The effects of Zn vacancies on ferromagnetism in Cu-doped ZnO films controlled by oxygen pressure and Li doping*

Ran Cong-Jun(冉从军), Yang Hai-Ling(杨海龄), Wang Yan-Kai(王延恺), Hassan Farooq M, Zhou Li-Gong(周丽宫), Xu Xiao-Guang(徐晓光)†, and Jiang Yong(姜 勇)

School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, *China*

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$Zn_{0.99}Cu_{0.01}O$ films were studied experimentally and theoretically. The films were prepared by pulsed-laser deposition on Pt(111)/Ti/SiO_2/Si substrates under various oxygen pressures to investigate the growth-dependence of the ferromagnetic properties. The structural, magnetic, and optical properties were studied, and it was found that all the samples possess a typical wurtzite structure, and that the films exhibit room-temperature ferromagnetism. The sample deposited at 600 °C and an oxygen pressure of 10 Pa showed a large saturation magnetization of 0.83 μ_B/Cu. The enhanced ferromagnetism in the (Cu, Li)-codoped ZnO is attributable to the existence of Zn vacancies (V_{Zn}), as shown by first-principles calculations. The photoluminescence analysis demonstrated the existence of V_{Zn} in both $Zn_{0.99}Cu_{0.01}O$ and (Cu, Li)-codoped ZnO thin films, and this plays an important role in the increase of ferromagnetism, according to the results of first-principles calculations.

Keywords: dilute magnetic semiconductor, Cu-doped ZnO, pulsed laser deposition, first-principles

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1. Introduction

A number of studies of ZnO have been conducted recently, since it was predicted to be an ideal diluted magnetic semiconductor (DMS) by Dietl *et al.*[1] Room-temperature ferromagnetism (RTFM) in transition metal (TM)-doped ZnO systems has been reported extensively.[2–7] However, further studies of the mechanism of RTFM have proved problematic. Moreover, it is difficult to rule out the possibility that the ferromagnetism might be caused by magnetic precipitation in the host semiconductors in the form of a secondary phase of either TM oxides or TM dopant clusters. To eliminate the obstacle of undetected magnetic precipitation, many researchers have turned their attention to the study of non-magnetic element-doped ZnO systems. Cu-doped ZnO has been studied both theoretically and experimentally.[8] Since Cu and all possible Cu-based secondary phases are non-ferromagnetic, the ferromagnetism observed in a Cu-doped ZnO system is undoubtedly an intrinsic property.[9] Additionally, the size mismatch is quite small, leading to low formation energy.[10] Hence, Cu is the appropriate doping element to avoid the controversies of ferromagnetism. However, the effects of donor or acceptor defects in Cu-doped ZnO (ZnO:Cu) are not clear. The experimental work of Li[11] and Gao[12] confirmed that the donor defects introduced in the system, such as oxygen vacancies (V_O), can enhance ferromagnetism in Cu-doped ZnO films. Nevertheless, the theoretical calculation results of Ye[13] and Huang[14] suggested that donor defects (such as V_O) weaken ferromagnetic (FM) stability, while acceptor defects (such as V_{Zn}) enhance FM stability. Therefore, it is necessary to clarify the effects of the defects (V_{Zn} or V_O) on the ferromagnetism in Cu-doped ZnO systems.

In this paper, we present our study of Cu-doped ZnO thin films, in which Li^+ cations serve as the acceptor to check the effects of defects on the ferromagnetism.

2. Experiments and computational methods

All the Cu-doped ZnO and (Cu, Li)-codoped ZnO thin films were grown by pulsed laser deposition (PLD) using a KrF excimer laser operating at 300 mJ/pulse and 5 Hz. The targets were prepared by sintering mixed ZnO (99.99%), CuO (99.99%), and Li_2CO_3 (99.99%) powders with the appropriate ratio in air at 950 °C for 90 min. The Cu concentration in all the targets was 1%, and the base pressure of the PLD chamber was better than 6.0×10^{-4} Pa. A series of $Zn_{0.99}Cu_{0.01}O$ thin films were deposited on Pt (111)/Ti/SiO_2/Si substrates at 600 °C under different oxygen pressures from 1.9 Pa to 23 Pa in order to study the effect of oxygen pressure on the growth of the films. Both Yi[15] and Chen[16] predicted that the replacement of Zn with Li atoms can generate holes and reduce the formation energy of V_{Zn}, and then stabilize the V_{Zn}-including system. Therefore, to further check the effects of acceptor defects on FM, $Zn_{0.94}Cu_{0.01}Li_{0.05}O$ films were deposited at 600 °C under an oxygen pressure of 10 Pa. The structure of the thin films was investigated by X-ray diffraction (XRD),

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†Corresponding author. E-mail: xgxu@ustb.edu.cn

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and the magnetic property of the films was measured using an alternating gradient magnetometer (AGM) at room temperature (RT). Photoluminescence (PL) spectra were employed to study the types of defects.

First-principles calculations based on density functional theory (DFT) were carried out using the Vienna *ab initio* Simulation Package (VASP).[17] The calculation method is the same as our previous calculations for the B-doped ZnO system.[18] The Cu-doped ZnO models were constructed by replacing one Zn atom with Cu in each $3 \times 3 \times 2$ ZnO supercell. Supercells with various defects (V_{Zn} or V_O) were also calculated, in which V_{Zn} or V_O was paired with a Cu atom.

3. Results and discussion

Figure 1 shows the XRD patterns of the Cu-doped ZnO thin films grown at different oxygen pressures. As we can see, only the (002) and (004) peaks can be detected in the recorded range, which indicates that all the thin films strongly prefer *c*-axis orientation. When the deposition oxygen pressure is 1.9 Pa, there is an impurity peak of CuO, as deduced from the XRD pattern. And this peak disappears as the deposition oxygen pressure is raised above 5.1 Pa. The lattice structure of the films is hexagonal wurtzite. Since the radii of Cu^{2+} and Zn^{2+} ions in a tetrahedral coordination are 0.72 Å (1 Å = 0.1 nm) and 0.74 Å[19], respectively, the Cu^{2+} dopants will not affect the XRD pattern of ZnO.

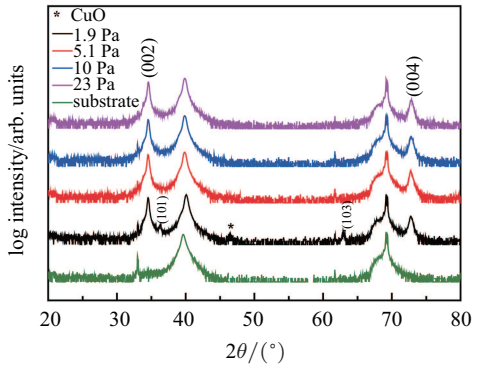


Fig. 1. (color online) The XRD patterns of $Zn_{0.99}Cu_{0.01}O$ thin films deposited under different oxygen pressures.

The magnetic properties of $Zn_{0.99}Cu_{0.01}O$ films were investigated using AGM at room temperature. Figure 2 shows the *M*–*H* loops of all the thin films grown at different oxygen pressures. It is obvious that all the films are ferromagnetic and the coercivity (H_c) can be observed from the right inset of Fig. 2. The value of the saturation magnetism (M_s) increases with the deposition oxygen pressure until 10 Pa, and then decreases as the oxygen pressure is increased further, as shown in the left inset of Fig. 2. Accordingly, moderate oxygen pressure can enhance the ferromagnetism of the Cu-doped ZnO thin films, but excess oxygen pressure will deteriorate it. The optimal oxygen pressure is about 10 Pa and the maximum saturation magnetization (M_s) is about 0.83 μ_B/Cu.

The monovalent alkali metal Li in ZnO can stabilize the Zn vacancies and produce holes at the same time. To explore the effects of acceptor defects on the ferromagnetism of Cu-doped ZnO systems, we deposited the $Zn_{0.94}Cu_{0.01}Li_{0.05}O$ thin film under 10 Pa at 600 °C. The *M*–*H* loops are shown in Fig. 3. It is clear that the M_s is dramatically enhanced from 0.83 μ_B/Cu to 1.13 μ_B/Cu by Li doping. For comparison, a pure ZnO thin film was fabricated under the same growth conditions and verified to be diamagnetic. Much work has been done to study the Cu-doped ZnO systems.[9–14,20,21] Our previous work[22] demonstrated that the RTFM is strongly correlated with the high-spin state of copper. Cu ions show a mixed valence state between +1 and +2. The configuration of the Cu^{2+} cation is $3d^9$, which provides one unpaired electron and results in the magnetism in $Zn_{1-x}Cu_xO$ films.[9,21] Therefore, monovalent Li doping drives Cu dopants to take on a bivalent state, which results in an enhanced RTFM.

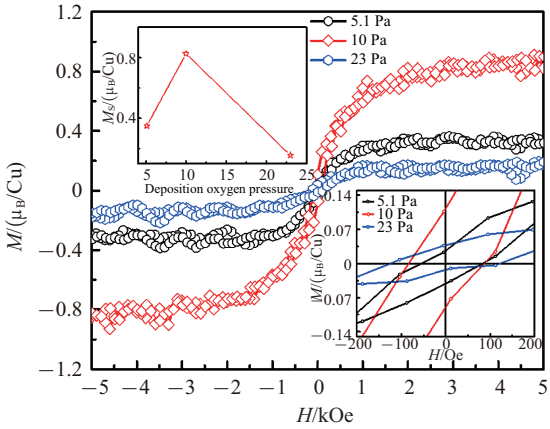


Fig. 2. (color online) The *M*–*H* loops of $Zn_{0.99}Cu_{0.01}O$ thin films deposited under different oxygen pressures, 1 Oe = 79.5775 A/m.

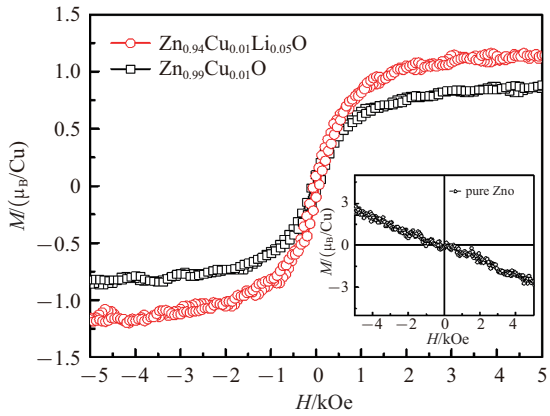


Fig. 3. (color online) The *M*–*H* loops of $Zn_{0.99}Cu_{0.01}O$ and $Zn_{0.94}Cu_{0.01}Li_{0.05}O$ thin films deposited under 10 Pa at 600 °C.

PL spectra were employed to study the effects of defects on the Cu-doped ZnO system. As shown in Fig. 4, there are two main emission bands in the spectra, the ultraviolet peak at

about 384 nm and the green peak at about 540 nm. The ultraviolet peak acts as the reference peak of the intrinsic free exciton emission,[23] with which the spectra are relatively normalized. The intensity of the green peak increases relative to the ultraviolet peak as the oxygen pressure increases up to 10 Pa, and then it decreases as the oxygen pressure is further increased. In addition, a weak blue peak at about 400 nm can be observed in the spectra under 10 Pa and diminishes as the oxygen pressure is increased. The visible luminescence band in the PL spectra is related to defects. There are six kinds of defects in ZnO: oxygen vacancy (V_O), zinc vacancy (V_{Zn}), interstitial zinc (Zn_i), interstitial oxygen (O_i), antisite zinc (O_{Zn}), and antisite oxygen (Zn_O). The V_O tends to have a high concentration due to its low formation energy and serves as a deep donor level in ZnO, while the Zn_i is unstable at room temperature.[24] It has been confirmed that the PL peak around 539 nm derives from V_{Zn},[15,25,26] which is quite close to the emission at 540 nm in Fig. 4. Therefore, the Cu-doped ZnO films have a large V_{Zn} density under oxygen pressure deposition. According to the PL spectra, the density of V_{Zn} increases with the increase in oxygen pressure under 10 Pa and decreases at oxygen pressures beyond 10 Pa, which is quite consistent with the trend of the magnetism results, indicating that V_{Zn} does play an important role in meditating the magnetism of Cu-doped ZnO thin films. Lin[27] has indicated that the V_O density is proportional to $PO_2^{-1/2}$, and the V_{Zn} density is proportional to $PO_2^{1/2}$, where PO_2 is the growth oxygen pressure. However, according to the study of Tao *et al.*,[28] the good crystallization of ZnO films under high oxygen pressure may give rise to a low concentration of defects in the ZnO:Cu films. Therefore, for the Cu-doped ZnO films in our study, the optimized oxygen pressure is 10 Pa. As reported,[29,30] the Cu^+ generates an acceptor energy level located at about 0.35 eV above the valence band maximum (VBM), and the transition from conduction band to this energy level corresponds to the emission at about 400 nm. Accordingly, the weak blue emission in the PL spectra may be attributed to the transition between the conduction band and the acceptor state of Cu_{Zn}. The diminution of blue emission with increased oxygen pressure indicates either a decreasing density of Cu_{Zn} acceptor defects or the formation of Cu^{2+} in the films. Figure 5 shows the PL spectra of (Cu, Li)-codoped ZnO films deposited at 10 Pa and 600 °C. For comparison, the pure ZnO film was deposited under the same conditions. Obviously, all the doped films show a green emission peak in the visible range, and the intensity of the green peak is greatly enhanced when an Li dopant is introduced into the Cu-doped ZnO. The high V_{Zn} defect concentration in the (Cu, Li)-codoped ZnO film is in accordance with the magnetism trend shown in Fig. 3. The yellow emission around 600 nm can be attributed to the interstitial oxygen.[26,31] According to the above analysis, the density of the V_{Zn} defects can be affected by both the deposition oxygen pressure and the Li dopants, and determines the magnetism of Cu-doped ZnO films.

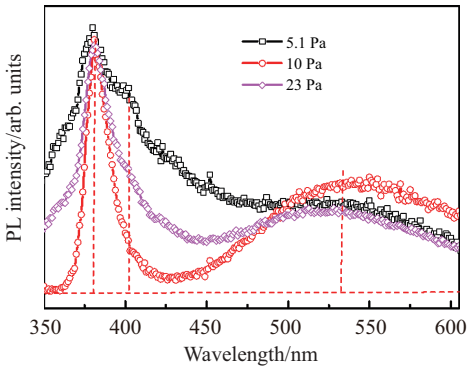


Fig. 4. (color online) The photoluminescence spectra of $Zn_{0.99}Cu_{0.01}O$ thin films deposited under different oxygen pressures.

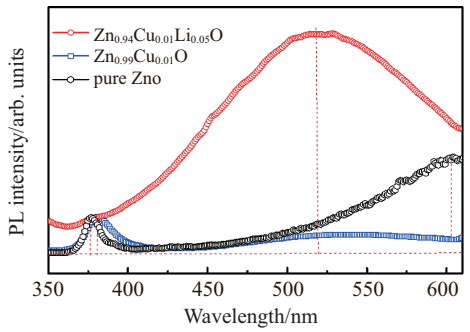


Fig. 5. (color online) The photoluminescence spectra of $Zn_{0.99}Cu_{0.01}O$, $Zn_{0.94}Cu_{0.01}Li_{0.05}O$ thin films deposited under 10 Pa at 600 °C.

To study the origin of ferromagnetism, we calculated the electronic structures of Cu-doped ZnO systems. The total density of states (DOS) and partial density of states (PDOS) of $Zn_{35}CuO_{36}$ and $Zn_{34}CuO_{36}$ are presented in Fig. 6. For the $Zn_{35}CuO_{36}$ supercell, the Cu-3d states (Fig. 6(b)) overlap with those of O-2p (Fig. 6(c)) near the Fermi level, indicating a strong exchange interaction between the O-2p orbitals and the Cu-3d orbitals. The majority spin states of Cu-3d and O-2p are fully occupied, while the corresponding minority spin states are partially occupied, which causes the spin splitting observed near the Fermi level. As a result, the $Zn_{35}CuO_{36}$ supercell has a magnetic moment of 0.94 μ_B, which comes mainly from the Cu-3d (about 0.6 μ_B) and O-2p (about 0.34 μ_B) orbitals, as listed in Table 1. Therefore, the magnetic moment of Cu is the main contributor to the magnetism of the vacancy-free $Zn_{35}CuO_{36}$ structure.

Table 1. Calculated magnetic moments in $Zn_{35}CuO_{36}$, $Zn_{34}CuO_{36}$, $Zn_{33}CuO_{36}$, and $Zn_{35}CuO_{35}$ supercells doped with various defects. M_{total} is the total magnetic moment per supercell and M_{Cu}, M_O are the local magnetic moments of the Cu and O atoms neighboring V_{Zn}.

System	M_{total}/μ_B	M_{Cu}/μ_B	M_O/μ_B
$Zn_{35}CuO_{36}$/(ZnO: Cu)	0.94	0.6	0.34
$Zn_{34}CuO_{36}$/(ZnO: Cu+V_{Zn})	2.52	0.74	1.53
$Zn_{33}CuO_{36}$/(ZnO: Cu+2V_{Zn})	4.07	0.77	2.77
$Zn_{35}CuO_{35}$/(ZnO: Cu+V_O)	0.59	0.22	0.32

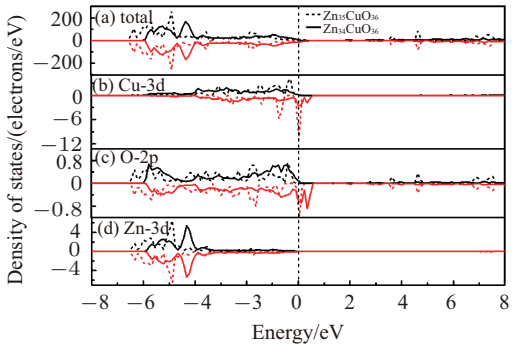


Fig. 6. (color online) The total DOS and PDOS for the $Zn_{35}CuO_{36}$ and $Zn_{34}CuO_{36}$ systems. The positive (negative) channel represents the spin up (down) states. The Fermi level is set to 0 eV.

To explore the effects of V_{Zn} on the magnetic properties of Cu-doped ZnO, one V_{Zn} was created by removing a Zn atom in each $Zn_{35}CuO_{36}$ supercell. The distance between the Cu atom and V_{Zn} has already been discussed. The $Zn_{34}CuO_{36}$ supercell with Cu and V_{Zn} in the neighboring sites is more stable ($\sim$0.43 eV) than that with Cu and V_{Zn} in sites separated further away. The total DOS and PDOS are presented in Fig. 6, and the magnetic moments of the supercell, Cu, and oxygen atoms are listed in Table 1. Comparing the total DOS of the $Zn_{35}CuO_{36}$ and $Zn_{34}CuO_{36}$ supercells, we find that the spin splitting is enlarged near the Fermi level by the existence of V_{Zn}. According to the PDOS, the spin splitting of Cu-3d states in $Zn_{34}CuO_{36}$ is slightly larger than that in vacancy-free $Zn_{35}CuO_{36}$. Moreover, the spin splitting of O-2p states shows a significant enhancement after V_{Zn} is introduced into the Cu-doped ZnO. As shown in Table 1, Zn vacancies cause the total magnetic moment to increase from 0.94 μ_B to 2.52 μ_B, which arises mainly from the magnetic moment increase of oxygen atoms coordinated with V_{Zn}. Therefore, the spin polarization of O-2p orbitals near the Fermi level is the main contributor to the enlargement of the spin splitting in the total DOS near the Fermi level. To further study the effects of Zn vacancy concentration on ferromagnetism, the $Zn_{33}CuO_{36}$ supercell was calculated. As shown in Table 1, the total and local magnetic moments show a large enhancement with the increased concentration of Zn vacancies. Besides, a ZnO:Cu system supercell with one V_O was also studied. It was found that the magnetic moments of the supercell and the Cu dopant decrease dramatically from 0.94 μ_B to 0.59 μ_B and from 0.6 μ_B to 0.22 μ_B, respectively. Therefore, we find that V_{Zn} is the key factor for the magnetism of Cu-doped ZnO systems, which agrees quite well with the experimental results.

4. Conclusion

$Zn_{0.99}Cu_{0.01}O$ films were prepared by pulsed-laser deposition on Pt (111)/Ti/SiO_2/Si substrates under various conditions. The film deposited at 600 °C and an oxygen pressure of 10 Pa shows the largest M_s, about 0.83 μ_B/Cu, increasing to 1.13 μ_B/Cu with Li doping. The PL spectra suggest that all the doped films have large concentrations of V_{Zn} defects, which play a key factor in increasing the RTFM. First-principles calculations indicate that the RTFM in Cu-doped ZnO systems comes mainly from the spin polarized Cu-3d states. The V_{Zn} defects can increase the RTFM due to the spin polarized O-2p states of the oxygen atom nearest the V_{Zn}, while V_O defects may decrease the RTFM.

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