Effect of various deposition conditions on the electrical properties of LAO/STO hetero interfaces

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Abstract. We have examined the effects of partial oxygen pressure and laser energy density on the electrical transport properties of thin LAO films grown on (100) TiO$_2$-terminated SrTiO$_3$ substrates. Films were grown by pulsed laser deposition monitored by in-situ reflection high-energy electron diffraction (RHEED). Layer-by-layer growth, as indicated by clear RHEED oscillations, can be obtained in a wide range of oxygen partial pressures from $10^{-6}$ to $5 \times 10^{-2}$ mbar. Transmission electron microscopy (TEM) analysis shows that the interface is coherent and atomically sharp for all deposition conditions. The STO substrate is oxygen self reduced at an oxygen pressure of $10^{-6}$ mbar and the electrical properties of the interface are dominated by the presence of oxygen vacancies. By increasing the oxygen pressure above $10^{-4}$ mbar, the substrate itself is insulating but the interface still shows metallic conductivity. However, the interface becomes insulating at an oxygen pressure of $5 \times 10^{-2}$ mbar. We also found that the interface exhibits insulator-to-metal transition by changing the laser fluence during the deposition of the film. The interface prepared at $5 \times 10^{-2}$ mbar shows metallic conductivity at high fluence, above 3.5 J/cm$^2$.

1. Introduction
Perovskite-structured oxides are complex materials which exhibit a vast number of functional properties. When two perovskite materials are brought together to form an interface, new phenomena may occur which normally are not present in the bulk. The interest of the interfaces between insulating perovskite oxides has rapidly grown since the observation of high electrical conductivity and mobility in the hetero interface formed between a thin LaAlO$_3$ (LAO) film deposited on a TiO$_2$-terminated SrTiO$_3$ (STO) substrate [1]. It was suggested that an atomically sharp interface is a prerequisite for the electrical properties of the interface. This implies that the interface properties may strongly depend on the deposition conditions.

The origin of the conductivity in the LAO/STO interface is not yet fully understood. One model suggests a polar discontinuity at the interface as a driving force. Due to different formal valences of Ti and Al, half of an electron charge per unit cell may be released at the interface to compensate for the growing electrostatic potential [2]. On the other hand, oxygen vacancies in the STO substrate can also give very similar electrical behavior [3]. In our previous study we have shown that oxygen vacancies may be present in the STO substrate near the LAO/STO interface prepared at low oxygen pressure, resulting in very high electrical conductivity and mobility values [4]. The strong dependence of electrical conductivity on the deposition pressure and the important role of oxygen vacancies were also indicated in other studies [5, 6]. Another work found that if the LAO/STO interface is prepared at higher oxygen pressure, $2 \times 10^{-3}$ mbar, the electrical conductivity is substantially suppressed, but the sheet charge carrier density is about the limit deduced from the polar discontinuity model [7].
Fig. 1. RHEED oscillations of the LAO films prepared at different laser fluence at 5x10^{-2} mbar oxygen pressure.

It was suggested that the oxygen vacancies in the STO substrate are filled at this oxygen pressure and the residual conductivity is due to only intrinsic doping at the interface. If this were the case, metallic electrical conductivity should be observed in interfaces prepared even at higher oxygen pressures, provided that the interface structure is the same.

We have prepared LAO/STO hetero interfaces by pulsed laser deposition (PLD) in a wide range of oxygen pressure from 10^{-6} up to 5x10^{-2} mbar. LAO films were grown in layer-by-layer mode under all deposition conditions. TEM studies show that the interface structure is clearly coherent and atomically sharp. The electrical conductivity of the interface is gradually decreasing with increasing oxygen pressure. Finally, an interface prepared at oxygen pressure 5x10^{-2} mbar shows no conductivity at all when the LAO film is deposited at our normal laser fluence – it becomes conducting if the fluence is increased three times. This indicates that it is still possible that oxygen vacancies dominate the electrical properties of the LAO/STO interfaces prepared at all oxygen pressures.

2. Sample preparation

We used a KrF excimer laser Lambda Physik Compex 205 (pulse duration ~25 ns, repetition rate 1 Hz) for pulsed laser deposition. In-situ reflection high-energy electron diffraction (RHEED) with electron energy of 35 kV and beam current of 1-50 µA was used to monitor the film growth and the surface morphology during the deposition process. The RHEED was equipped with a differential pumping unit which allows operation at high ambient pressures, up to 0.5 mbar.

Single crystal substrates of SrTiO_3 were cleaned in acetone and isopropanol alcohol, etched 30 s in commercially available Si etching solution (BHF, pH=5.5) and annealed for 2 hours at 950 °C and in pure oxygen flow. The atomically flat character of the substrate surface was confirmed by atomic force microscopy (AFM). The substrates were attached to a heater block using silver glue and heated to 70°C at ambient pressure for 15 min, then introduced into vacuum (10^{-7} mbar) and heated further at a rate of 10°C/min. At 250°C, oxygen gas was let into the chamber at the deposition pressure and the temperature was thereafter increased by 40°C/min up to 800°C. The stability at low pressure was limited by the precision of the mass-flow controller, but was better than ±2.5x10^{-7} mbar at all times. A LAO single crystal was used as ablation target. After deposition, samples were cooled down at a rate of 10 °C/min keeping the same oxygen pressure as during deposition. Laser energy was measured directly in the deposition chamber after all optical components to eliminate possible energy losses. The area of the beam spot was measured at the surface of a sintered STO target placed exactly in the position of the LAO target. The beam spot area and laser energy in the beam were varied in the range of 2-4 mm² and 50-75 mJ, correspondingly. Resulting laser fluence values were between 1.25 and 3.7 J/cm². Fig. 1 shows RHEED oscillations during the growth of LAO films at oxygen pressure 5x10^{-2} mbar.
Table 1. Electrical transport properties of the 15 unit cell thick LAO/STO hetero interfaces prepared at different partial oxygen pressure and laser fluence. All values are measured after removing photo-induced charge carriers in darkness.

| Sample | Oxygen pressure, mbar | Laser fluence, J/cm² | $R_s$ at 300 (2) K Ω | $n_s$ at 300 (2) K cm⁻² | $\mu_{ii}$ at 300 (2) K cm²/Vs |
|--------|------------------------|----------------------|---------------------|-----------------------|------------------------|
| 618    | $10^{-6}$              | 1.5                  | 50 $(10^{-2})$      | 3x10¹⁶(4x10¹⁶)       | 5 $(1.5x10^4)$         |
| 623    | $10^{-4}$              | 1.5                  | 6x10³ (150)         | 2x10¹⁵(2x10¹³)       | 5 $(2x10^3)$           |
| 676    | $5x10^{-2}$            | 1.5                  | > 10 GΩ             | n/a                   | n/a                    |
| 724    | $5x10^{-2}$            | 3.7                  | 1.2x10⁵ (n/a)       | n/a                   | n/a                    |

mbar and different laser fluence of 1.25, 1.5, 3.0 and 3.7 J/cm². In all cases, films are grown in layer-by-layer mode with similar growth rate. AFM showed step-like structure of LAO films similar to the STO substrate.

3. Results and discussion
Electrical measurements were performed in a four probe Van der Pauw configuration in the temperature range between 300 and 2 K. Electrical contacts were made by sputtering of Ti/Au pads through metal masks. The samples were kept in darkness for at least 24 hours in order to remove photo induced carriers.

First, we focus on transport properties of 15 unit cell thick LAO films deposited at different oxygen pressures and laser fluence of 1.5 J/cm². The resistances and Hall charge carrier densities of these samples are listed in Table 1. It is evident that the resistance increases with increased oxygen pressure and finally the sample becomes insulating at an oxygen pressure of $5x10^{-2}$ mbar. The charge carrier density decreases but saturates at $10^{-4}$ mbar. All conducting samples show metallic behavior in the temperature range 300-2 K.

We performed high resolution transmission electron microscopy studies (TEM) using a Philips CM 200 field emission gun TEM operating at 200kV in order to probe the intrinsic structure of the interface. TEM images of interfaces prepared at $10^{-6}$, $10^{-4}$ and $5x10^{-2}$ mbar are shown in Fig. 2. It shows that the interfaces are coherent and atomically sharp in all cases. No interstitial substitution and other defects could be seen.

Electrical resistance of samples prepared at $5x10^{-2}$ mbar depends on the laser energy density at the target surface during the deposition. At 3.0 J/cm², the LAO/STO interface shows conductivity in the light, but it vanishes in the darkness after some time. An interface prepared at even higher fluence of 3.7 J/cm² remains conducting also in darkness after very long time. The resistivity is higher than for samples prepared at lower oxygen pressure conditions, but the sample shows metallic behavior.

What is the reason for the dependence of electrical properties on different deposition parameters? If one assumes that intrinsic doping (i.e. polar discontinuity at the interface) causes the electrical conductivity at the LAO/STO interface, then it should be similar for any interface with the same thickness of LAO films prepared under different conditions, provided that the interface structure is not altered. Our results show that this is not the case: the electrical conductivity vanishes at high oxygen pressure, while the interface remains atomically sharp as shown by RHEED, AFM and TEM data. This indicates that the oxygen vacancies in the STO substrate may be a dominant mechanism of the electrical conductivity. Produced in the STO substrate at low oxygen pressures during the deposition of the LAO film, oxygen vacancies result in high electrical conductivity and mobility values. At higher oxygen pressures, however, all vacancies are filled and no conductivity can be detected. In this respect, the insulator-to-metal transition at high laser fluence interfaces is very important.

Since all deposition conditions (pressure, temperature, target-substrate distance and deposition rate) were...
kept constant, the only difference is the energy of oncoming particles hitting the surface of the STO substrate. At high energy, the formation of oxygen vacancies may be enhanced resulting in metallic conductivity at very high laser fluence.

The interface microstructure prepared at high laser fluence, however, may be different from normally deposited LAO films. Though we could not see any difference in the RHEED oscillations, it is still possible that the stoichiometry of the film may be altered. In order to eliminate this possibility, more studies of the interface microstructure need to be done. We are currently investigating this issue.

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