

The origin of oxygen in oxide thin films: Role of the substrate

C. W. Schneider, M. Esposito, I. Marozau,^{a)} K. Conder, M. Doebeli, Yi Hu, M. Mallepell, A. Wokaun, and T. Lippert^{b)}

Department of General Energy Research, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland;
Laboratory for Developments and Methods, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland;
and Ion Beam Physics, ETH Zurich, CH-8093 Zurich, Switzerland

(Received 13 October 2010; accepted 23 October 2010; published online 11 November 2010)

During the growth of oxide thin films by pulsed laser deposition, a strong oxygen substrate-to-film transfer has been experimentally observed for SrTiO₃ and LaAlO₃ thin films epitaxially grown on ¹⁸O exchanged SrTiO₃ and LaAlO₃ substrates by secondary ion mass spectrometry depth profiling. This oxygen transfer effect can seriously change the respective thin film properties. Taking the oxygen substrate contribution to the overall oxygen balance into account, original ways to design material properties of oxide thin films can be envisioned like a controlled charge carrier doping of SrTiO₃ thin films. © 2010 American Institute of Physics. [doi:10.1063/1.3515849]

The preparation of high quality complex oxide thin films and heterostructures with atomic precision has advanced in recent years considerably.^{1,2} Subsequently, the crystalline quality of these oxide films is comparable to semiconductors and oxide-semiconductors structures with designed properties have been prepared.^{3,4} These developments in thin film growth helped to investigate superconductivity in a single copper oxygen plane⁵ or to prepare highly conducting oxide interfaces between two insulators^{6–8} which show superconductivity⁹ and magnetism.¹⁰ To obtain the desired oxide materials properties, a specific oxygen stoichiometry is essential. The challenge associated with growing oxides is to provide and control the amount of oxygen during the growth to obtain the desired oxygen stoichiometry and hence appropriate physical properties of the respective oxide. For a deposition using pulsed laser deposition (PLD), it often seems to be sufficient to create the correct amount of plasma species within an oxygen background to form the chosen compound as a thin film on a suitable substrate and to supply the missing oxygen with a subsequent annealing step.

During a deposition, the only discussed and usually considered oxygen sources are the target and the background gas. The substrate is taken as the template for the film to be and to match the respective lattice constants to grow the oxide film, e.g., epitaxially, with a preferred crystalline orientation. For an oxygen substrate contribution, there is so far only circumstantial evidence from YBa₂Cu₃O_{7–δ} grown on SrTiO₃ (Ref. 11) and EuO grown on YSZ.⁴ Growing oxides with, e.g., a perovskite structure, the dielectric SrTiO₃ is a typically used substrate due to an acceptable lattice mismatch to most commonly investigated oxides. When doped with oxygen vacancies or metals SrTiO₃ becomes a *n*-type^{12,13} or *p*-type conductor¹⁴ and a superconductor.¹⁵ Recently, TiO₂-terminated SrTiO₃ (Ref. 16) served as a substrate for ultrathin LaAlO₃ layers grown by PLD where the polar discontinuity at the LaAlO₃/SrTiO₃ interface¹⁷ causes a highly conducting *n*-type layer with charge carriers confined within a few nm at the interface.^{6,9,18,19} Oxygen vacan-

cies, caused by the PLD process itself,²⁰ were briefly considered to be the origin of the observed conductivity. However, oxygen vacancies in SrTiO₃ are highly mobile²¹ and to localize them exclusively at an interface seemed unlikely.

The example of SrTiO₃ shows that the oxygen content plays a role for the respective material properties and it could even affect the properties of an oxide grown on it. This is revealed in Fig. 1 where the resistance of SrTiO₃ thin films grown by PLD on (100) SrTiO₃, (100) LaAlO₃, and (100) oriented MgO single crystalline substrates at a vacuum background pressure *p* of 1.5 × 10⁻⁵ mbar, a fluence *F*, of ~4 J cm⁻² and a substrate temperature *T*_S of 750 °C were measured between 4 and 300 K. After the deposition, the cooling-down took place at the vacuum base pressure. The sheet resistance of the SrTiO₃ thin film on SrTiO₃ clearly shows a metal-like temperature dependence, whereas SrTiO₃ grown on LaAlO₃ and MgO is semiconducting-like. The expectations have been to prepare SrTiO₃ with similar transport properties using the same growth conditions on different substrates. A difference of 10⁶ at 4 K for the measured resistance

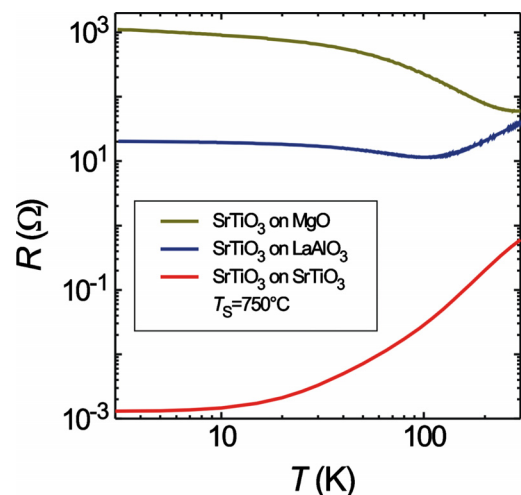


FIG. 1. (Color online) Temperature dependence of the sheet resistance of SrTiO₃ thin films grown on (100) MgO (top), (100) LaAlO₃ (middle), and (100) SrTiO₃ (bottom) single crystalline substrates at *T*_S = 750 °C. All films are ~100 nm thick and grown at a vacuum base pressure of 1.5 × 10⁻⁵ mbar, *F* ~ 4 J cm⁻², and a substrate temperature of 750 °C.

^{a)}Present address: Department of Physics, University of Fribourg, Chemin du Musée 3, CH-1700 Fribourg, Switzerland.

^{b)}Author to whom correspondence should be addressed. Electronic mail: thomas.lippert@psi.ch.

is unexpected and indicates a potential substrate contribution to the measured resistance. For SrTiO₃ grown on oxygen deficient SrTiO_{3-x}, a metal-like temperature dependence can be expected. Estimating the oxygen content of the SrTiO_{3-x} thin films using Rutherford backscattering (RBS), values of ~ 2.5 for the films shown in Fig. 1 have been obtained with an average composition of Sr_{0.97±0.03}Ti_{1.03±0.03}O_{2.52±0.06}. This raises the questions where does the oxygen in an oxide thin film grown on an oxide substrate come from, is oxygen supplied by the substrate, and how significant is the oxygen transfer for deposition techniques other than PLD?

To investigate the role of oxygen supplied by the substrate during a deposition, the oxygen diffusion properties of SrTiO₃ and LaAlO₃ thin films grown on ¹⁸O isotope exchanged SrTi¹⁸O₃ and LaAl¹⁸O₃ substrates were studied by dynamic secondary ion mass spectrometry (D-SIMS) which yields elemental depth profiles. SrTiO₃ and LaAlO₃ thin films have been prepared at three different deposition temperatures (nominal room temperature, 650 °C, and 750 °C) by PLD ($\lambda=248$ nm, 10 Hz) at a background pressure $p=1.5 \times 10^{-5}$ mbar and $F=4$ J cm⁻² on ¹⁸O₂ exchanged (100) oriented SrTi¹⁸O₃ and LaAl¹⁸O₃ substrates (non-terminated and TiO₂ terminated) with a total thickness of ~ 100 nm. Details to the oxygen exchange is given in Ref. 22. SIMS spectra were recorded using a quadrupole mass spectrometer (Hiden analytical EQS) operated with a 2.5 keV Ar ion beam focused to 150 μ m diameter rastering over a square of 1 × 1 mm with an effective sampling area of 500 × 500 μ m². The etched area is subsequently measured with a Dektak 8 profilometer to convert etching time into depth. In addition, a kinetic energy selection scheme is used to separate species with the same mass.²³

The ¹⁸O diffusion from SrTi¹⁸O₃ into SrTi¹⁸O₃ shows a pronounced dependence on the deposition temperature [Fig. 2(a)]. Whereas for a room temperature deposition, no traceable ¹⁸O diffusion into the film has been measured, the situation changes dramatically for elevated deposition temperatures. At 650 °C, there is considerable ¹⁸O diffusion from the substrate into the film, while at $T_s=750$ °C, there is no significant difference with respect to the amount of ¹⁸O measured in the film and substrate. Measuring Sr and Ti species from the substrate and film simultaneously with ¹⁶O and ¹⁸O, the elemental compositions of film and substrate are very similar. This implies that oxygen in the SrTiO₃ thin film is supplied by the substrate and the oxygen provided by the target seems to play a minor role for this system.

The ¹⁸O diffusion into LaAlO₃ from LaAl¹⁸O₃ differs significantly compared to SrTiO₃ on SrTi¹⁸O₃. No considerable oxygen diffusion from the substrate into the film is detected, in particular, at the interface region, irrespective of the studied deposition temperature (not shown). In the case of SrTiO₃ grown on LaAl¹⁸O₃, a significant and homogeneous oxygen contribution is measured for the SrTiO₃ film prepared at $T_s=750$ °C [Fig. 2(b)]. Even at 650 °C, there is still a significant ¹⁸O intake which can be detected up to the film surface. It is interesting to note the comparatively large difference in oxygen diffusion properties of the SrTiO₃ thin film considering a modest difference in T_s of 100 °C. This is probably due to the activation energy of oxygen diffusion in SrTiO₃ and that a film is inherently defect-rich which allows oxygen to diffuse more easily at elevated temperatures compared to a single crystal [$D_{\text{crystal}}=10^{-15}$ cm² s⁻¹; D_{defects}

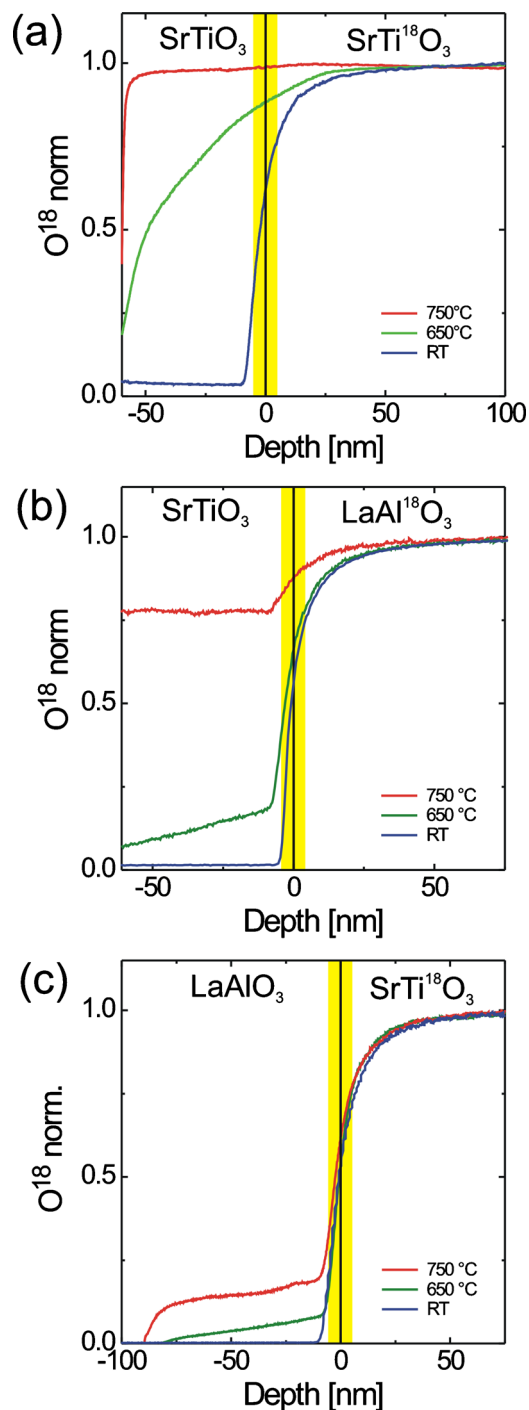


FIG. 2. (Color online) (a) ¹⁸O SIMS depth profile of SrTiO₃ on SrTi¹⁸O₃ grown at $T_s=750$ °C, 650 °C, and room temperature. The sharp drop of the ¹⁸O signal near the SrTiO₃ surface for the film grown at $T_s=750$ °C could be related to a back-exchange of ¹⁶O at room temperature. (b) ¹⁸O SIMS depth profile of SrTiO₃ on LaAl¹⁸O₃ grown at $T_s=750$ °C, 650 °C, and room temperature. (c) ¹⁸O SIMS depth profile of LaAlO₃ on SrTi¹⁸O₃ grown at $T_s=750$ °C, 650 °C, and room temperature. These samples have been grown at a vacuum base pressure of 1.5×10^{-5} mbar and a fluence of ~ 4 J cm⁻². The yellow area visualizes approximately the depth over which the information of the interface region is collected.

$= 10^{-11}$ cm² s⁻¹ [Ref. 21]). The large ¹⁸O concentration in SrTiO₃ thin films is unexpected if compared to LaAlO₃ on LaAl¹⁸O₃. This suggests that SrTiO₃ is a material which can either take or give oxygen during film growth, whereas LaAlO₃ is more likely to keep oxygen during the deposition. Oxygen diffusion into LaAlO₃ is more difficult to achieve

than into SrTiO₃. This becomes evident when depositing LaAlO₃ onto SrTi¹⁸O₃ [Fig. 2(c)]. The ¹⁸O concentration in the ≈100 nm thin LaAlO₃ films deposited at different temperatures is smaller than in SrTiO₃, still there is a significant amount of ¹⁸O at the film-substrate interface for the film grown at $T_S=750$ °C.

The growth of oxide thin films by PLD is a process influenced by its plasma species formed during the ablation process (positive and negative ions, neutrals²⁴), their kinetic energy and propagation velocity, and respective scattering events with a background gas. For a vacuum deposition, the only obvious oxygen source is the target. RBS measurements of these LaAlO₃ films show that a substantial amount of oxygen is transferred from the target to the film, at the same time ¹⁸O is supplemented from the substrate. The total amount of oxygen in the film is still smaller (approximately LaAlO_{2.9}) as compared to the SrTiO₃ substrate, indicating a substantial oxygen deficiency for the as-grown LaAlO_{3-x} with induced vacancies in the substrate. The ¹⁸O diffusion data have been reproduced, albeit with a reduced depth resolution by ERDA and essentially confirm the presented SIMS measurements. In addition, the diffusion data are independent of a substrate termination.

Frequently, electrical transport properties of as-grown oxides such as LaTiO_{3+δ} on SrTiO₃ and other substrates have been reported²⁵ which yield similar variations in conductivity to the data in Fig. 1. Like SrTiO₃, LaTiO_{3+δ} ($0 \leq \delta \leq 0.5$) will most probably draw oxygen from the substrate if available which would explain the observed conducting properties.²⁵ The additional substrate contribution is often eliminated if films are grown on oxides such as MgO or scandate substrates.

The work on the conducting LaAlO₃/SrTiO₃ interface shows that a combination of surface and interface engineering and controlled defect chemistry can give structure functionalities different from the bulk as shown for the conducting interfaces. Therefore, it seems possible to create structures where the controlled oxygen diffusion from or to SrTiO₃ or related oxides helps to prepare multilayers with a defined oxygen defect structure. This is potentially beneficial for oxide multilayers used for thermoelectric applications where the contradictory demands between low thermal conductivity and good electrical conductivity could be reduced by creating defect-rich interlayers leading to an enhanced conductivity. Also, the presented experiments are most likely not just restricted to PLD because the general diffusion kinetic of a substrate-film structure is not restricted to a specific deposition technique. Details will be different, but the deposition of a material which can take oxygen during the deposition will typically result in oxygen redistribution between substrate and film. To achieve the desired properties, the specific deposition conditions for the chosen deposition technique need to be adjusted accordingly.

In summary, we have demonstrated that the oxygen-substrate contribution has to be taken into the overall oxygen balance when growing oxide thin films. LaAlO₃ and SrTiO₃ thin films where deposited on ¹⁸O exchanged SrTiO₃ and LaAlO₃ substrates and the ¹⁸O diffusion profile studied by D-SIMS. A substantial oxygen transfer between substrate and as-grown thin film has been noted, which indicates that the initially formed film is oxygen deficient and a chemical

gradient is in favor of supplying oxygen via the substrate. This finding should also be applicable to other deposition techniques such as molecular beam epitaxy or sputtering if high deposition temperatures are involved.

This work was partially supported by SNF, Project No. 200020–117642, MaNEP, and the Paul Scherrer Institut. We also gratefully acknowledge fruitful discussions with A. Weidenkaff (EMPA), E. Pomjakushina, and P. Willmott (PSI).

¹D. G. Schlom, J. H. Haeni, J. Lettieri, C. D. Theis, W. Tian, J. C. Jiang, and X. Q. Pan, *Mater. Sci. Eng., B* **87**, 282 (2001).

²*Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials*, edited by R. Eason (Wiley Interscience, Hoboken, 2008).

³M. P. Warusawithana, C. Cen, C. R. Sleasman, J. C. Woicik, Y. L. Li, L. F. Kourkoutis, J. A. Klug, H. Li, P. Ryan, L. P. Wang, M. Bedzyk, D. A. Muller, L. Q. Chen, J. Levy, and D. G. Schlom, *Science* **324**, 367 (2009).

⁴A. Schmehl, V. Vaithyanathan, A. Herrnberger, S. Thiel, C. Richter, M. Liberati, T. Heeg, M. Ruckerath, L. F. Kourkoutis, S. Muhlbauer, P. Boni, D. A. Muller, Y. Barash, J. Schubert, Y. Idzerda, J. Mannhart, and D. G. Schlom, *Nature Mater.* **6**, 882 (2007).

⁵G. Logvenov, A. Gozar, and I. Bozovic, *Science* **326**, 699 (2009).

⁶A. Ohtomo and H. Y. Hwang, *Nature (London)* **427**, 423 (2004).

⁷M. Huijben, G. Rijnders, D. H. A. Blank, S. Bals, S. Van Aert, J. Verbeeck, G. Van Tendeloo, A. Brinkman, and H. Hilgenkamp, *Nature Mater.* **5**, 556 (2006).

⁸S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, and J. Mannhart, *Science* **313**, 1942 (2006).

⁹N. Reyren, S. Thiel, A. D. Caviglia, L. F. Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A. S. Ruetschi, D. Jaccard, M. Gabay, D. A. Muller, J. M. Triscone, and J. Mannhart, *Science* **317**, 1196 (2007).

¹⁰A. Brinkman, M. Huijben, M. Van Zalk, J. Huijben, U. Zeitler, J. C. Maan, W. G. Van der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, *Nature Mater.* **6**, 493 (2007).

¹¹L. S.-J. Peng, W. Wang, W. Jo, T. Ohnishi, A. F. Marshall, R. H. Hammond, M. R. Beasley, E. J. Peterson, and R. E. Ericson, *IEEE Trans. Appl. Supercond.* **11**, 3375 (2001).

¹²Y. Tokura, Y. Taguchi, Y. Okada, Y. Fujishima, T. Arima, K. Kumagai, and Y. Iye, *Phys. Rev. Lett.* **70**, 2126 (1993).

¹³H. P. R. Frederikse and W. R. Hosler, *Phys. Rev.* **161**, 822 (1967).

¹⁴H. Guo, L. Liu, Y. Fei, W. Xiang, H. Lu, S. Dai, Y. Zhou, and Z. Chen, *J. Appl. Phys.* **94**, 4558 (2003).

¹⁵C. S. Koonce, M. L. Cohen, J. F. Schooley, W. R. Hosler, and E. R. Pfeiffer, *Phys. Rev.* **163**, 380 (1967).

¹⁶M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, *Science* **266**, 1540 (1994).

¹⁷S. Okamoto and A. J. Millis, *Nature (London)* **428**, 630 (2004).

¹⁸M. Sing, G. Berner, K. Goss, A. Muller, A. Ruff, A. Wetscherek, S. Thiel, J. Mannhart, S. A. Pauli, C. W. Schneider, P. R. Willmott, M. Gorgoi, F. Schafers, and R. Claessen, *Phys. Rev. Lett.* **102**, 176805 (2009).

¹⁹M. Basletic, J. L. Maurice, C. Carretero, G. Herranz, O. Copie, M. Bibes, E. Jacquet, K. Bouzehouane, S. Fusil, and A. Barthelemy, *Nature Mater.* **7**, 621 (2008).

²⁰M. L. Scullin, J. Ravichandran, C. Yu, M. Huijben, J. Seidel, A. Majumdar, and R. Ramesh, *Acta Mater.* **58**, 457 (2010).

²¹A. E. Paladino, L. G. Rubin, and J. S. Waugh, *J. Phys. Chem. Solids* **26**, 391 (1965).

²²C. W. Schneider, M. Esposito, I. Marozau, K. Conder, M. Doebeli, Y. Hu, M. Mallepell, A. Wokaun, and T. Lippert, "The oxygen contribution of the substrate for oxide thin film growth" (unpublished).

²³H. T ellez, J. M. Vadillo, and J. J. Laserna, "Development of an energy-resolved method for SIMS in-depth analysis of metal-polymer interfaces," *Surf. Interface Anal.* (to be published).

²⁴M. Esposito, T. Lippert, M. Doebeli, C. W. Schneider, and A. Wokaun, "Negative ions: The overlooked species for oxide thin film growth using pulsed laser ablation" (unpublished).

²⁵F. J. Wong, S.-H. Baek, R. V. Chopdekar, V. V. Mehta, H.-W. Jang, C.-B. Eom, and Y. Suzuki, *Phys. Rev. B* **81**, 161101 (2010).