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Synthesis, Structural and Optical Properties of Mo-Doped ZnO Thin Films

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Transparent zinc oxide thin films doped with molybdenum have been prepared using a DC reactive magnetron sputtering on glass substrates from metallic ZnMo target. The three films, called A, B, and C, had 1.9 at.% Mo, 2.8 at.% Mo and 4.7 at.% Mo, respectively. The composition of the films was determined by X-ray photoelectron spectroscopy. The analysis of Mo $3d_{5/2}$ core level spectra indicated that Mo exist in the films in Mo⁶⁺ oxidation state irrespective of the Mo content in the film. The X-ray diffraction spectrum of film A showed a texture along the 002 orientation, while that of film B showed two peaks, one at $\theta \approx 34.5^{\circ}$ and the other at $\approx 36.5^{\circ}$ corresponding to 002 and 101 orientations, respectively. Film C showed two small peaks corresponding to 100 and 110 orientations. Optical measurements showed that all three films had a transmittance of about 80%. The energy band gap showed a linear increase as Mo concentration increases from 3.29 eV to 3.38 eV. The atomic force microscopy image of films A showed an inhomogeneous one.

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1. Introduction

Zinc oxide (ZnO) has attracted a considerable number of researchers over the last two decades because of the wide range of applications [1]. The development of nanotechnology induced an increasing interest for nanostructured semiconductors and ZnO appears to be a remarkable oxide that can be shaped in a vast variety of nanostructures such as nanorods [2], nanobelts [3], nanosheets [4], and nanospheres [5].

There have been many reports on the fabrication of transition-metal-doped ZnO bulk and thin film specimens. For example, studies have been reported on Ti--doped [6], V-doped [7], Cr-doped [8], Mn-doped [9], Fe--doped [10], Co-doped [11], Ni-doped [12], and Cu-doped [13] ZnO.

In a recent study [14], Mo-doped zinc oxide thin films with high transparency and relatively low resistivity was prepared by RF magnetron sputtering at room temperature under different Ar pressure. The films had hexagonal structure and a preferred orientation along the *c*-axis. The resistivity increased as Ar pressure increased. The lowest resistivity achieved was $9.2 \times 10^{-4} \Omega$ cm for the samples deposited at Ar pressure of 0.6 Pa with a Hall mobility of 30 cm² V⁻¹ s⁻¹ and a carrier concentration of 2.3×10^{20} cm⁻³. The average transmittance in the visible range exceeded 88% for all the samples. The optical band gap decreased from 3.27 to 3.15 eV with increasing Ar pressure. In another study [15] Mo-doped ZnO transparent conductive thin films were prepared by dc reactive magnetron. The structure, surface morphology, chemical state, optical and electrical properties of ZnMo films were studied. The films were polycrystalline with the hexagonal crystal structure, and the surface morphology measured by AFM demonstrated that the surface was smooth and compact. Chemical state analysis revealed that molybdenum atoms existed mainly in Mo^{6+} and Mo^{5+} ions. The energy bands increased from 3.37 eV to 3.8 eV with the increase in carrier concentrations.

In this work, we report on the synthesis of Mo doped ZnO thin films obtained by DC reactive magnetron sputtering technique. The objective is to investigate the effect of Mo doping on the optoelectronic properties of ZnO thin films. In addition, X-ray photoelectron spectroscopy (XPS) was used to determine the actual oxidation state of Mo in the films in order to confirm some published results which suggested the presence of both 5+ and 6+ oxidation states of Mo atoms in ZnO lattice [15].

2. Experimental procedure

Mo doped ZnO thin films were deposited by DC reactive magnetron sputtering on ordinary optical microscope glass slides. A disc of pure (99.999%) metallic Zn was used as a target. The target was covered by a varying number of high purity (99.99%) Mo wires starting with one wire and adding each time more wires to obtain films with different Mo concentrations. The XPS spectra were recorded using an Electron Spectrometer of the type VG-ESCALAB MKII. The structure of the thin films was studied using Shimadzu XRD-6000 X-ray diffractometer using a Cu anode. The microstructure and surface morphology was studied by atomic force microscopy (AFM) using INNOVA-Veeco AFM system in tapping mode. The optical transmittance of the films was measured between 200 nm and 800 nm using a JASCO V-570 Spectrophotometer.

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3. Results and discussion

Figure 1 shows the XRD patterns of the ZnO thin films with different Mo doping. It is clear from the figure that for sample A (1.9 at.% Mo), a single peak of ZnO (002) is observed at $2\theta = 34.36^{\circ}$. The 2θ value is close by less than that of the standard ZnO crystal (34.45°) . For sample B (2.8 at.% Mo), three peaks of ZnO (100), ZnO (002), and ZnO (101) are observed. The intensity of the 002 peak is much more that that of the 101 peak, while the intensity of the 100 peak is very small. For sample C(4.7 at.% Mo), the 002 and 101 peaks almost disappear while the 100 peak becomes stronger and a new peak (110) at $2\theta = 56.13^{\circ}$ appears. The position of 002 peak for sample B is $2\theta = 34.24^{\circ}$. This value is less that of ZnO crystal and less than that of sample A. A decrease in 2θ for the 002 peak with increase in Mo doping might indicate an increase in the c lattice parameter. The grain size can be estimated from the XRD diffraction peaks using Scherrer's formula. The (002) peak was used to estimate the grain size for samples A and B, since it is the most intense peak, while the (100) peak was used for sample C. The Scherrer formula gave an estimated grain size of about 17 nm, 34 nm, and 23 nm for films A, B, and C, respectively. The chemical states of oxygen and molybdenum atoms in these films were examined by XPS.



Fig. 1. XRD spectra of three ZnO films doped with Mo showing the change in structure of the film with Mo concentration.

The O 1s and Mo 3d XPS spectra of the as-deposited films are shown in Figs. 2a and 3a, respectively. The O 1s core level peaks shown in Fig. 2a have a binding energy (BE) of about 530.2 eV for all three films. There is an asymmetry on the higher BE side of the main peak due to moisture (hydroxide group). The O 1s peaks were all fitted with two contributions. Figure 2b shows the fitting of the O 1s of film A to two peaks, one at a BE of 530.2 eV with full width at half maximum (FWHM) of 2.5 eV due to oxygen in the ZnO structure and the other at a BE of 531.7 eV with a FWHM of 2.6 eV due to oxygen in hydroxide environment. The Mo $3d_{5/2}$ peak is symmetric and has a BE of about 232.5 eV for all three films. The standard values of the BE of Mo $3d_{5/2}$ for Mo^{6+} , Mo^{5+} , Mo^{4+} , Mo^{3+} and metallic Mo are 232.6 eV, 231.5 eV, 230.6 eV, 230 eV, and 228 eV [16, 17].



Fig. 2. (a) Core level XPS spectra of the three films, (b) XPS for the O 1s spectrum of x = 2.8% Mo film fitted with two contributions.



Fig. 3. (a) Core level spectra of the three films, (b) XPS for Mo 3d spectrum of x = 2.8% Mo film showing the spin-orbit doublet.

It can be noted from Fig. 3a that the Mo 3d spectra of the three films are symmetric and do no show any shoulder. We curve fitted the Mo 3d spectrum for film A as shown in Fig. 3b for film A. It is clear from the figure that a single narrow doublet peak fits well the spectrum. The BE of the fitted Mo $3d_{5/2}$ is 232.5 eV with a FWHM of 2.2 eV in agreement with previous work [17]. We conclude that Mo ions in our films are in the Mo⁶⁺ oxidation state forming MoO₃ structure. No lower oxidation states were detected by XPS in these films. This result may be related to the pure oxygen atmosphere that was used in this work while the partial pressure of oxygen was set to 5×10^{-2} Pa to 1.5×10^{-1} Pa.

The transmittance spectra in the wavelength range 200–2000 nm for the three films with different Mo doping level are shown in Fig. 4a. The average transmittance is about 80% for all samples indicating the good transparency of the films in the visible region. Changes in Mo content in the films did not affect the transmittance. However, there is a slight shift in the transmittance curves which indicate changes in the band gap energy $E_{\rm g}$. Figure 4b (inset) shows a quasi linear variation of the energy gap as a function of Mo doping within the explored doping range.



Fig. 4. (a) Transmittance spectra for the three Mo doped ZnO films and (b) $(E^* \ln T)^2$ vs. photon energy and energy gap vs. Mo content (inset).



Fig. 5. AFM image of (a) 1.9% Mo doped film showing a single [002] orientation of the grains and (b) 2.8% Mo doped film with less pronounced texture.

The AFM images of the Mo doped thin films are shown in Fig. 5 in a 2 μ m × 2 μ m region of the film. The AFM image of film A shows in Fig. 5a grains with small size of the order of 10 nm and a well defined unidirectional orientation (002) in agreement with the XRD pattern of this film. The AFM images of film B shown in Fig. 5b, indicate non-uniform films with non-well-defined grain having various orientations and much bigger size. The AFM image of film C, not shown here, shows a non-uniform film and probably with amorphous regions. These results are in agreement with the XRD findings.

4. Conclusion

Polycrystalline Mo doped ZnO thin films of various textures were deposited on glass substrate by DC reactive magnetron sputtering. With Mo doping the XRD pattern shows a texture change from a preferential orientation along [002] direction to [100] and [110] and an increase in grain size. The XPS data indicate that Mo is in the 6+ oxidation state irrespective of the Mo doping. The optical measurements indicate an 80% transmittance and an increase in band gap with increase in Mo content. The AFM images of the low Mo content indicate a uniform film, a 002 grains orientation and about 15 nm grain sizes.

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