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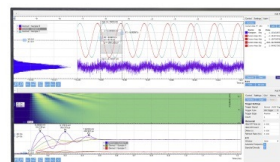
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Temperature-dependent optical studies of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$

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We present the results of Raman and photoluminescence studies on epitaxial anatase phase $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ films for $x=0-0.07$, grown by pulsed-laser deposition. The low-doped system ($x=0.01$ and 0.02) shows a Curie temperature of 700 K in the as-grown state. The Raman spectra from the doped and undoped films confirm their anatase phase. The photoluminescence spectrum is characterized by a broad emission from self-trapped excitons (STE) at 2.3 eV at temperatures below 120 K. This peak is characteristic of the anatase-phase TiO_2 and shows a small blueshift with increasing doping concentration. The Co-doped samples show two spin-flip emission lines at 2.77 and 2.94 eV. © 2003 American Institute of Physics. [DOI: 10.1063/1.1619212]

II-VI based dilute magnetic semiconductors, such as Mn-doped CdTe and ZnSe,¹ and III-Vs, such as Mn-doped GaAs,² have been studied extensively in the last decade due to their potential usage in spintronics. However, these materials undergo ferromagnetic phase transitions much below room temperature. The discovery of Curie temperatures above 300 K in cobalt-doped TiO_2 by Matsumoto *et al.*³ has generated a considerable amount of interest in this and similar systems. Epitaxial films of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ have been grown by various techniques, such as pulsed-laser deposition (PLD)⁴⁻⁷ and molecular-beam epitaxy (MBE).^{8,9} First-principles calculations of Co-doped TiO_2 have studied the microscopic distribution of Co atoms crucial for ferromagnetic ordering,^{10,11} but the exact nature of ferromagnetism still remains unclear. The PLD-grown films show evidence of clustering of Co for higher cobalt concentrations^{4,5,7} and the oxygen-assisted MBE-grown films seem to indicate that almost all of the Co substitutes for Ti in the lattice.⁹

Our motivation behind this work is twofold: assess defect structure and crystalline quality of as-grown $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ epitaxial films using Raman spectroscopy and probe the electronic structure using photoluminescence (PL) spectroscopy. Our PL studies also directly validate recent band structure calculations.^{10,11}

TiO_2 is a wide band gap semiconductor which occurs in three crystal structures: rutile, anatase, and brookite. The anatase phase of concern here has a very shallow donor level and high electron mobility.¹² Detailed investigations of the absorption edges in anatase and rutile phases by Tang *et al.* have shown that the excitonic states of the anatase phase are self-trapped, while those of the rutile phase are free.¹³

In this work, we present the results of Raman and PL

studies on epitaxial anatase phase $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ films for $x=0, 0.01, 0.02, 0.04$, and 0.07 , grown by PLD. Details regarding the growth and physical properties from these films are reported in Ref. 4. The Raman measurements were carried out in a perfect backscattering geometry using a fiberoptically coupled confocal micro-Raman system (TRIAx 320) equipped with a liquid N_2 -cooled charge-coupled detector. The 514.5-nm line of an Ar^+ ion laser was the excitation source. The microscope is equipped with a holographic super-notch filter to block the elastically scattered light. A $50\times$ microscope objective was used to focus and collect the scattered laser light, with a spatial resolution of about $5\text{ }\mu\text{m}$. The PL spectra were excited using the 363.8-nm line of an Ar^+ laser. The luminescence excitation was analyzed with a SPEX 0.85-m double monochromator equipped with a cooled GaAs photomultiplier tube and standard photon counting electronics.

The anatase and the rutile phases of TiO_2 belong to the symmetry space groups D_{4h}^{19} and D_{4h}^{14} , respectively.¹⁴ Group theory predicts six Raman active modes for the anatase phase; E_g : 147 cm^{-1} ; E_g : 198 cm^{-1} ; B_{1g} : 398 cm^{-1} ; A_{1g} and B_{1g} : 515 cm^{-1} ; and E_g : 640 cm^{-1} . The rutile phase has four Raman active modes, of which the predominant ones are E_g : 448 cm^{-1} ; A_{1g} : 612 cm^{-1} ; and B_{1g} : 827 cm^{-1} . Since the Raman peaks from each phase are clearly separated in frequency, the two phases are easily distinguishable by their Raman spectra.

Figure 1 shows the Raman spectra from $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ for various Co concentrations. The 485-cm^{-1} peak is from the LaAlO_3 substrate and serves as a good calibrant. The Raman peaks at 398 and 515 cm^{-1} clearly show that the samples are in the anatase phase. Within an experimental accuracy of a few wave numbers, there is no discernable shift of the Raman peaks with higher Co-doping concentration. However, for the higher Co-doped samples, the Raman peaks broaden.

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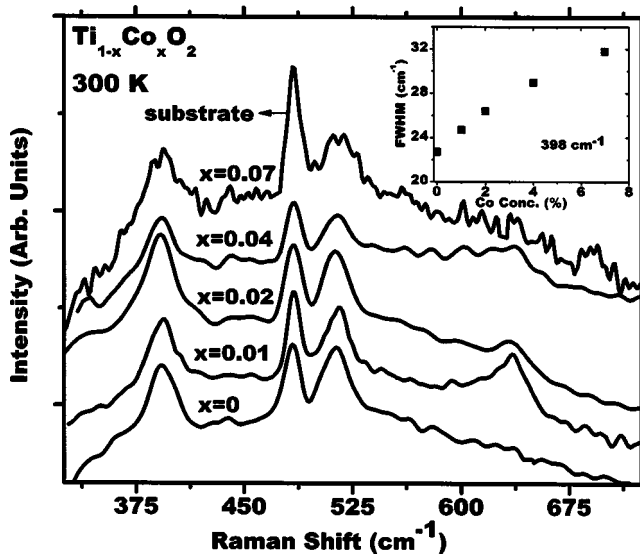


FIG. 1. Raman spectra of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ for various values of x at 300 K. The peak at 485 cm^{-1} is from the substrate. The inset shows the full width at half-maximum of the 398 cm^{-1} peak as a function of Co concentration.

The inset of Fig. 1 shows the broadening of the 398-cm^{-1} peak with increasing Co concentration. This may be an indication of limited Co solubility resulting in a disorder of the crystal structure. Recent work by Shinde *et al.* shows that higher Co doping (beyond $x=0.02$) without annealing results in the formation of Co clusters in $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$.⁴

Since the notch filter cuts off energy positions below 200 cm^{-1} , we do not observe the low-energy E_g Raman peaks. The doubly degenerate E_g modes are observed to be perpendicular to the c axis of the conventional unit cell. All the other modes are parallel to the c axis.¹⁵ The absence of the 640-cm^{-1} E_g mode in undoped TiO_2 indicates that for an epitaxial film, the c axis of the crystallites is oriented perpendicular to the substrate; the E_g modes may then be forbidden in a perfect backscattering geometry. A signature of the 640 cm^{-1} peak in $x=0.01$ and 0.02 samples shows that the crystallites have parallel components of the c axis. We point out that the E_g modes are observed in thicker films and in bulk anatase TiO_2 with a different scattering geometry.¹⁶

Although the absorption edge of anatase TiO_2 is at $\sim 3.2\text{ eV}$, the luminescence spectrum Stokes shifts by almost 1 eV . A broad greenish-yellow emission, centered at 2.3 eV , is observed from films and crystals of anatase TiO_2 .^{13,17} The TiO_6 octahedra in the anatase phase are distorted to lower symmetry, which lifts degeneracies and creates band splitting, resulting in a narrowing of the conduction band. The band-to-band excitation therefore results in self-trapped excitonic states due to a localization of the excited state whose energy is lowered by the lattice relaxation energy.¹³

Figure 2 shows the PL spectra of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ for various values of x , measured at 30 K. The spectra are characterized by a broad emission centered at 2.3 eV due to the self-trapped excitons (STE). The individual spectra have been normalized to the 2.3-eV emission and are vertically shifted for clarity. A recent work using polarized PL shows that this broad emission can be further resolved into at least two peaks centered at 2.2 and 2.4 eV .¹⁷ The center of the emission from STE blueshifts in energy with increased dop-

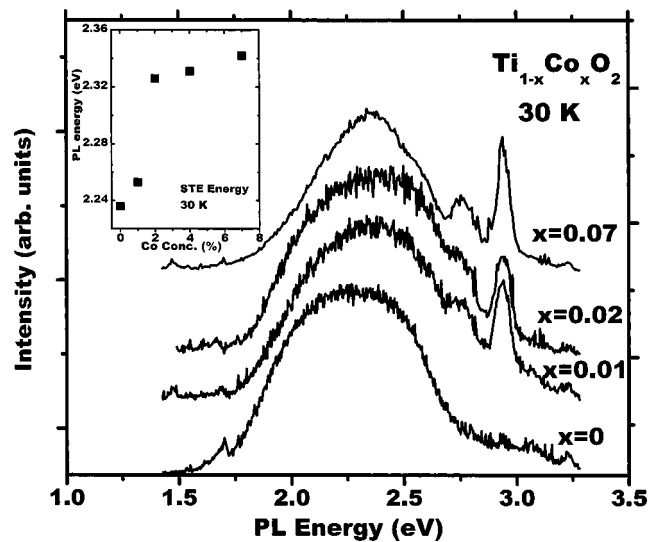


FIG. 2. PL spectra of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ for various Co concentrations at 30 K. The inset shows the center of the STE emission versus doping concentration.

ing concentrations, as seen in the inset. A saturation of the STE energy is observed for higher Co concentration, indicative of limited cobalt solubility at higher concentrations.

The most striking feature of Fig. 2 is the appearance of two peaks at 2.77 and 2.94 eV in the Co-doped samples which are absent in the undoped samples. At 30 K, the 2.77-eV peak appears as a weak shoulder in the low-doped samples. To understand the origin of these peaks, we have carried out a detailed temperature dependence study of the PL. Since higher cobalt doping leads to clustering in as-grown films,⁴ we compare the PL from undoped TiO_2 to the low Co-doped samples as a function of temperature.

Figure 3 shows the PL spectra for a few selected values of temperature for (a) $x=0.01$ and (b) $x=0$ samples. The spectra have been normalized to the STE emission. With increasing temperature the intensity of the STE drops and beyond 120 K it is barely visible. Each individual PL spectrum is fitted with four Gaussian peaks, as shown by the dotted line under the 32 K data for the $x=0.01$ sample. The individual peak positions of these four PL peaks (two of which are from STE) are plotted as a function of temperature in Fig. 4.

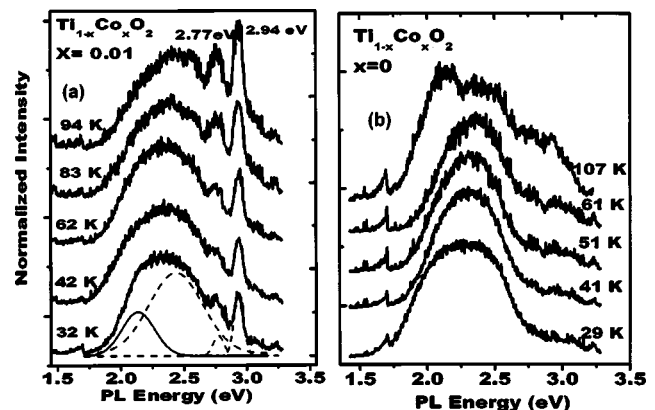


FIG. 3. PL spectra of (a) $\text{Ti}_{0.99}\text{Co}_{0.01}\text{O}_2$ and (b) undoped TiO_2 at selected temperatures.

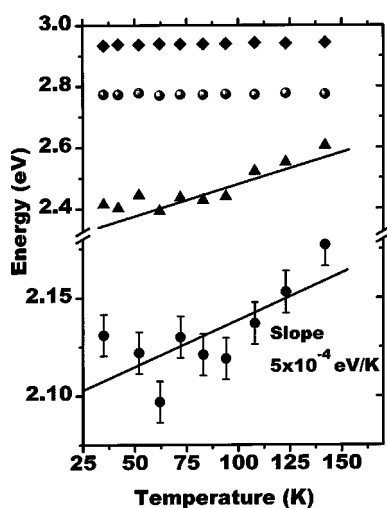


FIG. 4. PL transition energies of $\text{Ti}_{0.99}\text{Co}_{0.01}\text{O}_2$ as a function of temperature.

The 2.1 and the 2.4 eV PL energies from STE in the $x=0.01$ sample blueshift with increasing temperatures. This is in contrast to other doped system, such as Al-doped anatase TiO_2 , in which the STE redshifts by more than 500 meV from 5 to 150 K due to trapping of excitons at higher temperatures by Al acceptor levels; Al gets incorporated interstitially.¹³ We observe that the STE emission also blue-shifts with increasing temperature from undoped TiO_2 , similar to the work by Tang *et al.*¹³ Our results clearly show that cobalt does not result in any additional self-trapping mechanism, and in low-doped samples it is incorporated substitutionally. As seen from Fig. 4, the energy positions at 2.77 and 2.94 eV hardly shift with temperature, indicating that they originate from more localized levels.

The absolute intensities of the 2.77- and 2.94-eV PL peaks do not change significantly with temperature. Since the PL spectra are normalized to the STE peak in Fig. 3(a), it appears that the 2.94 and the 2.77 eV peaks gain intensity upon increasing temperatures. These two peaks are not related to any oxygen vacancies. We have compared the PL spectra (at different temperatures) from two halves of a $x=0.02$ sample: one half as-grown, and the other half annealed in an oxygen atmosphere. The PL spectra at all temperatures from both samples are identical, eliminating any issues related to oxygen vacancies. The difference in energy of 170 meV between the 2.77- and the 2.94-eV peaks may be related to states with a given spin and a spin-flipped state.

Band structure calculations show that the valence band derives primarily from oxygen p -levels, the conduction band from the Ti d -levels, and the crystal-field split Co d -levels fall within the energy gap. The local-spin-density approximation (LSDA) calculations by Park *et al.* show that the crystal-field splitting between t_{2g} and e_g states is larger than the exchange splitting between t_{2g} states, suggesting a low spin state of Co.¹⁰ The appearance of the 2.77- and the 2.94-eV energy levels in our PL spectra well below the absorption edge of 3.2 eV in $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$, show that they most probably

arise from the cobalt e_g energy levels. Moreover, the 170 meV difference between the two PL peaks agree well with the energy separation between the spin-up and spin-down e_g states of the LSDA calculation.¹⁰

The location of Co midgap levels also depends on the microscopic distribution of the Co atoms, as suggested by Yang *et al.*¹¹ The local oxygen nonstoichiometry (which influences the valence states of cations) also affects the band filling. Thus, the assignment of the observed levels to specific electronic states would require these inputs. Based on the total energies calculated for various configurations, Yang *et al.* suggest that cobalt ions in the $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ matrix would prefer nonuniform doping mode with short Co-Co distances.¹¹ Future work involving magneto-optical techniques should reveal the nature of magnetic coupling and magnetic excitations from various $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ configurations and their possible participation in optical processes.

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