
by

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ABSTRACT

Along with the fast development of science and technology, the studied materials are becoming more complicated and smaller. All these achievements have advanced with the fast development of powerful tools currently, such as Scanning electron microscopy (SEM), Focused Ion Beam (FIB), Transmission electron microscopy (TEM), Energy dispersive X-ray spectroscopy (EDX), Electron energy loss spectroscopy (EELS) and so on. SiTiO3 thin film, which is grown on Si (100) single crystals, attracts a lot of interest in its structural and electronic properties close to its interface. Valence EELS is used to investigate the Plasmon excitations of the ultrathin SrTiO3 thin film which is sandwiched between amorphous Si and crystalline Si layers. On the other hand, theoretical simulations based on dielectric functions have been done to interpret the experimental results. Our findings demonstrate the value of valence electron energy-loss spectroscopy in detecting a local change in the effective electron mass. Recently it is reported that ZnO-LiYbO2 hybrid phosphor is an efficient UV-infrared convertor for silicon solar cell but the mechanism is still not very clear. The microstructure of Li and Yb co-doped ZnO has been studied by SEM and EDX, and our results suggest that a reaction (or diffusion) zone is very likely to exist between LiYbO2 and ZnO. Such diffusion regions may be responsible for the enhanced infrared emission in the Yb and Li co-doped ZnO. Furthermore, to help us study the diffusion zone under TEM in future, the radiation damage on synthesized LiYbO2 has been studied at first, and then the electronic structure of the synthesized LiYbO2 is compared with Yb2O3 experimentally and theoretically, by EELS and FEFF8 respectively.
To my family
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CHAPTER 1
INTRODUCTION


Along with the fast development of science and technology, the scale of studied materials is becoming smaller and smaller, from micrometer scale to nanometer scale. On the other side, the materials are becoming more and more complicated, thus fine and subtle operations are required. For example as shown in Figure 1.1, even single atoms can be controlled. With all these knowledge and ability about the marvelous microscopic world we can create more and more valuable products to make our lives better. All these achievements cannot be finished without current powerful tools, such as Scanning electron microscopy(SEM), Focused Ion Beam(FIB), X-ray absorption microscopy(XAS), Transmission electron microscopy(TEM) and Electron energy loss spectroscopy(EELS) and so on, because we only have a very limited vision with our naked eyes. Any new upgrade and improved progress of the tools can lead us a smaller wonderful microscopic world of materials.

Figure 1.1 Famous IBM logo in 1989 with 35 xenon atoms by using Atomic Force and Scanning Tunneling Microscopes (STMs)
Among above mentioned tools, Transmission Electron Microscopy may be the mostly used technique in material science for several years. Associated with current improvement, recently EELS is becoming more and more popular as an analytical technique that measures the energy change of electrons after they have interacted with a specimen. Although the well known traditional x-ray absorption spectroscopy (XAS) can give us similar spectral information, XAS currently only has a lateral resolution of around 30 nm if carried out using synchrotron radiation, using electrons as probe in a modern TEM, EELS is capable of giving a spatial resolution down to the atomic level in good conditions. The electromagnetic lenses of the TEM can be used to focus them into a ‘probe’ of very small diameter (1 nm or even 0.1 nm) or to produce a transmitted-electron image of the specimen, with a spatial resolution down to atomic dimensions. In other side, the energy resolution is typically 1 eV but can approach 0.1 eV with an electron-beam monochromatic. Furthermore EELS can be combined with transmission imaging, electron diffraction and x-ray emission spectroscopy, all in the same instrument, the technique has become important for studying the physics and chemistry of materials.2

In my research, associated with the Transmission Electron Microscope (TEM), Electron Energy Loss Spectroscopy (EELS) is the most used technique to study the electronic structure or chemical composition of the materials. EELS was developed by James Hillier and RF Baker in the mid 1940s3 but was not widely used over the next 50 years, only becoming more widespread in research in the 1990s due to advances in microscope instrumentation and vacuum technology.4 The technique is able to take advantage of modern aberration-corrected probe forming systems to attain spatial resolutions down to ~0.1nm, while with a monochromated electron source and/or careful
deconvolution the energy resolution can be 100 meV or better. This has enabled detailed measurements of the atomic and electronic properties of single columns of atoms, and in a few cases, of single atoms.

<table>
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<th>Incident beam</th>
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Figure 1.2 Microanalysis Techniques using electron, ion and photon

Among a lot of analytical methods, TEM and EELS have their own distinguish features and advantages, of course some disadvantages. Thus we need to choose the proper methods for different materials and different purposes. As shown in Figure 1.2, the features of some important analytical methods are compared. Outstandingly, TEM and EELS have the highest resolution, which is very important for current demand of the nano-scale study on materials. Although relatively low energy electron beam methods are often considered as nondestructive, especially comparing with Ion beam methods, in practice the electron beam methods are not entirely so, since inelastic scattering of the incident electrons always results in some radiation damage according the rule of
conservation of energy, especially high energy electron beam techniques are very common nowadays. We will discuss radiation damage later in our real cases.

Among other microanalysis techniques, X-ray absorption spectroscopy (XAS) is most comparable with EELS. X-ray absorption edges, which occur at incident energy close to binding energy of atomic shell, are the closest analog to the ionization edges in EELS. Fine structure is also present as EELS up to hundreds eV above the edge (EXAFS) and in the near-edge region (XANES or NEXAFS). Although XAS has a low resolution but sample preparation is simple comparing to TEM/EELS. It is commonly used in large scale pure materials. Thus a lot of paper about XAS is available as reference for our EELS study.

Overall, as a microanalysis technique, EELS has a lot of advantages, such as high spatial resolution, relatively high core loss signal, available to structural information and ability of quantization. With different incident electron energy, the technique can be referred to as high resolution (energy) electron energy loss spectroscopy (HREELS) with low energy electron beam (100-1000eV), reflection energy loss spectroscopy (REELS) with about 30keV, and transmission EELS which is carried out with a TEM, such as JOEL 2010 which has a 200keV incident electron beam. This incident energy is high enough to penetrate a thin film up to about 100nm and the transmitted beam can give us the information of both the surface and bulk structure after interacted with the specimen.

1.2. Instrumentation

High spatial resolution EELS is often associated with TEM, thus before we talk about the instruments of EELS, we should also know some basic knowledge of TEM. The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group
developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939.\textsuperscript{7}
And the common structure of TEM can be shown in Figure 1.3. From top to bottom, firstly it is the electron gun, source of the electron beam. There are thermionic gun and field emission gun (FEG), while FEG is widely used for latest high resolution TEM for its high coherence of beam energy spread, while thermionic gun is also used widely for its larger beam size. After emission from electron gun, electrons incident into the TEM column, go through series of lenses and apertures. As same as in visible-light microscope, the lenses in TEM control all the basic operational functions. Instead of glass lens, magnetic electron lenses are used in TEM to control electron beam. The apertures are annular metallic plates, which are used to control the beam size, collection angle, the depth of field and the image contrast. The specimen stage is inserted into the middle of the column, just on the axis of electron beam. Finally, the transmitted electrons will form images or diffraction patterns on the fluorescent screen, or continue to incident into next instrument, such as EELS and EDX.

For EELS instrument, we focus on its core part, the magnetic prism spectrometer, which is used to form the electron energy loss spectra. As shown in figure 1.4 (a), in x-z plane, the electrons without energy loss are deflected along the solid line under the magnetic field B, which is outward of paper, finally focus at origin point. And other electrons with energy loss are deflected along the dashed line, finally focused above the origin point, and the more loss, the further from the origin point.

\[
R = \frac{m}{eB} v
\]

Thus we can get dispersive electron signals distribution corresponding to different energy loss. In figure 1.4 (b) shows the focusing program in y-z plane.
Figure 1.4 Focusing and dispersive properties of a magnetic prism

Figure 1.5(a) shows the simplest form of energy-loss system consists of a conventional TEM fitted with a magnetic prism below its image-viewing chamber. An alternative strategy is to incorporate a spectrometer into the TEM imaging column as shown in Figure 1.5(b). For image stability, it is important to preserve a vertical TEM column, so there are usually four magnetic prisms that bend the beam into the shape of a Greek letter Ω, hence the name “omega filter”. In Figure 1.5(c) a third type of system is based on the scanning-transmission electron microscope (STEM), in which a field-emission source and strong electromagnetic lenses are used to form a small probe that can be raster-scanned across the specimen.
Figure 1.5 The procedure of TEM-based energy-loss spectroscopy: (a) conventional (b) TEM incorporating an in-column imaging filter (c) STEM system\(^2\)

Originally energy loss spectra were recorded by photographic film at the spectrum plane. But now it is replaced by electronic acquisition. Firstly a serial-recording system was created, where a narrow slit is placed in the spectrum plane and the spectrum scanned past the slit by varying the magnetic field of the prism or the microscope high voltage. Recently parallel-recording system was developed without energy-selecting slit, so no electrons are wasted.\(^2\)
1.3. The Physics of EELS

The electrons interact with the material via electrostatic force, and based on the energy transfer or loss, it is convenient to divide the scattering into two categories: elastic and inelastic. If the electrons happen to interact with the nucleus, because of the huge mass of the nucleus comparable to electrons, as we learned in classical mechanics, the energy transfer of electrons can be negligible for the spectrometer energy resolution, especially for most electrons which travel further from the nucleus. While for head-on collision, the energy transfer can be larger than 1eV for 100keV incident beam, also in this case, light atoms can be knocked out of the specimen, which is one cause of radiation damage, but really rare, thus the elastic scattering can still be considered as zero loss interaction.

If the electrons interact with the atomic electrons around the nucleus, because of the comparable mass, inelastic scattering occurs. EELS mainly consider inelastic interaction, no matter with inner-shell or outer-shell electrons, these two processes dominate the different regions in the electron energy loss spectrum.

If a fast electron interacts with the atomic inner-shell electron which is hundreds or thousands of eV below the Fermi level, the ground state electrons can absorb this amount of energy to be excited to the unoccupied states, which is above the Fermi level. And the incident electron loses the same amount of energy. And then the excited electron will lose its excess energy, in the form of X-ray or kinetic energy of another atomic electron. Because of the high demand of energy loss, the collective effect is not important for inner-shell interaction, thus can be approximated as single electron mode of excitation very well.
In the other hand, the single electron excitation can also occur between incident electron and outer-shell electron, such as an interband transition of the valence electron across the band gap in semiconductor or insulator, or an intraband transition of the conduction electron to higher state in metal. Furthermore, the more general outer-shell interaction involves many atomic electrons. This collective effect of scattering can be named Plasmon resonance, and can be described in term of a quantum pseudoparticle, the Plasmon. The Plasmon resonance is an oscillation of the valence electrons due to the interaction of the incident electron beam.

Single electron excitation and Plasmon excitation are two different extreme modes of inelastic scattering. In a material in which the valence electrons can be treated as free particles, the Plasmon resonance dominates, while in other cases, Plasmon effect is weak or even disappears. But most materials are in between these two extremes.

The elastic scattering cross section has been studied very well for a long time. Here we only discuss the inelastic scattering cross section. The Bethe theory uses the first Born approximation, and gets the differential cross section for the transition, which is from an initial state $\psi_0$ to a final state $\psi_n$

$$\frac{d\sigma_n}{d\Omega} = \left(\frac{m_0}{2\pi\hbar^2}\right)^2 \frac{k_1}{k_0} \left| \int V(r)\psi_0 \psi_n \psi_n^* \exp (iq \cdot r) d\tau \right|^2$$

Where $k_1$ and $k_0$ are the initial and final wavevectors of the incident electrons respectively, and $q = k_0 - k_1$ is the momentum transferred to the excited atom. The interaction potential energy is generally presented as below for less than 300keV incident energy:
\[ V(r) = \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{1}{4\pi\varepsilon_0} \sum_{j=1}^{Z} \frac{e^2}{|r - r_j|} \]

Where the first term is contributed by Coulomb force from nucleus, the second term is from other electrons’ repulsive effect. And because the initial state \( \psi_0 \) and the final state \( \psi_n \) are orthogonal, the first term from nucleus effect will integrate to zero in the differential cross section equation, thus inelastic scattering involves only the interaction with atomic electrons, whereas elastic scattering involves both effects from nucleus and atomic electrons. Combine above two equations we can write down the equations as

\[ \frac{d\sigma_n}{d\Omega} = \left( \frac{4\gamma^2}{a_0^2 q^2} \right) \frac{k_1}{k_0} |\varepsilon_n(q)|^2 \]

The first term on the right side is the Rutherford scattering cross section from a single free electron. The second term is almost unity when incident energy is high. The third term is called the inelastic form factor or dynamical structure factor, which is a dimensionless modifying factor to the atomic electrons which are not free. It is the property of the material atoms. A more popular related quantity, the generalized oscillator strength (GOS) is defined as

\[ f_n(q) = \frac{E_n |\varepsilon_n(q)|^2}{R (qa_0)^2} \]

Here \( R = \frac{m_0 e^4}{2(4\pi\varepsilon_0 h)^2} = 13.6 \text{ eV} \) is the Rydberg energy and \( E_n \) is the energy loss. The generalized oscillator strength is the key point in the Bethe theory, which describes the response of an atom to the external excitation. Thus we need to calculate the GOS by several different methods. The first and also the simplest method is based on the hydrogen atom wave mechanics. A more accurate method which is simplification of the
Hartree-Fock procedure, the Hartree-Slater method, has already been applied for most atoms by iterative solution of Schrodinger equation with a self-consistent atomic potential.

1.4. Electron energy loss spectrum

Figure 1.6 Electron energy loss spectrum

Figure 1.6 shows a typical electron energy loss spectrum. First of all, it includes a zero loss peak, which is contributed by the elastic scattered electrons without any measurable energy loss and the unscattered electrons as well. The FWHM of the zero loss peak is a very important tuning parameter which can influence the energy resolution.
Secondly, the energy loss due to inelastic scattering from outer-shell electrons is generally in the region from 5eV to 50eV in the spectrum, which is called Plasmon peak. With increasing loss energy, the electron intensity drops quickly following power law approximately, and the energy loss from inner-shell scattering will appear like an edge rising rapidly on the tail of Plasmon peak and then drop slowly. And the sharp rising edge corresponds to the binding energy of the inner atomic shell, so called ionization threshold. All of the features are distinct for different elements and compounds, and can be explained by different processes if the specimen is thin enough.

Furthermore, if we view the spectrum in greater detail, we may find a fine structure among both the valence-electron peaks and the ionization edges, which reflects the crystallographic or energy-band structure of the specimen. Thus distinct fine structures can be produced for the same element in different phases.

As we mentioned above, if the specimen is thin enough, we can approximate that every electron only interact with the specimen once, thus we can correspond the spectrum features to distinct excitation process. But if the specimen is thick, probably the electrons can interact with the specimen more than once. Especially for outer-shell scattering, in which the interaction cross section is larger than inner-shell scattering, multiple scattering is more possible. Thus in the spectrum, maybe there are some features, which are sums of the individual scattering, presenting as a series of peaks at multiples of the Plasmon peak. This kind of plural scattering peaks is very common in a real spectrum because the common specimen thickness can compare even exceed the mean electron free path of the TEM electron beam. The plural scattering is unwanted and can be removed by deconvolution method.
1.4.1. The mechanism of Plasmon excitations

As similar as photons and phonons are quantization of light and mechanical vibrations, respectively, Plasma oscillation is the collective oscillation of the valence electrons which interact collectively with incident electrons via Coulomb force. In the simplest model, the valence electrons behave as free particles, so called free electron gas, also known as “jellium” A Plasmon is a quantum of plasma oscillation. In this model, the oscillation can be described as below equation:

\[ m \ddot{x} + m \gamma \dot{x} = -eE \]

If \( E = E \exp(-i \omega t) \), we can solve above equation and get

\[ x = \left( \frac{eE}{m} \right) (\omega^2 + i\gamma \omega)^{-1} \]

From the displacement we can get the electronic susceptibility

\[ \chi = \frac{-enx}{\varepsilon_0 E} \]

Thus we can get the dielectric function

\[ \varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} + \frac{i\gamma \omega_p^2}{\omega(\gamma^2 + \gamma^2)} \]

Here \( \omega \) is the angular frequency of the forced oscillation, which is directly related to the incident electrons in EELS, and \( \omega_p \) is the natural or resonance frequency for Plasmon oscillation, which is the natural feature of the materials

\[ \omega_p = \frac{\sqrt{n e^2}}{\sqrt{\varepsilon_0 m}} \]

Here \( n \) is the outer shell electron density per volume, and \( m \) is the electron effective mass in material. Furthermore, the energy loss function can be defined as
\[ Im \left[ \frac{-1}{\varepsilon(\omega)} \right] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} = \frac{\omega \Gamma \omega_p^2}{(\omega^2 - \omega_p^2) + (\omega \Gamma)^2} \]

And as we know

\[ \frac{d^2 \sigma}{d\Omega dE} = \frac{Im \left[ \frac{-1}{\varepsilon(\omega)} \right]}{\pi^2 a_0 m_0 v^2 n_a} \]

We can see that the energy dependence of the inelastic scattered intensity is proportional to \( Im \left[ \frac{-1}{\varepsilon(\omega)} \right] \), thus we can get the relation between the energy loss spectrum and the dielectric functions. This is very useful in the energy loss calculation when we know the dielectric function of the materials; it means we can get the energy loss spectrum through the calculation based on dielectric functions, which are very complete in science database. I have done some work on this topic, and the detail will be discussed in Chapter 2.

1.4.2. The Overall shape of inner-shell edges

The inner-shell electrons have binding energies which are mostly hundreds or thousands of eV. Their excitations will give the energy loss spectrum ionization edges, similar with the absorption edges in XAS. The ionization edges can be used to identify different elements due to their different inner-shell electrons’ binding energies. Thus it is very important and meaningful to study the inner-shell edges.

Due to the high binding energies of inner-shell electrons, the collective effects are not important. Inner-shell excitation can generally be considered as single-atom excitation approximately. Thus, to some extent, the K-, L-, M-shell ionization differential cross sections can be calculated by Bethe theory\(^1^0\) and the Hartree-Slater central model\(^1^1,1^2\) as we mentioned before. The calculated K-shell edges show “sawtooth” shape for elements B, C, N, O, which conform the experimental results very well except for
some pronounced fine structure.\textsuperscript{13,14} And the K-shell edges still remain the sawtooth shape for the third period elements.

Figure 1.7 L-edges of fourth-period elements measured using 120 keV electron beam and a collection semi-angle of 5.7 mrad\textsuperscript{15}

For L-edges, there are three components, the $L_1$ edge from $2s$ excitation, the $L_2$ edge from $2p_{1/2}$ and the $L_3$ edge from $2p_{3/2}$. The $L_1$ edge has the hydrogenic sawtooth shape but is relatively weak since it violates the dipole sum rule.\textsuperscript{2} For lower-Z elements, the thresholds are so close in energy that the two edges overlap and are described as $L_{23}$ edge as an entire one. However, the calculations of third-period elements shows that $L_{23}$
edges have a rounded profile because the effective potential is delayed by a centrifugal-barrier term.\textsuperscript{10} In Figure 1.7, the fourth-period elements give different L-edges, which are sharp peaks at the ionization edges, known as white lines. This is because of a high density of empty d-states just above the Fermi level. The separation of $L_2$ and $L_3$ is due to the spin-orbit splitting, and increases with increasing atomic number.\textsuperscript{15} The ratio of intensities of $L_2$ and $L_3$ is based on the relative occupancy of the initial-state levels.\textsuperscript{16}

Figure 1.8 M-edges of fifth-period elements measured using 120keV electron beam and a collection semi-angle of 5.7 mrad\textsuperscript{15}
As shown in Figure 1.8, $M_{45}$ edges are prominent for fifth-period elements, rounded with the intensity maximum delayed by 50 to 100 eV beyond the threshold because the centrifugal potential suppresses the optically preferred $3d \rightarrow 4f$ transitions just above the threshold.\textsuperscript{17} While for sixth-period elements, between Cs and Yb, for the rare earth elements, white line peaks occurs at the threshold due to a high density of unoccupied $f$-states. The splitting and the intensity ratio of $M_5$ and $M_4$ increase with atomic number.\textsuperscript{18,19} However after Yb, $M_4$ and $M_5$ edges come back to be rounded profiles. While $M_{23}$ edges of the beginning fourth-period elements is below 40 eV, superimposed on the Plasmon tail which makes them confused with Plasmon peaks. From the elements V to Zn, $M_{23}$ edges are sharp and resemble K-edges.\textsuperscript{20} $M_1$ edges are weak and difficult to be observed. $N_{67}, O_{23}$ and $O_{45}$ edges have been observed for some heavy elements.\textsuperscript{21} For example, in Th and U, $O_{45}$ edges are a double-peak.

1.4.3. Near-Edge Fine Structure (NLNES)

As we discussed before, besides the inner-shell edges, there are some pronounced fine structures, in the form of peaks or oscillations within 50 eV of the ionization threshold. Because most of these fine structures reflect the environment around the excited atoms, thus they are very useful for getting local structure information.

There are several approaches to explain ELNES. Firstly, let us discuss the density-of-state interpretation. The core-loss intensity $J_c(E)$ is represented by Fermi golden rule:\textsuperscript{22}

$$J_c(E) \propto \frac{d\sigma}{dE} \propto |M(E)|^2 N(E) \propto \frac{df}{dE} N(E)$$
Where M(E) is an atomic matrix element, closely related to the atomic oscillator strength $\frac{df}{de}$, and N(E) is the density of final state in the transition. M(E) gives the overall shape of the edge, while N(E) depends on the local chemical and crystallographic environment of the excited atom. Thus the fine structures, the variations in $J_c(E)$ represent the energy dependence of the unoccupied local density of states (LDOS) above the Fermi level. Further, N(E) is a symmetry-projected density of states, following the dipole selection rule. For example, the excitation of K-shell (1s) electrons reveals the density of empty $p$ states, while $L_2$ and $L_3 (2p)$ excitations show unoccupied $d$ and $s$ states. Besides that, N(E) is a joint density of states which convolutes the final states with the initial core states. However, the initial core state is relatively very sharp, can be approximated as delta function. Due to the uncertainty relation, the recombination rate for core level gives the initial state broadening, while the lifetime of the excited electron gives the final state broadening. The measured ELNES is also broadened by the instrumental energy resolution.

An alternative explanation of ELNES is in term of molecular orbital (MO) theory, which approximates the local band structure as a linear combination of atomic orbitals (LCAO) of the excited atom and its immediate neighbors. For example, in graphite, four valence electrons of each atom are $sp^2$ hybridized, resulting in three strong $\sigma$ bonds and the remaining $p$-electron contributes to a delocalized $\pi$ orbital. The corresponding antibonding orbitals are $\sigma^*$ and $\pi^*$, and they are the unoccupied states giving the fine structure in the K-edge spectrum.

Another approach is originally developed to explain extended X-ray absorption fine structure (EXAFS). And it can also be extended to interpret x-ray absorption near-
edge structure (XANES, or NEXAFS), further to interpret ELNES. This approach takes into account multiple scattering of the ejected core electron, and formally equivalent to a density of states interpretation of ELNES,\textsuperscript{24} multiple scattering approach are finished in real space. This feature is very useful for aperiodic systems.\textsuperscript{25} In my work, this approach has been applied with the program FEFF8. And I discuss it in detail in chapter 4.

1.5. The applications of Electron Energy Loss Spectroscopy

After previous review about EELS, we can find that EELS can be a very important technique in material characterization, associated with electron diffraction and imaging. Now we discuss about some applications.

Sometimes it is useful to know the local thickness of the TEM specimen, and EELS is relatively general and rapid among several methods. The easiest procedure is the log-ratio method based on the record of integration of zero-loss peak \( I_0 \) relative to the integration of the whole spectrum \( I_t \). And from the Poisson statistics of inelastic scattering, the thickness is given by

\[
\frac{t}{\lambda} = \ln \frac{I_t}{I_0}
\]

Here \( \lambda \) is the inelastic scattering mean free path. For thin specimens composed of light elements, \( I_t \) only need integrated up to 100 eV, but should be higher for thicker or high-Z specimens.\textsuperscript{6} To get the absolute thickness, we need to know the inelastic scattering mean free path. If no angle-limiting aperture is used, even with large aperture (\( \beta > 30 \text{ mrad} \)), we can consider \( \lambda \) a total mean free path. While if the collection angle is small enough to correspond to the dipole region of scattering, a \( \beta \)-dependent mean free path need to be calculated. Thus the accuracy of the log-ratio method depends largely on how well we
know the mean free path, which really depends on different materials, but generally the accuracy can be about 20% in most cases.²

Figure 1.9 Bulk Modulus plotted against Plasmon energy for various elements²⁴

In the energy loss spectrum, the Plasmon peak is related to material mechanical properties closely, large $E_p$ implies a high valence-electron density. And the elastic, bulk and shear modulus all relate with the square of the Plasmon energy.² In Figure 1.9, using this relation Oleshko and Howe have deduced the mechanical properties of metal-alloy precipitates which are too small to probed by nanoindentation techniques.²⁶ Furthermore, Gilman showed that $E_p$ also correlate with surface energy, Fermi energy, metals’ polarizability and semiconductor band gap.²⁷

While for the higher energy region, specific element has its particular ionization edge. Thus EELS can be used to identify the elements within the region of the probe. After remove the background, generally using a power-law energy dependence $AE^{-r}$ in
my work, where A and r are extrapolated from least-square fitting to pre-edge background, the remaining core-loss intensity provides a quantitative estimate of the element concentration. Then integration over 50eV beyond the edge threshold can average out the near edge fine structure and only represent the amount of the element, independent of its atomic environment.

For the near-edge fine structure, such as $L_3/L_2$ ratio in a transition metal can be used to identify the oxidation state of an element. Especially energy-filtered (EFTEM) imaging has been used to plot $L_3/L_2$ ratio as an intensity map directly to display the valence states of Mn and Co in mixed-valence specimens. ELNES is also very useful in the semiconductor industry, where integrated circuits become smaller and smaller, the oxide gate thickness in MOSFET can be around 1nm now. Combined with high-resolution STEM, core-loss EELS provides a way to detect the gate oxide properties which maybe depart from bulk properties due to the extreme small thickness. Generally speaking, NLNES can give useful information on inter-atomic bonding, but for quantitative results we should avoid the edges which are strongly affected by the core hole.

1.6. Layout of this Dissertation

In my work, TEM and EELS, as well as SEM and EDX are applied to study several valuable functional materials, which have different properties and different applications. At the same time, several theoretical calculations have been applied to help us to analyze and explain our experimental data as well, such as Dielectric function theory coding by MATLAB, and FEFF8 program based on the real space multiple
scattering (RSMS) approach. All they together show us the powerful characterization ability of EELS with TEM.

In detail, firstly valence electron energy-loss spectroscopy is used to investigate the Plasmon excitations of ultrathin SrTiO\(_3\) sandwiched between amorphous Si and crystalline Si. Two Plasmon excitations are observed, one at 15.8eV and the other at 28.7eV. Our calculations by MATLAB, based on dielectric-function theory have also been presented to help us to simulate different parameters, therefore to overcome the difficulty of some experimental limit.

Another functional material we discuss here is the ZnO-LiYbO\(_2\) hybrid phosphor. The diffusion region of the ZnO-LiYbO\(_2\) hybrid phosphor has been studied by SEM and EDX, to find the cause why the emission has been enhanced with co doping Li\(^{+}\) and Yb\(^{3+}\). As well the synthesized LiYbO\(_2\) has also been studies under TEM and EELS. Firstly the radiation damage effect on LiYbO\(_2\) has been studied by real time EELS and diffraction patterns to help us to find a “damage free” zone to study its electronic structure further. And then the EELS spectra of both LiYbO\(_2\) and Yb\(_2\)O\(_3\) are acquired in low loss and core loss region. Furthermore, FEFF8 program has been applied to simulate the core loss spectra and the projected density of states (DOS) for both LiYbO\(_2\) and Yb\(_2\)O\(_3\).
CHAPTER 2

VALENCE ELECTRON ENERGY LOSS SPECTROSCOPY OF ULTRATHIN SrTiO₃ FILMS GROWN ON SILICON (100) SINGLE CRYSTAL

2.1. Introduction

Recently functional oxides exhibit an incomparable variety of advantageous physical properties for electronic applications, such as high electron-mobility, high spontaneous polarization, and high superconducting-transition temperature.²⁹ To fully utilize these properties, it is very important to incorporate these materials into current dominant Si-based technology. Due to the demand of thinner gate dielectrics, the high dielectric constant \( k \) (about 310 at room temperature) of SrTiO₃ is a virtue we can apply to make it an alternative gate dielectric for SiO₂. Especially SrTiO₃ (STO) thin film can be grown on silicon (100) single crystals without forming silicon dioxide,³⁰,³¹,³² thereby making SrTiO₃ an outstanding gate dielectric material. In the STO/Si heterostructures, SrTiO₃ has a cubic perovskite structure while the single crystal Si has a diamond structure. Due to this crystal structural difference and also the chemical bonding difference, the properties of the interface are critical to its electrical performance. Therefore we are interested in the structural and electronic properties of the STO film close to the interface.³³,³⁴ However, we do not know how the electronic structure of changes under compressive strain or with a different interfacial structure.³⁵ EELS together with high resolution TEM, offers a powerful method for exploring local electronic structure with atomic-layer precision.⁶ Recently, the valence electron energy-loss spectroscopy (VEELS) technique was applied to characterize electronic- and electromagnetic structure. For example, Nelayah employed it to measure surface-bound
optical excitations in nanoparticles, Sanchez investigated the quantum dots-in-well structure using the bulk Plasmon peak, and Arenal et al. extracted the optical gaps of single boron-nitride nanotubes using EELS. In some previous report, it is proposed that employing the shift of the maximum loss peak to measure the porosity of nanoporous MgO. However, we should be cautious to link the EELS measurement with the physical properties, because of the delocalization contribution associated with Plasmon excitation and because of the multiple factors that might shift the peak, such as the quantum-confinement effect, the relativistic effect, the damping effect, and the effective response of dielectric medium.

In this chapter, we described our study using VEELS technique on an ultrathin STO film, sandwiched between an amorphous Si and a crystalline Si layer. We observed two predominant peaks in the low energy-loss regime within the ultrathin STO layer that do not match the corresponding peaks in the bulk STO. We undertook calculations based on dielectric theory and found that the shift of one of the main peaks in the STO layer is related to the coupling of the Si layers. We identified the other peak shift as reflecting the change in the band structure of STO.

2.2. Experimental

The experimental part has been done by Dr. Dong Su etc. As shown in Fig. 2.1 (a), an approximately 1 nm thin film of STO, corresponding to two and a half unit cells of STO with an (001) orientation, was grown on a (100) Si single crystal using molecular beam epitaxy. Then an amorphous Si layer was deposited on the STO film at room temperature. The growth sequence was optimized so that the terminal layer of STO close to the Si crystal is a Sr–O layer, consistent with previous reports. The specimens was
examined under a Hitachi-2700C dedicated scanning-transmission electron microscope (STEM). For these experiments, a 1.3 Å probe was used with a beam current of 5pA. EELS spectra were collected with a Gatan high-resolution spectrometer (Enfina ER), with an energy resolution of about 0.35eV, by measuring the full width at half maximum (FWHM). All the EELS spectra were deconvoluted using a Fourier-log method to remove the multiple-scattering effect. The relative thickness of the STO film ($t/\lambda$) was 0.55±0.05.

Figure 2.1 Cross-sectional high angle annular dark-field image of the sandwich structure, where $x_0 = 0$ sits at the center of STO thin layer.

2.3. **EELS simulations based on Dielectric function theory**

In principle, the valence electron in a solid can be thought as a set of coupled oscillators interact with a transmitted electron via electrostatic forces. The behavior can be described in terms of dielectric function as in Drude theory. Simply speaking, the energy–loss function can be given by:
\[ I(\omega) \propto Im \left[ -\frac{1}{\varepsilon(\omega)} \right] = Im \left[ \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \right] \]

Where \( Im \left[ -\frac{1}{\varepsilon(\omega)} \right] \) is the energy-loss function, and \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are the real and imaginary dielectric constants, respectively. However, in a nanoscale structure, the geometry of the surrounding material affects the energy-loss function. In particular, Moreau et al. derived the relativistic expression for the excitation probability of an electron traveling parallel to a sandwiched interface. This theory has been used to characterize the interface Plasmon of a 2 nm thick SiO\(_2\) layer sandwiched by silicon.

![Figure 2.2 Geometry of the interaction of a charged particle Ne, moving with velocity v, at a distance \( x_0 \) from the interface between media 1 and 2, with dielectric functions \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \), respectively.](image)
As we discussed in Chapter 1, there are several theories which can explain EELS spectrum. Specifically for the low loss region, both the bulk Plasmon and surface Plasmon can be explained by Dielectric function theory. Right now let us review it in first principle.\textsuperscript{49} Molina \textit{et al.} used the dielectric function approach to analyze the interaction of a relativistic electron beam, travelling parallel to the interface of the semi-infinite mediums.\textsuperscript{49} As shown in Figure 2.2, an electron beam \( Ne \) travel parallel to the interface between media \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) at \( \vec{v} \). To calculate the excitation probability and the energy loss of the electron beam, the Maxwell’s equations with Hertz vector \( \vec{Z} \) has been solved. At first, the electromagnetic field is given\textsuperscript{50}

\[
\vec{E} = \nabla(\nabla \cdot \vec{Z}) + \frac{\varepsilon \omega^2}{c^2} \vec{Z} \quad (1)
\]

\[
\vec{H} = -\frac{i \varepsilon \omega}{c} \nabla \times \vec{Z} \quad (2)
\]

Similarly, the current density is given\textsuperscript{50}, where \( c \) is the speed of light

\[
\vec{j} = \frac{i \varepsilon \omega}{4\pi} \left( \nabla^2 + \frac{\varepsilon \omega^2}{c^2} \right) \vec{Z} \quad (3)
\]

Where the Hertz vector is expressed as below

\[
\vec{Z}(\vec{r}, t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \vec{Z}(\vec{r}, \omega) \quad (4)
\]

The current density of the electron beam can also be defined by

\[
\vec{j}(\vec{r}, t) = Ne \nu \delta(z - \nu t) \delta(y) \delta(x - x_0) \quad (5)
\]

Due to the translational invariance parallel to the \( y-z \) plane we can get the Fourier transforms of the Hertz vector to integrate over \( y \) and \( z \)

\[
\vec{Z}(\vec{k}, \omega) = \int \frac{d^2k}{(2\pi)^2} e^{i\vec{k}\cdot\vec{r}} \vec{Z}(\vec{k}, \omega, x) \quad (6)
\]
Where \( \tilde{\rho} = (0, y, z), \tilde{k} = (k_x, k_y, k_z) \), thus Fourier transforming (5) according to (4) and (6) we can get

\[
f(\tilde{k}, \omega, x) = 2\pi Ne v\tilde{z}\delta(\omega - k_z v)\delta(x - x_0) \quad (7)
\]

From the y-z plane symmetry of the semi-infinite media, we can assume that \( Z = (Z_x, 0, Z_z) \) (equivalently we can also assume \( Z = (Z_x, Z_y, 0) \)), and then from equations (3) and (7) we can solve (1) for an external beam

\[
\left( \frac{d^2}{dx^2} - v_1^2 \right) Z_{z}^- = 0 \quad (8a)
\]

\[
\left( \frac{d^2}{dx^2} - v_1^2 \right) Z_{z}^+ = \frac{8\pi^2 Ne v}{\omega \varepsilon_1} \delta(\omega - k_z v)\delta(x - x_0) \quad (8b)
\]

\[
\left( \frac{d^2}{dx^2} - v_2^2 \right) Z_{x}^- = 0 \quad (8c)
\]

\[
\left( \frac{d^2}{dx^2} - v_2^2 \right) Z_{x}^+ = 0
\]

Where \( Z^\pm \) represents the Hertz vector for both sides of the interface \( x > 0 \) and \( x < 0 \) respectively, and

\[
v_1 = \sqrt{k^2 - \frac{\varepsilon_1 \omega^2}{c^2}} \quad (9)
\]

\[
v_2 = \sqrt{k^2 - \frac{\varepsilon_2 \omega^2}{c^2}}
\]

And the solution for equation (8) is

\[
Z_{z}^- = C e^{v_2x} \quad 10(a)
\]

\[
Z_{z}^+ = -\frac{4\pi^2 Ne v}{\omega \varepsilon_1 v_1} \delta(\omega - k_z v)e^{-v_1|x-x_0|} + Ae^{-v_1x} \quad 10(b)
\]

\[
Z_{x}^- = D e^{v_2x} \quad 10(c)
\]
$$Z^+_x = B e^{-v_1 x}$$  \hspace{1cm} 10(d)

Both $v_1$ and $v_2$ have a positive real part. And the four constant A, B, C, D can be get from the boundary conditions which is the continuity of the tangential component ($y$ and $z$) of the electric field $\vec{E}$ and $\vec{H}$, thus from (1), (2), (4) and (6) the boundary conditions can give equations at $x=0$

$$\varepsilon_1 Z^+_z = \varepsilon_2 Z^-_z$$

$$ik_z Z^+_z + \frac{\partial Z^+_z}{\partial x} = ik_z Z^-_z + \frac{\partial Z^-_z}{\partial x}$$  \hspace{1cm} (11)

$$\varepsilon_1 Z^+_x = \varepsilon_2 Z^-_x$$

$$\varepsilon_1 \frac{\partial Z^+_z}{\partial x} = \varepsilon_2 \frac{\partial Z^-_z}{\partial x}$$

Only the coefficients $A$ and $B$ are necessary here, and given by

$$A = \frac{v_1 - v_2}{v_1 + v_2} \Lambda$$  \hspace{1cm} 12(a)

$$B = 2ik_z v_1 \Lambda \frac{\varepsilon_2 - \varepsilon_1}{(v_1 + v_2)(\varepsilon_1 + v_1 \varepsilon_2)}$$  \hspace{1cm} 12(b)

$$\Lambda = -\frac{4\pi N_e v}{i\omega \varepsilon_1 v_1} e^{-v_1 x_0} \delta(\omega - k_z v)$$  \hspace{1cm} 12(c)

Its energy loss per unit path length is just the retarding force on the electron in the $-\hat{z}$ direction

$$-\frac{dW}{dz} = -N_e E_z(v t, 0, x_0, t) = -\frac{N_e}{(2\pi)^3} \int_{-\infty}^{\infty} dk_z \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} d\omega \ e^{i(k_z v - \omega) t} E_x(\vec{k}, \omega, x_0)$$  \hspace{1cm} (13)

Thus the probability of excitation of a frequency $\omega$ per unit path per unit frequency $\frac{d^2P}{dz d\omega}$ can be given$^5$

$$\frac{dW}{dz} = \int_0^\infty \frac{d^2P}{dz d\omega} \hbar \omega d\omega$$  \hspace{1cm} (14)
Following the same idea and similar formulism with Molina et al. as shown above, Moreau et al. have also derived the relativistic expression for the excitation probability of an electron traveling to an interface between two media. Furthermore they have extended their equations available for a double planar interface between three media with dielectric functions $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ and $\varepsilon_3(\omega)$ respectively as shown in Figure 2.3. This structure is so called the sandwich interface as we mentioned before, and $x_0$ is the impact parameter of the electron beam from the center of the intermediate layer $\varepsilon_2(\omega)$. To make the formulas simple, the integration is limited only in the $k_y$ direction with acceptable error. Then probability of excitation of an angular frequency $\omega$ per unit path per unit frequency can be expressed as

For $x_0 \geq \frac{d}{2}$,
\[
\frac{d^2 P}{dzd\omega} = \frac{e^2}{2\pi^2 \hbar \varepsilon_0 v^2} \text{Im} \left( \int_0^{k_{YM}} dk_y \left\{ \frac{-(1 - \beta^2 \varepsilon_3)}{\varepsilon_3} \right\} \Gamma + \Delta e^{-\nu_3 (x_0 - \frac{d}{\nu})} \right)
\]

Where

\[
\Gamma = \frac{e^{-2\nu_3 (x_0 - \frac{d}{\nu})}}{\nu_3} - \frac{2e^{-2\nu_3 (x_0 - \frac{d}{\nu})}}{J} \left[ (v_2 + v_1)e^{\nu_2 d} + (v_2 - v_1)e^{-\nu_2 d} \right]
\]

\[
J = (v_1 + v_2)(v_3 + v_2)e^{\nu_2 d} + (v_3 - v_2)(v_2 - v_1)e^{-\nu_2 d}
\]

\[
L = [(v_3 \varepsilon_2 + v_2 \varepsilon_3)(v_2 \varepsilon_1 + v_1 \varepsilon_2)e^{\nu_2 d} + (v_2 \varepsilon_1 - v_1 \varepsilon_2)(v_3 \varepsilon_2 - v_2 \varepsilon_3)e^{-\nu_2 d}]
\]

\[
\Lambda = \frac{1}{JL} \left\{ 8v_3 v_2^2 (\varepsilon_1 - \varepsilon_2) e^{-\nu_3 (x_0 - \frac{d}{\nu})} \right\}
\]

\[
+ \frac{2v_3}{\varepsilon_3}(\varepsilon_2 - \varepsilon_3)e^{-\nu_3 (x_0 - \frac{d}{\nu})} [(v_1 \varepsilon_2 + v_2 \varepsilon_1)e^{-\nu_2 d}
\]

\[
+ (v_2 \varepsilon_1 - v_1 \varepsilon_2)e^{\nu_2 d}][(v_1 + v_2)e^{\nu_2 d} + (v_2 - v_1)e^{-\nu_2 d}] \right\}
\]

\[
v_i = \sqrt{k_i^2 + \frac{\omega^2}{v^2}(1 - \beta^2 \varepsilon_i)}
\]

Similarly for \(0 \leq x_0 \leq \frac{d}{\nu}\),

\[
\frac{d^2 P}{dzd\omega} = \frac{e^2}{2\pi^2 \hbar \varepsilon_0 v^2} \text{Im} \left( \int_0^{k_{YM}} dk_y \left\{ \frac{-(1 - \beta^2 \varepsilon_2)}{\nu_2 \varepsilon_2} \right\} \left( (1 - \beta^2 \varepsilon_2) - (1 - \beta^2 \varepsilon_2) \frac{T}{J} + \frac{Y}{JL} \right) \right)
\]

Where \(J\) and \(L\) have the same definition as above and

\[
T = (v_2 + v_1)(v_2 - v_3)e^{2\nu_2 x_0} + (v_2 - v_1)(v_2 + v_3)e^{-2\nu_2 x_0} - 2(v_1 - v_2)(v_2 - v_3) e^{-\nu_2 d}
\]

\[
Y = \frac{2v_2^2}{\nu_2} \left\{ (v_2 \varepsilon_1 + v_1 \varepsilon_2)(v_1 + v_2)(\varepsilon_3 - \varepsilon_2)e^{2\nu_2 (x_0 + \frac{d}{\nu})} + (v_1 \varepsilon_2 - v_2 \varepsilon_1)(v_2 - v_1)(\varepsilon_3 - \varepsilon_2)e^{-2\nu_2 (x_0 + \frac{d}{\nu})} + (v_3 \varepsilon_2 - v_2 \varepsilon_3)(v_2 - v_3)(\varepsilon_1 - \varepsilon_2)e^{2\nu_2 (x_0 - \frac{d}{\nu})} + (v_2 \varepsilon_3 + v_3 \varepsilon_2)(v_2 + v_3)e^{2\nu_2 (x_0 - \frac{d}{\nu})} + 2v_2(v_3 + v_1)(\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_3) \right\}
\]

\[
32
\]
This expression for sandwich structure has been applied for our sample, in which SrTiO$_3$ (STO) thin films were grown between an amorphous Si and a crystalline Si layer, as same as the structure in Figure 2.3. In this study, we assumed that 1 nm STO layer still retains the dielectric property of the bulk STO, so that we can apply the dielectric functions from bulk STO to our system. The real and imaginary parts of the dielectric functions can be obtained from the Kramers–Kronig analyses of the EELS spectra.$^6$ And our dielectric functions are derived from the EEL spectra of bulk amorphous Si, bulk crystal Si, and bulk STO in the energy range of 5eV to 60eV. The calculation is realized by MATLAB, all the input equations are exactly the same as above formulas. However, as we can see the above formulas from Moreau et al. only consider the cases for $x_0 \geq 0$, while we want to go over both interfaces and all three media from $x_0 \leq -\frac{d}{2}$. To overcome this problem, we just do simulations in MATLAB for both amorphous-Si/STO/crystalline-Si and crystal-Si/STO/armophous-Si structures respectively, and then combine two simulations to complete the entire scan.

2.4. Results and discussions

In Figure 2.4 we plot the deconvoluted experimental EELS spectra of the amorphous Si (a-Si) layer, the STO ultrathin film, the crystalline Si (c-Si) layer, and the reference spectrum acquired in a bulk STO sample under the same conditions. These spectra were recorded by scanning the probe parallel to the interface. In both the amorphous and crystalline Si layers, the sharp peaks at 16.5eV and 16.6eV respectively, are due to their bulk Plasmon excitations. In the spectrum of the STO thin layer, we observed a small bump at about 8.0eV due to coupled interface Plasmon excitations.$^{41,48}$ There are two pronounced peaks, one around 15.8eV (peak A) and the other at 28.7eV
(peak B). Peak A is between the collective excitation in bulk STO at 14.2eV and the silicon Plasmon peak at around 16.5eV. Thus it is difficult to derive its origin straightforwardly. On the other hand, peak B is about 1.7eV lower than STO’s bulk-Plasmon peak at 30.4eV.

Figure 2.4 Comparison of deconvoluted EELS spectra of amorphous-Si, STO thin film, crystalline Si, and bulk STO

Based on the relativistic equations for the sandwich structure described by Moreau, the MATLAB code has been created. Firstly we calculated the spectrum of 1 nm STO layer sandwiched within infinitely thick a-Si and c-Si layers on two sides. Furthermore, to evaluate the contribution from the sandwiched Si exclusively, we carried
out the similar calculations in the same sandwiched geometry after replacing the thin STO layer with vacuum. Therefore the effect of STO has been excluded. In both models, the electron probes were set at the center of the STO, or vacuum layer, and we define $x_0 = 0$ at the center.

Figure 2.5 Comparison of the experimental spectrum of a-Si/STO/c-Si, the calculated spectra of a-Si/STO/c-Si and a-Si/vacuum/c-Si sandwich structures using dielectric function theory. All spectra are at the centers of the layers ($x_0 = 0$)

In Figure 2.5 we show the calculated results for these two models; and compared to the experimental EELS spectrum of STO layer from Figure 2.4. In the calculated
spectrum of STO layer, there are two peaks around 15 and 30eV, approximately corresponding to peaks A and B in the experiment respectively. However, in calculated spectrum of the vacuum layer, peak A remained but peak B disappeared. The position of peak A calculated for the sandwiched STO layer almost matched its experimental position. While the peak A calculated for vacuum layer is about 0.4eV lower than the peak A in the spectrum of the STO layer, implying that it originates mainly from the delocalization effect of the Si layers, but also partially affected by the STO layer. And we can also speculate that peak B may totally come from STO due to its disappearance in vacuum.

To further study the relationship between peak A and the local parameter of the sandwiched structure. Our detailed calculation with different widths of the STO layer in our a-Si/STO/c-Si system has been done and plot in Figure 2.6. We can see that the energy position of peak A declines with an increase of the width of the vacuum layer. These findings suggested that peak A mainly is generated by the coupling of the Plasmon of Si layers, and reflects the geometrical effect of the sandwiched structure. On the other hand, the fact that peak B is stronger in wider STO layer, but disappears in that of the vacuum layer indicates that it is associated with the STO, and can be related to the bulk Plasmon excitation of STO, which is at about 30.4eV. However, the experimental peak B position is 1.7eV lower than that in the bulk STO material and in the calculated spectrum of STO layer, and the peak B position in the calculated spectra keeps constant whatever the width of STO layer is, in other words, the peak B position shows no dependence on the distance from Si layers. Therefore we cannot interpret the shift of peak B being affected by the geometric effect.
To further verify the geometric effect, as shown in Figure 2.7 (a), we acquire EEL spectra by moving the electron probe across the STO layer from amorphous Si side ($x_0=-2.5$ nm) to crystal Si side ($x_0=2$ nm) step by step. Correspondingly, we also calculate the EEL spectra under the same conditions with a step of 0.4 nm (from $x_0=−3.2$ to 2.4 nm), as shown in Figure 2.7(b). And we observe that there are variations of the peak position when the electron beam is scanned.
Figure 2.7 The comparison of the peak A position with constant STO layer width 1.0nm. (a) The experimental EELS spectra crossing the STO layer, from -2.5nm to 2nm. (b) The calculated EELS spectra, crossing the STO layer, from -2.5nm to 2nm.

To see the variation clearly we plot the relative shift of the experimental and calculated positions of peak A to the Si bulk Plasmon energy in Fig. 2.8 (a) and similar comparisons of positions of peak B in Fig. 2.8 (b). In Fig. 2.8 (a), the calculations fit the experimental very well within the experimental error. Again, they confirm that peak A, observed in the STO ultrathin layer, is mainly caused by the coupling of collective excitations between crystal Si and amorphous Si layers (the geometric effect); interestingly, as shown in Fig. 2.8 (b) both the experimental and calculated positions of
peak B are little affected by the position of the electron probe. Thus the shift of peak B should be due to other reasons but not the geometric effect.

Figure 2.8 (a) Comparison of experimental and calculated values of the maximum loss position of peak A. (b) Comparison of STO Plasmon peaks’ positions of peak B.
Besides the geometric effect, several possible mechanisms might also cause a shift to lower energy in the maximum-loss peak. First, we can exclude the quantum confinement effect as the cause because this effect only shifts the peak to higher energy.\(^{42}\) As shown in Figure 2.9, Mitome et al. claimed that the Plasmon energy increases in proportion to the inverse square of the cluster size, which is due to the increase of the energy gap by the quantum confinement effect.

\[
\begin{align*}
E_p' &= E_{\text{max}} \sqrt{4E_{\text{max}}^2 + \Gamma^2} - E_{\text{max}}^2,
\end{align*}
\]

Figure 2.9 Size dependence of the Plasmon energy in the Si cluster.\(^{42}\)

Second, as shown in Fig. 2.1 (b), the Plasmon peak of STO thin film is broader than that of STO bulk, due to the damping effect.\(^8\) The strong damping effect in the ultrathin layer may shift the measured Plasmon peak downwards. According to Sanchez et al.,\(^{37}\) the actual Plasmon peak is at

\[
E_p' = E_{\text{max}} \sqrt{4E_{\text{max}}^2 + \Gamma^2} - E_{\text{max}}^2,
\]
where $E_p'$ is the modified bulk Plasmon energy in an insulator or semiconductor,

$$E_p'^2 = \bar{E}_g^2 + E_p^2/\varepsilon_c,$$

$\bar{E}_g$ represents an “average” band gap, $\varepsilon_c$ is the dielectric function of the core electrons and positive ions. $E_{\text{max}}$ is the measured maximum of plasmon peak, and $\Gamma$ is the damping constant which is approximately the FWHM of the plasmon peak, $\Delta E$. Here, the contribution of band gap was considered. $E_p$ is the free electron plasmon energy. By fitting the experimental data with Gaussian function, we estimated that in the ultrathin STO layer, $\Delta E$ is about 9.8eV; similarly, $\Delta E$ is estimated to be 4.6eV for the STO bulk Plasmon. Thus with calculations based on different $\Delta E$ respectively, the corresponding energy of peak B would be about 0.3eV lower than the value in STO bulk material. Undoubtedly, the damping effect can only partially contribute to the 1.7eV shift of peak B. We need to find other factors to shift the peak B.

According to the Drude theory, the bulk Plasmon energy is determined by the density of valence electron, $n$, and effective electron mass $m_{\text{eff}}$, i.e., as shown in Drude equation,

$$E_p = \frac{\hbar e \sqrt{n}}{\sqrt{\varepsilon_0 m_{\text{eff}}}}$$

As we know, the in-plane lattice parameter of STO is 1.7% smaller than that of Si due to the strain from Si compression. However, the out-of-plane lattice constant of STO is elongated due to the Poisson effect. Overall the volume change of the unit cell would be insignificant; in a similar case, the change in volume is reported only 0.19% for 5 ML STO layers on Si. Therefore, the energy shift due to the change in valence electron density can be negligible in our case.
After all the previous discussions, we can speculate that the only possible cause is an increase in the effective mass components in the plane crossing the electron incident beam at the electron wave vector $q \sim 0$. We calculated this enhancement as $11.5\pm2.0\%$, taking into account both geometrical and damping effects. To explain this enhancement, we note that the compressive strain in STO and the interfacial structure between Si and STO was shown to modify the electronic structure of STO thin films grown on silicon. For instance, density functional theory (DFT) calculations by Zhang et al.\textsuperscript{52} show the valence band offset is $2.26\text{eV}$, and the offset of the conduction band is $-0.13\text{eV}$, while Amy et al.\textsuperscript{53,54} reported that the maximum position of the valence-band shifted more than $2.0\text{eV}$, depending on the surface treatment; the conduction band’s minimum was below that of Si by a value from $0.2 \sim -0.46\text{eV}$ for the STO/Si interface. The band structural change at the interface may lead to a decrease in the width of the valence state, possibly by flattening the density of states in the valence band. This mechanism is consistent with our findings on the result of the enhancement of effective electron mass in this study.

2.5. Conclusions

In summary, we investigated the valence electron-loss spectroscopy of a c-Si/STO/a-Si sandwiched structure. We observed two peaks at around 15.8 and 28.7eV in the 1 nm STO ultrathin layer. Using dielectric function theory, we calculated the shifts in peaks induced by the geometry of the sandwiched structure. The peak at 15.8eV apparently results mainly from the coupling of Si plasmon peaks with a redshift. We can interpret the peak at 28.7eV as an STO bulk plasmon peak, with a 1.7eV redshift mainly due to the enhancement of the effective electron-mass in the STO layer. Our results demonstrate that the bulk plasmon can be observed, even in a 1 nm thick film. After
considering other possible effects, we consider that valence electron energy loss spectroscopy can be a valid method to detect local changes in effective electron mass.

We can see the valuable meaning of the dielectric theory in simulation of EELS and it can help us a lot to interpret the peak shift by analysis independently and free us from the real experimental material structure. For example, we have replaced the STO by vacuum in the sandwich structure, which is difficult to realize experimentally. However with the formula based on dielectric theory, we can do calculations for various structures whatever we want without extra cost, only by simply changing parameters of our MATLAB codes.
CHAPTER 3
THE MICROSTRUCTURE STUDY OF Yb AND Li CO-DOPED ZnO BY
SEM/TEM AND EELS

3.1. Introduction to ZnO-LiYbO₂ hybrid phosphor

In this chapter, the microstructure of Yb and Li co-doped ZnO has been studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Co-doping ZnO with Li and Yb by solid state reaction produces a LiYbO₂ phase. It is found that formation of the LiYbO₂ is intermediated by ZnO. Growth of LiYbO₂ occurs at ZnO surfaces and at grain boundaries. Detailed microstructure analysis suggests that the nucleation of LiYbO₂ may be catalyzed by ZnO. A reaction (or diffusion) zone is very likely to exist between LiYbO₂ and ZnO. Such diffusion regions may be responsible for the enhanced infrared emission that is observed from the Yb and Li co-doped ZnO.

Unintentionally-doped, as grown ZnO is usually an n-type semiconductor with a direct band gap of about 3.3eV. It is also an efficient luminescent material, which gives off a broad green emission under UV excitations. According to previous studies, such green emission from n-type ZnO is mainly due to the recombination of single ionized oxygen vacancies and photo-generated holes. ZnO has also been considered as a candidate for rare-earth doping, for applications in optoelectronics, including flat panel displays and solar cells. However, in reality such rare-earth(RE) doped ZnO can hardly find any practical applications, because their luminescent efficiencies are usually very low. The low efficiency was overwhelmingly interpreted as being due to the inability of RE ions to incorporate easily into ZnO lattice. This speculation was supported by X-ray diffraction (XRD) measurements, which showed that the lattice
parameters of ZnO demonstrate have no measurable change before and after doping.\footnote{64} Therefore, large efforts have been made “to increase the solubility of RE ions in ZnO”.\footnote{63,64} One successful method was to co-dope RE with Li ions.\footnote{63} In such RE and Li co-doped ZnO, the luminescence in the infrared region becomes remarkably strong. Extensive studies suggest that this strong infrared emission is due to the high efficiency of energy transfer from the ZnO host to the RE dopants.\footnote{62} XRD measurements in the Rare earth and Li co-doped ZnO did not show any measurable lattice parameter change either.\footnote{64} So far there is no definitive explanation for why RE and Li co-doping of ZnO works, but it is evident that single-doping of RE does not work, at least from a microstructure and doping point of view. Some considered that the co-doping Li\textsuperscript{+} ions might enhance the solubility of rare earth ions in the ZnO and hence increase the number of the luminescent centers,\footnote{62} or creates the oxygen vacancies that may act as the sensitizer for the energy transfer to the rare earth ions.\footnote{65} While it was also suggested that the Li\textsuperscript{+} in ZnO host may distort the local symmetry and structure around rare earth ions and thus enhance the energy transfer rate.\footnote{66}

Recently, the intense infrared emission associated with Yb\textsuperscript{3+} was observed in Yb and Li co-doped ZnO, which was synthesized using a solid state reaction method.\footnote{67} XRD measurements indicated that the lattice parameter of ZnO before and after doping have no measurable change. Interestingly, as shown in Figure 3.1, the XRD patterns from the non-doped ZnO, Yb\textsubscript{2}O\textsubscript{3} mixed ZnO and Li\textsubscript{2}O-Yb\textsubscript{2}O\textsubscript{3} co-mixed ZnO have been acquired. From this figure we can see that for the non-doped ZnO, all the diffraction peaks can be well indexed as hexagonal ZnO. In the mixture of ZnO and Yb\textsubscript{2}O\textsubscript{3}, the diffraction patterns contain both hexagonal ZnO and cubic Yb\textsubscript{2}O\textsubscript{3} peaks, and there is no detectable
change of the peak position from standard ZnO diffraction patterns. While in the Li$_2$O-Yb$_2$O$_3$ co-mixed sample, new diffraction peaks besides ZnO and Yb$_2$O$_3$ can be observed. After compare with the reference as shown in the figure, these new peaks can be indexed as LiYbO$_2$ phase. The LiYbO$_2$ phase was observed for the first time in the Yb and Li co-doped ZnO, and we named this production as ZnO-LiYbO$_2$ hybrid phosphor.

![XRD patterns](image)

Figure 3.1 XRD patterns of (a) non-doped ZnO, (b) 1 mol% Yb$_2$O$_3$ mixed ZnO, (c) 1mol% Li$_2$O-1 mol% Yb$_2$O$_3$ co-mixed ZnO, and (d) LiYbO$_2$ diffraction pattern, together with the enlargement of (c).

In Figure 3.2 the excitation and emission spectra in the ZnO-LiYbO$_2$ hybrid phosphor has been plot. In the right part of Figure 3.2, it shows the emission spectra under the excitation of 395 nm, we can observe a broadband visible green emission around 550nm due to the radioactive recombination of the electrons from the conduction
band edge with the deeply trapped holes in the ZnO\textsuperscript{57,58} as we discussed before. In addition the other infrared emission round 1000nm is originated from Yb\textsuperscript{3+} $^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$ transition.

Furthermore the excitation spectra for the ZnO 540nm green emissions and the Yb\textsuperscript{3+} 986nm infrared emission are shown in the left side of Fig. 3.2. The excitation spectrum for ZnO emission has a broadband shape in the near UV region and a very smooth edge around 395 nm. The excitation spectrum of Yb\textsuperscript{3+} infrared emission has not only a similar broadband structure in the near UV region, but also a sharp peak located at 395 nm.

![Figure 3.2 Excitation spectra of ZnO visible emissions at 540 nm, and Yb3+ infrared emission at 986 nm, and emission spectra under the excitation of 395 nm for ZnO-LiYbO2 hybrid phosphor.\textsuperscript{69}](image)

Figure 3.2 Excitation spectra of ZnO visible emissions at 540 nm, and Yb3+ infrared emission at 986 nm, and emission spectra under the excitation of 395 nm for ZnO-LiYbO2 hybrid phosphor.\textsuperscript{69}
Figure 3.3 Excitation spectra (green) of ZnO visible emission and emission spectra (blue) excited by 380 nm for (a) non-doped ZnO, (b) Yb$^{3+}$ single-mixed ZnO and 350 nm for (c) Li$^+$ single-doped ZnO.$^{69}$

As shown in above Figure 3.3, the excitation and emission spectra for the non-doped, Yb$^{3+}$ single-mixed and Li$^+$ single-doped ZnO samples have been plot and compared. Firstly we can observe that the excitation spectrum of the visible emission in the non-doped ZnO consists of a broadband in the near UV region and a sharp peak,
which are the band-band absorption and exciton absorption, respectively.\textsuperscript{70,71} For the \textsuperscript{Yb}$^{3+}$ single-mixed sample, only the green emission from ZnO can be detected and the excitation spectrum of the visible emission shows similar spectral profile with that of the non-doped ZnO. In contrast, for the \textsuperscript{Li}$^{+}$ single-doped ZnO visible emission, the sharp excitation peak due to exciton absorption disappears. The annihilation of the sharp excitation band for ZnO visible emission is also occurred in the ZnO-LiYbO\textsubscript{2} hybrid phosphor, although dominated in the \textsuperscript{Yb}$^{3+}$ excitation spectra.

Figure 3.4 \textsuperscript{Yb}$^{3+}$ emission spectra in the ZnO-LiYbO\textsubscript{2} hybrid phosphor and LiYbO\textsubscript{2} crystal under the excitation of 937nm LD. Inset shows \textsuperscript{Yb}$^{3+}$ emission spectrum in ZnO-LiYbO\textsubscript{2} hybrid phosphor under 395nm excitation.\textsuperscript{69}
Comparing Figure 3.2 and 3.3, the doping of Li$^+$ in ZnO may be the role which makes the difference by forming some defect energy levels. These defect energy levels may act as the annihilation center of excitons, and also acts as an efficient energy donor for Yb$^{3+}$ ions, which give intense infrared emission under the excitation of ZnO exciton absorption at 395 nm. And we need further study on this part.

Furthermore, in Figure 3.4 we compared Yb$^{3+}$ emission spectra in the ZnO-LiYbO$_2$ hybrid phosphor and LiYbO$_2$ crystal under the excitation of 937 nm LD. And Yb$^{3+}$ emission spectrum in ZnO-LiYbO$_2$ hybrid phosphor under 395 nm excitation was also shown as inset for comparing. It can be observed that the ZnO-LiYbO$_2$ hybrid phosphor shows intense Yb$^{3+}$ infrared emission with the same spectral profile as indirect excited ZnO with near-UV light at 395 nm, while the LiYbO$_2$ crystal shows much weaker Yb$^{3+}$ emission with different spectral profile. Because the structure of Yb$^{3+}$ emission spectra can be an indication of the similarities and differences for the local crystal field around, Figure 3.4 indicated that the enhanced infrared emission was not from the LiYbO$_2$ phase, but was associated rather with high-efficiency-energy-transfer from ZnO to Yb$^{3+}$ intermediately with Li$^+$. Therefore, we can speculate that there may be interdiffusion regions between LiYbO$_2$ and ZnO. In this study, to confirm the speculation, the microstructure of Yb and Li co-doped ZnO was studied using both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The overall distribution, detailed microstructure and the crystal growth of LiYbO$_2$ on ZnO were examined.
3.2. Experimental

The Yb and Li co-doped ZnO samples were sintered using a solid-state reaction method in a weak reductive atmosphere by placing a crucible filled with raw materials into a bigger graphite crucible at 1050 °C for 2.5 hours. The starting materials were pure ZnO powders, mixed with 2mol% of Li$_2$CO$_3$ (99.99%) and 2mol% of Yb$_2$O$_3$. XRD measurements were obtained using a Rigaku D/MAX-RA diffractometer using a Cu target. Scanning electron microscopy observations were carried out using a Nova 200 NanoLab UHR FEG-SEM/FIB and a FEI XL30 EFSEM. Energy dispersive characteristic X-ray analysis (EDX) was used for performing chemical analysis in conjunction with the FEI XL30 EFSEM. Transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) were carried out using a JEOL 2010F TEM operating at 200keV, and equipped with a Gatan Enfina electron spectrometer, with an energy resolution of 1.0eV. The TEM specimen was prepared by grading the sample in acetone and picking up using a Cu grid covered with lacy C films.

3.3. Results and Discussion

Figure 3.5 is a SEM micrograph of Yb/Li co-doped ZnO. The large smooth-surfaced particles are ZnO. The remaining Yb$_2$O$_3$ particles are of irregular shapes, with sharp edges and corners. It is also evident that some particles have “French bread” shapes, as indicated by arrows in Figure 3.5. These “French bread” shaped particles are LiYbO$_2$, which have a unique porous structure. We speculate that the porous nature of LiYbO$_2$ may be related to the decomposition of Li$_2$CO$_3$ at high temperature, which liberates CO$_2$ gas. Most interestingly, there are many small particles (shown as tiny bright dots in Figure 3.5) stuck on the ZnO surfaces. In some cases, the ZnO surfaces show...
concave areas underneath these small particles. Visually, these particles look like they are partly sunken into the ZnO surfaces. These particles can be vividly depicted as “sprouts” of ZnO, and they are called sprouts thereafter. EDX spectra show the presence of Yb in these sprouts. Unfortunately, Li cannot be detected by our currently used EDX system.

Figure 3.5 SEM image of Yb and Li co-doped ZnO

A closer look at the sprouts, along with LiYbO$_2$ particles and Yb$_2$O$_3$ nanoparticles, is presented in Figure 3.6. An Yb$_2$O$_3$ nanoparticle is indicated by a white arrow. It is attached on the ZnO surface, which is consistent with previous observations in Yb single-
doped ZnO. As shown in Figure 3.6 (a), each pit may contain single or multiple sprouts. Some sprouts appear to sink into the ZnO, as shown in the upper left in Figure 3.6 (a), while some may grow above the ZnO surface, as shown in the lower right in Figure 3.6 (a). An enlarged image of one sprout on the ZnO is presented in Figure 3.6 (b). It has an oval shape, and its size is slightly over 1 µm x 1.5 µm. The surface of the ZnO appears to be concave underneath this sprout. The sprout shows porous structure, which is similar to the structure of the LiYbO₂ particle sitting at the junction of three ZnO grains.

Figure 3.7 Elemental maps of Yb and Zn in the rectangle area in Figure 3.6(b). Yb L and Zn K-line X-ray emissions are used for the Yb and Zn mapping, respectively.

Composition maps were acquired using EDX in the rectangle area in Figure 3.6 (b), which contains one sprout (in the middle) and one piece of LiYbO₂ crystal (on the right). In the Yb map, the bright areas indicate Yb-rich regions. In the Zn map, the dark areas indicate strong absorption of Zn K-line emission. The composition maps indicate that the sprout contains Yb, but very low levels, if any of Zn. A closer look at the Yb map shows that, the edge of the sprout is blurred compared to the edge of the LiYbO₂ crystal. It is difficult to define the outline of the sprout from the Yb map. In comparison, in the
Zn map, the edge of the same sprout is quite sharp and the outline of the sprout is defined quite clearly. From visual investigation, it appears that the sprout size is slightly bigger in the Yb map than in the Zn map. Careful measurements of the dimensions also show that the sprout size in the Yb map is slightly larger than in the Zn map.

Figure 3.8 Linescan of x-ray emission intensities of Yb L and Zn K lines across the sprout shown in Figure 3.6 (b). The vertical dashed lines are guides for eyes, which indicate the possible boundaries of the sprout.

To further confirm this observation, we also performed a linescan across the same sprout. The results are plotted in Figure 3.8. Overall, the Yb concentrates in the sprout region, while the Zn is in deficient in the same region. On the right side, the Zn has a relatively constant intensity up to the marked position at 2.2µm (indicated by a dashed line), and then the Zn intensity drops quickly within a distance of approximately 0.1 – 0.2µm. On the left side, the Zn intensity is relatively low and is not constant. This is
likely due to the concave surface in the vicinity of the sprout. Nevertheless, we can still identify the marked position at about 1.0µm (indicated by a dashed line), from which the Zn intensity starts to drop rapidly toward the sprout. Therefore, it is evident that the line profile of Zn intensity has sharp edges within a spatial resolution of 0.1 – 0.2µm, which are consistent with the 2-d Zn mapping observation. The size of the sprout as measured by Zn K-line emission is about 1.2µm between the two dashed lines.

On the other hand, the line profile of Yb L-line emission is relatively smooth at the edges. The Yb intensities do not drop to zero at the marked edges (dashed lines) from the Zn K-line emission. Instead, meaningful signals of Yb K-line emission can still be measured beyond the marked edges, approximately at the positions marked by the arrows in Figure 3.8. This is also consistent with the 2-d Yb mapping observation, which shows blurred edges of the sprout. The size of the sprout measured by the Yb L-line emission is then slightly larger than the size measured by the Zn K-line emission.

It should be pointed out that the spatial resolution of EDX in SEM is limited by the electron interaction volume, which is generally larger than the probe size of the electron beam. (The probe size is about 3nm across in the FEI XL30 EFSEM used in this study.) An estimate of spatial resolution is obtained by comparing the Zn K-line profile with the secondary electron signals across an edge of the sprout, as shown in Figure 3.9. According to the secondary electron line-profile, the width of the edge is between 0.1 ~ 0.2 µm. Meanwhile, the width of the edge, as measured by the Zn K-line emission is also about the same, although it is slightly wider. Therefore, it is reasonable to consider that the spatial resolution in the linescan and 2-d mapping is about 0.1 – 0.2 µm. Therefore,
the blurring of the edge seen in the Yb map is not an artifact, and may be interpreted as due to the diffusion of Yb into ZnO.

Figure 3.9 Detailed comparison of Zn K line profile with simultaneously recorded secondary electron (s.e.) signals. The vertical double chained lines indicate the spatial resolution.

Although the exact composition and structure of the sprouts are not known, these sprouts are “nuclei” for LiYbO₂ crystals. There is evidence in our micrographs that LiYbO₂ particles can grow from these sprouts. An example is shown in Figure 3.10, indicated by a black arrow. The figure shows a long LiYbO₂ particle that lies on the ZnO, while still connected to its “root”. The appearance of the particle suggests that the LiYbO₂ crystal originally grows into a pillar perpendicular to the ZnO surface. The width
of the pillar is slightly larger than the diameter of the sprout, from which it grows, while its length can be as much as several micrometers. It is also noticeable that although the LiYbO$_2$ crystal has a smooth surface, it has a porous structure inside. As a result, it can easily fall off from the root. In this particular case (in Figure 3.10), the breaking off of the particle was due to the buckling. The compressive load (due to the weight of particle) results in bowing of the long particle, creating tension on the outer side of the particle and compression on the inner side. Although the LiYbO$_2$ single crystal may not have high ductility, the porous structure is more likely to be ductile. The tensile stress on one side will elongate the particle until it reaches the yield point, and then the particle will begin to neck. Such a neck is indicated by two short black arrows in Figure 3.10. When such necking occurs, stresses are further concentrated, and the radius of the neck decreases until the particle breaks off.

Figure 3.10 SEM image showing growth of a LiYbO$_2$ particle from a sprout
The particle then leaves a pancake-like remnant on the ZnO surface, which is indicated by the white arrow in Figure 3.10. The height of such pancake-like remnant is much smaller than the diameter. The diameters vary from slightly about a half micron to one micron. This suggested model can also explain the origin of the observed “French bread” shaped particles, which arise from the breaking away of LiYbO2 pillars that grow on the ZnO surface.

It is also evident from the micrographs that the porous LiYbO2 crystals are not exclusively in the “French bread” shape. They may also exist in irregular shapes. For example, they may grow from the junction of several ZnO grains as shown in Figure 3.6 (b) or between two ZnO grains as shown in Figure 3.11. Nevertheless, all of the LiYbO2 particles surveyed in this study are associated with ZnO. Therefore, we suggest that the nucleation of LiYbO2 occurs only on the ZnO, and the ZnO surface has catalytic role on the formation of LiYbO2 phase during the thermal synthesis.

Figure 3.11 SEM images showing radiation damage in the LiYbO2 particle.

In Figure 3.10, it is also noticeable that the pancake-like particles have a “shadow” around them on the ZnO substrate. The shadow is in fact induced, or exacerbated by
electron damage as discussed below. The damage can be seen in Figure 3.11. In Figure 3.11 (a), a porous LiYbO₂ particle grew at the interface between two ZnO particles. A narrow and faint shadow is visible around the particle. In Figure 3.11 (b), the same particle was recorded after 2 minutes of exposure to the electron beam. The shadow around the particle has become larger. However, the porous structure of the particle does not change at all. Although various mechanisms for beam damage have been proposed previously, it is likely that electric field induced ion migration⁷³,⁷⁴ is responsible for the shadow region around the LiYbO₂. It is known that the electron bombardment of glasses can drive alkali ions out of the illuminated region, resulting in the decay of alkali characteristic x-ray intensities.⁷⁵ There are several reasons that suggest that the same mechanism can be operational in the case of the LiYbO₂ crystals. First of all, beam damage was only seen in the LiYbO₂ particles, but not in the Yb₂O₃. The latter is very robust under electron beam in both SEM and TEM. Secondly, the microstructure of the LiYbO₂ particle remains unchanged after beam damage, as show in Figure 3.11. Furthermore, we have observed a similar beam damage phenomenon for LiYbO₂ in the TEM.

Figure 3.12 shows a time series of EELS spectra acquired from a reference LiYbO₂ crystal in TEM. The beam current density was 0.4nA/cm². Spectra A to E were recorded at a time sequence of initial, 2, 8, 22, and 30mins, respectively. The background subtracted Li K-edges are provided in the inset. The three-peak features between 25 and 45eV are Yb O₂³-edge.⁷² The Li K-edge is at about 60eV. It is seen that radiation damage causes a decrease in the bulk plasmon peak (18.6eV) of LiYbO₂, accompanying an increase in the peak at 16.2eV, which is very close to the bulk plasmon of Yb₂O₃. Beam
damage also results in the decay of the Li K-edge, as shown in the inset of Figure 3.12. These results indicate that beam damage causes a loss of Li.

Figure 3.12 A time series of EELS spectra recorded from a reference LiYbO$_2$ crystal

Two mechanisms can be involved in the damage process: one is knock-on damage due to kinetic energy transfer from energetic electrons to Li, and the other is electric-field induced Li migration. The electric field is created by ejection of secondary and Auger electrons into the vacuum in the TEM. Experimentally, it is difficult to confirm or reject the first mechanism, because the majority of the Li atoms are sputtered into vacuum by knock-on damage. In contrast electric-field induced damage mainly causes lateral migration of Li ions towards areas with lower or zero electric potential. Therefore if
electric-field induced Li migration does occur, it should be possible to detect Li in the adjacent C film.

Figure 3.13 (a) TEM image of LiYbO₂, (b) Low loss spectrum of LiYbO₂
As shown above, Figure 3.13 (a) is a TEM bright-field image showing a piece of porous LiYbO₂, which was obtained from the Yb and Li co-doped sample. After a short exposure to the electron beam, we acquired EELS spectrum from the adjacent supporting C film, as shown in Figure 3.13(b). From the figure, we can clearly observed Li K-edge around 60eV, detailed shown in the inset of Figure 3.13(b). This indicates that a significant amount of Li in the C film close to the porous LiYbO₂ particle. This evidence indicates that migration of the Li ions in the LiYbO₂ is being caused by the electric-field induced by processes (such as ejection of secondary and Auger electrons) that are caused by the incident electron beam.

In the case of SEM, electron-beam induced electric fields are mainly due to trapping of incident electrons inside the specimen. The buildup of incident electrons inside the sample may then attract positive ions, e.g. Li⁺ in LiYbO₂ into the sample. However, in the outmost layers, secondary and Auger electrons are likely to be ejected into vacuum, producing a thin positive charged region. Therefore, Li⁺ ions become unstable on surface. In some cases, metallic alkali can be observed at the surface. Since ZnO exhibits n-type conductivity, it is reasonable to consider that ZnO plays a similar role as in the case of the supporting C film in the TEM specimen. Therefore, the surface Li⁺ ions can be driven laterally to the nearby ZnO surface (due to electron charging of the LiYbO₂ particle), and may interact with the ZnO to form a heavily Li doped ZnO surface. The Li doped ZnO surface has different conductivity compared to the un-doped ZnO, and this difference will modify the emission of secondary electrons and therefore the contrast of SEM images. This process becomes more favorable in case of porous LiYbO₂, due to the large surface area in the porous particle. It is also noticeable that beam damage is
observed only in the small LiYbO$_2$ particles, but not in the sprouts. No matter how long the electron beam exposure, a similar shadow cannot be seen around the sprouts (Figure 3.6). One possible reason is the volume of sprout is small, and therefore total surface area is also small.

### 3.4. Conclusions

In conclusion, based on previous dedicated optical studies on Li and Yb co-doping ZnO, the formation of a LiYbO$_2$ phase by the thermal synthesis is observed to be intermediated by ZnO. Under SEM, we observed that the growth of LiYbO$_2$ particles is either from the ZnO surfaces or at grain boundaries. Strong evidence suggests that the nucleation of LiYbO$_2$ may not be just on the ZnO surface, but catalyzed by ZnO. Therefore, a reaction (or diffusion) zone is very likely to exist between LiYbO$_2$ and ZnO. This finding accords with previous studies by excitation-emission spectroscopy. And as we know, enhanced infrared emission was not from the LiYbO$_2$ phase directly, the diffusion regions may be responsible for the enhanced infrared emission in the Yb and Li co-doped ZnO. Therefore, the infrared emission may not be uniformly from the ZnO particles, but from the regions containing sprouts. In other words, the sprouts are probably the emission centers.

Limited by the spatial resolution of SEM, the direct evidence of such a diffusion zone might be obtained from the cross-section TEM observations. Though it is not a trial task to prepare a TEM sample for the cross section of the diffusion region, in principle the TEM sample can be prepared by FIB. However our study indicates that the challenge part of direct observation of diffusion zone in TEM is most likely the beam damage. Irradiation by energetic electron irradiation may not only sputter Li into vacuum, but also
cause lateral migration of Li, and therefore poison the diffusion zone. Therefore dedicated study of beam damage mechanism in the LiYbO₂ crystal is required to seek the damage-free conditions before we go further.
CHAPTER 4

ELECTRON ENERGY LOSS SPECTROSCOPY STUDY OF LiYbO₂

4.1. Introduction

LiYbO₂ is a fundamental and industrial important material, and it has been known since 1959. Its synthesis and crystal structure have been well studied later on. In brief, LiYbO₂ has a tetragonal structure with the space group I4₁/amd, and can be considered as an ordered rocksalt (NaCl) structure, in which the cation-ordering preserves an alternation of Yb³⁺ and Li⁺ along the tetragonal c-axis. Although the magnetic and optoelectrical properties of LiYbO₂ have been measured experimentally, there is no study on its electronic structure available in literature. However, as a rare earth oxide, the study of Yb₂O₃ optical absorption properties has been reported for a while. Yb₂O₃ has a cubic structure with the space group Ia₃. Although their crystal structures are different, Yb atoms are all in octahedral coordination in LiYbO₂ and Yb₂O₃, thus Yb₂O₃ can be used as reference for the study of LiYbO₂.

As stated in chapter 3, it is reported that the LiYbO₂ crystals were observed in the Yb³⁺ and Li⁺ co-doped ZnO using solid-state reaction method. Although it may not be directly caused by the LiYbO₂ phase itself, the microstructure study indicates that the LiYbO₂ phases are grown on the ZnO surfaces, and there is a reaction zone (or diffusion zone) between LiYbO₂ and ZnO. However the role of LiYbO₂ in the high intense Yb³⁺ emission is still unclear. Before we study the vulnerable diffusion region under TEM, the further study of radiation damage effect and the electronic structure of LiYbO₂ are necessary. In this chapter, firstly we study the radiation damage due to high energy electron beam on LiYbO₂. With damage results we try to find the “damage free zone”
where we can do study without detectable damage on the specimen. And then we acquire EEL spectra to study the electronic structure of LiYbO₂, also compared with Yb₂O₃ experimentally. To help us to understand the experimental results better, by using FFEF8 simulations we do calculations for low loss spectra and Li, O K-edges, as well as projected local density of states for every kind of ion in both LiYbO₂ and Yb₂O₃. The calculated results have been compared with the experimental results.

4.2. Experimental Details

The synthesized LiYbO₂ and commercial Yb₂O₃ (Alfa Aesar Inc.) crystals were used in this study. The LiYbO₂ crystals were synthesized using solid-state reaction method⁵¹, and the details of synthesis can be found elsewhere. Transmission electron microscopy (TEM) specimens were prepared by crushing LiYbO₂ or Yb₂O₃ crystals in acetone and then picking up by a Cu grid covered with lacy carbon thin films. The specimens were studied in a JOEL-2010F(S) TEM equipped with a Gatan Enfina electron spectrometer. The field-emission electron gun (FEG) worked at 200keV. The energy resolution of EELS was about 1.0eV measured at the full width at half maximum (FWHM) of zero peak. The dispersion of spectrometer was 0.1eV/channel, and the EELS entrance aperture was 3.0mm in diameter. Low energy-loss spectra and Li K-edge EELS were acquired in image mode and the VEELS spectra analyzed using KK analysis procedure, which was encoded in DigitalMicrograph. The O K-edge EELS are recorded in diffraction mode, and the backgrounds were fitted with a power-function and remove the original data. And in order to measure the lattice parameters from diffraction patterns, Au-spoiled Cu grid specimens have been used to calibrate the scale of the software at the same camera length 20 cm.
4.3. Radiation damage study in LiYbO₂ by high-energy electron beam

As we discussed in last paragraph, to study the diffusion zone between ZnO and LiYbO₂ by TEM, we have to overcome the radiation damage problem. Firstly, radiation damage induced by high-energy electron beam in LiYbO₂ has been studied by EELS and diffraction. Both structural and compositional changes during the damage process are observed in real time. The decomposition from crystal LiYbO₂ to polycrystalline Yb₂O₃ in the damage region has been observed by both diffraction and EELS in real time, therefore confirm that Li and O could be sputtered out and the damaged lattice would collapse to polycrystalline Yb₂O₃ in random lattice directions. The purpose of this part is to demonstrate that the damage mechanism of LiYbO₂ under high density and high energy electron beam, to prepare the TEM observation of the cross section specimens of the ZnO-LiYbO₂ hybrid phosphors’ diffusion region.

4.3.1. Results of radiation damage study by EELS

In Figure 4.1 a time series of low loss spectra of LiYbO₂ is shown, we can see there are three-peak features between 25 and 45eV, which are Yb O₂-edge. The Li K-edge is at about 60eV as shown in the inset. The spectra have been acquired under beam current 0.2nA/cm² at 0 minute, 5 minutes, 10 minutes, 16 minutes, 23 minutes, 31 minutes, 71 minutes, respectively in alphabetic order. It is seen that radiation damage causes the decrease of the dominant peak (18.6eV) of LiYbO₂, accompanying the increase of a dominant peak at 16.2eV, which may be due to the bulk plasmon of Yb₂O₃. And we can observe that the middle peak in the three-peak feature also decay a lot. Beside these, radiation damage also results in the decay of Li K-edge, as shown in the inset of Fig. 4.1. These results indicate that radiation damage causes the loss of Li.
Figure 4.1 A time series of EELS spectra recorded from a LiYbO$_2$ crystal. The beam current density was 0.2nA/cm$^2$. The background subtracted Li K-edge are given in the inset.

However, even after 71 minutes’ exposure to high energy electron beam, there is still a bump remained above 60eV although the Li K-edge peak has already disappeared. We can speculate that there is something else existing here besides Li K-edge. After
investigating reference, as shown in Figure 4.2 we found that Yb O$_1$-edge also locates here, which overlaps with the Li K-edge around 60eV. The Yb O$_1$-edge corresponds to Yb $5s \rightarrow 6p$ excitations.

Figure 4.2 EELS spectra of Li K-edge and Yb O$_1$-edge in LiYbO$_2$ low loss region

Besides the low loss spectra, for the same sample area the O K-edges have also been acquired simultaneously. Figure 4.3 shows a time series of EELS spectra of O K-edges in the LiYbO$_2$ specimen, and we can see that all the spectra have the double-peak structure of O-K-edge. And along with the radiation damage processing, the relative intensity of 1$^{\text{st}}$ peak to 2$^{\text{nd}}$ peak reduced a lot although there are no change of the two peaks’ positions. The spectrum G at final stage looks very similar with O K-edge in Yb$_2$O$_3$. Considering both the low loss spectrum and O K-edge for the final product after beam radiation damage, we can speculate that LiYbO$_2$ can decompose to Yb$_2$O$_3$ under radiation damage.
Figure 4.3 A time series of O K-edge spectra recorded from a LiYbO$_2$ crystal

4.3.2 Results of radiation damage study by diffractions

Besides the EELS study on the radiation damage, as shown in Figure 4.4 the diffraction patterns show several radiation damage stages of the same region on the specimen. Initially, pattern (a) shows that the illuminated area is a perfect LiYbO$_2$ crystal oriented along [110], and then the electron-radiation induced damage in this specimen
can be observed in the rest of diffraction patterns. Pattern (b) shows that some diffraction rings begin to appear, but the diffraction pattern from LiYbO₂ [110] still can be observed but dimmed; pattern (c) shows that the LiYbO₂ [110] diffraction pattern almost disappears; finally pattern (d) shows the high intensity diffraction rings after a long time exposure to electron beam.

Figure 4.4 SAED patterns of LiYbO₂ showing the damage process
To know the final product after radiation damage, we need to know the crystal parameters in Figure 4.4 (d). Because gold is a well studied material for its crystal structure, we sputter gold particles on the carbon film of the Cu grid, and then get the diffraction pattern as reference to do the calibration under the same conditions of TEM. This procedure makes sure the scale of instrument is accurate. As shown in Figure 4.5 (a), which is originally from Figure 4.4 (d), the radius of the five most visible bright rings have been measured. The standard X-ray diffraction data has also been simulated by software “CrystalDiffract” with the Yb$_2$O$_3$ unit cell, which created by software “CrystalMaker” by inputting the unit cell parameters of Yb$_2$O$_3$. Yb$_2$O$_3$ has a cubic structure with the space group $Ia\overline{3}$, and $a = b = c = 10.4405$ Å, $\alpha = \beta = \gamma = 90^\circ$. As shown in Figure 4.5 (b), although there are lots of diffraction peaks, clearly the five strongest ones distinguish themselves, from left to right, the first one and last four higher peaks with marked names.
The numerical result of Figure 4.5 is listed in Table 4.1. We can see that the diffraction parameters of the irradiation product match the X-ray diffraction data of Yb$_2$O$_3$ perfectly. The five rings correspond to [112], [222], [004], [044], [226].
diffractions of Yb$_2$O$_3$ outwards with negligible error. Till now the final radiation product from LiYbO$_2$ can be confirmed as Yb$_2$O$_3$, after loss of Li and O under high-energy electron beam for a long exposure time.

Table 4.1 Comparison between experimental diffraction rings and simulated X-ray diffractions

<table>
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<tr>
<th>Rings/Peaks</th>
<th>Ring Radius(1/nm)</th>
<th>Peak Position(1/nm)</th>
<th>Ring-Peak Error (%)</th>
<th>Peak Intensity (I/Imax, %)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>10</td>
<td>112</td>
</tr>
<tr>
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<td>3.332</td>
<td>3.314</td>
<td>0.55</td>
<td>100</td>
<td>222</td>
</tr>
<tr>
<td>3</td>
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<td>3.832</td>
<td>0.20</td>
<td>36.4</td>
<td>004</td>
</tr>
<tr>
<td>4</td>
<td>5.421</td>
<td>5.421</td>
<td>-0.01</td>
<td>38.3</td>
<td>044</td>
</tr>
<tr>
<td>5</td>
<td>6.383</td>
<td>6.355</td>
<td>0.45</td>
<td>32.2</td>
<td>226</td>
</tr>
</tbody>
</table>

As we discussed before, two mechanisms may be involved in the damage process, one is the knock-on damage due to kinetic energy transfer from energetic electrons to Li atomic nuclei, and the other is the electric field induced Li migration. The electric field is created by ejection of secondary and Auger electrons into vacuum in TEM. Actually the O atoms can also be sputtered if the sample is thin enough. This kind of O loss due to sputtering radiation damage has been reported in the TEM study of ZrSiO$_4$. However Yb atoms are quite robust under the high energy beam due to its high atom mass. Based on the conservation of momentum and kinetic energy in the elastic scattering, Egerton et al. give equations for the transferred energy from the incident beam. \[ E = E_{\text{max}} \sin^2(\theta/2) \]
\[ E_{\text{max}} = E_0 (1.02 + E_0 / 10^6)/(456.7A) \]

Where \( E \) is the energy transferred from the incident electron to the atomic nuclei, \( E_{\text{max}} \) is the possible maximum transferred energy when the incident electron has been head-on collided happened at \( \theta = 180^\circ \). And \( \theta \) is the deflected angle, \( \theta = 0 \) if no change, \( \theta = 180^\circ \) if head-on collide and so on. \( E_0 \) is the kinetic energy of the incident electrons \( A \) is the atomic mass number in the sample. Therefore, the light mass atoms will receive more collision energy for the same collision. With \( E \) we can tell if the atoms can be knocked out or sputtered from the sample surface when we compare \( E \) and the knocked out energy \( E_d \) or the sputtered energy \( E_s \), generally \( E_d > E_s \). Thus surface sputtering is easy to happen under the same beam condition.

4.4. The electronic structure study of LiYbO_2 and Yb_2O_3 by TEM and EELS

After we studied the radiation damage to LiYbO_2, to avoid artifacts induced by electron irradiation damage during the experiments, the diffraction patterns and EELS spectra have been checked routinely in real time. The damage was mainly caused by ejection of Li\(^+\) ions from the illuminated area into surroundings, driven by electric field. This type of damage is dose rate (or beam current density) dependent.\(^8^8\) It was found that radiation damage was not detectable under the current density lower than 100pA/cm\(^2\), which was the readout of the small view screen, especially for a relatively thick area (>100 nm). All the data presented here were recorded with the current density between 20 and 50pA/cm\(^2\).

In a one-electron approximation, EELS spectrum gives the fraction of incident beam electrons that have lost energy to the excitation of a core electron or valence electron from an initial to an unoccupied state. For small-angle scattering, the dipole
selection rules apply. According to the Fermi’s golden rule, the EELS intensity is the product of joint density of states (JDOS) of initial and final states and an atomic transition matrix. Since the atomic transition matrix is a smooth function of energy, EELS can be qualitatively interpreted as the JDOS. For core-edge EELS, the initial state can be considered as a delta function, and thus the JDOS can be simplified as dipole selected unoccupied DOS projected on a particular atom. For example, the Li K and O K-edge EELS probe the unoccupied Li 2p and O 2p DOS, respectively. For valence EELS (VEELS), the initial states consist of extended valence bands, and thus the unoccupied DOS must convolute the initial valence bands. In other words, the interpretation of VEELS requires the JDOS.

However, the peaks observed in VEELS do not directly correspond to the peaks in the JDOS. This is because in the low frequency (e.g. \( \hbar \omega < 50eV \)), the real part \( (\varepsilon_1) \) of dielectric response function \( \varepsilon (=\varepsilon_1+i\varepsilon_2) \) is not unit, and a peak in EELS is due to an absorption peak in \( \varepsilon_2 \) associated with an oscillation in \( \varepsilon_1 \). Therefore, to compare with calculated DOS it is more convenient to derive \( \varepsilon_2 \) using Kramers-Kronig (KK) analysis. Furthermore, the optical absorption strength or interband transition strength \( (J_{cv}) \) can be derived by \( J_{cv} \propto \Delta E^2 \cdot \varepsilon_2(E) \). In addition, in the low energy-loss region, the spectrum is dominated by the collective excitations, which include both surface and bulk plasmons. Although these plasmons themselves contain information of both atomic and electronic structures, they have to be removed in order to reveal interband transitions.

In this study, VEELS of LiYbO2 and the derived \( \varepsilon \) and \( J_{cv} \) are compared with Yb2O3. Although the VEELS study of Yb2O3 is not available either in literature, the well
documented optical and x-ray photoemission results can be used to compare to. In addition, the energy-loss near-edge fine structures (ELNES) of Li K- and O K-edge are also measured and analyzed. The interpretations are given with the aid of \textit{ab initio} DOS calculations by FEFF8.

The program FEFF8 is an \textit{ab initio} self-consistent RSMS code written in ANSI FORTRAN 77,\textsuperscript{90,91} which is based on the real space multiple scattering (RSMS) approach, and self-consistent field (SCF) RSMS theory is based on the interference between the outgoing electron wave and the electron wave backscattered from surround atoms,\textsuperscript{91} which are in a limited size cluster, actually as same as the real space Green’s function band theory. And it is based on a muffin-tin potential approximation. The advantage of SCF RSMS with respect to other methods is that it can obtain the contribution to Green’s function from a smaller cluster by using full MS calculations, making real space calculation convenient and efficient.

With the crystal structure information, the input files for FEFF8 can be generated by program named “ATOMES” coded in Perl, in which we input crystallographic data such as the type of crystal space group, lattice parameters and other variable parameters such as cluster radius in one file called “atom.inp”. To get better accuracy, we set up the cluster radius as 10nm, thus we got an output file which included about 330 atoms in the LiYbO\textsubscript{2} cluster. After running the program “ATOMES” we could get an output file called “feff.inp” containing atoms’ coordinates and other variable information. Before using “feff.inp” as input file for FEFF8, we set up some important parameters carefully, such as broadening parameter “\textit{vi} = 1 \text{ eV}”, the cluster radius of multiple scattering “\textit{r\_fms} = 7” and also including cole-hole effects by default.\textsuperscript{92} Based on the different demands of
interest, different experimental environments, a lot of parameters are adjustable, thus it is a useful tool to interpret ELNES quantitatively, based on simultaneous calculations of ELNES and projected local densities of states (DOS).

4.4.1. Results and Discussions of low loss spectra

First of all, the experimental VEEL spectra of LiYbO₂ and Yb₂O₃ are compared in Figure 4.6. The plural scatterings were deconvoluted using Fourier-log method⁸, surface losses were removed using KK analysis (the dotted line shows surface plasmon), and the zero-loss peaks were also removed. Although two spectra are more or less similar, there are still some differences in detailed feature. In Yb₂O₃, there is a dominant peak P at 16.2eV with a broad pre-peak shoulder A around 10eV and small post-peak shoulder B at about 20eV. However in LiYbO₂, the dominant peak P is at 18.6eV. Although the pre-peak shoulder A is also at around 10eV, the post-peak cannot be identified in LiYbO₂.

Furthermore around 24.0eV (indicated by arrows in Figure 4.6), a weak bump C can be recognized in both oxides. Between 25 and 45eV, both Yb₂O₃ and LiYbO₂ spectra have a three-peak feature, a broad peak (C) around 32eV and two peaks at about 38eV (D) and 43eV (E). These three peaks shift slightly to lower energy in LiYbO₂, comparing with those in Yb₂O₃. It is also noticed that the VEELS spectrum of Yb₂O₃ in Figure 4.6 is consistent with our previous results,⁷² in which the peak at 16.2eV was assigned to bulk plasmon peak and three-peak features between 25 and 45eV were assigned to the Yb O₂⁻³-edge. In the LiYbO₂, there are peaks around 60eV (F), which are not visible in Yb₂O₃ except a small step-like feature at about 55eV, as shown in the inset. The peak F in LiYbO₂ is from the Li K-edge. And we will discuss the small step-like feature in Yb₂O₃ later.
Figure 4.6 The deconvoluted VEELS spectra of LiYbO$_2$ and Yb$_2$O$_3$

The proper assignments of these peaks in VEELS needs to separate bulk plasmon excitations from the interband transitions, which can be carried out using the KK analysis. Both real and imaginary parts of dielectric functions derived from the KK analysis for LiYbO$_2$ and Yb$_2$O$_3$ are compared in Figure 4.7. Our derived dielectric functions for Yb$_2$O$_3$ are also consistent with previous results. Several absorption bands can be observed in the $\varepsilon_2$. These peaks and bumps in $\varepsilon_2$ are due to interband transitions. It is seen that the strong peaks observed in VEELS at 16.3eV in Yb$_2$O$_3$ and 18.6eV in LiYbO$_2$ do not shown in the imaginary part of dielectric function (Figure 4.7). And theoretically the plasmon peak should appear at $\varepsilon_1 = 0$. Instead, at 16.3eV $\varepsilon_1 = 0$ in Yb$_2$O$_3$ and $\varepsilon_2$ is
decreasing with a relatively small rate. These combinations result in a resonance peak in an energy-loss function $\text{Im}[-1/\varepsilon]$ at about 16.3 eV. Therefore, the sharp peak at 16.3 eV can be assigned to the bulk plasmon peak of Yb$_2$O$_3$. In LiYbO$_2$, $\varepsilon_1 = 0$ at 17.4 eV, but the resonance is about 1.2 eV above, at 18.6 eV. This is caused by the $\varepsilon_2$, which is rapidly decreasing at 17.4 eV. At about 19 eV, the decreasing rate of $\varepsilon_2$ is slowing down. The combination of $\varepsilon_1$ and $\varepsilon_2$ curves creates a resonant peak at 18.6 eV, which can be assigned to the bulk plasmon peak of LiYbO$_2$.

![Dielectric functions plot](image)

**Figure 4.7** The dielectric functions $\varepsilon_1$ and $\varepsilon_2$ for LiYbO$_2$ and Yb$_2$O$_3$

In *jellium* model, the valence electrons in these oxides can be considered as free particles, as in the Drude theory of electrical conduction in metals. In response to incident
electron beam, a collective oscillation of valence electrons occurs at a characteristic bulk plasmon energy $E_p$. This value can be evaluated by the Drude formula,

$$E_p = \left( \frac{\hbar e}{\sqrt{\varepsilon_0 m^*}} \right) \sqrt{n},$$

in which $n$ is density of valence electrons involved in plasmon excitation, and $m^*$ is effective mass for the electrons. In the calculations, O $2s^22p^4$ and Li $2s^2$ are considered as free electrons, which may involve in collective excitations. For Yb, its electron configuration is [Xe]Yb$4f^{14}6s^2$. Here we assume Yb $4f^{14}6s^2$ as valence electrons involved collective excitation, considering its 3+ formal valence state. Thus the valence electrons are 24 and 16 for Yb$_2$O$_3$ and LiYbO$_2$ respectively. Using their rest mass $m_0$, the calculated Drude plasmon energies for Yb$_2$O$_3$ and LiYbO$_2$ are 21.6eV and 21.4eV respectively. They are away from our experimental results because we assume an ideal condition for Drude model, but actually there is damping effect as we discussed in chapter 2. Both Yb$_2$O$_3$ and LiYbO$_2$ are insulators, and the damping effect can shift the plasmon energy to lower energy.

Furthermore, since rare-earth compounds are heavy fermions, their effective mass $m^*$ should be much larger than $m_0$. According to previous band structure calculations, top of valence bands and bottom of conduction bands of these oxides are relatively flat and narrow. Since $m^*$ is inversely proportional to $d^2E/dk^2$, the flat band usually results in large $m^*$. In other words, the calculations using the rest electron mass $m_0$ may overestimate plasmon energies.

In addition, the calculations show that the plasmon energies for Yb$_2$O$_3$ and LiYbO$_2$ are about the same, but there is clearly an about 2.3eV difference in experiment. Such a difference may be caused by the interference due to interband transitions, which will be discussed later.
Interband transition strength ($J_{cv}$), which we can also call optical absorption strength, can be evaluated from the derived $\varepsilon_2^{94}$ in “DigitalMicrograph”, and the results are compared between LiYbO$_2$ and Yb$_2$O$_3$ in Fig. 4.8. Due to the width and large tail of zero-loss peak, the data below 5eV are not reliable, and thus omitted in Figure 4.8. Several absorption bands have been marked by capital letters corresponding to the VEELS peaks observed in Figure 4.6.

![Figure 4.8 The interband transition strength $J_{cv}$ for LiYbO$_2$ and Yb$_2$O$_3$](image)

It is seen that although these absorption bands are very similar between LiYbO$_2$ and Yb$_2$O$_3$, there are still some differences, such as B and F. The absorption band F is due to the Li K-edge absorption, which does not exist in Yb$_2$O$_3$. In Yb$_2$O$_3$, absorption band B starts from around 16eV, thus no overlap with band A. While in LiYbO$_2$, band B starts from about 14eV with a width about 5–6eV, and thus it not only overlaps band A.
but also interferes with bulk plasmon excitations. Due to this absorption band, the bulk plasmon peak is pushed toward higher energy, resulting in 2.3eV difference between LiYbO2 and Yb2O3.

It is evident that the derived interband transition strength from Yb2O3 in Figure 4.8 is consistent with previous optics and synchrotron x-ray measurements. Interpretation of the absorption in Yb2O3 has been well studied, we can try to explain the features of J\textsubscript{cv} based on the research of Yb2O3 optical absorption properties. From left to right, for both LiYbO2 and Yb2O3 band A corresponds to O 2p \rightarrow Yb 5d6s and Yb 4f \rightarrow 5d6s; band B is due to O 2p \rightarrow 3s; peak C' may be from O 2s \rightarrow 3p. Here it is impossible to separate the Yb 5d and 6s states so we treat them as one state 5d6s. However, the main structure of the three-peak features-bands C, D, E are more complicated. Firstly, they are all from Yb 5p \rightarrow 5d6s, which can be named as Yb O\textsubscript{23}-edge. Due to spin-orbital interaction, Yb 5p can be separated into two parts, 5p\textsubscript{1/2} and 5p\textsubscript{3/2}, and the energy level of 5p\textsubscript{1/2} is 6.6eV lower than 5p\textsubscript{3/2}. The transition from 5p\textsubscript{3/2} gives rise to a broad band C (Yb O\textsubscript{3}-edge), while the transition from 5p\textsubscript{1/2} produced bands D and E (Yb O\textsubscript{2}-edge). The two-peak feature in Yb O\textsubscript{2}-edge originates from splitting of the unoccupied Yb 5d states. With interaction with O 2p states, Yb 5d can be separated into two parts of e\textsubscript{g} and t\textsubscript{2g} symmetries and the energy level of e\textsubscript{g} is higher than t\textsubscript{2g}. However, we can see that the energy interval between D and E are different for Yb2O3 and LiYbO2, which are 3.8eV and 4.6eV respectively. This should be due to the difference of the local crystal structure between LiYbO2 and Yb2O3 and then give some difference of the local density of states. We discuss this later together with FEFF8 simulations.
4.4.2. Results and Discussions of the calculated projected Local density of states from Yb$_2$O$_3$ and LiYbO$_2$

To help us to interpret EEL spectra and interband transitions, projected local density of states for both Yb$_2$O$_3$ and LiYbO$_2$ have also been simulated by FEFF8 as shown in Figure 4.9 and Figure 4.10 respectively. And we have already aligned Fermi energy at 0eV. To make the spectra to be observed easily, the intensity of some weak spectra has been multiplied by 3, but the shapes always keep the same, such as O $s$DOS, Yb $s$DOS and $p$DOS in Yb$_2$O$_3$, and LiYbO$_2$.

![Figure 4.9 Calculated local projected density of states (DOS) in Yb$_2$O$_3$](image)

Figure 4.9 Calculated local projected density of states (DOS) in Yb$_2$O$_3$
In Figure 4.9, at first the local density of states has been projected on O in $\text{Yb}_2\text{O}_3$. And as we know, O K-edge corresponds to $\text{O} 1s \rightarrow 2p$ excitation, our unoccupied $p$DOS is just above Fermi level. This feature matches that the two peaks of O K-edge which are
just above the ionization edge. However, the interval between the two main peaks in O $p$DOS doesn't match O K-edge very well, we need further discussion later. While for the DOS projected on Yb in Yb$_2$O$_3$, let us check unoccupied $d$DOS and $s$DOS at first, we can see there are two groups of peaks for $d$DOS. Also we can see that there is only one peak for $s$DOS, which is overlapped with the second group of $d$DOS peaks. This feature confirmed our speculation before, we can not separate Yb 5$d$ state and 6$s$ state, and we have to treat them together as 5$d$6$s$.

Furthermore we want to know why Yb 5$d$ state splits. In Yb$_2$O$_3$, Yb is octahedrally coordinated to O, although six O atoms are not in perfect octahedral corners. Even though five Yb5$d$ sub-orbitals do not generate as in an ideal octahedron, Yb 5$d_{z^2}$ and Yb 5$d_{x^2-y^2}$ are still approximately pointing toward O, resulting in stronger interaction with O 2$p$, while Yb 5$d_{xy}$, Yb 5$d_{yz}$ and Yb 5$d_{xz}$ are pointing between two O atoms, resulting in weaker interaction with O 2$p$. As a result, the unoccupied Yb 5$d$ state consists of two main portions, as shown in Fig. 4.9, in which the density between 0 ~ 5eV is mainly from Yb5$d_{xy}$, Yb5$d_{yz}$ and Yb5$d_{xz}$ and the density between 5 ~ 9eV is mainly from Yb5$d_{z^2}$ and 5$d_{x^2-y^2}$. In literature, these two portions are still referred to “$t_2g$” and “$e_g$”, respectively, although the explicit octahedral symmetry does not exist in Yb$_2$O$_3$.

Correspondingly, as we discussed before peak D and E observed in both EELS (Figure. 4.6) and interband transition (Figure.4.7) can be assigned to $t_2g$ and $e_g$, respectively and the split is different in Yb$_2$O$_3$ and LiYbO$_2$. According to crystal filed theory, the split of $t_2g$ and $e_g$ orbitals ($\Delta E$) in an octahedron is determined by bond lengths and bond angles. In general, the longer the bond length, the narrower the split, and the more it is deviated from a regular octahedron, the narrower the split. The average
Yb – O bond length (2.228 Å) in LiYbO₂ is slightly shorter than that in Yb₂O₃ (2.250 Å). In addition, although Yb octahedrons are irregular in LiYbO₂ and Yb₂O₃, it has higher symmetry in the former. Therefore, we can expect that \( \Delta E (\text{LiYbO}_2) > \Delta E (\text{Yb}_2\text{O}_3) \).

In Figure 4.10 for LiYbO₂, besides the DOS projected on O and Yb, the DOS projected on Li has also been presented. At first, let us check \( p \)DOS on O, we can see that there are three close peaks just above Fermi level, which may relate to the first peak in O K-edge, and the fourth peak may relate to the second peak in O K-edge of LiYbO₂. While for the DOS projected on Yb in LiYbO₂, the unoccupied \( d \)DOS and \( s \)DOS are slightly different from that in Yb₂O₃. The first peak in \( d \)DOS is relatively more stronger in LiYbO₂ than in Yb₂O₃, in which only a small bump. This feature confirms that the peak C in Figure 4.8 is stronger in LiYbO₂. Secondly, the \( s \)DOS is also overlapped with \( d \)DOS. For the \( p \)DOS on Li, we can see that the first peak is just above Fermi energy, which contribute the peak at around 58.9eV in Li K-edge. And as shown by the black arrow, the second and third peaks are close to each other, and contribute together to the second peak around 64.5eV in Li K-edge. Therefore, we can interpret that why the second peak in Li K-edge is broad by these two close peaks in Li \( p \)DOS.

Previously band B in Yb₂O₃ was assigned to the transition from top valence bands (O 2p/Yb 4f) to unoccupied O 3s states.⁸² According to our calculations, however, the unoccupied O 3s states mainly concentrate within the bottom of conduction bands, overlapping with the Yb 5d6s as shown in Figure 4.9. While we can see that the unoccupied Yb 6p states are just around 14eV, as shown by the black arrow in Figure 4.9. Therefore, band B is likely due to the transition from the top valence band to the unoccupied Yb 6p states in Yb₂O₃.
Interestingly, although the corresponding band B does not show in VEELS of LiYbO$_2$ (Figure 4.6) due to the overlap with plasmon peak, it can be clearly observed in the derived interband transitions (Figure 4.8). Compared with Yb$_2$O$_3$, this band has a relatively broader range in LiYbO$_2$, as shown in Figure 4.8. As a result, it partially overlaps with band A. Based on the calculations, as shown in Figure 4.10, Li 2$p$ has a maximum intensity between Yb 5$d$ and Yb 6$p$. Therefore, absorption band B in LiYbO$_2$ should be associated with both unoccupied Yb 6$p$ and Li 2$p$ states, and can be assigned to the transitions from the top valence band to these unoccupied states. In other word, it is probably due to the transitions associated with Li that results in the bulk plasmon shift to higher energy in LiYbO$_2$.

4.4.3. Results and Discussions of the experimental and calculated Li K-edge and O K-edge from Yb$_2$O$_3$ and LiYbO$_2$

![Figure 4.11 Comparison of experimental EELS spectra of the Li K with theoretical calculations by FEFF8](image)

Figure 4.11 Comparison of experimental EELS spectra of the Li K with theoretical calculations by FEFF8
Figure 4.12 Comparison of experimental EELS spectra of the O K-edges with theoretical calculations by FEFF8

We used Fourier-log method to deconvolute our experimental EELS spectra which included plural-scattering.\cite{ref13} The deconvoluted Li K-edge in LiYbO$_2$ is shown in Figure 4.11, and O K-edge in both LiYbO$_2$ and Yb$_2$O$_3$ are compared in Figure 4.12. Overall the spectral structure in both Li and O K-edges are similar, two sharp peaks followed by a broad feature. The two sharp peaks are at around 58.9eV and 64.5eV in the Li K-edge, while 534.1eV and 539.6eV in the O K-edge respectively. The separation between the two peaks, in the Li K-edge (5.6eV) is almost the same as that in O K-edge (5.5eV). Meanwhile, the relative intensity of the first peak is stronger than the second in the Li K-edge, but it is also narrower than the second one. And the asymmetry of the
second peak in Li K-edge is also observed. For the O K-edge in both oxides, although the peak positions are the same, the difference is that the first peak in LiYbO$_2$ is much stronger than that in Yb$_2$O$_3$.

To help us understand better, we applied program FEFF8 to calculate both Li and O K-edges based on the structure information of LiYbO$_2$ and Yb$_2$O$_3$ lattices. The Li and O calculated K-edges in LiYbO$_2$ and Yb$_2$O$_3$ by FEFF8 are shown under the experimental spectra for comparison in Figure 4.11 and Figure 4.12 respectively. To make it easy to compare, the band edges have been aligned to the thresholds of the experimental K-edges.

In Figure 4.11, the Li K-edge has been reproduced very well compared to the experimental spectra, but there are still some differences. For example, the first peak in Li K-edge is much weaker in FEFF8 simulation. Besides this, the bump is not very obvious due to the low signal-to-noise ratio in experimental spectra, while it is very clear in the simulation result. Furthermore, the 5.6eV difference is much less than the separation between the first and the second peak in Li 2p DOS, which is about 10eV in Figure 4.10. This difference is caused by the strong core-hole effect on Li K-edge. The presence of a hole in Li 1s orbital in calculation shifts Li DOS toward the band edge. However, the final state approximation is perhaps still not enough to simulate the real core-hole effect on Li K-edge. It is seen that the first peak is much stronger in the experiment than in calculation. Therefore, the origin of the double-peak feature in Li K-edge is different from O K-edge, as well as Yb O$_2$-edge. It does not reflect the crystal field of Yb d orbitals.

For the O K-edge, overall the features have been reproduced very well, especially the intense of the first peak can be reproduced in LiYbO$_2$, compared with that in Yb$_2$O$_3$. 

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The double-peak characteristic in O K-edge ELNES (or equivalent x-ray absorption near-edge structure, XANES) is very common in transition metal oxides,\textsuperscript{99,100,101} as well as in rare-earth oxides\textsuperscript{18,84}. As we mentioned before, such a character was interpreted as due to the crystal field splitting of the metallic $d$ orbitals into $t_{2g}$ and $e_g$ components, considering that O $2p$ orbitals interact with the $d$ orbitals of the metal.\textsuperscript{84,99,100} In a systematic study in rare-earth oxides,\textsuperscript{84} it is found that the splitting of $t_{2g}$ and $e_g$ components depends on the bond length and the distortion of octahedron. This is consistent with the above observation of Yb O$_2$-edge in Figure 4.6.

However, careful measurements in O K-edge ELNES show that the splitting are the same between LiYbO$_2$ and Yb$_2$O$_3$. This contradicts the observations in Yb O$_2$-edge in Figure 4.8. The discrepancy can be better understood if it is integrated with the intense first peak observed in LiYbO$_2$. According to the calculations in Figure 4.10, both O $2p$ and Li $2p$ unoccupied states have strong intensity near the band edge. This suggests that the first peak in O K-edge ELNES from LiYbO$_2$ is also highly related to the Li – O interaction besides the Yb – O interaction. By contrast, such interaction does not exist in Yb$_2$O$_3$. Relatively, Li – O interaction has less effect on the second peak in O K-edge ELNES. As we mentioned above, LiYbO$_2$ is susceptible to electron beam, resulting in loss of Li by exposing to electron irradiation. So the first peak in O K-edge ELNES will decreases relative to the second, if beam damage occurs. This deduction has been confirmed by our \textit{in situ} observation of O K-edge ELNES during irradiating LiYbO$_2$ in Figure 4.3.

Therefore, the splitting in O K-edge ELNES of LiYbO$_2$ is not only determined by the crystal field of Yb $d$ orbitals, but is also influenced by the Li – O interaction.
Although the double-peak feature can still be interpreted in general as a result of $d$ orbital splitting, $\Delta E$ between the two peaks cannot be used to quantify the strength of crystal field. Such Li – O interaction may also affect the allocation of Yb $5d$ DOS in LiYbO$_2$. This may also be responsible for the relatively intense “$t_{2g}$” peak in Yb O$_2$-edge in LiYbO$_2$, compared with that in Yb$_2$O$_3$, as shown in Figure 4.6 (peak D). Interestingly, this “$t_{2g}$” peak also decreases with the depletion of Li during in situ beam damage observations, and the results are also presented in Figure 4.1.

4.5. Conclusions

First of all, radiation damage by high-energy electron beam in LiYbO$_2$ has been studied thoroughly by using diffraction and EELS, and compared with the simulation results from several software tools. It is demonstrated that crystal LiYbO$_2$ could decompose to polycrystalline Yb$_2$O$_3$ with the loss of Li and O induced by radiation damage. These kinds of loss by radiation may involve two mechanisms, one is the knock on (sputtering) damage by kinetic energy transfer from energetic electron to Li and O, and the other is the electric field induced Li migration. Although LiYbO$_2$ is vulnerable to high energy beam, we can still work on it with a relative low beam current such as 100pA/cm$^2$ for a short time, such as less than 5 minutes. Under these conditions, we can assume that there is no serious radiation damage on the LiYbO$_2$ sample. It indicates the possibility for us to observe the cross-section specimen of the ZnO-LiYbO$_2$ hybrid phosphors’ diffusion zone in TEM under this “damage free zone”.

Furthermore, we acquire experimental EEL spectra for both LiYbO$_2$ and Yb$_2$O$_3$, both low loss and core loss. The dielectric response function and single-electron interband transition spectrum are derived from VEELS data for LiYbO$_2$, in the range of 5
– 70eV, using the Kramers-Kronig analysis method. Li K and O K-edge have been compared between experimental and calculated results, between LiYbO$_2$ and Yb$_2$O$_3$. The DOS projection on specific atoms has also been simulated by FEFF8, which help us interpret qualitatively the fine structure of electron band. The bulk plasmon is identified at 18.5 eV for LiYbO$_2$. Our interpretation of the interband transitions is given with the aid of comparison with Yb$_2$O$_3$, as well as ab initio calculations of density of states.

To a great extent, although similarities in the VEELS and O K-edge exist between LiYbO$_2$ and Yb$_2$O$_3$, differences are also noticed and explained in terms of composition and local structure differences around Yb. The fundamental information of LiYbO$_2$ electronic structure is essential for further understanding the composite phase LiYbO$_2$, as well as the active diffusion zone between ZnO and LiYbO$_2$. 
CHAPTER 5

SUMMARY

5.1. Summary

In this dissertation, to study the structural and electronic properties of functional materials, experimental characterizations have been done by TEM and EELS, as well as SEM and EDX, but the most used and important tool is EELS. At the same time, several theoretical methods have been simulated to help us to analyze and explain our experimental energy loss spectra as well. The first one is the relativistic expression based on dielectric function theory, which is realized by MATLAB. The other is the FEFF8 program based on the real space multiple scattering (RSMS) approach, which is coded by FORTRAN. Aided by both experimental and theoretical tools EELS can give us powerful ability for materials characterization.

The first functional material we studied in this dissertation is the 1nm ultrathin SrTiO3 layer sandwiched between amorphous Si and crystalline Si. We acquired the valence electron energy-loss spectra of the sample under a Hitachi-2700C STEM. Two Plasmon excitations were observed, one at 15.8eV and the other at 28.7eV. Our calculations of VEELS by Moreau’s equations, based on dielectric-function theory and realized by MATLAB, suggest that the former peak originates from the coupling of the amorphous Si and the crystalline Si layers, and it is dependent on the geometry of the structure, such as the width of STO layer, the position of the electron beam probe on the sample. While the latter peak at 28.7eV results from the SrTiO3 bulk Plasmon also has a red shift. And after trying different geometry parameters both experimentally and theoretically, we didn’t find obvious variations. Therefore we focused other factors and
found that the shift is mainly due to the enhancement of the effective mass close to the interface. Meanwhile we also demonstrated the value of valence electron energy-loss spectroscopy in detecting a local structure change at the interface.

The other functional material is the so called ZnO-LiYbO$_2$ hybrid phosphor. It is synthesized by co doping Li and Yb into ZnO. The enhancement of infrared emission has been observed. And also a new phase LiYbO$_2$ has been detected. However optical studies show that the LiYbO$_2$ is not the direct source of the enhanced emission. While the diffusion region between LiYbO$_2$ and ZnO may be the critical area. Therefore the diffusion region of LiYbO$_2$ has been studied by SEM and EDX to find the cause why the emission has been enhanced with co doping Li$^+$ and Yb$^{3+}$, and the growth mechanism of phase LiYbO$_2$ has been described. During our study, beam damage has been detected under SEM for LiYbO$_2$. Furthermore, we also observed radiation damage for LiYbO$_2$ in TEM.

The new phase LiYbO$_2$ attracts our interest because there is no study on its electronic structure in literature. Thus the synthesized LiYbO$_2$ has been studied under TEM and EELS. Firstly the radiation damage effect on LiYbO$_2$ has been studied by real time EELS and diffraction, and the decomposition from LiYbO$_2$ to Yb$_2$O$_3$ have been observed by both methods. Two mechanisms may be involved in the radiation damage of LiYbO$_2$. One is the knock-on or sputtering damage due to kinetic energy transfer from energetic electrons to Li and O atomic nucleus, and the other is the electric field induced Li migration. The electric field is created by ejection of secondary and Auger electrons into vacuum in TEM. However “the damage free zone” can still be found for further study by EELS. Because firstly the cross section is relatively low for the knock on or
sputtering damage, and then the electric field induced damage is dose dependent, we can control our beam current and exposure time to find the balance between radiation damage and our demand of high spatial resolution and high signal/noise ratio. Finally under the “damage free” conditions, experimental energy loss spectra have been acquired for both LiYbO₂ to Yb₂O₃. Meanwhile energy loss spectra and density of states have been simulated by FEFF8 program to help us compare and interpret the electronic structures of LiYbO₂ and Yb₂O₃.
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