Title
Electrostatic carrier doping of GdTiO3/SrTiO3 interfaces

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Two-dimensional electron gases (2DEGs) at interfaces between Mott insulators and band insulators have attracted significant attention because of unique properties, such as strong electron correlations, superconductivity, or magnetism. Furthermore, interfaces between the band insulator SrTiO$_3$ and the rare earth titanates (RTiO$_3$, where $R$ is a trivalent rare earth ion), which are Mott insulators, exhibit a fixed polar charge. In particular, $R^{3+}/O_2^−$ and $Ti^{4+}/O_2^−$ layers alternate along the (001) surface normal of RTiO$_3$, carrying formal $+1$ and $−1$ charges, respectively, which causes a diverging electrostatic surface energy due to the non-zero dipole moment on the RO-TiO$_2$ units. At the interface, these transition to a sequence of neutral layers, Sr$^{2+}/O_2^−$ and Ti$^{4+}/O_2^−$, of non-polar (001) SrTiO$_3$. The fixed interfacial charge can be compensated by a 2DEG, residing in the bands of the Mott and/or band insulator and bound to the interface by the fixed charge. In the absence of any other charge compensation, defects, interfacial mixing, roughness, and nonstoichiometry, the interface is expected to form an electronic boundary layer. All layers and superlattices were grown coherently strained to the LSAT. Aberration-corrected scanning transmission electron microscopy (FEI Titan G2 ChemiSTEM) was used to characterize the atomic structure of GdTiO$_3$/SrTiO$_3$ interfaces. Longitudinal and Hall resistivity measurements were made in Van der Pauw geometry using a Physical Properties Measurement System (Quantum Design PPMS). Ohmic contacts were 300 nm Au/20 nm Ni/40 nm Al for...
SrTiO	extsubscript{3} top layers and 300 nm Au/50 nm Ti for GdTiO	extsubscript{3} top layers. The top layer was Au for wire bonding with an Au wire.

The sheet resistances of GdTiO	extsubscript{3} grown directly on LSAT and of GdTiO	extsubscript{3} grown on SrTiO	extsubscript{3} buffer layers with different thicknesses are shown in Fig. 1(a). The GdTiO	extsubscript{3} film on LSAT with no SrTiO	extsubscript{3} buffer layer is insulating. While too resistive for meaningful Hall measurements, the Seebeck coefficient was measured and is positive (p-type), as found for stoichiometric GdTiO	extsubscript{3}. All bilayers are n-type and metallic if the SrTiO	extsubscript{3} thickness exceeded one unit cell (0.4 nm). Even the bilayer with one unit cell SrTiO	extsubscript{3} already exhibits a remarkable drop in resistance. The localized behavior for this sample is expected as the sheet resistance exceeds the critical Mott value ($\sim 10 \text{k}\Omega$). The sheet resistance should decrease with increasing SrTiO	extsubscript{3} thickness if the conductivity is due to the oxygen deficient SrTiO	extsubscript{3}. The constant sheet resistance for SrTiO	extsubscript{3} layers thicker than 20 nm indicates that it arises from a space charge layer of constant thickness and carrier density at the interface. The Hall resistance as a function of magnetic field $B$ was linear and n-type down to the lowest temperatures, in contrast to LaTiO	extsubscript{3}/SrTiO	extsubscript{3} (Refs. 15 and 16). All of the electrons contributing to the Hall resistance satisfy $\mu B \ll 1$. Although more than one subband with different mobility may be occupied, the Hall coefficient ($R_H$) is converted to an effective sheet density by $n_s = 1/eR_H$, where $e$ is the elementary charge. Figure 1(b) shows that $n_s$ is constant, $\sim 3.5 \times 10^{14} \text{cm}^{-2}$, for all bilayers, even for extremely thin SrTiO	extsubscript{3}. Thus there is little trapping at the LSAT/SrTiO	extsubscript{3} interface, at least on a scale of $\sim 3 \times 10^{14} \text{cm}^{-2}$. A similar result is obtained when the GdTiO	extsubscript{3} thickness is varied. The mobility increases with SrTiO	extsubscript{3} thickness [Fig. 1(b)]. Thus the decrease in sheet resistance for SrTiO	extsubscript{3} layers between 0.4 nm and 20 nm is due to an increase in mobility, not a change in sheet carrier concentration. The results are consistent with an interfacial mobile space charge layer of constant thickness with a sheet charge density of $\sim 3 \times 10^{14} \text{cm}^{-2}$. This carrier density closely corresponds to the $1/2$ electron per surface unit cell required to compensate for the polar discontinuity at the interface.

To further confirm the results, multilayer samples were investigated. Figure 2(a) shows the sheet carrier density for (SrTiO	extsubscript{3}/GdTiO	extsubscript{3}/SrTiO	extsubscript{3})	extsubscript{x} superlattices on LSAT as a function of the number of repeats $x$, each containing two GdTiO	extsubscript{3}/SrTiO	extsubscript{3} interfaces. If each repeat contributes the same sheet carrier density as the $x = 1$ trilayer, then the sheet

![FIG. 1. (Color online) (a) Sheet resistance as a function of temperature for GdTiO	extsubscript{3}/SrTiO	extsubscript{3}/LSAT structures with varying SrTiO	extsubscript{3} thicknesses, indicated by the labels. The GdTiO	extsubscript{3} film grown directly on LSAT is labeled “0 nm.” (b) Sheet carrier density and mobility at room temperature and 2.5 K.

![FIG. 2. (Color online) (a) Room temperature sheet carrier concentrations of SrTiO	extsubscript{3}/GdTiO	extsubscript{3}/SrTiO	extsubscript{3} multilayers as a function of multilayer repeats ($x$). The dashed line indicates the expected sheet carrier concentration scaling with number of repeats as calculated from the $x = 1$ sample. (b) High-angle annular dark-field scanning transmission electron microscopy image of the $x = 20$ multilayer.](https://doi.org/10.1063/1.3566011)
density should scale as shown by the dashed line. The experimental results closely follow the dashed line, independent of GdTiO₃ or SrTiO₃ thicknesses. The total carrier sheet density is not proportional to the total Gd in the superlattice nor is it proportional to the Gd concentration. It is proportional to the number of interfaces. The constant sheet carrier density per interface excludes interfacial intermixing as the source of the charge carriers, because the charge carrier density in this case should strongly depend on the precise interfacial composition.

Figure 2(b) shows a high-angle annular dark-field scanning transmission electron microscopy (HAADF/STEM) image of the sample with x = 20. Thicker sample regions appear to show intermixing of about one monolayer, but observation of thinner regions shows that the interface contains short steps, which overlap along the beam direction. Thus the interfaces are locally atomically abrupt. Comparison of sheet carrier densities of the x = 1 multilayer (two GdTiO₃/SrTiO₃ interfaces) with that of the GdTiO₃/SrTiO₃/LSAT structures (one interface) of Fig. 1(b) shows that the sheet carrier concentration of the multilayer is slightly less than twice that of a single interface. This is likely due to different electrostatic boundary conditions for GdTiO₃/SrTiO₃ and SrTiO₃/GdTiO₃ interfaces.

The interfacial space charge can be understood by noting that the fixed polar charge at the interface must be neutralized by negative space charge, mobile or fixed, and dictated by the available quantum states in the presence of the selfconsistent electrostatic fields/potentials. The SrTiO₃ is n-type (oxygen deficient) and GdTiO₃ is p-type. The fixed polar charge can be neutralized by an accumulation layer in the SrTiO₃, a hole depletion layer (negatively charged acceptors) in the GdTiO₃ and an inversion layer in the GdTiO₃. The mobile charge is close to that required to compensate the fixed polar charge at the interface: thus hole depletion in the GdTiO₃ is not sufficient to siphon off significant numbers of electrons from the mobile space charge. The interface may share the mobile charge between the SrTiO₃ and the GdTiO₃. The relatively strong temperature dependence of the electron mobility [Fig. 1(b)] and the absence of an anomalous Hall effect, potentially caused by the ferrimagnetism in the GdTiO₃, indicate that mobile charge is largely found on the SrTiO₃ side and that the conduction band alignment favors SrTiO₃ accumulation.

Because SrTiO₃ has the larger band gap, the band line-up must be of type II (staggered). First principle calculations confirm this.

The mobile charge distribution and band bending are modeled using a self consistent Poisson-Schrödinger solver, as shown in Fig. 3, using band lineups from first-principle calculations, a fixed interface charge of 3.4 × 10¹⁴ cm⁻² (modeled as a 0.2 nm layer with fully ionized dopants), an electron effective mass of 1, a 6-fold degeneracy of the conduction band, and dielectric constants of SrTiO₃ and GdTiO₃ of 300 and 30, respectively. The interfacial positive charge induces a high-density 2DEG. A deep quantum well is formed [Fig. 3(b)], but there is overflow of the electrons into the GdTiO₃. Despite the high effective mass/density of states, the high electron density drives the Fermi level above the SrTiO₃ conduction band minimum by approximately 0.7 eV, which is greater than the assumed conduction band offset. The GdTiO₃ conduction band is therefore near the Fermi level near the interface and the polar charges invert the p-type GdTiO₃ (Nₓ = 3 × 10¹⁹ cm⁻³), making it effectively n-type. From the simulations, the spatial extent of the quantum confined electron gas is ~3 nm. We note that the superlattice with only 4 nm SrTiO₃ is best described as a quantum well rather than two distinct interface space charge layers, yet the total electron density appears fixed by the polarization charge.

The model supports experimental observations, namely, that the mobile space charge density at the GdTiO₃/SrTiO₃ interface is perturbed very little by the LSAT even for small separations and that the transport is dominated by one carrier type. The electrical transport measurements indicate that the different 2DEG regions in multi-layer structures are not isolated, which may have been expected since the GdTiO₃ layers are p-type. Most importantly, the very tight binding of the electrons to the interface should allow for exploration of quantum and strong correlation effects. Figure 3 is based on an effective mass model that assumes slowly varying envelope wave functions. The wavefunctions are derived from d-bands that are likely better described by tight binding Hamiltonians with rapid spatial variations, far from the approximations used in conventional semiconductor heterostructures. Appropriate models need to be developed, especially those that also include electron correlations.

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Pseudocubic notation is used here for the orthorhombic RTiO$_3$.


M. Grundmann, BandEng program (unpublished).