

Charge modulated interfacial conductivity in SrTiO₃-based oxide heterostructures

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When depositing amorphous SrTiO₃ (STO) films on crystalline STO substrates by pulsed laser deposition, metallic interfaces are observed, though both materials are band-gap insulators. The interfacial conductivity exhibits strong dependence on oxygen pressure during film growth, which is closely related to the STO plasma expansion in the background gas of oxygen. By controlling the charge balance in the STO plasma with an external bias, V_{bias} , of $-10 \text{ V} \leq V_{\text{bias}} \leq 5 \text{ V}$ at an oxygen pressure of 10^{-4} Pa , the interfacial conduction can be tuned to be metallic or semiconducting. These results provide a new opportunity to tailor low-dimensional interface states of complex oxide heterostructures. © 2011 American Institute of Physics. [doi:10.1063/1.3598391]

Oxide heterostructures with artificially engineered interfaces have attracted considerable attention in recent years due to the emerging novel behavior which does not exist in the corresponding bulk parent compounds.^{1,2} This opens possibilities for future applications in oxide-based nanoelectronic as well as nanoionic devices. The recent discovery of a quasi-two-dimensional electron gas (q2DEG) at the interface of two insulating complex oxides LaAlO₃ (LAO) and SrTiO₃ (STO) represents an important milestone toward oxide electronics.³ It has become clear that the system offers the potential for possible future devices and is therefore of high interest.^{4,5} However, since the discovery of conductivity at the LAO/STO interface, one of the main challenges is to identify the source of the charge carriers. Up to date, in spite of intensive research effort, there is not yet a consensus on the origin and nature of the doping mechanism. The conductivity at the LAO/STO interface has been overwhelmingly ascribed to the polar discontinuity induced electronic reconstruction,³ or the La-intermixing-related doping at the interface.^{6–8} However, recent results indicate that the oxygen vacancies formed on STO side may account for the conducting behavior.^{9–12}

Oxygen vacancies are among the most important intrinsic ionic defects in oxides, the formation of which are usually associated with strong electron redistribution on neighboring cations. When a neutral O atom is missing in the ionic lattice of STO, two excess electrons are usually transferred to Ti cations, reducing Ti⁴⁺ to Ti³⁺.¹³ This can alter the wide-band insulator of stoichiometric STO into semiconducting, metallic, or superconducting states, depending on the concentration of the oxygen vacancies.¹⁴ Normally, the oxygen vacancies are quenched in the STO through thermal routes.^{15,16} When the STO is used as a substrate for growing oxide films at high temperatures, the oxygen ions in STO can be pumped out as an oxygen source for the film growth,^{17,18} which could result in a conducting interface under reduced conditions. More interestingly, it is recently found that the

outward diffusion of the oxygen ions in STO substrate and the resultant metallic interface can even be realized at room temperature.¹² This outward diffusion of oxygen ions at room temperature is probably activated by the reactivity of the plasma species during laser ablation, and provides an alternative way to create mobile charge carriers at complex oxide heterointerfaces. Here, we report that, by controlling the charge balance in plasma plume with an external bias without changing the oxygen pressure of film growth, the interfacial conduction of STO-based heterostructures with amorphous STO over-layers can be tuned to be metallic or semiconducting, which provides an *in situ* way to tailor low-dimensional interface states of complex oxide heterostructures.

STO films with a nominal composition of SrTiO_{3-x} and a thickness of about 25 nm were deposited on $5 \times 5 \times 0.5 \text{ mm}^3$ (001) TiO₂-terminated STO substrates¹⁹ from a single crystalline STO target by pulsed laser deposition (PLD) at room temperature. The target-to-substrate distance was fixed at 4.5 cm. A KrF laser ($\lambda=248 \text{ nm}$) with a repetition rate of 1 Hz and laser fluence of 1.5 J/cm^2 was adopted. The film deposition was performed under different oxygen pressures, P_{O_2} , ranging from 1×10^{-4} to 100 Pa. To influence the charge flux of the film growth plasma reaching the substrate during deposition, the STO substrate was surrounded with a truncated cone electrode on which an external bias was applied, as sketched in Fig. 1. All the obtained films were determined to be amorphous and insulating as described elsewhere.¹² The conductivity of the buried interfaces was measured in a four-probe Van der Pauw geometry with ultrasonically wire-bonded aluminum wires as electrodes. The dependence of the plasma parameters on P_{O_2} and the cone-electrode bias voltage, V_{bias} , during the ablation of STO target was measured by a planar Langmuir probe (see Fig. 1). The probe was made from a $5 \times 5 \times 0.5 \text{ mm}^3$ gold plate, which was placed at the same location as the STO substrate. The Langmuir probe was biased with a programmable power supply controlled by PC while the probe current was measured over a $10 \text{ } \Omega$ resistor using an instrumen-

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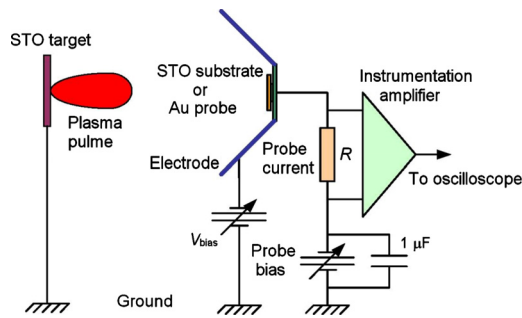


FIG. 1. (Color online) Schematic diagram for the PLD with a bias-controlled cone electrode and the plasma parameters measurement using a Langmuir probe.

tation amplifier with insulated ground connected to a fast digital oscilloscope. Both the cone electrode and the Langmuir probe were cleaned after each film deposition to remove the contamination due to the deposition of insulating STO films.

Figures 2(a) and 2(b) show the P_{O_2} dependence of the electron temperature, T_e , which corresponds to the mean kinetic energy of electrons, and the collected electrons per pulse, N_e , respectively, of the STO plasma for film growth at $V_{bias}=0$ V. Little changes are observed for both T_e and N_e at $P_{O_2} \leq 0.1$ Pa. This is consistent with the free expansion of the plasma in this oxygen pressure range.^{20,21} In contrast, when increasing P_{O_2} to 1 Pa, a large rise in T_e from 0.8 to 2.1 eV is observed. This suggests the appearance of strong interaction between the plume and the background oxygen gas. However, no increase in electron collection is observed here. When P_{O_2} is increased to 10 Pa, N_e increases four times due to the dramatic collisions between the oxygen molecules and the plasma species, which generally produce a large

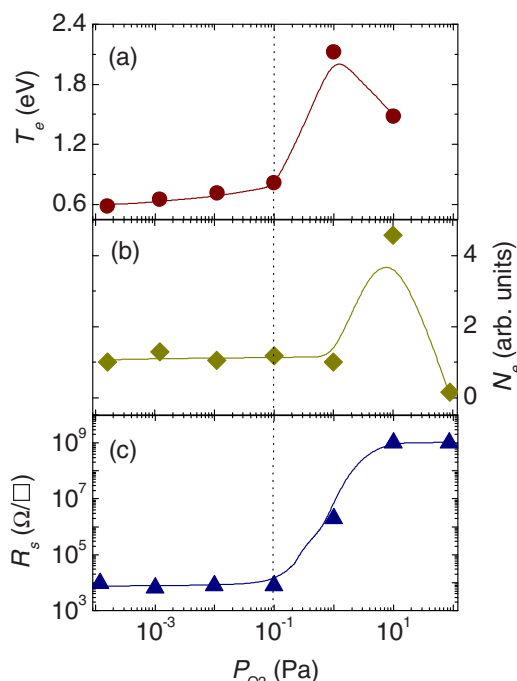


FIG. 2. (Color online) [(a) and (b)] The dependence of electron temperature, T_e , and the collected electrons per pulse, N_e , of a STO plasma, respectively, on the oxygen pressure, P_{O_2} at $V_{bias}=0$ V. (c) The corresponding room temperature sheet resistance, R_s , vs P_{O_2} of the formed STO/STO heterostructures. All lines are guide to the eyes.

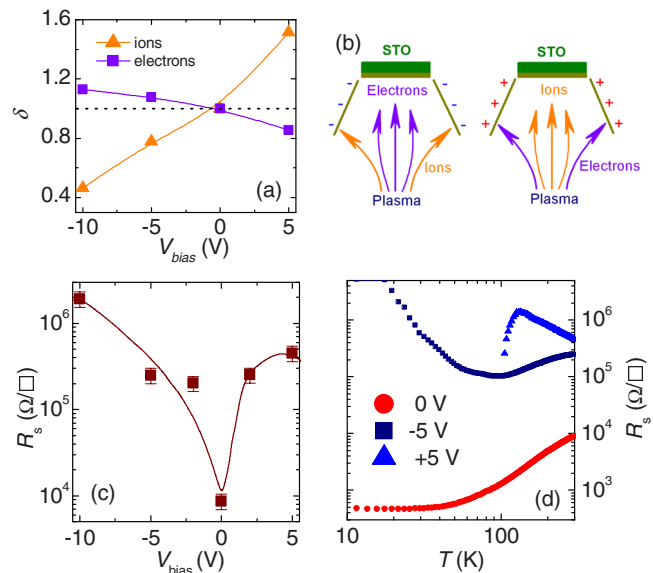


FIG. 3. (Color online) (a) The relative integrated charge, δ , of both ions and electrons at different V_{bias} of $-10 \text{ V} \leq V_{bias} \leq +5 \text{ V}$ in comparison with that of $V_{bias}=0$ V during film deposition at $P_{O_2} \approx 1 \times 10^{-4}$ Pa. (b) Sketches of the corresponding response of the plasma charge flux to the negative bias V_{bias} (left) and positive V_{bias} (right). (c) The V_{bias} dependent sheet resistance R_s of the amorphous STO/STO heterostructures, measured at room temperature. (d) The temperature dependent R_s of STO/STO heterostructures under different V_{bias} of -5 , 0 , and $+5$ V. All lines are guide to the eyes.

amount of atomic oxygen and change significantly the plasma composition by formation of diatomic oxides for reactive plume cations.^{20,21} For $P_{O_2} > 10$ Pa, a strong decay of plasma plume before reaching the substrate is observed. In short, substantial collisions and reactions of oxygen gas with plasma species occur at $P_{O_2} \geq 1$ Pa, which is consistent with previously reported results.^{20,21} Figure 2(c) shows the interfacial conductivity of the formed heterostructures versus P_{O_2} for $V_{bias}=0$ V. It is obvious that the highly conductive (metallic) interfaces at $P_{O_2} \leq 0.1$ Pa are linked to the free-expansion plasma, which probably results from the reactivity of the plasma compositions at low oxygen pressures as discussed elsewhere.¹²

Generally, the free-expansion plasma consists of a large fraction of energetic atomic neutrals, a small fraction of energetic atomic ions [in the range of 1%–5% (Ref. 21)], and electrons with energies below several electronvolts.^{20,21} To investigate the respective role of electrons and ions in the plasma plume on the interfacial conductivity during film growth, the charge flux balance at the substrate was modified by varying the V_{bias} applied on the truncated cone electrode at $P_{O_2} \approx 1 \times 10^{-4}$ Pa, as illustrated in Fig. 1. Figure 3(a) shows the relative integrated charge, δ , of both ions and electrons at different V_{bias} of $-10 \text{ V} \leq V_{bias} \leq +5 \text{ V}$ in comparison with that of $V_{bias}=0$ V, which is close to the plasma potential of 0.5 eV, during one pulse deposition (in a period of 40 μs). As shown in the figure, when a positive bias of $V_{bias} \leq +5$ V is applied, a confinement of more positive ions up to 51.1% in addition with a reduction in the electron flux by up to 13.5% at $V_{bias}=+5$ V is realized, which is sketched in Fig. 3(b). On the other hand, when a negative bias of $V_{bias} \geq -10$ V is applied, a deflection of more electrons to the substrate up to 14.1% in addition to a reduction in positive ion flux up to 54.2% is also observed. Interestingly, in both cases, a dramatic increase in R_s of more than one order

is observed at room temperature [Fig. 3(c)]. These results strongly indicate that both positive ions and electrons contribute to the interfacial conductivity. Note that further increasing V_{bias} to $V_{\text{bias}} > +5$ V or $V_{\text{bias}} < -10$ V results in a tendency toward decreasing R_s , thus increasing interface conductivity, which is not discussed in this letter. Figure 3(d) shows the typical temperature dependent R_s of the heterostructures deposited at $V_{\text{bias}} = -5, 0, \text{ and } +5$ V. The interface is metallic at $V_{\text{bias}} = 0$ V as reported previously.¹² While, a metal-to-insulator transition at around 100 K upon cooling is observed in the sample deposited at $V_{\text{bias}} = -5$ V. On the other hand, a semiconducting behavior is observed at $V_{\text{bias}} = +5$ V. These results are retrospective to the conducting behavior of LAO/STO samples deposited under higher oxygen pressures of $P_{\text{O}_2} \geq 0.01$ Pa,^{12,22} and strongly indicate that slight changes in the plasma composition may result in dramatic effects on the interfacial conductivity.

It has been indicated that the conductivity in the amorphous STO/STO heterostructures results from the oxygen vacancies formed on the crystalline STO substrate side due to the outward diffusion of oxygen ions to feed the oxygen-deficient capping films.¹² The increase in the interfacial sheet resistance as shown in Fig. 3(c) therefore indicates a reduction in the concentration of oxygen vacancies in STO substrates near the interface, which probably results from a higher oxygen incorporation process of the grown films from the ambient oxygen gas upon the application of V_{bias} . The incorporation of oxygen into the grown sample is a complex process,^{17,21,23} which could occur in all the steps during the growth of oxide thin films: during the time needed to stabilize the oxide substrate at high temperature before deposition, during the laser ablation itself, and during the sample cooling down after deposition.²³ Since our STO films are deposited at room temperature, there are negligible oxygen exchanges between the oxide system (the substrate and the film) and the background oxygen gas both before and after film deposition. Therefore, the oxygen uptake of the grown films occurs mainly during the laser deposition process itself, which is consistent with the *in situ* x-ray photoelectron spectroscopy measurements.¹² More specifically, the oxygen incorporation occurs only during the laser pulse where the plasma interacts with the sample surface (in a period of 40 μs) rather than the interval between pulses (with a period of 1 s).^{12,23} Generally, it is the atomic oxygen, which mainly comes from the ablation of the target and the dissociation of molecular oxygen by collisions with energetic particles in the plasma, that takes part in the oxygen incorporation process at each laser pulse.²³ However, when the STO is used as a substrate, the oxygen ions in STO can serve as a source of the oxygen incorporation even at room temperature for $P_{\text{O}_2} \leq 0.1$ Pa.¹² This results in oxygen vacancies dominant interfacial conductivity in our STO-based heterostructures. It is reasonable that the concentration of the oxygen vacancies in STO substrates and the resultant interfacial conductivity are related to the oxygen incorporation of the capping films from the background oxygen gas, which is determined not only by the oxygen incorporation due to the collisions with plasma species but also by chemical reactions on the sample surfaces.^{21,23} Since both electrons and ions will take part in these processes, at this moment, it is not clear yet whether the increase in R_s under V_{bias} is due to the enhanced amount

of atomic oxygen during collisions or due to the accelerated oxidization process at the sample surface.

In summary, the conductivity at the interface between crystalline STO substrates and amorphous STO films exhibits strong dependence on oxygen pressure of film growth by PLD. This is dominated by the dynamics of the PLD plasma expansion in the oxygen background gas. By controlling the charge balance in plasma plume with an external bias, the interfacial conduction of the heterostructures can be tuned to be metallic or semiconducting. This sheds light on the origin of the q2DEG in LAO/STO heterostructures and provides a new opportunity to tailor the low-dimensional interface states of complex oxide heterostructures.

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