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Role of donor-acceptor complexes and impurity band in stabilizing ferromagnetic order in Cu-doped SnO₂ thin films

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Our complementary magnetic and photoluminescence measurements reveal the correlation between the donor-acceptor complex and the ferromagnetic order in Cu-doped SnO₂ thin films. Oxygen vacancies (V_O) and Cu dopants form defect complexes of donor-acceptor pairs, and the associated spin-polarized impurity band leads to the narrowing of bandgap. Electronic structure calculations based on the first-principles method demonstrate that the Cu-V_O complex has low formation energy and can stabilize the ferromagnetic coupling. Our results suggest that intrinsic defects and their complexes with dopants play a key role for establishing the ferromagnetic order in doped wide-bandgap oxides. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4705419>]

Recently, diluted magnetic semiconductors (DMSs) have attracted much attention as they are promising to realize semiconductor-based spintronic devices, utilizing both charge and spin degrees of freedom.^{1–3} Wide-band-gap oxides doped with transition metal (TM) are perceived as promising material candidates toward achieving room temperature ferromagnetism,^{4–13} and the very recent developments and the important role of defects have been highlighted in a recent review by Ogale.¹⁴ So far, however, most of the research has been focused on the point defects such as oxygen and cation vacancies, and the physics of defect complexes involving more than one type of defect remains elusive.

SnO₂ is one of the prototypical functional oxides, and it is extensively applied in the fields of gas sensors, transparent conducting thin films, photocatalysis and solar cells due to its excellent optical and electrical properties.^{15–18} But compared to other wide-band-gap oxides, the magnetic properties of TM-doped SnO₂ have been less investigated, and the mechanism of introducing magnetism into SnO₂ can be different from other material systems. In some previous works,^{6,19,20} SnO₂ thin films doped with Co, Fe, and Ni have been explored, and giant magnetic moment was reported in the Co-doped case.⁶ In terms of TM dopants, Cu stands out as a prominent one because Cu and its relative oxides are nonmagnetic, thus clustering does not lead to parasitic magnetic signals. Furthermore, Cu-induced bands in wide-bandgap oxides are often located near the valence band edge, and as a result physical properties of the *n*-type oxides can be significantly modified. However, the synthesis and physical properties of Cu-doped SnO₂ thin films, as well as the correlations between doping, defects, and magnetism, have not been reported.

In the present work, we investigated the origin of ferromagnetism in Cu-doped SnO₂ thin films by combining both experiment and first-principles methods. We found that the oxygen vacancies (V_O) and the Cu dopants tend to bind to each other, forming donor-acceptor complexes. The synergistic interaction between the Cu dopants and V_O plays a critical role in stabilizing the ferromagnetism. Our results indicate that structural defects, electronic structure, and magnetic order are intricately correlated in TM-doped wide-bandgap oxides.

The Cu-doped SnO₂ films with a thickness of ~300 nm were fabricated on *c*-sapphire substrates using pulsed laser deposition (PLD), and the growth procedures are similar to the previous reports.^{21–24} During the growth process, the substrate temperature was 600 °C and the oxygen pressure was fixed at 2×10^{-3} Pa.²⁵ The Cu concentration in these films was determined using energy dispersive x-ray spectroscopy (EDS), as listed in Table I. In general, the Cu concentrations in the films are smaller than the nominal ones in the ceramic Cu-doped SnO₂ PLD targets. Optical absorption measurements were performed using an UV-visible-near infrared spectrophotometer, and photoluminescence (PL) was measured using the He–Cd laser line of 325 nm as the excitation source. Electrical properties and carrier concentrations were characterized with the van der Pauw configuration in a Hall effect measurement system. Magnetization measurements were carried out by using a superconducting quantum interference devices magnetometer (SQUID, Quantum Design, MPMSXL-5). The diamagnetic background of the sapphire substrates was carefully calibrated and subtracted from the raw data.

The x-ray diffraction data shown in Figure 1(a) indicate that the Cu-doped SnO₂ films have the rutile structure with a (200) orientation, and no impurity phase was observed. The electrical transport properties of the Cu-doped SnO₂ thin films are summarized in Table I. For the *n*-type SnO₂ films with Cu concentrations of 0, 1.2 and 2.2 at. %, the resistivity

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TABLE I. Doping concentrations and electrical properties of the Cu-doped SnO₂ thin films.

Sample No.	Cu conc. in target (at. %)	Cu conc. in film (at. %)	Carrier type	Resistivity ($\Omega\text{-cm}$)	Carrier conc. (cm^{-3})	Mobility (cm^2/vs)
S0	0	0	n	0.09	1.9×10^{19}	3.6
S1	2	1.2	n	0.62	4.8×10^{18}	2.1
S2	5	2.2	n	1.24×10^3	1.6×10^{16}	0.3
S3	7	3.5	—	Very high	—	—
S4	10	7.0	—	Very high	—	—
S5	15	10.4	p	2.04×10^3	5.6×10^{15}	0.5

significantly increases with the Cu concentration, which is a result of compensation of the intrinsic donors by the Cu acceptors. As the Cu doping concentration increases to 3.5 and 7.0 at. %, the samples are highly insulating, indicating heavy compensation and the resultant low carrier concentration. As the Cu concentration increases further to 10.4 at. %, the Hall effect measurements revealed that the conduction transforms into *p*-type with a low hole concentration on the order of 10^{15} cm^{-3} . Pan *et al.* also observed *p*-type conduction in nitrogen-doped SnO₂ films,²⁶ and the origin of the *p*-type conduction can be ascribed to the acceptor states of Cu dopants which substitute Sn atoms in the SnO₂ lattice.

Figure 1(b) shows magnetization vs. magnetic field (M-H) loops measured at room temperature for the Cu-doped SnO₂ thin films. It is clear that the Cu doping helps to boost the magnetism in SnO₂. A very weak magnetization ($\sim 0.2 \text{ emu/cm}^3$) was found in the pure SnO₂ thin film, which agrees with the previous reports of weak magnetic signal in undoped oxides such as ZnO, TiO₂, In₂O₃, and HfO₂ and can be attributed to intrinsic defects.^{27–29} As shown in Figure 1(c), the saturation magnetization of the samples monotonously increases with the Cu content. Furthermore, the highest saturation magnetic moment is estimated to be $\sim 0.6 \mu_B/\text{Cu}$. Up to now, no ferromagnetism has been reported in Cu-doped SnO₂ thin films. The magnetic signal reported here appears to be stronger than that of Cu-doped SnO₂ nanowires which present a magnetic moment of $\sim 0.25 \mu_B/\text{Cu}$.³⁰ The coercivity of the Cu-doped SnO₂ films is in a range of 72–128 Oe, and the weak anisotropy is common for dilute magnetic oxides.^{31–34}

PL is an effective tool to elucidate the band structure and the defect characteristics in wide-bandgap oxides, thus we carried out room-temperature PL measurements on the Cu-doped SnO₂ thin films to search for the possible defect-related origin of the ferromagnetism. As shown in Figure 2, the pure SnO₂ thin film is featured with a broad deep-level

emission (DLE) band centered at $\sim 2.4 \text{ eV}$ in the visible region, which can be ascribed to the transitions of excited optical centers at deep levels to the valence band. These deep levels are associated with the intrinsic defects of oxygen vacancies (V_O).³⁵ In order to confirm the origin of the DLE, a series of pure SnO₂ thin films were fabricated at various O₂ pressures. The intensity of DLE significantly weakens on increasing O₂ pressure,²⁵ suggesting its V_O -related origin. In contrast, for the Cu-doped SnO₂ thin films, an ultraviolet (UV)-violet emission peak emerges at $\sim 3.1 \text{ eV}$ and dominates in the sample with the highest Cu concentration (S5). Ma *et al.* also reported the 3.1 eV emission in Sb-doped SnO₂ and assigned it to the radiative recombination of donor-acceptor pairs.³⁶ In ZnO, V_O defects and Cu dopants can serve as donors and acceptors, respectively, and they pair up with intricate interactions. Recently, Heng *et al.* found the evidence of Cu- V_O complexes in Cu-doped ZnO films using soft x-ray magnetic circular dichroism (SXMCD) and proposed an indirect double-exchange model to explain the observed room-temperature ferromagnetism in Cu-doped ZnO.³⁷ In SnO₂, we also observed Cu^{2+} (d^9) using x-ray photoelectron spectroscopy (XPS),²⁵ and these spin-polarized Cu ions are presumably coupled magnetically via forming Cu- V_O complexes.

Generally, if there exists a large amount of compensated donor-acceptor complexes, a passivated impurity band will occur in the bandgap, which makes the bandgap narrower.³⁸ In a previous study on TiO₂, it was proposed that passivated co-doping Mo and C can effectively shift the valence band edge up while leaving the conduction band edge almost unchanged. In our case, similar band engineering is realized by co-doping V_O and Cu in the SnO₂ matrix. Figure 3 shows the optical absorption spectra for the various Cu-doped SnO₂ samples. Indeed, after Cu doping, a significant narrowing of band gap was observed with respect to the pure SnO₂ film, indicating the presence of the impurity band in the Cu-doped

FIG. 1. (a) XRD patterns and (b) room temperature magnetic hysteresis loops of the Cu-doped SnO₂ thin films with different Cu contents. Samples S0, S1, S2, S3, S4, and S5 correspond to Cu concentrations of 0, 1.2, 2.2, 3.5, 7.0, and 10.4 at. %, respectively. (c) Saturation magnetization as a function of the Cu concentration.

FIG. 2. Room-temperature PL spectra of Cu-doped SnO_2 thin films with Cu concentrations of 0 (S0), 2.2 at. % (S2) and 10.4 at. % (S5).

SnO_2 films. The data of absorption edge as a function of Cu concentration is shown in the inset of Figure 3.

To understand better the experimental results, we performed first-principles calculations using the VASP code with the projector augmented wave (PAW) potentials for electronic interaction and generalized gradient approximation (GGA) for electron exchange and correlation.^{39,40} Furthermore, on-site Coulomb repulsion U was taken into account as a result of the strong correlation effect at the Hartree-Fock level ($U = 8$ eV for Sn and 3 eV for Cu). The cutoff energy for the plane-wave basis set is 400 eV. We constructed a 72-atom $2 \times 2 \times 3$ supercell with the rutile structure. For the Brillouin zone integration, a $3 \times 3 \times 3$ Monkhorst-Pack k-point mesh was used; a more refined ($9 \times 9 \times 9$) k-point mesh was used for the density-of-states (DOS) calculations. In the calculations, all the atoms are allowed to relax until the Hellmann-Feynman forces acting on them become less than 0.01 eV/Å. The calculated band gap of pure SnO_2 is 3.7 eV,²⁵ in good agreement with the experimental value, which suggests that the parameters we selected in the calculations are reasonable. To simulate the

FIG. 3. Optical absorption spectra of Cu-doped SnO_2 thin films with various Cu concentrations. Inset: absorption edge of Cu doped SnO_2 films plotted as a function of Cu concentration, showing the monotonous decrease of band gap as the Cu concentration increases.

oxygen-deficient Cu-doped SnO_2 structure, a Cu atom substitutes a Sn atom (Cu_{Sn}) in the lattice, and the nearest-neighbor (NN) oxygen atom is removed for simulating a single Cu- V_O complex. To check the stability of possible magnetic couplings, we placed two Cu or Cu- V_O complexes with different distances in a supercell to examine the energy of the ferromagnetic (FM) or the antiferromagnetic (AFM) ground states.

In order to determine if the formation of the NN Cu- V_O complex is stable, we first calculated the complex binding energy $E_b = E_{\text{tot}}(\text{Cu}_{\text{Sn}} + \text{V}_\text{O}) + E_{\text{tot}}(\text{SnO}_2) - E_{\text{tot}}(\text{Cu}_{\text{Sn}}) - E_{\text{tot}}(\text{V}_\text{O})$, where E_{tot} is the total energy of the system calculated with the same supercell.⁴¹ A negative E_b indicates that the complex tends to bind to each other when both are present in the sample. The calculated binding energy E_b for the NN Cu- V_O complex is -2.8 eV, indicating that the

FIG. 4. First-principles calculated spin-polarized energy band structure and DOS of a 72-atom SnO_2 supercell with the Cu- V_O complex within the GGA+U approximation.

FIG. 5. Calculated SnO_2 rutile structure with two ferromagnetically coupled Cu-Vo complexes. In this particular case, the Cu-Cu distance is 6.93 Å.

complex is stable with respect to the isolated Cu dopant and V_O defect.

Figure 4 shows the calculated spin-polarized energy band structure and DOS of the SnO_2 supercell with Cu-Vo complex. The unoccupied V_O orbitals are found inside the band gap below the conduction-band minimum (CBM). The Cu-related impurity bands are located near the Fermi level, and the notable difference between the spin-majority (occupied) and the spin-minority (unoccupied) states indicates a significant energy splitting at the Fermi level, giving rise to spin polarization. We also calculated the energy difference $\Delta E_{\text{AFM-FM}}$ between FM and AFM states for both coupled Cu-Cu and (Cu-V_O) - (Cu-V_O) configurations. For the Cu-Cu coupling, only the NN configuration shows a FM state with $\Delta E_{\text{AFM-FM}} = 68$ meV. The examinations of second NN and other configurations show that $\Delta E_{\text{AFM-FM}}$ is almost zero, even negative, indicating a nonmagnetic or AFM state. However, for the (Cu-V_O) - (Cu-V_O) coupling, we found that stable FM states with $\Delta E_{\text{AFM-FM}} = 109$ and 287 meV when Cu-Cu distance is 5.94 and 6.93 Å, respectively. Figure 5 shows the optimized SnO_2 rutile structure with two Cu-Vo complexes. These results indicate that the Cu-Vo complex helps to stabilize the FM order in the Cu-doped SnO_2 system.

In summary, we have systematically investigated the magnetic and optical properties of Cu-doped SnO_2 thin films using complementary experimental and first-principles methods. Our results suggest that intrinsic defects and their complex with dopants play a key role for establishing ferromagnetic order in Cu-doped SnO_2 thin films. Such a scenario involving passivated donor-acceptor impurity bands may be generalized to other wide-bandgap oxides to exploit the potential magnetic and optical functionalities.

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