Conductivity of LaAlO$_3$/SrTiO$_3$ Interfaces made by Sputter Deposition

I. M. Dildar, D. B. Boltje, M. H. S. Hesselberth, and J. Aarts
Kamerlingh Onnes Laboratorium, Leiden University, The Netherlands

Q. Xu and H. W. Zandbergen
National Centre for High Resolution Microscopy, Kavli Institute for Nanoscience, Delft Technical University, Lorentzweg 1, 2628 CJ Delft, the Netherlands

S. Harkema
Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, the Netherlands
(Dated: November 23, 2011)

We have investigated the properties of interfaces between LaAlO$_3$ films grown on SrTiO$_3$ substrates singly terminated by TiO$_2$. We used RF sputtering in a high-pressure oxygen atmosphere. The films are smooth, with flat surfaces. Transmission Electron Microscopy shows atomically sharp and continuous interfaces while EELS measurements show some slight intermixing. The elemental ratio of La to Al measured by EDX is found to be 1.07. Importantly, we find these interfaces to be non-conducting, indicating that the sputtered interface is not electronically reconstructed in the way reported for films grown by Pulsed Laser Deposition because of the different interplay between stoichiometry, mixing and oxygen vacancies.

The formation of a two dimensional electron gas at oxide interfaces is a field of interest since its discovery in 2004 by Ohtomo & Hwang [1]. They reported that the interface of two band insulators LaAlO$_3$ and SrTiO$_3$ is conducting, which they ascribed to an intrinsic doping mechanism driven by the polar-nonpolar discontinuity. That this mechanism is important can be seen in the fact that a minimum LAO layer thickness of 4 unit cells is needed to create the conducting interface, and that the STO surface needs to be terminated with a TiO$_2$ layer. It was found in subsequent work that, at least when grown by Pulsed Laser Deposition (PLD), the interface properties strongly depend on the background oxygen pressure, and not only intrinsic doping but also oxygen vacancies (extrinsic doping) must play a role [2–4]. Moreover, cation intermixing at the interface was shown to play a role [5–7], and in a recent study on samples grown by Molecular Beam Epitaxy it was found that the La to Al ratio of the LAO layer needs to be smaller than 1 in order to activate the interface conductance [8]. This issue has not yet been addressed in PLD grown interfaces.

Here we report on the growth LAO/STO interfaces by sputter deposition using high oxygen pressure, which is a well-known deposition technique for oxide thin films. By various characterization methods we find the LAO films smooth and the interfaces atomically sharp, but we do not observe conductance. The La/Al ratio is 1.07, which indicates that stoichiometry also is part of the mechanism which yields conducting interfaces. We grow thin films of LAO on the TiO$_2$-terminated surface of STO by RF sputtering in oxygen at pressures from 0.8 mbar to 1.2 mbar at growth temperatures between 900°C and 940°C. The morphology of the films was characterized by Atomic Force Microscopy (AFM) in tapping mode. Thicknesses of the grown films were measured by X-ray reflectivity (XRR) using Cu-K$_\alpha$ radiation. The structural quality of the grown thin film of LAO has been measured by X-ray diffraction (XRD). Transmission Electron Microscopy (TEM) was used to characterize the interfaces. High Resolution TEM micrographs were recorded using a microscope (FEI Titan cubed TEM) equipped with an image forming Cs corrector and a High Resolution Gatan Image Filter (HR-GIF) operated at 300 kV. Scanning TEM (STEM) was used in Energy Dispersive X-ray (EDX) mode to determine the local stoichiometry of our LAO films. EDX profiles were acquired on a FEI Tecnai-200 system with the probe less than 0.38 nm. The spectra acquisition, drift correction and data analysis were all performed using the software TIA (Tecnai Imaging & Analysis).

Two critical parameters which control the growth in sputtering are the deposition temperature $T_{dp}$ and pressure $P_{dp}$. We determined a window for smooth and epitaxial growth in Table I which proved to be rather narrow. Growing outside this window results in rough and structurally defective films.

Good films were grown around $T_{dp} = 920°C$ and 0.8 mbar.

![FIG. 1: (Color on-line) (a) Morphology of a LaAlO$_3$ film on SrTiO$_3$ by atomic force microscopy (b) Height profile along the line drawn in (a)](image-url)
TABLE I: Sputter deposition parameters of LaAlO₃ on SrTiO₃. Given are the sputter gas pressure $P_{dp}$, the substrate temperature $T_{dp}$, the roughness of the LAO film, the out-of-plane lattice parameter $c_0$, and the LAO film thickness. The 20 nm films is LA051.

| $P_{dp}$ (mbar) | $T_{dp}$ (°C) | Rough. (nm) | $c_0$ (Å) | $d_{LAO}$ (nm) |
|-----------------|---------------|-------------|----------|----------------|
| 1.2             | 800           | 1.6         | x        | 5              |
| 1.2             | 840           | 1.7         | x        | 15             |
| 1.2             | 900           | 2.1         | x        | 8              |
| 1.2             | 1034          | 0.4         | 3.786    | 13             |
| 1.0             | 840           | 1.4         | 3.789    | 13             |
| 0.8             | 840           | 2           | 3.789    | 13             |
| 0.8             | 920           | 0.2         | 3.786    | 20             |
| 0.8             | 920           | 0.2         | 3.777    | 12             |
| 0.6             | 940           | 0.4         | 3.799    | 14             |
| 0.4             | 940           | 0.2         | x        | 15             |

FIG. 2: (color on-line) X-ray reflection data for the 20 nm film LA051 (LAO on STO). The drawn (black) line is a simulation.

Figure 1 shows the surface morphology of a 20 nm film (called LA051) measured by AFM. The corresponding profile (Fig. 1b) indicates a step size of unit cell height i.e., 0.4 nm. The roughness of the films is 0.2 nm over a scale of 1 μm. Figure 2 shows an XRR measurement on a 20 nm film. The Kiessig fringes are clearly visible and point to crystalline order of atomic planes perpendicular to the growth direction as well as flatness of surface and interface. For several films, the density profile was simulated by using Bruker XRD software. They have a constant density for each layer which indicates homogeneous films over whole thickness range.

The out-of-plane lattice constant $c_0$ of the LAO films was characterized by XRD. Figure 3 shows three representative films with thicknesses 12 nm, 20 nm (LA051) and 51 nm. The values of $c_0$ are given in Table I. Comparison with the bulk lattice constant of LAO ($a_0 = 3.789\text{Å}$) shows that the 12 nm film is fully strained, and the 51 nm film fully relaxed.

Figure 4 shows a TEM micrograph of the atomically sharp LAO-STO interface, made on film LA051. The diffractogram (Fig. 4b) shows a small splitting in the higher order diffraction spots, which point to a small misalignment between the out-of-plane crystallographic axes of LAO and STO. The elemental variation across the interface was probed with EDX (beam diameter 0.2 nm) and is given in Fig. 5. The signals are strong and stable beyond the interface region and allow to determine the elemental composition. EDX line scans were made across the LAO-STO interface, providing the atomic composition profiles as shown in Fig. 5. The La/Al ratio of the film was obtained by averaging over 92 data points from Region 1 and calibrated by using the averaged value obtained from a LaAlO₃ crystal. For an accurate calibration, the EDX experimental conditions for the crystal and the film were deliberately set up in the same way, including the cross-section sample preparation, the orientation of the sample in the holder and the TEM mode settings. In this way, the La/Al ratio of the film was found to be 7 percent higher than that of the crystal. Supposing the ratio there to be 1, the La/Al ratio in the film is therefore 1.07. It is of interest to note that in a recent study...
of growth of LAO on STO by PLD, it was found that the out-
of-plane lattice parameter $c_0$ of the LAO film is correlated to the La/Al ratio $[9]$. A typical value of 0.378 nm for our thin strained films (see Table I) would correspond to a La/Al ratio of 1.10, in very good agreement with the value we find from EDX. Finally, we determined the conductance of a number of films at room temperature. For this, wires were bonded for a 4-point measurement, with contacts in line. Typical values of the sheet resistance were $10^3$ Ω, but showed no variation in conductance. The picture from the data is then as follows. The LAO films, and the LAO/STO interfaces prepared by sputtering in a high oxygen pressure have crystallographic properties very similar to those grown by PLD or MBE, but the interface is not conducting. This points again to the important role of oxygen vacancies, and in that respect our results bear strong resemblance to a recent study of PLD-grown LAO/STO interfaces by Kalabukhov et al., where the oxygen pressure was varied between $10^{-4}$ mbar and $5 	imes 10^{-2}$ mbar $[10]$. The latter pressure is an order of magnitude higher than where conductance, in conjunction with magnetism, is still found $[2]$, and at this pressure the interfaces were not conducting. Apparently, both in high-pressure PLD and in high-pressure sputtering, the amount of oxygen vacancies produced in the growth process becomes too low to generate a doped interface. This may not be simply due to the high gas pressure, which might be thought to quench vacancy production by highly energetic particles in the PLD- or sputter-plasma. The off-stoichiometry also plays a role in the process. For instance, it was demonstrated by Schneider et al. that oxygen is drawn out of the STO substrate in the case of LAO films grown at low oxygen pressure ($1.5 	imes 10^{-5}$ mbar), and probably Al-rich $[11]$. Such a mechanism to create oxygen defects may not be present in La-rich films, as was surmised by Chambers $[12]$. Also, from first-principle density functional calculations, Hellberg concluded that in La-rich films, La does not substitute for Al but instead, Al vacancies are formed $[13]$. These vacancies can migrate to the interface and screen the polar discontinuity, so that the metallic interface does not form. This does not answer the question whether the La-enrichment results of the high oxygen pressure, but it does help to understand why La-rich LaAlO$_3$ on SrTiO$_3$ does not yield conductance.

In conclusion, we have grown LAO/STO interfaces by sputtering in high oxygen pressure. The LAO films are smooth, strained for small thickness, and show excess of La, while the interfaces are not conducting. Although sputtering is an important deposition technique, the materials science of the LAO/STO interfaces appears to be such that it cannot be simply utilized to produce such two-dimensional interface conductance.

This research was funded through a research grant of the Stichting FOM. I. M. Dildar is supported by the Higher Education Commission (HEC) of Pakistan and on study leave from the Department of Physics, University of Engineering and Technology (UET), Lahore, Pakistan.

[1] O. Ohtomo, H. Hwang, , Nature, 427 423 (2004).
[2] M. Huijben, A. Brinkman, G. Koster, G. Rijnders, H. Hilgenkamp and D. H. A. Blank, Adv. Mat. 21, 1665 (2009).
[3] G. Herranz, M. Basletic, M. Bihes, C. Carretero, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzic, J. -M.Broto, A. Barilemey, and A. Fert, Phys. Rev. Lett. 98, 216803 (2007).
[4] W. Siemons, G. Koster, H. Yamamoto, W. A. Harrison, G. Lucovsky, T. H. Geballe, D. H. A. Blank and M. R. Beasley, Phys. Rev. Lett. 98, 196802 (2007).
[5] A. Kalabukhov, R. Gunnarsson, J. Borjessen, E. Olsson, T. Claeson, D. Winkler, Phys. Rev. B 75, 121404(R) (2007).
[6] P.R. Willmott, S.A. Pauli, R. Herger, C.M. Schleputz, D. Martoccia, B. D. Patterson, B. Delley, R. Clarke, D. Kumah, C. Cionca and Y. Yacoby, Phys. Rev. Lett. 99, 155502 (2007).
[7] S.A. Chambers, M.H. Engelhard, V. Shuthandanand, Z. Z„ T.C. Droubay, L. Qiao, P.V. Sushko, T. Feng, H.D. Lee, T. Gustafsson, E. Garfunkel, A.B. Shah, J.-M. Zuo, Q.M. Ramasse, Surf. Sci. Rep. 65, 317-352 (2010).
[8] M.P. Warusawithana, A.A. Pawlicki, T. Heeg, D.G. Schiom, C. Richter, S. Paetel, J. MANNHART, M. Zheng, B. Mulcahy, J.N. Eckstein, W. Zander, and J. Schubert, Bulletin of the APS 55, nr. 2 (2010), abstract ID BAPS.2010.MAR.B37.1.
[9] L. Qiao, T. C. Droubay, T. Varga, M. E. Bowden, V. Shuthandanand, Z. Zhu, T. C. Kaspar, and S. A. Chambers, Phys. Rev. B 83, 085408 (2011).
[10] A. Kalabukhov, Y. A. Boikov, I. T. Serenkov, V. I. Sakharov, J. Borjesson, N. Ljustine, E. Olsson, D. Winkler and T. Claeson, Europhys. Lett. 93, 37001 (2011).
[11] C. W. Schneider, M. Esposito, I. Marozau, K. Conder, M. Dobe, T. Hu, M. Mallepell, A. Wokaun, and T. Lippert, Appl. Phys. Lett. 97, 192107 (2010).
[12] S. A. Chambers, Surf. Sci. 605, 1133 (2011).
[13] C. S. Hellberg, Bulletin of the APS 56, nr. 1 (2011), abstract ID BAPS.2011.MAR.A34.5.