_3$ structure is so far indirect. The bulk composition of the AlPSi$_3$ films was found to invariably reflect the stoichiometry of the reactants according to the equation in Ref 16. Furthermore, the lattice parameter is close to the Vegard’s law average between Si and AlP, suggesting a genuine alloy behavior in the classical sense. Raman spectra, described below, are consistent with the disordered tetrahedral structure, and the measured dielectric function is close to ab initio predictions. Nevertheless, a detailed understanding of the actual nanostructure and its impact on optoelectronic behavior is still lacking, particularly with regard to the placement of the Al and P atoms in the lattice. Since the uniformity of the bonding configuration depends on growth conditions, a range of structural arrangements at the atomic scale are formed of which some may in fact contain the predicted motif of isolated Al-P units or others contain multiple Al-P or Si-Si domains. Different bonding arrangements in the crystal are likely generated (as is the case for most complex alloy relatives) by disproportionation of AlP(SiH$_3$)$_3$, which may be unavoidable due to fluctuations of growth temperature, deposition rate, reactor configuration, or variations of
conditions innate to the gas-source molecular beam epitaxy (MBE) processing techniques used in the film synthesis.

In this chapter, a deeper understanding of these issues pertaining to the Al-P-Si system is developed, allowing a meaningful study and interpretation of their optical properties. The nano-scale structure, elemental distribution and local bonding environment of selected AlPSi₃/Si(100) samples are investigated in order to gain insight into the local bonding environment of the Al, Si and P atoms in the lattice for the first time using element-selective electron-energy-loss spectroscopy (EELS) and STEM techniques. Structural models are then developed using ab initio methods to explain the new experimental observations and predict the concomitant effect of the crystal structure on the dielectric function of the alloy.

### 2. Synthesis Concepts

From a precursor development perspective, the isolation of the hypothetical AlH₃:P(SiH₃)₃ shown in Figure 12 as a stable single source compound may not be practical due to possible dissociation channels that eliminate silanes (SiH₄) under normal conditions. In pursuing a model adduct AlMe₃: P(SiH₃)₃ analogous to AlH₃:P(SiH₃)₃ by combining P(SiH₃)₃ and Me₃Al, the stable product obtained via elimination of MeSiH₃ was (SiH₃)₂PAI Me₂. To circumvent this issue, the deposition approach involves thermally activated reactions between the (H₃Si)₃P compound and Al atoms generated from a Knudsen cell in a gas source molecular beam epitaxy (GSMBE) chamber. The (H₃Si)₃P molecule is stable and highly volatile liquid with a significant vapor pressure of 18 Torr at 22°C, well suited for film growth by low pressure CVD.
3. Bonding Elucidating from Simulation and Raman spectroscopy

First-principles density functional theory calculations were conducted to study the structural and bonding properties of the new system at both the molecular and the solid-state level and compared to the experimental data. In view of the nano-scale assembly theme described above, one objective was to elucidate the structural changes associated with the incorporation of the “Al-P-Si₃” molecular units into the crystal. For this purpose, the “Al-P-Si₃” core is decorated with hydrogen atoms to form the neutral gas-phase H₃Al-P(SiH₃)₃ hydride molecule. The Gaussian 03 quantum chemistry package was used to obtain the optimized molecular structure at LDA level using a 6-311G+(3df, 3pd) basis set. The resulting static equilibrium structure, shown in Figure 13, can be viewed as an alane-P(SiH₃)₃ Lewis acid complex, in which the apical angle of alane (AlH₃) unit is only slightly smaller (~1-2°) than its isolated value and the -P-(SiH₃)₃ unit adopts essentially its free molecular value. First, it is shown that the Al-P bond length in the crystal is compressed to the expected value relative to that in the adduct while the P-Si bond becomes slightly dilated. Together, these two effects lead to regulation of the tetrahedral cores, as shown in Figure 13 where the edge lengths in the molecular core vary by more than 0.5Å while a much smaller difference of 0.04Å is found in the isolated core.

Accordingly, the resulting crystal structure assembled from these cores is expected to adopt a diamond-like topology. Next, the properties of the solid using DFT at the LDA level using the VASP code is investigated. Ultrasoft pseudopotentials were employed to treat the [Ne] cores of the Al, Si and P atoms with an overall energy cutoff of 400 eV. Reciprocal space integrations were carried out using a Monkhorst-Pack grid of between 20 and 40 irreducible k-points. Under these conditions, residual atomic forces and cell
stress were reduced to levels below 0.01 eV/A and 0.01 kbar, respectively, to yield well-converged crystalline structures close to the LDA limit.

The initial calculations for the solid phases, correspond to the crystal in Figures 14a and 15. The fully converged equilibrium structure shows that the 20-atom primitive cell has C1c1 symmetry (space group no. 9) with lattice parameters \(a_0 = 8.523 \, \text{Å}\), \(b_0 = 8.553 \, \text{Å}\), and \(c_0 = 5.448 \, \text{Å}\), and cell angles \(\alpha = \beta = 90^\circ\) and \(\gamma = 90.32^\circ\) (the point group in this case is Cs). The ground state for this simplest ordered structure is thus monoclinic, with basal dimensions \(a_0\) and \(b_0\) differing by \(~0.35\%\). This slight asymmetry is due entirely to the bias in the cell shape induced by the highly ordered arrangement of Si\(_3\)AlP units, as shown in Figure 15a. To make contact with the experimental structure, the basal dimensions can be averaged to yield a nominally tetragonal structure with

\[a_0^T = 8.538 \, \text{Å} \quad \text{and} \quad c_0^T = c_0 = 5.448 \, \text{Å},\]

and a c/a ratio of 0.6381. The latter value is slightly different from the ideal value of 0.6325 obtained for a 20-atom diamond cubic unit cell with dimensions \(a \times (5/2)^{1/2} \times a\), indicating that the relaxed equilibrium structure is expected to exhibit deviations from the cubic symmetry. The equivalent crystallographic value for the basal plane dimension, referenced to a silicon lattice, is \(a_0^T/(5/2)^{1/2} = 5.400 \, \text{Å}\). Adding 0.8\% of this value to account for LDA’s underestimate then gives a predicted value of 5.4432 Å, while the corresponding corrected value for the c-axis dimension is 5.4916 Å. A similar analysis for the structure in Figure 14b yields virtually identical estimates for the lattice constants and the degree of tetragonal distortion. The theoretically predicted c/a ratio based on these values is 1.0089 and increases to c/a = 1.013 if such a system is pseudomorphically grown on a (001) Si
substrate. This appears to contradict the experimental results, which show c/a = 1.003, a ratio that can be explained in terms of epitaxial strain without invoking any intrinsic tetragonal distortion. It should be noted, however, that the deviations from cubic symmetry predicted by simulation are likely attributable to the structural bias induced by the specific spatial arrangements of the building blocks within the nano-scale primitive cells employed. It is possible that these deviations will be substantially reduced in a supercell simulation containing a more isotropic arrangement of AlPSi$_3$-units.

Strong evidence for the residual orientational disorder that might lead to an average cubic structure is obtained from the Raman spectrum of the Si$_3$AlP films, shown in Figure 16. The spectrum was collected in the same scattering configuration for which Raman scattering in bulk Si is allowed. It is dominated by a strong peak at 512 cm$^{-1}$, which is assigned to Si-like optical vibrations. This peak is asymmetrically broadened, as is the case in tetrahedral semiconductor alloys. A broad feature that peaks around 450 cm$^{-1}$ and a significant scattering background covering the entire spectral range up to the main peak are shown. These spectral characteristics confirm that the idealized structures in Figure 14 are not obtained experimentally. On the other hand, the Raman spectrum also suggests that our Si$_3$AlP is considerably less disordered than the analogue Ge$_{1.2}$(GaAs)$_{0.4}$ alloy grown by conventional methods. The Raman spectrum of Ge$_{1.2}$(GaAs)$_{0.4}$ is dominated by a Ge-like feature, with a line shape similar to the Si$_3$AlP spectrum in Figure 16 of Ge$_{1.2}$(GaAs)$_{0.4}$ in Ref 69, the FWHM of the main peak is 8% of its frequency, whereas in our Si$_3$AlP sample, the FWHM is only 4% of the peak frequency. Second, in Ge$_{1.2}$(GaAs)$_{0.4}$, the peak is downshifted from the Raman peak of bulk Ge by 4% of the bulk Ge frequency, whereas in our sample the equivalent downshift is only 1.7% of the
bulk Si frequency. Because the force constants in tetrahedral semiconductors are very similar,\textsuperscript{70} it is expected that all shifts and widths in the two systems to be comparable when expressed as a percentage of the corresponding bulk parent material. Therefore, the observed discrepancies point to structural differences between the two systems, and the reduced width observed could be interpreted in terms of a more ordered compound, as expected from a growth mechanism that proceeds via incorporation of preformed tetrahedra. The vertical bars at the bottom of Figure 16 show the calculated zone-center frequencies for the ordered compound in Figure 15, rigidly upshifted by 6.7cm\textsuperscript{-1}, which is the difference between experimental and calculated frequencies for pure Si. The presence of modes over the entire spectral range of the measurements explains the enhanced background relative to the Si reference. The accumulation of modes in the 450-
475 cm\(^{-1}\) range matches well the broad experimental shoulder in that range, modes involving Al-P optical vibrations are expected.\(^1\) The highest predicted frequency is 506 cm\(^{-1}\), somewhat below the experimental value, but this discrepancy may also be due to the use of a fully ordered 20-atom structure in the phonon calculation.

### 4. 10 atoms unit cell

Among the large number of ordered structures obtained by permuting the Al atoms in the available sites, the lowest energy ones (including the ground state \(C1c1\) structure) often possess the highest symmetry. Accordingly we describe here a 10-atom primitive cell setting derived from the cubic diamond lattice using lattice vectors \(\bar{a}_1 = a_0(1,0,0)\), \(\bar{a}_2 = a_0\sqrt{3}(\frac{1}{6}, \frac{1}{3}, \frac{1}{2})\), and \(\bar{a}_3 = a_0\sqrt{3}(\frac{1}{6}, -\frac{1}{2}, \frac{1}{2})\). (Fig. 17)

![Figure 17](image)

**Figure 17.** (left) Silicon lattice with lines designating the monoclinic 10-atom \((C1c1)\) representation containing two III-V-(IV)\(_3\) units (green tetrahedral, central panel). Atomic coordinates are listed in the adjoining table, where \(U, U'\) designate group-V atom positions and the \(\{V_k\}\) and \(\{V'_k\}\) sites represent the group III/group IV atom positions. Note: For clarity, the origin has been shifted so that the tetrahedral units appear within the cell as drawn.

<table>
<thead>
<tr>
<th></th>
<th>(U)</th>
<th>(U')</th>
<th>(V_1)</th>
<th>(V_1')</th>
<th>(V_2)</th>
<th>(V_2')</th>
<th>(V_3)</th>
<th>(V_3')</th>
<th>(V_4)</th>
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<td>0.75, 0.50, 0.50</td>
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<td>0.00, 0.00, 0.00</td>
<td>0.35, 0.10, 0.70</td>
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Here, as in the case of the 20-atom cell, the Cartesian components are aligned with the conventional cubic (100), (010) and (001) directions in the parent crystal, respectively, facilitating a systematic comparison of calculated and observed Raman spectra. For
AlPSi$_3$ this setting accommodates two tetrahedral Al-P-Si$_3$ building units with the central P in fractional positions $U = \left( \frac{1}{2}, \frac{1}{3}, \frac{1}{12} \right)$ and $U' = \left( \frac{1}{2}, \frac{1}{4}, \frac{1}{12} \right)$, and the neighboring atoms at $V_n = \left\{ \left( \frac{1}{2}, \frac{1}{3}, \frac{1}{3} \right), \left( 0, 0, 0 \right), \left( \frac{1}{2}, \frac{1}{3}, \frac{1}{3} \right), \left( \frac{1}{2}, \frac{1}{4}, \frac{1}{4} \right) \right\}$ and $V'_n = \left\{ \left( \frac{1}{2}, \frac{1}{4}, \frac{1}{4} \right), \left( \frac{1}{2}, \frac{1}{4}, \frac{1}{12} \right), \left( \frac{1}{2}, \frac{1}{4}, \frac{1}{4} \right), \left( \frac{1}{2}, \frac{1}{4}, \frac{1}{12} \right) \right\}$, respectively, where $n=1,\ldots,4$, as shown in Fig. 17. The optimized ground state structure cell parameters are found to be $a_1=5.537$ Å, $a_2=6.736$ Å, $a_3=6.758$ Å, $\alpha=80.42^\circ$, $\beta=65.827^\circ$ and $\gamma=65.729^\circ$. Here the Al atoms are located at sites $V_1$ and $V'_3$, and resulting crystal has energy $\sim1$-2 meV/atom below that of the weighted sum of elemental constituents (FCC Al, hexagonal P, and diamond silicon) while a second ordered phase with only slightly higher energy ($\sim38$ meV/atom) is obtained by placing Al atoms on sites $V_1$ and $V'_3$ (structures with intermediate energies been identified in supercells which allow a symmetry reduction).

5. Nanoscale structure

Two representative samples designated 04, 06 were produced using procedures previously reported in our original description of the AlPSi$_3$ synthesis and used to conduct the analyses described in this chapter. One of the samples 04 is fully coherent to the Si substrate while sample 06 exhibits slight relaxation leading to slightly smaller in-plane lattice dimensions ($a_0 = 5.4377$ Å) as evidenced by high resolution XRD measurements. The corresponding molar volume of the latter is slightly smaller in spite of the fact that the bulk compositions of both samples, as measured by Rutherford Backscattering (RBS), are very close to the ideal AlPSi$_3$.

Initial examination of the thin film microstructure was conducted by transmission electron microscopy (XTEM) using a JEM-4000EX high-resolution electron microscope operated at 400keV and with a structural resolution of 1.7 Å. Studies of sample 04
showed uniform low defectivity layer with planar surface and well-defined interface (see Figure 18).

![Figure 18: TEM diffraction data of AlPSi$_3$/Si(001). (a) Cross-sectional micrograph showing the full epilayer grown lattice-matched on Si(100) wafer. The arrow denotes the interface. Panels (b) and (c) show diffraction patterns taken along 110 and 100 zone axes, respectively, indicating Si-like symmetry with no evidence of 200 spots due to zincblende structure in (c). High-resolution electron micrographs reveal a highly coherent interface exhibiting exact alignment of the \{111\} lattice planes between the film and the Si wafer due to the very close matching of the lattice dimensions. Selected area electron diffractions patterns taken in \{110\} projection indicated that the crystal has diamond cubic structure akin to Si as expected on the basis of previously reported structural models of diamond-like AlPSi$_3$.\textsuperscript{16} To probe for the possible existence of zincblende phase and/or AlP precipitation, diffraction patterns were recorded in [001] projection using plan-view specimens. The data from sample 04 showed the typical array of spots characteristic of bulk Si with no evidence of 200 reflections corresponding to cubic zincblende symmetry, as shown in Figure 18 panel (c). In this case, the TEM camera length was calibrated using a GaSb ($a_0 = 6.095$ Å) standard to measure the lattice constant of the film which was]
found to be of 5.44 Å, effectively identical to that determined by XRD. The XTEM images of sample 06 showed a uniform monocrystalline layer with a morphology comprising large contiguous swaths of defect-free material extending from the interface to the free surface. The boundaries of these regions exhibit threading defects. The interface of the film with the substrate is fully epitaxial but somewhat defected, showing some accumulation and bunching of short stacking defects. Selected area electron diffraction patterns along 001 taken from multiple areas within the film showed predominately diamond-like structure consistent with that of sample 04. In one isolated region an array of very weak 002 spots reminiscent of zincblende structure was observed in sample 06. While this diffraction behavior does not appear to be representative of the bulk film, it suggests that the atomic structure varies over isolated regions across the layer, particularly in the vicinity of the dislocated domains. In this case non-uniform bonding arrangements could presumably lead to locally segregated structures at the crystal boundaries producing the 002 spots. In spite of the latter there is no evidence shown by XRD and TEM imaging or compositional non-uniformities shown by EELS elemental profile measurements (described below) to support the existence of substantial phase separation.

Further structural and chemical analyses were made using EELS and aberration-corrected STEM to enable a detailed atomic-level elucidation of the bonding configurations and compositional profiles for samples 04 and 06 which show no structure inhomogeneity. These experiments were performed on a NION UltraSTEM100 microscope equipped with an Enfinium EELS spectrometer operating at 100kV. High-angle annular-dark-field (HAADF) microscopy was performed in STEM mode yielding
Figure 19: High-angle annular-dark-field (HAADF) image of AlPSi$_3$ film in [110] projection. The rectangular region analyzed by EELS (see Fig. 21) is shown by the green box. The white spots correspond to projections of atomic columns of dimers or “dumbbells” comprising Al, Si and P. These features are aligned with the 100 growth direction as indicated by the arrows in the inset.

[110] projection images such as that shown in Figure 19, for the representative case of sample 06 which consist of pairs of bright spots corresponding to the projection of dimers (or dumbbells) of the diamond-like lattice. The EELS spectra were acquired using a probe size of 0.13 nm, beam current of 120 pA, convergence semi-angle and collection angle of 30 mrad and ~ 45 mrad, respectively. The analysis was refined within a smaller sample region with lateral dimensions of 0.88x0.6 nm$^2$, shown by the green box in Figure 19. The thickness of the specimen at this spot was ~30 nm, as determined by the low-loss spectra. Approximately 400 energy loss-spectra each spanning a range of 1300-2400 eV were collected by rastering through this area with a uniform step size of 0.035 nm, with a typical exposure time of 0.1s and dispersion of 0.5 eV/channel. All scans revealed distinct peaks at 1560 eV, 1839 eV and 2146 eV, corresponding to the K-edges of Al, Si and P, respectively, in every sub-nanometer area probed, indicating the homogeneous presence of all three elements, as shown in Figure 20. The elemental concentrations were determined to be 20% Al, 20% P and 60 % Si in all cases with an experimental
uncertainty of 5%. Long line scans across 250 nm were also performed using EELS and the analyses were in agreement with the results obtained from the local areas.

**Figure 20.** EELS spectrum of sample 06 acquired from an area with 15 nm thickness. The spectrum show three distinct peak features after the ionization edge.

**Figure 21:** (top row) Elemental Si, Al and P maps for the 0.88x0.6 nm² area defined by the green box shown in Figure 19. Bottom row colored circles mark the positions of atomic columns. The colored panel at far right shows superposition of the elemental maps (top) and the overlay of the individual atomic column positions represented by circles (bottom). The apparent alignment of the Al-P pairs in the experimental map is confirmed by the overlaid atom positions obtained directly from the intensities within the individual elemental maps. Si, Al and P are designated by blue, green and pink circles, respectively.
The Al, Si and P K-edges in the EELS spectra for sample 06 were used to create individual elemental maps of the atomic columns within the area marked by the green box in Figure 19. The resultant intensity maps are shown on the panels in the top row of Figure 21. The brightest intensity pixels correspond to atomic positions within dimer columns (equivalent to the dumbbell in the HAADF image) while the intervening darker regions correspond to empty space in the lattice (dark areas on the HAADF image). The bright spots on the Si map (top row panel) have a rectangular shape elongated along the 001 direction corresponding to a full Si-Si dumbbell, as expected. This is shown in the lower Si panel where blue circles are superimposed to indicate the positions of the Si-Si atomic columns in the dimer. The bright spots in the Al and P maps are very similar in shape and size and appear to correspond to projections of individual atomic columns (1/2 dimer) rather than full dimers. The Al and P column positions are indicated by green and pink circles in the lower panels, respectively. From this graphic it is clear that the P atomic column positions are laterally displaced relative to those of Al atomic column positions, indicating that their projections when combined correspond to individual AlP like dimer columns along the [110] crystal direction. Superposition of the Al, P and Si spots produces the pattern shown in the bottom right panel with green, pink and blue circles, which corroborates that the Al and P atomic column positions each coincide with a Si-Si dimer position within the same dimer column. Furthermore, the Al and P sites exhibit preferential ordering of the atomic columns in a manner consistent with the existence of Al-P dimers with a common alignment relative to the growth direction, with the Al orienting toward the free surface and with the P atoms on the interface side. This is consistent with the colored overlay of the Si, Al and P sites shown in the top right
panel of Figure 21. The results indicate that the Al-P ordering coexists with a complete mixing of the three components Si, Al and P, yielding the Si$_3$AlP stoichiometry within the sample volume defined by the 0.88 x 0.6 nm$^2$ area of the green box and the 30 nm projected specimen thickness used to produce these elemental maps.

![Elemental Maps](image)

**Figure 22**: Si, P and Al maps for a 1.8 x 0.6 nm$^2$ area showing Si-Si dimer rows and P/Al single atom sites in 110 projection. The hybrid map on bottom left panel illustrates that the later atoms combine to form corresponding P-Al pairs exhibiting preferential alignment from left to right of each crystal column.

The Al-P ordering in this sample was further confirmed by analyzing multiple areas with varying sizes throughout the film. Figure 22 shows elemental maps extracted from a region with lateral dimensions of 1.8 x 0.6 nm$^2$ and a thickness of 30 nm, twice the size of the green box described above. The blue features in the Si map correspond to the Si-Si dumbbells while the green and red spots represent projections of the Al and P atoms, respectively. The combined Si/Al/P map on the bottom left panel of the figure clearly demonstrates that the atomic distribution is uniform and the P/Al constituents occupy left/right sites on the rectangular lattice, indicating preferential alignment of the dimers along the growth direction.

Next we compare the observed Al-P arrangements with theoretical predictions for the AlPSi$_3$ system, starting with the lowest energy $C1c1$ structure consistent with the
existence of isolated Al-P pairs. These are based on the assembly of integral AlPSi$_3$ building units which link to produce a diamond-like lattice with either ordered or rotationally disordered arrangements of isolated AlP pairs embedded within the parent Si matrix, as discussed in this chapter’s introduction. With the current resolution of our elemental images, the EELS maps of sample 06 can not be matched to any bonding configuration containing isolated Al-P pairs. Furthermore, matching these maps to segregated nano-scale arrangements of zinc blende AlP domains and pure Si within the sample volume probed by EELS is not successful. Although this type of structural motif may be energetically favored, there is no definitive evidence to support the existence of phase segregation into AlP zinc blende and Si diamond domains. In fact, the atomic-scale EELS analyses confirm the existence of a single-phase alloy with AlPSi$_3$ composition at the nano-scale. On the macro-scale, the single-phase character of the samples is corroborated by high-resolution triple axis XRD analysis of 004, 111 and 224 reflections, and XRD investigations of a range of AlPSi$_3$ samples which invariably yield a unique cubic lattice constant ($a_0$) in the range of 5.436 – 5.440 Å irrespective of layer thickness and growth conditions (T ~ 500-550 °C). The $a_0$ values for the alloy in all cases are found to be intermediate to those of the AlP and Si phases and closely follow the expected compositional dependence on the basis of Vegard’s Law. Furthermore, as mentioned previously electron diffraction patterns in the 100 zone axis did not show evidence of characteristic zinc blende spots (Figure 18) except in isolated regions of sample 06.

To explain the Al-P orientations observed in the EELS maps a model derived from the previous DFT ordered C1c1 structures is adopted. In this case the building block
units are allowed to partially dissociate so as to form short-range Al-P-Al-P-Al-P bonding arrangements. A simple structure, which retains the AlPSi$_3$ stoichiometry and the diamond–like symmetry, is shown in Figure 23 and is described as a 10 atom cell containing a short chain of Al-P bonds rather than isolated Al-P pairs. In this case, all P atoms are bonded to two Al and two Si atoms. Due to the formation of multiple Al-P bonds, the energy of this system is slightly lowered relative to that of the structures containing isolated AlP units (see table 1 below), but remains metastable relative to the zincblende AlP and Si. Moreover, the molar volume is virtually unchanged and the average lattice structure remains diamond-cubic. Figure 23 (bottom panel) shows a [110] projection of this AlPSi$_3$ model in which the Al, P and Si atoms are shown as violet, green and blue spheres (respectively) to simplify comparison with the EELS maps in Figure 21 above. While this model clearly accounts for the pattern observed in the EELS maps, it is stressed that the “chain” structure cells can be combined with the other “isolated Al-P pair” counterparts, provided that the latter structure is more prevalent. For example in addition to the model shown in Figure 23 the related chain-like structures of AlPSi$_3$ featuring simpler and shorter (Al-P)$_2$ linkages which are isolated within the Si matrix are simulated. These also reproduce the orientational alignment of the Al-P dimers along 110
Figure 23: (a) Ten atom unit cell model of a Si₃AlP structure containing multiple Al-P-Al-P bonds in the form of short chains (Si: gold, Al: blue, P: pink). (b) Extended representation of this model in [110] projection showing that the Al (green) and P (pink) atoms appear in a unique row. The Al-P dimers are aligned along the growth direction as shown in (c) where the bonds are omitted to facilitate comparison with experimental maps in Figure 21. Note that the Si (blue) are interleaved between the Al-P in an alternating manner down each atomic column.

projection like the above analog. This family of variants will be discussed in future work.

Here let us focus on the most plausible case from an experimental perspective with medium size chains (shown in Figure 23). From the point of view of synthesis, the modification of the tetrahedral Al-P(SiH₃)₃ intermediates and corresponding AlPSi₃ building blocks needed to produce the chain-like structure in the model of Figure 23 (or its variant) is rather minimal. In fact not all building blocks need to dissociate, thereby minimizing the prospect for energetically costly interdiffusion of the atoms at the growth front. The local bonding modifications can readily occur as a result of minor variations of the synthetic conditions. For example, the loss of a silyl (SiH₃) group from Al-P(SiH₃)₃
induced by temperature fluctuation may lead to AlPSi$_2$ cores which then combine with an integral AlPSi$_3$ cores to form the atomic Al-P-Al-P- bonding sequence (seen in figure 24) while Si from the remaining SiH$_2$ group inserts locally into the crystal to maintain the overall AlPSi$_3$ stoichiometry which is consistently obtained in our studies under a range of conditions. Specifically, the same bulk AlPSi$_3$ composition is reproducibly obtained over a 500-550 °C temperature range without any evidence of degradation of the bulk alloy properties, such as band gap and molar volume. In this context the prior work on the AlPSi$_3$ system has demonstrated that increasing the temperature above 550 °C also leads to the dissociation of the tetrahedral intermediates to enhance the Si content via possible loss of volatile P-hydrides.

On the basis of the assembly of the decomposed fragments shown in Figure 24, a wide range of crystalline representations incorporating the new Al-P-Al-P bonding motif were constructed. The simple ten-atom description employed in prior work yielded several low energy structures of which a representative example was shown in Figure 23. Here The VASP code$^{72}$ was used to simulate the ground state properties of AlPSi$_3$ alloys in both this proposed “chain-like” structure, and the ordered C1c1 phase described in prior work,$^{16,17,18}$ as well as those of the their “end members” diamond Si and zinc-blende AlP. Exchange and correlation effects were treated using the Ceperley-Alder form of the local density approximation (LDA) and the corresponding standard ultrasoft pseudopotentials included with VASP were used to replace the core electrons of the Al, P and Si atoms. Wavefunctions, potentials and densities were expanded in a plane-wave basis up to an energy cutoff of 400 eV, and a 6x6x6 Γ -centered $k$-point grid was used for all reciprocal space integrations. These parameters yielded well-converged ground state
Figure 24: Proposed decomposition mechanism of the “Al-P-Si₃” units at the growth front leading to the formation of stoichiometric AlPSi₃ material containing –Al-P-Al-P- bonding motifs needed to explain the atomic map patterns in the 110 projection.

structures with atomic forces and cell stress below 0.01 eV/Å and 0.1 kBar, respectively.

To facilitate comparison among the simulated crystalline systems a common 10-atom primitive cell setting¹⁸ based on the diamond structure archetype with cubic lattice parameter a₀. The lattice vectors are chosen to be \( \vec{a}_1 = a_0\left(-\frac{1}{2},1,-\frac{1}{2}\right) \), \( \vec{a}_2 = a_0\left(-\frac{1}{2},1,\frac{1}{2}\right) \) and \( \vec{a}_3 = a_0\left(\frac{1}{2},-\frac{1}{2},0\right) \) such that the Cartesian components are aligned with the conventional crystallographic (100), (010) and (001) directions. Our key results are summarized in Table 2, which lists the ground state energies and equilibrium static lattice structures of AlPSi₃ (both ordered and “chain-like”), diamond Si and zinc-blende AlP, all with respect to a common 10-atom unit cell. In the case of silicon and the AlP binary, the structures are found to be cubic with crystallographic (LDA) lattice constants of 5.386 Å and 5.420 Å, respectively, in excellent agreement with previously reported calculations. For these
perfectly cubic systems the primitive cell dimensions are trivially related to the crystallographic lattice constant by $|\vec{a}_i| = |\vec{a}_j| = a_0 \sqrt{\frac{2}{3}}$ and $|\vec{a}_3| = a_0 \frac{\sqrt{10}}{3}$ (we also note that $|\vec{a}_1|/|\vec{a}_3| = \sqrt{\frac{5}{3}} \sim 1.291$). In the case of the ordered AlPSi$_3$ system ($C1c1$ space group symmetry), the structure predicted by the LDA calculations agrees with previous work\textsuperscript{19} and indicates very small departures from cubic symmetry ($|\vec{a}_1|/|\vec{a}_3| \sim 1.284$) and $\langle a_0 \rangle = 5.417$ Å, while the value of $a_0$ based on the length of the equilibrium $\vec{a}_i$ and $\vec{a}_3$ lattice vectors is 5.422 Å and 5.392 Å, yielding a weighted average of 5.412 Å similar to $\langle a_0 \rangle$. The fractional Al, P and Si atomic positions listed in the table also indicate small deviations (0.01-0.02) from the corresponding perfect diamond-Si parameters, as found for this system in previous work.\textsuperscript{19} The formation energy of the ordered AlPSi$_3$ alloy is calculated as $\Delta E = E[AlPSi_3] - E[AlP] - 3 E[Si]$ yielding $+188$ meV per atom in agreement with prior work. This indicates that the system is metastable with respect to disproportionation into AlP and Si, as expected. However, this configuration is the lowest energy structure possible under the assumption that the Al-P-Si$_3$ units remain intact, with the constraint of no near-neighbor Al-Al bonds. Next the ground state properties of the AlPSi$_3$ analog structure ($AlP-Si_3$ in Table 1) containing the “chain-like” –Al-P-Al-P- motifs is calculated, as shown in Figure 23 (previous section). The most striking distinction with the ordered $C1c1$ phase is the significant lowering of the crystal energy by $59$ meV/atom, due to the presence of linked -Al-P- bonds, while the corresponding formation energy of this system is $+129$ meV per atom (e.g., less metastable than the ordered phase). Perhaps more interestingly, the molar volume of “AlP-Si$_3$” phase is only reduced by 0.4%, indicating that the change in the effective cubic lattice constant relative to the ordered structure is virtually negligible. A similar volume invariance was recently
reported in the related AlAsSi$_3$ system upon introducing orientational disordering of the Al-As-Si$_3$ units.$^{73}$

**Table 2:** Ground state energy and structure of ordered AlPSi$_3$, its “chain-like” analog (designated AlP-Si$_3$ above), diamond Si and zinc-blende AlP as predicted using the LDA in a common 10-atom setting. The effective cubic LDA lattice parameters, listed as $\langle a_0 \rangle$ in the table, were obtained from the diamond-like optimized structures by $(8 \Omega_0)^{1/3}$ where $\Omega_0$ is the volume per atom of a given system.

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The EELS spectra of sample 04 were acquired from 40 regions throughout the layer in 110 projection using the same procedures and instrumental setting as for sample 06 described above. Each region analyzed had an approximate volume defined by an area of 0.9x 0.6 nm$^2$ and a depth of 20 nm containing between 100-200 formula units of AlPSi$_3$. Figure 25 shows a representative EELS plot illustrating a continuous sequence of K-edges corresponding to Al, Si and P atoms within a relatively narrow energy range from 1300 to 2400 eV due to the close proximity of the three atoms in the periodic table. As in the case of sample 06, it is also found that quantitative fitting of these spectra in all cases.
gave the stoichiometric composition AlPSi$_3$ consistent with the bulk values measured by RBS indicating homogeneous elemental distributions at the nanoscale.

**Figure 25:** EELS plots of AlPSi$_3$ showing Al, Si and P K-edges. Inset compares the Si signal with that of the substrate indicating significant differences in spectral features shape and intensity as expected due to the distinct bonding environments of the atoms in bulk Si vs the alloy. Reference spectra of SiO$_2$ and Si$_3$N$_4$ also show similarly different peak profiles relative to bulk Si, as expected.

The EELS spectra acquired for sample 04 and 06 in Figure 25 and Figure 20 exhibit pronounced fine structures in the form of peaks and the basic spectral features are qualitatively similar to each other indicating the same coordination number of 4. The bonding types are different in both structures, which are confirmed by the different intensity ratio of the near-edge peaks. The intensity ratio of the peaks is 20:19:16:14 in sample 04 as opposed to 44:38:33:28 in sample 06. We know from Ref 49, these peaks correspond to different transitions in the samples, if the ratio is quite different, that means the bonding configurations are different. As a matter of fact, the bonding type in various forms of carbon and carbon alloys was measured from the $\pi^*/\sigma^*$ ratio at the carbon K
edge in Ref 49 P356. The further investigation of bonding types based on the transition peaks is beyond the scope of this thesis.

A close inspection of the Si K-edge fine structure in the spectra reveals distinct differences from the corresponding spectrum of the elemental Si reference acquired from the substrate during the course of the experiment. This is shown in the inset of Figure 25. In particular, the AlPSi$_3$ spectrum shows a very sharp and distinct peak at the onset of the Si K-edge compared to that observed in pure Si. In the alloy case a series of weaker but well-defined higher energy features riding on the tail of the K-edge are shown. These peaks also appear to be present in the Si wafer spectrum and the spectrum of sample 06 except they are more pronounced and broader in shape and size, as shown in Figure 25. This finding further confirms that the bonding configurations in sample 04 and 06 are similar compared to that of elemental Si.

The above spectra were subsequently used to create spatial elemental maps of the Si, Al and P atomic column positions shown in Figure 26. The Si map contains sharp and well-defined dimers characteristic of the classic Si diamond structure. The distinct pattern of dumbbell shapes of these features within the entire sample volume in 110 projection indicates that Si local bonding environment is highly uniform. Figure 26 also shows that the Al and P maps (colored green and red, respectively) for sample 04 display a dumbbell shape in stark contrast to the corresponding maps of sample 06 where Al and P atomic columns occupied only a half of a dumbbell unit thus creating the preferential arrangement of the atomic pairs depicted in Figure 21. This is evident from the superimposed Al, P and Si maps shown in the overlay panel of Figure 26, which clearly
indicates a homogeneous mix of the three elemental contributions within all dimer columns visible.

**Figure 26:** Element selective lattice maps extracted from the EELS spectra of Si$_3$AlP. The Si map shows distinct Si-Si dimer columns colored blue. Analogous maps of Al and P colored green and red, respectively, exhibit similarly shaped dimer-like features. The overlay panel at bottom left is a hybrid map of Al, Si and P illustrating uniform distribution of the green, blue and red features. This result indicates that all atoms occupy the same lattice and that the Al and P pairs are randomly located along the [110] projected crystal column. The atom dimers in the panels above are identified by yellow box.

This observation can be explained using our original low energy model for AlPSi$_3$, which confirms this absence of preferential Al-P orientation when viewed along the 110 projection in Figure 27. The latter shows an extended region of the C1c1 ordered structure on the top panel illustrating that the Al and P atoms alternate in position looking down any dimer row (note that the interleaving Si dimers are omitted for clarity). Thus a projection of this pattern generates a distribution identical to that shown in the elemental maps of Figure 26 namely the projected dimers have no preference for Al or P direction. In Figure 27, bottom panel, an orientationally disordered variant of the C1c1 structure which essentially yields the same outcome even though the individual Al-P units are
randomly aligned in the parent Si matrix is shown. Accordingly, if the alloy adopts the previously proposed structures in which the Al-P pairs are isolated then the change of orientations down a dimer column will never result in clear ordering of the atoms as visible in sample 06 above.

Figure 27: Models of AlPSi$_3$ C1c1 ordered structure (top) and orientationally disordered analog (bottom) showing the positions of Al (green) and P (pink) atomic column pairs in 110 projection. The interleaving Si dimers are omitted from the lattice to emphasize that in both cases the crystal columns show a random arrangement of Al-P dimers. Both structures share a common P-atom sub lattice devoid of Al-Al bonds.

Collectively, the EELS elemental mapping of the above samples indicates that a range of structural arrangements are possible spanning systems in which the Al-P units are isolated (as proposed for sample 04) and others, because of growth conditions, forming multiple Al-P bonding assemblies generated by the partial decomposition of the precursor
intermediates (as proposed for sample 06). In fact it is possible to envision situations in which the conditions promote large-scale dissociation of the Al-PSi$_3$ tetrahedra, leading to local AlP-rich domains at the nanoscale. The Al-P-Al-P type chain structure discussed above, which is presumably produced by breaching the integrity of Al-PSi$_3$ building blocks, represents the first step toward phase disproportionation. The fate of the final composition under this scenario is not clear. For example, more extended zinc-blende crystallites of Al-P-Si with Al-P rich stoichiometries containing variable amounts of Si, though thermodynamically favored, might be hindered by large diffusion barriers requiring energy beyond that provided by the synthesis process. This suggests that the most controlled outcomes will be achieved using the lowest possible growth temperatures at highest possible growth rates.

When the “AlP-Si$_3$” chain structure is viewed in (110) projection, the apparent common alignment of Al and P atoms within dimer rows becomes quite evident. This corroboration of the atomic structure observed in our EELS elemental mapping of sample 06, together with the favorable energy lowering and simultaneous molar volume conservation, suggest that the “AlP-Si$_3$” chain structure describes a very plausible bonding arrangement.

6. Optical Properties

The alternative Al-P bonding scheme suggested to explain the result of the nanostructural chemical characterization of our alloys raises new questions concerning the optical properties of the alloys, which were previously interpreted in terms of the structures arising from combinations of intact tetrahedra. A fundamental question is then
to what extent these optical properties are expected to depend on the formation of chain-like structures.

Accordingly, spectroscopic ellipsometry measurements of the dielectric function of samples 04 and 06 at room temperature were performed using a variable-angle spectroscopic ellipsometer (VASE from J.A. Woollam Co.) with a computer-controlled compensator. The data were collected over an energy range spanning 0.56-4.52eV using an incident angle of 70°. The pseudo-dielectric functions were obtained using a three-layer model incorporating the Si substrate, the bulk-film AlPSi$_3$ layer and an additional outer layer to account for the surface roughness. The latter layer is modeled as a thin film consisting of a 50% AlPSi$_3$ layer and 50% voids in the Bruggeman approximation with corresponding thicknesses of 2.5nm and 3nm, respectively. Excellent fits of the dielectric function of AlPSi$_3$ are obtained using two Tauc-Lorentz oscillators and one Drude oscillator$^{74}$, and the results are confirmed by point-by-point fits that do not assume any particular model. The absorption coefficients corresponding to the measured dielectric functions are plotted on the top panel of Figure 28 which shows that both samples have an extended absorption relative to Si for $E<3.2$ eV. In the case of sample 06 (aligned Al-P dimers) the magnitude of the absorption is slightly weaker than that of sample 04, in which there appears to be no orientational alignment of Al-P units.

Complementary *ab initio* calculations of the optical properties of both the newly proposed chain structure and the ordered C1c1 phase were carried out to confirm that the observation of similar absorption spectra is consistent with the two distinct structures. For this purpose meta-GGA exchange and correlation function as implemented in the
ELK code is used.\textsuperscript{75} Optimized 10-atom structures given in table 1 were used in the calculation of the dielectric function over a range of energies from 0-8 eV. Default species parameters (such as muffin-tin radii, etc) were used as provided by in release 2.10 of the ELK code. A dense \textit{k}-point grid of 12x12x12 points for the reciprocal space integration and 20 empty states above the highest occupied state are used. The resulting dielectric functions were smoothed by convoluting with a Gaussian of width 50 meV.

\textbf{Figure 28:} Comparison of the absorption coefficient dependence on nanostructure. The top panel shows that absorption in AlPS\textsubscript{i} sample 06 (aligned Al-P dimers) is enhanced relative to Si for E<3.2 eV, but slightly slightly reduced relative to that of sample 04, which shows no apparent bond alignment. This trend is corroborated by \textit{ab initio} (meta-GGA) calculations where it is found that the absorption coefficient of AlPS\textsubscript{i} systems in which “Al-P” units are no longer isolated, is only slightly reduced compared to that of the idealized C\textsubscript{1c1} structure.
Figure 28 (bottom panel) compares the calculated absorption coefficient obtained from the resulting dielectric functions for pure Si, and the $C1c1$ and chain variants for AlPSi$_3$. The results show excellent agreement with experimental data and confirm that the two structures have very similar absorption spectra. In fact, theory predicts that the chain-like structure has a slightly reduced absorption compared to that of its ordered $C1c1$ analog, suggesting that the very small difference observed experimentally in Fig. 28 might be real. Finally the agreement between theory and experiment is not limited to the spectral line shape of the absorption but the predicted absorption magnitudes are also in excellent agreement with the measurements.

Raman spectroscopy is a sensitive probe of local atomic bonding structure such as rotational disordering of III-V pairs substituted within Si matrix. Accordingly we apply the same technique to elucidate the subtle vibrational affects associated with the localized bonding arrangements observed in samples 04 and 06. Figure 29 shows the Raman spectra for the two AlPSi$_3$ samples, after subtraction of the dominant substrate peak. This substrate peak is also shown in the figure for comparison. The peaks observed are assigned to the Si-Si vibration in the AlPSi$_3$ system. The peak from sample 04 is weaker due to its smaller thickness. The downshift from the bulk Si frequency is substantial, and it is further increased after a correction to adjust for the slight compressive strain in both samples, using the Si-Si mode strain coefficient of $-955$ cm$^{-1}$ measured for Si$_{1-x}$Ge$_x$ alloys, it is estimated that the peaks in Fig. 29 are upshifted by $1.5$ cm$^{-1}$ (sample 04) and $3.0$ cm$^{-1}$ (sample 06). Therefore, the total downshift from bulk Si is $8.4$ cm$^{-1}$ (sample 04) and $7.5$ cm$^{-1}$ (sample 06).
Figure 29: Room temperature Raman spectra of two AlPSi$_3$ samples after subtraction of the Si substrate Raman peak. The spectra were excited with a 532 nm laser line, and collected in a Raman-allowed backscattering at the 001 crystal surface. The Raman spectrum of the Si substrate is also shown as a shaded shape. All peaks are normalized to the same height. The dip near 525 cm$^{-1}$ in the Sample 04 spectrum may be an artifact from the substrate peak subtraction.

The observed downshift in the Si-Si mode is caused by disruption of the Si lattice due to the presence of “foreign atoms”, in this case Al and P. Since the masses of Al and P are much closer to that of Si than the mass of Ge, the perturbation is weaker than in the case of Si$_{1-x}$Ge$_x$ alloys, where Ge atoms do not participate in Si-like vibrations. This is confirmed by the magnitude of the equivalent downshift in Si$_{0.6}$Ge$_{0.4}$ alloys, which is estimated to be $\sim$ 20 cm$^{-1}$. Computer simulations of this effect indicate that the peak frequency will be closer to bulk Si, and the corresponding Raman peak narrower, the larger the average size of the pure Si clusters in the alloy. Because of the proposed formation of Al-P chains in sample 06, Si clusters in this sample are expected to be larger than those in sample 04 and therefore we might expect a somewhat higher Raman frequency and narrower Raman width in sample 06, as observed experimentally. Therefore, the observed Raman spectra appear to be consistent with the structural models for both samples. Overall, both theory and experiment indicated that changes in the
optical properties due to the formation of Al-P chains are rather subtle. This implies that full control of the structure at the nano-scale level may not be necessary for applications.

6. Si-rich alloys

This chapter is concluded with a study of Si-rich alloys, which, in addition to having applications on their own, may contribute to the understanding of the structure and properties of the parent compound AlPSi$_3$.

As the temperature increases, the Si : P ratio increases from the 3:1 value to levels as high as 12:1 at 650°C. Si-enriched, but highly homogeneous crystal lattice comprised of tetrahedral AlPSi$_3$ units interlinked with Si are obtained. All films grown at 500-550°C possessed a nominal Si$_3$AlP stoichiometry which can also be expressed as 40% AlP and 60% Si. The Si fraction (1-2y/5) of (Si)$_{5-2y}$(AlP)$_y$ films grown between 575 and 650°C were measured to be in the range of 70%-90%. The concomitant reduction in lattice dimensions was measured by high-resolution x-ray diffraction (HR-XRD), which was also used to determine phase purity and strain properties. The θ/2θ scans (Figure 30) showed a single reflection in the vicinity of the Si (004) peak. No other Bragg peaks were detected in the 20°-90° range, indicating that the samples were single-phase alloys possessing diamond-like monocrystalline structures orientated along the Si (100) substrate normal. The (004) alloy peaks exhibited a remarkably strong and sharp profile similar to that of
Figure 30. (Color online) (Left) (004) reflections for a series of alloys with Si concentrations between 60% and 90% indicating a decrease in vertical lattice dimension with increasing Si fraction. (Right) (224) reciprocal space maps of a sample containing 83% Si showing perfect vertical alignment (full coherence) between the film and the substrate.

The underlying Si, which was in fact sufficient to allow clear resolution of their angular position despite the close similarity in d-spacing. Accordingly, in spite of the minute 0.02 Å deviation between lattice parameters of AlP(5.451 Å) and Si, a measureable and systematic reduction of the vertical (c) constant is found, in the sequence of c=5.445, 5.437, 5.435, 5.434 and 5.433 Å for %Si=60, 70, 75, 83 and 88, respectively. The thickness fringes, resolved near the base line of alloy peaks for the thinner samples (~200nm), confirm the presence of highly registered and crystalline overlayers. Off-axis (224) reciprocal space maps were used to extract the in-plane (a) lattice constant. In all cases, the alloys were found to be perfectly lattice-matched to the substrate with a=a_{Si}.

Finally, the shape and intensity distributions in the diffraction maps for a typical alloy and the substrate were virtually identical. This remarkable similarity between the grown film and the Si reference is further testament to the high degree of crystalline perfection.
For the highest Si concentration (88%), the a- and c- parameters were 5.4312 Å and 5.4340 Å indicating minimal strain relative to the relaxed value $a_o=5.433$ Å, obtained from classical elasticity theory. This is remarkably close to $a_{Si}$, corroborating the near cubic symmetry of the alloy.

![Graphs showing Si-Si Raman peak frequency and E1 transition energy](image)

**Figure 31.** (Left) Si-Si Raman peak frequency in $Si_{5-2y} (AlP)_y$ alloys. The solid line represents the compositional dependence of the same mode in $Si_{1-x}Ge_x$ alloys. The inset shows selected Raman spectra after substrate peak subtraction. (Right) Compositional dependence of the $E_1$ transition energy in $Si_{5-2y} (AlP)_y$ alloys. The solid line is a quadratic fit to the data, giving a bowing parameter of 1.0 eV. The inset shows the actual ellipsometry data from which the energies were extracted. The second derivatives of the imaginary part of the dielectric function show the $E_1$ and $E_2$ transitions.

The near-perfect crystalline quality of the above samples motivated a study of their optical properties. Raman scattering experiments were carried out at room temperature in the back-scattering configuration using 532nm excitation. Representative spectra, corresponding to Si-Si like optical vibrations, are presented in Figure 31 (left) (inset). The frequency of this mode is shown in the main panel of Fig 31(Left). The continuous frequency shift as a function of the Si concentration corroborates the formation of
(Si)$_{5-2y}$(AlP)$_y$ alloys. The compositional dependence of the Raman peak frequency is much weaker than the corresponding dependence in Si$_{1-x}$Ge$_x$ alloys, which is shown as a solid line. As indicated earlier, the Ge mass in Si$_{1-x}$Ge$_x$ alloys is so much larger than the Si mass so that the Ge atoms can not participate in Si-like optical vibrations, leading to a frequency downshift which is akin to phonon confinement. In addition, the stretching of Si-Si bonds to accommodate the larger size of the Ge atoms produces an additional frequency downshift. The mass substitution effect accounts for about 70% of the Si-Si mode shift in Si$_{1-x}$Ge$_x$ alloys, whereas bond stretching is responsible for the remaining 30%. These two effects are significantly reduced or suppressed in (Si)$_{5-2y}$(AlP)$_y$ alloys. Bond length changes are minimal, due to the similarity in atomic sizes. In addition, the masses of Al, Si, and P are very similar, and therefore, the Al and P atoms are likely to participate in what we call Si-Si vibrations, reducing the mass effect considerably. This is confirmed by the similarity between the Si ($\omega_0=521$ cm$^{-1}$) and the AlP ($\omega_{LO}=501$ cm$^{-1}$, $\omega_{TO}=439$ cm$^{-1}$, Ref 79). The expected weak bond and mass contributions qualitatively explain the experimental findings, which show a variation of less than 5 cm$^{-1}$ over a composition range of 60% Si. Furthermore, the data are consistent with the single-phase character of this crystal in which all Al-P pairs are isolated within a Si-like matrix. Figure 31 (right) shows spectroscopic ellipsometry measurements of the dielectric function of Si$_{5-2y}$(AlP)$_y$ alloys. The sharp feature close to 3.4 eV is mainly due to the so-called E$_1$ transition at the L-point of the diamond/zincblende Brillouin zone. Using experimental E$_1$ data for pure AlP$^{80}$, the compositional dependence of the E$_1$-transition energy is fit with a quadratic polynomial and a moderate bowing (quadratic) parameter of 1.0 eV is obtained, much less than that calculated for (Ge$_2$)$_{1-x}$(GaAs)$_x$ alloys.$^{12}$
Figure 32. The band structure for this system, indicates an indirect band gap of (Color online) (Top left) Primitive 10-atom cell of Si$_3$AlP containing two fundamental “Al-P-Si3” units. (Bottom) LDA band structure of Si$_3$AlP indicating an indirect band gap of 0.6eV from C to a point close to Z along the Z - M line (red arrow in top right panel).

The rather weak bowing of the $E_1$ transition prompted us to undertake a series of preliminary density functional theory (DFT) calculations to investigate its origin and obtain an initial picture of the nature and magnitude of the valence and conduction bands in the vicinity of the band gap. The limiting 60% silicon composition of (Si)$_{3-2y}$(AlP)$_y$ (e.g., $y=1$), comprised exclusively of interlinked fundamental III-V-(IV)$_3$ building units, can be described by a high-symmetry 10-atom primitive cell, thereby making detailed electronic structure calculations both possible and relevant. Band structure calculations were carried out for this ordered pseudo-cubic phase of crystalline Si$_3$AlP with a base-centered monolithic C1c1 space group symmetry. The FPLAPW ELK code $^{75}$ was used to calculate the electronic structure with an 8×8×8k-point grid and a $R_{K_{\text{max}}}$
structure of 10, within the local density approximation (LDA). Using these parameters, highly converged structures with residual forces <0.01 eV/Å and cell stress <0.01 kbar were obtained. The band structure for this system shown in figure 32 indicates an indirect gap of ~0.6 eV from Γ to a point close to Z along the Z-M line, while corresponding calculations for diamond-phase Si and zincblende AlP systems yield well-known results for the band structure and indirect band gap of $E_g=0.58$ and 1.4 eV, respectively. From a linear interpolation of these end-member band gaps, we find that the 60% Si alloy (Si$_3$AlP) exhibits a slight negative bowing, in qualitative agreement with the experimental results. Empirical scaling of these LDA values for the AlP and Si band gaps then yields a corresponding predicted Si$_3$AlP indirect band gap of ~1.3 eV, which is only 0.3 eV less than the value predicted using a weighted Vegard average of the experimental Si and AlP band gaps (~1.1 and 2.5 eV, respectively).

7. Conclusion

The ordering of the AlP and Si components in AlP$_3$Si$_3$ alloys was studied via aberration-corrected annular-dark-field imaging and atomic column elemental mapping, which is capable of detecting atomic-column-by-atomic column orientation motifs and bonding configurations. EELS analysis of both samples reveals that the films are single phase alloys with uniform elemental distributions at the atomic scale and not a mixture of phase segregated domains of the zincblende AlP and Si diamond. Atomic column elemental mapping identified two distinct patterns for the Al-P units in the lattice; one with an apparent displacement of the Al and P atoms along the growth direction (sample 06) and another in which the pairs appear to be randomly oriented (sample 04). In both cases the Si component is uniformly arranged throughout the individual crystal columns,
consistent with a diamond lattice structure. Measurements of the dielectric function indicated that both samples show higher absorption than bulk Si in the visible range but the strength of absorption is slightly higher in the 04 sample. These trends are corroborated with \textit{ab initio} simulations of two distinct structural models, one containing isolated Al-P pairs designated C1c1 and another in which Al-P units are bonded in the form of short -Al-P-Al-P- chains. In addition to predicting the observed absorption behavior, the latter motif also correctly accounts for the orientation alignment of the Al-P pairs along the 110 projection in the elemental maps. The data indicate that the nano-scale configurations of Al-P from sample to sample might be dependent on subtle changes in synthesis conditions. The optical properties of the samples can be correlated to their proposed structures via \textit{ab initio} simulations, and we find excellent agreement between theory and experiment. These results suggest that a theoretical search for specific electronic properties, such as particular bandgap values, may yield attractive synthetic targets for additional fine-tuning of the properties of this system.
CHAPTER 5

SYNTHESIS, STRUCTURE AND OPTICAL PROPERTIES OF \([\text{Al(As}_{1-x}\text{N}_x)]_y\text{Si}_{5-2y}\) ALLOYS


1. Introduction

The synthesis of AlPSi$_3$ and related alloys represents a significant breakthrough in the quest for novel group-IV/III-V alloys. However, the structural similarities between AlP and Si and the wide-gap nature of AlP suggest that AlPSi$_3$ may not be ideal when it comes to develop an alloy with significant absorption in the visible range that overlaps with the solar radiation spectrum as filtered by the Earth’s atmosphere. In fact, the measurements of the imaginary part of the dielectric function discussed in Chapter 4 show that the AlPSi$_3$ spectrum is similar to a broadened Si spectrum. Accordingly, it is worth exploring the effect of substituting P with As or N. The former may lower the absorption edge due to the lower band gap of AlAs relative to AlP. In the case of N,
while it is true that AlN has very large band gaps, the substitutional incorporation of N into dimensionally disparate III–V materials such as GaAs(N) and InGaAs(N) has been pursued for the past 10 years precisely because of the dramatic N “impurity”-induced bowing of the direct gap and the potential applications of this effect in photovoltaics. Moreover, by combining As and N one may be able to control strain issues arising from the mismatch of alloy lattice constants relative to the Si substrates.

Recent work led to the successful demonstration of AlAsSi$_3$ layers on Si using similar reaction pathways and deposition protocols to those employed in our original studies on AlP$_3$. The AlAsSi$_3$ compound contains an Al–As bonds with natural lengths about 4% larger than those in Si. Accordingly, relatively large epitaxial strains- as large as ~1.7% -are expected on the basis of Vegard’s law. This significant misfit strain leads to a bimodal growth mechanism in which a thin (~40nm) initiation layer is formed which provides a template for the subsequent bulk-like crystal growth. The lattice mismatch between AlAsSi$_3$ and Si can be mitigated via intermediate Al(As$_{1-x}$P$_x$)Si$_3$ alloys, which were obtained using straightforward stoichiometric combinations of the corresponding As(SiH$_3$)$_3$ and P(SiH$_3$)$_3$ precursors. However, since the cubic average lattice constant of AlP$_3$ is slightly larger than that of Si, the mismatch strain with the substrate can never be completely eliminated within this system. In addition, the re-introduction of P may not lead to the desired optical properties. On the other hand, the substitution of arsenic by the markedly smaller nitrogen can lead to perfect lattice matching with Si, aside from the above-mentioned electronic effects. Using literature lattice parameter data for cubic AlN (a = 4.38 Å), AlAs (a = 5.66 Å), and Si (a = 5.431 Å), we estimate on the basis of Vegard’s law that the lattice constants of Al(As$_{1-x}$N$_x$)Si$_3$ should decrease from 5.52 Å for...
x = 0 (e.g., pure AlAsSi$_3$) to 5.431 Å (e.g., silicon lattice match) for a nitrogen content corresponding to $x \sim 0.18$.

The strain-minimized Al(As$_{1-x}$N$_x$)Si$_3$ and [Al(As$_{1-x}$N$_x$)]$_3$Si$_{5-2y}$ materials described in this chapter are created via reactions of Al atoms with appropriate mixtures of As(SiH$_3$)$_3$ and their planar N(SiH$_3$)$_3$ analogue. While the AsSi$_3$ cores in these molecules are inherently pyramidal, the NSi$_3$ core is planar and far less reactive toward nucleophilic attack. Nevertheless, as is shown below, under appropriate conditions the N(SiH$_3$)$_3$ compound reacts with Al to form trigonal prismatic intermediates which can then be readily inserted into the structure as intact Al-NSi$_3$, leading to significant incorporation of N up to 11% in the case of Al(As$_{1-x}$N$_x$)Si$_3$, far beyond the 5% level typically accessible in pure III–V analogues using metal–organic chemical vapor deposition (MOCVD).

2. Synthesis and Characterization of Al(As$_{1-x}$N$_x$)Si$_3$ and [Al(As$_{1-x}$N$_x$)]$_3$Si$_{5-2y}$ Alloys.

The N(SiH$_3$)$_3$ and As(SiH$_3$)$_3$ compounds used in this study were prepared as colorless liquids and were purified by fractional distillation to obtain semiconductor-grade gas-source products. The compounds are found to possess significant room temperature vapor pressures of ~320, 20 and 10 Torr, respectively, well suited for the low pressure CVD conditions employed throughout our experiments. The target alloy layers were grown directly on Si(100) using gas-source MBE techniques in a UHV chamber equipped with Knudsen cells charged with high-purity aluminum metal. The substrates were rectangular segments with dimensions of $2 \times 1$ cm$^2$ cleaved from double-side polished p-type wafers possessing a nominal resistivity of 1–10 Ω·cm. Prior to growth the substrates were degreased by sonication in methanol and isopropanol baths and then dipped in a 10% HF–methanol solution to etch the native oxide. They were then clamped onto the sample
holder using two metal electrodes and inserted into the UHV reactor through a load lock. The chamber was then pumped to a base pressure of $10^{-10}$ Torr, and this was followed by “flash heating” at 1100 °C for 10 s by passing current through the samples to obtain a deposition-clean surface. To begin crystal growth the temperature was typically set in the 530–630 °C range, as measured by a single color pyrometer, depending on the requirements of the specific experiment. The gaseous sources were subsequently inserted into the chamber and allowed to combine in the vicinity of the substrate surface with the Al atoms at a nominal molar ratio of 1:1 and a constant flow/flux rate over the course of the 1–2 h experiment.

2.1 AlNSi₃ System.

To pursue the above synthetic strategy a series of control experiments were carried out to establish the relative reactivity of N(SiH₃)₃ in relation to its As(SiH₃)₃ analogues. In the initial experiments the gas phase N(SiH₃)₃ compound was reacted with Al atoms to form “Al–N(SiH₃)₃” intermediate complexes, intended to serve as the source of Al–N–Si₃ building blocks to assemble the corresponding solid. These reactions produced crystalline films with nominal AlNSi₃ compositions as measured by Rutherford Backscattering (RBS) on Si (100) wafers at 550 °C. Detailed cross-sectional transmission electron microscopy (XTEM) analysis showed that the films exhibited a reasonable degree of heteroepitaxial alignment at the interface, as evidenced by the coincidence of the substrate (111) lattice planes with those of the epilayer. This is presumably either pure Si or diamond-like Si-rich material whose lattice constant is close to that of the underlying Si wafer. The bulk portions of the film consisted of large and highly defective domains possessing distinct orientations and a definite cubic symmetry, as well as no
obvious evidence of hexagonal AlN phase precipitation. On the other hand, our TEM analysis also revealed “diffraction rings” overlapping with the major diffraction spots of the substrate, strongly suggesting Si segregation within the layer. At 600 °C these reactions again yielded films with the expected AlNSi$_3$ composition, but a significantly inferior crystalline quality and possible phase segregation, while reducing the reactions below 550 °C produced no discernible film growth. From Vegard’s law, the cubic lattice parameter of AlNSi$_3$ is estimated to be $a = 5.01$ Å. Thus the absence of single phase formation within the optimal growth temperature range (550–600 °C) is likely due to the significant 7.8% lattice mismatch with the Si substrate, which thwarts the epitaxial stabilization of the desired product structure and is also far too great for epitaxy-driven synthesis via “templating” through an initiation layer, as found in the case of AlAsSi$_3$. However, the condensation of solid products with average AlNSi$_3$ composition, irrespective of temperature, strongly suggests the persistent formation of sufficiently stable gas phase “Al–N(SiH$_3$)$_3$” intermediates over the temperature and pressure range explored in these experiments, validating our proposed general concept for the synthesis of (III–V)(IV)$_3$ solids based on reactions of V–(IVH)$_3$ molecules with III atoms.

2.2. Al(As$_{1-x}$N$_x$)Si$_3$ System.

The experiments above involving N(SiH$_3$)$_3$ thus provide a clear conceptual path to the lattice matching problem via substitution of As by N to produce a range of Al[As$_{1-x}$N$_x$]Si$_3$ alloys with lattice dimensions more compatible with those of Si template. For example Al(As$_{1-x}$N$_x$)Si$_3$ alloys might be envisioned to form via idealized reactions of Al atoms with an appropriate stoichiometric mixture of N(SiH$_3$)$_3$ and As(SiH$_3$)$_3$, following the reaction path
\[ x\text{As}(\text{SiH}_3)_3 + (1-x)\text{N}(\text{SiH}_3)_3 + \text{Al} \rightarrow x\text{“Al-As(SiH}_3)_3”} + (1-x)\text{“Al-N(SiH}_3)_3”} \rightarrow \text{AlAs}_x\text{N}_{1-x}\text{Si}_3 + 9/2\text{H}_2 \]

as in the case of the Al(As\(_{1-x}\text{P}_x\))Si\(_3\) analogues, which formed readily using corresponding P(\text{SiH}_3)_3 and As(\text{SiH}_3)_3 in stoichiometric proportions. In practice,

**Figure 33.** (left) 2 MeV RBS spectrum of Al(As\(_{0.95}\text{N}_{0.05}\))Si\(_3\)/Si(100) showing distinct signals for the Al, Si, and As atoms obtained from a RUMP model (red trace) fit to the random spectrum (black trace). The aligned spectrum (green trace) shows a fully commensurate epilayer. (right) SIMS depth profiles of the film illustrating the presence of nitrogen throughout the epilayer as well as uniform elemental profiles.

however, this simple stoichiometry-based approach to Al(As\(_{1-x}\text{N}_x\))Si\(_3\) alloys leads to no measurable nitrogen incorporation in the 525–550 °C range, as evidenced from secondary ion mass spectrometry (SIMS) profiles. In fact it was empirically determined that within this temperature range the ratio of gas-phase N(\text{SiH}_3)_3 and As(\text{SiH}_3)_3 co-reactants must exceed 3:1 in order to incorporate even minute amounts of N into the solid. This indicates that the reaction rate of Al atoms with N(\text{SiH}_3)_3 is significantly lower than that with As(\text{SiH}_3)_3. When the precursor gas ratio was increased from the threshold 3:1 value to 4:1, substantial N incorporation in the range of 3–5%, as measured by SIMS, was achieved at 560 °C. A typical elemental profile of the latter 5% sample is
shown on the right of Figure 33, illustrating a uniform distribution of all the constituent elements throughout the layer thickness. The nitrogen content in this case was determined by comparisons with known nitride standards. The full elemental content was corroborated by RBS, as shown in the left panel of Figure 33, which indicates a composition of AlAs$_{0.95}$N$_{0.05}$Si$_3$ and also yields a film thickness of 120–160 nm. Most importantly, the aligned RBS spectrum reveals the same degree of channeling in all constituent elements, which is consistent with the existence of a single-phase material where all atoms occupy substitutional diamond lattice sites. High-resolution X-ray diffraction (HRXRD) measurements of the (224) reciprocal space maps and on-axis plots of the (004) reflections (not shown) indicate that the material is tetragonally distorted with lateral and perpendicular lattice parameters of $a = 5.4557$ Å and $c = 5.531$ Å, respectively. Appropriately averaged elastic constants of Si, AlAs, and AlN were then employed to obtain a relaxed lattice constant $a_0 = 5.497$ Å, which agrees with the Vegard’s law estimate of 5.497 Å for the AlAs$_{0.95}$N$_{0.05}$Si$_3$ composition. In view of the virtually ideal stoichiometric character of this phase (60% Si and 40% AlAs$_{1-x}$N$_x$), the agreement is consistent with complete N substitution within the (III–V)(IV)$_3$ prototype structure, in which the III–V pairs are completely isolated from one another and the group V atoms constitute a third-nearest-neighbor sublattice. From these XRD data we also conclude that the film possesses a significant compressive strain −0.76%.

In subsequent experiments, it is found that the substitutional N content in these alloys could be systematically increased up to 11% by raising the growth temperature from 560 to 600°C while maintaining an essentially fixed precursor ratio of 4:1, which represents a vast excess of the N(SiH$_3$)$_3$, as indicated above. Under these conditions the growth rates
remained within the range of 1.5-2 nm/min to yield films with thicknesses of 100-150nm. For slower deposition rates of ~1nm/min we also noticed a slight but systematic enhancement in Si content from approximately 60% for the stoichiometric materials to an upper limit of 65−70%, indicating that straightforward adjustments in process conditions—including reactant flow and aluminum flux—can be used to fine-tune the expected stoichiometry. HR-XRD measurements show that samples with a nominal stoichiometry of AlAs$_{0.89}$N$_{0.11}$Si$_{3.8}$ [from here on we use for Si-rich alloys of the form (III−V)$_y$(IV)$_{5−2y}$, the equivalent notation of III−V(IV)$_{5−2y}$/y, which provides the same compositional information in a more compact form] are lattice-matched to the underlying Si wafer and represent the highest N incorporation achieved to date in this class of materials. The diffraction data corroborate the monocrystalline character and average cubic structure akin to that of pure elemental silicon. Figure 34 shows high-resolution measurements of the 004 and 224 reflections for the AlAs$_{0.89}$N$_{0.1}$Si$_{3.8}$ sample which correspond to in-plane
and perpendicular lattice parameters of $a = 5.4305 \, \text{Å}$ and $c = 5.5128 \, \text{Å}$, respectively, yielding a relaxed cubic cell length of $a_0 = 5.475 \, \text{Å}$. This value is significantly lower than $a_0 = 5.52 \, \text{Å}$, which was obtained for the pure AlAsSi$_3$ phase. The dramatic reduction in lattice dimensions for these supersaturated alloys and their adherence to Vegard’s law is entirely due to complete substitutional incorporation of the smaller N atoms in the lattice.

The closer lattice-matching of this AlAs$_{0.89}$N$_{0.1}$Si$_{3.8}$ alloy with the Si substrate enabled by the substitution of As by N facilitates formation of fully coherent layers devoid of misfit-induced defects. Not surprisingly, all samples containing 9–11% N substitution are found to exhibit a significantly improved crystalline quality compared to their AlAsSi$_3$ parent material, which invariably grows partially strained at the expense of forming threading defects that somewhat degrade the microstructure.

**Figure 35.** (a) High resolution micrograph of the interface region for sample AlAs$_{0.9}$N$_{0.1}$Si$_{3.8}$ showing full epitaxial registry. (b) Diffraction contrast micrograph of the material show low defectivity and single phase character. (c) low magnification of Z contrast image, which indicates that the film has higher Z than the substrate and the columns which may be due to growth mechanism. (d) high resolution Z contrast image, it shows sharp interface and some contrast variation in the film.
The XTEM micrograph in Figure 35 shows that the surface of the AlAs$_{0.89}$N$_{0.10}$Si$_{3.8}$ alloy sample is relatively flat and it possesses a uniform microstructure across the entire film thickness of 200 nm. Furthermore, the bulk material shows low levels of threading defects and occasional \{111\} type stacking faults within the field of view of approximately 400 nm, with no sign of phase separation, as expected on the basis of the stability of all related materials produced to date. The corresponding high resolution micrograph of the interface indicates a high degree of registry on the basis of the exact alignment of the Si (111) lattice fringes with those of the epilayer. This defect-free appearance is also consistent with the XRD results indicating that the film is closely lattice-matched to the underlying silicon substrate. The composition homogeneity was confirmed by Z contrast image in Figure 35 (c) and (d) showing uniform contrast across the epilayer. The contrast of the film is brighter than for the Si substrate indicating the overall higher atomic number.

![Image](image_url)

**Figure 36.** EDS survey image for sample AlAs$_{0.89}$N$_{0.10}$Si$_{3.8}$ shows the line scan across the interface and the line scan on the film as identified by green lines.
Energy Dispersive Spectroscopy (EDS) analysis with a small focused probe of 1nm was used for studying the compositional uniformity of the AlAs$_{0.9}$N$_{0.1}$Si$_{3.8}$ alloy sample. This analysis for Al, As, N, Si was carried out by mapping the Al K edge (1.49 keV), Si K edge (1.74 keV), As L edge (1.28 keV) and N K edge (0.39 keV) across the interface over 67nm and along the film for 30nm, as indicated by the green line in figure 36 which served as a survey image. The four element profiles Al, As, N, Si are uniform across film in Figure 37 (left) confirming homogeneous composition. The elemental profiles across the interface in Figure 37 (right) indicate that it is chemically abrupt, at least to the resolution limit of the EDS technique.

Figure 37. EDS analysis of AlAs$_{0.9}$N$_{0.1}$Si$_{3.8}$ across the film (left) indicating uniform composition and across the interface (right) revealing a sharp interface.

In summary, the nitride samples synthesized for this study possess compositions close to the idealized AlAs$_{3-x}$N$_{1-x}$Si$_3$ stoichiometry and were obtained by reactions of ~80/20 molar ratio of the N(SiH$_3$)$_3$ and P(SiH$_3$)$_3$ precursors combined with a slight excess of Al flux. The substitutional N incorporation varied from ~ 3 to 11% depending on the reaction conditions (increasing temperature) to produce a host of materials with specific stoichiometries of AlAs$_{0.97}$N$_{0.03}$Si$_3$ or AlAs$_{0.95}$N$_{0.05}$Si$_3$, AlAs$_{0.93}$N$_{0.07}$Si$_3$, and
AlAs$_{0.9}$N$_{0.1}$Si$_3$. The 3–7% N alloys were found to be partially strained while those with 10–11% N appeared to be fully coherent with the Si wafer as expected due to the closer lattice matching induced by the higher N content. The relaxed lattice parameters of the cubic structure varied in the sequence of 5.4974 Å, 5.487 Å, and 5.480 Å for 5%, 7%, and 10% N, respectively, which is in close agreement with the Vegard’s Law estimates of 5.597 Å, 5.485 Å, and 5.470 Å. Minor variation of growth conditions at the high end of the 375–600 °C temperature range of the experiments yielded slightly higher Si contents in the films than the stoichiometric 60% value. In this case the N content remained near 10–11% in all samples with nominal compositions AlAs$_{0.9}$N$_{0.1}$Si$_{3.8}$ and AlAs$_{0.9}$N$_{0.11}$Si$_{4.8}$. These materials were fully lattice-matched with the Si wafer in the lateral direction and exhibited ($a_0$) values of 5.475 Å and 5.457 Å, respectively.

2.3 [Al(As$_{1-x}N_x$)$_3$]$_5$Si$_{5-2y}$ System

The limited amount of N obtained in the Al(As$_{0.90}$N$_{0.10}$)Si$_3$ films above prompted attempts to enhance the nitrogen incorporation by raising the reaction temperature from 600°C to 625°C while keeping the precursor ratio fixed at 4:1. In this case the growth experiments produced Al(As$_{1-x}N_x$)Si$_5$ alloys that were notably enriched in silicon as measured by RBS, and also contained larger amounts of nitrogen relative to As. In this case the Si enrichment is due to the same mechanism involved in the formation of the corresponding AlAsSi$_5$ parent phase. Here the N source does not decompose and the excess Si is presumably furnished almost exclusively from byproducts of secondary As(SiH$_3$)$_3$ reaction channels. The temperature-induced N incorporation and simultaneous increase in Si content indicates that the synthesis of Al(As$_{1-x}N_x$)Si$_5$ is not limited to a fixed Si stoichiometry but represents a general pathway to the formation of alloys with
even more broadly tunable properties compared to the Al(As$_{1-x}$N$_x$)Si$_3$ system described above. It is found that the resultant epilayers exhibited uniform morphology, flat surfaces and single-phase structures that grew fully lattice-matched strained to the Si platform as evidenced by HR-XRD, AFM and cross-sectional transmission electron microscopy (XTEM). The RBS plots of the samples revealed strong signals for the constituent Al, Si and As atoms with concentration determined to be close to AlAs$_{1-x}$N$_x$Si$_5$ using fits of the 2 MeV spectra, as shown in Figure 38. These analyses again provided an estimate of $\sim x=0.17$-0.20 for the more elusive bulk N concentration, which is in good agreement with the x levels of up to 0.20±0.03 measured by nitrogen resonance depth profiles for several representative samples, including AlAs$_{0.80}$N$_{0.20}$Si$_5$ and AlAs$_{0.83}$N$_{0.17}$Si$_5$. This is consistent with SIMS measurements which clearly indicated a relative increase in the nitrogen content. In contrast to the Al(As$_{0.90}$N$_{0.10}$)Si$_3$ mentioned above, the RBS nitrogen peaks of the Si-rich films are sufficiently intense and distinctly resolved to allow standard

![Figure 38](image.png)

**Figure 38.** (Color online) Standard 2 MeV RBS spectrum of an AlAs$_{0.80}$N$_{0.20}$Si$_5$ layer grown on Si(100). Inset shows the 3.74 MeV nitrogen resonance plot in which the N signal is clearly resolved. The fits of the data in both cases (red line) give the above composition, which corresponds to an absolute N content of $\sim 3\%$.
modeling of the N concentration and establish the uncertainties in the fitting procedure using the RUMP program. A nominal ±0.03 error in x was estimated by comparing deviations between various fits of the same data. As expected, this error is significant, since the nitrogen represents only a very small fraction (~3 %) of the total alloy stoichiometry. In general, the nitrogen contents obtained from RBS resonance are also consistent with those obtained indirectly by explicit XRD lattice constants determinations, supporting the notion that the simultaneous increase of N and Si incorporation into the parent AlAsSi$_3$ structure leads to close lattice-matching with bulk silicon.

**Figure 39.** HR-XRD on-axis plot (blue trace) showing the 004 reflections of the film and substrate. The 224 reciprocal space maps (inset) reveal a perfect vertical alignment of the peak maxima, indicating that the epilayer is compressively strained to the underlying Si.

The HR-XRD measurements were also used to corroborate the single-phase character and diamond-like structure of the alloys based on detailed analysis of the on-axis 004 peaks and off-axis 224 reciprocal space maps (see Figure 39). Using these data for the AlAs$_{0.80}$N$_{0.20}$Si$_5$ film the in-plane lattice parameter is found to be exactly matched to that of the substrate ($a = a_{Si} = 5.430$ Å) while the out-of-plane counterpart is slightly dilated to
5.469 Å due to a residual compressive strain in the epilayer. The corresponding relaxed lattice constant \((a_0)\) was calculated to be 5.45 Å compared to the Vegard average of 5.43 ± 0.02 corresponding to \(x=0.20±0.03\), as determined by RBS resonance.

**Figure 40.** TEM and STEM Z contrast images acquired by 4000EX and JEOL JEM 2010F. (a) The diffraction contrast image (b) high resolution phase contrast image (c) low magnification Z contrast image (d) high magnification Z contrast image.

The XTEM studies (see figure 40) reveal uniform layers with flat surfaces (AFM RMS roughness of 1-2 nm) and average thickness of 95-100nm, which is comparable to those measured by RBS and ellipsometry. The local microstructure shows sporadic networks of stacking defects scattered throughout the middle and upper portions of the epilayer. The origin of these features may be traced back to the intact incorporation of the highly irregular AlNSi3 building blocks furnished by the N(SiH3)3 precursor, as described in Ref. 19. Simulated structural models predict that the tetrahedral AlNSi3 units likely induce significant steric stress within the parent Si matrix at the atomic scale, in contrast to the
perfectly normal (regular) AlAsSi$_3$ analogs that are incorporated with minimal
deformation of the local structure. The resultant strain can then be relieved via generation
of stacking dislocation along 111 as observed in Figure 40(a).

High resolution images of the interface show a high degree of epitaxial registry, as
expected due to close similarity in cell dimensions as shown in Figure 40(b). Collectively,
the XTEM lattice images showed a uniformly homogeneous microstructure akin to cubic
Si throughout the layer, with no evidence of AIAs or AlN phase segregation. It is also
confirmed by EDS analysis in Figure 42 and the Z-contrast images in Figure 40 (c) and
(d). The RBS aligned spectra also suggest structural imperfections, presumable due to
lattice distortions in the crystal. The spectra (not shown) revealed a significant level of
de-channeling toward the film surface, which was attributed to stacking faults extending
from the middle to the upper portion of the layer. In fact, the intensity of the channeled
signal in most samples remained essentially unchanged across the entire peak width of
the random spectrum from the surface to the interface, as expected from the near uniform
spatial distribution of these defects. The ratio of the aligned versus random peak heights
($\chi_{\text{min}}$) of the Al, As and Si signals exhibited values of \(~ 55\%\) (and higher) which are
attributed to the defective upper layer, since XTEM reveals nearly perfect epitaxy at the
interface with the substrate.
Figure 41. Survey image of EDS analysis for sample AlAs$_{0.83}$N$_{0.17}$Si$_5$, the green lines indicate EDS scans.

EDS analysis with a small focused probe was performed on the AlAs$_{0.83}$N$_{0.17}$Si$_5$ sample across the interface and across the film along lines of length scale 45 and 47nm, respectively. The signal profiles of Al, As, N, Si in the left panel of Figure 42 suggests uniform composition across the film. The As and Al line profiles shown in the right panel of Figure 42 indicate the interface is certainly abrupt to less than about 3nm.

Figure 42. EDS analysis of the film AlAs$_{0.83}$N$_{0.17}$Si$_5$ indicating uniform composition (left) and across the interface (right) revealing a sharp interface.

It is emphasized that increasing the reaction temperatures from 575-625°C while maintaining a vast excess of the N(SiH)$_3$ co-reactant invariably incorporates a near stoichiometric amount of nitrogen such that the lattice constants of the target
AlAs$_{1-x}$N$_x$Si$_{5-x}$ systems are very close to the calculated counterparts. Under these process conditions any possible competing reactions producing AlAs$_{1-x}$N$_x$ phase segregation or amorphous Si-N-H precipitates via unimolecular decomposition of N(SiH$_3$)$_3$ are suppressed, facilitating the assembly of crystalline layers as evidenced by our HR-XRD and XTEM characterizations. The stabilizing effect of the silicon matrix allows a significant substitution of As by N and a precipitous increase in Si content from 60 to 70% without compromising the phase integrity and microstructure quality of the material as evidenced by XTEM.

The general finding is that increasing the temperature above 650 °C during the growth process moves the system away from stoichiometry and dramatically hinders the crystallization of single phase materials. Competing processes at high temperatures include a plethora of reaction channels involving possible AlN precipitation and unimolecular decomposition of the N(SiH$_3$)$_3$ and As(SiH$_3$)$_3$ compounds, leading to phase segregation and formation of elemental impurity precipitates. It is interesting to note that the stabilizing effect of the silicon matrix in our systems actually allows a significantly larger degree of N to be substituted in place of As than found in the related Ga(As$_{1-x}$N$_x$) pseudobinary alloy in which only ~5% N has been reported. Finally, efforts to increase the N composition through a concomitant increase in the N(SiH$_3$)$_3$/As(SiH$_3$)$_3$ reactant ratio beyond the ~4:1 value used above did not succeed (single phase or fully crystalline materials were not produced). The disparity between the As/N ratios in the alloys (~9:1) and that of the corresponding molecular sources As(SiH$_3$)$_3$ and N(SiH$_3$)$_3$ used in the growth reactions (~1:4) represents a factor of approximately 30, indicating that the
reactivities of these coreactants are incompatible, leading to a highly inefficient use of the nitrogen source.

3. Optical Properties

Raman study is carried out to gain insight into the bond distortions induced in the Si matrix by the presence of the III–V elements, and parallel spectroscopic ellipsometry studies are conducted focusing on possible enhancements of the optical absorption in the visible range relative to pure Si.

3.1 Raman Studies

Ultraviolet (UV) micro-Raman measurements were performed with the 3.41 eV (363.8 nm) line from a Spectra-Physics 2065 argon ion laser at an average power of 1 mW. Excitation and photocollection were in the backscattering configuration.

The Si-like Raman peak of the alloy is shown in the inset of Figure 43 for a representative sample. The peak is significantly broader than its pure Si counterpart, which is also shown in the inset for comparison. Notice that the substrate Si peak does not appear in the film spectrum, indicating that the 3.41 eV photons are completely absorbed in the epilayer. While orientational disorder of the (III–V)–(IV) tetrahedra that make up the alloys likely contributes to the width, even in perfect (III–V)–(IV) crystals with 10 atoms per unit cell theory predicts a few closely spaced Si–Si-like Raman peaks, which explains much of the increased width of the observed peak. The alloy peaks are also shifted with respect to pure Si, and the peak frequencies for several samples are shown in Figure 43 as a function of the fraction of non-Si atoms in the crystal and the average cubic lattice constant of the alloy. There are three main effects that contribute to a shift in the observed Raman frequency with respect to pure Si. The first effect is
extrinsic and due to the epitaxial strain as the film accommodates the lattice parameter of the substrate. The shift is given by $\Delta \omega = b \varepsilon$, where $\varepsilon = (a - a_0)/a_0$. Here $a$ is the in-plane and $a_0$ is the relaxed lattice constant of the film. The coefficient $b$ is not known from our alloys; therefore, this shift is approximated by using the value $b = -769$ cm$^{-1}$ for pure Si.

The data in Figure 43 are shown after correction for epitaxial strain shifts, so that only intrinsic effects are displayed. The choice of $b$ for this correction may introduce a systematic error but will not alter the trends observed in Figure 43. The two intrinsic effects contributing to the shifts of the Si–Si Raman peak in the alloys are as follows. First, both N and As have masses that are very different from that of Si, and therefore the Si–Si vibrations become confined to the Si matrix. This “mass effect” lowers the frequency of the mode, as observed in most alloy semiconductors. The second intrinsic contribution is a “bond effect” mainly related to
Si–Si bond compressions and/or expansions which track the difference in lattice parameter between the alloy and pure Si. If the cubic lattice constant of the alloy is larger than that of Si, the Si–Si bonds will be on average stretched, and this lowers the mode frequency. Conversely, if the cubic lattice constant of the alloy is smaller than that of Si, the resulting bond compression will lead to an increase in the Raman frequencies. These effects are illustrated in Figure 43. We see that the mode frequency decreases as a function of the fraction of the non-Si atoms. This represents the mass effect. In addition to this contribution, color coding is used to indicate the average lattice parameter, and we see that for a given non-Si fraction (for example at 0.4) the alloys with the smaller lattice constant have higher Raman frequencies.

3.2 Spectroscopic Ellipsometry

The complex dielectric functions of our alloy films are measured using a variable angle spectroscopic ellipsometer with incident angles of 65°, 70°, and 75°. The samples are described as a three-layer system consisting of a Si substrate, an [Al(As_{1-x}N_x)]_ySi_{5-2y} layer, and a surface layer to mimic roughness. The fitted thickness of the surface layer is typically ~ 5nm, consistent with the small value of the RMS surface roughness measured by AFM. The surface layer is modeled as a thin film consisting of 50% [Al(As_{1-x}N_x)]_ySi_{5-2y} layer and 50% voids in the Bruggeman approximation. For the dielectric function of the [Al(As_{1-x}N_x)]_ySi_{5-2y}, a combination of two Tauc-Lorentz oscillators provides an excellent fit of the data. It may seem counterintuitive to fit the optical properties of ostensible crystalline films using model functions developed for amorphous materials, but theoretical calculations of the dielectric function of AlPSi_3 show that, to a first approximation, the dielectric function of this material can be viewed...
as a broadened version of that of pure Si.\textsuperscript{22,87} Figure 44 shows the imaginary part $\varepsilon_2$ of the dielectric function obtained for selected samples.

For pure Si, the maximum value of the imaginary part of the dielectric function at room temperature is higher than $\varepsilon_2 = 45$.\textsuperscript{88} The dielectric function of the films in Fig. 44 has a lower maximum and extended tails into the visible. The overall agreement with the theoretical calculations of Ref. 22 for AlPSi$_3$, both in the lineshape of $\varepsilon_2$ and its magnitude,

![Figure 44](image)

Figure 44. The solid black lines show the imaginary part of the dielectric function of selected [Al(As$_{1-x}$N$_x$)$_y$]$_5$Si$_{2-y}$ films on Si obtained from Tauc-Lorentz fits as described in the text. The thick grey lines show the imaginary part of the Si dielectric function broadened to match the maximum value for each film. The Lorentzian broadening parameter (FWHM) used for the Si dielectric function is indicated in each panel.

is quite impressive. The observed low energy tails are important for photovoltaic applications because they lead to a significant enhancement of the optical absorption over the visible range. To quantify the distortion of the dielectric function in the films relative to that of Si, the Si dielectric function is convolved with a Lorentzian. The Lorentzian-broadening $\Gamma$ is chosen in such a way that the maximum of the broadened Si $\varepsilon_2$ is made equal to the maximum value of $\varepsilon_2$ for the corresponding film. The broadened Si dielectric function is also shown in Fig. 44, and it provides a good, and for some samples an excellent, approximation of the measured dielectric function. In Fig. 45, it is shown that the optical absorption at 3.0 eV is strongly correlated with the Lorentzian broadening, confirming that $\Gamma$ is a good parameter to quantify the overall dielectric response of the
Figure 45. Measured optical absorption at 3.0 eV for several \([\text{Al(As}_{1-x}\text{N}_x)_{y}\text{Si}_{5-2y}]\) films plotted as a function of the broadening parameter used to match the imaginary part of the Si dielectric function with that of the film. The horizontal line shows the absorption coefficient of bulk Si at the same photon energy.

Films. Notice the up-to-five-times higher absorption coefficient of the films relative to that of pure Si. The dependence of \(\Gamma\) on the compositional parameter \(y\) and the N concentration \(x\) is shown in Fig. 46. There seems to be a trend for an increase in \(\Gamma\) as a function of \(x\), which might be expected in view of the large bond distortions caused by the presence of N substituting As. On the other hand, one might also expect the largest broadening for \(y = 1\), which corresponds to the highest III-V concentration in the Si matrix. However, this trend is not observed. If anything, the broadening seems to be less for \(y = 1\). One intriguing possibility is that \(y = 1\) films maintain some residual ordering of the tetrahedral orientations that is not easily detected with Raman spectroscopy\(^1\) but still causes a narrower dielectric function. For \(y < 1\), on the other hand, the orientational ordering is completely disrupted by the addition of extra Si atoms, leading to maximum disorder that manifests itself as a broad dielectric function. This interpretation suggests that alloys with \(y < 1\) are the best candidates for photovoltaic applications due to their
increased visible absorption. As a cautionary note however, it is emphasized that this analysis may be too simplistic because films with different values of y were grown at different temperatures; therefore, a different structural origin for the trends observed in Fig. 46 can not be ruled out.

![Figure 46](image)

**Figure 46.** The broadening parameter used to match the imaginary part of the Si dielectric function with that of \([\text{Al(As}_{1-y}\text{N}_y)]_{5-y}\text{Si}_{2-y}\) as a function of the III-V concentration y and the N concentration x. The latter dependence is shown using a color scale.

Sharp optical transitions in solids arise from critical points in the joint density of states. The effect of these critical points on the dielectric function \(\varepsilon(E)\) can be easily displayed by computing higher order derivatives \(d^n\varepsilon(E)/dE^n\). A fit of these derivatives with model expressions that depend on the character of the critical point gives the strength, width, and energy of the transitions. For this purpose, however, the dielectric function based on Tauc-Lorentz oscillators is not appropriate, because a model function that provides a good fit of \(\varepsilon(E)\) does not necessarily give a good fit of its derivatives. Instead, we perform a so-called point-by-point fit in which the layer thicknesses are held fixed at the values
determined from the Tauc-Lorentz fits, so that the only remaining adjustable parameters are the real and imaginary part of $\varepsilon(E)$ for the film. A comparison of this point-by-point $\varepsilon(E)$ with the model functions in Fig. 44 shows an excellent agreement, corroborating the Kramers-Kronig consistency of the point-by-point fits and the general self-consistency of the fit procedure. However, as indicated above, the agreement between the functions does not necessarily translate into an agreement between their derivatives. Accordingly, only second-order numerical derivatives of the point-by-point dielectric functions, which are computed using 25 Savitzky-Golay coefficients is used for subsequent analysis. These numerical second derivatives are fit with expressions combining terms of the form

$$\frac{d^2 \varepsilon}{dE^2} = \frac{Ae^{\delta}}{(E - E_t + i\Gamma)^{3/2}}$$

where $A$, $E_t$, $\phi$, and $\Gamma$ are the amplitude, transition energy, phase, and broadening, and $i$ is the dimensionality of the critical point ($i = 0$ for excitonic transitions). Results are shown in Fig. 47.

**Figure 47.** Circles show numerical second derivatives of the real (top) and imaginary (bottom) dielectric functions of selected [Al(As$_{1-x}$N$_x$)]$_y$Si$_{5-2y}$ films on Si. The solid black lines are fits with Eq. (6.1) using $E_0^*$, $E_1$, and $E_2$ critical points, as described in the text. The thick gray lines show to the second derivative of the dielectric function of Si, broadened to match the width of the $E_1$ transition in the alloy films. The vertical arrows mark the energies of the three transitions obtained from the fits.
The second derivative of the bulk Si dielectric function over the energy range of Fig. 47 is well characterized by three critical points. The lowest energy one, near 3.32 eV at room temperature, corresponds to the so-called E_0' transition and is best fitted with a two-dimensional (2D) critical point. A second critical point, called the E_1 transition, appears at about 0.1 eV higher and is associated with a much larger joint density of states. This feature is well represented by an excitonic transition. The third critical point corresponds to the maximum of ε_2 in Si and is called the E_2 transition. It is best represented by a 2D critical point. Whereas E_0' and E_1 arise from narrow regions of the Brillouin zone (near the Γ point and along the Γ-L line, respectively), E_2 is a complex combination of contributions from regions near the X point as well as along the Σ line. Above room temperature, E_0' can no longer be distinguished in the ellipsometric spectra, and the dielectric function near 3.3 eV is well described by a single, broadened E_1 transition. Accordingly, the second derivative of the Si dielectric function at room temperature is reasonably well represented, over the range of Fig. 47, by an excitonic and a 2D critical point. Similar fits, however, give much worse results for the [Al(As_{1-x}N_x)]_ySi_{5-2y} alloys, for which the E_0' critical point must be added to obtain satisfactory agreement with the experimental data. The results of such fits are shown as solid black lines in Fig. 47. The good fit for both the real and imaginary parts provides strong support for the critical point analysis, since the point-by-point fit used to obtain the original ellipsometric data does not impose Kramers-Kronig consistency. The main difference between [Al(As_{1-x}N_x)]_ySi_{5-2y} and Si, in this context, is that the E_1-E_0' separation increases from 0.1 eV in Si to up to 0.66 eV in [Al(As_{1-x}N_x)]_ySi_{5-2y}, so that the two transitions can no longer be represented by a single critical point. This is illustrated
in Fig. 47, where it is shown that the second derivatives of the Si dielectric function, broadened in such a way that the width of the E₁ transition matches that of the corresponding [Al(As₁₋ₓNₓ)]ₓSi₅₋₂ₓ film. (The broadening values are similar to those in Fig. 44.) A close similarity between the two derivatives is observed, except for the additional low energy E₆'-like transition in the films.

![Graph showing band structures of AlAsSi₃ and Si](image)

**Figure 48.** Comparison of the band structures of AlAsSi₃ and Si in a 10-atom unit cell structure, as described in Ref. 17. The arrows indicate the lowest-energy direct transitions at the center of the Brillouin zone, which in the case of Si correspond to the so-called E₆' transition between p-bonding and p-antibonding states (the spin-orbit interaction is not included in the calculation). The experimental value of E₆' in Si is 3.32 eV. The discrepancy is a well-known shortcoming of the local density approximation, but calculated relative trends are usually much more accurate.

Theoretical simulations of AlPSi₃ and AlAsSi₃ indicate the existence of optical transitions at lower energies than those in Si, as shown for example in Chapter 4.¹⁸,²² The band structure of an ordered III- VSi₃ compound can be viewed as that of Si folded into the smaller Brillouin zone of the compound and further split and shifted due to the perturbation represented by the III-V atoms. From this perspective, the low-energy transitions in AlPSi₃ or AlAsSi₃ are seen to originate at the Γ point of the Brillouin zone.
from precisely the same states that contribute to the $E_0'$ transition in pure Si, which are split and shifted in energy by the lower symmetry of the III-VSi$_3$ compound relative to Si. Figure 48 shows side-by-side our calculated band structure of AlAsSi$_3$ for the 10-atom unit cell of its ground structure and the band structure of pure Si for the same supercell. These calculations are performed with the VASP code within the LDA; Therefore, the absolute energies are underestimated by a significant amount (~0.7 eV). The energy differences between the two structures in Fig. 48 should, however, be much less affected by the LDA error. The largest downshift of the transition energies derived from $E_0'$ is 0.67 eV in Fig. 47, and the average downshift is 0.34 eV. These are comparable to the observed shifts of the low energy transitions in our [Al(As$_{1-x}$N$_x$)$_y$Si$_{5-2y}$]$_y$ films, consistent with the assignment of the lowest feature to $E_0'$. Since the splittings due to the lower symmetry are present even in stoichiometric AlAsSi$_3$ compounds, the additional disorder induced by the incorporation of nitrogen for $x>0$ and extra Si atoms for $y<1$ can only induce some inhomogeneous shifts of the state energies, which manifest themselves as an increased broadening and lead to observation of a single rather than several optical transitions in this energy range. It can also be speculated that this additional disorder increases the downshift of the $E_0'$-like transitions due to additional level-repulsion channels, making them easier to observe due to the increased separation with the $E_1$ transitions.

The energies of the measured transitions are given in the Table 3. The values quoted have been corrected for the residual epitaxial strain using deformation potential theory. Since the strains are relatively small and it is hard to resolve any strain-related splitting, it
Table 3. Critical point energies for selected [Al(As\(_{1-x}N\_x\)]\(_{y}\)Si\(_{5-2y}\) samples obtained from the fits in Fig. 47 corrected for strain shifts as discussed in the text. Typical errors in the fit energy values are in the 0.01 eV range.

<table>
<thead>
<tr>
<th></th>
<th>(E_0) (eV)</th>
<th>(E_1) (eV)</th>
<th>(E_2) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlAs(<em>{0.97}N</em>{0.03})Si(_3)</td>
<td>2.90</td>
<td>3.29</td>
<td>4.33</td>
</tr>
<tr>
<td>AlAs(<em>{0.90}N</em>{0.10})Si(_3)</td>
<td>3.02</td>
<td>3.21</td>
<td>4.11</td>
</tr>
<tr>
<td>AlAs(<em>{0.85}N</em>{0.15})Si(_3)</td>
<td>2.98</td>
<td>3.16</td>
<td>4.51</td>
</tr>
<tr>
<td>AlAs(<em>{0.90}N</em>{0.10})Si(_4)</td>
<td>2.66</td>
<td>3.24</td>
<td>4.29</td>
</tr>
<tr>
<td>AlAs(<em>{0.85}N</em>{0.15})Si(_5)</td>
<td>2.78</td>
<td>3.12</td>
<td>4.20</td>
</tr>
<tr>
<td>AlAs(<em>{0.80}N</em>{0.20})Si(_5)</td>
<td>2.92</td>
<td>3.27</td>
<td>4.27</td>
</tr>
<tr>
<td>AlAs(<em>{0.86}N</em>{0.11})Si(_6)</td>
<td>2.54</td>
<td>3.20</td>
<td>4.31</td>
</tr>
</tbody>
</table>

is reasonable to use only the hydrostatic component of the strain for the corrections. For the \(E_1\) and \(E_2\) transitions, the strain shifts is written as

\[
\delta E = \sqrt{3} D_{i1} \left( 2 \epsilon_\parallel + \epsilon_\perp \right) \tag{6.2}
\]

where \(\epsilon_\parallel\) and \(\epsilon_\perp\) are the components of the strain in the growth plane and in the growth direction, respectively. Obviously, no deformation potentials are available in the literature for III-VSi\(_3\) compounds, so we use Si values. The deformation potential \(D_{11}\) is taken as \(D_{11} = -9.72\) eV (\(E_1\) gap) and \(D_{11} = 2.6\) eV (\(E_2\) gap) (Ref 93,106). For the \(E_0\)’ gap, the only study of the strain dependence of the transition energy appears to be the work of Munguía and co-workers.\(^{94}\) If their measured shifts are modeled with an expression of the form

\[
\delta E = D \left( 2 \epsilon_\parallel + \epsilon_\perp \right) \tag{6.3}
\]
then $D = -7.8$ eV from fitting these data. It is difficult to extract clear compositional dependence trends from the data in Table 3, particularly because the compositional dependence space is 2D in x and y, combined with the aforementioned difference in the growth conditions as a function of y.

### 2.3. Conclusion

In this chapter we have characterized AlAs$_{1-x}$N$_x$Si$_3$ samples grown from reactions of Al with mixtures As(SiH$_3$)$_3$ and N(SiH$_3$)$_3$, which produced AlAsSi$_3$, and AlNSi$_3$ building units. These units interlink to form single phase alloys as monocrystalline and fully lattice matched layers on Si wafers. The incorporation of smaller but ideal AlNSi$_3$ limits the amount of N that can be substituted into the group V sublattice to levels of $\sim 11\%$. Although the latter is not sufficient to achieve a bulk lattice constant equal to Si, it nevertheless reduces the strain difference to a level that promotes growth of fully coherent layers devoid of threading defects.

Raman spectra of the fabricated alloys are consistent with structural models in which the tetrahedral building blocks are orientationally disordered. The optical studies show that distinct absorption transitions calculated for the ordered ground state structures are still observable in these disordered phases, demonstrating that such transitions are robust against orientational fluctuations.

This work suggests that Si-rich [Al(As$_{1-x}$N$_x$)]$_y$Si$_{5-2y}$ alloys with $y \sim 0.7$ are optimal for applications in photovoltaics due to their maximally broadened dielectric function with respect to Si, with tails in the imaginary part that extend into the visible range, enhancing the absorption by one order of magnitude. The narrower dielectric function observed for
$y = 1$ suggests that these compounds may have some residual ordering that does not manifest itself in the Raman spectra but has a clear influence on the optical properties.
CHAPTER 6

COMPOSITIONAL DEPENDENCE OF THE DIRECT AND INDIRECT BAND GAPS IN $\text{Ge}_{1-x}\text{Sn}_x$ ALLOYS FROM ROOM TEMPERATURE PHOTOLUMINESCENCE: IMPLICATIONS FOR THE INDIRECT TO DIRECT GAP CROSSOVER IN INTRINSIC AND N-TYPE MATERIALS


I. Introduction

The growth of $\alpha$-Sn films on InSb and CdTe substrates and the epitaxial stabilization of their diamond structure beyond the bulk $\alpha \rightarrow \beta$ transition temperature led to the speculation that a similar synthetic route might enable the growth of $\text{Ge}_{1-y}\text{Sn}_y$ alloy films,95 thereby bypassing the very limited miscibility of the Sn-Ge system. The interest in the $\text{Ge}_{1-y}\text{Sn}_y$ alloy stems from the observation that an interpolation of the band structures of its end members Ge and $\alpha$-Sn suggests that the material should be a direct gap semiconductor over a broad compositional range $y > 0.2$. This estimate was confirmed by microscopic calculations within the virtual crystal approximation (VCA).96 While several III-V and II-VI compound systems feature direct band gaps over the same energy range, the very weak ionic character of the Ge-Sn bond guarantees the near absence of polar phonon scattering, which in III-V and II-VI systems is one of the major factors that limit carrier mobility. Moreover, while the integration of zincblende materials
with Si substrates is problematic due to the appearance of anti-phase domains, such domains are expected to be absent in Ge$_{1-y}$Sn$_y$ alloys due to their average diamond structure.

The experimental confirmation of the above ideas has proven extremely difficult, both from the synthetic and optical characterization standpoints. The first optical studies of the direct-indirect transition in Ge$_{1-y}$Sn$_y$ alloys were performed in samples grown by low energy ion-assisted Molecular Beam Epitaxy (MBE). The direct and indirect gaps were extracted from optical absorption measurements. To obtain good agreement with experiment, an Urbach tail contribution, representing localized states, had to be added to the model. The results indicated that the compositional dependence of the direct gap deviates strongly from the predicted nearly linear interpolation between Ge and α-Sn. The non-linear dependence was found to be well described by a term of the form $-b y(1-y)$, with a bowing parameter $b = 2.8$ eV. For the indirect gap, the deviations from linearity were found to be less pronounced, implying that the crossover composition is much less than $y_c = 0.2$.

The significant bowing in the compositional dependence of the direct gap has since been confirmed by several groups. However, the reliability of the indirect gap energies determined from absorption measurements is not firmly established. This is because the direct and indirect edges have very different strengths—by about two orders of magnitude—while being in close proximity from each other. This poor contrast is exacerbated by alloy broadening. In fact, ellipsometric studies of the near-band gap optical properties in Ge$_{1-y}$Sn$_y$ alloys show that the energy dependence and magnitude of the optical absorption is in excellent agreement with calculations that assume a broadened
direct edge, without inclusion of indirect or Urbach contributions.\textsuperscript{97,98} These studies were performed on Ge\textsubscript{1-y}Sn\textsubscript{y} alloys grown by chemical vapor deposition (CVD) using Ge\textsubscript{2}H\textsubscript{6} and SnD\textsubscript{4} as Ge and Sn precursors, respectively.\textsuperscript{99} The CVD method yielded films that not only could be deposited directly on Si substrates, achieving the goal of integrating the Ge\textsubscript{1-y}Sn\textsubscript{y} system with Si technology, but had a high level of crystalline perfection, as demonstrated from direct structural studies, from the fabrication of diodes with good electrical and optical characteristics,\textsuperscript{36,98,100} and from the observation of band gap photoluminescence (PL) and electroluminescence.\textsuperscript{35,101} The room-temperature PL signal from Ge\textsubscript{1-y}Sn\textsubscript{y} alloys shows contributions from the direct and indirect band gaps. The simultaneous observation of emission from the two edges is a unique property of Ge-like materials, resulting from the very small (~0.1 eV) separation between them. In bulk Ge, the higher-energy direct gap emission signal is largely suppressed by self-absorption,\textsuperscript{102} but it becomes very prominent in films with thicknesses on the order of a few microns or less.\textsuperscript{103-107}

The observation of distinct direct and indirect gap peaks in PL spectra makes this technique a superior alternative to absorption for the determination of the gap energies. However, while in most low-temperature PL studies of semiconductors the identification of the peak maximum with the associated band gap energy is sufficient for practical purposes, a detailed lineshape analysis is needed for room temperature studies. In the case of indirect gap PL, this analysis must include the possibility of phonon emission and absorption. The need for a detailed lineshape analysis that yields accurate band gap energies is very acute for the Ge\textsubscript{1-y}Sn\textsubscript{y} system if the purpose of the study is the determination of the crossover composition \(y_c\), since small systematic changes in the
slope of the compositional dependence of either gap translate into significant changes in
the predicted value of \( y_c \). In this chapter, the results of an in-depth study of PL from a
large set of Ge\(_{1-y}\)Sn\(_y\) samples with compositions in the \( 0 < y < 0.08 \) range is presented. A
fit of the direct gap emission using a generalized van Roosbroeck-Shockley formula,
combined with an accurate model expression for the absorption coefficient, yields values
of the direct band gap \( E_0 \) in the limit \( y \to 0 \) in excellent agreement with the known value
for bulk Ge. The compositional dependence of this transition can be determined with
meV-level accuracy. For the indirect gap, on the other hand, it is shown that the standard
textbook expressions for the absorption coefficient are inadequate for Ge-like materials,
especially for Ge\(_{1-y}\)Sn\(_y\) alloys. As a result of this limitation, the indirect edge energy \( E_{\text{ind}} \)
can only be extracted from the energy of the indirect PL peak by assuming a constant
shift that is chosen to make the value of \( E_{\text{ind}} \) for \( y = 0 \) agree with the known value of \( E_{\text{ind}} \)
for pure Ge. The crossover composition deduced from these studies is \( y_c = 0.073 \pm 0.007 \).

2. Experiment

2.1 Samples

The PL measurements were performed on Ge\(_{1-y}\)Sn\(_y\) films grown on Si substrates using
CVD methods. Some of the samples were deposited using the CVD precursors Ge\(_2\)H\(_6\) and
SnD\(_4\), as described in several references.\(^{97,99,108}\) Other samples, particularly those with
high-Sn concentrations, used Ge\(_3\)H\(_8\) as the Ge-source.\(^{109}\) Typical thicknesses required for
the observation of good PL signals are about 500 nm. A subset of the samples were
grown on Ge-buffered Si substrates, and these samples typically display a stronger PL
signal, presumably due to the fact that the Ge\(_{1-y}\)Sn\(_y\)/Ge interface is less defected than the
Ge\(_{1-y}\)Sn\(_y\)/Si interface. A detailed comparative study of Ge\(_{1-y}\)Sn\(_y\)/Ge/Si and Ge\(_{1-y}\)Sn\(_y\)/Si
samples will be presented elsewhere. Unfortunately, PL studies of Ge$_{1-y}$Sn$_y$ films on Ge-buffered samples are difficult for $y \leq 0.02$ due to overlap between the film and buffer signals.

The study also includes $n$-type samples doped with P using the P(GeH$_3$)$_3$ precursor.\textsuperscript{110,111,112} The carrier concentrations in the samples were determined from Hall measurements and infrared spectroscopic ellipsometry. The agreement between the two techniques is generally excellent.

The structural properties of the films were monitored using Nomarski microscopy, Atomic Force Microscopy, Rutherford Backscattering (RBS) and x-ray diffraction (XRD). These studies reveal smooth surfaces (RMS roughness $\sim$ 3 nm), very good epitaxial alignment and low defectivity, as evidenced by a drastic reduction of the signal in a channeling geometry. XRD measurements of (224) reciprocal space maps yielded the in-plane and out-of-plane lattice parameters from which the strain could be computed. The 004 -rocking curve scans exhibited full width half maxima (FWHM) close to 0.6 °, depending on thickness, which were reduced to the 0.1-0.3° range after two or three cycles of Rapid Thermal Annealing at temperatures that were adjusted between 550 °C and 700 °C, depending on Sn concentration. The emission from samples with low Sn-concentrations is significantly enhanced after a passivation annealing cycle in an H$_2$ atmosphere.

The Sn concentration in the films were determined from their relaxed cubic lattice parameter using the compositional dependence of this parameter measured by Beeler \textit{et al.}\textsuperscript{113} This dependence was obtained by fitting the measured $a_0$ from tens of
$\text{Ge}_{1-y}\text{Sn}_y$ samples as a function of their Sn concentration determined from RBS. Accordingly, it is expected that the Sn-concentrations determined from x-ray measurements in our samples to be in close agreement with direct RBS determinations, and this is indeed the case. However, since the x-ray measurements of the lattice parameter are considerably more precise than the RBS fit parameters, plots of the band gap energy versus compositions derived from x-ray measurements are less noisy than equivalent plots using concentrations extracted directly from RBS.

Since the size difference between Ge and Sn is much larger than that between Si and Ge, non-random atomic arrangements are more likely in $\text{Ge}_{1-y}\text{Sn}_y$ alloys than in their $\text{Ge}_{1-x}\text{Si}_x$ counterparts. Since these effects might have an impact on the compositional dependence of optical transitions, we have carried out detailed experiments to map the Sn distribution in our films. Electron energy loss spectroscopy (EELS) on a JEOL ARM 200F microscope equipped with a GATAN Enfinium spectrometer is performed. The EELS spectra were collected from $2 \times 2 \text{ nm}^2$ areas (green box in Figure 49 a) with spatial resolution of 0.12 nm and electron beam penetration depth of 60 nm. The latter was measured by the low loss spectra. Multiple scans throughout each sample revealed sharp and well defined ionization peaks corresponding to the characteristic Ge (L) and Sn (M) core edges at 1217 eV and 483 eV, respectively, indicating that the material is a pure and crystalline $\text{Ge}_{1-y}\text{Sn}_y$ alloy. The spectral features were then used to create atomic resolution maps for the Sn and Ge constituents shown in Figure 49 b-d. In the case of Ge (panel b) a uniform pattern of distinct dimer rows in the (110) projection of the cubic lattice in the crystal is shown. The Sn map (panel c) displays a similar arrangement of features corresponding to a two dimensional projection of the Sn atoms within a sample.
column with dimensions of 2 nm × 2nm × 60nm probed by EELS. Collectively the maps confirm that the Sn atoms are evenly distributed throughout the Ge matrix and occupy random substitutional sites in the diamond lattice. Finally, the Sn atom map was overlaid onto the Ge map to construct a composite representation of the chemical distribution in the lattice, as shown in panel 56 d, which indicates a close alignment of the Ge and Sn dimer.

Figure 49. STEM micrographs and EELS maps of the Ge and Sn atoms in a Ge$_{0.96}$Sn$_{0.04}$ sample. (a) Survey image of the film identifying the ~ 2 × 2 nm region analyzed by EELS; (b) Ge atom map created from the L edge showing the characteristic dimer rows colored green; (c) Corresponding Sn map colored red was created from the M edge; (d) Overlay of Ge and Sn maps illustrating a uniform distribution of the atomic species over the same average alloy lattice, and a close correspondence of the dimer Ge/Sn rows. The sample thickness used for this analysis was 60 nm.
rows along the individual (001) columns. No diffraction intensity above background levels between the dimer projections rows is visible, indicating that the Sn and Ge atoms occupy the same tetrahedral lattice devoid of precipitates and interstitials.

2.2 Optical Measurements

Photoluminescence was measured at room temperature from samples excited by ~400 mW of 980 nm laser radiation, focused to a ~20 µm spot. The emitted light was collected with a Horiba 140 mm f/3.9 Czerny-Turner micro-HR™ spectrometer equipped with a liquid-nitrogen-cooled InGaAs detector. The system response was carefully calibrated using a 10 W tungsten-halogen lamp (Newport Corporation catalog #6318). This calibration, discussed in Appendix A, is important because of the broad spectral range covered by the observed peaks and the fact that the detector’s responsivity drops sharply near 2300 nm. Long-pass filters were used during the measurements to block the PL signal from the Si substrate and the laser radiation, which appears as a strong peak at 1960 nm due to second-order diffraction from the 600 gr/mm grating. In many spectra, a residual laser peak is seen at 1960 nm and subtracted from the data by fitting it with a Gaussian profile. From the width of the Gaussian we determine the spectral resolution of the measurements (FWHM), which is found to be 16 meV.

3. Results

Figure 50 shows photoluminescence spectra for a few selected samples. The spectra consist of a main peak, assigned to the direct band gap, and a weaker peak at lower energy that is assigned to the indirect gap. Both peaks shift to lower energy as the Sn-concentration is increased, but their separation decreases. At the highest Sn concentrations, a single peak is observed. The solid lines in Fig.50 correspond to a fit that
is discussed below. At concentrations above 5.5%, the two emission peaks appear completely merged.

**Figure 50.** Room temperature photoluminescence spectra from representative Ge$_{1-x}$Sn$_x$ films. The main peak is assigned to direct gap emission, and the weaker feature at lower energies corresponds to indirect gap emission. The solid lines show fits using a simple Gaussian for the indirect gap and an Exponentially Modified Gaussian for the direct transition.
4. Theory

The spontaneous emission transition rate \( R \) per unit sample volume, for photons with energy \( E \) emitted into solid angle \( d\Omega \), is given by in Eq. 2.78\textsuperscript{54,114}

It is assumed that in a sample under steady-state photoexcitation, quasi-equilibrium conditions are reached separately in the conduction and valence bands. The absorption coefficient \( \alpha(E) \) that appears in Eq. (2.78) results from the difference between the absorption and stimulated emission rates. In the case of vertical (direct) transitions between isotropic parabolic bands, it is given by Eq. (2.70)

\[
\alpha(E) = \alpha_0(E) \left[ f_v(E) - f_c(E) \right],
\]

where \( \alpha_0(E) \) is the absorption coefficient for empty conduction bands and full valence bands and we use the Fermi functions (2.71)

\[
f_c(E) = \frac{1}{\exp\left[\frac{E_c(E) - E_{FC}}{k_BT}\right] + 1}
\]

\[
f_v(E) = \frac{1}{\exp\left[\frac{E_v(E) - E_{FV}}{k_BT}\right] + 1}
\]

Here \( E_c(E) \) and the \( E_v(E) \) are the energies of the electrons in the conduction and valence band states, respectively, vertically separated by an energy \( E \).

The empty-band absorption coefficient \( \alpha_0(E) \) that appears in Eq.(2.70) is not accurate enough for our purposes because it does not include excitonic effects. An analytical expression that includes these effects was introduced in Refs. 97, 98 and 106. This expression reproduces the bulk Ge absorption curve over a range of up 0.1 eV above the direct band gap based on standard band structure parameters, without introducing any additional parameter to adjust for the absorption strength. It also lends itself to its use in
Ge$_{1-y}$Sn$_y$ alloys by extrapolating the relevant band structure parameters from bulk Ge using $k\cdot p$ expressions. A comparison of the emission lineshape predicted by this theory with simpler textbook models is presented in Appendix B.

The effect of strain is easily incorporated in our calculated emission using deformation potential theory. Table 4 shows the deformation potentials used for these calculations.

For pure Ge, the hydrostatic deformation potential for the direct gap is obtained by plotting the pressure dependence of $E_0$, measured by Goñi et al. (Ref. 116) as a function of the relative volume change $\Delta V/V$, and fitting a linear function up to $\Delta V/V = 2.5\%$. For the indirect gap, we use experimental data from Ahmad and Adams. For $\alpha$-Sn, there are no experimental measurements of deformation potentials. For the $E_0$ gap, Li et al. (Ref. 118) calculated the hydrostatic deformation potential for both Ge and $\alpha$-Sn. For Ge, the theoretical value must be multiplied times a factor 0.94 to match the experimental value. The theoretical value for $\alpha$-Sn is multiplied by the same factor to obtain the deformation potential we use for this material. For the indirect gap, the same procedure is followed, but this time theoretical data from Schmid et al. (Ref. 119) and Brudevoll et al. (Ref. 120) is adopted. For the alloy, linear interpolation is applied between Ge and $\alpha$-Sn. For the shear deformation potential of measurements or calculations for $\alpha$-Sn is

<table>
<thead>
<tr>
<th>Table 4 Deformation potentials used to calculate strain effects on the direct gap transitions in Ge$_{1-y}$Sn$_y$ alloys.</th>
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</thead>
<tbody>
<tr>
<td>Direct gap hydrostatic deformation potential $a_{E0}$ (in eV)$^a$</td>
</tr>
<tr>
<td>-9.46+2.33y</td>
</tr>
<tr>
<td>Indirect gap hydrostatic deformation potential $a_{ind}$ (in eV)$^b$</td>
</tr>
<tr>
<td>-3.6+1.77y</td>
</tr>
<tr>
<td>Valence band shear deformation potential $b$ (in eV)$^c$</td>
</tr>
<tr>
<td>-1.88 eV</td>
</tr>
</tbody>
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$^a$References 54 and 117, as discussed in text.

$^b$References 116, 118, and 119, as discussed in text.

$^c$Reference 120.
unknown, so we use the result $b = -1.88$ eV for Ge obtained by Liu et al.\textsuperscript{121} Recently, Lin et al.\textsuperscript{122} presented measurements from compressively strained Ge$_{1-y}$Sn$_y$ alloys from which they extracted a value $b = -4.07\pm0.91$ eV. Their hydrostatic deformation potential is about 15\% larger than the value in Table 4, whereas the data from Liu et al.\textsuperscript{121} is in nearly perfect agreement with the pressure measurements by Goñi and co-workers.\textsuperscript{116} Theoretical calculations, for example Ref. 123, are closer to the Liu et al. value. The major difference between the Liu and Lin experiments is that the former were obtained in films under tensile strain, whereas the latter correspond to compressive strain. This suggests that a careful comparative study of the elastic properties of Ge under tensile or compressive strain is warranted. In our case, since most of our samples experience a slight tensile strain after annealing, the values from Liu et al is used.\textsuperscript{121}

Eq. (2.78) is also valid for indirect transitions,\textsuperscript{124} but Eq. (7.1) is not, and therefore the calculation of the absorption coefficient is less straightforward. Moreover, as shown in Chapter 2, the standard expression for indirect gap absorption in Eq. (2.103) is not appropriate for Ge. The reason for this behavior is that the direct gap $E_0$ and the indirect gap $E_{\text{ind}}$ are very close in energy. In Ge$_{1-y}$Sn$_y$ alloys the two gaps are even closer, and Eq. (2.103) should be expected to break down completely. It is also important to point out that even if a more rigorous expression is developed to replace Eq.(2.103), the inclusion of excitonic effects at room temperature is likely to be important in a quantitative theory of indirect gap emission, in much the same way that excitonic effects are crucial to explain the shape and strength of the direct gap absorption at room temperature.\textsuperscript{97,98} Moreover, to the extent that Ge$_{1-y}$Sn$_y$ alloys deviate more strongly from a virtual crystal approximation than Ge$_{1-x}$Si$_x$ alloys, one cannot rule out a strong no-phonon contribution
to the indirect gap emission, which would render the theory significantly more complex. Due to these complications, the development of a quantitatively rigorous theory of indirect gap spontaneous emission in Ge$_{1-y}$Sn$_y$ alloys is beyond the scope of this thesis, but the lack of appropriate theoretical expressions creates a challenge when it comes to extracting values of the indirect gap from the measured PL spectra.

5. Data Processing

While the direct gap component of the spectra in Fig. 50 can be fitted using Eq. (2.78) combined with Eq. (7.1) and the analytical expression for the absorption coefficient in Refs. 97 and 98, the lack of an equivalent expression for the indirect gap emission makes it impossible to fit the entire PL spectrum consistently using physically motivated lineshape expressions. Therefore, a two-step modeling approach is adopted in which standard function is used first, available in most curve-fitting software packages, to separate the direct and indirect components. For this purpose the observation that the theoretically predicted emission lineshapes from Eqs. (2.78) and (7.1) [and also those obtained using Eqs. (2.78) and Eq.(2.103)] are extremely well described by so-called Exponentially Modified Gaussian functions (EMG). Thus the first step of our data processing approach consists in fitting the raw experimental data (corrected for the instrument response) as a combination of a simple Gaussian, representing the indirect gap, and an EMG representing the direct gap contribution. These fits are shown as solid lines in Figure 50.

In the second modeling step we fit the EMG component from our first step (representing direct gap emission) with the theoretical expression using Eq. (2.78) combined with Eq. (7.1) and the analytical expression for the absorption coefficient in
The agreement between the theoretical expression and the EMG lineshapes is excellent. An example and a detailed discussion is given in Appendix B. In principle the fit contains only two adjustable parameters: the direct gap energy $E_0$ and the photoexcited carrier density $n_{ex}$. This carrier density determines the quasi-Fermi levels.

For the conduction band, our simulation includes the two valleys around the $\Gamma$ and $L$ points. Neglecting non-parabolicity corrections, it is straightforward to show that the carrier density in the conduction band satisfies

$$\frac{n_{ex}}{(k_BT)^{3/2}} = K_L F_{1/2}(z) + K_\Gamma F_{1/2}(z'), \quad (7.3)$$

where $K_L = m_{cl}^{3/2} / \left( \sqrt{2} \pi^{3/2} \hbar^3 \right)$, $K_\Gamma = 4 m_i^{1/2} m_f / \left( \sqrt{2} \pi^{3/2} \hbar^3 \right)$, $z = E_{Fe} / k_BT$, and $z' = z - \Delta_{\Gamma L} / k_BT$. Here $m_{cl}$ is the effective mass at the $\Gamma$ point and $m_i$, $m_f$ are the longitudinal and transverse masses at the $L$ point, respectively. The quantity $\Delta_{\Gamma L}$ is the energy separation between the two valleys. The function $F_{1/2}$ that appears in Eq. (7.3) is the Fermi-Dirac integral of order $1/2$ as defined by Van Halen and Pulfrey. The photoexcited hole density $p_{ex}$ satisfies the similar equation

$$\frac{p_{ex}}{(k_BT)^{3/2}} = K_{lh} F_{1/2}(z) + K_{hh} F_{1/2}(z'), \quad (7.4)$$

if we include the heavy hole ($hh$) and light hole ($lh$) bands. Here $K_{hh} = m_{hh}^{3/2} / \left( \sqrt{2} \pi^{3/2} \hbar^3 \right)$, $K_{lh} = m_{lh}^{3/2} / \left( \sqrt{2} \pi^{3/2} \hbar^3 \right)$, $z = E_{Fe} / k_BT$, and $z' = z - \Delta_s / k_BT$. The quantity $\Delta_s = E_{vl} - E_{vh}$ is the energy separation between light-and heavy holes at the $\Gamma$-point of the Brillouin zone (zero unless there is strain), and $m_{lh}$, $m_{hh}$ are the corresponding hole effective masses.

Eqs. (7.3) and (7.4) are solved numerically for the quasi-Fermi levels, under the constraint $p_{ex} = n_{ex}$. In the case of doped $n$-type samples, the doping concentration is

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added to the parameter $n_{\text{ex}}$. Adjusting $n_{\text{ex}}$ shifts the peak emission slightly and affects the high-energy tail in the emission spectra. For the values of broadening used in the calculation of the direct gap emission (discussed below), the lineshape is quite insensitive to the value of $n_{\text{ex}}$ if $n_{\text{ex}} < 10^{18} \text{ cm}^{-3}$. The highest value obtained from the fits was $n_{\text{ex}} = 6 \times 10^{19} \text{ cm}^{-3}$, but most samples are fitted with $n_{\text{ex}}$ values in the $10^{17}$-$10^{18} \text{ cm}^{-3}$ range. In some cases, the predicted high-energy tail is somewhat broader than the experimental one even at the lowest photoexcited carrier concentrations. Self-absorption is included in the latest simulation.

The treatment of broadening in the calculated emission is important for the accuracy of the band gap fit parameter $E_0$. As indicated in Ref. 98, the best agreement between calculated and experimental absorption in Ge and Ge$_{1-x}$Sn$_x$ alloys is obtained using Gaussian broadening. Accordingly, the absorption $\alpha_0$ is broadened by convoluting the calculated function with a Gaussian with a FWHM $w_{\text{abs}}$. The emission in Eq. (2.78) is calculated using the broadened absorption, and then this calculated emission is convolved with a Gaussian with FWHM $w_{\text{res}}$ to account for the instrumental resolution. In earlier work, a simplified approach is used in which the absorption is calculated without any broadening and we performed a single Gaussian convolution step after calculating the spontaneous emission. This step was supposed to account effectively for the absorption broadening and instrumental resolution. However, this leads to band gap values that are systematically shifted to lower energies by about 10 meV. The two-step broadening procedure described here, on the other hand, is more physically appealing and leads to excellent agreement with the expected band gap in the case of pure Ge films.
In principle, the broadening \( w_{\text{abs}} \) is not an adjustable parameter in the second data processing step because, as shown in appendix B, it is related to the FWHM \( w \) of the Gaussian component of the EMG function by

\[
w = \sqrt{w_{\text{abs}}^2 + w_{\text{res}}^2}
\]  

(7.5)

Thus \( w_{\text{abs}} \) is obtained from Eq. (7.5) using the EMG broadening parameter from the first step and the known resolution broadening \( w_{\text{res}} = 0.016 \) eV. The quality of this approximation decreases in the presence of strain, because our absorption calculation includes the separate light- and heavy hole edges explicitly, but a single EMG function is applied in the first step. In these cases the fit of the EMG with the theoretical expression for the emission can be further improved by taking \( w_{\text{abs}} \) as a third adjustable parameter, and typically values within 90\% of those calculated are obtained from Eq.(7.5).

The temperature \( T \) that appears in the above expressions was taken as \( T = 316 \) K. This value was obtained by performing a few preliminary fits in samples measured at increasing laser power densities, for which we observed a downshift in the \( E_0 \) energy. If this shift is attributed to laser heating, based on the known temperature dependence of the direct gap in Ge, the laser power used for the measurements will raise up temperature by about 23 K. At this temperature, the expected direct band gap of Ge is \( E_0 = 0.796 \) eV,\(^{106}\) whereas the fits for the pure Ge films gives \( E_0 = 0.798 \pm 0.005 \) eV. It is thus fair to claim that the method makes it possible to determine the band gap \( E_0 \) within a few meV.

Further confirmation of this is seen in Fig. 51, where the \( E_0 \) gaps are plotted for our Ge\(_{1-x}\)Sn\(_x\) samples as a function of the Sn concentration, and the data points follow a line with small fluctuations from sample to sample. It is important to
Figure 51. Compositional dependence of the direct gap $E_0$ (circles) and the indirect gap $E_{\text{ind}}$ (squares) in Ge$_{1-y}$Sn$_y$ alloys. The solid lines represent linear fits to the data, and the dotted lines correspond to quadratic fits for the entire compositional range $0 \leq y \leq 1$ using the end values at $y = 0$ and $y = 1$ as fixed parameters. The shaded area around the crossover point indicates the error in the crossover concentration.

Point out here that since the calculated direct gap absorption deviates strongly from the expected $(E-E_0)^{1/2}$ dependence for free electron-hole pairs (due to excitonic effects), the difference between the band gap $E_0$ and the maximum of the calculated emission cannot be expected to be $k_B T/2$, as commonly assumed. This is shown in detail in Appendix B.

For the indirect gap emission, as explained above, a theoretical expression that can be fit to the Gaussian function used in the first modeling step is lack. Moreover, it can be argued that assuming a simple Gaussian in the first step represents an oversimplification. A considerably more sophisticated approach is explored, in which the indirect emission is modeled with three EMG’s (for phonon emission, phonon absorption, and no-phonon
transitions), and excellent fits are obtained, which appear to indicate that the no-phonon transitions increase in relative intensity as a function of the Sn concentration. However, a fundamental limitation of this approach is finding a reliable way to extract the desired $E_{\text{ind}}$ value from these fits in the absence of a theoretical model of indirect emission as available for the direct gap. The “location” parameter of the EMG functions is not related to the desired $E_{\text{ind}}$ in any obvious way. This is confirmed by performing EMG fits of theoretical direct-gap emission spectra calculated for a fixed value of $E_0$ but varying $w_{\text{abs}}$ and/or $\Delta F$. In all cases, the location parameter does not remain constant. The same should be true for the indirect emission, and this precludes the use of EMG-based fits to determine the value of the indirect gap. On the other hand, the simple Gaussian curve has the virtue that the position and width are completely “decoupled”, and therefore it is recommended to use the location of this Gaussian as a way to determine the compositional dependence of the indirect gap. Of course, the peak of the Gaussian cannot be identified as the indirect gap, but it is assumed that it is shifted from $E_{\text{ind}}$ by a constant amount, independent of composition, that can be determined from PL experiments in pure Ge films for which the indirect band gap is known. By using this procedure, and assuming that for the very modest values of strain in our samples the indirect emission is dominated by transitions to the heavy-hole band, and that the indirect band gap of pure Ge at 316 K is 0.655 eV,\textsuperscript{128} it is found that the constant shift that must be applied to the data is 0.031 eV. This value is consistent with the energies of the zone edge LA/LO (0.027/0.031 eV) and TO (0.035 eV) phonons in Ge. The expected compositional dependence of these phonon energies is rather weak for $y < 0.1$, which justifies the use of the same rigid shift of 0.031 eV for all Ge$_{1-y}$Sn$_y$ samples. The results of the fit for all
Ge$_{1-y}$Sn$_y$ samples for which the indirect band gap emission was observed is shown in Fig. 51, and it is seen that the data is significantly noisier than the direct band gap results. However, this higher noise is not due to the *ad hoc* nature of our fitting approach but to the fact that the indirect band gap emission is considerably weaker, and sometimes nearly merged, with the stronger direct gap emission.

6. Discussion

6.1 Compositional Dependence

The simplest fits to the data in Fig. 51 are linear expressions given by (in eV):

\[
E_0(y) = 0.796 - (3.43 \pm 0.04)y \\
E_{\text{ind}}(y) = 0.655 - (1.64 \pm 0.10)y
\]  

(7.6)

The fits are shown as solid lines in Fig. 51. Here the independent term is fixed to match the known Ge values. If both coefficients are adjustable, similar results are obtained (in eV) \( E_0(y) = (0.790 \pm 0.002) - (3.33 \pm 0.06)y \) and \( E_{\text{ind}}(y) = (0.662 \pm 0.005) - (1.82 \pm 0.16)y \)

As expected from the introduction, extrapolation of Eq. (7.6) to \( y = 1 \) leads to values drastically different from those measured in \( \alpha \)-Sn, so that the linear expression in Eq. (7.6) can only be valid over the range of our measurements. To extend the results to the entire compositional range, it is usually assumed that the compositional dependence is quadratic.

The quadratic term is proportional to a bowing parameter \( b \) defined by

\[
E_0(y) = E_0^{\text{Ge}}(1-y) + E_0^{\text{Sn}}y - b_y(1-y) \\
E_{\text{ind}}(y) = E_{\text{ind}}^{\text{Ge}}(1-y) + E_{\text{ind}}^{\text{Sn}}y - b_{\text{ind}}y(1-y)
\]

(7.7)

If both end values for \( y = 0 \) and \( y = 1 \) are taken as equal to the corresponding values in Ge and \( \alpha \)-Sn, a fitting function that contains the bowing coefficient as its only adjustable parameter is left. Using \( E_0^{\text{Ge}} = 0.796 \) eV, \( E_0^{\text{Sn}} = -0.413 \) eV (Ref. 129), \( E_{\text{ind}}^{\text{Ge}} = 0.655 \) eV,
and $E_{\text{Sn}}^\text{ind} = -0.035$ eV (Ref. 130), thus $b_0 = 2.37 \pm 0.04$ eV and $b_{\text{ind}} = 0.99 \pm 0.11$ eV. One potential difficulty with this approach is that $\alpha$-Sn is not stable at room temperature. Its low temperature properties were measured in the 1970’s, but extrapolation to room temperature is problematic. $\alpha$-Sn films that were metastable beyond room temperature were grown in the 1980’s on InSb and CdTe substrates. Extensive work was done on the optical properties of the metastable films, but the low-energy band structure has not been revisited. The value $E_0^\text{Sn} = -0.413$ eV that we used for our $E_0$ fit was determined by Groves et al. from magnetoreflection experiments at low temperatures. This value is in good agreement with theoretical calculations based on semi-empirical methods. No temperature dependence was found below 100K, but assuming the same value at room temperature may introduce an unknown error. The indirect gap was determined at low temperatures using free-carrier reflectivity ($E_{\text{ind}} = 0.115$ eV) and electrical measurements ($E_{\text{ind}} = 0.092$ eV). The agreement with theory is not particularly good. Chelikovsky and Cohen predict $E_{\text{ind}} = 0.140$ eV (Ref. 133), whereas Brudevoll et al find $E_{\text{ind}} = 0.175$ eV. The indirect transition has a relatively strong temperature dependence that has been measured only to 250 K in Ref 134. Extrapolating the results to room temperature, we obtain $E_{\text{ind}} = -0.035$ eV, and this value was used to obtain the bowing parameter. If the theoretical value $E_{\text{Sn}}^\text{ind} = 0.175$ eV is used, the bowing parameter fit would have been $b_{\text{ind}} = 1.2 \pm 0.1$ eV. These results illustrate the need for specifying the end values when comparing bowing parameters from different authors. For this reason, the simple fit in Eq. (7.6) may be preferable.

Earlier PL work on samples with $y \leq 0.03$ indicates $b_0 = 1.8$ eV, significantly below the value reported here. The band gap values in Ref. 35 were assumed to be equal to the
PL maximum. Given the far more sophisticated lineshape analysis in the present chapter, the extended compositional range, and the much larger data set, the results reported here are more accurate than those in Ref. 35. On the other hand, earlier $E_0$ measurements using spectroscopic ellipsometry and photoreflectance also yield $b_0 = 1.94 \pm 0.04$ eV. However, this value corresponds to an extended compositional range $y \leq 0.14$. The ellipsometric data are in very good agreement with the PL data in Fig. 51 over the overlapping range $y \leq 0.08$. The different bowing parameters obtained over different compositional ranges suggest a possible compositional dependence of the bowing parameter itself, i.e. a deviation from the quadratic dependence in Eq. (7.7). This is in principle not entirely surprising, since there is no profound theoretical reason in support of the functional form in Eq. (7.7). However, Pérez Ladrón de Guevara and co-workers obtain $b_0 = 2.3 \pm 0.1$ eV, in good agreement with our PL results, from absorption measurements on seven samples with $y \leq 0.14$ grown by rf sputtering on Ge substrates. The apparent discrepancy with Ref. 34 can be traced back to the measured band gaps at the highest Sn concentrations. For example, for $y = 0.14$, Perez Ladron de Guevara et al. find $E_0 = 0.33$ eV, whereas for the same concentration D’Costa et al. find $E_0 = 0.41$ eV. It is difficult to compare the results from the two references, since the samples were grown using a different method, the compositions were determined differently, and the band gaps were extracted from the optical data using a different methodology. Most importantly, however, the determination of possible deviations from Eq. (7.7) will require a very large set of samples covering a compositional range beyond that in Fig. 50.

In Ref. 122, Lin et al. presented photoreflectance results from four samples with $y < 0.064$. The reported bowing parameter is $b_0 = 2.42 \pm 0.04$ eV, in good agreement with our
PL data. Chen et al. also reported photoluminescence results from five samples in the compositional range $0 < y < 0.09$. The band gap is simply identified with the PL peak maximum. The resulting bowing parameter is $b_0 = 2.1 \pm 0.1$ eV. Given the different methodologies and reduced sample set, the agreement with our data is satisfactory.

Experimental work on the compositional dependence of the indirect band gap is much more scarce. Tonkikh et al report low-temperature PL results from samples in the $0.06 \leq y \leq 0.09$ range. They obtain a bowing parameter $b_{\text{ind}} = 0.80 \pm 0.06$ eV by assuming that the photoluminescence peak corresponds to the no-phonon line, and $b_{\text{ind}} = 0.17 \pm 0.06$ eV if they assume that the peak corresponds to emission of an LA phonon. Recent PL experiments in GeSn quantum wells by the same group suggest instead a lower limit $b_{\text{ind}} > 1.47$ eV. The fit value presented here is intermediate between the different bowing parameters proposed by Tonkikh et al. Mathews et al. (Ref. 35) did not give an explicit compositional dependence of the indirect transition, but their measured dependence of the $E_0-E_{\text{ind}}$ difference suggests a direct-indirect cross-over near $y_c = 0.09$, somewhat higher than cross-over value discussed below.

The failure of early theoretical predictions regarding the compositional dependence of the direct gap has motivated a renewed theoretical interest in Ge$_{1-y}$Sn$_y$ alloys. Using 64-atom quasi-random structures to simulate the alloy, Yin et al. predict $b_0 = 2.55$ eV and $b_{\text{ind}} = 0.89$ eV, in good agreement with our results. Their calculated direct-indirect crossover concentration is $y_c = 0.063$. Using smaller (16 atom) cells, Chibane and Ferhat predict a compositional dependent bowing parameter close to $b_0 = 2.9$ eV for $y = 0.06$ and approaching $b_0 = 1.9$ eV for $y = 0.19$. For the indirect gap, Chibane and Ferhat predict $b_{\text{ind}} = 0.9$ eV, leading to $y_c = 0.105$. The strong compositional dependence
of $b_0$ is in contrast with the results from Yin et al., who find a weak compositional dependence for this parameter. A non-monotonic compositional dependence of $E_0$ is predicted by Lee et al based on even smaller 8-atom cells. Using similar cells but with an empirical pseudopotential method, Moontragoon et al. (Ref. 141) predict $b_0 = 2.49$ eV and $b_{\text{ind}} = 2.28$ eV, which lead to $y_c = 0.17$. Perhaps the most important conclusion from a comparison of all these theoretical predictions with our experimental data is that the best agreement is obtained for 64-atom supercells, suggesting that this is probably the minimum supercell size for meaningful comparisons with experiment. It is interesting to point out in this context that an empirical correction to the VCA was introduced by Gupta and coworkers. Here a local disorder correction is added to the VCA pseudopotential. This correction includes a free parameter that is adjusted to reproduce the experimental bowing coefficient for the direct gap, which is taken as $b_0 = 2.1$ eV. The calculations predict $b_{\text{ind}} = 0.91$ eV, which is close to our experimental value. Unfortunately, the predictions from this approach have not been compared with the experimental bowing coefficients for higher-energy transitions, which might provide a more complete assessment of the validity of this intriguing method.

6.2 Crossover Concentration

Since the difference in slopes for the two lines in Fig. 51 is not too large, small slope errors translate into a relatively large uncertainty regarding the crossover concentration $y_c$ between the direct and indirect band gaps. From the slopes determined above and their uncertainties, we obtain $y_c = 0.073 \pm 0.007$. In principle, the crossover concentration can
be determined directly from low-temperature PL or from measurements of the infrared Drude reflectivity in doped samples. However, the much larger electronic density of states at the $L$ valley minimum, compared with the $\Gamma$ minimum, make these experiments challenging. In the case of doped samples, for example, simulations show that the predicted Drude response only reflects the lower effective mass of carriers at the $\Gamma$ minimum at concentrations much higher than $y_c = 0.073$, for which there is a substantial population of the $\Gamma$ valley. It is also possible that the alloy perturbation will partially mix the conduction band states when they overlap in energy, further blurring the abruptness of the transition.
The results obtained can be used to estimate the compositional dependence of the direct and indirect edges in Ge$_{1-y}$Sn$_y$ films fully strained to Ge substrates. Figure 52 shows the predicted dependence using the fits in Fig.51 and standard deformation potential theory, with parameters from Table 4. Compressive strain increases the separation between the direct and indirect edges, which is predicted to be 0.076 eV at the crossover composition $y_c = 0.073$ for the relaxed alloy. If the calculation is continued to higher Sn-concentrations, a direct-indirect crossover is predicted for fully-strained Ge$_{1-y}$Sn$_y$ at $y_c = 0.19$, not too different from the value $y_c = 0.17$ estimated by Tonkikh et al.\textsuperscript{136} However, the compressive strain value at such composition would be 2.7%. At this level of strain both the linear elasticity and deformation potential theories underlying the calculation will break down, so that the estimate may be affected by a significant systematic error. However, regardless of the precise crossover value, it is apparent that fully strained Ge$_{1-y}$Sn$_y$ direct gap semiconductors would be of very limited practical interest.

6.3 Doped Samples

The effect of phosphorus doping on the band gap energies of Ge has been somewhat controversial as of late. A clear band gap renormalization was reported by Haas in 1962 (Ref. 143) for both $E_0$ and $E_{\text{ind}}$, and reproduced theoretically.\textsuperscript{144} More recently, however, room temperature PL experiments on highly doped Ge films on Si were interpreted as showing a negligible $E_0$ renormalization.\textsuperscript{103} Subsequent PL work, on the other hand, showed clear evidence for an $E_0$ renormalization shift that is comparable to Haas’ earlier work.\textsuperscript{106,145,146} Our results make it possible to extend the study of band gap renormalization effects to Ge$_{1-y}$Sn$_y$ alloys.
Figure 53. Direct gap $E_0$ (circles) and indirect gap $E_{\text{ind}}$ (squares) obtained from the PL spectra of $n$-type Ge$_{1-y}$Sn$_y$ films. Colors indicate the carrier concentration. The solid lines are the best fits for the direct and indirect gap in undoped films, from Fig 51. The inset shows the band gap renormalization extracted from the data (black circles). The white circles are results for bulk Ge from Ref. 62. The solid line is a fit to the data as described in the text.

In Fig. 53 the measured values of $E_0$ and $E_{\text{ind}}$ in our doped Ge$_{1-y}$Sn$_y$ films are compared with the corresponding results for undoped samples, shown as solid lines extracted from the best fit lines in Fig. 51. It is apparent that the energies of both direct and indirect edges are reduced in the presence of donor atoms, as expected from theory. The band gap renormalization can be extracted by simply subtracting the measured values in doped samples from the best prediction for the band gap of an undoped sample with the same concentration. The resulting data might be expected to be much noisier than measurements in pure Ge films, because of fluctuations in the undoped gap value on the order of those seen in Fig. 51. In the case of the $E_0$ gap, however, a clear trend is seen as a function of the doping concentration, shown in the inset in Fig. 53. Comparing our Ge$_{1-y}$Sn$_y$ data with band gap renormalization measurements in pure Ge (white circles), it appears that band gap renormalization is largely independent of the Sn concentration over
the measured range. The solid line in the inset shows a fit of the data with the function

\[ \Delta E_0 = -A \sqrt{\frac{n}{10^{18} \text{ cm}^{-3}}} \], with \( A = 8.22 \text{ meV} \). A somewhat better agreement with the data using a linear fit is obtained, as proposed in Ref. 146, but the square-root function gives the correct dependence for \( n \to 0 \). It is important to point out that our analysis of the PL results include the possible effects of band filling and associated shifts of the peak emission, so that these results represent a measurement of the true band gap renormalization. Finally, the agreement of the renormalization shifts measured in our Ge\(_{1-y}\)Sn\(_y\) alloys with those reported in literature for pure Ge provides additional indirect evidence for the accuracy of the underlying compositional dependence of \( E_0 \), which is used to compute the renormalization shifts. For the case of the indirect gap, however, the results are too noisy to identify a clear trend beyond a reduction in band gap energy with doping.

7. Conclusion

In summary, a study of the compositional dependence of the direct and indirect band gap edges in Ge\(_{1-y}\)Sn\(_y\) alloys using room temperature photoluminescence is presented. This technique is in principle the most attractive one for the determination of the two gaps, because they produce distinct features in the same spectrum. However, a detailed theoretical analysis is needed to extract the needed gap values from the broadened room-temperature spectra, and this need is particularly acute in the Ge\(_{1-y}\)Sn\(_y\) system because small errors in the compositional dependence of either gap leads to a large uncertainty in the value of direct-indirect crossover. The required accurate model for the direct gap transition is developed and shown that it allows for the determination of the energy \( E_0 \) with meV precision. On the other hand, it is shown that current models of indirect gap
emission are inadequate for Ge-like Ge_{1-y}Sn_y alloys. The indirect gap energies were extracted from the peak energy of the emission by subtracting a constant energy that was found to be approximately equal to the energy of the phonons involved in this transition. Further theoretical work will be needed to improve this aspect of the analysis and fit the indirect emission with a realistic physical model of the process.

The results presented here for both direct and indirect transitions indicate a crossover concentration $y_c = 0.073 \pm 0.007$. This is substantially less than predicted from theoretical models within the virtual crystal approximation. Explicitly incorporating alloy effects via large supercells brings the theoretical predictions much closer to the experimental data. The low value of the predicted crossover concentration indicates that direct-gap Ge_{1-y}Sn_y can be easily fabricated using current growth approaches. However, the very different density of states between the $L$ and $\Gamma$-valleys in the conduction band of Ge_{1-y}Sn_y semiconductors suggest that optical and electrical behavior of the alloys may not reflect their direct-gap character until the Sn concentration is significantly higher than $y_c$. 
CHAPTER 7

DEVELOPMENT OF LIGHT EMITTING GROUP IV TERNARY ALLOYS ON SI PLATFORMS FOR LONG WAVELENGTH OPTOELECTRONIC APPLICATIONS

Reprinted with permission from “Development of Light Emitting Group IV ternary Alloys on Si Platforms for Long Wavelength Optoelectronic Applications” Liying Jiang, Chi Xu, James D. Gallagher, Ruben Favaro, Toshi Aoki, José Menéndez, and John Kouvetakis Chemistry of Materials DOI: 10.1021/cm403801b. American Chemical Society. My work in this chapter is part of photoluminescence measurement and electron microscopy.

1. Introduction

A major issue with Ge$_{1-y}$Sn$_y$ is the low thermal stability of highly concentrated samples with Sn contents near the direct gap threshold, and this creates problems for applications requiring high temperature processing (above 500 °C). An attractive and thermally robust alternative to Ge$_{1-y}$Sn$_y$ alloys is the Ge$_{1-x-y}$Si$_x$Sn$_y$ system. This latter represents the first viable ternary semiconductor among group IV elements with independently tunable lattice parameter and electronic structure. Ge$_{1-x-y}$Si$_x$Sn$_y$ photodiodes with state of the art optical and electrical properties have already been developed, paving the way for a variety of applications in Si-based photonics, including photovoltaics. Additionally, Ge$_{1-x-y}$Si$_x$Sn$_y$ exhibits an enhanced thermodynamic stability relative to Ge$_{1-y}$Sn$_y$ analogs due to its increased mixing entropy for the same Sn content. The incorporation of Si not only improves the thermal stability but changes the electronic structure (see schematic in Fig.54). Its main effect is to shift the direct gap energy toward higher values, since the $E_0$ direct transition in Si has an energy of 4.1 eV at room temperature. In addition, the separation between the direct edge and the indirect
edge associated with the $L$-valley is also predicted to increase as a function of the Si concentration, both from an interpolation between the corresponding energy eigenvalues in the elemental semiconductors$^{149}$ and from detailed calculations.$^{150}$ The discovery of a large negative bowing in the direct gap of the ternary alloy$^{151,152}$ does not change this picture substantially, because as the Si concentration is increased, the indirect gap switches rapidly to Si-like.$^{149,153}$ The Si indirect gap is associated with a valley with a minimum along the (001) direction ($\Delta$-line) in the Brillouin zone of the diamond-structure crystal. The energy of this valley above the maximum of the valence band is about the same for Si, Ge, and $\alpha$-Sn.$^{153,154}$ Thus a very weak compositional dependence of the indirect gap associated with the $\Delta$-minimum is expected, and this approximately constant energy represents an upper limit for the value of any indirect band gap in the ternary alloy. This qualitative analysis is corroborated by detailed calculations.$^{149}$

The above considerations suggest that the way to recover Ge-like emission properties from ternary Ge$_{1-x-y}$Si$_x$Sn$_y$ alloys is to overcompensate the electronic contribution of Si by further increasing the Sn concentration. This idea was recently validated with the observation of direct-gap photoluminescence from Ge$_{1-x-y}$Si$_x$Sn$_y$ films with $y > x$ grown on Si substrates.$^{155}$ In this chapter, we report structural and optical studies of Ge$_{1-x-y}$Si$_x$Sn$_y$ films with $y > x$ grown on Ge-buffered Si. The results demonstrate that the separation of the direct and indirect edges can be made smaller than in Ge even for non-negligible Si concentrations, confirming that with a suitable choice of compositions the ternary alloy Ge$_{1-x-y}$Si$_x$Sn$_y$ reproduces all features of the electronic structure of the binary Ge$_{1-y}$Sn$_y$. Since our luminescent Ge$_{1-x-y}$Si$_x$Sn$_y$ films have $y \geq x$, they are not lattice matched to the Ge buffer layers, and their thickness is such that the epitaxial strain is
largely relaxed. Still, the starting lattice mismatch is drastically reduced relative to previous Ge$_{1-x-y}$Si$_x$Sn$_y$/Si films. Accordingly, the Ge$_{1-x-y}$Si$_x$Sn$_y$/Ge interface is expected to be substantially less defected than the direct Ge$_{1-x-y}$Si$_x$Sn$_y$/Si interface, where the carrier recombination velocity could be as high as 4000 m/s. It is possible that this is the underlying reason for the much enhanced photoluminescence signal from these films.

2. Results and Discussion

2.1 Growth of Ge Buffer

In this new class of Ge$_{1-x-y}$Si$_x$Sn$_y$ alloys the Si content is maintained nearly constant at 3-4 % Si, which is considered to be sufficient to imbue the desired thermal stability in the ternary alloy, while the Sn composition was varied from 4-10 %, spanning the range where the direct gap transition is reported to occur for the Ge$_{1-y}$Sn$_y$ binary alloys. These samples were grown using two distinct methods previously described in Ref157. Briefly, the first method utilized a single-wafer gas-source MBE reactor and combinations of
tetrasilane (Si$_4$H$_{10}$), tetragermane (Ge$_4$H$_{10}$) and stannane (SnD$_4$) chemical sources to produce alloys with 3-4 % Si and 5-6 % Sn, grown at 260 °C. The main advantage in this case is that the growth of the film is conducted in one step in the same chamber starting with the buffer and followed by in situ growth of the epilayer using similar protocols and chemical sources. This approach avoids exposure of the wafers to the ambient and ensures minimal contaminations of background impurities which are detrimental to the optical performance of the materials. Furthermore, the hydride co-reactants possess comparable reactivities enabling low temperature growth of uniform layers across the 4” wafers exhibiting low defectivity, flat surfaces and large thicknesses near the 500 nm threshold to generate PL emission from these materials. However, the main drawback of this method is that thick films with higher Sn contents above 5% are difficult to produce, since the lower temperatures needed to systematically increase the Sn content while maintaining reasonable growth rates are outside the range of optimal reaction efficiency under the conditions allowed by the reactor geometry. For this reason the samples reported here utilize an alternative set of

![Figure 55](image_url)

**Figure 55:** (a) Equilibrium mixture of Ge$_4$H$_{10}$ isomers at growth conditions. (b) XTEM image of as-grown Ge on Si buffer layer showing no threading defects within the field of view. (c) Corresponding plan view TEM image shows sporadic dislocations (marked by arrows) with an estimated density of 2x10$^7$ cm$^{-2}$. 
sources (Si$_4$H$_{10}$, Ge$_2$H$_8$, SnD$_4$) and a conventional UHV CVD technique used in prior work to synthesize GeSn alloys. In this arrangement the reactants are subjected to additional activation by preheating them before reaching the substrate surface to initiate crystal growth. This leads to the formation of highly concentrated layers with 4-10% Sn and ~3-4% Si between 330 and 290 °C, respectively. This synthetic pathway also provides access to a wider range of operating temperatures and pressures relative to MBE. This process flexibility in turn delivers higher growth rates and significantly lower residual strain in the as-grown samples due to the higher temperatures employed, which more effectively relax the compressive stresses formed during crystal assembly. Nevertheless, the samples produced using both methods provide valuable insight into the influence of the reaction environment and the precursor chemistry (chemical and physical compatibility among co-reactants) on the optical performance of the target materials, as evidenced by the quality and strength of the PL emission peaks as described in later sections.

The Ge buffer layers were grown on 4” Si(100) wafers using the gas source MBE method via thermolysis of the Ge$_4$H$_{10}$ (Fig. 55a) using recently developed protocols reported in detail elsewhere. Briefly, the gaseous compound was diluted with high purity H$_2$ in 1:20 by volume and the mixture was then delivered onto the wafer surface via an injection manifold at a steady rate controlled by a high-precision leak valve. The substrate temperature was set at 370 °C and the growth pressure was maintained at 1x10$^{-4}$ Torr throughout the course of the experiment. Under these conditions high crystal quality Ge films were grown at a rate of 25 nm per minute to a final thickness of 1.5 µm. All samples underwent post-growth annealing at 750°C for 60 seconds on the wafer stage to
reduce residual threading defects and improve uniformity in crystal orientation and alignment. Standard quality control characterizations with Nomarski and atomic force microscopies (AFM) were routinely conducted and the results revealed optically smooth and atomically flat layers (AFM RMS roughness of 0.5 nm) devoid of cracks and surface defects, as expected. Furthermore, XRD analysis of the films showed the full width at half maxima (FWHM) of the 004 rocking curves to be in the range of 120 to 150 arcseconds. The samples were further characterized by transmission electron microscopy both in plan-view and cross sectional (XTEM) geometries to verify the flat surface morphology and estimate the bulk dislocation density (Fig. 55b, c). The plan-view images reveal intermittent dislocations scattered throughout the layer as illustrated with a representative image in Figure 55c. Quantitative examination of multiple images gave an average defect density of 2x10^7 cm^-2. The latter likely represents an upper limit to the actual number of defects penetrating to the top surface, since corresponding XTEM images show either no defects present (see Fig. 55b) or only occasional dislocations terminating within the lower segment of the film. Given the relatively low thickness of this film and the difficulty to gauge how far down into the layer our plan view images extend, it is possible that our analysis may include defects confined to the vicinity of the interface region along with those propagating through the entire layer. Notwithstanding, the representative micrograph shown in Figure 55(b) demonstrate that the bulk layer microstructure does not contain threading defects within the field of view of the experiment. The XTEM images also confirmed that the strain mismatch of the film with the Si platform is fully compensated by a pseudoperiodic, Lomer-type, edge dislocations as commonly seen for integration of highly dissimilar group IV materials.
Figure 56. AFM images (top) and XTEM micrographs (bottom) of Ge$_{0.911}$Sn$_{0.036}$Si$_{0.053}$ sample. The phase contrast image shows the full Ge buffer and epilayer with corresponding thicknesses of 500 nm and 1200 nm. The interfaces are defective in both cases while the bulk crystal segments are mostly devoid of threading defects. The AFM images of the film surface show cross-hatched surface patterns as a consequence of interface misfit dislocations. The RMS roughness for the 20x20 um and 5x5 um scan areas at top left and right panels are 1.6 and 2.6 nm, respectively.

Finally, each of the fabricated Ge-buffered Si wafers was cleaved into four quadrants, which were then used as substrates for subsequent heteroepitaxy of the Ge$_{1-x-y}$Si$_{x}$Sn$_{y}$/Ge/Si(100) samples using the UHV CVD method.$^{155}$

Initial inspections of the bulk film microstructure were conducted by cross-sectional transmission electron microscopy (XTEM) using a JEM-4000EX high-resolution electron microscope operated at 400keV and with a structural resolution of 1.7 Å. Studies of selected samples revealed uniform layers with planar surfaces and well-defined interfaces,
as shown in Figure 56 for a 500 nm thick Ge$_{0.911}$Si$_{0.036}$Sn$_{0.053}$ film grown on 1200 nm Ge buffer layer. In this case the bulk layer above the interface shows a low-defectivity microstructure as indicated by the homogeneous contrast of the image. Corresponding high resolution data (not shown) reveal edge-type dislocations confined to the interface plane. Although the 500 nm film thickness in Figure 56 significantly exceeds the expected critical thickness, extended defects beyond the interface region within a field of view of the XTEM images are not visible. In this case the Ge platform absorbs the differential strain by developing localized defects whose cores do not seem to propagate through to the top surface. In contrast, XTEM images of films with higher Sn contents above 7 % reveal occasional stacking faults propagating well above the growth plane into the bulk film. These defects further accommodate the increasing lattice strain as a function of Sn composition due to the highly dissimilar lattice dimensions of the two materials. The observed interface microstructure is consistent with AFM images which reveal cross-hatch surface patterns aligned along the 011 crystallographic direction, as typically observed for similarly mismatched Si$_{1-x}$Ge$_x$ films grown on Si wafers as shown in Figure 56 top section. These features are known to directly correlate to the interface dislocations. For our materials the cross-hatch patterns become more prevalent with increasing misfit in the 4-10 % Sn composition range, yielding correspondingly increasing AFM RMS roughness of 1.5-3.5 nm.

Further structural and chemical characterizations were conducted using a JEOL ARM 200F atomic resolution microscope to investigate strain, defect microstructure and elemental distribution of the alloys. High angle annular dark field (HAADF) and bright field (BF) techniques in STEM mode were implemented to enable atomic level
interpretation of the structural and compositional properties beyond the average stoichiometric understanding of the bulk structure afforded by RBS and XRD. STEM images of the samples corroborated the presence of smooth, uniform and mono-crystalline layers exhibiting highly coherent hetero-interfaces, marked by arrows in Figure 57 for a Ge$_{0.915}$Si$_{0.035}$Sn$_{0.05}$/Ge/Si sample annealed 550°C. The elongated bright spots on panels 1 and 2 of the figure correspond to pairs of Ge-Sn-Si atoms or “dumb-bells” in the diamond cubic lattice. The dark contrast areas indicate the presence of edge dislocations accommodating the interfacial misfit strain between the two materials. The type of these defects was identified by first Fourier transform (FFT) processing the lattice images to simulate the diffraction patterns. Next a reverse FFT was applied to two selected pairs of diffraction spots \{(-1,-1,1) (1,1,-1) and (-1,1,-1) (1,-1,1)\} to generate corresponding pairs of filtered images displayed on panel 1a and 1b respectively. In both cases we see two lattice planes terminating at the same position at the interface indicating that the defect is a Lomer (LO) dislocation Fig 57(1a)(1b). The same operation was applied to the image on panel 2. Here we see that only one plane terminates at the interface, indicating that the defect is a 60° dislocation (Figure 57 (2a) and 64(2b)). Using this approach, the distribution of dislocations could be qualitatively estimated, and the types of defects at the interfaces could also be identified. Examinations of multiple electron diffraction images indicate that the 60° dislocations are the most frequently encountered defects and are typically found to be well separated and evenly distributed. The Lomer analogs are found to be infrequent and randomly scattered throughout the heterointerfaces. Notwithstanding their low initial concentration in our samples, the latter defects appear to form in an increasing proportion via combinations of
60° pairs by post growth RTA processing of the crystals. In this case the local strain fields found in the vicinity of the 60° defects (see panel 2a)

Figure 57: STEM HAADF images showing enlarged view of the Ge_{0.915}Si_{0.035}Sn_{0.05}/Ge interface marked by arrows on panel 1 and 2. The dark contrast areas indicate the location of Lomer (LO) and 60° dislocations. Inverse FFT images of selected {111} planes near the dislocation area are shown on panels (1a, 1b) and (2a, 2b) identifying the specific types of LO and 60° dislocations marked by arrows. Note that the 60° defect (panel 2a) is inherently accompanied by local strain fields as evidenced by the deformation of the lattice fringes.

likely play a key role in promoting their interaction, leading to the formation of the more stable Lomer counterparts. From a lattice mismatch accommodation perspective, the thermodynamically favored Lomer defects are also more effective in relaxing interfacial strains and in our case facilitate the development of virtually cubic epilayers irrespective
of composition allowing a straightforward interpretation of the PL properties discussed as a later section.

2.2 Atomic Level Chemical Mapping by STEM and EELS

Elemental analysis and atom-selective mapping of lattice columns was next performed by electron energy loss spectroscopy (EELS) using a GATAN En finium spectrometer with spatial resolution of 0.12 nm. The objective here is to elucidate the chemical bonding arrangements in the crystal in order to gain insights into the substitutional distribution of the Sn atoms in the lattice. The EELS spectra were recorded from a sample volume of 4x4 nm$^2$ in the lateral direction marked by the green box in Figure 58 panel (a) and a penetration depth of 25-30 nm measured via the low loss spectra. The EELS scans of the samples showed distinct core peaks at 483 and 1217 eV corresponding to Sn M 4,5 and Ge L ionization edges, respectively. These were then used to extract atomic resolution maps after background subtraction and the results are presented in Figure 58 panels (a-d). In the case of Ge (panel b) we see a distinct pattern of rectangular features corresponding to Ge-Ge dimers. The latter represent the dominant building block of the host alloy lattice and marked with a red box on the panel. The Sn map (panel c) shows a pattern of bright red spots representing a two dimensional projection of the Sn sites within the sample volume probed by EELS. The data in this case indicates that the Sn atoms do not form well-defined dimers, as expected due to their random distribution and low concentration in the lattice. These features appear to represent single isolated Sn atoms that are sparsely dispersed within the surrounding crystal matrix indicating that the atomic substitution is fully random precluding the presence of interstitial Sn atoms or
segregated clusters. Similar mapping of the Si sites was not possible in these experiments due to the low molar concentration (3 %) of the element, yielding low intensity core-loss signals which proved to be unsuitable for further analysis. Panel (d) is a colored overlay of panels (b) and (c) showing a near perfect alignment of the Sn and the Ge contributions along the 001 columns of the lattice. The latter hybrid map essentially reproduces the same STEM HAADF image outlined by the green box on panel (a), with no intensity observed between the dimer column projections, as expected for a fully substitutional Sn concentration. The above demonstrated capability of visualizing the heavy atoms in our
sample by EELS confirms the RBS channeling data in that the alloys do not show interstitial incorporation or Sn clustering. Collectively the RBS data and the element-selective EELS mapping provide complementary stoichiometric and average nano-scale level, respectively, and unequivocal evidence of compositional uniformity and atomic substitutionality. In the case of the diamond lattice the data shows that the Sn atoms occupy random tetrahedral sites and thus preserve a near ideal alloy structure with extended crystalline perfection.

![Image](image_url)

**Figure 59.** (left) Sn maps across the interface, the intensity corresponds to Sn composition. (right) Sn relative composition profile across the interface.

The interface sharpness was characterized with EELS in the same instrumental setting but a large sampling area of around 100nm ×100nm. Typical elemental maps were generated with the same processing described above. Take Sn maps in the left panel of Figure 59 for example, the left side with higher intensity corresponds to Ge$_{0.915}$Si$_{0.035}$Sn$_{0.053}$ film and the right side corresponds to Ge buffer, which does not contain Sn atoms. The two dimensional maps is then divided to a series of line scans across the interface and average along the interface. This process generated a profile of
Sn as a function of horizontal distance plotted on the right panel of Figure 59. The fluctuations on the Ge buffer are due to data processing and uncertainty of the technique. Assuming the interface is Gaussian-broadened with a standard deviation $\sigma$, and fit it with error function as indicated by the solid line in the right panel of Figure 59. It gives a broadening value of $\sigma=12.27\text{nm}$.

The above fabrication of mostly strain-relaxed GeSiSn alloys is a testament to recent advances in developing suitable Ge-on-Si buffer technologies using improved deposition chemistries based on novel high order Ge hydrides. As described above, these buffers are implemented as low energy platforms to engineer the interface defects of $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ epilayers by providing significant reductions in the starting mismatch relative to previous $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ films grown directly on Si. Accordingly the new $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$/Ge interfaces are found to be less defective and presumably with lower non-radiative recombination velocities than the direct $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$/Si counterparts.

2.3 Optical properties

Detailed photoluminescence (PL) studies were conducted to demonstrate that the gains in structural stability enabled by the incorporation of Si into the Ge-Sn lattice do not come at the expense of dramatically altered optical properties. Specifically, tunable direct band gaps below those of Ge, a reduced separation between the direct and indirect edges, and a concomitant increase in the emission intensities represent characteristic optical features of binary $\text{Ge}_{1-y}\text{Sn}_y$ alloys that can also be observed in the more stable $\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y$ system.

All photoluminescence experiments were carried out at room temperature. Figure 60 shows results for several samples whose Si concentration is close to $x = 0.04$, while the
Sn concentration is varied over a broad range from 5.1 to 8.3%. The main peak is assigned to emission across the direct gap $E_0$, and the shoulder to the low energy side is related to the indirect gap $E_{\text{ind}}$. Excellent fits are obtained by representing the indirect-gap emission by a simple Gaussian function and using an exponentially modified Gaussian (EMG) to represent direct gap emission, as described in Chapter 6. The direct and indirect gap energies are extracted from these fits using the procedure described in Chapter 6.

It is apparent from Figure 60 that both gaps shift to lower energies as the Sn fraction increases, that their separation is also reduced, and that the peak intensity increases as a function of the Sn concentration. In Figure 61 we show the compositional dependence of the band gap energies. The solid and dashed lines in the figure correspond to the bilinear compositional dependencies determined in Ref. 160 (in eV): $E_0=0.79+2.21x-3.79y$ and $E_{\text{ind}}=0.67+0.65x-1.75y$ which suggest a direct-indirect crossover near $y = 0.09$. In Figure 62 we show the area of the EMG profile used to fit the direct gap emission as a function of the direct-indirect gap separation. In spite of the inherently noisy nature of intensity measurements, a clear trend is observed. The trend is compared with a theoretical calculation of the emission intensity for pure Ge$_{1-y}$Sn$_y$ alloys with the same direct-indirect gap separation. The calculation uses the Roosbroeck-Shockley theory for spontaneous emission, as described in Chapter 3. The conduction band quasi-Fermi level needed for the Roosbroeck-Shockley expression is computed by taking into account the
Figure 60. PL spectra from several Ge$_{0.96-y}$Si$_{0.04}$Sn$_{y}$ samples with Si concentrations very close to 4%. The main peak is assigned to direct gap emission, and the low energy shoulder to indirect gap transitions. A weak feature above 0.75 eV is direct emission from the Ge buffer layer. The inset shows details of the fits used to determine the band gap energies as well as the strength and width of each transition.

Two conduction band minima associated with the direct and indirect gaps, following the expressions in Chapter 6. The separation between these gaps affects the calculated intensities very strongly because the population of the conduction band minimum responsible for direct-gap emission is a strong function of this separation. The agreement is good, although the theoretical dependence is somewhat stronger, perhaps due to some additional non-radiative recombination channels at the highest Sn concentrations. We see, as expected, a trend for higher intensities in thicker samples, but the dependence on annealing treatment is rather weak. This is quite surprising, because there is a noticeable improvement in the structural properties upon annealing, as seen from the X-ray studies.
Figure 61. Sn-fraction dependence of the direct and indirect edges in samples with the approximate composition \( \text{Ge}_{0.96-y} \text{Si}_{0.04} \text{Sn}_y \). The squares represent the energies extracted from theoretical fits of the PL spectra. The lines correspond to bilinear fits of the compositional dependence of both gaps in \( \text{Ge}_{1-x-y} \text{Si}_x \text{Sn}_y \) alloys.

While the effect of annealing is not obviously apparent in the measured intensities, we do see sizable effects in the spectral widths. The EMG function used in the lineshape fits in Figure 60 is a convolution of a Gaussian with an exponential, and one of its adjustable parameters is the Gaussian width \( \sigma_{\text{EMG}} \). Physically, the width is caused by the absorption broadening. This is clearly illustrated in Chapter 6, where we show the strong correlation between the two quantities.

The absorption width obtained from the PL fits is shown in Figure 63 as a function of the Sn concentration and annealing conditions. A systematic decrease of the width upon annealing is observed. The widths of the annealed samples are similar to those observed in pure Ge-on-Si samples (~30 meV, while the absorption width in bulk Ge is 16 meV at
room temperature\cite{161}). This, combined with the weak dependence on Sn concentration, indicates that intrinsic alloy broadening plays a minor role. These results suggest that smaller broadenings might be obtained by growing alloys directly on Ge wafers. However, such samples are difficult to study with photoluminescence due to the very strong indirect gap PL from the Ge substrate. In addition our initial attempts to grow such materials using the gas source MBE methods produced fully compressive layers which proved difficult to relax using RTA processing. In contrast, the GeSiSn films grown on Ge buffered Si exhibit significant relaxation “as grown”. If the annealing treatment improves crystallinity and reduces the width of the emission, one might expect a concomitant increase in the emission intensity, since the defects eliminated by the annealing should contribute to non-radiative recombination. However, as noted above,

**Figure 62.** Integrated photoluminescence intensity for the direct gap emission from Ge$_{1-x}$Si$_x$Sn$_y$ samples. The line represents a theoretical calculation for Ge$_{1-y}$Sn$_y$ alloys with the same direct-indirect separation. The relative scale between theory and experiment is arbitrary, so only the energy dependence can be compared.
this predicted increase in intensity is in general not observed. One possibility is that the annealing procedure, while improving the bulk properties of the film, increases the surface recombination velocity, in such a way that the two contributions tend to cancel out in our samples. A hint that this may indeed be the case was obtained from PL measurements of epi-ready Ge substrates, which show a weaker emission after thermal annealing under conditions similar to those used for our GeSiSn samples.

![Graph](image)

**Figure 63.** Absorption widths (FWHM) extracted from the photoluminescence fits using the EMG profile, as described in the text. The data correspond to samples as grown (blue markers) and annealed (red markers). The annealing temperatures are indicated next to the data points.

3. Conclusions

The structural and optical properties of Ge$_{1-x-y}$Si$_x$Sn$_y$ alloys grown on virtual Ge on Si platforms via reactions of Ge$_3$H$_8$, Si$_4$H$_{10}$ and SnD$_4$ were studied. The resultant films are largely relaxed and exhibit significantly improved crystal quality relative to similar samples produced directly on Si in prior studies. Element-selective mapping of the atomic columns of the layers using EELS and STEM provide unequivocal evidence that
the constituent atoms occupy random tetrahedral sites thus preserving a near ideal alloy structure with extended crystalline perfection. Photoluminescence spectra were measured for samples with a fixed 3-4 % Si content and progressively increasing Sn content in the 4-10 % range. It is found that for $y > x$ the optical emission from these films is strong enough to allow the determination not only of the direct gap—as done previously with $\text{Ge}_{1-x} \text{Si}_x \text{Sn}_y / \text{Si}$ films—but also of the indirect edge that represents the lowest band gap in the system over a broad compositional range. The enhanced optical emission compared to $\text{Ge}_{1-x} \text{Si}_x \text{Sn}_y / \text{Si}$ is seen in spite of the fact that all of our films exceed the critical thickness for growth on Ge and their strain is mostly relaxed. These observations suggest that for the same level of strain relaxation, the defect structure in $\text{Ge}_{1-x} \text{Si}_x \text{Sn}_y / \text{Ge}$ and $\text{Ge}_{1-x} \text{Si}_x \text{Sn}_y / \text{Si}$ are very different. This is consistent with direct AFM and TEM studies of both types of film. The photoluminescence results presented here indicate that the main features of the electronic structure of $\text{Ge}_{1-x} \text{Sn}_y$ films, namely the close proximity of the direct and indirect edges and the closing of their separation with respect to pure Ge, can be reproduced in the $\text{Ge}_{1-x} \text{Si}_x \text{Sn}_y$ ternary system, with the benefit that films approaching the direct-indirect cross-over can be annealed at temperatures as high as 700 °C without causing any measurable Sn segregation.
CHAPTER 8

CONCLUSIONS

1. Introduction

In this work spectroscopic ellipsometry, electron microscopy, and Raman spectroscopy are used to characterize different semiconductor alloy systems developed for the first time at Arizona State University, which have a intriguing potential for optoelectronic applications. III-V/IV alloys such as \((\text{AlP})_y\text{Si}_{5-2y}\), and \([\text{Al(As}_{1-x}\text{N}_x)]_y\text{Si}_{5-2y}\) systems are nearly lattice-matched to Si substrates while displaying a higher absorption coefficient than Si over the UV-Visible range relevant for photovoltaics. \(\text{Ge}_{1-y}\text{Sn}_y\) and \(\text{Ge}_{1-x-y}\text{Si}_x\text{Sn}_y\) systems make it possible to tune the band gaps above and below that of Ge and achieve direct gap conditions in a purely group-IV system.

2. \((\text{AlP})_y\text{Si}_{5-2y}\) System

STEM/EELS experiments provided the first evidence that in some AlPSi3 alloys the Al and P atoms are preferentially ordered. This ordering cannot be explained if the AlP pairs are completely isolated, as expected if tetrahedral AlPSi3 units are incorporated intact to the growing film. A “short chain” structure consisting of Al-P-Al-P units was proposed to explain the findings, and it was shown that a single precursor decomposition step was sufficient to explain the formation of such chains. The “short chain” structure was also shown to be consistent with the Raman data and the ellipsometry results. A series of \((\text{AlP})_y\text{Si}_{5-2y}\) samples were analyzed and the compositional dependence of Si-Si like vibrational mode was determined.
3. [Al(As1-xN_x)]ySi5-2y System

The characterization of the [Al(As1-xN_x)]ySi5-2y system is presented in the thesis. Z contrast image and EDS analysis was performed on selected samples revealing uniform element distribution. Raman Spectroscopy was performed on these samples and the compositional dependence of the Si-Si mode was obtained. The imaginary part of the dielectric constant was extracted from ellipsometry data and compared with that of broadened Si. The numerical second derivative of the imaginary part of the dielectric constant revealed the existence of a direct gap lower than that of Si, which was confirmed with band structure calculations. The direct gap transitions E0', E1 and E2 of selected samples were presented.

4. Ge1-xSn_y system

STEM/EELS elemental maps show that Sn is evenly distributed in the Ge matrix in a way that is consistent with a random alloy atomic distribution. Photoluminescence studies on intrinsic and n type Ge1-xSn_y samples were performed. The direct and indirect band gaps were extracted with two-step modeling approach. The compositional dependence of direct and indirect band gaps and crossover concentration of y=0.073±0.007 were obtained.

5. Ge1-x-ySi_xSn_y System

A series of Ge1-x-ySi_xSn_y/Ge/Si were characterized with electron microscopy and photoluminescence. XTEM characterization of the Ge buffer suggests a defect density of 2×10^7 cm^-2. Bright field image in STEM mode reveals the existence of 60° dislocations as a result of the slight lattice mismatch. EELS/STEM elemental mapping was performed revealing the uniform distribution of Sn in Ge matrix. Si maps were not obtained due to
low molar concentration. The PL spectra of several Ge$_{1-x-y}$Si$_x$Sn$_y$ samples with Si concentration close to 4% were presented and direct gap and indirect gap dependence on composition were determined.

6. Future work

The alloy systems discussed in this thesis are relatively new, and they were either developed at ASU for the first time (III-V/IV alloys, SiGeSn), or their growth method was developed at ASU (GeSn alloys). Accordingly, in spite of the great progress achieved, as demonstrated in this thesis, there remain notorious gaps in our understanding that need to be filled over the next few years. From the point of view of optical applications, the determination of the fundamental gap is critically important, and optical methods are not conclusive when the material has an indirect band gap. Spectroscopic ellipsometry is not sensitive enough to indirect band gaps, and the determination of the indirect gaps via photoluminescence is problematic. At the same time, traditional absorption methods, which require extremely thick (mm range) samples, are difficult to implement with thin films. An intriguing alternative is the possibility of determining the band gaps via EELS measurements on monochromated microscopes. Moreover, STEM/EELS element selective maps obtained from these microscopes make it possible to obtain structural information at the nanometer-scale that was not previously accessible to experiments. By correlating these observations with the growth conditions, it will be possible to fine-tune the synthesis protocols for a much more precise control of the structure/properties relationship.

For Ge$_{1-y}$Sn$_y$/Ge/Si$_x$Ge$_{1-x-y}$Si$_x$Sn$_y$/Ge/Si systems, very accurate values for the compositional dependence of the band gaps were obtained, and the structural properties
show dramatic improvements over earlier growth experiments, particularly in the case of samples grown on Ge buffer layers. These advances should lead rapidly to the development of GeSn and GeSiSn lasers as an alternative to Ge-on-Si devices.
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APPENDIX A

SPECTROMETER CALIBRATION
1. Lamp Measurement

The measurement of the instrument response is important for an accurate determination of band gap energies. The standard approach to carry out this calibration is to measure the emission spectrum of an incandescent lamp that follows the blackbody radiation law. A non-trivial complication of this approach is the uncertainty about the spectral dependence of the transmission curve of the lamp’s glass bulb. Most commercial lamps are designed for use in the visible, where the bulb transmission approaches unity, but in our case we require a knowledge of the lamp’s optical properties well into the near-IR to at least 2300 nm. Accordingly, we use a 10 W tungsten-halogen lamp with a quartz envelope (Newport Corporation catalog #6318) with a nominal color temperature of 3200 K, whose emission properties are provided by the manufacturer between 400 nm and 2400 nm. Figure A1 shows the lamp’s spectral irradiance we obtained by digitizing the data from the Newport catalog.

Figure A1 Spectral irradiance from calibrating lamp (dots) and fit with Eq. (1) times the tungsten emissivity in Fig. A2.
The blackbody spectral irradiance is given by:

\[
I(\lambda)\,d\lambda = \frac{2hc^2}{\lambda^5} \frac{d\lambda}{\exp\left(\frac{hc}{k_B\lambda T}\right) - 1}
\]  

(A.1)

The filament radiation deviates from Eq. (A.1) due to the fact that the emissivity of tungsten has a spectral dependence. Newport also provides the tungsten emissivity, shown in Fig. A2. The solid line in Figure A.1 is a fit of the lamp’s spectral irradiance times the emissivity of tungsten. The fit indicates that temperature is 2829 K, considerably below the nominal value of 3200 K.

![Tungsten emissivity from Newport’s catalog.](image)

**Figure A2.** Tungsten emissivity from Newport’s catalog.

Since the lamp’s irradiance peaks near 1000 nm, and we are interested in the instrument’s response near 2000 nm, we need to rule out the possibility that light emitted at 1000 nm is detected at 2000 nm due to second-order diffraction at the instrument’s grating. To eliminate this effect, we insert a long-pass filter with a cutoff near 1000 nm between the lamp and the spectrometer. For this purpose we use a RG1000 colored glass
filter from Schott’s catalog (purchased from Reynard Corporation). This filter has two significant advantages: its spectral transmission is very well calibrated by Schott, and it does not present any sharp features as the transmission curves of interference filters do. Using the RG100 filter, we can define a correction function as

\[
\text{Correction} = \frac{\text{True Lamp irradiance} \times \text{RG100 Transmittance}}{\text{Measured lamp irradiance with RG100 filter}}
\]  

(A.2)

The correction function so determined is shown in Figure A3.

Figure A3  Measured and predicted correction functions. The curves have been normalized to agree at \( \lambda = 2000 \text{ nm} \).

2. Discussion

The three main contributions to the correction function are the grating efficiency, the detector responsivity, and the bandwidth correction.
Grating efficiency

We use a 600 grooves/mm grating nominally blazed at 2 µm. The grating efficiency, provided by Horiba, is shown in Figure A4.

Figure A4  Grating efficiency for 600 g/mm grating blazed at 2 µ.
Detector responsivity

The detector responsivity curve was obtained from Horiba and is shown in Fig. A5.

![Detector responsivity curve](image)

**Figure A5** LN2-cooled extended InGaAs detector responsivity

Bandwidth correction

To match the blackbody spectrum in Eq. (A.1), the measurements must be performed at a constant bandwidth $\Delta \lambda$ as the wavelength is scanned. However, the measurements are actually carried out at a constant slit opening, which due to the spectrometer optics, does not correspond to a constant $\Delta \lambda$. Thus a correction is needed.

From the Horiba tutorial at [http://www.horiba.com/scientific/products/optics-tutorial/diffraction-gratings/#c3712](http://www.horiba.com/scientific/products/optics-tutorial/diffraction-gratings/#c3712) we have the diagram in Fig. A6.
The sign convention is such that the angle $\beta$ is positive and the angle $\alpha$ is negative, as measured from the normal to the grating. The angle $D_v$, which we are also going to call $2\phi$, is therefore

$$D_v = 2\phi = \beta - \alpha$$  \hspace{1cm} (A.3)

Notice that the angle $D_v$ (and therefore $\phi$) is fixed for a given instrument.

The diffraction equation for first order is, using our sign convention:

$$\sin \alpha + \sin \beta = n\lambda$$  \hspace{1cm} (A.4)

where $n$ is the groove linear density. Now let’s suppose that we are doing a measurement with a certain exit slit. This means that there is a certain angle $d\beta$ that will be collected by the detector, and this corresponds to a certain wavelength width $d\lambda$. We can compute this spectral bandwidth from the angular width by differentiating Eq. (A.4) while keeping $\alpha$ fixed. This gives
\[
\frac{d\lambda}{d\beta} = \frac{\cos \beta}{n} \tag{A.5}
\]

If the slit width is \(\Delta x\) and the focal length of the instrument is \(f\), then we have that the spectral bandwidth collected is

\[
\Delta \lambda = \frac{\cos \beta}{nf} \Delta x \tag{A.6}
\]

It is convenient to re-express these equations in terms of the angles \(\phi\) and \(2\rho = \alpha + \beta\), since the angle \(\phi\) is a constant. We then rewrite Eq. (A.4) as

\[
\sin \rho \cos \phi = \frac{n\lambda}{2} \tag{A.7}
\]

and Eq. (A.6) becomes

\[
\Delta \lambda = \frac{\cos (\rho + \phi)}{nf} \Delta x \tag{A.8}
\]

For the MicroHR instrument, we can fit \(\phi\) from the statement in the brochure and the spectral dispersion at 400 nm with 1200 grooves/mm gratings is 5.25 nm. Using this we determine \(\phi = 13.8^\circ\). Eq. (A.8) can be expressed as a function of the wavelength by obtaining \(\rho\) from Eq. (A.7) and using \(f = 140\) mm and \(\Delta x = 1\) mm. The result is shown in Fig. A7.
Predicted correction

From the foregoing discussion, the correction function must satisfy

\[
Correction(\lambda) \propto \frac{1}{\text{Detector responsivity}(\lambda) \times \text{Grating efficiency}(\lambda) \times \text{Bandwidth}(\lambda)} \quad (A.9)
\]

Combining the results from Figs A.5-7, we show this computed correction as a dotted line in Fig. A.3. We notice that the agreement with the measured correction is reasonably good.

Conversion to energy scale

For comparison of the measured photoluminescence with theoretical predictions, we convert the spectra to an energy scale. This conversion must be done with care. By applying bandwidth correction to our data, we are effectively converting our data to
constant bandwidth. In other words, our corrected spectra are equivalent to a measurement in which $\Delta \lambda$ is constant. When converting to an energy scale, on the other hand, we require $\Delta E = \text{constant}$. However, since

$$dE = -\frac{hc}{\lambda^2} d\lambda = -\frac{E^2}{hc} d\lambda \quad ,$$

(A.10)

we must not only convert the $\lambda$-axis to an $E$-axis but multiply the corresponding data points times $\frac{hc}{E^2}$. This ensures that the integral of the entire spectrum over its energy range equals the integral over the corresponding wavelength range.
APPENDIX B

THEORETICAL CALCULATION OF THE EMISSION RATE AND EMG FIT
In this appendix we provide details on our theoretical calculation of the emission rate and on the EMG functions used in the intermediate data processing steps. The solid line in Fig B1 shows the emission obtained from Eq. (2.78) and (7.1) using our model for $a_0$, calculated for the case of pure Ge with a photoexcited carrier concentration $n = 5 \times 10^{18} \text{ cm}^{-3}$. A simpler expression of the form $K (E - E_0) \exp\left[-\frac{(E - E_0)}{k_B T}\right]$, where $K$ is a constant appears in most textbooks and is often applied to the analysis of PL data. The simplified expression follows from Eq. (2.78) under the assumption of Boltzmann statistics and direct recombination of free electron-hole pairs from parabolic energy bands. It is easy to show that the maximum of this function is located at $E_{\text{max}} = E_0 + k_B T/2$, independent of the difference $\Delta F$ of quasi-Fermi levels, which only appears in the energy-independent factor $K$. On the other hand, we show in Fig. B2 the

![Figure B1 EMG fit of a theoretical direct gap emission lineshape. The horizontal axis is given in terms of the normalized energy $(E-E_0)/w$, where $w$ is given in Eq. (7.5). The vertical grey line indicates the value of the “location” parameter of the EMG, which corresponds to the center of its Gaussian component. The inset shows the Gaussian width fit parameter from the EMG (circles) from fits of theoretical lineshapes with different absorption broadenings. The solid line is from Eq. (7.5).](image_url)
difference $E_{\text{max}}-E_0$ as a function of $\Delta F$ for the theoretical lineshape in Fig.B1. For low values of $\Delta F$, $E_{\text{max}}-E_0$ is independent of $\Delta F$, as in the simplified expression above, but the separation $E_{\text{max}}-E_0$ is closer to $k_B T/4$. This is directly related to the inclusion of excitonic effects in the absorption model. As shown in Ref. 97, the rise of the absorption coefficient above the direct gap $E_0$ is much steeper when the effect of excitons is accounted for, and this shifts the peak of Eq. (2.78) towards the band gap $E_0$. The error incurred by using the standard $k_B T/2$ correction is about 6 meV at room temperature, which is small compared with the accuracy with which band gaps are known in semiconductors, but amounts to a not entirely negligible 4% of the direct-indirect separation in pure Ge, and an even larger fraction of this separation in Ge$_{1-y}$Sn$_y$. Using $E_0 = E_{\text{max}}-k_B T/4$, on the other hand, gives excellent direct gap values without the need of any fitting, but becomes less accurate in the presence of strain due to the different weights of the contributions from the split heavy- and light-hole bands.

Figure B2. Separation between the location of the maximum $E_{\text{max}}$ of the theoretical direct gap emission and the band gap value $E_0$, in units of $k_B T/2$ for $T = 300K$ as a function of the difference in quasi-Fermi levels between the conduction and valence bands.
For $\Delta F > 0.45$ eV, the peak energy in Fig. B2 shifts to higher values, reflecting band filling effects. The value $\Delta F = 0.45$ eV corresponds to a carrier concentration $n \sim 10^{17}$ cm$^{-3}$. Larger band filling effects are computed for Ge$_{1-y}$Sn$_y$ alloys due to the reduced separation between the direct and indirect minima in the conduction band. Fig. B2 could be used to read off the direct band gap values from the observed $E_{\text{max}}$ values in unstrained Ge, except that one needs to take into account the finite spectrometer resolution, which leads to an additional upshift because the theoretical profile is asymmetric. For the conditions of our experiment, where the resolution is about one-half of the absorption broadening, the upshift is $\sim 1.3$ meV, which is rather small.

Since our model expressions account realistically for excitonic, strain, and band-filling effects, the accuracy of the $E_0$ gaps determined with the method used here is considerably improved. However, our method relies on an intermediate step in which we fit the experimental data with an EMG profile, and we need to investigate the quality of these fits to determine if our fitting process could induce systematic energy shifts. The dotted line in Fig. B1 is a fit of the theoretical emission using an EMG, and we see that the agreement is extremely good. (In the practical application we use the reverse procedure, in which we fit the raw data with an EMG, followed by a fit of the EMG with Eq. (2.78), but the quality of the fit is of course identical). We repeated the fits for theoretical emission lineshapes computed for different values of the absorption broadening $w_{\text{abs}}$ and a fixed $w_{\text{res}} = 0.016$ eV, as in our experiments. The solid line in the inset corresponds to Eq. (7.5), and the dots represent the FWHM of the Gaussian component of the EMG obtained from the fit. It is apparent from the plot that Eq. (7.5) (although in principle exactly valid for the convolution of two Gaussians), is in excellent agreement with the
simulations. This justifies the procedure, discussed above, by which the absorption width is determined in the final fits used to extract the $E_0$ gap energies.

Figure B1 also illustrates the shortcomings of the EMG function for the determination of transition energies, as discussed above in the context of the indirect gap. The horizontal axis is normalized so that the zero corresponds to the energy of the direct gap $E_0$. The vertical grey line shows the “location” parameter in the EMG fit (corresponding to the location of the Gaussian component). We see that the two values do not agree, and both are shifted from $E_{\text{max}}$. As indicated above, these relative shifts depend in a complicated way on the other fit parameters, making it virtually impossible to extract reliable $E_0$ values from the EMG parameters. Only when the EMG is fitted with a physically motivated expression it is possible to determine $E_0$ with the required accuracy.
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