Kondo effect with tunable spin–orbit interaction in LaTiO$_3$/CeTiO$_3$/SrTiO$_3$ heterostructure

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Abstract
We have fabricated epitaxial films of CeTiO$_3$ (CTO) on (001) oriented SrTiO$_3$ (STO) substrates, which exhibit highly insulating and diamagnetic properties. X-ray photoelectron spectroscopy was used to establish the $3^+$ valence state of the Ce and Ti ions. Furthermore, we have also fabricated $\delta$ (CTO) doped LaTiO$_3$ (LTO)/SrTiO$_3$ thin films which exhibit variety of interesting properties including Kondo effect and spin–orbit interaction (SOI) at low temperatures. The SOI shows a non-monotonic behaviour as the thickness of the CTO layer is increased and is reflected in the value of characteristic SOI field ($B_{SO}$) obtained from weak anti-localization fitting. The maximum value of $B_{SO}$ is 1.00 T for $\delta$ layer thickness of 6 u.c. This non-monotonic behaviour of SOI is attributed to the strong screening of the confining potential at the interface. The screening effect is enhanced by the CTO layer thickness and the dielectric constant of STO which increases at low temperatures. Due to the strong screening, electrons confined at the interface are spread deeper into the STO bulk where it starts to populate the Ti $d_{xz/yz}$ subbands; consequently the Fermi level crosses over from $d_{xy}$ to the $d_{xz/yz}$ subbands. At the crossover region of $d_{xy} - d_{xz/yz}$ where there is orbital mixing, SOI goes through a maximum.

Keywords: 2DEG, weak antilocalization, magnetoresistance

(Some figures may appear in colour only in the online journal)
from the positively charged (LaO)\textsuperscript{2+} planes [18]. This potential confines the electrons at the interface resulting in 2DEG. The confined electrons reside on the Ti 3d subbands (d\textsubscript{xy}, d\textsubscript{yz}, d\textsubscript{zx}) of the STO [19].

In rare earth titanates (RTiO\textsubscript{3}, R = rare earth ions), magnetic structure depends on the f-orbital occupancy. As we go across the lanthanide series from La to Gd, f-orbital electron occupancy increases and R–O–Ti interaction becomes significant in addition to the existing Ti–O–Ti interaction; consequently magnetism in RTiO\textsubscript{3} switches from antiferromagnetic to ferrimagnetic for R = La and Gd, respectively [20]. R = Ce with f\textsuperscript{3} electronic configuration presents the case for the onset of R–O–Ti interactions. Bulk CeTiO\textsubscript{3} (CTO) crystallizes in the orthorhombic perovskite structure. The Ce and Ti ions in CTO are trivalent (Ti ions in d\textsuperscript{1} configuration) and exhibit insulating behaviour [21]. CTO is antiferromagnetic (AF) and neutron diffraction studies have attributed the AF ordering to Ce\textsuperscript{3+} ions, where it was revealed that the AF moments were in a canted state, resulting in a weak ferromagnetic behaviour of the type G\textsubscript{F}\textsubscript{c1} or G\textsubscript{F}\textsubscript{c2} [22]. Where G\textsubscript{F}\textsubscript{c1} indicates G-type canted AF ordering along the x-crystallographic axis which results in a net ferromagnetic ordering along the z-axis.

Similar to polar LTO and LAO, due to the trivalent Ce and Ti ions, CTO exhibits strong prospect for the formation of 2DEG in CTO/STO thin films. The objective of the paper is two-fold: first to grow epitaxial films of CTO on STO substrate and to study its electrical and magnetic properties. Second, since CTO is similar to LTO (La substituted by Ce), δ doping of the LTO/STO interface with CTO (LTO/CTO(δ)/STO) will allow further insight on the role of the rare-earth ion on the interface phenomena associated with 2DEG. This paper is divided into two section. In section 3.1 we discuss the experimental details and results obtained on CTO/STO film; in section 3.2 we discuss the electrical and magnetotransport properties of δ doped LTO/STO films.

2. Experimental

Pulsed laser deposition technique was used to fabricate epitaxial thin films of LTO and CTO on TiO\textsubscript{2} terminated STO (001) substrate, using KrF excimer laser (Lambda Physik COMPexPro, λ = 248 nm). The targets for LTO and CTO were fabricated by standard solid state reaction method. Stoichiometric ratios of La\textsubscript{2}O\textsubscript{3}–TiO\textsubscript{2} and CeO\textsubscript{2}–TiO\textsubscript{2} for LTO and CTO, respectively, were ground using a mortar and pestle. The powders were then calcined in a furnace for 12 h each at 900 °C, 1000 °C and 1100 °C. The powders were finally pressed into a pellet and sintered at 1300 °C for a period of 12h. STO substrates were etched in a solution of NH\textsubscript{4}F, deionized water and HF acid for 30 s, to achieve TiO\textsubscript{2} termination at its surface. Prior to deposition, the TiO\textsubscript{2} terminated STO (001) substrates were annealed for 1 h at 800 °C in an oxygen pressure of 7.4 × 10\textsuperscript{-4} mbar to attain a defect free surface. Furthermore, to achieve layer by layer growth of the film, the laser was fired at a repetition rate of 2 Hz and fluence of ~ 0.8 J cm\textsuperscript{-2}, which translated to a slow growth rate of 0.10 Å s\textsuperscript{-1}. CTO films of thickness 20 Å (5 u.c), 40 Å (10 u.c), 80 Å (20 u.c), 200 Å and 300 Å were deposited on the annealed substrate. The O\textsubscript{2} pressure and temperature of the substrate were maintained at 1 × 10\textsuperscript{-3} mbar and 800 °C, respectively. After deposition, the film was cooled at the rate of 10 °C min\textsuperscript{-1} while maintaining the deposition pressure in the chamber. The same deposition conditions were followed for LTO/STO. The viability of these deposition conditions has been well established by our group, and was used to fabricate excellent epitaxial films of LTO/STO and LAO/STO [10, 11, 15-17].

For the δ doped LTO/STO samples the deposition procedure is as follows: first, δ unit cells (u.c) of CTO was deposited on the annealed TiO\textsubscript{2} terminated STO substrate. Immediately after, 20 u.c of LTO was deposited on top of CTO(δ u.c)/STO. Same deposition procedure (including the temperature and pressure), as used for CTO/STO films were maintained. δ doped LTO films (LTO(20 u.c)/CTO(δ u.c)/STO) with δ = 0, 6, 8 and 10 u.c were fabricated. X-ray diffractometer (PANalytical X’Pert PRO), equipped with a Cu-K\textsubscript{α1} source (λ = 1.5405 Å) was used to study the crystalline structure of the deposited films. X-ray photoelectron spectroscopy (XPS) was done using PHI 5000 Versa Probe II, FEI Inc. fitted with an Al K\textsubscript{α} x-ray source (hv = 1486.6 eV). Magnetization measurements were carried out in SQUID magnetometer (Cryogenic Limited). The transport properties were measured in a Quantum Design Physical properties measurement system (PPMS). For transport measurements, Ag/Cr electrodes were deposited in the Van der Pauw and four probe geometry using shadow mask. For resistivity and MR measurements electrical contacts on 2 mm × 5 mm samples were made in the four probe geometry. For out-of plane MR, an external magnetic field was applied perpendicular to the sample plane, whereas for in-plane MR, the field was applied along the sample plane and perpendicular to the current direction. Hall measurements were carried out on 3 mm × 3 mm samples in the Van der Pauw geometry (Ag/Cr pads were deposited at the corners for electrical contacts) with an applied external magnetic field, perpendicular to the sample plane.

3. Results and discussion

3.1. CTO/STO

3.1.1. Structure. Figure 1 shows the results of x-ray diffraction measurement done on 300 Å CTO/STO film. The presence of only (0 0 2) film peaks in the θ = 2θ scan (figure 1(a)) confirms the epitaxial growth of CTO on STO (001). From the (002) peak of CTO (figure 1(b)) the film lattice parameter was determined to be 3.846 Å, which is smaller than the pseudocubic lattice parameter (a\textsubscript{0} = 3.939 Å) calculated from the bulk orthorhombic CTO lattice parameter reported in [22]. Since the lattice parameter of STO (a\textsubscript{0} = 3.905 Å) is smaller than that of bulk CTO (a\textsubscript{0}), an in-plane compressive strain acts on CTO films grown on STO, which should lead to an increase of out-of-plane lattice parameter (c). The decreased c despite the in-plane compressive strain, may be due to defects such as cation non-stoichiometry [23].
XRD-ω scan (figure 1(c)) about the (0 0 2) CTO film peak reveals a full width at half maximum (FWHM) of 0.14°, which indicates good crystalline structure of the film. The φ scan of both the film and the substrate (figure 1(d)) shows four peaks appearing at an interval of 90° which suggests a fourfold symmetry of the CTO film, furthermore the four peaks in the film and the substrate appear at the same value of φ confirming a good epitaxial growth of the CTO film on the STO substrate.

In order to determine the valence states and stoichiometry of the Ce and Ti in CTO we have carried out XPS measurement on 300 Å CTO/STO film. To compensate for the charging effect in the samples, adventitious C 1s peak has been set at 285 eV. The core level XPS spectrum of Ce 3d, Ti 2p and O 1s confirm a good epitaxial growth of the CTO film on the STO substrate.
O 1s is presented in figure 2. XPS peakfit 4.1 software was used to fit the XPS spectrum. A combination of Lorentzian–Gaussian function and Shirley background was chosen for the fitting purpose. Ce 3d spectrum (figure 2(a)) shows two spin–orbit split peaks, 3d_{5/2} and 3d_{3/2} at an interval of 18.5 eV. Deconvolution of 3d_{5/2} and 3d_{3/2} peaks reveals two component each, labelled as (v_{0, v}) and (u_{0, u}) respectively. The multiplet splitting of 3d_{5/2} and 3d_{3/2} occurs due to the final state effect, whereby the core hole potential perturbs the valence electrons and transfer of electrons between Ce 3d and O 2p valence band takes place. The presence of only two components each in 3d_{5/2} and 3d_{3/2} confirms Ce to be in the 3+ state [24]. However, small quantity of Ce^{4+} is also present as is evident from the small nondescript peak at 916.6 eV which is attributed to Ce^{4+} valence state. Figure 2(b) shows the Ti 2p spin–orbit doublet at separation of 5.6 eV. The deconvoluted components of 2p_{3/2} at 457.9 eV and 458.6 eV corresponds to Ti^{3+} and Ti^{4+}, respectively. O 1s peak is observed at 529.5 eV (figure 2(c)) with a FWHM of 1.4 eV, the peak at 531.5 eV is attributed to hydroxyl (OH) species [25].

From the fitting of the XPS data it is seen that both Ce 4+ and Ce 3+ states are present in our sample. However, from the peak area, the concentration of Ce^{4+} is negligible as compared to Ce^{3+}. From the ratio of the peak area of Ce (3d_{5/2}) and Ti (2p_{3/2}) (scaled by their relative sensitivity factor (RSF)), we obtain Ce:Ti = 0.7:1. We have used RSF value of 30.50 and 5.22 for Ce (3d_{5/2}) and Ti (2p_{3/2}), respectively [26]. The low Ce content, indicates the presence of Ce vacancies in the CTO lattice. Cation vacancies have been known to result from the polar catastrophe model, whereby the core hole potential perturbs the valence electrons and transfer of electrons between Ce 3d and O 2p valence band takes place. The presence of only two components each in 3d_{5/2} and 3d_{3/2} confirms Ce to be in the 3+ state [24]. However, small quantity of Ce^{4+} is also present as is evident from the small nondescript peak at 916.6 eV which is attributed to Ce^{4+} valence state. Figure 2(b) shows the Ti 2p spin–orbit doublet at separation of 5.6 eV. The deconvoluted components of 2p_{3/2} at 457.9 eV and 458.6 eV corresponds to Ti^{3+} and Ti^{4+}, respectively. O 1s peak is observed at 529.5 eV (figure 2(c)) with a FWHM of 1.4 eV, the peak at 531.5 eV is attributed to hydroxyl (OH) species [25].

3.1.2. Electrical and magnetic properties. Electrical resistivity measurements were carried out on 20 Å, 40 Å, 80 Å and 200 Å thick CTO/STO films. The films exhibit very high resistance that could not be measured (the resistance exceeded 100 MΩ). CTO is a polar perovskite oxide, which is diamagnetic in the CTO film as opposed to TiO2 terminated STO substrate, subjected to the same pressure and temperature conditions used during the deposition of CTO film. The temperature dependent FC magnetization profile of the bare STO substrate exhibits a diamagnetic behaviour (shown in the inset of figure 3). However, strength of the diamagnetic signal of the CTO film is greater by nearly a factor of 2 as compared to the bare STO substrate. At T < 80 K, a paramagnetic like upturn in the magnetization data is observed for CTO/STO as well as bare STO substrate. Such upturn in M(T) of STO substrates has been reported earlier [31], which was ascribed to the presence of (few ppm) contaminants like Fe^{3+} and Ni^{2+} in the STO substrate. Due to similar upturn in M(T) of STO itself, we are unable to say anything conclusive regarding the contribution of CTO to the observed magnetization upturn in CTO/STO.

3.2. δ (CTO)—doped LTO/STO

3.2.1. Electrical transport. Figure 4(a) shows the temperature dependent sheet resistance R_{SC}(T) of the LTO(20 u.c)/CTO(δ u.c)/STO samples with δ = 0, 6 and 10 u.c. Metallic behaviour in all the three samples is evident from the decreasing R_{SC}(T) measurements were carried out at an applied field of 0.2 tesla under zero field cooled (ZFC) and field cooled (FC) conditions. The results are plotted in figure 3. From M(T) data, a diamagnetic behaviour is observed in the CTO film as opposed to the antiferromagnetic behaviour observed in bulk CTO. Antiferromagnetism in bulk CTO is attributed to the unpaired Ti^{3+} d^{1} electrons. In contrast, the emergence of diamagnetism in CTO film suggests the oxidation of Ti^{3+} to Ti^{4+} with completely empty d^{0} bands i.e. absence of unpaired electrons, all the lower orbitals are completely filled. STO substrate with empty Ti^{4+} d^{0} orbital is known to exhibit diamagnetism [30, 31]. For reference we also carried out M(T) measurement on a bare TiO2 terminated STO substrate, subjected to the same pressure and temperature conditions used during the deposition of CTO film. The temperature dependent FC magnetization profile of the bare STO substrate exhibits a diamagnetic behaviour (shown in the inset of figure 3). However, strength of the diamagnetic signal of the CTO film is greater by nearly a factor of 2 as compared to the bare STO substrate. At T < 80 K, a paramagnetic like upturn in the magnetization data is observed for CTO/STO as well as bare STO substrate. Such upturn in M(T) of STO substrates has been reported earlier [31], which was ascribed to the presence of trace amount of (few ppm) contaminants like Fe^{3+} and Ni^{2+} in the STO substrate. Due to similar upturn in M(T) of STO itself, we are unable to say anything conclusive regarding the contribution of CTO to the observed magnetization upturn in CTO/STO.
as a function of temperature. However, the resistance of the sample increases with δ layer thickness. Das et al [15] have reported a similar $R_{\square}(T)$ behaviour on LaCrO$_3$ (δ layer) doped LTO/STO system. Using electron energy loss spectroscopy (EELS), they observed that the LaCrO$_3$ δ layer traps the electrons that are being transferred from the LTO to the STO side, which enhances $R_{\square}(T)$ [15]. We anticipate a similar mechanism for the enhancement in $R_{\square}(T)$ for our δ doped samples. Hall measurement performed on these samples at 300 K and 2 K reveals an inverse relation of the interface carrier concentration ($n_e$) with the δ layer thickness (inset of figures 5(a) and (b)). Thus, the electrons transferred from LTO to STO due to polar reconstruction is trapped by the CTO layer, which results in enhanced $R_{\square}(T)$. This picture also lends strong credibility to polar reconstruction being responsible for the formation of 2DEG at the LTO/STO interface.

Another notable feature of the $R_{\square}(T)$ data is the resistance minimum in the temperature range of 20–30 K. In order to emphasize the resistance increase, we have plotted $\Delta R_{\square}(T) = R_{\square}(T) - R_{\square}(2 K)$ versus $T$ in figure 4(b). Below the resistance minimum temperature ($T_{\text{min}}$), $R_{\square}(T)$ gradually increases and tends to saturate below 10 K. A fit to the experimental data below $T_{\text{min}}$ exhibits $\ln(T)$ behaviour (black solid line in figure 4(b)). The $\ln(T)$ rise in $R_{\square}(T)$ at low temperatures could be associated with a number of quantum scattering phenomena viz. weak localization (WL) [32–34], Kondo scattering [15–17] and electron–electron interaction (EEI) [35–39]. The origin of WL is purely quantum mechanical, which occurs due to the diffusive motion of electron in disordered system. The time reversed partial waves of the electrons undergo constructive interference, which increases the probability of backscattering and hence a resultant increase in resistance of the material results. On the other hand, Kondo scattering is prominent in low temperature region where, scattering due to phonons is minimal. Magnetic impurities in the lattice interact with conducting electrons in the system which leads to anti-parallel alignment of the spins between the electrons and the magnetic impurity ions. At low temperatures the contribution of Kondo scattering to the electrical resistivity is proportional to $\ln(T)$. As the temperature is further lowered the spin of the impurity ions is screened by the spins of the conductions electrons, and below a characteristic temperature (Kondo temperature ($T_K$)), the resistance gradually saturates. Similarly, EEI also introduces a logarithmic correction to the resistance [38, 40, 41].

In figure 4(b), at low temperatures ($T \ll T_{\text{min}}$) $R_{\square}(T)$ goes to a saturation. This behaviour of $R_{\square}(T)$ suggests the presence of one more scattering phenomena, the weak antilocalization (WAL) [42–45]. WAL effect occurs at low temperatures, in the presence of SOI which introduces a phase difference between the backscattered electron partial waves, leading to a destructive interference; this results in reduced backscattering of electrons and hence a saturating behaviour in $R_{\square}(T)$.

Figure 4. (a) Sheet resistance of the LTO/STO and CTO(δ) doped LTO/STO film (with δ layer thickness of 6 and 10 u.c) as a function of temperature. At lower temperatures the resistance of the films displays an upturn followed by saturation. (b) To properly emphasize the low temperature upturn in the resistance, $\Delta R_{\square}(T) = R_{\square}(T) - R_{\square}(2 K)$ has been shown at low temperatures. The black solid line represents $\ln(T)$ fit to the $R_{\square}(T)$ data.

Figure 5. Hall resistance measured as a function of magnetic field for various δ doping thickness at (a) 300 K and (b) 2 K. The negative slope indicates the charge carriers to be electrons. Carrier density as a function of δ layer thickness at 300 K and 2 K is shown in the inset of (a) and (b), respectively. Inverse relation between charge carrier density and δ layer thickness is observed.

\[ R_{\square}(0) \propto n_e \]

\[ R_{\square}(\delta) \propto n_e^{1/2} \]

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3.2.2. Magneto transport. In order to understand the mechanism behind the resistance upturn below $T_{\text{min}}$, we study the magneto transport properties of the $\delta = 0, 6$ and 10 u.c samples at 2, 5 and 20 K. To determine the charge carrier density we have performed Hall measurement on these samples at 2 and 300 K, shown in figure 5. The negative slope of $R_H$ versus $B$ plot suggests the majority charge carriers at the interface are electrons. The insets of figures 5(a) and (b) show the charge carrier density as a function of $\delta$ layer thickness at 300 K and 2 K, respectively. It is observed that $n_e$ has an inverse relation with $\delta$ layer thickness at both temperatures. At 300 K, $R_H - B$ plots for $\delta = 6$ and 10 u.c exhibit non-linear behaviour at low fields. Kim et al [46] have observed similar non-linear behaviour in $R_H - B$ data of LTO/STO superlattice, which occurs due to multiband occupancy of the charge carriers.

In figure 6 we show the plot of MR data with the magnetic field applied perpendicular to the sample plane. We define MR$\% = \frac{R(B) - R(0)}{R(0)} \times 100$, where $R(B)$ is the resistance at an applied field $B$. All the three samples display positive MR. External magnetic field has profound impact on WL, WAL and EEI, and can be used as a tool to distinguish between them. Backscattering is suppressed in the presence of a magnetic field which introduces a phase difference between the time reversed electron partial waves and destroys the constructive interference. Thus WL exhibits negative MR. Whereas for WAL the magnetic field destroys the existing destructive interference [47] and hence leads to positive MR.

In the case of EEI, Zeeman splitting by an amount of $g\mu_B B$ [48, 49] leads to a decrease in conductivity. Therefore magnetic field leads to a negative magnetoconductivity in case of EEI and in the 2D limit, it is given by [50]

$$\Delta \sigma(B) = -\frac{e^2 F}{4\pi^2 \hbar} A \left( \frac{g\mu_B B}{k_B T} \right)$$  \hspace{1cm} (1a)

$$A \left( \frac{g\mu_B B}{k_B T} \right) = \begin{cases} 
\ln \left( \frac{1}{0.084} \frac{g\mu_B B}{k_B T} \right)^2, & \frac{g\mu_B B}{k_B T} \gg 1 \\
0.084 \left( \frac{g\mu_B B}{k_B T} \right)^2, & \frac{g\mu_B B}{k_B T} \ll 1 
\end{cases} \hspace{1cm} (1b)
$$

Where, $\Delta \sigma(B) = \sigma(B) - \sigma(0)$, $F$ is the electron screening factor, $k_B$ is the Boltzmann constant, $g$ is the electron $g$-factor and $\mu_B$ is the Bohr magneton. The positive MR at perpendicular fields rule out WL as the mechanism for scattering
below $T_{\text{min}}$. Therefore, the observed positive parabolic MR in our samples seems to suggest a contribution from EEI or classical orbital effect. At 2 K, the maximum limit of $B$ for parabolic contribution to MR from EEI is $\sim 1.5$ T (equation (1b)). Thus, $B^2$ dependence of MR at higher fields suggests the contribution of classical MR as well. Classical MR follows Kohler’s rule, $\Delta R/R_{\text{C}}(0) = k(B/R_{\text{C}}(0))^2$ [51–53]. Kohler’s plot for the doped samples at 2 K is shown in the inset of figure 6(a). All the samples exhibit linear behaviour at higher fields, which indicates the presence of classical MR. Figure 7(a) shows the classical $B^2$ fit to the $R$-$H$ data for $\delta = 0$ u.c sample at 2 K. It is seen that the $B^2$ dependence provides a good fit to the experimental data for $B > 6$ T only, and at $B = 0$ T the $B^2$ fit gives a value of $R_{\text{C}}(B = 0)$ greater than that obtained experimentally (figure 7(a)). The deviation of experimental data from $B^2$ fit at low field and low temperature may be attributed to WAL which decreases $R_{\text{C}}(B = 0)$; for $B \neq 0$ WAL is suppressed and $R_{\text{C}}(B)$ increases. A theoretical model developed by Hikami, Larkin and Nagaoka (HLN) gives an account of the WAL contribution to MR for 2D systems and is expressed as [17, 32, 42, 54–56]

$$\Delta \sigma(B) = -e^2/2\pi h \left[ \frac{1}{2} \Psi \left( \frac{1}{2} + \frac{B}{B_{\text{WAL}}} \right) - \frac{1}{2} \ln \left( \frac{B_{\text{WAL}}}{B} \right) - \frac{1}{2} \Psi \left( \frac{1}{2} + \frac{B_{\text{SO}} + 2B_{\text{WAL}}}{B} \right) + \frac{1}{4} \ln \left( \frac{B_{\text{SO}} + 2B_{\text{WAL}}}{B} \right) \right] .$$

(2)

Where, $\Psi(x)$ is the digamma function, $B_{\text{WAL}} = h/4L_{\varphi}^2$ is the dephasing field with $L_{\varphi}$ as the effective dephasing length, $B_{\text{SO}} = h/4L_{\varphi_{\text{SO}}}$ is the characteristic field related to SOI; $L_{\varphi}$ is the spin relaxation length. HLN theory only takes $k$-cubic SOI into account.

The experimental data in the lower field range ($-0.3$ T $< B < 0.3$ T), can be fitted to a good precision using WAL effect (equation (2)). This fitting is shown in the inset of figure 7(a) for $\delta = 0$. The MR plot at 2 K for $\delta = 6$ and 10 u.c shows a cusp at lower field values (figure 6(a)). Such a cusp in MR data has been observed in previous studies [15, 17, 38, 42, 45], and is attributed to the WAL effect. In order to verify the WAL contribution, equation (2) is used to fit the experimental data (after subtracting the classical Lorentz $B^2$ background) for the low field region ($-6$ T $< B < 6$ T). Excellent fitting of experimental data with equation (2) justifies the presence of WAL (figure 7(b)). This result is consistent with our $R_{\text{C}}(B)$ data which exhibits a saturating tendency in this temperature range. The fitting parameters are shown in table 1. $B_{\text{SO}}$, which is a measure of the strength of SOI shows a non-monotonic behaviour with $\delta$ (or $n_d$), it is maximum for $\delta = 6$ u.c and decreases for $\delta = 0$, 8 and 10 u.c. This observation generates new possibilities for tuning the SOI with $\delta$ doping.

We further perform in-plane MR measurement to get a better insight about the scattering mechanism. The in-plane MR ($MR_\parallel$) data for $\delta = 0, 6$ and 10 u.c samples at $T = 2$ and 10 K is shown in figures 8(a) and (b). It is observed that $MR_\parallel$ increases with $\delta$ layer thickness. At 10 K all the three samples exhibit negative MR. At 2 K, $\delta = 0$ u.c sample exhibits negative MR, whereas $\delta = 6$ and 10 u.c samples exhibit an interesting MR behaviour: the MR of these $\delta$ doped samples show a cusp around $B = 0$ T, with a positive maximum at 4 T and as the field is increased beyond 7 T the MR becomes negative. This behaviour in MR suggests the presence of more than one scattering mechanisms in $\delta$ doped samples at 2 K. A similar cusp in in-plane MR has also been observed in LAO/STO [57], Bi [58], Mg [59] and topological insulators [39, 45] and was attributed to WAL effect. On the other hand, magnetothermopower measurements have unambiguously confirmed the presence of Kondo scattering in LTO/STO thin films [16]. In our thin film samples, the ln ($T$) behaviour of the $R_{\text{C}}(T)$ below $T_{\text{min}}$ coupled with the observed negative $MR_\parallel$ is strongly suggestive of Kondo scattering. Thus the experimental observations point to the presence of both Kondo and WAL effect in the $\delta$ doped samples at 2 K. To confirm Kondo...
scattering, we fit our experimental at 2 and 10 K with a simple Kondo model [60]:

\[
R^{\text{model}} = R_0 + R_K \left( B_\| / B_\| \right) . \tag{3a}
\]

Where, \( R_0 \) is the residual resistance, \( B_1 \) is a field scale related to \( T_K \) and density of electrons at the Fermi level. As the density depends on temperature, \( B_1 \) is temperature sensitive. \( R_K \left( B_\| / B_\| \right) \) is the magnetoresistance of the Kondo impurity at 0 K and is given by:

\[
R_K \left( B_\| / B_\| \right) = R_K \left( B_\| = 0 \right) \cos^2 \left( \frac{\pi}{2} M \left( B_\| / B_\| \right) \right) . \tag{3b}
\]

\( M \left( B_\| / B_\| \right) \) is the magnetization of the Kondo impurity at 0 K, calculated using the Bethe-ansatz technique and is expressed as:

\[
M \left( B_\| / B_\| \right) = \left\{ \begin{array}{ll}
\sum_{k=0}^{\infty} \left( -\frac{1}{2} \right)^k (k!)^{-1} (k + \frac{1}{2})^{(k-1)} e^{-(k+\frac{1}{2})} \left( \frac{b_1}{b_1} \right)^{2k+1} , & B_\| \leq \sqrt{2} B_1 \\
1 - \pi^{-3/2} \int d\phi \sin(\pi t) e^{-\alpha_\| (\phi)} \left( \frac{b_1}{b_1} \right)^{2} \Gamma(\frac{1}{2}t + \frac{1}{2}) , & B_\| \geq \sqrt{2} B_1
\end{array} \right.
\]

Equation (3a) is used to fit the experimental data in figures 8(a) and (b) (black solid line). The Kondo fit shows good agreement with our experimental data at 2 and 10 K. The fit parameters are shown in table 2. This result supports the presence of Kondo scattering at low temperatures. However, unlike in conventional Kondo effect, total cut off of the ln(T) divergence at low temperatures due to screening of impurity ions is not observed in the \( R_\| (T) \) data (figure 4(b)). On the other hand, SOI is known to result in significant underscreening of the impurity ions [61]. Thus our experimental observation is consistent with Kondo effect in presence of SOI at low temperatures. The origin of Kondo scattering in the LTO/STO \( (\delta = 0) \) can be attributed to the presence of localized polaronic unpaired electrons \( (S = 1/2) \) that act as magnetic scattering centers to the delocalized electron gas at the interface [62]. However in \( \delta \) doped samples, just the interaction between the delocalized and localized unpaired electrons is not enough to describe the Kondo scattering. If it were the case then \( MR_\| \) should decrease with increase in thickness of the \( \delta \) layer, as \( n_e \) decreases. However, \( MR_\| \) as well as \( \Delta R_\| (T) \) (figure 4(b)) increases with \( \delta \) layer thickness. The increase in Kondo resistance with concentration of magnetic impurity ion has been firmly established in the past [63]. Thus our results indicate that the \( \delta \) layer introduces magnetic impurities in the system. Kondo behaviour has been reported in many Ce bulk systems [64–68]. Thus the enhancement in the Kondo effect is ascribed to the presence of Ce\(^{3+}\) ions whose concentration increases on \( \delta \) doping.

\[
\Delta R_\| (B) = \frac{e^2}{2\pi h} \ln \left( 1 + \beta e^{\phi B_\parallel / 4h} B_\parallel^2 \right) . \tag{4}
\]

Where, \( d \) is the film thickness, \( B_\parallel \) is the dephasing field and \( \beta \) is a parameter that depends on the ratio of mean free path \( (l_e) \) and the film thickness. The ratio \( l_e / d \) characterizes the parallel field transport into three regimes, viz. Altshuler–Aronov (AA) regime, where \( l_e < d \), \( \beta = 1 / 3 \), Dugaev–Khmelnitskii (DK) regime, where \( l_e \gg d \), \( \beta = 1 / 16 l_e \) andBeenakker–van Houten (BvH) regime, where \( l_e \) is comparable to \( d \) and \( \beta < 1 / 3 \). The mean free path is given by, \( l_e = h \sqrt{2\pi k_B T / e, n_e, \mu} \) are the carrier density and mobility obtained from Hall measurements. For \( \delta = 6 \) and 10 u.c samples at 2 K, \( l_e = 92 \) Å and 75 Å which is comparable to the electron confinement in the STO side (12 nm) [7], thus \( \beta \) lies in the BvH regime. In order to justify the contribution of both Kondo and WAL effect to \( MR_\| \) for \( \delta = 6 \) and 10 u.c, we fit the experimental data by adding equations (3a) and (4). The excellent fit (solid orange line) in figure 8(a) supports our argument. The obtained fit parameters are shown in table 3.

It was observed in our \( \delta \) doped LTO/STO system that the SOI can be tuned by the \( \delta \) layer thickness. SOI at the interface of STO based 2DEG can also be modulated by applying a back gate voltage \( (V_g) \). Positive \( V_g \) tends to increase \( n_e \) whereas a negative \( V_g \) lowers \( n_e \). Liang et al [56] reported

| Table 2. Fitting parameters extracted from the Kondo fit to the in-plane MR data at 10 K. |
|---|---|---|
| Sample | \( R_0 \) (Ω/□) | \( R_K \) (Ω/□) | \( B_1 \) (T) |
| \( \delta = 0 \) u.c | 435 | 212 | 39.8 |
| \( \delta = 6 \) u.c | 515 | 1147 | 38.3 |
| \( \delta = 10 \) u.c | 557 | 1701 | 36.6 |

| Table 3. Fitting parameters obtained from WAL + Kondo fit to the in-plane MR data at 2 K. |
|---|---|---|---|
| Sample | \( R_0 \) (Ω/□) | \( R_K \) (Ω/□) | \( B_1 \) (T) | \( \beta \) |
| \( \delta = 0 \) u.c | 435 | 212 | 50.6 | — |
| \( \delta = 6 \) u.c | 515 | 1147 | 16.8 | 0.21 |
| \( \delta = 10 \) u.c | 557 | 1701 | 14.54 | 0.14 |
a non-monotonic change in the SOI of LAO/STO and LVO/STO as a function of $V_g$, on increasing positive $V_g$, SOI first increases goes through a maximum and then decreases again. A large SOI has been predicted at the crossover region of $d_{xy} - d_{xz/yz}$ subbands (SOI is minimal at $d_{xy}$ and $d_{xz/yz}$ subbands), where orbital mixing induces large orbital angular momentum [71]. This explains the observations of Liang et al [56], where the increasing $n_\delta$ first populates the lower energy $d_{xy}$ subband followed by the higher $d_{xz/yz}$ subbands and in the process Fermi energy ($E_F$) crosses the $d_{xy} - d_{xz/yz}$ interface leading to enhanced SOI. Contrary to the experimental observations of Liang et al [56], we observe an increase in SOI with decreasing $n_\delta$ (increasing $\delta$ layer thickness). We attempt to explain our observations based on the screening effect of the interface potential. As the thickness of the $\delta$ layer increases, the (LaO)$^+$ planes which provide the confining potential for the charge carriers at the interface is further isolated from the STO surface. Furthermore, at lower temperatures the dielectric constant $\varepsilon$ of STO increases by two orders of magnitude [46]. These two effects strongly screen the confining potential at the interface, as a result of which the electron density spreads away from the interface, into the bulk of STO. As the confinement potential decreases the energy splitting of $d_{xy}$ and $d_{xz/yz}$ subbands also decrease [72]. At the interface, $d_{xy}$ subband has lower energy; however, away from the interface, in the bulk of STO the energies for the $d_{xz/yz}$ subbands are lower and hence are easily populated by the electrons [73, 74]. Thus, the enhanced $\varepsilon$ of STO at low temperatures and increasing thickness of the $\delta$ layer facilitates the spread of electrons away from the interface, where it starts occupying $d_{xz/yz}$ subbands; this results in the crossover of $E_F$ from $d_{xy}$ to $d_{xz/yz}$ subbands leading to observed non-monotonic behaviour in SOI. Our arguments can be further supported if we look at the $k$-dependence of SOI of the $d_{xz/yz}$ subbands. $d_{xz/yz}$ subbands possesses only $k$-cubic dependence on SOI [75]. Furthermore, HLN theory accounts for only $k$-cubic SOI [56]. Hence the excellent fitting of WAL effect obtained using the HLN theory in our $\delta$ doped samples confirms the presence of only $k$-cubic SOI in our 2DEG system, which in turn implies the contribution of electrons in the $d_{xz/yz}$ subbands to the MR for the $\delta$ doped samples.

4. Conclusions

In summary, we have successfully deposited epitaxial thin films of CTO on TiO$_2$ terminated STO substrates. The CTO/STO films show an insulating behaviour which is attributed to the absence of 2DEG formation at the interface. XPS studies carried out on CTO/STO film show majority of the Ce and Ti to be in the $3+ \text{ valence state}$, although some amount of Ti$^{4+}$ and negligible amount of Ce$^{4+}$ are also present. The Ce:Ti ratio of $0.7$, indicates the presence of Ce vacancies ($V_{Ce}$) in the CTO lattice. We ascribe the presence of Ti$^{4+}$ ions in CTO to $V_{Ce}$, which incidentally results in the lack of 2DEG at the interface. The resulting cation offstoichiometry also explains the decrease in the out-of-plane lattice parameter of CTO obtained from XRD. $M(T)$ measurements on CTO/STO film exhibits diamagnetic behaviour, which is different from the antiferromagnetic behaviour reported in the bulk CTO. We have also deposited $\delta$ unit cells of CTO at the LTO/STO interface. It has been observed that the electron density at the interface decreases with $\delta$ layer thickness. This provides strong evidence in favour of polar reconstruction being responsible for 2DEG formation at LTO/STO interface. At low temperatures, magneto transport measurement reveals the presence of Kondo scattering, EEI and SOI in the LTO/CTO/STO heterostructure. The strength of Kondo scattering increases with $\delta$ layer thickness. The increase in Kondo scattering is attributed to Ce$^{3+}$. SOI displays a non-monotonic behaviour with $\delta$ layer thickness, which is related to the screening of the electron confining potential at the interface. The decrease in confining potential decreases the energy splitting between the $d_{xy}$ and $d_{xz/yz}$ subbands and also spreads 2DEG deeper into the STO bulk, where it starts to populate the Ti $d_{xz/yz}$ subbands. As $E_F$ crosses over to the $d_{xz/yz}$ subbands, a large SOI is observed at the crossover region of $d_{xy} - d_{xz/yz}$ where orbital mixing induces a large orbital momentum. Our results show that CTO $\delta$ layer can be used as an alternative to back gate voltage for SOI modulation in STO based 2DEG.

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