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Tuning ferromagnetism in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films by band gap and defect engineering

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We investigate the room temperature ferromagnetism in band gap tunable $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($x \leq 0.22$) alloy thin films and find that ferromagnetism is significantly enhanced in p-type $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($x \geq 0.17$) compared with the n-type counterparts ($x \leq 0.15$). Temperature-dependent photoluminescence measurements reveal the correlation between the p-type behavior, enhanced ferromagnetism, and zinc vacancies. First-principle calculations demonstrate that the formation energy of zinc vacancies decreases with the increasing Mg content and the zinc vacancies in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys stabilize the ferromagnetic coupling. Our results suggest a viable route to tune the magnetic properties of oxides through band gap and defect engineering. © 2010 American Institute of Physics. [doi:10.1063/1.3485058]

Dilute magnetic semiconductors (DMSs) with cations being partially replaced by magnetic atoms are of interest as potential semiconductor-compatible magnetic components in spintronics.^{1,2} In the past decade, ZnO-based DMSs doped with transition metals (TMs) have attracted much attention due to the claims of room temperature ferromagnetism (RTFM) (Refs. 3–5) although careful experiments are often needed to establish the intrinsic and robust magnetism. Recently, defects and nonmagnetic impurities are recognized to play important roles in inducing RTFM in ZnO,^{6–8} which on one hand explains the discrepancies often reported in experiments, on the other hand offers new opportunities to search for the underlying mechanisms. Notably, Yi *et al.* achieved RTFM in Li doped ZnO through defect engineering and proposed that the origin of RTFM is related to zinc vacancies (V_{Zn}) induced by the Li doping.⁷ However, many open questions still remain regarding the precise control of defect characteristics, and answering these questions entails further in-depth research.

ZnO is also considered as a promising material in the field of ultraviolet (UV) optoelectronics due to its high excitation binding energy of ~ 60 meV.⁹ $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ternary alloy is particularly interesting because of its tunable band gap which is controlled by the Mg content. Hence, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy is an important barrier material for realizing the high efficient UV light emission in the quantum well structure,¹⁰ and spintronic functionalities can be envisioned if a DMS barrier is used. Furthermore, the magnetic properties may be tailored in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ because a large amount of defects, in particular V_{Zn} , are introduced as Mg is alloyed into ZnO.¹¹ To investigate this scenario, we synthesized $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films and studied their magnetic properties of in detail. Indeed, we found that RTFM can be tuned in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$

($0 \leq x \leq 0.22$) alloy thin films, and the first-principle calculation confirmed its defect-related origin.

The $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin films were fabricated on c-sapphire substrates by using pulse laser deposition (PLD), and the Mg content in films was controlled by using different $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ targets. The RT optical absorption measurements were performed using an UV-visible-near infrared spectrophotometer, and the temperature-dependent photoluminescence (TDPL) was measured using the He–Cd laser line of 325 nm as the excitation source. Electrical properties 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.

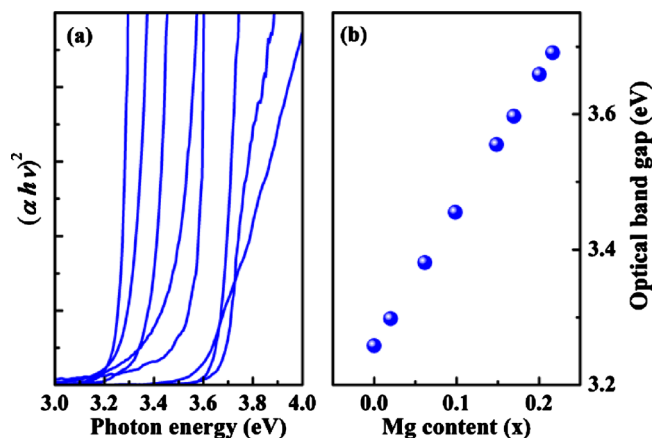


FIG. 1. (Color online) (a) Optical absorption spectra of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin films with the Mg content (x) increasing from 0 to 0.22. (b) Corresponding optical band gap of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys.

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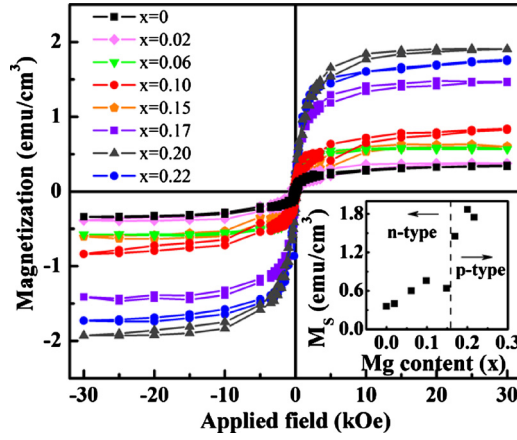


FIG. 2. (Color online) Room temperature magnetic hysteresis loops of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy films with different Mg content. The inset shows the saturation magnetization as a function of the Mg content.

The x-ray diffraction measurements indicate that the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ samples have the wurtzite structure with a preferential c-axis orientation, and no phase separation was observed for the samples with the Mg content up to 22 at.%. Figure 1(a) shows the optical absorption data of $(\alpha h\nu)$ (Ref. 2) versus $h\nu$, where α is the absorption coefficient and $h\nu$ is the photon energy. Using the relation: $\alpha(h\nu) \propto (h\nu - E_g)^{1/2}$, the band gap E_g of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films were evaluated to be 3.258 eV, 3.298 eV, 3.381 eV, 3.455 eV, 3.555 eV, 3.597 eV, 3.659 eV, and 3.691 eV, respectively, which is consistent with the expected increasing Mg content. Furthermore, using the relation between band gap and composition,¹² the Mg content x in the films were determined as 0, 0.02, 0.06, 0.10, 0.15, 0.17, 0.20, and 0.22, respectively. The optical band gap as a function of the Mg content is shown in Fig. 1(b).

Figure 2 shows M-H loops measured at RT for the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin films. A weak magnetization was found in the pure ZnO film, which agrees with the previous reports of RTFM in undoped oxides such as ZnO, TiO_2 , In_2O_3 , and HfO_2 .^{13–15} The inset shows the saturation magnetization (M_s) of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ as a function of the Mg content. The values of M_s are in the range of 0.3–0.7 emu/cm^3 for the Mg content $x \leq 0.15$, and increase significantly to 1.4–1.9 emu/cm^3 for $x \geq 0.17$. The electrical transport properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy films are summarized in Table I. With the higher Mg content, RT resistivity (carrier concentration) of the samples increases (decreases), as a result of the increasing donor ionization energy.^{16,17} As the Mg content goes above 0.17, the carrier type shows a transformation from n to p type with a low hole concentration of

TABLE I. Electrical properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin films.

Mg content	Resistivity ($\Omega \text{ cm}$)	Carrier concentration (cm^{-3})	Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Carrier type
0	0.07	5.6×10^{18}	15.2	n
0.02	0.19	2.4×10^{18}	14.3	n
0.06	5.3	7.6×10^{17}	1.6	n
0.10	1.3×10^2	5.7×10^{17}	0.2	n
0.15	1.8×10^4	1.5×10^{14}	2.3	n
0.17	1.2×10^3	1.1×10^{15}	4.8	p
0.20	9.7×10^2	7.0×10^{15}	1.1	p
0.22	1.5×10^2	3.7×10^{15}	6.8	p

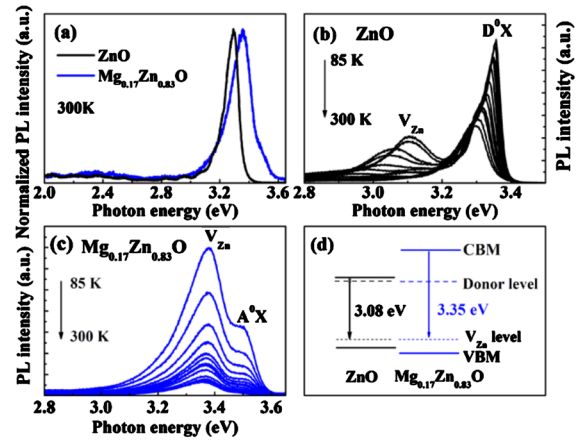


FIG. 3. (Color online) (a) Room temperature and (b) and (c) temperature-dependent PL spectra measured in ZnO and $\text{Mg}_{0.17}\text{Zn}_{0.83}\text{O}$ thin films. (d) Corresponding schematics of energy band diagrams showing transitions from the CBM to the V_{Zn} levels.

$\sim 10^{15} \text{ cm}^{-3}$. The p-type conversion was also observed previously, and the origin of p-type conduction was contributed to V_{Zn} .¹⁸

To elucidate the origin of the enhanced ferromagnetism in the p-type $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films, TDPL measurements were performed. Figure 3(a) compares the normalized RT data of the n-type ZnO and the p-type $\text{Mg}_{0.17}\text{Zn}_{0.83}\text{O}$ films. No obvious deep level emission was observed for both films, indicating that the deep level defects, such as interstitial oxygen, oxygen vacancy and antisite oxygen, have very low concentration if exist.^{19–21} The near band edge spectra of the n-type ZnO and the p-type $\text{Mg}_{0.17}\text{Zn}_{0.83}\text{O}$ films are shown in Figs. 3(b) and 3(c), respectively. For the n-type ZnO film, the 85 K spectrum shows a sharp peak at 3.36 eV and a weaker peak at 3.08 eV, which originate from the neutral-donor-bound excitons ($D^0\text{X}$) and the electron transition from the conduction band minimum (CBM) to the V_{Zn} level, respectively.^{22,23} The appearance of $D^0\text{X}$ emission agrees with the n-type conduction in the pure ZnO film, and V_{Zn} may be related to the observed weak magnetism. In contrast, for the p-type $\text{Mg}_{0.17}\text{Zn}_{0.83}\text{O}$ film, there is a strong peak at 3.38 eV and a shoulder at 3.51 eV in the 85 K PL spectra. The intensity of the 3.51 eV peak decreases rapidly with increasing temperature. By fitting the PL intensity, the ionization energy was estimated to be 229 meV by the Haynes rule.²⁴ Thus this peak at 3.51 eV can be assigned to the neutral-acceptor-bound excitons ($A^0\text{X}$) related to V_{Zn} ,¹⁸ which also agrees with the report by Hierro *et al.* who found high-concentration traps at $E_v + 280 \text{ meV}$ in the $\text{Mg}_{0.18}\text{Zn}_{0.82}\text{O}$ alloy.²⁵

The schematic energy band diagrams of ZnO and $\text{Mg}_{0.17}\text{Zn}_{0.83}\text{O}$ are shown in Fig. 3(d). Based on the absorption spectra, the band gap difference between ZnO and $\text{Mg}_{0.17}\text{Zn}_{0.83}\text{O}$ is about 0.34 eV. Their conduction-band offset (CBO) can be determined to be 0.27 eV by using the ratio of CBO to the valence-band offset.¹⁶ Since the emission peak at 3.08 eV in ZnO originates from the electron transition from the CBM to the V_{Zn} level, it can be deduced that the analogous emission in $\text{Mg}_{0.17}\text{Zn}_{0.83}\text{O}$ alloy should peak at 3.35 eV, which is very close to the observed strong peak at 3.38 eV. Thus, we attribute the 3.38 eV peak in Fig. 3(c) to electron transition from the CBM to the V_{Zn} level. As a result, we hypothesize that the ferromagnetic enhancement in the

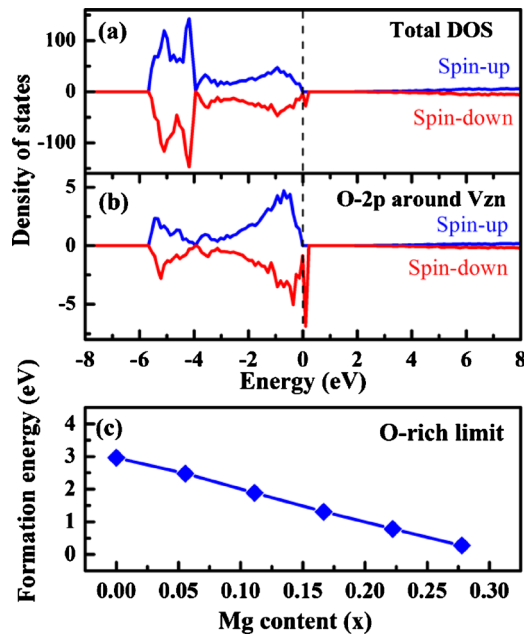


FIG. 4. (Color online) (a) Total DOS of $\text{Mg}_8\text{Zn}_{26}\text{O}_{36}$ system and (b) corresponding partial DOS of O 2p nearest neighbors to V_{Zn} . (c) Formation energy of V_{Zn} as a function of Mg content under the O-rich limit.

$\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy films is correlated with V_{Zn} .

To shed light on the experimental results, electronic structure of V_{Zn} in MgZnO were calculated by using the first-principle density-functional theory.²⁶ The calculations were carried out with the VASP code²⁷ using the projector augmented-wave method.²⁸ Figures 4(a) and 4(b) illustrate the spin-resolved total and partial density of states (DOS) of O 2p nearest neighbor to V_{Zn} in the $\text{Mg}_8\text{Zn}_{26}\text{O}_{36}$ system with FM configuration, respectively. There is a significant splitting around the valence-band maximum, which are contributed from the partially unoccupied p -orbitals of oxygen around V_{Zn} . The calculated magnetic moment of V_{Zn} increases slightly from 1.85 to 2.04 μ_B as the Mg content increases from 0 to 0.28. More importantly, we found that the formation energy of V_{Zn} decreases with the increasing Mg content, indicating that the formation of V_{Zn} is favored at the higher Mg content. It is in agreement with the strong V_{Zn} related emission observed in the PL spectra of $\text{Mg}_{0.17}\text{Zn}_{0.83}\text{O}$ as well as the recent positron annihilation spectroscopy measurements.¹¹

Furthermore, the energy difference between the AFM and the FM states of coupled V_{Zn} in ZnO is 41 meV, consistent with the calculated result of 44 meV by Wang *et al.*²⁹ Since it is larger than the RT thermal energy, RTFM can be established in the undoped ZnO, which was confirmed experimentally here as well by others.³⁰ For the $\text{Mg}_8\text{Zn}_{26}\text{O}_{36}$, we found that the energy difference increases to 116 meV, much larger than that in ZnO, indicating a stronger ferromagnetism. These results support the scenario that V_{Zn} is responsible for the enhanced ferromagnetism in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy films.

In summary, we found the strong correlation between ferromagnetism and engineered defects in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy thin films by experiments and first-principle calculations. Our work illustrates that tailoring the band gap and engineer-

ing the defects are effective in tuning the RTFM in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy, which is promising to be generalized to other oxides to establish RTFM and to construct functional devices.

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