Origin of the two-dimensional electron gas at LaAlO$_3$/SrTiO$_3$ interfaces - The role of oxygen vacancies and electronic reconstruction

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The relative importance of atomic defects and electron transfer in explaining conductivity at the crystalline LaAlO$_3$/SrTiO$_3$ interface has been a topic of debate. Metallic interfaces with similar electronic properties produced by amorphous oxide overlayers on SrTiO$_3$ [Y. Chen et al., Nano Lett. 11, 3774 (2011); S. W. Lee et al., Nano Lett. 12, 4775 (2012)] have called in question the original polarization catastrophe model [N. Nakagawa et al., Nature Mater. 5, 204 (2006)]. We resolve the issue by a comprehensive comparison of (100)-oriented SrTiO$_3$ substrates with crystalline and amorphous overlayers of LaAlO$_3$ of different thicknesses prepared under different oxygen pressures. For both types of overlayers, there is a critical thickness for the appearance of conductivity, but its value is always 4 unit cells (∼1.6 nm) for the oxygen-annealed crystalline case, whereas in the amorphous case the critical thickness could be varied in the range 0.5 to 6 nm according to the deposition conditions. Subsequent ion milling of the overlayer restored the insulating state for the oxygen-annealed crystalline heterostructures but not for the amorphous ones. Oxygen post-annealing removes the oxygen vacancies, and the interfaces become insulating in the amorphous case, but the interfaces with a crystalline overlayer remain conducting with reduced carrier density. These results demonstrate that oxygen vacancies are the dominant source of mobile carriers when the LaAlO$_3$ overlayer is amorphous, while both oxygen vacancies and polarization catastrophe contribute to the interface conductivity in unannealed crystalline LaAlO$_3$/SrTiO$_3$ heterostructures, and the polarization catastrophe alone accounts for the conductivity in oxygen-annealed crystalline LaAlO$_3$/SrTiO$_3$ heterostructures. Furthermore, it was found that the crystallinity of the LaAlO$_3$ layer is crucial for the polarization catastrophe mechanism in the case of crystalline LaAlO$_3$ overlayers.

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The two-dimensional electron gas (2DEG) appearing at the interface between the band insulators LaAlO$_3$ (LAO) and SrTiO$_3$ (STO) has attracted much attention since its discovery by Ohtomo and Hwang [1]. It has stimulated a substantial body of experimental and theoretical work [2-25], but, its origin is still controversial [26]. Three different mechanisms have been proposed. First is interface electronic reconstruction to avoid the polarization catastrophe induced by the discontinuity at the interface between polar LAO and nonpolar STO [2-4]. Second is doping by thermal interdiffusion of Ti/Al or La/Sr atoms at the interface [13]. A third possible mechanism is creation of oxygen vacancies in STO substrates during the deposition process [9-11,27,28]. Oxygen vacancies are known to introduce a shallow intragap donor level close to the conduction band of STO [29], and their action may be specific to this one substrate. The thermal interdiffusion mechanism was discounted in recent work [25], which studied the effect of a mixed interface layer. It is also in conflict with the experimental results that p-type LAO/STO interfaces [1] and interfaces created by growing STO films on LAO are insulating [30].

In 2007, Shibuya et al. [28] associated the metallic conductivity at interfaces between room temperature-deposited amorphous CaHfO$_3$ films and STO single crystal substrates with the bombardment of STO substrates by the plume during the pulsed laser deposition process. Later, Chen et al. [31] demonstrated metallic interfaces between STO substrates and various amorphous oxide overlayers including LAO, STO and yttria-stabilized zirconia thin films fabricated by pulsed laser deposition. The origin of the 2DEG in such amorphous heterostructures was attributed to formation of oxygen vacancies at the surface of the STO. Moreover, metallic interfaces between Al-based amorphous oxides and STO substrates have also been realized by other less energetic deposition techniques such as atomic layer deposition [32] and electron beam evaporation [33]. The electronic properties of STO-based amorphous heterostructures [31,32] are, to some extent, similar to those of crystalline LAO/STO
heterostructures [7,8], including the metallicity accompanied by the presence of Ti$^{3+}$ ions and a sharp metal-insulator transition as a function of overlayer thickness. These results call into question the polarization catastrophe model.

In this paper, we present a detailed comparison of amorphous and crystalline LAO/STO heterostructures based on electrical and optical measurements. By comparing the electronic properties of these two interfaces, we are able to distinguish the two different mechanisms mainly responsible for the 2DEG observed in amorphous and crystalline LAO/STO heterostructures.

Amorphous LAO films were deposited from a single crystal LAO target on untreated (100)-oriented STO substrates by pulsed laser deposition (KrF laser $\lambda = 248$ nm) at room temperature and different oxygen partial pressures. Crystalline LAO films were fabricated on TiO$_2$-terminated (100)-oriented STO substrates at 750 °C in 10$^{-3}$ Torr oxygen partial pressure. During deposition, the repetition rate of the laser was kept at 5 Hz and the laser fluence was fixed at 1.3 J/cm$^2$. The deposition rate of amorphous LAO films was calibrated by transmission electron microscopy measurements and the growth of crystalline LAO films was monitored in situ by reflectance high energy electron diffraction (RHEED). Electrical contacts onto $5 \times 5$ mm$^2$ samples were made with Al wires using wire bonding and electrical measurements were performed in a Quantum Design physical property measurement system. While the sheet resistance and Hall effect of all LAO/STO heterostructures was measured in the van der Pauw geometry, the magnetoresistance (MR) measurements were performed in the four-probe linear setup, which were 1.7 and 0.8 ˚A/s for amorphous LAO and crystalline LAO layer, respectively.

Figure 1(a) shows a cross-section transmission electron microscopy image of a 20 nm amorphous LAO film grown on an untreated STO substrate at room temperature and 10$^{-6}$ Torr oxygen partial pressure. The LAO layer is seen to uniformly cover the STO substrate. The zoom-in image of an interface region in the inset of Fig. 1(a) demonstrates the amorphous feature of the LAO overlayer, with one or two oriented layers at the interface, which confirms the room-temperature amorphous growth of LAO films on crystalline STO substrates. The first monolayer of the LAO is well oriented, while subsequent layers are increasingly disordered.

The photoluminescence (PL) spectra (excited by a 325 nm laser) of an as-received STO substrate and 20 nm amorphous LAO films deposited on STO substrates at different oxygen partial pressures ranging from 10$^{-1}$ to 10$^{-6}$ Torr are shown in Fig. 1(b). Although the PL intensity of the as-received STO substrate is weak, the characteristic PL peaks of oxygen vacancies at wavelengths ranging from 380 to 420 nm [29,34] in STO can still be seen. The PL intensity of amorphous LAO/STO heterostructures is enhanced by a factor of five to nine relative to the as-received STO substrate, depending on oxygen partial pressure. Moreover, the multiple PL emission peaks are much more pronounced, and the PL intensity increases with decreasing oxygen partial pressure. Considering that 20 nm amorphous LAO films grown on Si substrates present no PL signal [35] and the PL peaks from various defects in LAO bulk crystals appear only at ~600 nm and above [36], we are able to attribute the large enhancement of PL intensity between 350 and 475 nm in amorphous LAO/STO heterostructures to the creation of oxygen vacancies in the STO substrates near their interface during deposition.

The temperature-dependent sheet resistance ($R_s$-$T$) of the 20 nm amorphous LAO/STO heterostructures fabricated in different oxygen partial pressures from 10$^{-3}$ to 10$^{-6}$ Torr is shown in Fig. 2(a). As can be seen, the heterostructures exhibit metallic behavior in the whole temperature range. The room temperature sheet resistance increases with oxygen partial pressure. The corresponding carrier density and mobility data are illustrated in Fig. 2(b). The room-temperature carrier density of $\sim$10$^{14}$ cm$^{-2}$ is comparable to that of unannealed crystalline LAO/STO heterostructures [8,19], which were directly cooled down to room temperature in the deposition oxygen pressure after high temperature growth. Moreover, both the temperature-dependent carrier density ($n_s$-$T$) and mobility of such amorphous LAO/STO heterostructures are similar to those of unannealed crystalline LAO/STO heterostructures [5,8,19], including the carrier freeze-out effect below $\sim$100 K.

To examine the conductivity and band gap of amorphous LAO, we deposited 150 nm amorphous LAO films on large band gap substrates MgO and Al$_2$O$_3$. By electrical and ultraviolet-visible spectroscopy measurements, it was found that amorphous LAO is highly insulating with a band gap greater than 5 eV [35], similar to crystalline bulk LAO. Furthermore, any possible built-in potential in amorphous LAO-STO heterostructures should be negligible and only confined to the first or two quasi-crystalline layers of LAO at the interface. The PL spectra in Fig. 1(b) indicate the presence of oxygen vacancies in STO substrates. We are therefore led to conclude that the conductivity emerging at the interface between amorphous LAO films and STO substrates originates largely from oxygen vacancies created in STO near the interface during film deposition.

The $R_s$-$T$ curve of a 20 nm amorphous LAO/STO heterostructure [35] fabricated at 10$^{-2}$ Torr behaves differently from other heterostructures fabricated at lower
FIG. 1: Structural and optical properties of amorphous LaAlO$_3$/SrTiO$_3$ (LAO/STO) heterostructures. (a) Transmission electron microscopy image of a LAO film deposited on an untreated STO substrate at room temperature and $10^{-6}$ Torr oxygen pressure. Inset: zoom-in image of an interface region. (b) Room-temperature photoluminescence (PL) spectra of an as-received STO substrate and 20 nm amorphous LAO films deposited on untreated STO substrates at different oxygen partial pressure ranging from $10^{-1}$ to $10^{-6}$ Torr.

FIG. 2: Electrical transport properties of amorphous LAO/STO heterostructures. (a) The temperature dependence of sheet resistance ($R_s$-$T$) and (b) sheet carrier density ($n_s$-$T$) and the corresponding mobility for 20 nm amorphous LAO/STO heterostructures fabricated at different oxygen pressures from $10^{-3}$ Torr to $10^{-6}$ Torr.

We systematically examined the LAO layer thickness dependence of sheet resistance for amorphous LAO/STO heterostructures fabricated in different oxygen partial pressures ranging from $10^{-1}$ to $10^{-6}$ Torr. For samples deposited at $10^{-1}$ Torr, no measurable conductivity was ever detected up to a 100 nm LAO layer thickness. As shown in Fig. 3(a), for samples prepared at $10^{-2}$ Torr and lower pressure, a sharp drop by more than four orders of magnitude in sheet resistance occurs at a certain LAO layer thickness, which strongly depends on oxygen pressure. Indeed, there is a sheet resistance minimum at $\sim$18 K, which was also observed in crystalline LAO/STO heterostructures [8]. Moreover, the sheet resistance of an amorphous LAO/STO heterostructure can be tuned by a back gate voltage. The large tunability in the sheet resistance (60% variation between $\pm$60 V) and in the MR [35] is comparable to the electric field effect in a crystalline heterostructure [17].
The critical thickness for appearance of conductivity in amorphous LAO/STO heterostructures was observed as a function of overlayer thickness. A similar transition in resistance increases by a factor of seven in the oxygen-annealed crystalline LAO/STO case, compared to the oxygen-annealed crystalline heterostructures with a thickness of 4 unit cells (UC) [7]. In contrast, the activation energy of carriers in oxygen-annealed crystalline LAO/STO samples is much smaller, 0.5 meV. As shown in Fig. 4(d), the PL intensity of the post-annealed crystalline sample exhibits a little temperature dependence, changing from 1.62 × 10^{13} cm^{-2} at 300 K to 1.38 × 10^{13} cm^{-2} at 5 K. Such post-annealing experiments are reproducible [35]. The carrier freeze-out effect in unannealed crystalline LAO/STO samples, which also exists in oxygen-deficient STO films [29], is characterized by an activation energy ϵ of 4.2 meV (fitted from n_s ∝ e^{(-ϵ/k_B T)}). 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FIG. 4: Oxygen-annealing effect. (a) Room-temperature sheet resistance of 20 nm amorphous LAO/STO heterostructures prepared at different oxygen pressures before and after oxygen-annealing in 1 bar of oxygen gas flow at 600 °C for 1 h. (b) PL intensity of the 20 nm amorphous LAO/STO heterostructures fabricated at 10^{-6} Torr before and after oxygen-annealing. (c) $R_S$-$T$, (inset) $n_s$-$T$ and (d) PL spectra of a 10 unit cell (uc) crystalline LAO/STO heterostructure prepared at 10^{-3} Torr and 750 °C before and after oxygen-annealing in 1 bar of oxygen gas flow at 600 °C for 1 h.

LAO/STO sample generates the same critical thickness of 4 uc for maintaining the interface conductivity (hollow stars). On the other hand, Ar-milling the unannealed crystalline heterostructure from 10 uc down to 2 uc produces little change in conductance (open circles), because the conduction is dominated by oxygen vacancies.

To facilitate control of the Ar-milling rate in the amorphous overlayer case, where the milling rate of LAO was more than twice that of the crystalline case, we intentionally arranged the critical thickness of heterostructures to be 6 nm by increasing the substrate-target distance and decreasing the laser fluence. Figure 5(b) illustrates the LAO layer thickness dependence of conductivity (solid squares) for amorphous LAO/STO samples. As the top amorphous LAO layer is removed, one nm at a time, from a 6nm LAO/STO sample, the conductivity of the heterostructures is retained (hollow diamonds). To check the possible effect of the Ar milling on the conductivity of STO single crystals, an insulating 2 nm amorphous LAO/STO sample was used as reference. After the removal of the top 1 nm of amorphous LAO, the heterostructure remains insulating. This proves that no conductivity is created by the Ar-milling process.

The Ar-milling experiment further confirms that the conductivity in amorphous LAO/STO heterostructures originates principally from oxygen vacancies in the STO.
...LAO/STO heterostructures fabricated at 10^{-3} Torr and 750 °C, showing a critical thickness of 4 uc. The red hollow diamonds denote that the conductivity of the 4 uc sample disappears after the removal of the top 1 uc LAO by Ar-milling. Moreover, the blue hollow circles represent the conductance of an unannealed 10 uc crystalline LAO/STO heterostructure and after the removal of the top 8 uc LAO by Ar-milling. The black hollow stars represent the conductance of another oxygen-annealed 10 uc crystalline LAO/STO sample after step-by-step Ar milling. (b) Thickness dependence (green solid squares) of room-temperature conductance of amorphous LAO/STO heterostructures fabricated at 10^{-3} Torr, showing a critical thickness of 6 nm. The green hollow diamonds represent the conductivity of the 6 nm sample that remains after the removal of the top LAO layer 1 nm at a time by Ar-milling. All the arrows represent the Ar-milling process.

For comparison, another re-growth experiment was performed. We first fabricated a 3 uc crystalline LAO/STO heterostructure, which was ex situ measured to be highly insulating. Then one more unit cell of LAO was deposited on such a heterostructure. No surface reconstruction was seen over the entire deposition process [Fig. 6(c)]. During the re-growth, periodic RHEED intensity oscillation was obtained [35]. The re-grown sample was subsequently oxygen-annealed and the $R_s$-$T$ curve shows a typical metallic behavior [Fig. 6(d)]. Such re-growth experiments demonstrate that the good crystallinity of the LAO layer is crucial for the polarization catastrophe mechanism for the case of crystalline LAO overlayers.

In addition, there are three intriguing features in Fig. 3 that demand further explanation: i) the sharp conductivity transition, ii) the oxygen pressure dependence of the critical thickness, and iii) the saturation of the sheet resistance with the amorphous overlayer thickness. When depositing the overlayer, chemically reactive species such as Al [40] have a strong propensity to attract oxygen ions from the surface of the STO, even at room temperature. The conductivity transition is explained by percolation of the electrons associated with the oxygen vacancies. The wave function of these electrons will be Bohr-like orbitals with radii of a few nm [35], resulting from the large dielectric constant of STO ($\varepsilon_r = 300$ at 300 K) and the large effective mass ($\sim5m_e$) [41]; the percolation carrier density is $\sim10^{13}$ cm$^{-2}$ in one monolayer [35]. The oxygen-depletion process from the STO surface will depend on how much reactive oxygen is available in the ambient atmosphere during deposition, thereby explaining why the critical thickness decreases at lower oxygen pressures. At the carrier densities required for percolation, the vacancy concentration at the STO surface is of the order of a few percent, a value that is already high...
After the 4th unit cell growth

Oxygen annealed

FIG. 6: Re-growth experiment. (a) Reflection high energy electron diffraction (RHEED) pattern after depositing a new LAO layer (estimated to be 2 uc) on a crystalline LAO/STO heterostructure with the LAO layer etched from 4 uc to 3 uc. (b) $R_s$-T curves of the re-grown sample stated in (a) before and after oxygen annealing. (c) RHEED pattern after depositing one uc LAO on an as-grown 3 uc crystalline LAO/STO heterostructure. (d) $R_s$-T curve of the re-grown sample described in (c) after oxygen annealing.

and the further formation of vacancies will be inhibited [42]. This explains the saturation of the sheet resistance.

In conclusion, despite there being a critical overlayer thickness of LAO for appearance of conductivity at the LAO/STO interface for both crystalline and amorphous forms of LAO, the explanation in the two cases is different. Unlike the 4 uc critical thickness for the oxygen-annealed crystalline heterostructures, there is no universal critical thickness when the LAO is amorphous. The critical thickness then depends sensitively on deposition conditions, and oxygen vacancies in the STO substrate account for the interface conductivity. Oxygen vacancies also contribute substantially to the conductivity of crystalline LAO/STO heterostructures which have not been annealed in oxygen post deposition. The reversible thickness dependence of conductivity across the critical thickness of 4 uc in oxygen-annealed crystalline heterostructures indicates that the interface electronic reconstruction due to the potential build-up in LAO overlayers is ultimately responsible for the conductivity in that case. Moreover, our experiments demonstrate that the crystallinity of the LAO layer is crucial for the polarization catastrophe. Moreover, reproducing similar experimental procedures as reported here would be crucial to reveal the origin and mechanism of the recently reported anisotropic 2DEG at the LAO/STO (110) interface [43] and conductivity at the LAO/STO (111) [44] and other STO-based oxide interfaces.

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