Nanoscale Dichotomy of Ti 3d Carriers
Mediating the Ferromagnetism in Co:TiO$_2$ Anatase Thin Films

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We study the surface and bulk electronic structure of the room-temperature ferromagnet Co:TiO$_2$ anatase films using soft and hard x-ray photoemission spectroscopy with probe sensitivities of $\sim$1 nm and $\sim$10 nm, respectively. We obtain direct evidence of metallic Ti$^{2+}$ states in the bulk, which get suppressed to give a surface semiconductor, thus indicating a surface-bulk dichotomy. X-ray absorption and high-sensitivity resonant photoemission spectroscopy reveal Ti$^{2+}$ electrons at the Fermi level (E$_F$) and high-spin Co$^{2+}$ electrons occurring away from E$_F$. The results show the importance of the charge neutrality condition: Co$^{2+} + V_O^{2-} + 2$Ti$^{2+} \leftrightarrow$ Co$^{2+} + 2$Ti$^{3+}$ ($V_O$ is oxygen vacancy), which gives rise to the elusive Ti 3d carriers mediating ferromagnetism via the Co 3d-O 2p-Ti 3d exchange interaction pathway of the occupied orbitals.

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Dilute ferromagnetic oxides have been at the forefront of a paradigm shift in the search for spintronics and magneto-optic device materials [1-4]. However, for achieving reliable thin-film device performance, it is necessary to ensure the surface and bulk electronic properties of candidate materials. This is particularly true for high Curie-temperature oxide ferromagnets for spintronics which can be synthesized only in thin film form, such as Co:TiO$_2$ [2], Mn:ZnO [3], Cr:In$_2$O$_3$ [4], etc. The main question that still remains enigmatic: What changes drive the long-range coupling of local moments in an insulating parent? The pre-runners, namely, dilute magnetic semiconductors (DMSs) which consisted of magnetic 3d transition metal (TM) ions doped in III-V and II-VI compounds, showed a Curie-temperature ($T_c$) well-below room temperature e.g. InMnAs, GaMnAs, ZnCrTe, etc [7-9]. Theoretical studies of carrier-mediated ferromagnetism played a pivotal role in predicting high-$T_c$ ferromagnets in the dilute substitution limit [10]. The spin-charge degrees of freedom and the anisotropic character of the dopant TM d-orbitals results in a directional dependence of exchange energies and $T_c$'s of upto 170 K [11-12]. The limitation of $T_c$'s significantly lower than room temperature motivated studies on alternative parents, like oxides and nitrides. The discovery of ferromagnetism in Co-doped TiO$_2$ (Co:TiO$_2$), with a $T_c$ exceeding 300 K [2], was crucial in expanding the field to oxides, leading to a rapid increase of new materials and phenomena arising from a synergistic marriage of semiconductor physics and strongly correlated systems.

From extensive magnetic and transport studies, it is now well-accepted that Co:TiO$_2$ films grown in a reducing environment or annealed in vacuum result in Co segregation [13-14], while films grown in an oxidizing condition are intrinsically ferromagnetic with high spin Co$^{2+}$ [15-16]. While initial x-ray magnetic circular dichroism (XMCD) measurements and annealing in vacuum concluded that the ferromagnetism was extrinsic due to segregated Co metal clusters [14], subsequent XMCD studies showed intrinsic ferromagnetism in Co:TiO$_2$ grown in oxidizing conditions [13]. A soft x-ray surface-sensitive photoemission study indicated the importance of exchange interaction between the occupied Co $t_{2g}$ and conduction band Ti $t_{2g}$ states [18], but concluded that anatase Co:TiO$_2$ are wide band gap semiconductors. Recent experimental studies have emphasized the importance of oxygen vacancies ($V_O$) in Co:TiO$_2$ [13,18]. The above results are consistently explained by the theoretical model of a hydrogenic spin-split donor-impurity band interacting via ferromagnetic exchange with the localized spins to realize high-$T_c$ ferromagnetism [20]. However, the experimental results are still not conclusive about the origin of the donor band: whether it is derived from shallow oxygen vacancies or cation vacancies, singly occupied vacancies or doubly occupied vacancies, or due to Co$^{2+}$-$V_O$ complexes [19]. This is a critical missing input to the mechanism of ferromagnetism in Co:TiO$_2$. In this work, we address this issue using surface and bulk-sensitive photoemission spectroscopy (PES), x-ray absorption (XAS) and high-sensitivity resonant(R) PES. Our results unambiguously show that the carriers are the occupied Ti$^{3+}$ 3d electrons, a possibility completely neglected to date, and these electrons exhibit a nanoscale surface-bulk dichotomy of the electronic structure of Co:TiO$_2$ which would play a crucial role in real device applications.

Co:TiO$_2$ thin films were fabricated on SrTiO$_3$(100) single crystal substrates by pulsed laser deposition (PLD) method. A KrF excimer laser (Lambda Physik, $\lambda$ = 248 nm) was used to ablate sintered pellet target.
(Ti_{0.95}Co_{0.05}O_2). The laser fluence and repetition rate were set to 1.2 J/cm^2/pulse and 3 Hz, respectively. During deposition, the oxygen partial pressure \((P(O_2))\) and substrate temperature were fixed at 1 × 10^{-6} Torr and 650 °C, respectively. X-ray diffraction (XRD) measurements confirmed the epitaxial growth of these films in (001)-oriented anatase phase (See [22] for details of characterization), which also showed ferromagnetism at room temperature [6].

Hard x-ray(HAX)-PES measurements were carried out at undulator beamline BL29XU at SPring-8 using a photon energy of 7940 eV and Gammadata-Scintia R4000-10kV electron energy analyzer [21]. The total energy resolution was set to 250 meV. The soft x-ray(SX)-PES measurements were carried out at undulator beamline BL17SU of SPring-8. The PES spectra were obtained using a Gammadata-Scintia SES-2002 electron energy analyzer. The total energy resolutions were set to 240 meV with \(h\nu = 1200\) eV and 230 meV for RPES measurements, respectively. The Fermi level \((E_F)\) of the samples was referred to that of an Au film deposited on the sample substrate. The XAS spectra were taken in the total electron yield mode and were calibrated by measuring Au 4f PES peak excited with first- and second-order light. All the measurements were performed at room temperature.

Figure 1 shows the Ti 2p core-level spectra of Co(5 at%)/TiO_2 thin films grown epitaxially on a SrTiO_3(100) substrates. The inset shows the hysteresis at 300 K confirming the ferromagnetism [22]. The Ti 2p core-level spectra measured with SX-PES (\(h\nu = 1200\) eV) and HAXPES (\(h\nu = 7940\) eV) show a main Ti 2p_{3/2} peak at 459.4 eV and 2p_{1/2} peak at 465.2 eV due to Ti^{4+} states, accompanied by charge-transfer satellites at 13 eV higher binding energies [23]. In addition, a fine structure is observed at 1.8 eV lower binding energy to the main peak. We plot the SX-PES and HAXPES on an enlarged (×5) scale and normalized to the main peak intensity (inset Fig. 1), which clearly shows that this feature is enhanced in the HAXPES data compared to SX-PES. This feature is not observed in the case of stoichiometric Ti^{4+} (\(d^0\) state) titanates, but shows up in reduced/electron-doped titanates indicative of Ti^{3+} states [24, 25]. A similar behaviour was recently found for the 2D-electron gas at SrTiO_3-LaAlO_3 interface using HAXPES [25]. The present results indicate that Ti^{3+} components in Co:TiO_2 thin films are clearly present in bulk-sensitive HAXPES with a probing depth of ∼10 nm and they are suppressed in the top 1-2 nm, as probed by surface sensitive SX-PES. For \(\delta\) oxygen vacancies, 2\(\delta\) electrons are introduced into valence band states consisting of Ti 3d and O 2p electrons [27]. In addition, if Co is doped as Co^{2+} (as confirmed below), oxygen defects are also necessary to keep charge neutrality. If the carriers are trapped, these are described as Co^{2+} + V_0^{2-} complexes [19]. However, our core-level O 1s spectra show a clean single peak [22] but with a small shift in binding energies, suggestive of negligible role of oxygen vacancies. Taken together with the presence of Ti^{3+}, it indicates the following charge neutral transformation, Co^{2+} + V_0^{2-} + 2Ti^{4+} ↔ Co^{2+} + 2Ti^{3+}. This is consistent with no changes in Co co-ordination using extended x-ray absorption fine structure (EXAFS), suggesting that the defects are mobile and not localized to the first co-ordination shell of Co^{2+} ions [13].

In order to confirm Ti^{3+}, we measured the valence band spectra with SX-PES and HAXPES (Fig. 2). Non-doped anatase TiO_2 is a wide-gap semiconductor with a band gap of 3.2 eV [28], and the observed gap in Fig. 2 seems to confirm it (green arrow in Fig. 2). This indicates that \(E_F\) is pinned at the bottom of the conduction band. However, in the inset of Fig. 2 we plot high signal-to-noise ratio near-\(E_F\) data on an enlarged (×85) y-scale, and it clearly shows in-gap states. More importantly, the spectra show a depletion of states at \(E_F\) for the SX-PES data while the HAXPES data shows a clear Fermi-edge step. This indicates a nanoscale surface-semiconductor: bulk-metal dichotomy. Next, we investigate the electronic character of the in-gap region in detail, using Co 2p-3d and Ti 2p-3d XAS and RPES measurements which provides unoccupied and occupied element/site-projected and orbital-selective 3d partial density of states (DOS), respectively.

Figure 3(a) shows the experimental XAS spectrum of anatase Co:TiO_2 at the Co L_3-edge, compared with...
FIG. 2. Valence band PES of Co:TiO$_2$ thin film by HAXPES (blue) and SX-PES (red). The spectra are normalized by the peak area. A green arrow indicates the position of reported band-gap value [28]. The inset is the enlargement of the spectra ($\times 85$) near-E$_F$. A green line is the fitting curve of HAXPES spectrum. HAXPES spectrum clearly shows Fermi-edge step (marked by black arrow).

the theoretically calculated low-spin and high-spin Co$^{2+}$ spectrum of Co ions [23]. The rich structure found in the experimental spectrum of Fig. 3(a) shows very good correspondence with the calculated high-spin Co$^{2+}$ spectrum and also rules out the low spin Co$^{2+}$ configuration. It is also quite similar to that of rutile Co:TiO$_2$ [17]. The results thus confirm a high-spin Co$^{2+}$ ion substituted in the Ti$^{4+}$ site for Co:TiO$_2$.

Figure 3(b) shows the Co 2$p$-3$d$ valence band RPES of Co:TiO$_2$ obtained with photon energies A-H marked in Fig. 3(a). A comparison of the off-resonance spectrum (A) with on-resonance spectra (B-H) indicates that the spectral changes observed at $\sim$1 to $\sim$3.5 eV binding energy corresponds to the new Co 3$d$ states obtained in the gap, while changes in the O 2$p$ states result from hybridization changes accompanying the doping. From Fig. 3(b), we also verify that the Co 3$d$ states are not located at E$_F$, thus indicative of localized Co 3$d$ electrons.

Figure 4 shows the Ti 2$p$-3$d$ XAS and RPES of Co:TiO$_2$ thin films measured to clarify the Ti 3$d$ states in the electronic structure. The wide energy scale RPES spectra are shown in Fig. 4(a) while the near-E$_F$ in-gap region spectra are shown in Fig. 4(b). The photoemission intensities are normalized by photon flux and the high-sensitivity near-E$_F$ spectra are magnified ($\times 160$) in order to characterize the spectral features. Off-resonant spectrum ($h\nu$ = 454 eV) shows no striking changes from the valence band PES shown in Fig. 2. In contrast, the on-resonant spectra show two clear features: a weak feature at E$_F$ and another higher intensity feature at $\sim$1 eV binding energy, arising from coherent and incoherent features of $d^1$ Ti$^{3+}$ states in the Mott-Hubbard picture of strongly correlated electrons [29]. Interestingly, we have plotted the integrated intensity of the in-gap states as a function of incident photon energy in Fig. 4(c), and at first glance, it shows no correspondence with sharp features in the Ti 2$p$-3$d$ XAS spectrum. However, a comparison with the Ti 2$p$-3$d$ XAS of Ti$_2$O$_3$ (Ti$^{3+}$) single crystal fractured in vacuum (blue line in Fig. 4(c)) shows a very good match with the peak at 459.2 eV. Hence, the resonant enhancement around 459 eV is due to the Ti$^{3+}$ component in Co:TiO$_2$.

Thus, while the core level and valence band spectra of Figs. 1 and 2 clearly show Ti$^{3+}$ states, the RPES results show that the in-gap states (inset of Fig. 2) are actually derived from Co 3$d$ and Ti 3$d$ states. The magnetic Co
by a carrier-induced mechanism involving Ti $3d$ states, consistent with a donor exchange mechanism proposed earlier \cite{19}, but with the occupied Ti $3d$ orbitals playing the role of the donors.

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