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Effect of oxygen vacancies in the $SrTiO_3$ substrate on the electrical properties of the $LaAlO_3/SrTiO_3$ interface

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We experimentally investigated optical, electrical, and microstructural properties of heterointerfaces between two thin-film perovskite insulating materials, $SrTiO_3$ (STO) and $LaAlO_3$ (LAO), deposited at different oxygen pressure conditions. Cathode and photoluminescence experiments show that oxygen vacancies are formed in the bulk STO substrate during the growth of LAO films, resulting in high electrical conductivity and mobility values. In both high and low oxygen pressure interfaces, the electrical Hall mobilities follow a similar power-law dependence as observed in oxygen reduced STO bulk samples. The results are confirmed on a microscopic level by local strain fields at the interface reaching 10 nm into the STO substrate.

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Perovskite-structured oxides are complex materials which exhibit a broad spectrum of functional properties. High-temperature superconductivity in the cuprates, colossal magnetoresistance in the manganites, and ferroelectricity in doped perovskites are some examples of important phenomena in these materials. The microscopic properties of oxide interfaces may have a strong impact on the electrical transport properties at and near these interfaces. It was recently shown that high electrical conductivity and mobility can be obtained in the system of an ultrathin $LaAlO_3$ (LAO) film deposited on a $SrTiO_3$ (STO) substrate.[1–3] In the ideal interface between STO and LAO, a polar discontinuity may arise due to different valences of Sr and La atoms.[1] However, other factors like strain or oxygen vacancies may drastically change the interface properties.

STO and LAO are well studied dielectric materials with wide band gaps of about 3.2 and 5.6 eV at 300 K, respectively.[4–7] While LAO is not very critical to defects and dopants,[8,9] the properties of STO can easily be modified with a small compositional change. By replacing only a small fraction of Sr with Nb, La, or Ta the material will become highly (*n*-type) conducting with a charge carrier concentration of 10^{19} cm^{-3} and superconducting below 0.4 K.[10–12] The material properties can also be modified by reducing stoichiometric STO to introduce oxygen vacancies. There are three ways to create oxygen deficient STO: (i) by annealing at high temperature (800–1400 °C) in vacuum, in H_2 gas or in presence of Ti metal acting as an oxygen getter,[13,14] (ii) deposition of inherently oxygen reduced STO thin films,[13] and (iii) by Ar-ion bombardment.[15,16]

We show in this report that oxygen vacancies are also introduced during the deposition of LAO films on STO substrates resulting in similar properties recently reported for LAO/STO heterointerfaces.[1–3] We found that this interface gave a similar or identical bluish cathode luminescence [using electrons from our *in situ* reflection high-energy electron diffraction (RHEED) gun] as Ar-ion milled STO substrates,[16] and that oxygen can reversibly be driven in and out of the structure. Finally, high-resolution transmission electron microscopy (TEM) studies of LAO/STO heterointerfaces reveal strain fields originating from misfit dislocations, enhancing the formation of oxygen vacancies extending 10 nm into the substrate.

Ultrathin LAO films were grown on TiO_2-terminated[17,18] (100) STO substrates by pulsed laser deposition (PLD) using a KrF excimer laser. Deposition was done at the temperature of 800 °C and in two different oxygen pressure regimes: low (10^{-6} mbar) and high (10^{-4} mbar). The thickness of the LAO films was varied in the range of 7–15 unit cells (u.c.). *In situ* RHEED was used to monitor the film growth and the surface morphology during the deposition process. Well defined RHEED oscillations indicate an atomic layer-by-layer growth in all conditions. To reduce oxygen in STO single-crystal substrates we exposed them for 10 min to an Ar-ion beam with an acceleration voltage of 300 eV and a current of 0.2 A/cm^2. The detailed information about samples preparation can be found in Ref. 19.

After deposition of LAO films at low oxygen pressure (10^{-6} mbar) the samples changed color from transparent white to grey hue, which is characteristic for oxygen reduced STO.[20] After irradiating of the as-deposited heterointerfaces with an electron beam using the RHEED *e*-gun, strong blue light emission was observed from these samples, see Fig. 1(a). We also treated STO substrates under the deposition conditions (T=800 °C, oxygen pressure 10^{-6} mbar) but without the actual film deposition and observed that the intensity of the light is comparable independent on whether there was a film on top of the substrate or not, Fig. 1(b). This shows that low oxygen pressure annealing is sufficient for the STO substrate alone to become cathode luminescent. Cathode luminescence (CL), though with much weaker intensity, was also observed from films produced at higher oxygen pressure (10^{-4} mbar), Figs. 1(c) and 1(d). The light had the same color from LAO/STO heterointerfaces and reduced STO substrates: annealed in oxygen at 10^{-6} mbar and Ar-ion bombarded, Fig. 1(e).

We performed room-temperature photoluminescence (PL) experiments using a 350-nm argon laser to compare oxygen reduced substrates and LAO/STO heterointerfaces. Two samples with different LAO film thicknesses (7 and 15 u.c.) and an Ar-ion bombarded STO were studied. The results of the PL measurements are presented in Fig. 1(g). The wave-

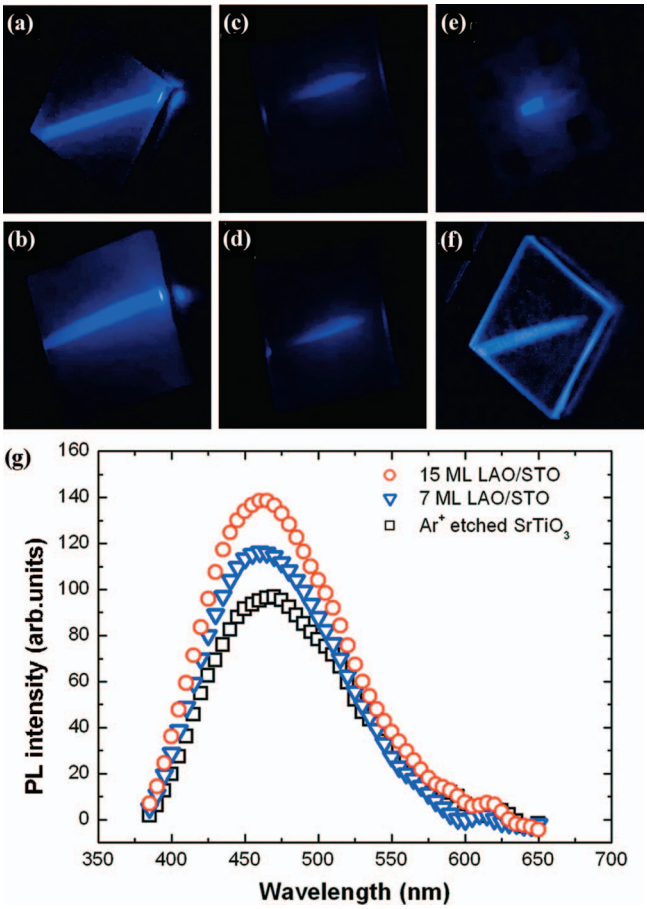

FIG. 1. (Color) Cathode and photoluminescence from various STO substrates and LAO/STO systems: (a) STO substrate annealed at 10^{-6} mbar O_2, 800 °C, and (b) after deposition of LAO film in the same conditions. (c) Substrate annealed at 10^{-4} mbar O_2, 800 °C and (d) after LAO deposition. (e) Ar-ion bombarded STO single-crystal substrate. (f) Cathode luminescence from an as-received LAO single-crystal substrate. (g) Photoluminescence measurements of LAO/STO films grown under low oxygen pressure conditions and of an Ar-ion bombarded STO substrate.

length of the emitted light (460 nm) from both the LAO/STO heterointerface and Ar-ion bombarded STO substrate is the same within the precision of the experiment. The position of the PL peak agrees well with the wavelength of light emitted from Ar-ion bombarded STO reported in Ref. 16, where it is ascribed to trapped states within the band gap created by oxygen vacancies. Light emitted from samples processed at high-pressure conditions was too weak to be detected using our PL equipment. The PL results are in good agreement with previous reports, where the PL was observed only from oxygen reduced strontium titanate.[21]

CL was also observed in single-crystal LAO substrates, Fig. 1(f), but it is more whitish in color than the light from STO, and the CL is even whiter from oxygen reduced LAO. Hence these results show that the CL in the LAO/STO heterointerface is produced in the bulk STO substrate rather than in a film.

Finally, we monitored the CL in a LAO/STO sample prepared at low oxygen pressure at different annealing processes, see Fig. 2. After re-entering oxygen by exposing the sample to 500 mbar oxygen at 600 °C for 2 h the intensity is considerably decreased, but still visible. In order to reduce the sample again, we annealed it *in situ* for 2 h in vacuum (10^{-7} mbar) at 600 °C for 2 h. The intensity of the CL was then recovered, see Fig. 2(c). The sample was then brought *ex situ* to a furnace and kept in a strongly reducing H_2/Ar environment at 700 °C for 17 h. This procedure increased the intensity of the luminescent light even more [Fig. 2(d)].

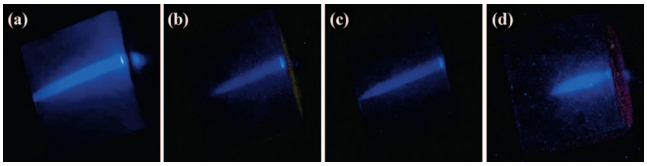

FIG. 2. (Color) Cathode luminescence from LAO/STO heterointerfaces: (a) as deposited at 10^{-6} mbar O_2, (b) after re-oxygenation, (c) after vacuum annealing (10^{-7} mbar) at 600 °C, and (d) after H_2/Ar annealing.

So far, we have shown that blue-light cathode luminescence can be observed in both LAO/STO heterostructures and intentionally oxygen depleted STO (i.e., Ar-ion bombarded), as well as in STO substrates treated in the same way and using exactly the same conditions as during film deposition (except for the actual deposition itself). We therefore conclude that oxygen vacancies can be formed in the STO substrate without deposition of LAO films at low oxygen pressure.

Electrical measurements were made in a four-point van der Pauw configuration[22] in the temperature range 2–300 K and in magnetic field up to 5 T. Gold contact pads were fabricated by sputtering using a Ti adhesion layer. The temperature dependence of the sheet resistance R_{XX}, the Hall mobility μ_H, and the charge-carrier density n_S are presented in Fig. 3.

First we focus on the electrical properties of the samples prepared at low oxygen pressure. The sheet resistance shows metallic temperature behavior and saturates at around 10 K. The low-temperature resistance value is about 10^{-2} Ω/□ for both the LAO/STO films made at low oxygen pressure and STO substrates annealed in deposition conditions. The Hall mobility deduced from the resistivity and Hall measurements are the same for the LAO/STO films, annealed in the deposition conditions and the Ar-ion bombarded STO substrates (10^4 cm^2 V^{-1} s^{-1}).

If LAO films, first deposited at low oxygen pressure, are oxidized at 500 mbar during cooling, they show much higher resistivity, about 1 kΩ/□ at 4 K. The same value of resistance is found for LAO films grown at high oxygen pressure. Further oxidation of the films at 600 °C in 500 mbar oxygen for 1 h had only a minor influence on the sheet resistivity and the Hall mobility. Finally, we made a deposition of LAO film at much higher oxygen pressure, 5×10^{-2} mbar, at 800 °C, which resulted in an insulating state.

In general, the behavior of our samples agrees well with the temperature dependence presented earlier for LAO/STO heterointerfaces,[1,2,23] on Ar-ion bombarded STO,[16,24] and vacuum annealed STO.[10,11] The observation of high con-

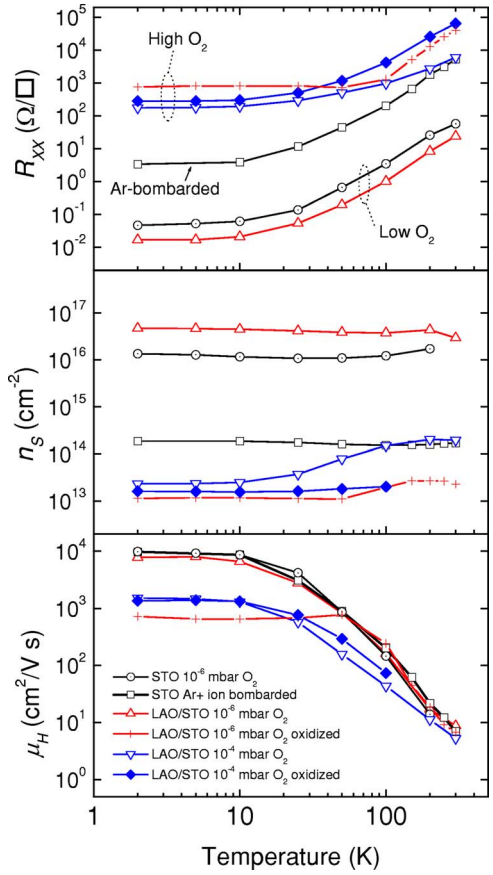

FIG. 3. (Color online) Sheet resistivity R_{XX}, charge-carrier density n_S, and Hall mobility μ_H for STO substrates annealed in deposition conditions (10^{-6} mbar O_2, 800 °C) and Ar-ion bombarded (U=300 eV, J=0.2 mA/cm^2) (open and solid circles); LAO/STO heterointerfaces prepared at low oxygen pressure (10^{-6} mbar) as well as annealed at 500 mbar during cooling (open and solid diamonds); LAO/STO heterointerfaces prepared at high oxygen pressure (10^{-4} mbar) and annealed at 500 mbar during cooling (open and solid triangles).

ductivity in STO substrates annealed in low-pressure (10^{-6} mbar) deposition conditions contradicts the results by Ohtomo and Hwang.[1] However, it is known that the properties of the STO substrates are very sensitive to the actual environmental conditions regarding temperature and pressure. We found that even minor differences in the actual procedures during heating and cooling may result in either insulating or conducting state. To eliminate this problem, we have introduced a very well defined route where the substrate treatment was kept unchanged for all samples.

The Hall mobilities at temperatures above 100 K follow a power-law temperature dependence similar to the one reported in Ref. 10 for oxygen reduced and Nb-doped single-crystal STO: $\mu_H \approx 3\times 10^7\ T^{-2.7}\ cm^2\ V^{-1}\ s^{-1}$.

A critical issue is the exceptionally high charge-carrier density observed in the LAO/STO heterointerfaces in Refs. 18 and 20. We observed $n_S = 10^{16}-10^{17}\ cm^{-2}$. This is two orders of magnitude higher than the estimated value for a polar interface between LAO and STO.[23] Thus our data suggest that the charge carriers are not localized only at the interface, but rather in the bulk of the substrate. This was also indicated by Siemons *et al.*[23] We note that the STO substrate treated in deposition conditions at high oxygen pressure (10^{-4} mbar) shows cathode luminescence, but at the same time no conductivity. A possible explanation for this could be clustering of oxygen vacancies, which has previously been observed in Ref. 14 in $SrTiO_{3-\delta}$. In addition, the maximum magnetic field we applied to the sample (up to 5 T, perpendicular to the sample) in magnetoresistance measurements was not sufficient to observe Shubnikov–de Haas oscillations. This type of oscillation is well known to occur in conducting STO,[25] and has been reported also in structures of oxide thin films grown on STO substrates.[26,27] Herranz *et al.*[27] deduced from the observation of Shubnikov–de Haas oscillations that the conducting layer at the LAO/STO interface extends over hundreds of microns into the STO substrate.

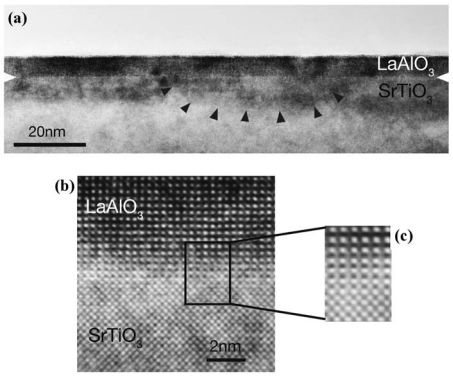

FIG. 4. TEM cross-section micrographs of the LAO/STO interface for a film deposited at an oxygen pressure of 10^{-6} mbar. (a) U-shaped dark contrast is marked with arrows. (b) High-resolution electron microscope image showing details of the LAO/STO interface between misfit dislocations. (c) A fast Fourier-transform filtered image of the coherent interface between the dislocations.

The congruence of the electrical properties as well as the strong effect on the oxygen pressure suggests that the high electrical conductivity and the mobility observed in the LAO/STO heterostructures are due to oxygen vacancies in the bulk of the STO substrate.

In order to understand the microscopic origin of these effects in the LAO/STO systems we performed high-resolution transmission electron microscopy (TEM). Figure 4 shows TEM cross-section micrographs of the 15-u.c.-thick LAO film deposited at an oxygen pressure of 10^{-6} mbar. The incident electron beam was parallel to the [100] axis of the STO substrate. The orientation relationship between LAO and STO is [100]LAO//[100]STO and [010]LAO//[010]STO. In Fig. 4(a), a U-shaped dark contrast can be seen in the STO substrate near the film-substrate interface reaching up into the film at several positions and coinciding with misfit dislocations at the interface. On a large scale, the average distance between these dislocations is approximately 15 nm. Figure 4(b) shows the STO/LAO interface between the dislocations with higher resolution, and Fig. 4(c) shows a fast Fourier transformed filtered image of Fig. 4(b). A clear coherence of the film-substrate interface can be seen in Figs. 4(b) and 4(c), though the TEM investigation shows the presence of misfit dislocations. Considering the orientation rela-

tionship between the LAO and the STO (see above) and the corresponding lattice mismatch of 3%, the expected distance between dislocations for a fully relaxed film is 11 nm, which is slightly smaller than the observed 15 nm. Thus the overall film is not completely relaxed. The LAO unit cell is smaller than the STO and the residual strain in the STO at the interface will therefore be compressive along the [100] and [010] directions. In addition, the contrast observed in the TEM images in the vicinity of the dislocations shows that they give rise to local strain fields in the STO reaching about 10 nm into the STO substrate. A similar result is also reported by Siemons *et al.*[28]

It is known that crystalline defects in STO can enhance the diffusion of oxygen.[29] Based on the perovskite tolerance factor t,[30] we can estimate the activation energy for oxygen vacancy diffusion. For STO (t=0.8072) it is 0.75 eV, and for LAO (t=0.8857) we find 2.2 eV. Hence it is reasonable to believe that during the initial growth of LAO on STO in a low-pressure environment the oxygen is more easily removed from STO than transported through LAO. This may explain why STO substrates annealed at high oxygen pressure are not conducting, in contrast to LAO/STO heterostructures prepared under the same conditions.

In summary, our findings strongly suggest that oxygen vacancies in STO are responsible for the conductivity in LAO/STO heterostructures prepared even at high oxygen pressures. However, at this stage we cannot completely exclude the possibility that other mechanisms, like polar discontinuity between LAO and STO or cation substitution at the interface, could have a minor effect on the electrical properties.

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