

Characterization of the Electronic Structure and Optical Properties of Al_2O_3 , ZrO_2 and SrTiO_3 from Analysis of Reflection Electron Energy Loss Spectroscopy in the Valence Region

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Abstract

Characterization of thin surficial films of oxides has become the focus of increased interest due to their applications in microelectronics. The ability to experimentally determine the electronic structure and optical properties of oxide materials permits the direct study of the interband transitions from the valence to the conduction band states. In the past years there has been much progress in the quantitative analysis of transmission electron energy loss spectroscopy (TEELS) in the electron microscope

Here we employed reflection electron energy loss function (REELS) as well as vacuum ultraviolet (VUV) spectroscopy to determine the dielectric functions of oxide materials, i.e. Al_2O_3 , ZrO_2 and SrTiO_3 . The two main steps in the analysis are the removal of the effects of multiple scattering from the REELS spectra followed by application of the Kramers-Kronig dispersion transforms to the single scattering energy loss function to determine the conjugate optical variable and then the complex dielectric function. The surface and bulk plasma resonance spectra for these oxide materials have been determined from VUV and REELS, along with the influence of primary electron energy on the REELS results. The relative contribution of surface and bulk plasmon oscillation in REELS has been investigated. Comparison with VUV results and existing TEELS results indicate that Kramers-Kronig analysis can also be applied to REELS spectra and the corresponding conjugate optical properties can be obtained. Quantitative studies of the electronic structure and optical properties of thin surficial films using VUV and REELS or TEELS, represent a new avenue to determine the properties of these increasingly important films.

1. Physical basis of REELS

Reflection electron energy loss spectroscopy (REELS) consists in bombarding the surface of a sample with a beam of monoenergetic electrons and detecting the energy distribution of the backscattered electrons.¹ The REELS spectrum consists of two regions: first the elastic peak is due to electrons that have lost no energy (elastic backscattering); the other structures, at lower kinetic energies, correspond to electrons that have lost part of their energy through electronic excitations or phonon excitations within the solid, as being shown in the Schematic of Figure 1.

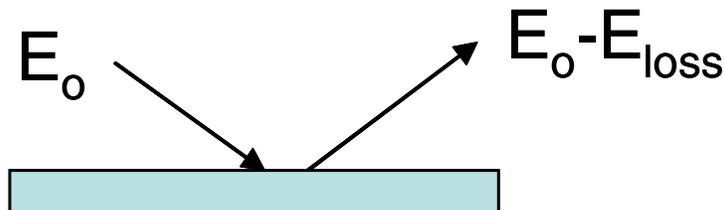


Figure 1. Principle of a REELS experiment

The losses produced by interactions with the phonons can be observed only if the experimental resolution is high (a few meV), as in high-resolution electron energy loss spectroscopy (HREELS). In this

work, we focus our interest on electronic interactions, the study of which can be performed with an experimental resolution of typically 0.5-1 eV, which can be estimated from the full width at half maximum (FWHM) of the elastic peak. The surface sensitivity of the method depends on the small value of the inelastic mean free path (imfp) for low-energy electrons, as shown in the figure. For primary energies of electrons between 150 eV and 550 eV, typically used, the imfp varies between 0.6 and 1.5 nm², the IMFP values for different materials are exhibited in Figure 2.. This surface sensitivity makes this technique particularly well suited for surficial films with about 1 nm thickness.

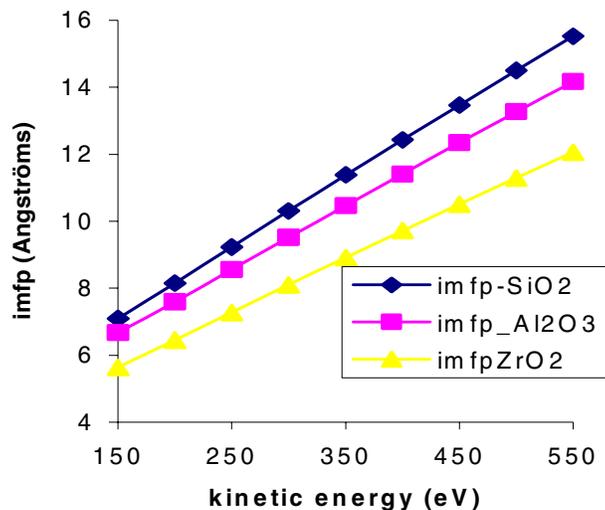


Figure 2. Inelastic mean free path of electrons (imfp) as a function of kinetic energy.

2. REELS on Metal Al

The surface sensitivity of REELS is well illustrated by the evolution of the REELS spectrum of aluminium metal as a function of primary energy: 200 eV (imfp=0.9 nm); 450 eV (imfp=1.5 nm); 850 eV (imfp=2.4 nm) and 1400 eV (imfp=3.5 nm), being seen in Figure 3.. The main structures appearing in the REELS spectrum of aluminium are the bulk plasmon at an energy loss of 15 eV and the surface plasmon at an energy loss of 10.5 eV. While the bulk plasmon peak is the most intense at the higher electron primary energies, the intensity of the surface plasmon peak increases significantly at the lowest ones.

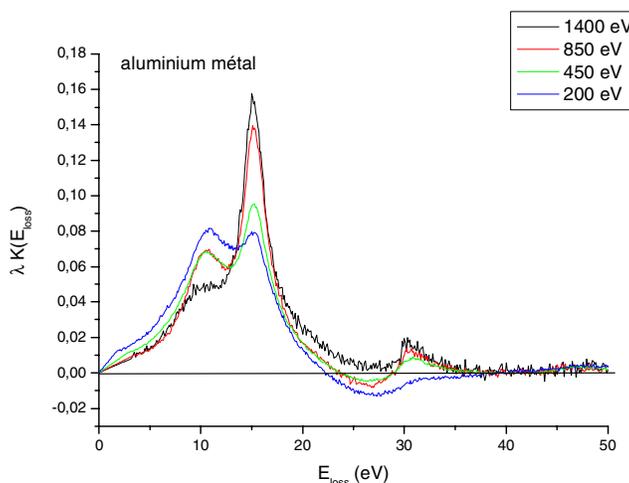


Figure 3. Single scattering cross section of metallic aluminum derived from REELS experiments at different primary electron energies.

The two main steps in the quantitative analysis of REELS for electronic structure information are the removal of the effects of multiple scattering from the REELS spectra³ followed by application of the Kramers-Kronig dispersion transforms to the single scattering energy loss function to determine the conjugate optical variable and then the complex dielectric function. Figure 4 shows the REELS spectra of

metal aluminium after removing the multiple losses contribution upon different primary electron energy. The spectrum exhibits a single scattering cross section $\lambda K(E_{\text{loss}})$, related to the probability of an electron of primary energy E_0 to lose an energy E_{loss} in one inelastic scattering event. The multiple scattering correction used in Figure 3 is inaccurate, as can be seen by the negative cross sections above 20 eV, too much multiple scattering correction has been applied. In a more quantitative way, this single scattering cross section can be related to the energy loss function (ELF) and if a conjugate pair of the optical property variables (for example the bulk ELF, $\text{Im}[-1/\epsilon(\omega)]$, and $\text{Re}[-1/\epsilon(\omega)]$), are known then the complex dielectric function $\epsilon(\omega)$, where $\hbar\omega = E_{\text{loss}}$ can be calculated algebraically. The complex dielectric function can also be derived from VUV optical measurement of the reflectance $R(\omega)$, followed by Kramers Kronig analysis (KK) to give the reflected phase $\theta(\omega)$, once the reflectance and its conjugate pair are known then the real and imaginary parts of any other optical property can be determined algebraically.⁴ In transmission electron energy loss spectroscopy (TEELS), the multiple scattering correction is performed using Fourier log deconvolution (FLD) and then the single scattering cross section is related to the bulk electron energy loss function $\text{Im}[-1/\epsilon(\omega)]$.⁵ Again, using KK analysis, the function $\text{Re}[-1/\epsilon(\omega)]$ is determined through application of the Bulk ELF KK transform, and then $\epsilon(\omega)$. In REELS, which is surface sensitive, the situation is complicated by two factors, the multiple scattering correction is more complex than can be accomplished by application of FLD, and secondly the fact that both bulk energy loss function and the surface energy loss function ($\text{Im}[-1/\epsilon(\omega)+1]$) are present in the REELS spectra, they both have to be taken into account. This requires knowledge of the surface KK transform for the Surface ELF, and conventional KK analysis bulk ELF to determine the conjugate optical property variables $\text{Re}[-1/\epsilon(\omega)]$, and the $\text{Re}[-1/(1+\epsilon(\omega))]$.^{6, 7}

3. REELS on SrTiO₃

Typical single scattering energy loss function derived using the Fourier log deconvolution method from REELS is shown in Figure 4, , where the effects of penetration depth and primary beam energy are observed. For higher primary electron energy, the inelastic mean free path of electrons in the sample increases and so does the penetration depth. More bulk scattering signals occurs for higher PBE, and the single scattering REELS spectrum is more representative of the bulk ELF than that of surface ELF. Therefore, removal of bulk ELF from EELS spectrum becomes significant for the KK analysis of surface ELF from REELS spectrum.

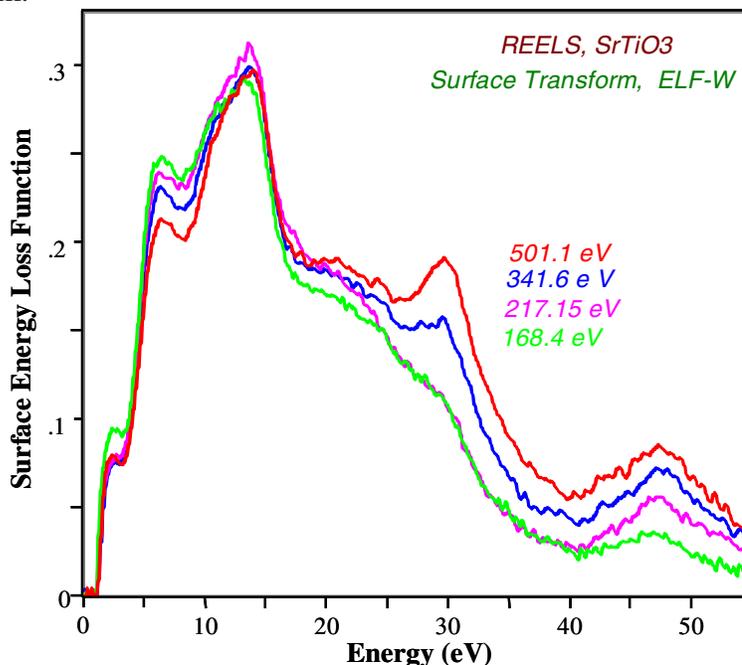


Figure 4, Surface energy loss function for SrTiO₃, derived from REELS spectra by surface KK transform.

In our previous studies of SrTiO₃ we have reported the band structure⁸ and the optical properties and interband transitions from VUV spectroscopy and TEELS⁹. The measurement for the surficial band gap in the surface layers of SrTiO₃ can be obtained by REELS spectrum. Figure 5 shows the low loss energy part of REELS spectra taken at low primary electron energies. The flat part of the spectrum near the elastic peak corresponds to the band gap, with a width of about 3.7 eV, in good agreement with the recent work¹⁰ of Frye, French and Bonnell¹⁰ for oxidized SrTiO₃.

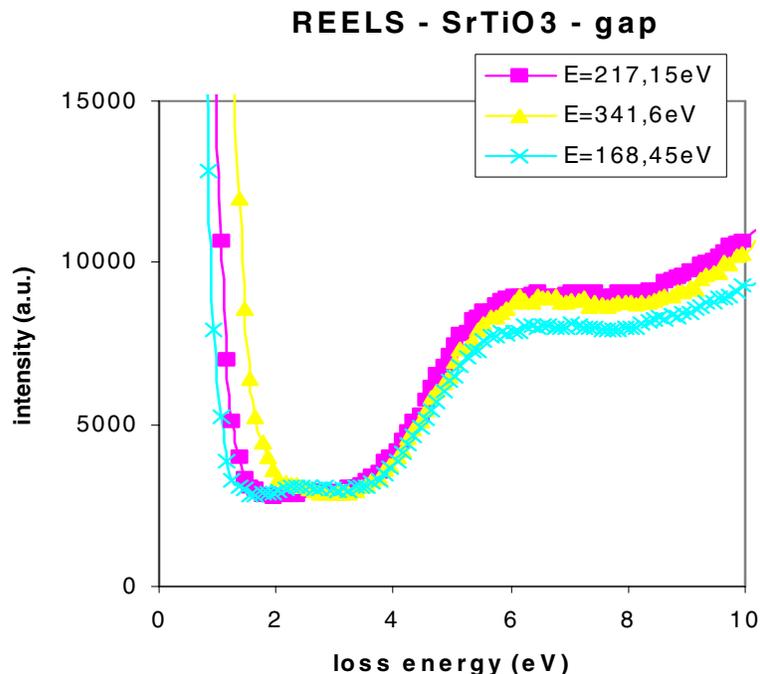


Figure 5, Band gap region of the REELS spectrum of single crystal SrTiO₃ at different electron energies

For the lowest primary energy (168.45 eV) in REELS first derivative spectrum in Figure 6, we clearly see a small structure at an energy loss at 2.5 eV, not seen at higher primary energies. This structure is likely due to a surface defect, already observed by V. Henrich¹¹, in the first derivative mode.

REELS first derivative

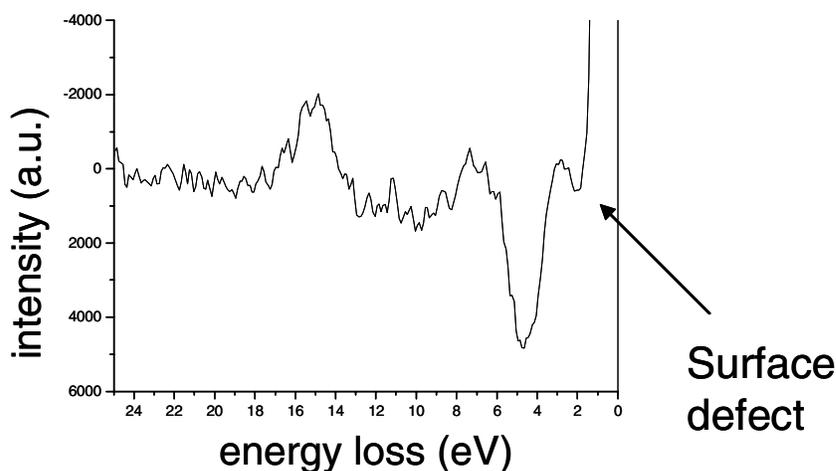


Figure 6. First derivative of the REELS spectrum of SrTiO₃ (primary energy = 168.45 eV)

In this earlier work, a 2.2 eV loss structure appeared after ion bombardment of the surface. The nature of this defect was not precisely determined, but it was likely attributed to oxygen vacancies. For comparison, we show the first derivative of our REELS spectrum for a primary energy of 168.45 eV in Figure 6.. It should be mentioned that in the earlier REELS work¹¹ the spectra were for technical reasons recorded in the derivative mode, which made impossible to measure the band gap.

4. REELS on Al₂O₃

REELS spectrum of bulk Al₂O₃ was taken on its surface with primary electron beam energy at 245 eV. After multiple scattering correction process and surface KK transformation calculation, surface energy loss function spectrum has been derived from the original REELS spectrum, which is shown in Figure 7. A typical surface plasmon at 22.5 eV can be easily observed in Figure 7. The bulk plasmon of Al₂O₃ based on bulk energy loss function $\text{Im}(-1/\epsilon)$ is locating at around 25 eV for bulk Al₂O₃,¹² which is not seen in this surface energy loss spectrum due to the low primary electron beam energy of 245 eV, probing only the surface plasmon. Once the primary electron beam energy is increased, (i.e. up to 800eV), then bulk plasma resonance should dominate the single scattering ELF

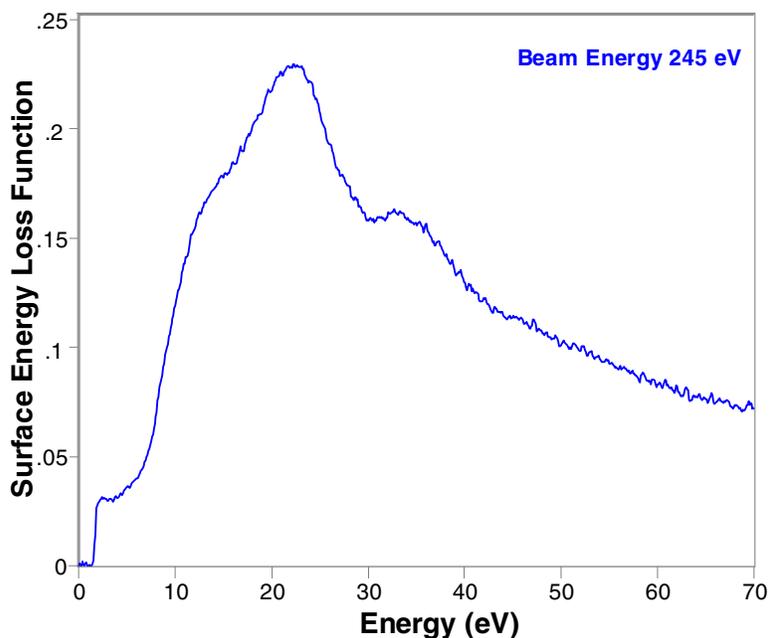


Figure 7, Surface energy loss function of Al₂O₃ derived from REELS spectrum.

5. REELS on ZrO₂

Typical single scattering energy loss function of ZrO₂ derived from REELS using Fourier log deconvolution is shown in Figure 8, where the energy dependent ELF variation in the spectrum as the ratio of surface and bulk loss processes changes can be seen. In Figure 9, we show a comparison of the energy loss function determined from REELS to the energy loss function determined previously from VUV spectroscopy. Similar features are seen, but quantitative agreement has not yet been achieved.¹³

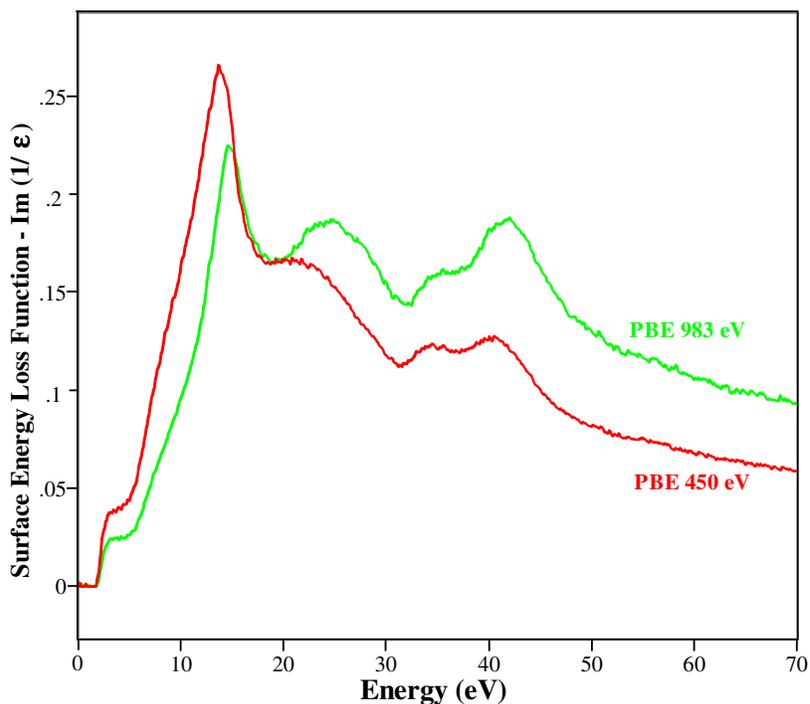


Figure 8, Surface energy loss function of ZrO_2 determined from REELS through surface KK transformation

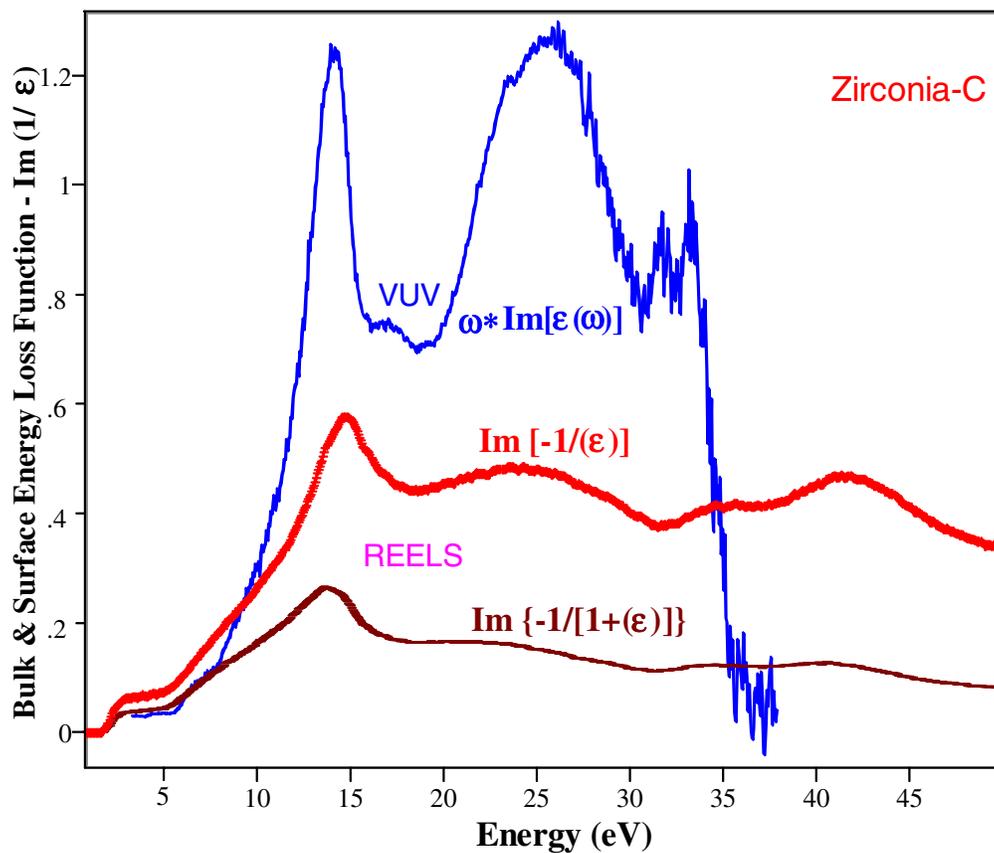


Figure 9, Bulk and Surface Energy Loss Function determined from VUV and REELS.

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