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Research Article

Zinc Vacancy-Induced Room-Temperature Ferromagnetism in Undoped ZnO Thin Films

Hongtao Ren,[1] Gang Xiang,[1] Gangxu Gu,[1] Xi Zhang,[1] Wenjun Wang,[2] Peng Zhang,[3] Baoyi Wang,[3] and Xingzhong Cao[3]

[1] *Department of Physics and Key Laboratory for Radiation Physics and Technology of Ministry of Education, Sichuan University, Chengdu 610064, China*
[2] *Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, China*
[3] *Key Laboratory of Nuclear Analytical Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China*

Correspondence should be addressed to Gang Xiang, gxiang@scu.edu.cn and Xi Zhang, xizhang@scu.edu.cn

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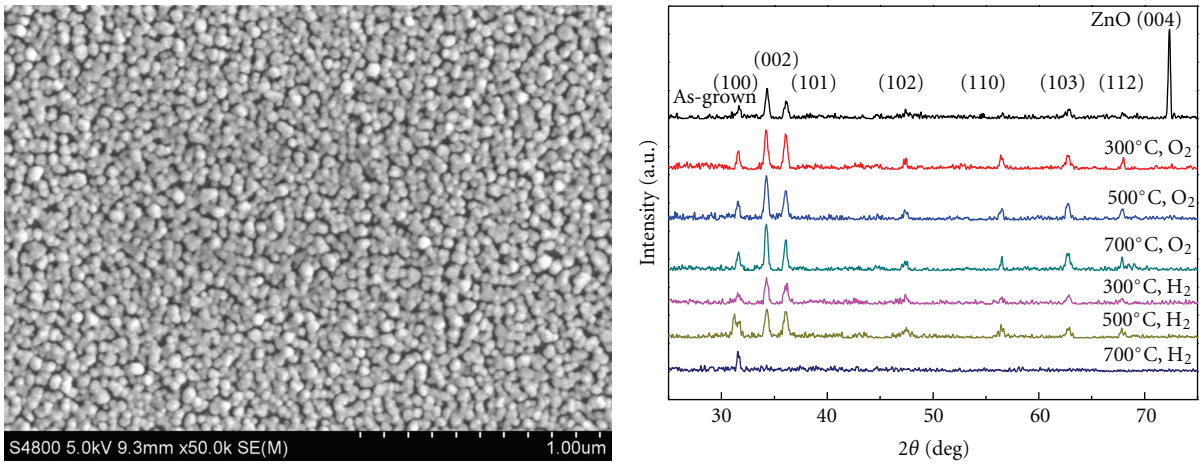
Undoped ZnO thin films are prepared by polymer-assisted deposition (PAD) and treated by postannealing at different temperatures in oxygen or forming gases (95% Ar + 5% H_2). All the samples exhibit ferromagnetism at room temperature (RT). SQUID and positron annihilation measurements show that post-annealing treatments greatly enhance the magnetizations in undoped ZnO samples, and there is a positive correlation between the magnetization and zinc vacancies in the ZnO thin films. XPS measurements indicate that annealing also induces oxygen vacancies that have no direct relationship with ferromagnetism. Further analysis of the results suggests that the ferromagnetism in undoped ZnO is induced by Zn vacancies.

1. Introduction

The dilute magnetic semiconductors (DMSs) have attracted increasing attention due to the potential applications in spintronic devices in recent years [1, 2]. Since the room-temperature (RT) ferromagnetism in Co-doped ZnO has been predicted by Dietl et al. with the Zener model of ferromagnetism [3], extensive theoretical and experimental studies have been performed on ZnO [4–12]. Various mechanisms, such as intrinsic defects [4–6] (zinc vacancy (V_{Zn}), oxygen vacancy (V_O), etc.), extrinsic defects [7–10] (TM and non-TM dopants), and the correlation of intrinsic and extrinsic defects [11, 12] have been declared to induce the room-temperature (RT) ferromagnetism in ZnO. However, magnetic properties of ZnO still remain a heavily controversial issue: the theoretical and experimental results were often found contradictory to each other; the origin of ferromagnetism and the influence of the complex interactions between different defects on magnetic properties of ZnO are still not well understood. Among them, the ferromagnetism induced by intrinsic defects, such as Zn vacancies and oxygen vacancies, and the correlation between the magnetic properties and intrinsic defects are of particular interest, since intrinsic-defects-induced mechanism may suggest new pathways for preparing ZnO-based spintronic devices and the physics of the simple system without dopants may be more straightforward.

In this paper, we systematically investigated the correlation between the magnetic properties and the intrinsic defects in undoped ZnO. Undoped ZnO thin films were first grown on (0001) sapphire (Al_2O_3) substrates by polymer-assisted deposition (PAD) [13, 14] and then treated by postannealing at different temperatures in different atmospheres. We then measured the structures and the magnetic properties of the ZnO thin films.

The crystalline structure of the films was characterized by using X-ray diffractometer (XRD) with Cu Kα radiation. The morphology of the samples was observed by a field emission scanning electronic microscopy (SEM). Magnetic measurements were performed using superconducting



(a) (b)

Figure 1: (a) SEM of nanocrystalline ZnO thin films (b) XRD spectra of ZnO thin films: as-grown, annealed at different temperatures in O_2 or H_2 atmosphere.

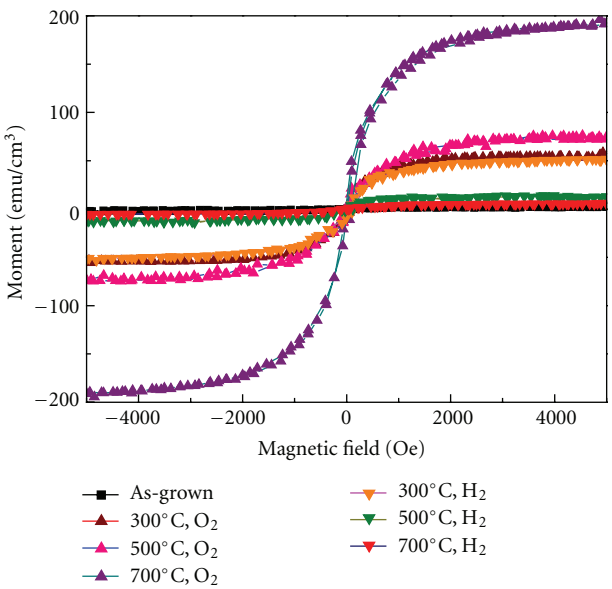


Figure 2: (a) M versus H of undoped ZnO thin films before and after annealing at different temperatures in H_2 gas. (b) M versus H of undoped ZnO thin films before and after annealing at different temperatures in O_2 gas.

quantum interference device (SQUID) magnetometer with the magnetic field applied parallel to the film surface at 300 K. The chemical state of oxygen was measured by X-ray photoelectron spectroscopy (XPS). Cation vacancies were detected by positron annihilation spectroscopy (PAS).

2. Experimental

ZnO thin films were prepared by PAD of Zinc nitrate hexahydrate (purity ≥ 99.0%) and ethylene imine polymer (purity = 99%). To prepare Zn-polymer solution, 2.5 g zinc nitrate hexahydrate was dissolved in 40 ml deionized water, and then 2 g ethylene imine polymer was added into the mixed solution. After stirring, the solution was purified by Amicon Ultra Centrifugal Filters with a 10,000 molar weight-off membrane. The solution was spin coated on (0001) R-cut sapphire substrates at the rates of ~600 rpm for 18 s and ~2600 rpm for 30 s. The resultant coatings were gradually heated from room temperature to 500°C and stayed at that temperature for a period of about 1 h to burn out the polymer under an oxygen atmosphere. These as-grown films, which served as the precursors, were put into a horizontal quartz tube furnace for 3 minutes of heating at 900°C. The heating and cooling rates were 75°C/s for all the cases. After deposition, the samples were treated by post-annealing in oxygen gas or forming gas of 5% H_2 and 95% Ar gases (we use H_2 to denote the forming gas for simplicity later) at 300,500 and 700°C for 30 minutes.

3. Results and Discussions

We first measured the structure and morphology of the ZnO samples. Figure 1(a) shows that the prepared as-grown samples are nanocrystalline ZnO thin films. The average crystallite size of the samples is about 50 nm and the film thickness is about 100 nm. No crack or obvious protuberance can be observed within the visual field. As shown in Figure 2(b), XRD results indicate that all the thin films are polycrystalline wurtzite-type ZnO and no second peaks can be observed. After post-annealing, the (004) main peak in as-grown sample disappears, indicating formation of more defects in ZnO samples. The diffraction peaks of samples annealed in O_2 at different temperatures are strong and similar to each other, while those of samples annealed in H_2 at 700°C get much weaker, indicating the deteriorated quality of the sample. This is probably because H_2 is a reducing gas and taking more amounts of oxygen atoms away from the sample at higher temperatures.

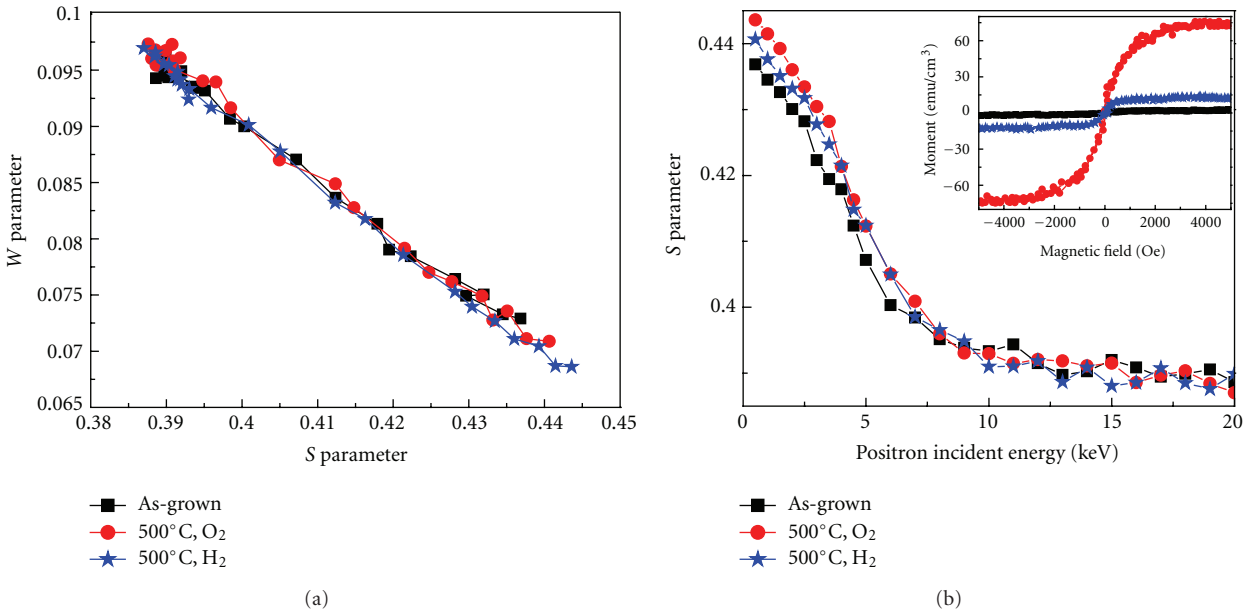


Figure 3: (a) Doppler-broadening parameter "S" as a function of incident positron energy for the ZnO samples: as-grown, annealed at 500°C in O_2 and annealed at 500°C in H_2 atmosphere. (b) The spectra of W parameter versus S parameter.

The magnetization of the undoped ZnO thin films was measured by SQUID at room temperature, as shown in Figure 2. All the samples exhibit a clear hysteresis loop, indicating that these films are ferromagnetic at RT. The as-grown undoped sample shows weak ferromagnetism (M~ 2.5 emu/cm^3). There are reports indicating that surface defects of the oxide thin film could cause ferromagnetism [15, 16]. After post-annealing treatment at different temperatures in O_2 or H_2 gas, ferromagnetic ordering of all the samples was improved. As shown in Figure 2, in the case of annealing in O_2 gas, the measured magnetization increases as annealing temperature increases, while in the case of annealing in H_2 gas, the magnetization decreases as annealing temperature increases. However, the annealing effect at the same temperature in O_2 atmosphere is always stronger than that in H_2 in terms of enhancement of ferromagnetism in undoped ZnO thin films. Since annealing in oxygen atmosphere tends to prevent the formation of oxygen vacancies but promote the formation of Zn vacancies while annealing in hydrogen the opposite, the results above suggest that the enhancement of ferromagnetism of undoped ZnO thin films is related to the Zn vacancies in the sample.

In order to confirm the Zinc vacancies concentration, we carried out the positron annihilation analysis (PAS) measurements for a series of samples: as-grown, annealed at 500°C in O_2 gas and annealed at 500°C in H_2 gas. As shown in Figure 3(a), the linear S-W spectra suggest that there is only one type of cation vacancies, that is, zinc vacancies in the samples. The relationship between the S values and positrons energy for the films is shown in Figure 3(b). The increase in the S values in the annealed samples indicates that annealing introduces more Zn vacancies. In addition, the S value in the sample annealed in O_2 is bigger than that annealed in H_2 at the same temperature. Since the magnetization of annealed samples increases and the magnetization of the samples annealed in O_2 is bigger than that annealed in H_2 at the same temperature, as shown in the insert of Figure 3(b), we see clearly positive correlation between the Zn vacancies and the magnetization of the undoped ZnO samples. In fact, theoretical studies show that the ferromagnetism can be induced by Zn vacancies instead of oxygen vacancies, in ZnO samples, and the magnetic moment mainly arises from the unpaired 2p electrons at O sites surrounding the Zn vacancies [17]. Therefore the ferromagnetic ordering can be enhanced by introducing more Zn vacancies.

On the other hand, we also investigate the variation of oxygen vacancies in the samples using XPS analysis. XPS O 1s scans of typical ZnO thin films are shown in Figures 4(a)–4(c). Two Gaussians were fitted to separate oxygen species. Then the profile can be fit by two symmetrical peaks, which are normally assigned as low-binding-energy component (LBEC) and high-binding-energy component (HBEC). Since the HBEC peak develops with increasing loss of oxygen, the development of the HBEC peak obviously leads to the asymmetry of the main peak. Changes in the ratios of HBEC/LBEC peak may result from the variations in the concentration of oxygen vacancies.

The variations of oxygen vacancies and the magnetization in the samples are shown in Figures 4(d)–4(f). As shown in Figure 4(e), when annealing in H_2, the magnetization decreases while oxygen concentration increases as annealing temperature increases. The negative correlation between the magnetization and the oxygen vacancies indicates that oxygen cannot be the origin of the ferromagnetism in these samples. In the case of annealing in hydrogen atmosphere, the oxygen vacancies are preferred, which results in higher

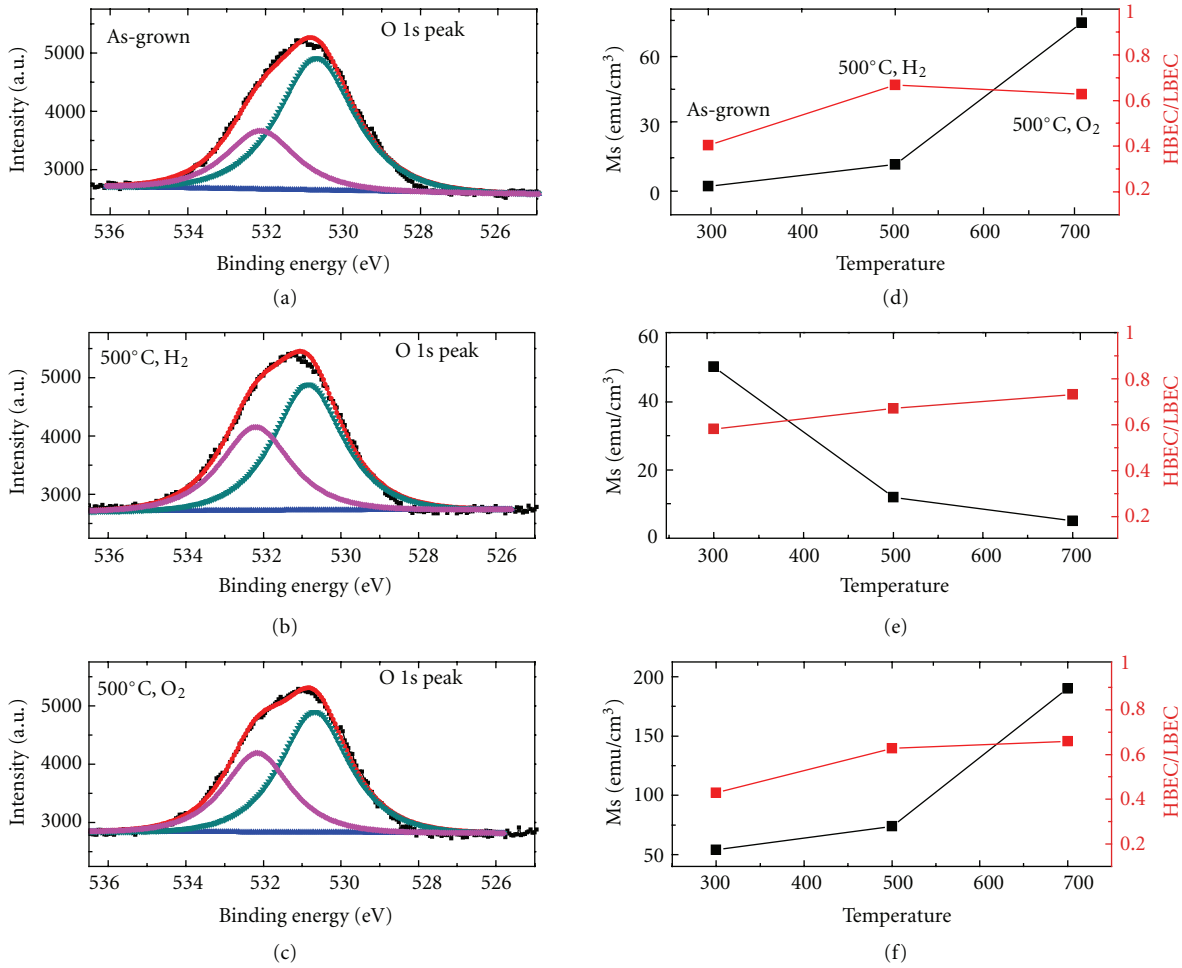


Figure 4: (a–c) Normalized XPS O 1s scans of ZnO samples: as-grown, annealed at 500°C in H_2 atmosphere, and annealed at 500°C in O_2 atmosphere; (d) The ratio of HBEC/LBEC peak and magnetization of as-grown, annealed (500°C + H_2), and annealed (500°C + O_2) ZnO samples; (e-f) Corresponding ratios of HBEC/LBEC peak and magnetizations of samples annealed at different temperatures in H_2 and O_2 atmosphere, respectively.

oxygen concentration than the case of annealing in oxygen atmosphere, as shown in Figure 4(d). Since the oxygen vacancies have no positive contribution to the ferromagnetism and the reducing H_2 gas may result in deterioration of sample quality at high temperature, the magnetization decreases as the annealing temperature increases. As shown in Figure 4(f), when annealing in O_2, both the magnetization and the oxygen vacancies increase as the annealing temperature increases, but the increasing rate of magnetization is higher than that of oxygen vacancies. This can be understood as follows: annealing in oxygen atmosphere promotes the formation of Zn vacancies, so Zn vacancies increase more rapidly than oxygen vacancies; since the ferromagnetism is induced by Zn vacancies, the magnetization also increase more rapidly than that of oxygen vacancies.

4. Conclusions

In summary, we have grown undoped ZnO thin films by polymer-assisted deposition. All the ZnO thin films show RT ferromagnetism. The enhancement of magnetization is observed after the samples are annealed at different temperatures in O_2 or H_2 gas. The clearly positive correlation between the magnetization and Zn vacancies indicates that Zinc vacancies are the origin of the ferromagnetism. Our results may be useful for the design and fabrication of spintronic devices based on ZnO DMS without dopants.

Acknowledgments

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