Dielectric properties of pure and Nb-doped SrTiO$_3$ surfaces: a reflection electron energy loss spectroscopy study

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Abstract. Reflection Electron Energy Loss Spectroscopy (REELS) is a valuable tool to characterize the electronic structure of insulating surfaces and nanometric films. The REELS inelastic single scattering cross section obtained after removing multiple losses is related to the complex dielectric function in the surface layers. Moreover the probing depth can be varied by changing the primary energy of electrons. One can expect in essence to obtain non-destructive REELS depth profiles, where the evolution of the REELS spectrum translates to the in-depth evolution of the dielectric constant. We present a REELS study of pure and Nb-doped SrTiO$_3$ single crystals, with primary energies ranging from 200 eV to 1500 eV so as to vary the probing depth between 0.7 and 3 nm. The resulting variations in the shape of the spectra are qualitatively interpreted by considering the energy loss functions corresponding to a double interface SrTiO$_3$ / carbon monolayer/vacuum, on the basis of the experimental dielectric function derived from TEELS measurements on strontium titanate and amorphous carbon.

1. Introduction

Reflection Electron Energy Loss Spectroscopy (REELS) consists in measuring the energy spectrum of electrons which have been inelastically backscattered from a solid surface. This technique is very surface sensitive, as the probing depth is related to the electron inelastic mean free path, between 0.5 and 3 nm [1] for electrons with a primary energy in the range 100–1500 eV. This technique is well-suited to characterize nanometric oxide layers, relevant to spin electronic applications (e.g. tunnel barriers in magnetic tunnel junctions) or to future development of microelectronics (e.g. high $k$ gate dielectrics thin films on Si).

From a REELS spectrum it is in principle possible to derive the optical dielectric constant $\varepsilon(\omega)$ and several models have been developed to quantitatively calculate the experimental REELS spectra [2][3][4][5][6]. In other works, a simplified model has been used in which the REELS scattering cross section is described as a linear combination of bulk $\text{Im}(-1/\varepsilon)$ and surface $\text{Im}(-1/1+\varepsilon)$ energy loss functions [7][8][9][10]. As the probing depth can be varied by changing the primary energy of the electron beam, one can expect in essence to obtain non-destructive REELS depth profiles, where the evolution of the REELS spectrum translates to the in-depth evolution of the dielectric constant. Such an approach is challenged by the requirement of obtaining clean surfaces, representative of a true
vacuum-sample interface for the analytical models to be applied. However obtaining REELS depth profiles of dielectric constant is very appealing with real samples, on which a small residual carbon contamination is not always possible to remove without altering the composition and structure of the sample surface. In this case, the evolution of the REELS spectrum with the primary energy is then not only due to a different weight in the surface/bulk electron energy loss contributions, but also to an increased contribution of the electron energy loss function of the carbon contamination layer when the primary energy decreases.

The purpose of the present paper is to show that even when a small carbon surface contamination is unavoidable, useful information can be gained from REELS experiments with varying primary energy. We report here a REELS study of pure and Nb-doped SrTiO$_3$ single crystals. Even though several ways of preparing the surfaces were attempted, a residual monolayer of carbon atoms could not be removed. We show that the influence of this latter on the REELS spectra is to lower the influence of the surface electron energy loss function, as the vacuum / SrTiO$_3$ interface is replaced by a carbon / SrTiO$_3$ interface. The REELS spectra can nevertheless be interpreted on the basis of available SrTiO$_3$ TEELS data, by taking into account the presence of the carbon / SrTiO$_3$ interface. While quantitative REELS studies are basically restricted to atomically clean samples, this work shows that REELS can also be qualitatively applied to real technological samples.

2. Experimental

The samples studied were a pure SrTiO$_3$(001) single crystal and a 0.5wt% Nb-doped (001) single crystal. They were cleaned ultrasonically in ethanol before loading into ultra-high vacuum. Several procedures were followed to remove the surface contamination: sputter cleaning with 2.4 kV Ar$^+$ for 120 s or annealing at 400°C under an oxygen partial pressure of 1.10$^{-5}$ mbar for 190 minutes. The oxygen flow was kept during cooling stage for 45 minutes in order to prevent surface reduction.

The REELS experiments were performed in a VG Instruments, Inc., ESCALAB Mark II, fitted with an electron gun LEG 200, and with a non-monochromatized X-ray source (AlK$\alpha$). The base pressure was less than 2.10$^{-10}$ mbar. The primary energy of electrons could be varied between 200 and 1500 eV. The hemispherical analyzer was fitted with a five-channeltron multidetector system. The electron beam was at 35° from the surface normal, while the analyzer axis was at 15° from the surface normal. With a pass energy of 20 eV, the full width at half maximum (FWHM) of the elastic peak varied between 0.9 eV for the lowest primary energy up to 1.2 eV at 1500 eV. The electron current was a few nanoamperes. Notwithstanding undoped SrTiO$_3$ sample is insulating, no noticeable charging effect occurred in REELS experiments.

The REELS spectra have been recorded for a set of different primary energies. From each of them a single scattering cross-section $\lambda K(h\theta)$ was obtained using the QUASES REELS software [11]. The surface composition was checked by X-ray photoelectron spectroscopy (XPS) in the same experimental set-up.

3. Result and discussion

3.1. REELS spectra

REELS spectra recorded on doped and undoped samples before surface cleaning (not shown) were similar. Due to the surface sensitivity of REELS, the carbon contamination observed by XPS on the “as received” samples led to a blurring of the loss structures. So it proved essential to remove the contamination layer as much as possible, without changing the surface composition and stoichiometry.

Under our experimental conditions, ion etching allowed a complete removal of the carbon contamination (checked by XPS). On the other hand, annealing did not allow the complete removal of the surface contamination layer, the thickness of the residual carbon layer was estimated to be less than one monolayer from the XPS C/Sr intensity ratio.

REELS spectra of the etched Nb-doped sample are displayed on the left hand side of Figure 1 and the spectra of the annealed undoped single crystal are shown on the right hand side. Spectra were
recorded at primary energies that ranged from 200 eV to 1500 eV. The Nb concentration is very low and no structures arising from Nb states were identified on REELS spectra. The difference between the two series of spectra is not due to doping but to the different surface preparations.

![Graphs](image)

**Figure 1:** Experimental REELS spectra of annealed and ion-etched SrTiO$_3$ (001) single crystals.

REELS single scattering cross-sections of etched and annealed samples are compared in Figure 2 for four primary energies (900, 650, 400 and 230 eV). The main loss features of the single scattering cross-sections related to the annealed sample show up at 6.2 eV (a), 14 eV with a shoulder at 12 eV (b), 22 eV (c), 30 eV (d) and 42 eV - 48 eV (e). With the etched sample, the peaks positions are basically the same but the width and the relative intensities are dissimilar. First, the (b) contribution is larger and broader, resulting in the vanishing of the (a) structure. Secondly, for a given primary energy, the main difference arises in the (c) feature, which is the major contribution of the single scattering cross-sections of the annealed sample, especially at low primary energy, while its intensity is notably reduced on the single scattering cross-sections of the etched sample.

The origin of the SrTiO$_3$ loss structures have been extensively discussed in [12] and can be interpreted as follows: structures (a) and (b) are due to interband transitions from O2p to Ti3d and Sr4d states; structure (c) from Sr4p to Ti3d and Sr4d states; the loss structure at 30 eV (d) is mainly due to the bulk plasmon of SrTiO$_3$; the loss structure (e) is due to transitions originating from the Sr 4s and Ti3p deeper electronic levels.

Amorphous carbon is known to induce characteristic loss structures on REELS spectra, especially a broad one around 20 eV corresponding to the excitation of the bulk plasmon [13]. Thus, the structure (c) of the single scattering cross section of the annealed sample contains also a contribution of the bulk plasmon from the carbon contamination monolayer, while its intensity is strongly decreased in the case of the ion etched sample, free of carbon contamination. However, the ion etching not only removed the carbon contamination layer, thus leading to the strong decrease of the (c) peak, but also led to the disappearance of structure (a), while broadening peak (b). Loss structures (a) and (b) are the ones involving the O2p states, very sensitive to the local order and stoichiometry. These changes in the REELS spectrum are to be related to a change of the chemical state of the surface induced by ion etching. A broadening of the XPS cation photoelectron lines was indeed observed, indicating a slight reduction of the SrTiO$_3$ surface.

Therefore, the cleaning procedure relying on simple annealing was considered preferable: a residual carbon contamination monolayer could not be removed, but the chemical state of the SrTiO$_3$ surface was not altered.
3.2. Comparison with TEELS

From a REELS spectrum it is theoretically possible to derive the optical dielectric constant $\varepsilon(\omega)$, following the well-established approach used in transmission electron energy loss spectroscopy (TEELS) [14]. The TEELS spectrum can be envisioned as the optical energy loss function $\text{Im}[1/\varepsilon(\omega)]$, once multiple scattering is removed. The REELS single scattering cross section obtained after removing multiple scattering can be, in a simplified model, described by a combination of bulk $\text{Im}[-1/(1+\varepsilon(\omega))]$ and surface $\text{Im}[-1/(1+\varepsilon(\omega))]$ energy loss function (Eq.(1)).

$$\lambda K(E_p) = A \text{Im} \left[ \frac{-1}{\varepsilon(\omega)} \right] + B \text{Im} \left[ \frac{-1}{1 + \varepsilon(\omega)} \right]$$

with

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

$$\text{Im} \left[ \frac{-1}{\varepsilon(\omega)} \right] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}$$

$$\text{Im} \left[ \frac{-1}{\varepsilon(\omega) + 1} \right] = \frac{\varepsilon_2}{(\varepsilon_1 + 1)^2 + \varepsilon_2^2}$$

**Figure 2:** Single scattering cross-sections derived from the experimental REELS spectra of annealed and ion-etched SrTiO3 (001) single crystals.
Figure 3: Comparison between REELS single scattering cross-section of the annealed sample at the highest primary energy (1444 eV) and the bulk and surface energy loss functions (ELF) of SrTiO₃ derived from TEELS data.

Figure 3 shows a comparison between the REELS single scattering cross-section of the annealed sample at the highest primary energy (1444 eV) and the bulk and surface energy loss functions of SrTiO₃ derived from TEELS data [15]. The surface energy loss function was calculated from the dielectric function derived from the experimental bulk energy loss function by Kramers Kronig analysis. The overall shapes of the energy loss functions are rather close; the widths and the intensities of the peaks are different but the energy positions of the REELS single scattering cross-section loss structures are clearly intermediate between the bulk and surface energy loss functions.

3.3. Evolution of the REELS energy loss functions with the primary energy
In a previous paper, we had made the assumption that the REELS scattering cross section of SrTiO₃ could be described by a linear combination of bulk and surface energy loss functions [16]. We had found that, although the overall evolution of the intensities of the different structures could be accounted for by an increased contribution of the surface energy loss function when the primary energy decreased, no satisfying agreement with a linear combination of bulk/surface energy loss function could be obtained in the region of peak (c) (20-25 eV). We re-visit this interpretation on the basis of the new set of data presented here.

Figure 4 shows the REELS single scattering cross-sections of the annealed sample at different primary energies. When increasing the primary energy, the intensity of the peak (d) at 30 eV, corresponding to the SrTiO₃ bulk plasmon, increases, as expected from an increased contribution of the bulk energy loss function. In the same time, the overall intensity around 22 eV (peak (c)) decreases. On the contrary, the intensity of the (a) and (b) structures do not change with the primary energy.

Clearly these REELS scattering cross sections can not be described by a linear combination of the SrTiO₃ bulk and surface energy loss functions. First, an increasing weight of the surface energy loss function at low primary energies would lead to higher intensities in the low energy loss region (see Figure 3), which is not what is observed. Moreover, the intensity of the structure (c) is due not only to the energy loss characteristic of SrTiO₃, but also to the carbon bulk plasmon, as proved from the comparison of the REELS spectra of the ion etched samples and annealed ones (Figure 2). In fact, the increase of the intensity of peak (c) when the primary energy decreases, is due to an increased
contribution of the carbon overlayer when the probing depth decreases. This behavior is quite similar to the one observed by Schammi et al. [13] in a TEM study of SrTiO$_3$. Carbon contamination occurred in the microscope as a function of irradiation time under the electron beam and led to a significant perturbation of the TEELS signal intensity over a domain extending mainly from 17 eV to 30 eV, the remaining of the spectrum being unchanged.

Figure 4: Single scattering cross-sections derived from the experimental REELS spectra of the annealed sample at different primary energies.

The evolution of the REELS scattering cross-section with primary energy can then be understood by considering, instead of a simple SrTiO$_3$ / vacuum interface, a SrTiO$_3$ surface covered by a thin carbon top layer as described in Figure 5. Two interfaces (SrTiO$_3$ / C and C / vacuum) have to be considered instead of only one (SrTiO$_3$ / vacuum). In this way, following the approach described in our previous work [16], we do not have to consider a linear combination of the surface and bulk energy loss functions of SrTiO$_3$, as would be the case for a genuine SrTiO$_3$ / vacuum interface. The REELS scattering cross section is rather the sum of contributions coming from the bulk SrTiO$_3$ energy loss function Im[-1/$\varepsilon_{\text{SrTiO}_3}(\omega)$], the SrTiO$_3$ / carbon interface energy loss function Im[-2/($\varepsilon_{\text{SrTiO}_3}+\varepsilon_c$)], the carbon bulk energy loss function Im[-1/$\varepsilon_c(\omega)$] and the carbon surface energy loss function Im[-1/($1+\varepsilon_c(\omega)$)] (Eq.(2)).

$$\lambda K(E_p) = A \text{Im}\left[\frac{-1}{\varepsilon_{\text{SrTiO}_3}}\right] + B \text{Im}\left[\frac{-2}{\varepsilon_{\text{SrTiO}_3} + \varepsilon_c}\right] + C \text{Im}\left[\frac{-1}{\varepsilon_c}\right] + D \text{Im}\left[\frac{-1}{1 + \varepsilon_c}\right]$$ (2)

Figure 5: The different energy loss functions for a SrTiO$_3$ substrate covered by an amorphous carbon layer.
Figure 6: Bulk and Surface energy loss functions of C, C / SrTiOₓ interface energy loss function and SrTiOₓ bulk energy loss function derived from TEELS data (normalized to the same area).

Figure 6 shows the shape of these four energy loss functions. They were calculated on the basis of the dielectric functions extracted from TEELS data from amorphous carbon and SrTiOₓ samples [17], and normalized to a unit area for comparison. In Figure 7, the experimental single scattering cross sections at 232, 653 and 906 eV are compared to linear combinations of the bulk, surface, and interface energy loss functions displayed in Figure 6. The calculated energy loss functions are normalized to a unit area, keeping the same B, C and D coefficients with B=C=D. Only the A coefficient was changed (A=0.3B, A=0.5B and A=B), in order to mimic an increased contribution of the SrTiOₓ bulk energy loss function, as it is the case when the primary energy increases. Keeping B=C=D is an approximation, because an increase of the primary energy not only will increase the A coefficient, but also will affect the other ones. However the increase of the A coefficient is expected to be the leading effect.

The evolution of the relative intensities of peaks (c) and (d) is qualitatively well reproduced. Decreasing the primary energy leads to a strong surface sensitivity. As a consequence, contributions of bulk and surface energy loss function of carbon go up and the intensity of feature (c), at 22 eV, increases. In the same way, deeper probing depths, linked with higher primary energies, allow an increasing weight of the SrTiOₓ contributions: as a result the (d) peak, related to SrTiOₓ bulk plasmon takes off. No marked changes are observed in the region of peaks (a) and (b).

The peaks positions of the calculated energy loss functions are in good agreement with those of experimental single scattering cross sections. No further attempt was done to better fit the width of the REELS loss structures, so as to take into account the q-dependence of the dielectric function, where q is the momentum transfer. Our purpose here was only to qualitatively understand the evolution of the REELS spectra with primary energy taking into account the presence of the thin carbon contamination overlayer.

As a result, our simple model considering a SrTiOₓ / carbon overlayer interface instead of a true SrTiOₓ / vacuum interface explains why the low energy part of the REELS single scattering cross section does not change much when the primary energy decreases. For a true SrTiOₓ / vacuum interface, the increased weight of the surface electron energy loss function would lead to an increase of the REELS intensity at low loss energies. On the contrary, replacing the SrTiOₓ / vacuum interface by a SrTiOₓ / carbon overlayer interface weakens the contribution of the SrTiOₓ surface electron energy loss function, while introducing a contribution of the carbon bulk and surface electron energy
loss function, whose weight increase when the primary energy decreases, making peak (c) take off, with a very small influence on the low loss part of the spectrum.

![Experimental and Calculated Energy Loss Spectra](image)

**Figure 7:** Experimental single scattering cross sections at 232, 653 and 906 eV compared to linear combinations of the C-bulk, C-surface, C / SrTiO₃ - interface and SrTiO₃ bulk energy loss functions.

4. Conclusion

We have reported a REELS study of pure and Nb-doped (100) SrTiO₃ single crystals. No effect of doping could be evidenced from the REELS spectra. Two different procedures were used to clean the sample surface, based on argon ion etching and annealing. The REELS spectra of the ion etched surface, which was carbon free, did not show all characteristic loss structures of SrTiO₃, due to an alteration of the chemical state of the surface induced by ion etching. The annealing procedure was thus found more suitable, because the chemical state and stoichiometry of the SrTiO₃ surface was preserved, even though a monolayer of carbon atoms could not be removed.

We have shown that the evolution of REELS spectra with primary energy can be understood by taking into account the contribution of the carbon bulk and surface electron energy loss function. The presence of a carbon / SrTiO₃ interface instead of a true vacuum / SrTiO₃ interface weakens the contribution of the surface SrTiO₃ electron energy loss function, the increasing weight of which would be expected to drive the evolution of the REELS spectrum with decreasing primary energy, in the case of a clean surface. While quantitative REELS studies are basically restricted to atomically clean samples, this work shows that REELS can also be qualitatively applied to real technological samples.
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References
[1] Tanuma S, Powell C J and Penn D R 1991 Surf. Interface Anal. 17 911
[2] Yubero F, Sanz J M, Ramskov B and Tougaard S 1996 S Phys. Rev. B 53 9719
[3] Werner W S M 2003 Surf. Interface Anal. 35 347
[4] Ding Z J and Shimizu R 2000 Phys. Rev. B 61 14128
[5] Tung C J, Chen Y F, Kwei C M and Chou T L 1994 Phys. Rev. B 49 16684
[6] Chen Y F and Chen Y T 1996 Phys. Rev. B 53 4980
[7] Colavita E, De crescenzi M, Papagno L, Scarmozzino R, Capui L S, Rosei R and Tosatti E 1982 Phys.Rev. B 25 2490
[8] Chiarello G, Colavita E, De Crescenzi M and Nannarone S 1984 Phys. Rev. B 29 4878
[9] Barreca F, Mezzasalma A M, Mondio G, Fortunato F, Trusso S and Vasi C 2000 Phys. Rev. B 62 16893
[10] Aliev A A, Ruzibaeva M K and Kim A E 2000 Vacuum 57 243
[11] QUASES-XS-REELS software package, www.quases.com
[12] Van Benthem K, Elsässer C and French R H 2001 J. Appl. Phys. 90 6156
[13] Schamm S and Zanchi G 2001 Ultramicroscopy 88 211
[14] Egerton R F 1986 Electron Energy-Loss Spectroscopy in the Electron Microscope, Second edition, Plenum, New York
[15] C. Koch, unpublished data
[16] Paumier F, Fouquet V, Guittet M J, Gautier-Soyer M, French R H, Tan G, Chiang Y M, Tang M, Ramos A and Chung S Y 2006 Mat. Science and Eng. A 422 29
[17] http://www.cemes.fr/~eelsdb