Relaxation of transport properties in electron doped SrTiO$_3$

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We electron-dope single crystal samples of SrTiO$_3$ by exposing them to Ar$^+$ irradiation and observe carrier mobility similar in its magnitude and temperature dependence to the carrier mobility in other electron-doped SrTiO$_3$ systems. We find that some transport properties are time-dependent. In particular, the sheet resistance increases with time at a temperature-dependent rate, suggesting an activation barrier on the order of 1 eV. We attribute the relaxation effects to diffusion of oxygen vacancies - a process with energy barrier similar to the observed activation energy.

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Perovskites attract considerable interest for their wide range of intriguing properties, including colossal magnetoresistance in manganites [1, 2], high-$T_C$ superconductivity in cuprates [3], ferroelectricity in titanates [4], and itinerant magnetism (ferromagnetism and antiferromagnetism) in ruthenates [5, 6]. In addition to their individual intriguing properties, for applications, it is particularly appealing that perovskite-based heteroepitaxial structures can be grown epitaxially, commonly on SrTiO$_3$, thus enabling a wide spectrum of new functionalities which may form the basis for future oxide electronics.

In addition to serving as a substrate for perovskite films, SrTiO$_3$ may be used to produce high mobility conductors that would be useful in future oxide electronics. A familiar way to obtain a SrTiO$_3$-based high mobility conductor is by electron doping [7, 8]. Recently it has been demonstrated that SrTiO$_3$-LaAlO$_3$ heterostructures prepared in a particular way also yield high mobility conductivity. Some groups attributed this phenomenon to the formation of a quasi two dimensional electron gas at the SrTiO$_3$-LaAlO$_3$ interface due to polarity discontinuity [9, 10], while others argue that it is related to the formation of oxygen vacancies [11, 12, 13].

Both methods yield high mobilities on the order of 10,000 cm$^2$V$^{-1}$s$^{-1}$ at 4.2 K [7, 8, 9, 11, 12, 13], suggesting SrTiO$_3$ may be an important component in oxide-based electronic devices. Some possibilities for such use have been demonstrated already in its use as a gate [14] and a channel [15, 16] in field effect transistors.

Electron doping SrTiO$_3$ is commonly achieved by creating oxygen vacancies which transform SrTiO$_3$ into SrTiO$_3$-$\delta$. Oxygen vacancies may be induced in various ways including high-temperature annealing in oxygen reduced pressure, and Ar$^+$-irradiation [7, 8, 17, 18, 19]. Ar$^+$ irradiation is also the method that we use to electron-dope our samples.

For any future applications of electron-doped SrTiO$_3$, it is important to elucidate the stability of its electrical properties over time. For this reason, in this report we focus on relaxation effects of electrical transport in electron-doped SrTiO$_3$. We have irradiated single crystal samples of SrTiO3 with Ar$^+$ and explored the changes in the sheet resistance, mobility and magnetoresistance (MR). We find that while the sheet resistance changes with time (although qualitatively it remains unchanged), the mobility and the MR are time-independent. Our analysis indicates that the activation energy for the observed relaxation is about 1 eV which is the energy scale observed for diffusion of oxygen vacancies. This suggests that diffusion of oxygen vacancies is responsible for the observed relaxation effects.

Our samples are commercially available [20] one sided polished SrTiO$_3$ crystals (5 x 5 x 0.5 mm$^3$). The SrTiO$_3$ samples were irradiated with Ar$^+$ ions, accelerated with 4 kV and the beam’s fluence was about 10$^{15}$ ions per second per cm$^2$. The estimated penetration depth of the ions, L, in Å is given by the empirical formula [21, 22]

$$L = 1.1 \frac{E^{2/3}W}{\rho(z_t^{2/3}+z_i^{2/3})},$$

where E is the energy in eV, W is the atomic weight of the target in atomic mass units, $\rho$ is the target density, and $z_i$, $z_t$ are the atomic numbers of the ions and the target, respectively (since SrTiO$_3$ is a compound, we use for the target the weighted average of the atomic weights and numbers). In our case $L \approx 120\,\AA$; therefore, we expect that the thickness of the conducting layer will be on this order.

The samples become conducting when the irradiation time exceeds 30 sec and no more changes in conductivity are observed after several minutes of irradiation. To irradiate specific parts of a substrate in shapes that will allow resistivity and Hall measurement, we use conventional photolithography that leaves 1 micron-thick photoresist on the samples except for windows in the desired shapes.

Figure 1a shows sheet resistance of Ar$^+$-irradiated SrTiO$_3$, determined with four point measurements. At low temperatures a quadratic behavior is observed for the sheet resistance ($R_{\|}$), $R_{\|} = a + bT^2$, typical for electron-electron interactions (except for samples with very high sheet resistance that exhibit resistivity minima). We note that the residual resistivity ratio (RRR) in our samples exceeds in some cases 500. Similar and even higher values of RRR have been reported for electron-doped SrTiO$_3$ and SrTiO$_3$-LaAlO$_3$ heterostructures [11].

The sheet resistance decreases significantly with irra-
radiation as a function of $R$ (+). The lines are fits to a linear function. (b) $R_R$ waiting, as a function of sheet resistances measured after different doses of irradiation (except for the range of temperatures with resistivity minima - if it exists). This indicates that in this range of doping there is no qualitative change in the resistivity.

Time-dependent measurements (Figure 1b) show that the sheet resistance of the irradiated sample changes with time at a temperature-dependent rate. Similar to the relation between sheet resistance with different doses of irradiation, we find a linear relation also between sheet resistances measured after different waiting times (see inset of Figure 1a); namely, there is no qualitative change in the resistivity behavior.

To extract the relevant energy scale for the relaxation in the sheet resistance, we explore the temperature dependence of the relaxation rate. As seen in the inset of Figure 1b, this rate is well fitted with Arrhenius law, $\alpha e^{-E/kT}$, where $E \approx 0.97 eV$. This activation energy is practically identical to the activation energy of oxygen vacancies in $\text{SrTiO}_3$ [24], and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ [23]. Hence, the observed relaxation is very likely due to diffusion of oxygen vacancies. While we do not address here the change in the conducting regions due to this diffusion, we note that irradiated regions which are few microns apart remain electrically disconnected.

In the following we explore how this diffusion affects other transport properties.

Figure 2 shows the mobility and sheet resistance of one of our irradiated samples after 60 and 90 seconds of irradiation. In contrast to the resistance, the change of the mobility with irradiation dose and relaxation time is hardly detectable. The observed mobility is consistent in magnitude and temperature dependence with previous reports [11].

Figure 3 shows the MR at various temperatures measured after two different relaxation times. Similar to the mobility, the magnetoresistance $\Delta \rho/\rho$ does not change with relaxation time or irradiation dose (not shown here) despite the significant change in resistance. The inset of Figure 3 shows that the MR data at temperatures higher than 50K obey Kohler’s rule 25; namely, $\Delta \rho/\rho$ scales with $H/\rho$, implying it is a function of $H\tau$ alone (where $H$ is the magnetic field and $\tau$ is the scattering time). That the MR does not change between different relaxation times or different irradiation times suggests that the scattering time is practically unchanged.
In passing, we also note that, the MR below 50K does not obey Kohler’s rule and the angular dependence is different, indicating that the mechanism of the MR at low temperatures is not the same as above 50K.

The linear relation between sheet resistances with different doses of irradiation and the linear relation between sheet resistances measured after different waiting times, indicate that the qualitative behavior of the resistivity does not change in a detectable way. Together with the fact that the mobility and the scattering time do not change when the sheet resistance changes, it may suggest that the diffusion of the oxygen vacancies decreases the number of charge carriers while hardly affecting the scattering rate of the remaining charge carriers. It remains to be checked how this observation is correlated with time dependent variation in the thickness of the conducting layer and the spatial variation of charge carriers density within this layer. Answers to these questions are important for the potential use of electron-doped SrTiO$_3$ in future oxide electronics.

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