Electron energy loss spectroscopy determination of Ti oxidation state at the (001) LaAlO$_3$/SrTiO$_3$ interface as a function of LaAlO$_3$ growth conditions

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Abstract – After the epitaxy of LaAlO$_3$ on a TiO$_2$-terminated (100) surface of SrTiO$_3$, a high-mobility electron gas may appear, which has been the object of numerous works over the last four years. Its origin is a subject of debate between the interface polarity and unintended doping. Here we use electron energy loss “spectrum images”, recorded in cross-section in a scanning transmission electron microscope, to analyse the Ti$^{3+}$ ratio, characteristic of extra electrons. We find an interface concentration of Ti$^{3+}$ that depends on growth conditions.

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Introduction. – In a pioneering work, Ohtomo and Hwang [1] have discovered that growing LaAlO$_3$ (LAO) by pulsed laser deposition (PLD) onto a TiO$_2$-terminated (001) surface of SrTiO$_3$ (STO), produces a metallic system, while both materials are insulators with respective band gaps of 5.6 eV and 3.2 eV [2]. This observation has been the signal for many studies of this system: among remarkable results are the superconductivity observed below 200 mK [3], the magnetism around 300 mK [4], and the field effect on conductivity [5].

In the ionic limit, the perfect interface carries a global positive charge, because the last TiO$_2$ plane of STO is neutral and faces a first plane of LAO that has composition LaO and carries an uncompensated charge +1/2 per surface unit cell. Such a configuration would lead to a polar instability [6] if it were not balanced by electron or ion rearrangements. In the present case, the capacity of Ti ions to bear a mixed valence may provide the necessary screening, some Ti$^{4+}$ (valence in bulk STO) becoming Ti$^{3+}$. This most simple scheme — essentially confirmed by calculations [7–9] — 1/2 extra electron per surface unit cell is necessary to maintain electrical neutrality [1]. The spreading of the electron cloud associated with such a delta-doping has been evaluated by solving Poisson’s equation: at 300 K, electron concentration should be $\sim$1.3×10$^{21}$ cm$^{-3}$ (≈8% of the Ti concentration) at the interface, and it should fall to $\sim$8×10$^{20}$ cm$^{-3}$ (5%, the present detection limit, see below) at only 1 nm into the bulk [10].

Several authors have associated the n-type conductivity they have measured with such screening electrons [1,5,11]. However, growth by PLD is a complex process, which will hardly create “perfect” materials [12,13]. Thus this scheme of interpretation, based on the interface being atomically sharp and chemically stoichiometric, is the object of intense discussion. It is now recognised that the oxygen vacancy plays a dominant role when the oxygen partial pressure has been maintained below 10$^{-3}$ Pa during the growth process [14,15]. The question remains of its spatial distribution. Our previous observations indicate that in such conditions, this defect invades the whole substrate so that sample conductivity is not an interface property [14,16].

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But even when the substrate was uniformly doped, we have recently shown, using conducting-tip atomic-force microscopy (CT-AFM) on cross-sections, that the interface region did exhibit a specific, enhanced, conductivity [16]. We also found that this specificity depended on growth conditions so that it must be associated with extrinsic causes. These may be various: let us site the existence of a thin layer of metallic La$_{1-x}$Sr$_x$TiO$_3$ at the interface deduced by Willmott et al. from X-ray diffraction data [13]. It is thus mandatory to characterise the doping level at the interface itself, as a function of growth conditions.

Our high-resolution transmission electron microscopy (HRTEM) observations in cross-section have shown the existence of a distortion at the interface [17], and also exhibited noisy contrasts [9], which could be consistent with the presence of La$_{1-x}$Sr$_x$TiO$_3$.

Detection of Ti$^{3+}$ by electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM), by David Muller’s group [3,18] and ours [9] could also fit in such a model. To be conclusive, however, such experiments have to be quantified. This is what we attempt to do here.

In this paper we bring new STEM-EELS data, obtained in two extreme cases: one representing the highest probability of an influence of point defects, with a sample grown at 10$^{-4}$ Pa (10$^{-6}$ mbar) during 200 s, macroscopically conductive, “low pressure”, and one representing the lowest probability of an influence of point defects, with a sample grown at 40 Pa (0.4 mbar) during 50 s, macroscopically insulating, “high pressure”. Our results evidence, for the first time to our knowledge, the role of growth conditions on the microscopic interface atomic structure: oxygen pressure in the growth chamber tends to decrease the apparent interface doping. The latter is therefore not only due the intrinsic polarity, but also to extrinsic point defects.

We also present a combined HRTEM, electron-diffraction, and atomic-force microscopy study of the two samples, which shows a fundamental change in growth mode as the pressure increases, which we associate with a large difference in point-defect content.

Methods. – Pulsed laser deposition (PLD) of LAO was performed following a process described in detail in ref. [16], at a deposition temperature of $T = 750\degree$ C, with a growth rate of about 1 Å s$^{-1}$ that resulted in a thickness of 20 nm for the low-pressure sample and 5 nm for the high-pressure one. Once the film deposition was finished, the samples were cooled down to room temperature at the growth oxygen pressure (10$^{-4}$ and 40 Pa, respectively). The transport properties of the low-pressure sample are among the best published to date (mobility > 10$^5$ cm$^2$ V$^{-1}$ s$^{-1}$ at 4 K, see details in ref. [14]).

The LAO/STO cross-sectional samples for TEM and STEM-EELS were prepared using standard tripod polishing, without water for the last ~5 µm on each face. It was completed by a prolonged, grazing incidence, ion milling with 2 keV Ar ions. A problem was to minimise, in EELS, the Ti$^{3+}$ signal coming from the damaged foil surfaces. This thinning procedure, on which we finally decide after testing several others, gave the best results. We otherwise minimised the influence of surfaces in EELS recordings by selecting relatively thick regions (~30–40 nm), with fairly parallel faces (see the profiles in fig. 5). We checked by HRTEM the defects created by STEM-EELS recording, and kept only those data sets where they remained invisible. The STEM-EELS measurements were performed with a VG HB501 microscope operated at 100 kV, TEM and HRTEM observations were carried out on a Topcon 002B, working at 200 kV.

We analysed the spatial variations of electron energy loss spectra using spectrum images (3-dimensional data boxes that consist in $n \times m$ arrays of p-channel spectra [19]) acquired by scanning a focused probe step by step and recording a spectrum at each step. We typically recorded images consisting in 2 to 8 64-pixel lines perpendicular to the interface, with a pixel size of 0.33 nm to 0.74 nm and a channel size of 0.2 eV. The dwell time varied between 0.2 and 1 s. In order to increase signal/noise ratio, the profiles finally used, such as those presented below, were obtained by summing, parallel to the interface, the 2 to 8 lines. Before this, the drift, measured as the shift of the interface from one line to the next, was corrected on pixel position and size. The effective size of the interaction volume was calculated by deconvoluting the measured Ti concentration profiles, assuming a step function for the actual profiles. The intensity distribution of the probe thus defined was quasi-Gaussian with a width at half maximum of ~2 nm in the experiments presented below. The energy resolution of the spectrometer was better than 0.6 eV (width at half-maximum of zero-loss peak).

The evaluation of the Ti$^{3+}$ ratio was carried out using the high sensitivity on this ratio of the fine structure of Ti-$L_{2,3}$ edge [20–22]. Indeed, this edge corresponds to transitions from 2p discrete levels to the 3d band, which is empty for Ti$^{3+}$ in bulk STO, and contains half an electron per site in the simplest model of Ti$^{2+}$/Ti$^{4+}$ at the interface. Figure 1 compares the Ti-3d molecular electronic structure in the case of the octahedral crystal field of STO and that of the distorted site [9] at the abrupt LAO-STO interface. The move of energy levels, when going from bulk STO to the interface, will appear in spectra as a fine structure smoothing.

More specifically, both the Ti-$L_{2}$, and Ti-$L_{3}$ edges in STO are made of two well-defined peaks corresponding to the $e_g$ and $t_{2g}$ levels separated by the crystal field (see fig. 4 and ref. [20]): a shift of valence towards 3+ will show as a progressive fading of these peaks and an increase of signal in the valley in between (see arrows in fig. 4). Of course, there is no charge redistribution without geometrical change, and vice versa. Thus, for the sake of simplicity, in the analysis presented below, we have
EELS determination of Ti oxidation state at the LaAlO$_3$/SrTiO$_3$ interface

![Diagram of Ti oxidation states](image)

Fig. 1: (Colour on-line) Evolution of the 3$d$ electronic structure of Ti as a function of valence and surroundings. Degeneracy in the case of Ti$^{4+}$ in bulk STO is partially lifted by the octahedral crystal field (middle), separating 3$d$ into $t_{2g}$ and $e_g$ levels. The two corresponding peaks are well visible in EELS Ti-$L_2$ and Ti-$L_3$ edges (see A, B in fig. 4) [20,22]. In the case of Ti at the interface (right), both valence and site symmetry are different, which organises the 3$d$ levels in quite a different way [9]. The levels presented correspond to molecular calculations, an additional spreading will occur in the actual crystal. This will transform the two peaks into a broad one in the EELS edges.

considered that all changes of line shape were associated with a valence change.

We further assumed following Ohtomo et al. [21], that the global Ti-$L_{2,3}$ cross-section did not depend on the oxidation state of Ti, so that all experimental spectra be linear combinations of pure Ti$^{4+}$ and Ti$^{3+}$ spectra. We performed least-squares fits of the experimental Ti-$L_{2,3}$ edges with reference Ti$^{4+}$ and Ti$^{3+}$ spectra. The fits were performed after background subtraction, and after normalising the integral of the remaining signal. The reference Ti$^{4+}$ spectrum was picked from the substrate contribution in the same profile where the analysed spectrum came from and the Ti$^{3+}$ spectrum was taken in ref. [21].

In such measurements, sources of error are numerous [23]. In order to increase the signal/noise ratio, we also applied the least-squares analyses to Ti-$L_{2,3}$ edges obtained after summing as many comparable interface spectra as possible. The summed edges totalised more than $2.5 \times 10^6$ counts (background subtracted), in both the cases of low and high growth pressure (see fig. 4).

Even in such conditions, the error in our measurements, taken as the standard deviation between data points from the experimental and fitting spectra, remained of the order of 3%, which made in turn our detection limit ($3\%: \sim 5 \times 10^{20}$ cm$^{-3}$).

**Point defects in LAO.** – We show in the present section that the two samples have undergone different relaxation processes of the epitaxial strain, which we associate with different point-defect contents. We focus in the following on the high-pressure sample, where growth appears to be quite different from that usually observed in the LAO/STO system.

Figure 2 shows an atomic-force micrograph of this sample where the surface appears significantly rough, contrary to what is generally observed with low-pressure growth. We associate this roughness with 3-dimensional growth. The structural analysis of this high-pressure sample by TEM (fig. 3) indicates that strain relaxation is also 3D: selected area electron diffraction pattern (b) of the high-pressure sample in (010) cross-section. As can be seen with the lateral shift of the 302 spot, the in-plane parameter is different in film and substrate, which does not occur in the low-pressure sample (not shown, see, e.g., ref. [17]). The arrows in (a) indicate valleys between relaxed 3D regions.

In similar TEM experiments carried out on the low-pressure sample (not shown), the LAO lattice parameters came out at $a_{\text{LAO}} = 0.3873$ nm and $c_{\text{LAO}} = 0.3748$ nm ($+/−$ 0.001 nm). Correlatively with the in-plane mismatch, we found some misfit dislocations, but not enough to allow for all the difference measured. 3-dimensional relaxation thus appears to be associated with the 3D growth mode. When compared to the equilibrium pseudo-cubic lattice parameter of LAO (0.3792 nm), the parameters found indicate a volume extension, which may be attributed to an elastic distortion with a Poisson ratio of about 0.22.

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low-pressure film thus appeared to be fully strained to the substrate, with a relatively small elastic relaxation out-of-plane as has been noticed previously [3,17]. These values indicate a unit cell volume much larger than in the high-pressure case, which is consistent with the presence of a much larger amount of point defects. And indeed, in the observation of a \{110\} cross-section of a sample grown in identical conditions (not shown), we have evidenced the existence of a superstructure which could not be simulated using the exact equilibrium rhombohedral LaAlO$_3$ unit cell, and had to be due to ordering of large amounts of point defects.

Therefore, the two samples would strongly differ in point-defect content, consistently with their growth conditions: the low-pressure sample would contain a much higher level of point defects than the high-pressure one.

**EELS results.** – Figure 4 presents raw experimental spectra, whose treatment has been limited to background subtraction and averaging over several spectrum images. In fig. 4, the data have been deduced from the spectra by the fitting procedure described in the section Methods. The experimental conditions were quite similar (probe effective size and current, spectrometer setting), so that the two samples in each figure can be directly compared.

In fig. 4, the mean experimental interface spectra are superimposed on bulk spectra, giving the reference Ti$^{4+}$. The effect of the interface on the Ti-$L_{2,3}$ edge is clearly visible in the low-pressure sample, while it is significantly smaller in the high-pressure case. The fit with reference Ti$^{3+}$ and Ti$^{4+}$ spectra as described in the section Methods gives 20% Ti$^{3+}$ in the former case and only 10% Ti$^{3+}$ in the latter.

**Discussion.** – In this section, after a deeper analysis of our data, we conclude on point defects being at the origin...
associate the present profile of fig. 6a with the profile of electron donors having diffused during growth such as oxygen vacancies or La substituted for Sr. Let us now examine the thermodynamics and kinetics of growth to decide which of these two dopants is the most probable at the interface.

The properties of a given point defect naturally vary with concentrations of other point defects and the presence of extended defects, but the following references give useful orders of magnitude. Regarding the oxygen vacancy in STO, Ishigaki et al. report different Arrhenius plots of the diffusivity that give, at our growth temperature of 750°C, a value between $\sim 10^{-6}$ cm$^2$s$^{-1}$ and $\sim 10^{-4}$ cm$^2$s$^{-1}$ [24]. This makes a minimum diffusion length of $\sim 150 \mu$m for a one-minute growth. On the other hand, Shin et al. give an equilibrium concentration of vacancies in Al-doped STO at 800°C that varies from 0 at the oxygen partial pressure of 1 Pa to $10^{18}$ cm$^{-3}$ at $10^{-4}$ Pa [25]. Moreover, the formation barrier of these defects will be much lower during growth as it is no longer necessary to evaporate an oxygen atom to create a vacancy. Thus, oxygen vacancies cannot be absent from the bulk of the substrate of our low-pressure sample.

However in PLD, kinetics may also play an important role. For instance in the conditions we use, the energy range of landing species extends above 100 eV in the $10^{-2}$–$10^{-4}$ Pa pressure range [26], which will undoubtedly create not only oxygen vacancies, but also cation-related defects. Thus after a low-pressure growth, the film that will be reservoir of point defects may contain a concentration much higher than the equilibrium one. This will further increase oxygen vacancy introduction, but it will also accelerate cation interdiffusion. As the base diffusivity of cations is very low (see, e.g., ref. [27]) this second process will take place only in the close vicinity of the interface. But if the cation solubility is high [28,29] it will be possible to form an interface alloy, as has been observed recently [13].

Thus in the present cases, we would indeed have two extremes: the low-pressure case should include an almost uniformly doped substrate, due to oxygen vacancies. At the interface, the oxygen vacancy would have no specific reason to be in a significantly higher concentration than elsewhere in the substrate; the most likely specific interface dopant would be lanthanum. In contrast, the high-pressure case should not be extrinsically doped, at least by oxygen vacancies or irradiation-induced defects.

That the high-pressure case (fig. 6b) be closer to a model of intrinsic polarity is thus confirmed. But it remains quite surprising that it be the mobile-carrier version of the model, as the sample was macroscopically insulating. An explanation, perhaps difficult to check, would be that conductivity in this sample would not only depend on Ti valence at the interface, but also on the epitaxial stress, which may strongly indeed influence the electronic structure (cf. fig. 1), and which varies on a small scale (arrows in fig. 3).

Fig. 6: (Colour on-line) The Ti$^{3+}$ profiles of fig. 5 in the low- (a) and high- (b) pressure samples compared with the EELS response applied to published Ti$^{3+}$ distributions. “Intrinsic delta”: localised electrons that would neutralise the intrinsic polarity in the form of a delta distribution at the interface; “Delta + Poisson”: same surface density of electrons, but spread into the bulk following the solution of Poisson equation [10]; Willmott et al.: distribution of Ti$^{3+}$ given in fig. 3a of ref. [13].

of the signal in the low-pressure case. We then discuss the conditions of growth in regard with thermodynamic and kinetic data from the literature to decide on the type of defect.

We start by comparing our experimental profiles with different models of electron distributions, convoluted with our Gaussian experimental response (fig. 6). Let us first note that, once the Ti$^{3+}$ profiles from the literature are convoluted, they only slightly emerge from the present detection limit (for the present profiles, the sensitivity is worth $\sim 5\%$ or $\sim 8 \times 10^{20}$ cm$^{-3}$, of course not as fine as that mentioned above for summed spectra). Thus it is not only justified, but even mandatory, to include our high-pressure profile, even though it is almost flat, in such comparisons.

Quite surprisingly, in both our cases of low (fig. 6a) and high (fig. 6b) pressures, the best fit is obtained with a model of intrinsic polarity. However, the low-pressure —conducting— case appears to fit with a model of localised interface electrons (“Intrinsic delta” in fig. 6a), while the high-pressure —insulating— case fits on the contrary with a model of mobile electrons (“Delta + Poisson” in fig. 6b). As this is precisely the opposite of what is expected, we have to attribute an extrinsic contribution to at least one of the two cases.

Given that electrons could hardly stay localised in the conducting low-pressure specimen, and given that we have made it so as to increase extrinsic effects, we may appoint it to represent the extrinsic case. Thus, we would rather
Conclusion. – We have measured the concentration profiles of Ti$^{3+}$ ions in the STO substrate in the vicinity of the TiO$_2$-terminated (001) interface with LAO using STEM-EELS in cross-section. We have studied two growth conditions: 200 s and 10$^{-3}$ Pa on the one hand, and 50 s and 40 Pa on the other hand, so that point-defect effects be maximum in the former case, and minimum in the latter. The concentration of Ti$^{3+}$ ions appears to depend significantly on growth conditions: in the low-pressure, thicker sample, Ti$^{3+}$ surface concentration comes out at more than twice that in the high-pressure specimen. In the former case, there is thus an additional doping. Among the different possibly active point defects, cations in substitution appear more likely candidates than oxygen vacancies, in qualitative agreement with previous observations [13].

In summary, we have thus shown that Ti ions bearing valence 3+ are indeed present at the polar interface between LAO and TiO$_2$-terminated (001) STO, but we have also shown, for the first time to our knowledge, that their concentration depends on growth conditions, so that their origin is, at least partially, extrinsic.

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