Non-conducting interfaces of $LaAlO_3/SrTiO_3$ produced in sputter deposition: The role of stoichiometry

I. M. Dildar, D. B. Boltje, M. H. S. Hesselberth, J. Aarts' , Q. Xu, H. W. Zandbergen, and S. Harkema

Citation: Appl. Phys. Lett. **102**, 121601 (2013); doi: 10.1063/1.4798828
View online: http://dx.doi.org/10.1063/1.4798828
View Table of Contents: http://aip.scitation.org/toc/apl/102/12
Published by the American Institute of Physics

RIGHTSLINK

Non-conducting interfaces of $LaAlO_3/SrTiO_3$ produced in sputter deposition: The role of stoichiometry

I. M. Dildar,[1] D. B. Boltje,[1] M. H. S. Hesselberth,[1] J. Aarts,[1,a)] Q. Xu,[2] H. W. Zandbergen,[2] and S. Harkema[3]
[1]*Kamerlingh Onnes Laboratorium, Leiden University, Leiden, The Netherlands*
[2]*National Centre for High Resolution Microscopy, Kavli Institute for Nanoscience, Delft Technical University, Lorentzweg 1, 2628 CJ Delft, The Netherlands*
[3]*Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands*

(Received 23 August 2012; accepted 18 March 2013; published online 26 March 2013)

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 sharp and continuous interfaces with some slight intermixing. The elemental ratio of La to Al, measured by the energy dispersive X-ray technique, 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 interplays among stoichiometry, mixing, and oxygen vacancies. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4798828]

The properties of the two dimensional electron gas at the interface between the band insulators $LaAlO_3$ (LAO) and $SrTiO_3$ (STO), and the mechanisms behind its formation have been a field of interest ever since its discovery in 2004 by Ohtomo and Hwang.[1] They ascribed it to an intrinsic doping mechanism driven by the polar-nonpolar discontinuity. This mechanism of electronic reconstruction is important, as can be seen in the facts 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, furnishing Ti 3d orbitals at the interface. It is not the only mechanism however, and surprisingly, there is still considerable debate about the relative importance of the different factors which conspire to produce a conducting interface.[2] Of particular importance is the question of oxygen deficiencies, as can be appreciated from the fact that the properties of the LAO/STO interface crucially depend on the pressure of the background oxygen, at least when grown by Pulsed Laser Deposition (PLD).[3–5] In general, the conductivity decreases with increasing oxygen pressure, and it was recently reported that at a pressure of 5×10^{-2} millibars, which is close to the upper limit for the PLD process, the interface became insulating.[6] On the other hand, Cancellieri *et al.* showed that interfaces grown at 10^{-2} millibars were superconducting when subjected to a postanneal treatment.[7] Clearly, the mobility of oxygen through the different layers during and after growth is a relevant parameter. Also cation intermixing at the interface was shown to play a role,[8–10] and it was found that the oxygen octahedra at the interface are rotated under the influence of strain, which should have bearing on the electronic reconstruction.[11] Finally, 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.[12] This issue has not yet been addressed at all in PLD grown interfaces.

The overwhelming majority of studies of the LAO/STO interface has been performed on PLD-grown samples. Given the promise for applications in oxide electronics,[2,13] the question is valid whether interfaces with similar (conducting) properties can be prepared by sputter deposition, a question which has not yet been addressed, although the electron microscopy study mentioned above[11] was partly performed on sputtered samples. Sputter deposition of oxides takes place at high oxygen pressures (typically 1 millibar), in order to suppress backsputtering effects, which otherwise can damage the growing film. This again raises the issue of the behavior of oxygen atoms and vacancies. Here, we report such experiments. By various characterization methods, we find the sputtered LAO films smooth and the interfaces epitaxial, with (La,Sr) intermixing in roughly 2 unit cells, very similar to what is seen in PLD-grown samples. We do not observe conductance nor can render the interface conducting after postannealing. Moreover, in the $LaAlO_3$ film, we find a La/Al ratio of 1.07. It appears that this ratio is connected to the high pressure and is also material in allowing oxygen diffusion to and from the interface.

Films of LAO were grown on the TiO_2-terminated surface of STO by RF sputtering in oxygen at pressures from 0.8 millibars to 1.2 millibars 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-Kα radiation. The structural quality of the grown thin film of LAO was 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

a)E-mail: aarts@physics.leidenuniv.nl

 © 2013 American Institute of Physics

RIGHTSLINK

TABLE I. Sputter deposition parameters of $LaAlO_3$ on $SrTiO_3$. 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 film is LA51.

P_{dp} (millibars)	T_{dp} (°C)	Roughness (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

at 300 kV. Scanning TEM (STEM) was used in Energy Dispersive X-ray (EDX) mode to determine the local stoichiometry of the LAO films. EDX profiles were acquired on a FEI Tecnai-200 system with the probe less than 0.38 nm. The acquisition of spectra, the drift correction, and the data analysis were all performed using Tecnai Imaging & Analysis software. Conductance was measured with a physical properties measuring system, on samples with wire-bonded leads in order to contact the interface.

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 as shown in Table I, which proved to be rather narrow. Growing outside this window results in rough and structurally defective films.

Smooth films were grown around $T_{dp} = 920\,°C$ and 0.8 millibars. Figure 1(a) shows the surface morphology of a 20 nm film (called LA51) measured by AFM. The corresponding profile (Fig. 1(b)) 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. Thickness fringes are clearly visible, which indicates a uniform film thickness. The measured data could be well fitted with a model consisting of a 20.33(9) nm thick LAO film of uniform density. The film/air interface has a roughness of 0.21(3) nm; the roughness of the STO/LAO interface was found to be 0.6(2) nm. Both values for the roughness are indications for epitaxial interfaces. For several

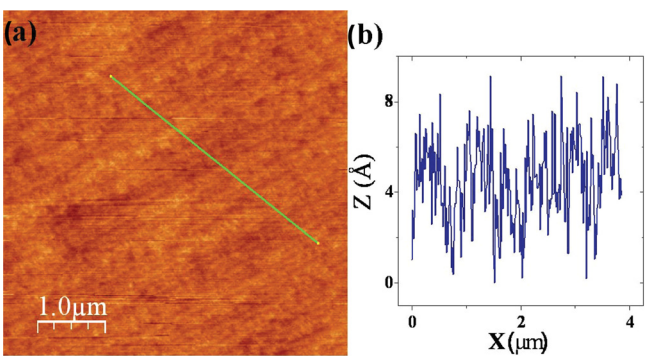

FIG. 1. (a) Morphology of a $LaAlO_3$ film on $SrTiO_3$ measured by atomic force microscopy. (b) Height profile along the line drawn in (a).

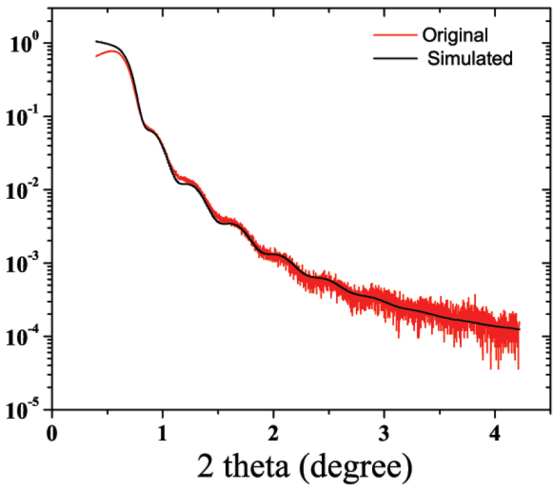

FIG. 2. X-ray reflection data for the 20 nm film LA51 (LAO on STO). The drawn (black) line is a simulation.

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 ($a_0 = 3.789$ Å) shows that the 12 nm film is fully strained and the 51 nm film fully relaxed. Figure 4(a) shows a micrograph of an LAO/STO interface, made on film LA51. The diffractogram (Figures 4(b) and 4(c)) shows a small splitting in the higher order diffraction spots, which points to a small misalignment between the out-of-plane crystallographic axes of LAO and STO. Similar observations were made on PLD-grown films and ascribed to the effects of strain.[10] The sharpness and the amount of interface cationic mixing were investigated in the following way. Starting with the micrograph of Fig. 4(a), the original picture was subtracted from the same picture but shifted over half a unit cell along the [110]-direction. Next, the intensity variation was derived for cross-sectional lines

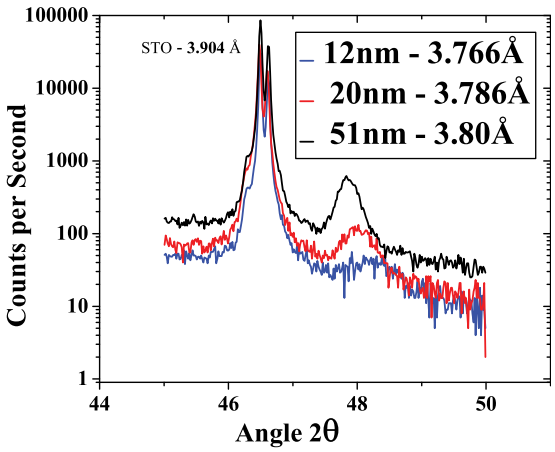

FIG. 3. XRD data of three representatives films of LAO at angles around the (002) reflection. The (002) STO peak corresponds to a lattice parameter of 0.3904 nm. The black line shows a 51 nm thick LAO film, the red line is for a 20 nm film (LA51), and the blue line is for a 12 nm film. Also given are the lattice parameters of the films as calculated from the intensity peaks.

RIGHTSLINK

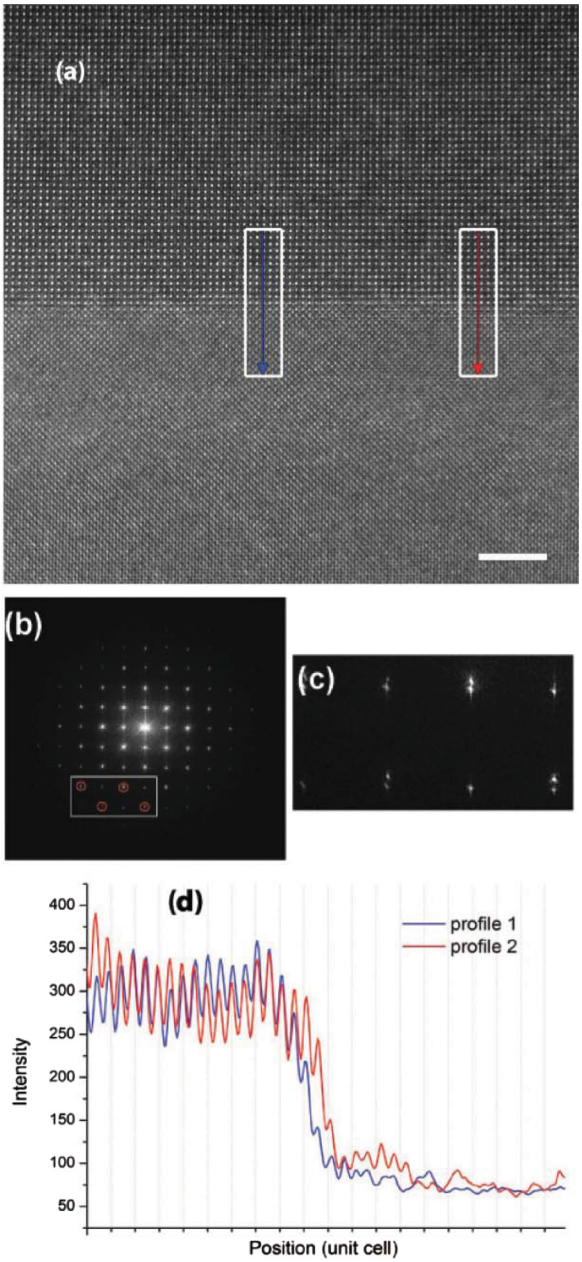

FIG. 4. (a) High resolution TEM picture of the LAO/STO interface for film LA51. (b) Diffraction pattern from an area at the interface. (c) Enlarged part of the region of the marked spots, showing a slight splitting which indicated some misalignment between film and substrate. (d) Intensity variation along the two lines shown in (a), derived by subtracting the image from a copy of itself which was shifted by half a unit cell along the [110]-direction (see text). Note that profile 1 (left in (a)) is shifted over one unit cell with respect to profile 2.

along a direction perpendicular to the interface. Two such lines are shown in Fig. 4(a), with the corresponding intensity variation in Fig. 4(d). On the LAO side of the interface, intensity still remains on the atomic positions, because of the difference in scattering factors for La and Al. On the STO side of the interface, the Sr and Ti signals are very similar, and the subtraction brings the signal close to zero. In this way, the crossover in the interface region gives a good estimate for the amount of intermixing, which can be seen to be of the order of two to three unit cells.

The elemental variation across the interface was probed with EDX and is given in Fig. 5. The variation of the elemental

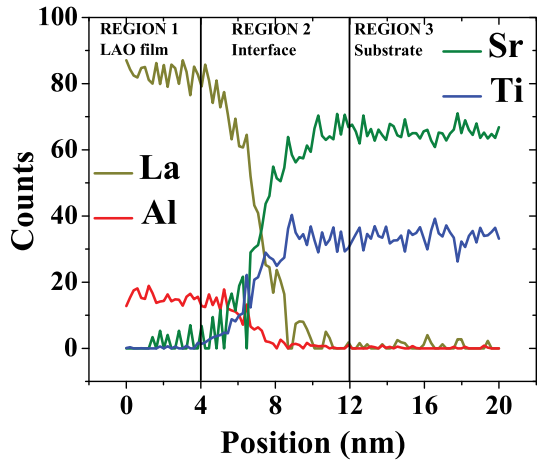

FIG. 5. STEM/EDX elemental profile of the LAO/STO sandwich across the interface. The elemental ratios La/Al and Sr/Ti were determined in regions 1 and 3, respectively.

intensity is somewhat larger than the two unit cells mentioned above, which is due to the thickness of the sample slice (about 50 nm) which gives rise to electrons scattering over 1 to 2 nm. The signals are strong and stable and allow to determine the elemental composition beyond the interface region. 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 $LaAlO_3$ 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% higher than that of the crystal. Supposing the ratio in the single crystal to be 1, the La/Al ratio in the film is therefore 1.07(2). This number can be compared to the number which can be obtained from the out-of-plane lattice parameter c_0 of the LAO film. In a recent study of growth of LAO on STO by PLD, it was found that c_0 is correlated to the La/Al ratio.[14] 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. Following up on this result, we used a La-deficient ($La_{0.94}Al_{1.06}Al_3$) target. Films from this target showed similar properties with respect to morphology (AFM) and structure (XRD) as those from the stoichiometric target. The EDX analysis of the La/Al ratio yielded 1.06, which within the accuracy of the measurement is the same as the number from the stoichiometric target. Finally, we determined the room temperature conductance of a number of films grown under optimal growth conditions. For this, wires were bonded for a 4-point measurement, with contacts in line. Typical values of the sheet resistance were 10 MΩ and above. Since the sheet resistance is known to increase significantly with thickness,[15] we included samples with thicknesses of 2.4 nm, 4 nm, 7 nm, and 9 nm, which is a range in which conductances of order 10 kΩ to 100 kΩ might be expected. Four films were cooled down to 10 K but showed no variation in conductance. PLD-grown films measured in the same way did show the expected conductance. Post-annealing did not change this. After the deposition, some samples were cooled down in vacuum to 580 °C. The oxygen pressure was then raised to 0.2 bars, while the

RIGHTSLINK

sample cooled further to 530 °C in about 15 min. These conditions were maintained for 1 h before cooling down to room temperature. Such samples still did not show 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 and in that respect our results bear strong resemblance to the results on PLD-grown LAO/STO interfaces by Kalabukhov *et al*. as mentioned before.[6] 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 (1.5×10^{-5} millibars), which were probably Al-rich.[16] 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.[17] 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 is a result of the high oxygen pressure, but it does help to understand why La-rich $LaAlO_3$ on $SrTiO_3$ does not yield conductance. Another remark should be made on the effects of post-annealing. The results of Cancellieri *et al*.[7] strongly suggest that their LAO film allows the oxygen content of their interface to be varied. Since they can produce a conducting interface, the LAO film is probably La-deficient. Our La-rich films apparently do not allow to change the interface anymore, which again hints at the importance of understanding the role of stoichiometry. Finally, we find that the stoichiometry cannot be simply changed by tuning the target. A reason for this may be that Al is light and scatters easily in the high gas pressure. Lowering the pressure is no option however, since this results in films with poor morphology.

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 nor can be rendered conducting by a post-anneal treatment. Apart from the practical implications with respect to sputtering as a technique to fabricate such conducting interfaces, the results point to the importance of the stoichiometry issue in relation to the physics.

This research was funded in part through a research grant of the Stichting FOM. I. M. Dildar was 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 and H. Hwang, Nature **427**, 423 (2004).
[2]D. G. Schlomm and J. Mannhart, Nature Mater **10**, 168 (2011).
[3]M. Huijben, A. Brinkman, G. Koster, G. Rijnders, H. Hilgenkamp, and D. H. A. Blank, Adv. Mater **21**, 1665 (2009).
[4]G. Herranz, M. Basletic, M. Bibes, C. Carretero, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzic, J.-M. Broto, A. Barthelemy, and A. Fert, Phys. Rev. Lett. **98**, 216803 (2007).
[5]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).
[6]A. Kalabukhov, Yu. A. Boikov, I. T. Serenkov, V. I. Sakharov, J. Börjesson, N. Ljustina, E. Olsson, D. Winkler, and T. Claeson, Europhys. Lett. **93**, 37001 (2011).
[7]C. Cancellieri, N. Reyren, S. Gariglio, A. D. Caviglia, A. Féte, and J.-M. Triscone, Europhys. Lett. **91**, 17004 (2010).
[8]A. Kalabukhov, R. Gunnarsson, J. Börjessen, E. Olsson, T. Claeson, and D. Winkler, Phys. Rev. B **75**, 121404(R) (2007).
[9]P. R. Willmott, S. A. Pauli, R. Herger, C. M. Schleputz, D. Martcoccia, B. D. Patterson, B. Delley, R. Clarke, D. Kumah, C. Cionca, and Y. Yacoby, Phys. Rev. Lett. **99**, 155502 (2007).
[10]S. A. Chambers, M. H. Engelhard, V. Shutthanandan, Z. Zhu, T. C. Droubay, L. Qiao, P. V. Sushko, T. Feng, H. D. Lee, T. Gustafsson, E. Garfunkel, A. B. Shah, J.-M. Zuo, and Q. M. Ramasse, Surf. Sci. Rep. **65**, 317–352 (2010); see also S. A. Chambers, Surf. Sci. **605**, 1133 (2011).
[11]C. L. Jia, S. B. Mi, M. Faley, U. Poppe, J. Schubert, and K. Urban, Phys. Rev. B **79**, 081405(R) (2009).
[12]M. P. Warusawithana, A. A. Pawlicki, T. Heeg, D. G. Schlom, C. Richter, S. Paetel, J. Mannhart, M. Zheng, B. Mulcahy, J. N. Eckstein, W. Zander, and J. Schubert, Bull. Am. Phys. Soc. **55**, BAPS.2010.MAR.B37.1 (2010).
[13]B. Förg, C. Richter, and J. Mannhart, Appl. Phys. Lett. **100**, 053506 (2012).
[14]L. Qiao, T. C. Droubay, T. Varga, M. E. Bowden, V. Shutthanandan, Z. Zhu, T. C. Kaspar, and S. A. Chambers, Phys. Rev. B **83**, 085408 (2011).
[15]C. Bell, S. Harashima, Y. Hikita, and H. Y. Hwang, Appl. Phys. Lett. **94**, 222111 (2009).
[16]C. W. Schneider, M. Esposito, I. Marozau, K. Conder, M. Doebeli, Ti Hu, M. Mallepell, A. Wokaun, and T. Lippert, Appl. Phys. Lett. **97**, 192107 (2010).
[17]C. S. Hellberg, Bull. Am. Phys. Soc. **56**, BAPS.2011.MAR.A34.5 (2011).

RIGHTSLINK