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Two-dimensional electron gas in a modulation-doped $SrTiO_3/Sr(Ti, Zr)O_3$ heterostructure

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A two-dimensional electron gas (2DEG) in $SrTiO_3$ is created via modulation doping by interfacing undoped $SrTiO_3$ with a wider-band-gap material, $SrTi_{1-x}Zr_xO_3$, which is doped n-type with La. All layers are grown using hybrid molecular beam epitaxy. Using magnetoresistance measurements, we show that electrons are transferred into the $SrTiO_3$, and a 2DEG is formed. In particular, Shubnikov-de Haas oscillations are shown to depend only on the perpendicular magnetic field. Experimental Shubnikov-de Haas oscillations are compared with calculations that assume multiple occupied subbands. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4819203]

Two-dimensional electron gases (2DEGs) at interfaces between $SrTiO_3$ and other complex oxides exhibit unique phenomena, including superconductivity,[1] Rashba spin-orbit coupling,[2] and magnetism.[3–7] Most studies thus far have focused on 2DEGs at polar/nonpolar interfaces, such as $LaAlO_3/SrTiO_3$,[8–10] $LaTiO_3/SrTiO_3$,[11,12] and $GdTiO_3/SrTiO_3$.[13,14] Mobile carriers in these heterostructures arise from a polar discontinuity at the interface, which gives rise to extremely high carrier densities on the order of $\sim 3 \times 10^{14}\,cm^{-2}$ ($LaAlO_3/SrTiO_3$ interfaces typically have lower densities, for reasons that are not yet well understood[9]). An alternative route to high-mobility 2DEGs is modulation doping, originally developed for III–V heterostructures,[15] leading to devices such as high-electron mobility transistors,[16,17] and scientific discoveries, such as the fractional quantum Hall effect.[18] This approach spatially separates the mobile charge from the ionized dopants by transferring it into an undoped layer. A heterostructure that has suitable conduction band alignments is therefore essential for modulation doping.

Here, we show that a 2DEG in $SrTiO_3$ can be created by modulation doping. We use $SrTi_{1-x}Zr_xO_3$ as the doped, wider band gap perovskite, i.e., the analog of AlGaAs in GaAs/AlGaAs structures. $SrTi_{1-x}Zr_xO_3$ is a solid solution of cubic $SrTiO_3$ and orthorhombic $SrZrO_3$. The band gap of $SrZrO_3$ (5.6 eV (Ref. 19)) is substantially larger than that of $SrTiO_3$ (3.2 eV). The band alignment between $SrTiO_3$ and $SrZrO_3$ is Type I, with a conduction band offset, ΔE_c, of 1.9 eV.[20] Given the large ΔE_c, reasonable band offsets should be achievable even for small x, which serve to reduce the substantial lattice mismatch between $SrTiO_3$ ($a = 3.905$ Å) and $SrZrO_3$ (pseudocubic unit cell, $a \approx 4.1$ Å), and facilitate doping, which would likely be difficult in a wide band gap material such as $SrZrO_3$.

Figure 1 shows a sketch of a modulation doped $SrTiO_3/SrTi_{0.95}Zr_{0.05}O_3$ heterostructure, along with a band diagram of the conduction band edge, Fermi level and the electron density, as calculated using a 1D Poisson solver.[21] A ΔE_c of 95 meV was estimated using Vegard's law. The $SrTi_{0.95}Zr_{0.05}O_3$ layer is n-type, doped with La to a carrier density of $2 \times 10^{19}\,cm^{-3}$. A 2DEG resides in the $SrTiO_3$.

Experimentally realizing this structure requires the growth of epitaxial, stoichiometric $SrTiO_3$ and $SrTi_{1-x}Zr_xO_3$ thin films, to ensure high mobility, avoid charge trapping, and allow for doping of the $SrTi_{1-x}Zr_xO_3$. Here, we use hybrid molecular beam epitaxy (MBE), previously developed for high-mobility $SrTiO_3$.[22,23] In this approach, both Ti and Zr are supplied from high-purity (99.999%) metal-organic precursors, titanium tetra isopropoxide (TTIP), and zirconium tert-butoxide (ZTB), respectively.

The $SrTi_{0.95}Zr_{0.05}O_3/SrTiO_3$ heterostructure discussed in this paper consists of a 120 nm undoped $SrTiO_3$ layer grown on (001) $SrTiO_3$, followed by growth of a 30-nm-thick La-doped $SrTi_{0.95}Zr_{0.05}O_3$ layer (see Fig. 1). For $SrTi_{1-x}Zr_xO_3$, both precursors were co-evaporated, and the beam equivalent pressures were adjusted relative to

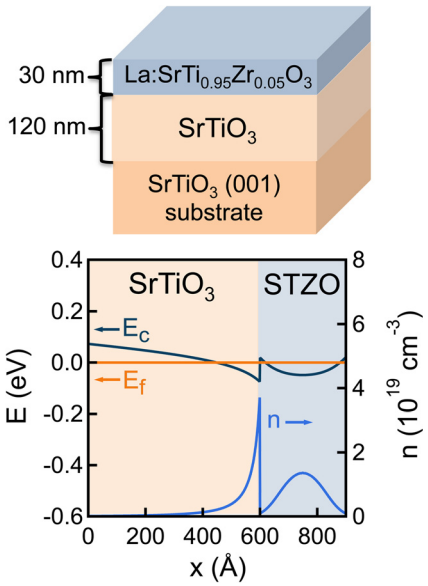

FIG. 1. Schematic of a modulation-doped $SrTi_{0.95}Zr_{0.05}O_3/SrTiO_3$ heterostructure and corresponding band diagram. The conduction band offset was estimated using experimental values for $SrZrO_3/SrTiO_3$ (Ref. 20) and assuming Vegard's law. The conduction band edge (E_c), Fermi level (E_f), and carrier density (n) were calculated using a 1D Poisson solver.[21] The dopant density in the $SrTi_{0.95}Zr_{0.05}O_3$ and the surface pinning potential were assumed to be $2 \times 10^{19}\,cm^{-3}$ and 0.1 eV, respectively. The $SrTiO_3$ layer is nominally undoped with $\sim 10^{16}\,cm^{-3}$ residual donor-type defects (an upper limit established by doping studies for these high-quality MBE films).

that of Sr to give A:B site stoichiometric films (where A = Sr and B = Ti or Zr) of the desired Zr content (x). Growth optimization to obtain the correct A:B site ratio closely followed our approach for $SrTiO_3$,[23] and details will be reported elsewhere. Oxygen was supplied by an rf plasma source. The substrate temperature was 900 °C as measured by thermocouple. La was evaporated from a solid source effusion cell to obtain a carrier concentration of $2 \times 10^{19}\,cm^{-3}$. Doping calibrations were carried out using thick, uniformly doped layers, which confirmed n-type doping of the $SrTi_{0.95}Zr_{0.05}O_3$ layers, but showed much lower mobilities than the modulation doped samples investigated here. *In-situ* reflection high-energy diffraction (RHEED) patterns were streaky during and after growth for all films and showed periodic oscillations in intensity at the beginning of growth, indicating layer-by-layer growth.[24] 2θ-ω x-ray diffraction scans in the vicinity of the $SrTiO_3$ 002 reflection showed a single, separate 002 peak for the $SrTi_{1-x}Zr_xO_3$ film and clearly defined Laue oscillations.[24] The composition x was calibrated by comparing the unstrained unit cell volume, obtained from lattice parameter measurements, to that of bulk $SrTi_{1-x}Zr_xO_3$.[25] The sample was post-growth annealed in a rapid thermal annealing furnace in 1 atm of oxygen at 800 °C for 30 s to ensure oxygen stoichiometry. Hall and longitudinal resistance measurements at temperatures between 300 K and 2 K and magnetic fields (B) up to 14 T were performed in van der Pauw geometry using a Physical Properties Measurement System (Quantum Design). Ohmic contacts (40 nm-Al/20 nm-Ni/400 nm-Au) were deposited by electron beam evaporation through a shadow mask onto the corners of a square sample. The longitudinal magnetoresistance was measured using a standard lock-in technique in a He^3 cryostage at temperatures ranging from 0.45 K to 3 K. Data at low B showed positive magnetoresistance at low temperatures, with a sharp dip near $B = 0$, possibly due to weak antilocalization. Magnetoresistance measurements as a function of the angle θ that B makes with the surface normal were performed at 2 K using a horizontal sample rotator stage ($\theta = 0°$ indicates that B is perpendicular to the interface).

To confirm the existence of a 2DEG and to probe the dimensionality of the electron system in the $SrTi_{0.95}Zr_{0.05}O_3$/$SrTiO_3$ heterostructure, we investigate Shubnikov-de Haas oscillations that appear in the longitudinal magnetoresistance in a quantizing magnetic field. In particular, for a 2DEG, the periodicity of these oscillations, which are due to quantization into Landau levels, should only depend on the component of B that is normal to the interface.

Figure 2 shows the longitudinal magnetoresistance at different temperatures. At 0.45 K, Shubnikov-de Haas oscillations are observed for $B > 5$ T. Oscillations persist to temperatures up to 3 K. The oscillating component of the magnetoresistance, ΔR_{xx}, was obtained by subtracting the non-oscillating background using multiple polynomial fits. Figure 3(a) shows ΔR_{xx} as a function of $1/B$ [$\Delta R_{xx}(1/B)$] at 0.45 K. A Fourier transform (FT) of $\Delta R_{xx}(1/B)$ is shown in the inset and exhibits multiple peaks, which will be further discussed below. Figure 3(b) shows Shubnikov-de Haas oscillations for different θ, measured at 2 K and plotted against $(B\cos\theta)^{-1}$. Resistance maxima and minima appear

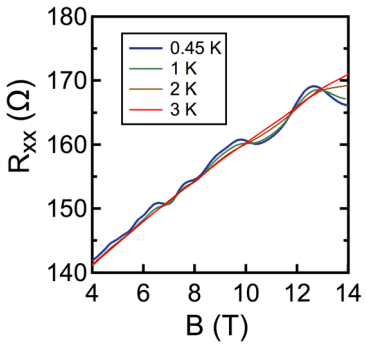

FIG. 2. Longitudinal magnetoresistance (R_{xx}) measured at temperatures between 0.45 K and 3 K.

at the same values of $(B\cos\theta)^{-1}$ for θ up to 60°, confirming the two-dimensionality of the electron system. Therefore, as suggested by the band diagram in Fig. 1, a 2DEG has been created on the $SrTiO_3$-side of the interface.

Shubnikov-de Haas oscillations allow for the extraction of important characteristics, including the effective masses (m^*) for the subbands and the quantum scattering time (τ_q) or Dingle temperature (T_D). For 2DEGs with a single subband, values for m^* and T_D are determined from the decay in the amplitude of oscillations with increasing temperature and by constructing a Dingle plot at a fixed temperature, respectively. Multiple subbands (or spin splitting) complicate such analyses, since oscillations contain contributions from several components. Therefore, we fit the experimental data, $\Delta R_{xx}(1/B)$, at 0.45 K to the standard equation[26]

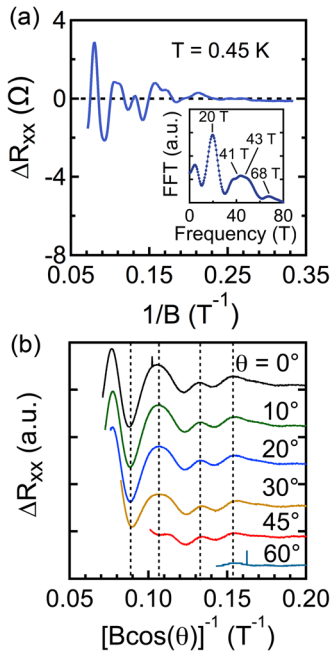

FIG. 3. (a) Shubnikov-de Haas oscillations, $\Delta R_{xx}(1/B)$, measured at 0.45 K and $\theta = 0°$. The inset shows a Fourier transform of the data. Approximate positions for four peaks are labeled. (b) Shubnikov-de Haas oscillations measured at 2 K at various tilt angles θ (the angle between B and the interface plane normal) and plotted as a function of the inverse perpendicular component of the magnetic field, $(B\cos\theta)^{-1}$.

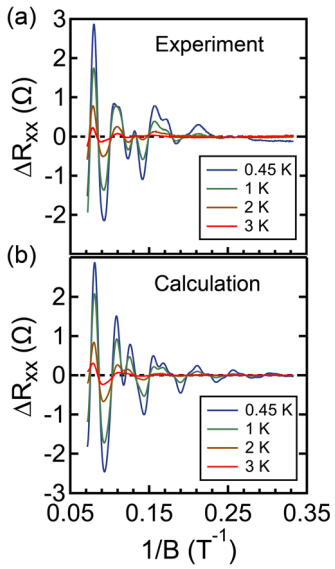

FIG. 4. (a) Temperature-dependent Shubnikov-de Haas oscillations, $\Delta R_{xx}(1/B)$, measured at $\theta = 0°$ and at temperatures between 0.45 K and 3 K. (b) Calculated [Eq. (1)] Shubnikov-de Haas oscillations for temperatures between 0.45 K and 3 K, using the parameters listed in Table I.

$$\frac{\Delta R_{xx}}{R_0} = \sum_{i=1}^{l} 2A_i \exp\left(-\frac{2\pi^2 k_B T_{D,i}}{\hbar\omega_c}\right) \frac{X}{\sinh(X)} \cos\left(\frac{2\pi f_i}{B} + \pi\right), \tag{1}$$

where i is the subband index, l is the number of occupied subbands, A_i are amplitude factors associated with intrasubband scattering probabilities, k_B is the Boltzmann constant, $T_{D,i}$ is the Dingle temperature of each subband, $\hbar$ is the reduced Planck's constant, ω_c is the cyclotron frequency, f_i are the oscillation frequencies (in $1/B$), and $X = (2\pi^2 k_B T)/(\hbar\omega_c)$. Figure 4 shows experimental and calculated $\Delta R_{xx}(1/B)$ at temperatures between 0.45 K and 3 K for $l = 4$. The temperature-dependence was calculated and the m^*'s adjusted to match the experimentally observed behavior. The parameters obtained from the fits and the extracted sheet carrier density (n_s), τ_q, and quantum mobility (μ_q) for each subband are shown in Table I. The frequencies are in good agreement with those obtained in the FTs shown in Fig. 3(a). The lowest value for m^* (0.95 m_0, where m_0 is the free electron mass) is consistent with a d_{xy}-derived subband.[27–30] Spin-orbit coupling can hybridize d_{xy}-derived with d_{xz}/d_{yz}-derived subbands.[29] This results in a heavier in-plane mass. Theoretical calculations support multiple occupied subbands at this carrier density.[29] Alternative models and fits to the experimental Shubnikov-de Haas oscillations were also explored (see Ref. 24), including whether multiple frequencies could arise from two spin-split subbands. A good qualitative match with the data could be obtained, and at present, we cannot distinguish between these models.[24] These uncertainties place limitations on the accuracy of the extracted values in Table I. The extracted μ_q's of around 2000 $cm^2V^{-1}s^{-1}$ are consistent with the onset of magnetoresistance oscillations around 4–5 T, i.e., when $\mu_q B > 1$.

The total sheet density estimated from Table I is approximately $8.4 \times 10^{12}\,cm^{-2}$, which is only 19% the Hall density, $n_{s,H} = 4.46 \times 10^{13}\,cm^{-2}$, measured at 300 K. The remaining carriers can be reasonably assumed to reside in the La-doped $SrTi_{0.95}Zr_{0.05}O_3$ layer. Carrier distributions calculated in Fig. 1 confirm this picture qualitatively. Using reasonable assumptions for the mobilities and carrier densities in both layers, a Hall coefficient can be calculated from a multicarrier model and compared with experimentally measured values. Good agreement is found.[24] The two spin-split subband interpretation of the data (see Ref. 24) results in lower carrier densities. Prior studies of 2DEGs in $SrTiO_3$ found upwards of 60%–95% of carriers in the 2DEG to not give rise to oscillations,[14,31–34] which is likely due to disorder limiting the mobility of a significant fraction of the carriers, preventing oscillations to be resolved for all subbands.

Discrepancies exist between calculated and experimental ΔR_{xx} in all models. One possible explanation is intersubband scattering,[35,36] which was neglected in Eq. (1). The energy spacing between subbands, ΔE, is very small

$$\Delta E = \frac{q\hbar\Delta f}{m^*}, \tag{2}$$

where Δf is the difference in oscillation frequencies between any two subbands, and q is the elementary charge. From Table I, ΔE ranges from 0.15 meV to 5 meV. Intersubband scattering may thus be significant. It is generally more significant at low B[35,36] and could thus potentially affect finer features that would otherwise appear in the measured resistance. At present, a complete theory of magnetoresistance oscillations of 2DEGs in $SrTiO_3$ is still lacking.

In summary, we have shown that modulation doping provides an alternative route to 2DEGs in $SrTiO_3$. Future studies should be dedicated to a complete understanding of the quantum oscillations, and to further improving the mobility in these structures. For example, remote ionized impurity scattering can be mitigated by inserting an undoped $SrTi_{1-x}Zr_xO_3$ spacer. Lower-density 2DEGs can be obtained by optimizing the doping and Zr content of the $SrTi_{1-x}Zr_xO_3$, which determine the band offsets.

TABLE I. Parameters extracted from fits of the experimental Shubnikov-de Haas oscillations measured at 0.45 K to a four-subband model [Eq. (1)]. Also shown are the sheet carrier densities (n_s), quantum scattering times (τ_q), and quantum mobilities (μ_q) of each subband extracted from the fits. The effective mass m^* is determined from the cyclotron frequency $\omega_c = eB/m^*$, τ_q is calculated from $\tau_q = \hbar/(2\pi k_B T_D)$, and n_s is calculated from $f = nh/2q$, where h is Planck's constant.

Subband index i	R_0A (Ω)	f (T)	m^* (m_0)	T_D (K)	n_s (cm^{-2})	τ_q (s)	μ_q ($cm^2V^{-1}s^{-1}$)
1	0.8	68.4	1.2	0.8	3.30×10^{12}	1.52×10^{-12}	2225
2	6.5	43	1.5	1.1	2.08×10^{12}	1.10×10^{-12}	1288
3	2	41.2	1.4	0.8	1.99×10^{12}	1.52×10^{-12}	1907
4	2	21.2	0.95	0.9	1.02×10^{12}	1.35×10^{-12}	2496

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