Low temperature transport measurements on atomically smooth metallic and oxygen deficient strontium titanate

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Abstract. Atomically smooth, TiO$_2$ terminated SrTiO$_3$ (STO) substrates were prepared using a combination of chemical and thermal annealing treatments. The TiO$_2$ terminated surface was obtained by etching with aqua regia solution and thermal annealing at 1000 °C for 30 min. The subsequent vacuum annealing at 830 °C for 10 min generated an atomically smooth and metallic surface of STO. In this paper, we report low temperature transport measurements down to 50 mK on these samples which clearly exhibit a metallic temperature dependence in the resistance. The samples show no sign of superconductivity down to the lowest temperatures. The $R(T)$ data provide information on the physical origin of metallic behavior in STO, which might also be relevant to the current research interest in oxide interfaces.

1. Introduction
For the past decade SrTiO$_3$ (STO) has been on the vanguard of complex oxide physics. Perhaps the most intriguing discovery is the existence of a metallic state at the heterointerface of LaAlO$_3$/SrTiO$_3$, which also displays Shubnikov-de Hass oscillations [1]. This junction was later shown to undergo a superconducting transition around 200 mK [2]. The authors demonstrate that the superconducting transitions is Kosterlitz-Thouless-like indicating the two dimensional nature of the electron gas at the interface. Interestingly, a two dimensional electron gas has been observed on the surface of cleaved STO in vacuum, using angle resolved photo emission spectroscopy [3]. Metal-insulator transitions have also been observed in bulk and thin film STO [4, 5]. A superconducting ground state has also been observed in bulk, oxygen deficient STO for carrier concentrations as low as $5.5 \times 10^{17} cm^{-3}$ [4]. Apart from the interesting physics of intrinsic STO, it is also valuable as a substrate for growing materials such as thin films of perovskite oxides. A prerequisite for epitaxial crystal growth is an atomically smooth substrate. There are several methods for making atomically smooth STO [6, 7, 8]. However, producing atomically smooth metallic STO has proven to be a formidable task. Doping STO by vacuum annealing for long periods of time ($\sim$ 1-10 hr) has led to rough surfaces [9], unacceptable for epitaxy.

We have produced atomically smooth TiO$_2$ terminated samples that exhibit metallic behavior down to 50 mK. The procedure is relatively simple and the results are reproducible. The annealing time used is relatively short, so it is expected that only a thin film on the surface of the substrate is conducting. In this paper we present transport measurements on two samples prepared in the same manner and an estimation of the conducting layer thickness.
Figure 1. Temperature dependence of the normalized resistance for two samples by the resistance at 294 K. \( R(294 \text{ K}) \) is 34.8 \( \Omega \) and 19.8 \( \Omega \) for sample 1 and 2, respectively.

2. Sample Preparation
The samples are prepared from commercially available STO substrates from the CrysTec company. The substrates used in this study are 0.5 mm thick and oriented in the (100) direction. The samples are treated further to obtain the atomically smooth TiO\(_2\) terminated surface with a conducting layer. The atomically smooth TiO\(_2\) layer was obtained using a wet-etch technique [6]. The untreated samples are first cleaned with ethanol for 5 min. They are then soaked in 50 \(^\circ\)C DI water for 30 min. After the soak the samples are etched with an aqua regia solution (3:1 HCl to HNO\(_3\)) for 12 min. The soaking and etching take place in a sonicator. After etching, the samples are rinsed with DI water. Additional cleaning with acetone and ethanol is performed before annealing the samples in air at 1000 °C for 30 min. In order to obtain the metallic surface the samples are annealed at 830 °C for 10 min. in vacuum (10\(^{-7}\) Torr). Vacuum annealing is known to cause oxygen deficiency in STO, and the oxygen vacancies introduce charge carriers [9]. Removal of an oxygen atom from STO leaves behind a doubly charged (+) oxygen vacancy and introduces two free electrons. Therefore, it is expected that the charge carriers from oxygen vacancy doping are electrons. This has been confirmed by preliminary Hall effect measurements which indicate negative charge carriers. This result will be published elsewhere. Samples made using this process have been characterized by AFM and LFM. The samples have an rms surface roughness of about 1.7 Å with wide terraces of unit cell height (3.9 Å).

3. Metallic Layer Thickness
One quantity of particular interest is the thickness of the conducting layer. Currently no experiments have been done to directly determine this quantity. However, the thickness can be estimated from the diffusion constant of oxygen in STO and the annealing time:
Figure 2. Resistance measurement scheme: $R = V_{CD}/I_{AB}$ and $R' = V_{AD}/I_{BC}$. As an example, $V_{CD}$ indicates the voltage measured across contacts C and D. Sheet resistance is plotted against temperature in Fig. 3.

$$\ell = \sqrt{Dt},$$

where $\ell$ is the thickness of the metallic layer, $D$ is the diffusion constant, and $t$ is the annealing time. The diffusion constant of oxygen ions in single crystal STO has been measured by Paldino et al. [10]. For the temperature used in annealing the samples, one can estimate the diffusion constant to be $5 \times 10^{-11}$ cm$^2$ s$^{-1}$, which combined with an annealing time of 10 min gives a thickness of roughly 2 $\mu$m.

4. Resistance Measurements

Resistance measurements were made on two samples. Both samples were prepared using the same method described above. The resistance was measured down to 145 mK for one sample and 58 mK for the other. The resistance was measured using a standard four wire technique. The measurements were made with a 13 Hz ac driving current and the voltage across the sample was measured using a lock-in referenced at that frequency. At low temperature, the excitation current was 9.7 $\mu$A. This current was chosen to minimize heating to the sample. The resistance of each sample was measured while cooling and warming the cryostat. Each sample was measured on a different run of the cryostat. The whole range of $R$ vs. $T$ for both samples is shown in Fig. 1. The samples show metallic behavior down to the lowest temperatures measured. The RRR of both samples, inferred from Fig. 1, is about 3000, indicating high purity. In Fig. 1 the resistance of each sample is normalized by the resistance value at room temperature: $R(294 \text{ K})$ is 34.8 $\Omega$ for sample 1 and 19.8 $\Omega$ for sample 2. The dependence on sample size and lead placement is removed by taking the ratio of the resistance to a value at a reference temperature. The two curves lie on top of each other for most of the temperature range and only begin to deviate below $\sim 1$ K, implying that this process produces reproducible metallic samples.

It was observed that in a thin film of vacuum annealed STO with a thickness $\sim 2.5$ $\mu$m a metal-insulator transition, attributed to carrier freeze-out, occurred at 78 K [5]. The thin film was annealed at 950 °C at $\sim 10^{-7}$ Torr for one hour, where it is expected that the distribution of carriers in the film is homogenous. The expected conducting film thickness of our samples is similar to that of the aforementioned thin film. However, we do not observe a clear metal-insulator transition in our samples down to the lowest temperature, although sample 1 exhibits a slight increase in resistance below 0.7 K of about 3% indicating the presence of weak localization.
Figure 3. Sheet resistance $R_\square$ of both samples. The upper curve is for sample 1, and the lower curve is for sample 2. Warming and cooling data are included for both graphs.

This behavior might be caused by a large gradient in charge carrier density where the metallic behavior is confined to a small layer on the surface.

The sheet resistance of both samples was calculated, at room temperature, using the van der Pauw method [11]:

$$R_\square = \frac{\pi}{\ln(2)} \frac{1 + R'/R}{2} f \left[ \frac{R}{R'} \right] R,$$

(2)

$R$ and $R'$ are defined in Fig. 2 and $f$ is a slowly varying function given in [11]. The sheet resistance at temperatures lower than room temperature is inferred from the ratio of sheet resistance to sample resistance at room temperature. The value of the ratio $R_\square/R$ is 1.69 and 1.98 for sample 1 and 2, respectively. It is assumed that the change of this ratio with temperature is negligible. The sheet resistance for the whole temperature range is shown in Fig. 3.

5. Conclusion

It was shown that samples of TiO$_2$ terminated STO which were subsequently vacuum annealed at 830 °C for 10 min show metallic behavior down to 58 mK. After normalization the resistances curves of both samples fall directly onto of one another, indicating the reproducibility of the procedure. It was also estimated, based on the diffusion of oxygen atoms in STO, that the thickness of the conducting layer is approximately 2 $\mu$m. Although, it is more likely the metallic behavior is contained in a thinner layer near the surface.

Acknowledgments

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