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Effects of doping concentration on properties of Mn-doped ZnO thin films*

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This paper reports that the radio frequency magnetron sputtering is used to fabricate ZnO and Mn-doped ZnO thin films on glass substrates at 500 °C. The Mn-doped ZnO thin films present wurtzite structure of ZnO and have a smoother surface, better conductivity but no ferromagnetism. The x-ray photoelectron spectroscopy results show that the binding energy of $Mn_{2p3/2}$ increases with increasing Mn content slightly, and the state of Mn in the Mn-doped ZnO thin films is divalent. The chemisorbed oxygen in the Mn-doped ZnO thin films increases with increasing Mn doping concentration. The photoluminescence spectra of ZnO and Mn-doped ZnO thin films have a similar ultraviolet emission. The yellow green emissions of 4 wt.% and 10 wt.% Mn-doped thin films are quenched, whereas the yellow green emission occurs because of abundant oxygen vacancies in the Mn-doped ZnO thin films after 20 wt.% Mn doping. Compared with pure ZnO thin film, the bandgap of the Mn-doped ZnO thin films increases with increasing Mn content.

Keywords: Mn-doped ZnO, radio frequency magnetron sputtering, x-ray photoelectron spectroscopy, photoluminescence

PACC: 7865K, 6180C, 7155G, 7855E

1. Introduction

Mn-doped ZnO (ZnMnO) is recognized as a best candidate for diluted magnetic semiconductors in the recently emerged field of spintronics.[1−6] Spintronics focuses on the creation of functional devices based on the control of ferromagnetic ordering by an electric field or light.[7] According to a theoretical prediction by Dietl, ZnMnO is expected to be ferromagnetic material with a high Curie temperature.[8] Therefore a transparent ferromagnetic material could be created. As a matter of fact, although several groups have confirmed the ferromagnetic properties[9,10] of ZnMnO samples, some experiments have not found any ferromagnetic ordering in ZnMnO thin films.[11,12] These controversial results seem to come from the defect concentration, the growth condition and the grain size of the textured ZnMnO films. On the other hand, it is believed that the Mn concentration in ZnMnO thin films relates to their microstructures and properties, thus, in this paper we try to investigate ZnMnO thin films with different Mn concentrations by an economic and popular technique,[13,14] radio frequency (RF) magnetron sputtering, and the optical, electrical and magnetic properties of the thin films were measured and compared.

2. Experiments

The targets were prepared from high purity ZnO powder and mixed with 4 wt.%, 10 wt.% and 20 wt.% MnO_2 powder respectively, then sintered at 500 °C for 16 h in air. The substrates were ultrasonically cleaned in de-ionized water, acetone, rinsed in alcohol and then dried in hot air. The sputtering chamber was pumped down to 3×10^{-4} Pa before deposition and the target was placed at a distance of 5 cm paralleled to substrate which kept at 500 °C during deposition. The pressure of the chamber was kept 0.3 Pa during 4 h deposition time. Ar:O_2=16 sccm:16 sccm. X-ray photoelectron spectroscopy (XPS) (AXIS ULTRA) was used to analyze the chemical state. Conventional x-ray diffraction (XRD) studies on the films were carried out in a diffractometer (D/Max2550VB+/PC) using Cu Kα line of 0.154 nm radiation to investigate the crystal quality and crystal orientation of the thin films. Atom force microscope (AFM) (SPM-9500J3) was used to observe the surface morphology. A vibrating sample magnetometer (VSM) (Lakeshore Model

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665) was used to measure magnetic property. UV-VIS spectrophotometer was used to measure the optical transmission of the thin films. Edinburgh optical instrument F900 was used to measure the photoluminescence of the thin films. Four-point probe method and Hall-effect apparatus were used, to examine the electrical properties of the ZnMnO thin films.

3. Results and discussion

The XPS spectra were used to investigate the composition and chemical bond configuration of the ZnMnO thin films. In the first stage, the Mn concentrations in the ZnMnO thin films, fabricated with 4 wt.%, 10 wt.% and 20 wt.% Mn contents targets, were detected to be 2.20 wt.%, 4.54 wt.% and 8.33 wt.%, respectively. The XPS patterns of Mn, O and Zn chemical bonds in ZnMnO thin films were shown in Figs.1(a), 1(b) and 1(c). Their binding energies were calibrated by C_{1s} peak (284.8 eV) as reference in spectroscopy. After compensated the shift, the determined binding energies of $Mn_{2p3/2}$ and $Mn_{2p1/2}$, O_{1s}, $Zn_{2p3/2}$ and $Zn_{2p1/2}$ were listed in Table 1. From Fig.1 and Table 1, it can be seen from all three samples that two peaks of Mn and the main peaks have a satellite structure on the higher binding-energy side. This fact indicates a divalent state for the Mn ions in the ZnMnO thin films.[15] Both the binding energy (Table 1) and the intensity (Fig.1(a)) of the $Mn_{2p3/2}$ peak in the thin films increase with increasing Mn content. The binding energy of O element in the thin films was also investigated and the Gaussian method of fitting multi-peaks was used to analyse the peaks of O element in Fig.1(b). The O_{1s} peak of the thin films is divided into two peaks, the low energy peak is associated with Zn–O or Mn–O bond (O_1) in lattice while the high energy peak is associated with the chemisorbed oxygen impurity such as O^{2-}, O^- and O_2^- (O_a),[16] which can probably produce oxygen defects. It should also be noted that with increasing Mn content the intensity of O_1 decreases but the O_a increases, suggesting a great possibility of too many oxygen defects in the films after doping excessive Mn. Additionally, in Fig.1(c), the $Zn_{2p3/2}$ main peaks located at 1021.60 eV or 1021.70 eV show a high energy shift in comparison to the metallic $Zn_{2p3/2}$ peak located at 1021.50 eV. This means that the majority of the Zn atoms in all films remains in the same formal valence states of Zn^{2+} within ZnO matrix. Therefore, the Zn peak is not observed in the following XRD patterns of ZnMnO thin films accords to this conclusion.

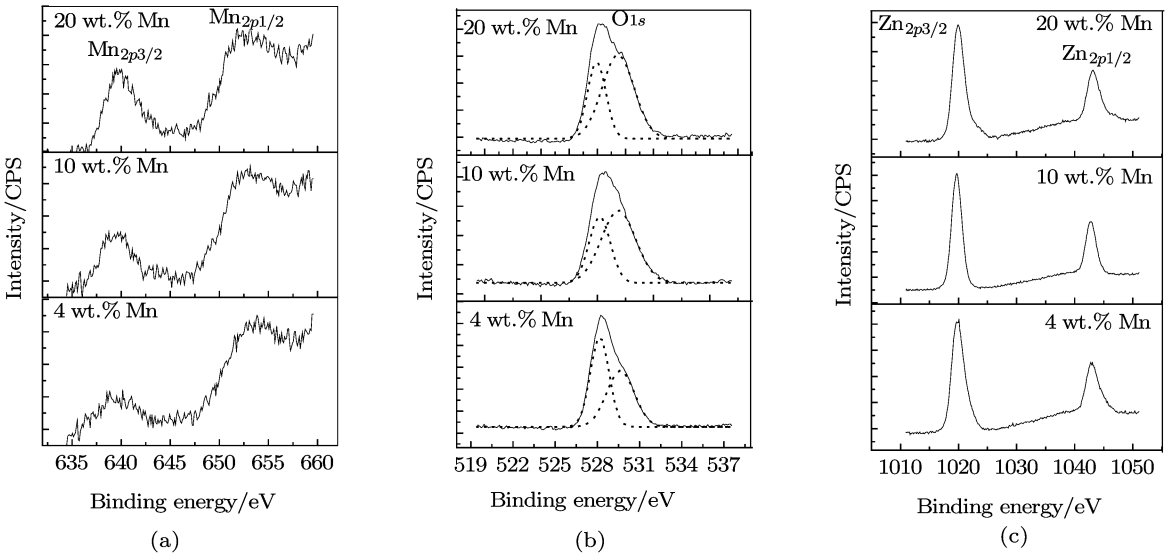


Fig.1. The XPS patterns of (a) Mn, (b) O and (c) Zn chemical bonds in ZnMnO thin films.

Table 1. Binding energy of Mn, O and Zn in ZnMnO thin films.

sample	$Mn_{2p3/2}$/eV	$Mn_{2p1/2}$/eV	O_{1s}/eV	$Zn_{2p3/2}$/eV	$Zn_{2p1/2}$ (eV)
20 wt.% Mn	641.79	656.95	529.71 531.24	1021.60	1044.30
10 wt.% Mn	641.30	657.33	531.24 531.59	1021.60	1044.70
4 wt.% Mn	640.75	657.23	529.74 531.30	1021.70	1044.94

Figure 2 shows the ZnMnO thin films XRD patterns in which all the peaks are found to be from the wurtzite structure of ZnO and without any second phases. The 4 wt.% and 10 wt.% ZnMnO thin films have a unique (002) peak, whereas the 20 wt.% ZnMnO thin film has not only a (002) peak but also a (103) peak. The appearance of the (103) peak indicates that the orientation of this film is complex after doping excessive Mn. It can be observed from Fig.2 that the (002) peak of the ZnMnO thin films shifts to lower angle with increasing Mn content. In detail, the 2θ positions of the (002) peak are located at 34.42°, 34.37° and 34.30° for 4 wt.%, 10 wt.% and 20 wt.% ZnMnO thin films respectively, furthermore all of these 2θ positions are lower than that of 34.45° for the pure ZnO thin films.[17] This is because the radius of Mn^{2+} 0.083 nm is larger than the radius of Zn^{2+} 0.072 nm. According to Bragg formula: $2d\sin\theta = n\lambda$, after Mn^{2+} substituted the position of Zn^{2+}, the interplanar distance of (002) planes became larger, so the value of 2θ shifted to lower angle. The values of the full-width at half-maximum (FWHM) of the (002) peak for all the ZnMnO thin films are only about 0.51°, such small FWHM values but very intensive intensity indicate that high-quality ZnMnO thin films have been fabricated especially for lower Mn contents. The appearance of a weak (103) peak in 20 wt.% ZnMnO thin film shows a degraded (002) texture. As an example, we only present an AFM image of 10 wt.% ZnMnO film to show morphology characteristic of these ZnMnO thin films in Fig.3. It can be seen that the ZnMnO thin films have a smoother surface with uniform grains. From vibrating sample magnetometer (VSM) measurements, we did not find any ferromagnetism in all samples at room temperature. Initially, theoretical predictions proponed only p-type ZnMnO leading to ferromagnetism,[8] and none of the theories predicted ferromagnetism in insulating or n-type ZnMnO, but lately Hou found that the ferromagnetism also existed in n-type ZnMnO semiconductor.[15] In fact, recent experimental studies have shown that appropriate growth conditions are very crucial factors for obtaining room temperature ferromagnetism.[18,19] So, further research is needed

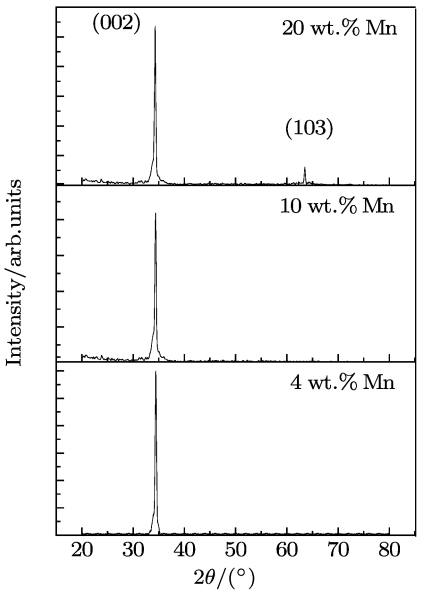


Fig.2. The XRD patterns of ZnMnO thin films.

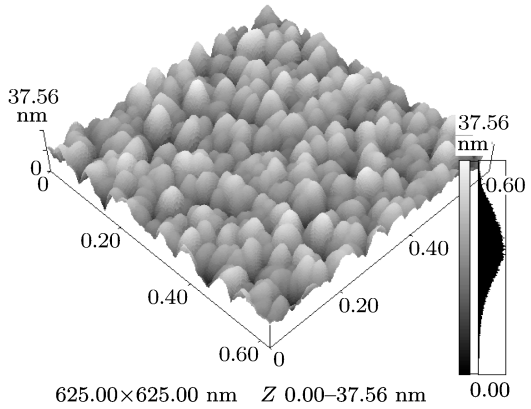


Fig.3. The AFM image of 10 wt.% ZnMnO thin film.

The colours of the ZnMnO thin films change from light yellow to amber with increasing Mn content from 4 wt.% to 20 wt.%. The transmittance spectra of ZnO and ZnMnO thin films with different Mn contents are shown in Fig.4. It can be observed that the average optical transmission of the films decreases with increasing Mn content. The large decrease in transmission for 20 wt.% ZnMnO thin film may be resulted from an obviously degraded (002) texture. Furthermore, the absorption edges also become mild from steep with increasing Mn content. The formula: $(\alpha h\nu)^2 = (h\nu - E_g)$[20] (where α is the absorption coefficient) was used to draw the curves of α^2 versus $h\nu$ in Fig.5 and the bandgap of ZnMnO thin films can be extrapolated from a linear fit. It is observed that the bandgap of ZnMnO thin films also increases with increasing Mn content.

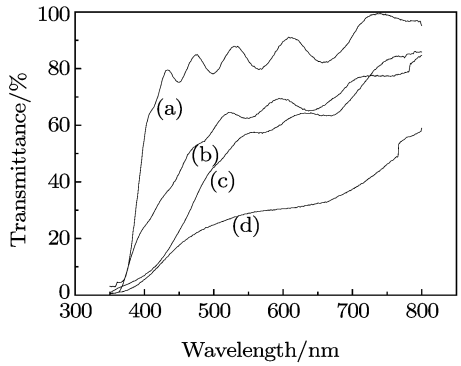


Fig.4. Optical transmittance spectra of (a) ZnO and (b) 4 wt.%, (c) 10 wt.%, (d) 20 wt.% ZnMnO thin films.

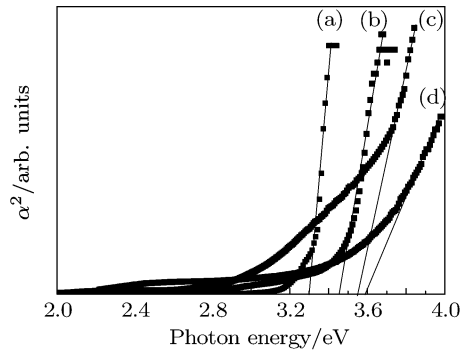


Fig.5. The α^2 vs. $h\nu$ curves for the optical bandgap determination in (a) ZnO and (b) 4 wt.%, (c) 10 wt.%, (d) 20 wt.% ZnMnO thin films.

Two important characteristics can be found from the photoluminescence (PL) spectra of the ZnMnO thin films doping 4 wt.%, 10 wt.% and 20 wt.% Mn as is shown in Fig.6. First, their ultraviolet (UV) emissions locate at 391 nm, 381 nm and 380 nm respectively; secondly, their FWHM becomes wider with increasing Mn content. The Gaussian analysis method of fitting multi-peaks was used to investigate the UV emission peaks of ZnMnO thin films and the results were listed in Table 2 together with initial UV emissions. It was clearly found that the near band emission (left partial peak) peak position blue-shifts while Mn content increases. This could be explained by the Burstein–Moss effect.[21] When ZnO films are doped with more Mn impurities, providing the excessive carriers to fill the conduction band edges, blocking the low energy transitions and widening the bandgap of the ZnMnO thin films (see Fig.5), therefore, a larger $h\nu$ transition obviously results in a blue shift. The right partial peak around 390 nm (3.168 eV) is due to accompanied phonon replicas.[22] Additionally, 20 wt.% Mn-doped ZnO thin film has a green emission which is understood to be associated with oxygen vacancies whereas the green emissions of 4 wt.% and 10 wt.% Mn-doped ZnO thin films are quenched. It is suggested that Mn^{2+} substitutes the position of Zn^{2+} without degrading the quality of the crystal at low Mn concentration. When increasing Mn content, it brings about excessive Mn atoms, the interstitial Mn atoms degrade the crystal quality, and then oxygen vacancies are produced, green emission can be observed.

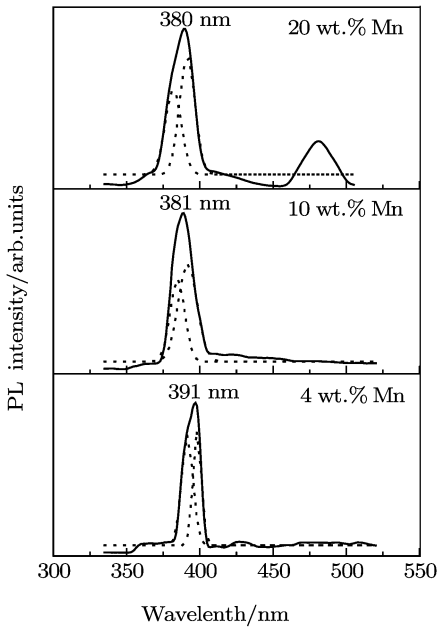


Fig.6. The PL spectra of ZnMnO thin films.

Table 2. Peak analysis of photoluminescence (PL) spectra of ZnMnO thin films.

sample	UV emission/nm	Gaussian multi-peaks fit to UV emission/nm	
20 wt.% Mn	380	374	390
10 wt.% Mn	381	380	391
4 wt.% Mn	391	383	396

Table 3. The electrical properties of the ZnMnO thin films.

samples	$\rho/\Omega\cdot$cm	carrier type
20 wt.% Mn	1.5×10^{-3}	n
10 wt.% Mn	3.2×10^{-4}	n
4 wt.% Mn	7.1×10^{-4}	n
ZnO	8.9×10^{-2}	n

The four-point probe method and Hall-effect apparatus were used to examine the electrical properties of the ZnMnO thin films and the results were listed in Table 3 together with those of the ZnO film. Compared with the electrical resistivity of pure ZnO film, the high level conductivity (low level resistivity) of the ZnMnO thin films is caused by increasing Mn carrier concentration in the thin films.[23] However, a slight increase in the electrical resistivity for 20 wt.% ZnMnO thin film may be resulted from the excessive Mn contents which also bring about a vast number of defects and degrade the quality of the film crystal, thus, increase the resistivity of the film.

4. Conclusions

In the present work, ZnO as well as 4 wt.%, 10 wt.% and 20 wt.% Mn-doped ZnO thin films were deposited by RF magnetron sputtering on glass substrates at 500°C. The following conclusions were obtained: ZnMnO thin films fabricated by RF magnetron sputtering have the same crystal wurtzite structure of preferential growth orientation of (002) at low Mn concentration (≤10 wt.%) whereas the microstructure is degraded at high Mn concentration (20 wt.%); The thin films have a smoother surface, better quality crystal but none of ferromagnetism in all samples at room temperature. The XPS results show that the binding energy of $Mn_{2p3/2}$ increases with increasing Mn content slightly. The PL spectra of ZnMnO thin films have a similar UV emission. The yellow green emissions of 4 wt.% and 10 wt.% ZnMnO thin films are quenched, whereas the yellow green emission occurs because of abundant oxygen vacancies in the ZnMnO thin films doped 20 wt.% Mn content. The bandgap of the ZnMnO thin films increases in comparison with pure ZnO thin film with increasing Mn content. After doping Mn, the thin films have a better conductivity than that of pure ZnO thin film because of abundant carriers in the ZnMnO thin films.

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