Defect characterization and magnetic properties in un-doped ZnO thin film annealed in a strong magnetic field*

Ning Shuai(宁 帅), Zhan Peng(战 鹏), Wang Wei-Peng(王炜鹏),
Li Zheng-Cao(李正操), and Zhang Zheng-Jun(张政军)†

State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, *China*

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Highly *c*-axis oriented un-doped zinc oxide (ZnO) thin films, each with a thickness of ∼ 100 nm, are deposited on Si (001) substrates by pulsed electron beam deposition at a temperature of ∼ 320 °C, followed by annealing at 650 °C in argon in a strong magnetic field. X-ray photoelectron spectroscopy (XPS), positron annihilation analysis (PAS), and electron paramagnetic resonance (EPR) characterizations suggest that the major defects generated in these ZnO films are oxygen vacancies. Photoluminescence (PL) and magnetic property measurements indicate that the room-temperature ferromagnetism in the un-doped ZnO film originates from the singly ionized oxygen vacancies whose number depends on the strength of the magnetic field applied in the thermal annealing process. The effects of the magnetic field on the defect generation in the ZnO films are also discussed.

Keywords: magnetic semiconductors, magnetic annealing, defects, zinc oxides

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1. Introduction

Zinc oxide (ZnO) is a unique semiconductor material of particular interest with wide applications ranging from photonic crystals, photodetectors, and gas sensors, to solar cells, owing to its wide band-gap (3.37 eV), large exciton binding energy (60 meV), and specific electrical and optoelectronic properties.[1,2] In recent years, it has also been considered as a promising candidate of diluted magnetic semiconductors (DMSs) in the field of spintronics, owing to its room-temperature ferromagnetism (RTF)[3–5] that was theoretically predicted and experimentally obtained. Many research groups have paid considerable attention to the RTF in ZnO doped with some magnetic ions,[6–9] which are partially filled with d or f electrons. However, metallic clusters and secondary phases may occur in the doped samples, and they are detrimental to applications of DMSs.[10]

RTF has also been observed in un-doped oxides, such as ZnO,[11] SnO_2,[12] TiO_2,[13] HfO_2,[14] ZrO_2,[15] and Al_2O_3,[16]; however, it is very weak. This type d^0 ferromagnetism motivated researchers to understand the origin of RTF in un-doped oxides, and to manage to enhance this RTF. For example, studies published in the literature suggested that the RTF in un-doped ZnOs probably originates from the intrinsic point defects such as oxygen vacancy (V_O),[17–20] oxygen interstitial (O_i),[21] zinc vacancy (V_{Zn}),[22,23] and zinc interstitial (Zn_i).[24] However, which kind of defect is responsible for this RTF is still an open question. It has been reported that the growth conditions and post-growth treatments do play an important role in forming the ferromagnetic nature of the material as they greatly influence the creation of defects in the oxide semiconductor, and that applying an external strong magnetic field during post annealing may significantly affect the ordering kinetics, structure, defect, and magnetic properties of the material.[25,26] It is therefore of great interest to investigate the defect generation in un-doped ZnO by applying a strong magnetic field during annealing, to gain a better understanding of the origin, and to search for a way to enhance the RTF in un-doped ZnO thin film.

In this study, we report the characterization of the defects generated in the un-doped ZnO thin film annealed in a strong magnetic field, the relationship between the RTF and the defect generated in the film, as well as the dependence of the defect generation on the strength of the magnetic field applied. The mechanism for the strong magnetic field affecting the defect generation in the film is also discussed.

2. Experimental procedure

Highly *c*-axis oriented ZnO films each with a thickness of ∼ 100 nm were deposited on the (100)-oriented silicon substrates by pulsed electron beam deposition (Neocera Inc.). The detailed deposition process was reported elsewhere.[20] The as-deposited ZnO films were then annealed in flowing argon in a tube furnace, which was installed in a superconducting magnetic system (9 T, Cryomagnetics Inc.). The temperature inside the tube furnace was raised to 650 °C at a rate of 10 °C/min and was maintained for two hours, during which the

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†Corresponding author. E-mail: zjzhang@tsinghua.edu.cn

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magnetic field was set at 0, 1, 3, 5, and 7 T, sequentially. After that, the tube furnace was cooled to room-temperature gradually. During the annealing the direction of the magnetic field was set to be parallel to the surface normal of the samples.

The samples were examined by X-ray photoelectron spectroscopy (XPS, PHI5400ESCA), positron annihilation analysis (PAS), and electron paramagnetic resonance (EPR, JEOL JES-FA200). Before the XPS measurements, all of the samples were etched by Ar^+ ions sputtering for five minutes to remove the surface contaminations. All spectra were obtained using Mg Kα of 1253.6 eV as a radiation source and were calibrated with 1s peak of carbon at 284.6 eV. For the PAS analysis, Doppler broadening spectra were measured with a slow positron beam, whose energy was adjusted continuously in a range of 0.18 keV–20 keV, and about 4×10^5 counts were accumulated for each given energy for accuracy. The EPR spectra were obtained at a temperature of -150 °C, with the magnetic field direction being parallel to the surface of the samples.

The room-temperature optical properties were analyzed by photoluminescence (PL) measurements using a Raman spectrometer (LabRam Aramis) equipped with a 325-nm He–Cd laser. The magnetic properties were measured on a superconducting quantum interface device (SQUID) magnetometer (MPMS XL-7) with the magnetic field direction being parallel to the surface of the samples at room-temperature. In order to make a comparison, the EPR intensity and magnetization of the samples were all normalized to the mass of film measured by induced-coupled-plasma atomic emission spectra (ICP-AES) using an ELAN DRC-e ICP-AES system.

It should be mentioned that we carefully avoided contacting samples with any magnetic materials during the sample treatments, and used non-magnetic tweezers to handle samples to eliminate unintentional ferromagnetic contaminations.[27]

3. Results and discussion

Figure 1(a) shows a typical XPS spectrum of un-doped ZnO film. The absence of the peaks at 638.8, 706.8, and 777.9 eV indicates that the film is free from contamination by magnetic elements of Mn, Fe, and Co. With the spectrum one can calculate the atomic ratio of oxygen to zinc. The inset of Fig. 1(a) shows the variation of the ratio of oxygen to zinc with the strength of the magnetic field applied to the annealed samples during annealing. It is seen that all annealed samples are oxygen-deficient, and the deficiency of oxygen is very dependent on the strength of the magnetic field applied. At a field strength of 3 T, the oxygen deficiency is at its smallest where a maximum ratio of oxygen to zinc is achieved, i.e. 0.99. When the field strength is weaker or stronger than 3 T, the oxygen deficiency in the annealed film increases, suggesting that the film loses oxygen after annealing and the oxygen loss is strongly dependent on the strength of the magnetic field applied.

We also perform the high-resolution analysis of Zn $L_3M_{45}M_{45}$ Auger peak appearing in the XPS spectra. As reported in Ref. [28], the Zn LMM Auger peak is more sensitive to the chemical environment than Zn 2p peak. Figures 1(b) and 1(c) show the spectra of the LMM Auger peak and its position versus the strength of the magnetic field applied during annealing. It is seen that the peak position for the sample annealed at 3 T corresponds to the highest energy, and that it shifts to lower energy when the field strength is weaker or stronger than 3 T. From Ref. [29] it follows that the Zn LMM Auger peak may shift from high energy to low energy, owing to the oxidation state decreasing. It is seen that the oxygen deficiencies become larger in number when the field strength is weaker or stronger than 3 T, which is consistent with the calculation as shown in Fig. 1(a).

To further clarify this point, we perform high-resolution scans of O 1s peak for all of the annealed samples, and the results are shown in Fig. 1(d). One sees that all of the spectra of O 1s can be fitted by two Gaussian peaks, i.e. one is the lower binding energy at 531.7 eV (O_a) which is ascribed to O^{2-} ions in wurtzite structure of hexagonal ZnO, and the other is the higher binding energy peak located at 533.6 eV (O_b) which can be attributed to O^{2-} ions in the oxygen-deficient regions in the matrix of ZnO.[17,30] Thus it is clear that all of the annealed samples are oxygen-deficient. Naturally, the ratio of the area of the O_b peak to the total area of peaks O_a and O_b can be considered as a measure of the concentration of oxygen vacancies (V_O) in the film. Figure 1(e) shows this ratio as a function of the strength of the magnetic field applied during annealing. One sees that the number of oxygen vacancies is at its smallest in the film annealed at 3 T, and when the field strength is weaker or stronger than 3 T, the number of the oxygen vacancies increases. It is thus concluded that all annealed samples are oxygen-deficient, and that the number of oxygen vacancies is dependent on the applied magnetic field strength with a minimum of 3 T.

As is well known, the motion of the electron–positron pair prior to annihilation may lead to the Doppler broadening of the 511-keV annihilation line and can be characterized by the line-shape parameter S (valence annihilation parameter).[31] Anion vacancies (mainly V_O) in ZnO are positively charged and thus have a small positron affinity, while cation vacancies (mainly V_{Zn}) are negatively charged and act as effective positron traps. The parameter S is believed to be more sensitive to cation vacancies than anion vacancies.[32] Therefore, we perform PAS analyses for the samples annealed at field strengths of 0, 3, and 7 T, respectively, to obtain an idea of the zinc vacancies generated in these annealed samples. Figure 2(a) shows the variations of parameter S with the energy of

the incident positrons in different magnetic fields. At energies below 3.5 keV, the $S(E)$ curve represents the annihilation only within the ZnO film, while at energies > 3.5 keV, the influence of the substrate becomes also visible. Figure 2(b) shows the variations of the core annihilation parameter W with the parameter S in different magnetic fields for the three samples. From the figure, one observes a good linear relationship between parameters S and W, suggesting that there is only one type of trapping site of the positron, i.e. V_{Zn},[33] in the ZnO film. As observed in Fig. 2(a), there is almost no difference in the value of the parameter S among these three samples at energies below 3.5 keV. It indicates that there is almost no change in the concentration of cation vacancies (V_{Zn}) in each of the three samples. Combined with XPS analysis results, it is believed that the number of zinc vacancies (V_{Zn}) in the sample is negligible, while the number of oxygen vacancies (V_O) is considerable, which is strongly dependent on the strength of the magnetic field applied during thermal annealing.

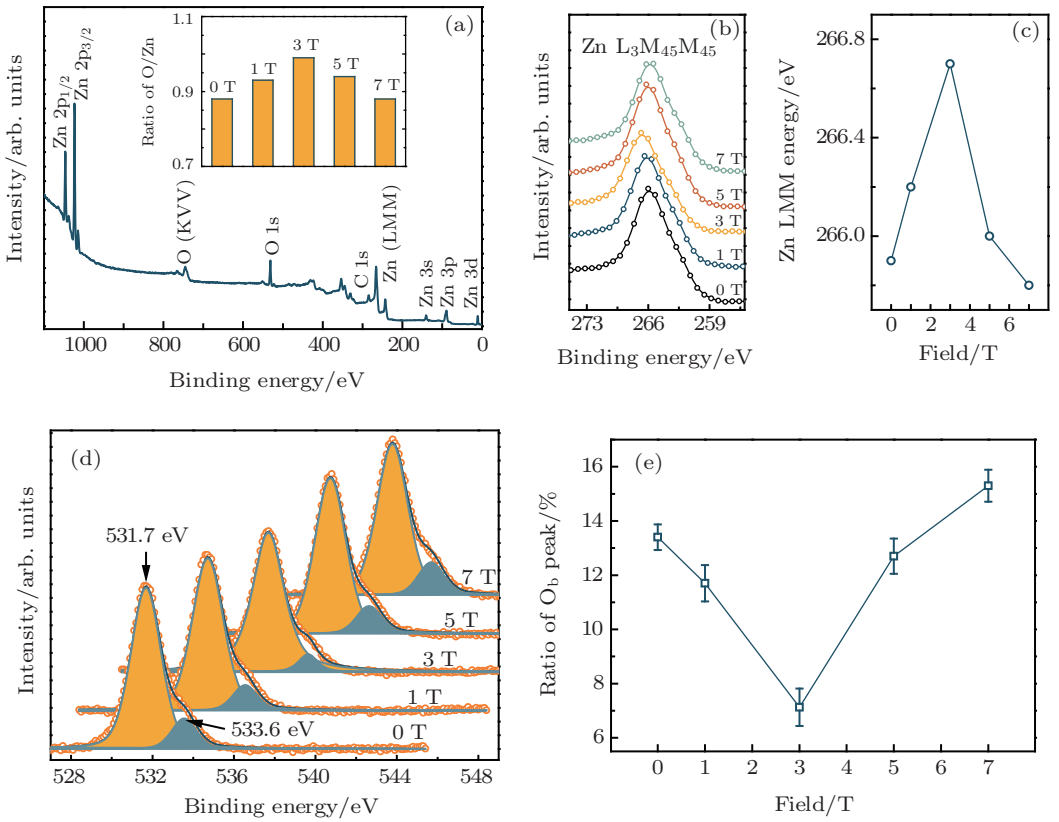


Fig. 1. (color online) (a) A typical XPS spectrum of ZnO film after Ar^+ sputtering for five minutes; inset shows the ratio of O/Zn in the annealed samples versus the magnetic field applied in the annealing process; (b) the Zn LMM Auger peaks of ZnO films annealed at different magnetic field strengths; (c) the position of the Zn LMM Auger peak versus the strength of the magnetic field applied during annealing; (d) the high-resolution O 1s peaks of different samples and the fitting results; and (e) the ratio of the peak O_b (at ~ 533.6 eV), defined as $O_b/(O_a+O_b) \times 100\%$, versus the strength of the magnetic field.

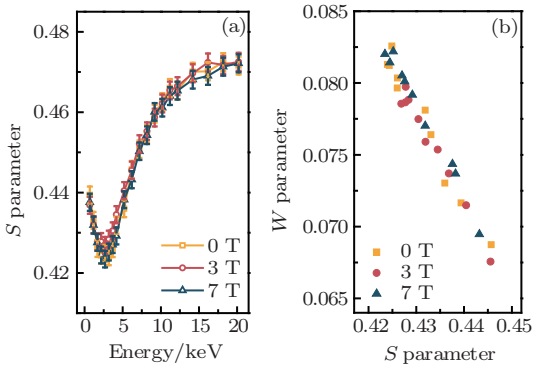


Fig. 2. (color online) (a) Variations of parameter S with the energy of incident positrons, measured in the ZnO films annealed in magnetic fields of 0, 3, and 7 T, respectively; and (b) the relationships between the core annihilation parameter W and the parameter S for different magnetic fields.

Previous studies have shown that the existence of oxygen vacancies in ZnO could induce visible light emission.[34–36] We therefore perform PL measurements on these samples. Figure 3(a) shows room-temperature PL spectra of all samples in the visible light region. We notice that these emission peaks can be well fitted by two Gaussian peaks centered at ~ 525 nm and ~ 580 nm, respectively. As an example, figure 3(b) shows the fitting results of the PL spectrum of the ZnO film annealed at 7 T. Figure 3(c) indicates the integrated intensity of two PL emissions as a function of the strength of the magnetic field applied in the thermal annealing process. Following Refs. [37] and [38], the emission at ~ 580 nm can be ascribed to the doubly ionized oxygen vacancy (denoted as V_O^{2+}), and the emis-

sion centered at ∼ 525 nm can be assigned to either the zinc vacancy (V_{Zn}) or the singly ionized oxygen vacancy (V_O^+). As shown by the above analysis, however, the numbers of V_{Zn} vacancies in these samples are negligible. Thus the ∼ 525-nm emission should be ascribed to V_O^+.[19] Figure 3(d) shows the integrated intensity of the two emissions as a whole versus the amount of oxygen vacancies calculated by the XPS analysis. The good linear relationship between them suggests that the two emissions are induced by oxygen vacancies generated in ZnO film.

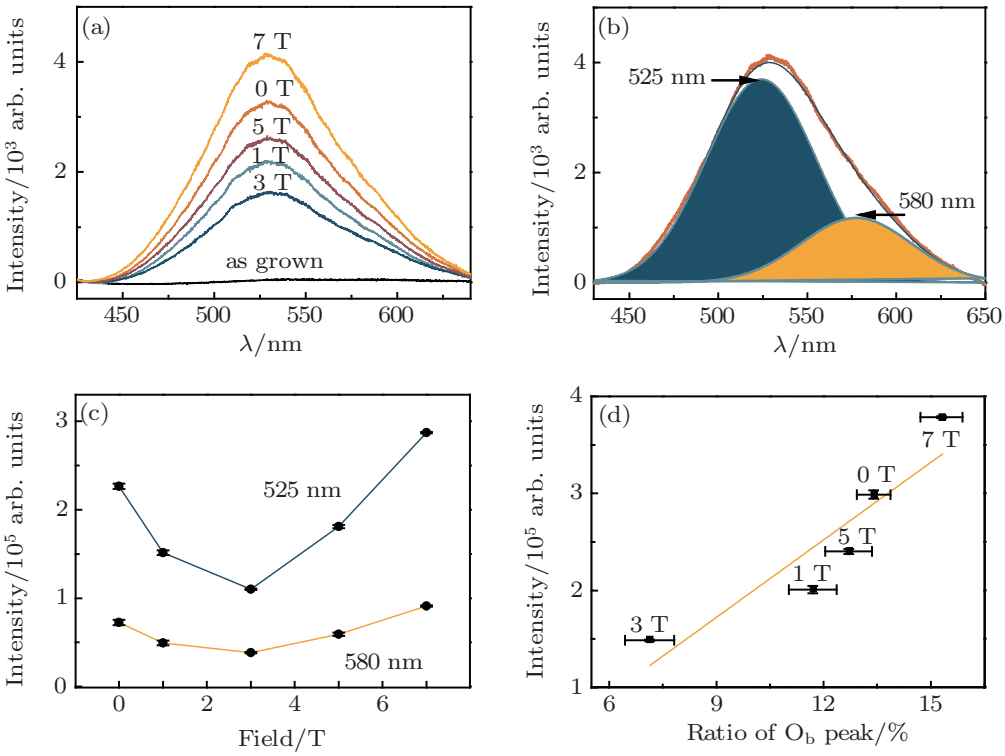


Fig. 3. (color online) (a) PL spectra of the as-deposited and annealed ZnO films in the visible light range; (b) the fitting results of the PL spectrum of the film annealed at 7 T; (c) the intensities of the two PL emissions versus the strength of the magnetic field applied during thermal annealing; and (d) the intensities of the two emissions versus the ratio of the O_b peak calculated from the XPS analysis.

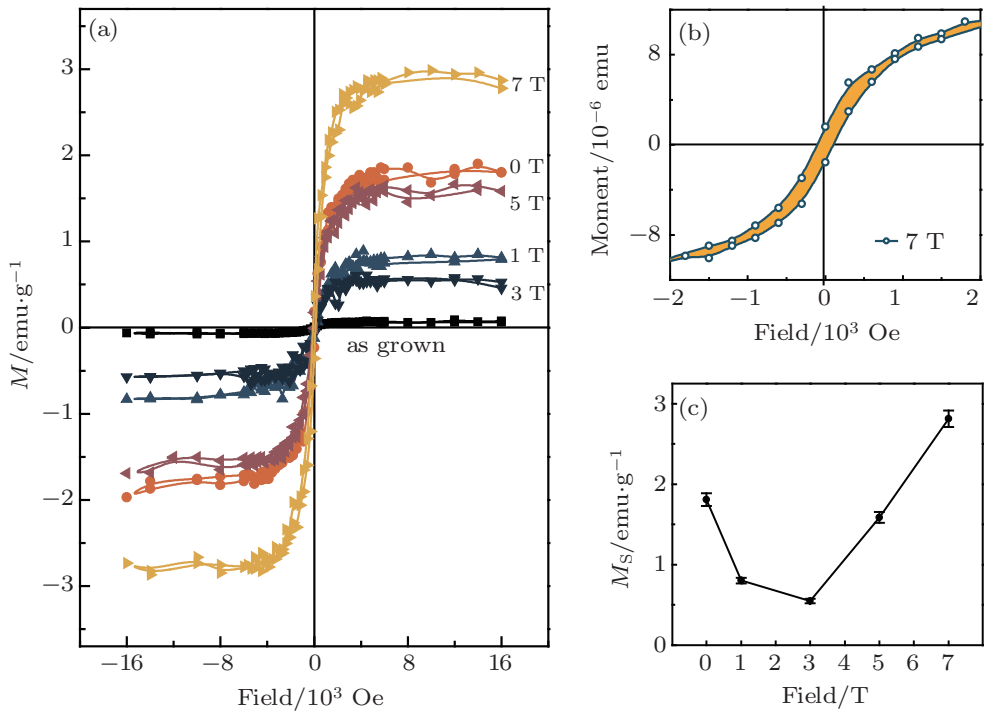


Fig. 4. (color online) (a) Normalized *M*–*H* loops of the as-deposited and thermally annealed ZnO films, measured at room temperature; (b) the magnified *M*–*H* loop of the ZnO film annealed at a magnetic field of 7 T; and (c) M_S of the annealed ZnO films versus the strength of the magnetic field applied during thermal annealing.

It is reported that the existence of oxygen vacancies could induce RTF in un-doped ZnO film.[17–20] We thus measure the magnetic properties of these samples at room temperature. Figure 4(a) shows their hysteresis loops measured by SQUID. It should be noted in Fig. 4(a) that the diamagnetic background is subtracted from the silicon substrate and plastic measuring tubes, and that all hysteresis loops are normalized to the mass of the ZnO film measured by ICP-AES. Figure 4(b) shows the magnified hysteresis loop of the sample annealed at 7 T, where a coercivity of $\sim$ 150 Oe (1 Oe = 79.5775 A·m^{-1}) is observed. From the figures it is seen clearly that all annealed ZnO films exhibit RTF, and that the normalized saturated magnetization (M_S) is dependent on the strength of the magnetic field applied in the thermal annealing process. Figure 4(c) shows the normalized M_S versus the strength of the magnetic field. One sees that the normalized M_S is $\sim$ 1.81 emu/g without applying a magnetic field during thermal annealing, and decreases to a minimum of $\sim$ 0.55 emu/g when annealed at a magnetic field of 3 T. Then it increases to $\sim$ 2.81 emu/g when the magnetic field is 7 T. This behavior is very similar to the dependences of the calculated concentration of oxygen vacancies (see Fig. 1(e)) and the PL intensity (see Fig. 3(c)) on the strength of the magnetic field applied during the thermal annealing process.

As is well known, there are different electron states of oxygen vacancies, such as V_O, V_O^+, and V_O^{2+}. In fact, both V_O and V_O^{2+} have no net spin magnetic moments and cannot make any contribution to the ferromagnetism. As a result, V_O^+ is considered to most likely originate from the RTF in our samples. It is therefore of interest to evaluate the numbers of V_O^+ vacancies generated in these samples after annealing, which can be done by the EPR analysis, as it is sensitive to the number of paramagnetic defects.[17,39] Figure 5(a) shows EPR spectra of these films annealed in different magnetic fields. From the figure it follows that each of all the spectra exhibits a peak at a g factor of $\sim$ 2.003, which was reported to be from V_O^+, a kind of typical paramagnetic defect.[40] It suggests that V_O^+ vacancies are created in all annealed ZnO films, and their numbers are dependent on the strength of the magnetic field applied. As the EPR spectra are normalized to the mass of the ZnO film, we might use the height of this EPR signal (from peak to valley) as a measure of the number of V_O^+ vacancies generated in the film. Figure 5(b) shows the EPR signal height as a function of the strength of the magnetic field applied in the thermal annealing process. Comparing the results in Fig. 5(a) with the dependences of the $\sim$ 525-nm PL emission (see Fig. 3(c)) and the normalized M_S (see Fig. 4(c)) on the strength of the magnetic field, one can see that they have a very good similarity. For simplicity, we plot the intensity of $\sim$ 525-nm PL emission and the normalized M_S versus the EPR signal height in Figs. 5(c) and 5(d), respectively. Good linear relationships between the intensity of the $\sim$ 525-nm PL emission and EPR signal and between the M_S and EPR signal are obtained. These results suggest that the singly ionized oxygen vacancy (V_O^+) should be responsible for the $\sim$ 525-nm PL emission and the RTF observed in the annealed ZnO film.

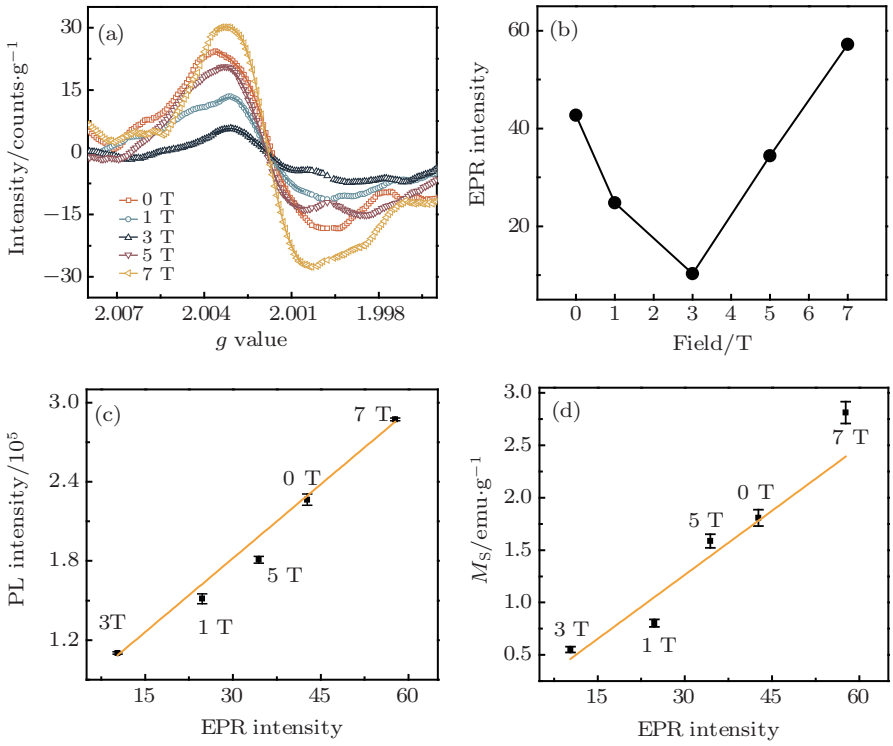


Fig. 5. (color online) (a) Normalized EPR spectra of ZnO films annealed in different magnetic fields; (b) the EPR signal intensity corresponding to V_O^+ ($g = 2.003$) versus the strength of the magnetic field; and (c) the PL intensity of the emission at $\sim$ 525 nm and (d) the normalized M_S versus the EPR signal intensity of V_O^+ (at $g = 2.003$).

The influence of the magnetic field applied during thermal annealing on the generation of defects in the ZnO film is intriguing. It has been reported that a strong magnetic field could help to improve the crystallinity and reduce point defects in crystals,[26] or affect the crystal orientation to some extent due to the magnetic anisotropy[41,42] and generate strains or structural defects. In fact, there is a prerequisite of realignment of crystal orientation that the energy obtained from the external magnetic field should be large enough to overcome the resistance including the thermal vibration energy, lattice distortion, and diffusion in the realignment process. These views can give us some insight into the effects of the strong magnetic field on the defect generation in our samples during thermal annealing. When the magnetic field is above 3 T, it is strong enough to stimulate the realignments of orientation in ZnO films, thus creating more defects, specifically oxygen vacancies, in the ZnO films annealed in an oxygen-deficient environment. When the magnetic field is below 3 T, however, it cannot cause the orientation realignments but restricts the diffusion and defect generations. This may be the reason why the defect generation is suppressed in the ZnO film at fields below 3 T, and is enhanced at fields above 3 T. More studies, theoretical and experimental, are still required to gain a clearer understanding of the effect of a magnetic field on the defects generation.

4. Conclusions

We observed that the defect generation in un-doped ZnO film, when annealed in a strong magnetic field, is strongly dependent on the strength of the field, and that the major defects generated in the un-doped ZnO film are oxygen vacancies. Detailed analyses suggest that the singly ionized oxygen vacancy (V_O^+) should be responsible for the room-temperature ferromagnetism and the PL emission at $\sim$ 525 nm in the un-doped ZnO films. The present study also provides a way to enhance the ferromagnetism induced by oxygen vacancies in ZnO.

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