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Local Co structure in epitaxial $\mathbf{Co_xTi_{1-x}O_{2-x}}$ anatase

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We have used Co *K*-shell near-edge and extended x-ray absorption fine structure to investigate the charge state and local structure surrounding Co in epitaxial Co-doped TiO_2 anatase grown on $LaAlO_3(001)$. Co is in the +2 formal oxidation state throughout the film, and substitutes for Ti in the lattice, creating a nearby oxygen vacancy in the process. There is no evidence for either elemental Co or CoO in the films.

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The quest for diluted magnetic semiconductors (DMS) that retain their magnetism at and above room temperature is spanning several classes of materials. Such materials are critically important in the development of spintronics as spin injectors for semiconductor heterostructures that can operate without cryogenic cooling. Group IV, III-V, and II-VI DMS materials typically exhibit Curie temperatures (T_c) well below ambient due to weak interaction of the magnetic impurities. Calculations based on the Zener model of magnetism suggest that the strongest interaction is that mediated by holes, and experimental studies carried out to date have borne out this prediction.[1] One notable exception is that of Mn-doped GaN, which grows *n*-type by gas-source molecular-beam epitaxy under certain conditions, and appears to be ferromagnetic at room temperature.[2] In addition, it has recently been shown that at least one oxide semiconductor—Co-doped TiO_2 anatase—is ferromagnetic well above room temperature when doped *n*-type by oxygen vacancies,[3–5] but the mechanism of magnetism remains unknown. Critical to elucidating the mechanism of magnetism in this material is a determination of the local structure surrounding the magnetic impurity. The geometric and associated electronic structures directly determine the magnetic properties. Relevant questions have surfaced concerning the possibility that elemental Co nanocrystals form in this material either during or after growth. Such nanocrystals would trivially explain the room-temperature ferromagnetism exhibited by this material. In contrast, Co substitution at Ti lattice sites would render the material a doped semiconductor, and, in addition, a true DMS, if it can be established that the observed magnetization is indeed due to the coupling of Co dopants by itinerant electrons. The purpose of this investigation is to determine the local structure surrounding Co in crystallographically and compositionally well-defined specimens of Co-doped TiO_2 anatase.

The growth of epitaxial $Co_xTi_{1-x}O_2$ on $LaAlO_3(001)$ by oxygen-plasma-assisted molecular-beam epitaxy (OPAMBE) has been described in detail elsewhere.[6] Activated oxygen was supplied by an electron cyclotron resonance oxygen source. $LaAlO_3(001)$ substrates were ultrasonically cleaned on the bench using acetone and isopropanol, and then annealed at ~650 °C for ~5 min in the oxygen plasma at a pressure of $\sim 2\times 10^{-5}$ torr. This procedure resulted in well-ordered, flat surfaces that were free of carbon, as determined by reflection high-energy electron-diffraction (RHEED) and x-ray photoelectron spectroscopy. The substrate temperature during growth ranged from 600 to 700 °C. The growth rate was ~0.01 mm anatase/sec, and the Ti and Co fluxes were set with the goal of achieving a Co mole fraction (x in $Co_xTi_{1-x}O_2$) of 0.05. The as-grown films were either semiconducting or insulating, depending on the oxygen plasma power and flux.[6] In all cases, the majority phase was single-crystal anatase with some level of Co doping. In some cases, the surface was quite flat, with no evidence of particles. In other cases, some density of oriented Co-enriched TiO_2 anatase particles nucleated along with the flat single-phase epitaxial film. The characteristics of these particles have been discussed in more detail elsewhere.[7] In all cases, the RHEED patterns indicated single-crystal anatase with the epitaxial relationship to the substrate being $(001)_{\mathrm{ana}}\|(001)_{\mathrm{LAO}}$ and $[100]_{\mathrm{ana}}\|[100]_{\mathrm{LAO}}$.

Here, we present Co *K*-shell x-ray absorption spectra for two representative films to determine the local structure surrounding the Co dopant. One film is a flat, single-phase epitaxial film with Co uniformly distributed throughout and no particles. This specimen was grown under oxygen-rich conditions, and is insulating. The other is a majority-phase epitaxial film that exhibits a low density of particles which have been shown to be oriented Co-enriched anatase in other films grown using similar conditions.[7] In this particular case, the particles have an average diameter and height of 26±2 and 7±2 nm, respectively, and constitute ~1% of the surface. This specimen was grown under slightly oxygen-poor conditions and is semiconducting, with a resistivity of ~100 Ω cm.

Following growth and *in situ* characterization, the samples were transferred through air to the Advanced Photon Source at Argonne National Laboratory to measure Co *K*-shell x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS). The latter two measurements were done at the PNC-CAT beamlines using a bend magnet (BM) and insertion device (ID) for parallel (*s* polarization) and perpendicular (*p* polarization) orientation of the electric-field vector relative to the surface, respectively. For both measurements, the sample surface made an angle of ~1° with respect to the beam direction. A focusing mirror was used for harmonic rejection, and to focus the beam to about 50 μm on the BM line and 5 μm on the ID line. The fluorescence signal was detected using a 13-element Ge detector. The monochromators used Si(111) crystals giving an energy resolution of about 1.1 eV. The

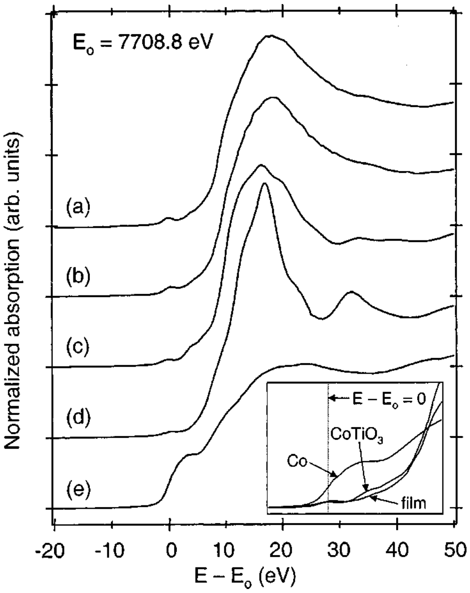

FIG. 1. Co *K*-edge XANES for a 27-nm-thick film of $\mathrm{Co}_x\mathrm{Ti}_{1-x}\mathrm{O}_2$ on $\mathrm{LaAlO}_3(001)$ which showed a low density of Co-enriched anatase particles on the surface (a). The value of x taken from the fluxes is ~0.05 when averaged over the entire film. Also shown are spectra for a 22-nm-thick film of $\mathrm{Co}_{0.06}\mathrm{Ti}_{0.94}\mathrm{O}_2$ on $\mathrm{LaAlO}_3(001)$ without particles (b), CoTiO_3 (c), CoO (d), and Co metal foil (e). E_0 was taken as the first inflection point in the Co metal edge at 7708.8 eV. These spectra were obtained in p polarization. The spectra obtained in s polarization reveal negligible differences relative to those measured with p polarization. In the inset the near-threshold regions are directly overlapped for the 22-nm-thick film, CoTiO_3, and Co metal.

energy calibration was monitored using a Co foil, and the first peak in the derivative of the metal spectrum was set at 7708.8 eV.

In order to determine the charge state of Co throughout the film, and infer something about local structure, we have measured Co *K*-edge XANES for these two films and compared to reference spectra for various Co-containing materials. The results are summarized in Fig. 1. In addition to having a depth sensitivity that exceeds the film thickness, Co *K*-shell x-ray absorption has the advantage of high sensitivity to low concentrations of Co; submonolayer equivalents can be easily measured.[8] There is a high degree of similarity between the epitaxial film spectra for specimens with and without Co-enriched anatase particles. Moreover, these spectra strongly resemble that of CoTiO_3, but are considerably different from that of CoO. These results indicate that Co is in the +2 formal oxidation state in the films, whether or not Co-enriched anatase clusters are present, and that the local structural environment is much more like that of CoTiO_3 (distorted octahedral cage) than CoO (undistorted octahedron). The film spectra are also very different from that of Co metal, allowing us to rule out the presence of Co precipitates. There is a large chemical shift between Co(0) and Co(II), as evidenced by the different threshold energies, making the detection of Co(0) straightforward. The threshold region is magnified in the inset of Fig. 1, making the comparison easier. The weak pre-edge resonance at $E-E_o=0$ eV is not due to small quantities of Co(0), but rather to a $1s$ to $3d$ transition which is strictly dipole forbidden, but weakly allowed if there is mixing of Co $3d$ and O $2p$ character in the first unoccupied state in the conduction band.[9] The presence of this feature in the reference spectra for CoTiO_3 and CoO, which do not contain any Co(0), support the conclusion that this feature is not due to Co metal. The absence of Co metal has also been corroborated by x-ray diffraction and transmission-electron microscopy measurements for other samples grown under similar conditions. However, the Co *K*-edge XANES results are more convincing because of the inherently high sensitivity of the technique and the fact that it averages over a reasonably large film area ($\leqslant\sim 50\ \mu\mathrm{m}\times\leqslant 3$ mm).

It is noteworthy that the Co *K*-edge spectrum is much more sensitive to local structural than Co *L*-edge XANES.[6] Based on the latter, Kim *et al.*[10] have concluded that Co in $\mathrm{Co}_x\mathrm{Ti}_{1-x}\mathrm{O}_2$ grown by pulsed laser deposition (PLD) under oxygen-rich conditions forms a high-spin CoO-like phase. These authors compared their epitaxial film spectra with that of CoO, and observed a strong resemblance, as we have previously noted.[6] However, they did not compare to CoTiO_3, which also exhibits a high degree of similarity in its *L*-edge spectrum to that for $\mathrm{Co}_x\mathrm{Ti}_{1-x}\mathrm{O}_2$ epitaxial films. In fact, Co *L*-edge spectra are virtually indistinguishable for CoO and CoTiO_3. Thus, Co *L*-edge XANES cannot discriminate between CoO and CoTiO_3.

In order to determine the detailed structural environment of Co(II) in $\mathrm{Co}_x\mathrm{Ti}_{1-x}\mathrm{O}_2$, we turn to Co *K*-shell EXAFS. The k^2-weighted EXAFS are shown for the films with (a) and without (b) Co-enriched anatase particles in Fig. 2 for both s and p polarizations. Some interference from Bragg peaks is seen in the data in Fig. 3(a) at $k>\sim 8\ \text{Å}^{-1}$. However, the two films exhibit very similar oscillations for $k<\sim 8\ \text{Å}^{-1}$, indicating similar local structural environments. The absence of Bragg interference in Fig. 2(b) allows us to carry out a detailed analysis. We show Fourier transforms in Fig. 3 for both x-ray polarizations. The peak characteristic of the first coordination shell falls at nearly the same value of R for s and p polarization. These data were further analyzed using the AUTOBAK and IFEFFIT programs.[11] Model standards were calculated using FEFF7.[12] The amplitudes were calibrated by fitting to CoO and CoTiO_3. Both gave identical amplitude reduction factors of 0.80. Simultaneously fitting the data obtained using s and p polarizations yields the following structural parameters: $R_{ab}=2.04\pm 0.01$ Å and $\sigma_{ab}^2=0.0096$, $R_c=2.01\pm 0.01$ Å, and $\sigma_c^2=0.011$, and $N=5.45\pm 0.3$. Here, $R_{ab}(\sigma_{ab}^2)$ and $R_c(\sigma_c^2)$ are the Co-O bond lengths (Debye-Waller factors) in the ab plane and along the c direction, respectively, and N is the spherically-averaged effective coordination number for the Co. These bond lengths are intermediate between those found in pure anatase [$R_{ab}=1.94$ Å $(4x)$ and $R_c=1.97$ Å $(2x)$], and the larger Co-O bond lengths in CoTiO_3 [2.08 Å $(3x)$ and 2.20 Å $(3x)$] and CoO [2.13 Å $(6x)$]. Thus, local strain fields may be present at substitution sites. In addition, the Debye-Waller factors are higher than expected for Co-O bonds at room temperature,[13] the most probable cause being the presence of structural dis-

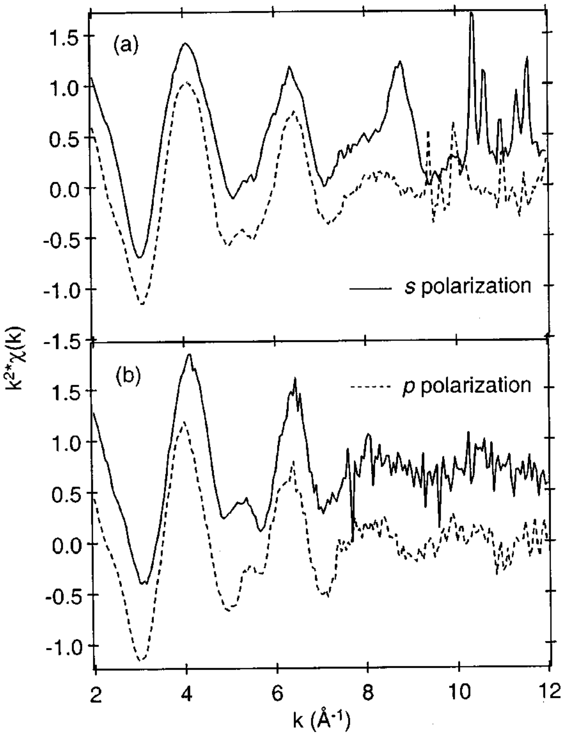

FIG. 2. Co *K*-shell EXAFS for the same two films depicted in Fig. 1 in both *s* and *p* polarizations, with k^2 weighting: (a) 27-nm-thick film of $Co_xTi_{1-x}O_2$ on $LaAlO_3(001)$ with a low density of Co-enriched anatase particles and (b) 22-nm-thick film of $Co_{0.06}Ti_{0.94}O_2$ on $LaAlO_3(001)$ without particles.

order at Co sites resulting from strain and thin-film growth. Finally, *N* is less than 6.00, the value expected for an ideal substitutional site, indicating the presence of an oxygen vacancy in the vicinity of substitutional Co(II), as discussed below. Individually fitting the *s* and *p* polarization data gave a similar reduction in coordination for both the Co-O bonds in the *ab* plane and along the *c* axis. Transforming the data in Fig. 2(a) up to $k = 8$ Å^{-1} yields similar results, but with larger uncertainties. *N* is found to be less than 6.0, and $R_{ab} = R_c = 2.01$ Å.

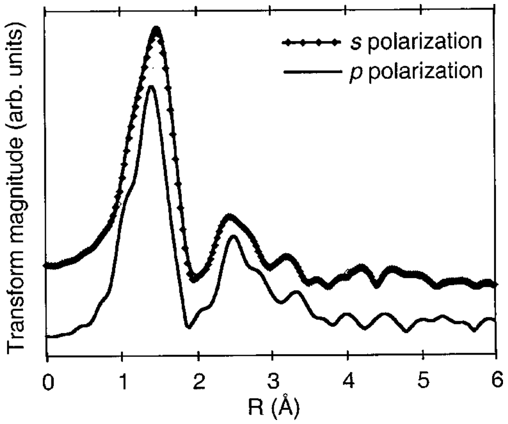

FIG. 3. Fourier transforms of the Co *K*-shell EXAFS shown in Fig. 2(b) over the range $k = 1.5-12$ Å^{-1}. Transforming the data in Fig. 2(a) up to $k = 8$ Å^{-1} yields essentially the same results, but with larger error bars.

The strain introduced into the lattice by Co substitution for Ti explains the facts that (i) Co is in the +2 formal oxidation state and (ii) *N* is less than 6. Strain relief can be achieved by expelling oxygen from the lattice. The formal charge on a Co will be lowered if adjacent oxygen vacancies exist. In fact, one oxygen vacancy must be created for every Co(II) that substitutes for Ti(IV) in the lattice in order to maintain charge neutrality. Thus, the correct empirical formula for Co-doped TiO_2 is $Co_xTi_{1-x}O_{2-x}$. A value of *N* equal to 5.00 is expected if these vacancies are perfectly correlated with substitutional Co(II). If, on the other hand, these vacancies are randomly distributed throughout the lattice, *N* will equal 5.82 for $x = 0.06$.[14] The fact that *N* assumes an intermediate value reveals significant, but incomplete structural correlation between oxygen vacancies and substitutional Co(II). Interestingly, we have found that oxygen vacancies associated with substitutional Co do *not* contribute to the electrical conductivity of the material. Films grown at high oxygen flux are consistently insulating, whether or not they are doped with Co. Conductivity in these films is directly correlated with the oxygen pressure and plasma power level used during growth. We have found a monatomic relationship between film resistivity and oxygen pressure and/or plasma power level for pure TiO_2 anatase growth.[6] In addition, we have found that for a given oxygen flux, the resistivity of the film is higher when Co is included than when a pure TiO_2 film is grown. It has been shown that oxygen vacancies in anatase produce shallow donor levels that dope the material *n* type.[15] We have found empirically that oxygen vacancies in excess of those needed to compensate substitutional Co(II) in $Co_xTi_{1-x}O_{2-x}$ anatase are required to make the material semiconducting.

These results are highly significant, in that they establish there is no detectable Co metal in OPAMBE grown Co-doped TiO_2 anatase. Yet, this material has been shown to be ferromagnetic at and above room temperature, provided enough free electrons are present to make it semiconducting.[4–6] This result is in stark contrast to that obtained for PLD grown $Co_xTi_{1-x}O_{2-x}$.[10,16] Here, it was found that Co inclusions inevitably resulted when the growth was not done with a high oxygen background pressure in the chamber. Co was directly detected by spectroscopic, TEM imaging, and selected area diffraction methods, and indirectly by the presence of magnetic hysteresis loops that strongly resemble those of Co metal.[17] At sufficiently high oxygen pressure ($P \geq \sim 1 \times 10^{-5}$ torr in Ref. 10), there was no evidence for Co metal, but the magnetization was either very low ($\sim 0.5\mu_B$ per Co), or zero. In addition, these PLD-grown films remained highly conductive, even when grown at high oxygen pressure, revealing the presence of a high concentration of what are presumably oxygen vacancy defects. In contrast, our OPAMBE-grown material is found to contain only Co(II) which appears to substitute for Ti(IV) at cation lattice sites. The moment is consistently found to be $1.1\mu_B - 1.2\mu_B$ per Co, but the remanence varies inversely with the conductivity. This finding is consistent with, but does not unambiguously establish that OPAMBE-grown Co-doped TiO_2 anatase is a true DMS. Exclusion of free carriers by growing under oxygen-rich conditions would prevent carrier mediated exchange interaction, leaving behind uncoupled Co spins in the lattice. A detailed study of the dependence of magnetic properties on growth conditions and specimen temperature is underway and will be published at a later date.

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[17] A magnetic moment of $1.3\mu_B$–$1.7\mu_B$ per Co was detected in these films, and the value for Co metal is $1.7\mu_B$ per Co.