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Surface depletion in doped SrTiO$_3$ thin films

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Strong effects of surface depletion have been observed in metallic La-doped SrTiO$_3$ thin films grown on SrTiO$_3$ substrates by pulsed-laser deposition. The depletion layer grows with decreasing temperature due to the large temperature-dependent dielectric response of SrTiO$_3$. When the depletion layer becomes comparable to or exceeds the thickness of the doped film, the Hall mobility shows significant enhancements as more of the electron distribution extends into the undoped substrate, in conceptual analogy to modulation doping in compound semiconductor heterostructures.

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Electron-doped SrTiO$_3$ is a good metal, exhibiting low-temperature Hall mobility in excess of 10 000 cm$^2$/V s.~$^{1-3}$ The presence of a nearby ferroelectric instability provides significant screening by polar phonons, resulting in metallic conduction with increasing mobility as temperature decreases, while the electron density remains nearly temperature independent. This is despite a large effective mass estimated at $\sim 10m_0$.~$^1$ Substitutional doping of Nb on the Ti site or La on the Sr site forms hydrogenlike donor states which generate conduction electrons. The semiconductor characteristics of SrTiO$_3$, as well as the availability of high-quality SrTiO$_3$ substrates lattice matched to many transition metal oxides, have made thin-film studies of SrTiO$_3$ central to the notion of “oxide electronics.”

Controlled doping during thin-film growth of SrTiO$_3$ is complicated by the role of oxygen vacancies, which also generate conduction electrons. This mechanism often dominates below oxygen partial pressures $P_{O_2}$ of $10^{-4}$ Torr in pulsed-laser deposition (PLD).~$^4$ However, it has also been observed that robust electron doping by Nb substitution during PLD is unsuccessful above a threshold $P_{O_2}$, which varies depending on the individual growth system.~$^5-7$ This propensity is suppressed for La-doped films, although the low-temperature carrier mobility is significantly reduced from levels achieved with Nb substitution.~$^8$ Despite this compromise, many perovskite heterostructures place a premium on well-controlled robust dopant profiles for their function. In this vein, the surface electronic structure of doped and undoped SrTiO$_3$ has been subject to intensive photoemission studies. Although theoretical studies have predicted a large density of intrinsic surface states,~$^9$ the effects of surface depletion have not been established in this material,~$^{10}$ unlike most compound semiconductors.

In this letter, we report the observation of significant surface depletion in metallic La-doped SrTiO$_3$ thin films. This phenomenon is unusually strong even at high carrier densities, due to the large dielectric background of SrTiO$_3$, orders of magnitude higher than in most semiconductors. We estimate a surface pinning potential of $\sim 0.7$ eV, as deduced from transport measurements and x-ray photoelectron spectroscopy (XPS). For very thin films, we find that the conduction electrons are spatially separated from the doped film and pushed into the substrate by the built-in potential due to surface bandbending, enhancing the low-temperature carrier mobility. Surface depletion is a likely contribution to surface dead layers discussed in many oxide thin films, which are often characterized by large dielectric constants and polar surfaces.

Doped SrTiO$_3$ films were grown in an ultrahigh-vacuum chamber by PLD, using a single crystal target of La (5 at.%)-doped SrTiO$_3$. A KrF excimer laser with a repetition rate of 5 Hz was used with fluence at the target surface of $\sim 1.7$ J/cm$^2$, and a target–substrate distance of 45 mm. Buffered HF-etched (001) SrTiO$_3$ substrates, presenting a TiO$_2$-terminated surface,~$^{11}$ were used to grow 100–1000 Å films at 800 °C. The thickness was monitored observing unit-cell reflection high-energy electron diffraction (RHEED) oscillations. Molecular O$_2$ and atomic O, generated by an rf radical source, were used at various partial pressures. After the growth, the temperature was lowered at a constant rate of 50 °C/min, keeping the oxidant gas pressure constant. The transport properties of the films were measured in a conventional Hall bar geometry with ohmic contacts obtained by laser annealing~$^4$ and Al evaporation. XPS was performed at room temperature for some of the films in a separate analysis chamber.

The basic experimental observation we wish to address can be seen in Fig. 1(a), which shows the temperature-dependent resistivity $\rho(T)$ for a series of films of La$_{0.05}$Sr$_{0.95}$TiO$_3$ with varying thickness, grown in 0.1 Torr of O$_2$. At these high oxygen pressures, oxygen vacancies in the film are suppressed. With decreasing thickness, $\rho$ increases dramatically, roughly by an order of magnitude going from 1000 Å to 100 Å. The Hall coefficient $R_H$ for the films was measured between 2 K and 300 K, using the film thickness $d$ determined from RHEED oscillations. The Hall effect was linear in magnetic field up to 14 T, and showed no additional structure for all temperatures. The temperature-dependence of the effective three-dimensional carrier density $n$ is given in Fig. 1(b), where $n = -1/(\epsilon R_H)$ and $\epsilon$ is the electron density.
charge, which has been found to be an accurate description in bulk (La,Sr)TiO$_3$ in this doping range. With decreasing temperature, the carrier densities of all of the films decrease markedly, in contrast to the nearly temperature independent $n$ observed in doped bulk single crystals. However, the loss of carriers is inconsistent with freeze-out, following rather a power law temperature dependence and saturating at a finite value. It is also noteworthy that thinner films show smaller $n$ at all temperatures.

A common interpretation of Fig. 1 is the existence of an insulating dead layer. To consider this issue, we first note that there was no evidence of diminished crystallinity near the surface, from either RHEED or x-ray diffraction. Therefore, we focus on the loss of carriers at the surface over a constant surface, from either RHEED or x-ray diffraction. Therefore, there was no evidence of diminished crystallinity near the insulating dead layer. To consider this issue, we first note that at all temperatures.

The temperature dependence of $d_0$ can be understood by considering the expression for a depletion layer

$$d_0 = (2\epsilon(T)\epsilon_0 V_B / e n)^{0.5},$$

where $\epsilon$ and $\epsilon_0$ are the SrTiO$_3$ and vacuum dielectric constants, respectively, and $V_B$ is surface pinning potential. Using $n = [La^{3+}]$ (asymptotically approached with increasing film thickness and temperature), and a typical value for the dielectric constant of thin-film SrTiO$_3$ $\epsilon(300 K) = 300$, one obtains $V_B = 0.7$ eV to reproduce the observed $d_0$ at room temperature, taking the value of $V_B = 0.7$ eV and $n$ as constant (consistent with bulk and thick film measurements), $\epsilon(T)$ can be estimated from $d_0(T)$, as shown in Fig. 2(b). The temperature dependence of $\epsilon$ is quite similar to that measured in films, rising by an order of magnitude at low temperatures, but significantly suppressed when compared to bulk single crystals. Therefore, we conclude that the intrinsic carrier density in the films is temperature independent, but the temperature dependence of the depletion layer reduces the total carrier number.

As an independent measure of surface depletion, ex situ XPS was performed for several La$_{0.05}$Sr$_{0.95}$TiO$_3$ films and a bare SrTiO$_3$ substrate. Figure 3(a) shows spectra near the valence-band maximum $E_V$ for three films of constant thickness (1500 Å) grown in $1 \times 10^{-6}$ Torr of O$_2$ (A), $1 \times 10^{-5}$ Torr of O$_2$ (B), and 0.1 Torr of O$_2$ (C). The carrier density of each film was measured as $8 \times 10^{20}$, $1 \times 10^{21}$, and $8 \times 10^{20}$ cm$^{-3}$, respectively, and all showed metallic conductivity down to low temperature. Films A and B, containing oxygen vacancies, have carrier densities higher than the La$_{3+}$ concentration ($8.4 \times 10^{20}$ cm$^{-3}$). Considering first the SrTiO$_3$ substrate, the valence-band edge is consistent with the chemical potential $\mu$ fixed close the conduction band by residual impurities and oxygen vacancies. Film C, grown in conditions identical to those in Figs. 1 and 2, shows a decrease in $|E_V - \mu|$, opposite to what would be expected from a Burstein shift. A similar trend is also observed in the shift of the peak positions. With increasing carriers (films B and A), $|E_V - \mu|$ systematically increases, consistent with degenerate semiconductor statistics and conduction-band filling, leading to a typical Burstein shift with respect to film C.

These systematic trends support the picture of bandbending at the surface deduced from transport measurements, since the XPS probing depth (<20 Å) is shorter than the depletion layer thickness ($d_B$). Figure 3(b) shows a scheme...
matic energy diagram of the La$_{0.05}$Sr$_{0.95}$TiO$_3$ film. The surface pinning potential can be estimated as $V_B = E_g - |E_V - \mu|$, where $E_g$ is room-temperature bandgap of SrTiO$_3$, giving $V_B \approx 0.69$ eV, in reasonable agreement to $V_B$ obtained previously. A quantitative analysis of the trend from films C to A is difficult, as the dielectric response of the film may evolve, and the depletion layer at high carrier densities is abruptly enhanced. In this configuration, the $E_0$, $E_2$, and $E_0$ donar sites, and distribute into the substrate by the built-in potential arising from surface bandbending. The mobility enhancement arises from this separation, as the conduction electrons are less sensitive to scattering by the ionized La$^{3+}$ impurities. This effect is significant despite the decrease in mobility due to a growing contribution of diffuse surface scattering with decreasing film thickness. Although La-doped SrTiO$_3$ exhibits relatively low mobility, these results demonstrate, in principle, that the notion of offset doping can be applied to oxide heterostructures as a means of increasing carrier mobilities.

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