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Experimental and first-principles study of ferromagnetism in Mn-doped zinc stannate nanowires

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Room temperature ferromagnetism was observed in Mn-doped zinc stannate (ZTO:Mn) nanowires, which were prepared by chemical vapor transport. Structural and magnetic properties and Mn chemical states of ZTO:Mn nanowires were investigated by X-ray diffraction, superconducting quantum interference device (SQUID) magnetometry and X-ray photoelectron spectroscopy. Manganese predominantly existed as Mn^{2+} and substituted for Zn (Mn_{Zn}) in ZTO:Mn. This conclusion was supported by first-principles calculations. Mn_{Zn} in ZTO:Mn had a lower formation energy than that of Mn substituted for Sn (Mn_{Sn}). The nearest neighbor Mn_{Zn} in ZTO stabilized ferromagnetic coupling. This observation supported the experimental results. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4815884]

I. INTRODUCTION

Room temperature ferromagnetism in binary oxides doped with transition metal (TM) or rare-earth elements has been extensively reported. Examples include Mn-, Cr-, Ni-, Co-, Fe-, Cu-, Nd- and Gd-doped, ZnO, and SnO₂.¹⁻²⁴ TMdoped ternary oxides including SrTiO₃, exhibit physical properties and have potential application in spintronics.²⁵ Zinc stannate (Zn₂SnO₄, ZTO) is a cheap, transparent, conducting nontoxic oxide that can be prepared as films with varying nanostructures.²⁶⁻²⁹ ZTO is a prototypical ternary functional oxide and has been applied in solar cells, transparent conducting films, and photocatalysts.^{30–32} Numerous experimental and theoretical studies have investigated the structural, electrical, and optical properties of ZTO.^{27,33,34} The magnetic properties of TM-doped ZTO have received far less attention, and the mechanism of magnetism in ternary oxides may differ from that in binary oxides. Mn is an attractive TM-dopant because of its d⁵ electron configuration and large magnetic moment.

Herein, an experimental and theoretical study of the magnetic properties of Mn-doped ZTO (ZTO:Mn) nanowires, prepared by chemical vapor transport, is reported. The influence of Mn on ferromagnetism is investigated. Magnetic moments introduced by Mn^{2+} doped at Zn sites are proposed to explain the observed ferromagnetism. This is supported by first-principles calculations.

II. EXPERIMENTAL

Undoped and Mn-doped ZTO nanowires were synthesized by chemical vapor transport in a horizontal tube furnace. Two mixtures were used in a typical ZTO and ZTO:Mn nanowire growth procedure. One was of ZnO and graphite powders. The other was of SnO₂, graphite and MnO₂ powders. The former had a ZnO:graphite weight ratio of 3:2. The latter had SnO₂:MnO₂:graphite weight ratios of 2:1:1 and 2:2:1, thus producing ZTO doped with two different concentrations of Mn. A quartz boat containing a powder mixture was placed in the centre of the furnace tube. Au catalyst films ca. 3 nm thick were sputter-coated on 5×5 mm silicon wafers. These substrates were placed a few centimeters downstream of the powder mixture. The furnace was evacuated to ca. 1 mbar to remove O_2 . A constant 100 cm³/min flow of 95.5% Ar/0.5% O₂ was introduced to the tube during growth. The tube pressure was fixed at 8 mbar, and the furnace temperature was increased to 950 °C and held there for 10 min. The furnace was cooled to room temperature, and the products characterized.

Morphologies were analyzed by field-emission scanning electron microscopy (SEM) using a JEOL JSM-6700 F instrument. Crystal structures were determined by X-ray diffraction (XRD) using a diffractometer with CuK α radiation ($\lambda = 0.15418$ nm). Chemical bonding states and compositions were determined by X-ray photoelectron spectroscopy (XPS). Binding energies were determined with respect to the adventitious C 1s peak at 284.6 eV. XPS indicated that ZTO:Mn nanowires from the 2:1:1 and 2:2:1

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reactant weight ratios had Mn contents of 1.4 (denoted ZTO:Mn-1) and 2.3 (ZTO:Mn-2) at. %, respectively. Magnetization measurements were carried out using a superconducting quantum interference device magnetometer (SQUID, Quantum Design, MPMSXL-5). The diamagnetic contribution of the substrate was calibrated and subtracted from the measurements.

III. RESULTS AND DISCUSSION

Fig. 1 shows SEM images of ZTO and ZTO:Mn. Samples were composed of large quantities of dense straight nanowires. Insets show enlarged views of individual nanowires. Nanowire lengths and diameters were several tens of micrometers and 70–100 nm, respectively. Their surfaces appeared faceted, which differed from the smooth nanowires reported in the literature.³⁵ They exhibited morphologies resembling necklaces of rhombohedra, and their periodic axial surface structure was similar to a previous report.³⁴ The morphology of ZTO:Mn samples in Figs. 1(b) and 1(c) was similar to that of undoped ZTO in Fig. 1(a).



FIG. 1. SEM images of (a) ZTO nanowires, and ZTO:Mn nanowires with Mn contents of (b) 1.4 and (c) 2.3 at.%. Insets show magnified images of individual nanowires.



FIG. 2. XRD patterns of ZTO and ZTO:Mn nanowires with Mn contents of 1.4 and 2.3 at.%.

XRD measurements were used to characterize structural properties. Fig. 2 shows XRD patterns of undoped ZTO and ZTO:Mn. The products were highly crystalline, and were indexed to a face-centered cubic spinel structure (JCPDS PDF No: 040736). No impurity phases were detected. These results greatly improve on the purity of ZTO nanowires in previous reports.^{34,36} Raman spectra were recorded to further check for impurities. Fig. 3 shows room temperature Raman spectra of undoped ZTO and ZTO:Mn. The peak at 520 cm⁻¹ was attributed to the Si substrate, and that at 665 cm⁻¹ to the ZTO phase.^{27,34,37} No Raman modes of other phases such as ZnO, SnO₂ or SnO were observed. Samples were of a highly pure single phase.

XPS measurements were used to investigate chemical compositions and bonding states. Fig. 4 shows the XPS spectrum of the Mn 2*p* spectral region of ZTO:Mn-2 nanowires. The Mn 2*p*_{3/2} and 2*p*_{1/2} peaks were observed at ca. 640.3 and 655.6 eV. Fitting results of the Mn 2*p*_{3/2} peak are shown inset in Fig. 4. The fitted peak at 640.3 eV was attributed to Mn²⁺ (640.4 eV).^{22,37} XRD did not detect any undesirable Mn²⁺



FIG. 3. Room temperature Raman spectra of ZTO and ZTO:Mn nanowires with Mn contents of 1.4 and 2.3 at.%.



FIG. 4. XPS spectrum of the Mn 2p region of ZTO:Mn nanowires with Mn content of 2.3 at.%. Inset shows an enlargement of the Mn $2p_{3/2}$ peak and fitted curve (red).

phases, so the XPS results suggested that Mn^{2+} most likely replaced Zn^{2+} in ZTO:Mn.

Fig. 5(a) shows raw magnetization versus magnetic field (M-H) loops measured at 300 K for ZTO, ZTO:Mn-1 and ZTO:Mn-2 nanowires, without subtracting the substrate contribution. M-H curves clearly indicated ferromagnetic behavior. Measuring the contribution from the bare substrates ensured that their contrition was solely diamagnetic.³⁸ These diamagnetic contributions were subtracted from the raw data according to sample weights, as shown in Fig. 5(b). Details of this method can be found elsewhere.³⁵ Very weak magnetization was observed in undoped ZTO nanowires, in agreement with previous reports of undoped oxides ZnO and In₂O₃, where it was attributed to intrinsic defects.^{39–42} Mn doping clearly increased the magnetism in ZTO nanowires. The saturation magnetization monotonously increased with increasing Mn content: The saturated room temperature magnetic moment of ZTO:Mn-2 was twice that of ZTO:Mn-1, which indicated that magnetic properties correlated closely with Mn content. Saturation magnetizations at 1 T were 0.14 and 0.15 $\mu_{\rm B}$ /Mn, for ZTO:Mn with Mn contents of 1.4 and 2.3 at. %, respectively. This indicated the contribution of each Mn²⁺ to total magnetization was similar for both

FIG. 5. (a) Magnetization versus magnetic field for ZTO and ZTO with Mn contents of 1.4 and 2.3 at.%, at 300 K. (b) Corresponding ferromagnetic hysteresis loops after subtracting the diamagnetic contribution from the substrate.

FIG. 6. ZTO supercell with spinel structure. Large red balls: O; Gray balls: Zn; Purple balls: Sn. Sites marked A and B indicate NN Sn atoms, C and D indicate NN Zn atoms, and B and C indicate NN Sn and Zn atoms.

samples. Potential secondary phases containing Mn include Mn⁰, MnO and MnO₂, which are paramagnetic or antiferromagnetic and do not contribute to ferromagnetism.^{43–45} However, no secondary phases were observed within experimental detection capabilities.

First-principles calculations using the plane-wave projector augmented-wave (PAW) method were undertaken.^{46,47} The semilocal Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁴⁸ was applied, as implemented in the VASP code.^{49,50} A 56 atom spinel ZTO cell was constructed to simulate the ZTO:Mn system. Two Mn atoms substituted two nearest neighbor (NN) cation sites. The nanowire dimensions were too large to construct models simulating modified surface band structures.⁵¹ Thus, the calculations focused on the effect of defects on magnetic order. Three occupied configurations: (i) two NN Sn atoms,

FIG. 7. Formation energies of neutral Mn_{Sn} , Mn_{Zn} and Mn_{Sn} - Mn_{Zn} complexes in ZTO:Mn under O-, Zn-, Mn- and Sn-rich conditions.

TABLE I. Calculated magnetic moments (μ_B/Mn) and energy (E) differences (meV) between AFM and FM states.

Configuration	Mn _{Sn} -Mn _{Sn}	Mn _{Sn} -Mn _{Zn}	Mn _{Zn} -Mn _{Zn}
$\mu_{\rm B}$	2.9	2.2	3.3
$E_{\rm AFM}$ - $E_{\rm FM}$	25	41	176

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FIG. 8. (a)–(c) Calculated total and partial DOS and (d)–(f) spin density distributions of different substitution configurations in ZTO:Mn. Filled areas in (a)–(c) represent partial DOS of Mn-3d states. The Fermi level is set at zero. Atom coloring in (d)–(f) is as in FIG. 6.

(ii) two NN Zn atoms and (iii) NN Sn and Zn atoms, were replaced by two Mn atoms. These three configurations were denoted Mn_{Sn} , Mn_{Zn} and Mn_{Sn} - Mn_{Zn} , respectively, and are shown in Fig. 6. A $3 \times 3 \times 3$ Monkhorst-Pack k-point mesh was used for the Brillouin zone integration. A more refined $6 \times 6 \times 6$ k-point mesh was used for density of states (DOS) calculations. In the calculations, all atoms were allowed to relax until the Hellmann-Feynman forces acting on them was <0.01 eV/Å.

To determine the stable state of the ZTO:Mn system, the formation energies of Mn_{Sn}, Mn_{Zn} and Mn_{Sn}-Mn_{Zn} in ZTO were calculated under O-, Zn-, Mn- and Sn-rich conditions. The results are shown in Fig. 7. Mn_{Zn} exhibited the lowest formation energy, suggesting that Mn_{Zn} was the predominant substitution defect in the ZTO:Mn system, in agreement with the experimental results. Total energies of the NN Mn_{Sn}-Mn_{Sn}, Mn_{Zn}-Mn_{Zn} and Mn_{Sn}-Mn_{Zn} complexes with ferromagnetic (FM) and antiferromagnetic (AFM) configurations were calculated. This was done to check the stability of magnetic couplings for the three configurations. Table I lists magnetic moments and energy differences between AFM and FM states, for the three configurations. The FM state always exhibited a lower energy than the AFM state in the three configurations, indicating that the FM state was stable in ZTO:Mn. The NN Mn_{Zn}-Mn_{Zn} configuration exhibited the strongest FM coupling and the largest magnetic moment, indicating that NN Mn_{Zn} could stabilize FM ordering in ZTO:Mn. Its EAFM- $E_{\rm FM}$ value reached 176 meV, which was well above the room temperature energy (25 meV). This supported the observed room temperature magnetism.

Spin-resolved DOS were calculated to explain the origin of magnetic moments in ZTO:Mn. Figs. 8(a)-8(c) show spinresolved total DOS and partial DOS of Mn 3d states in ZTO:Mn in the FM ground state, for the Mn_{Sn}-Mn_{Sn}, Mn_{Sn}-MnZn and MnZn-MnZn configurations. For the MnSn-MnSn configuration, a strong splitting of the Mn 3d state was observed at the bottom of the conduction band. This indicated the magnetic moment predominantly originated from the Mn-3d states. A weak energy band splitting was also observed at the top of the valence band, where the Fermi level passes through the majority-spin states. Thus, some of the magnetic moment was contributed by partially unoccupied O 2p orbitals. Fermi levels in the other two configurations were located at the bottom of the conduction band, and the split was predominantly from the Mn 3d states. In general, magnetic moments arose from the contribution of Mn 3d states in the three FM configurations. Figs. 8(e)-8(g) show the spatial distributions of spin density for the three FM configurations. Most of the spin densities were localized in the vicinity of Mn dopants, which was consistent with results from the DOS calculations.

IV. CONCLUSIONS

Room temperature ferromagnetism was observed in Mndoped ZTO nanowires with a spinel structure. Mn^{2+} in ZTO was important in obtaining ferromagnetic coupling. Complementary first-principles calculations indicated that most Mn^{2+} in ZTO substituted at Zn sites. Strong ferromagnetic coupling was observed between nearest neighbor Mn_{Zn} dopants. ZTO:Mn nanowires are a promising ternary oxide for room temperature ferromagnetism.

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