# Engineering of electronic and optical properties of ZnO thin films via Cu doping*

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ZnO thin films doped with different Cu concentrations are fabricated by reactive magnetron sputtering technique. XRD analysis indicates that the crystal quality of the ZnO:Cu film can be enhanced by a moderate level of Cu-doping in the sputtering process. The results of XPS spectra of zinc, oxygen, and copper elements show that Cu-doping has an evident and complicated effect on the chemical state of oxygen, but little effect on those of zinc and copper. Interestingly, further investigation of the optical properties of ZnO:Cu samples shows that the transmittance spectra exhibit both red shift and blue shift with the increase of Cu doping, in contrast to the simple monotonic behavior of the Burstein–Moss effect. Analysis reveals that this is due to the competition between oxygen vacancies and intrinsic and surface states of oxygen in the sample. Our result may suggest an effective way of tuning the bandgap of ZnO samples.

**Keywords:** ZnO thin films, Cu doping, optical properties, bandgap tuning

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## 1. Introduction

ZnO is an inexpensive, wide band gap semiconductor with excellent optical and electronic properties, which has great potential in applications such as transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers, thin film transistors, optoelectronic and piezoelectric applications, surface acoustic wave devices, and so on.[1–7] Recently, the transition metal-doped ZnO thin films have aroused a lot of interest and attracted much attention due to their importance both in basic science and technological applications.[8–12] Among them, Cu-doped ZnO is of particular interest, because Cu has a similar electronic shell structure to that of Zn, and hence similar physical and chemical properties to those of Zn, and is expected to not be difficult to enter into the ZnO lattice.[13] In fact, the modification of the physical properties of ZnO thin films via Cu doping has been reported.[9,13] However, the mechanism behind this modification is still under debate. Furthermore, the detailed studies of chemical states of Cu-doped ZnO are still absent, which is of key importance for us to understand the effects of the variation of Cu-doping on optical and electronic properties of ZnO.

In this paper, Cu-doped ZnO thin films are first prepared by radio frequency co-reactive magnetron sputtering technique. The optical and electronic properties of ZnO thin films are then systematically studied. The effects of doping level on the physical properties of ZnO are analyzed and the possible mechanism is discussed.

## 2. Experiments

A high-purity Zn target (purity 99.999%, 60 mm in diameter) and glass substrates were used in the experiments. The substrates were ultrasonically cleaned in acetone and rinsed in deionized water. The distance between target and substrate was 50 mm. The base pressure in the deposition chamber was evacuated to $3.0\times10^{-4}$ Pa. The sputtering was performed in an argon/oxygen mixture atmosphere with gas flow rates 6 sccm for Ar and 6 sccm for $O_2$. The working pressure during deposition was fixed at 2.6 Pa, RF power was 80 W, and the substrate temperature was maintained at 200 °C. In order to dope Cu into ZnO, Cu foils were spread on the Zn target covering a specific sputtering area. The films prepared with the Cu foil covering about 0.8%, 1.6%, and 2.4% of the effective target area are denoted as samples A, B, and C, respectively. All the films were deposited for 2 h.

The crystal structures of the thin films were characterized by using X-ray diffraction (XRD, X'Pert Pro). The electronic states of zinc, oxygen, and copper in Cu-doped ZnO film were investigated by XPS on ESCA LAB 220-XL photoelectron spectrometer (VG Scientific, USA). The transmission and absorption spectra were measured by employing Lambda35UV/VIS, and all spectra were taken at room temperature.

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## 3. Results and discussion

### 3.1. Structural properties

Figure 1 shows the XRD patterns of ZnO:Cu films with different Cu concentrations. As shown in Fig. 1, for all the ZnO:Cu films, the peaks at 34.25 °C, 34.15 °C, and 34.25 °C for samples A, B, and C are from the diffraction of the ZnO (002) plane, and no other peaks can be observed in the patterns, which implies that copper atoms have entered into the hexagonal lattice and/or copper atoms have resided in the non-crystalline region in grain boundary. The intensity of (002) peak increases with Cu-doping content increasing at the same sputtering condition. The enhancement in the extent of *c*-orientation may be due to the fact that a moderate quantity of Cu atoms exist as interstitials that share the oxygen with Zn atoms, thereby improving the (002) orientation.[14] However, as the Cu doping level further increases (sample C), the crystallinity slightly decreases. This trend suggests that Cu dopant starts to create newer nucleation centers, which in turn, would change the nucleation type from homogeneous to heterogeneous, thereby deteriorating the crystalline structure at high doping level.[15]

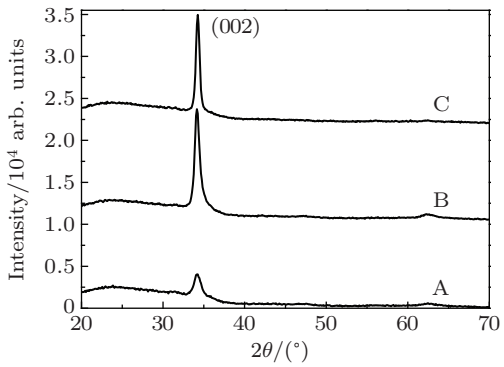



**Fig. 1.** XRD patterns of ZnO:Cu films fabricated for Cu doping levels. Sample A: 0.8%, sample B: 1.6%, and sample C: 2.4%.

### 3.2. Chemical states

To obtain the electronic states of the different atoms in the thin films, we measure the XPS spectra of the samples. Figure 2 shows the typical XPS data of Zn $2p_{3/2}$ in the Cu-doped ZnO film with different Cu doping concentrations. The peak of Zn $2p_{3/2}$ is located at about 1022.4 eV and does not shift with the variation of Cu doping, which indicates that Zn exists only in the oxidized state,[16] and the Cu doping level has no evident influence on the chemical state of Zn.

The XPS spectra of Cu in the films with different Cu doping levels are shown in Fig. 3. It shows that the peaks of Cu $2p_{3/2}$ also have no evident shift with the variation of Cu doping. The peaks of Cu $2p_{3/2}$ are located at about 933.28 eV, which reveals that the majority of Cu exists in the oxidized state.[14,17]

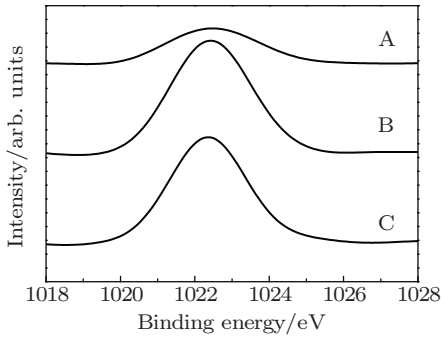



**Fig. 2.** XPS spectra of Zn $2p_{3/2}$ of ZnO:Cu films for Cu doping levels. Sample A: 0.8%, sample B: 1.6%, and sample C: 2.4%.

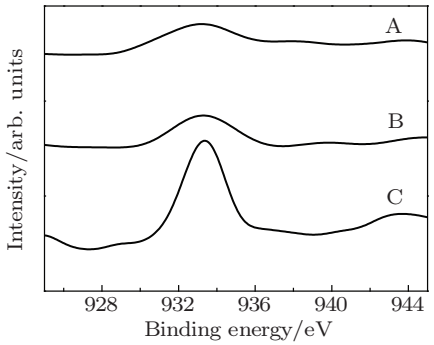



**Fig. 3.** XPS spectra of Cu $2p_{3/2}$ of ZnO:Cu films for Cu doping levels. Sample A: 0.8%, sample B: 1.6%, and sample C: 2.4%.

The XPS peaks of O 1s of the doped films are shown in Fig. 4(a) and evident changes of the spectra can be seen from the spectra. The binding energy peak of O 1s of sample A is located at 531.19 eV, which indicates that the majority of $O^{2-}$ ions exist in the oxygen deficient regions,[18–20] while the binding energy peak of O 1s shifts toward the lower energy as Cu doping level increases. In order to perform a further analysis of the O 1s spectra, the Gaussian curve fitting method is used for samples B and C, and the results are shown in Figs. 4(b) and 4(c). For sample B, the peak can be decomposed into two components, which are located at 529.90 eV and 533.30 eV, respectively. The strong intensity component with a binding energy of about 529.90 eV indicates that the majority of $O^{2-}$ ions exist at the intrinsic sites and no $O^{2-}$ ions in the oxygen deficient regions are detected.[18–20] The high binding energy component located at 533.30 eV is usually attributed to the presence of loosely bound oxygen on the surface of ZnO film, belonging to a specific species, e.g., $-CO_3$, which adsorbs $H_2O$ or $O_2$.[18–20] Finally, the peak of O 1s of sample C can be deconvoluted into three components, which are centered at 529.90 eV, 531.19 eV, and 533.30 eV, corresponding to the intrinsic state, oxygen deficient state, and surface state of oxygen elements, respectively. Clearly, our results indicate that Cu-doping level has a complicated and strong effect on the chemical state of O in the ZnO:Cu film. Moderate Cu doping level is conducive to the good stoichiometry of the film.

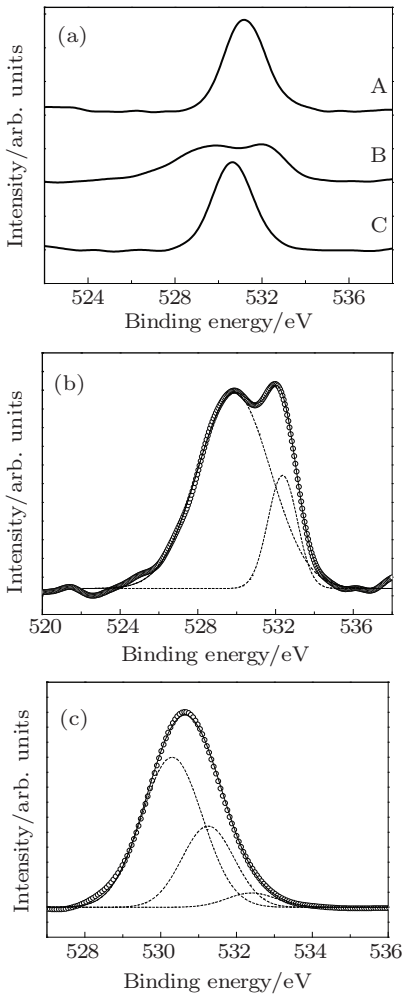



**Fig. 4.** XPS spectra of O 1s of ZnO:Cu films for Cu doping level. Sample A: 0.8%, sample B: 1.6%, and sample C: 2.4% (a), and XPS spectra (open circles) and simulated lines of O 1s in samples B (b) and C (c).

### 3.3. Optical properties

The optical properties of the samples are studied. The transmittance and absorption spectra of samples A, B, and C are shown in Fig. 5. A change in the optical band gap for each of the ZnO films is revealed. The average optical transmission decreases substantially at short wavelengths near the ultraviolet range.

In order to distinguish the relationship of the bandgap change as the variation of Cu doping levels, the optical gap ($E_g$) of the film is obtained by plotting $(\alpha h\nu)^2$ against $h\nu$ ($\alpha$ is the absorption coefficient and $h\nu$ is the photon energy) and extrapolating the straight line portion of this plot to the energy axis according to the absorption spectra.[21] Band gap values of about 3.16, 3.21, 3.18, and 3.68 eV are obtained for the pure ZnO and the ZnO compounds with different Cu concentrations (samples A, B, and C). The bandgaps change evidently with the Cu doping level increasing. According to the Burstein–Moss effect, the bandgap change is simple and in one direction: with the increase of doping level, the bandgap will be blue-shifted due to the increase of carrier concentration, which is donated by interstitial zinc atoms or oxygen vacancies at room temperature.[13] Interestingly, our results reveal much more complicated variation behaviors and imply richer physics behind them: the bandgap of ZnO:Cu is first blue-shifted, then red-shifted, and finally blue-shifted. As shown by the above XPS analysis, the chemical states of oxygen elements change nonlinearly with the increase of doping level of Cu: oxygen vacancies are dominant at low doping level, then intrinsic and surface states of oxygen take over at moderate doping level, and finally oxygen vacancies become the majority of oxygen elements with intrinsic and surface states coexisting at higher doping level. Since the carrier concentration in the sample is mainly donated by oxygen vacancies, the bandgap changes in a complicated manner with Cu-doping level. We can then conclude from our experimental observation that when the oxygen vacancies are dominant and the intrinsic and surface states of oxygen are not detected (sample A), which is probably because of the scarcity of oxygen in the sample, the optical spectra (and bandgap) shows blue shift; when the intrinsic and surface states are dominant and the oxygen vacancies are not detected, which is probably because of the abundance of oxygen in the system (sample B), the optical spectra shows red shift; when both oxygen vacancies and intrinsic and surface states of oxygen are detected (sample C), the optical spectra result from the competition between the three states of oxygen. Our results show that one can modulate the bandgap of ZnO back and forth via Cu doping, and the narrowest bandgap

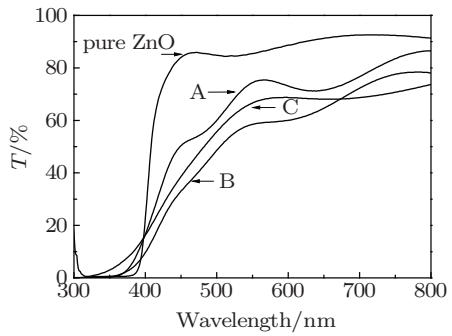



**Fig. 5.** Transmittance spectra of ZnO:Cu films for Cu doping levels. Sample A: 0.8%, sample B: 1.6%, and sample C: 2.4%.

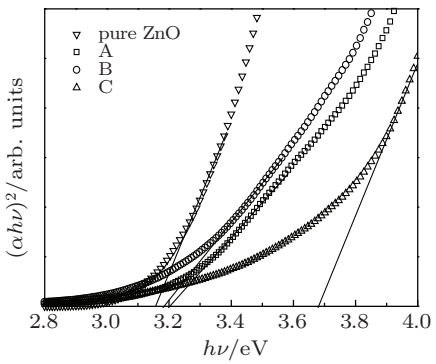



**Fig. 6.** Curves of $(\alpha h\nu)^2$ versus $h\nu$ of ZnO:Cu films for Cu-doping levels. Sample A: 0.8%, sample B: 1.6%, and sample C: 2.4%.

occurs in sample B, where no $O^{2-}$ ions in the oxygen deficient regions are detected in the XPS spectra. This may suggest an effective way for the bandgap engineering of ZnO samples.

## 4. Conclusion

In this paper, ZnO:Cu thin films are first prepared by reactive magnetron sputtering technique. XRD measurements then reveal that ZnO doped with moderate Cu dopant could enhance the crystallinity of ZnO thin film. The XPS spectra of zinc, oxygen, and copper results show that the chemical states of zinc and copper do not change with Cu-doping level, but the chemical states of O change dramatically with Cu-doping level. The measurements of optical and electronic properties of the samples reveal that the bandgap variation is not monotonic, in contrast to the simple one way variation of the Burstein–Moss effect.[13] Instead, the bandgap can be varied back and forth, and the transmittance spectra show both red shift and blue shift, due to the complicated variations of chemical states of oxygen with the increase of Cu doping. Our results may be important both for the understanding of the foundation of transition-metal-doped ZnO and for the potential applications based on the bandgap engineering of ZnO.

## References


[1] Kim H, Horwitz J S, Kim W H, Qadri S B and Kafafi Z H 2003 *Appl. Phys. Lett.* **83** 3809

[2] Nelson S F, Levy D H and Tutt L W 2012 *Appl. Phys. Lett.* **101** 183503

[3] Kim Y J, Cho J, Hong Y J, Jeon J M, Kim M, Liu C and Yi G C 2010 *Nanotechnology* **21** 55303

[4] Shi L B, Li M B, Ren J Y, Wang L J and Xu C Y 2009 *Chin. Phys. B* **18** 726

[5] Zhang F C, Zhang Z Y, Zhong W H, Yan J F and Yong J N 2009 *Chin. Phys. B* **18** 2508

[6] Fu W Y, Cao J, Li Y X and Yang H B 2011 *Acta Phys. Sin.* **60** 067505 (in Chinese)

[7] Liu D F, Tang D S, Ci L J, Yan X Q, Liang Y X, Zhou Z P, Yuan H J, Zhou W Y and Wang G 2003 *Chin. Phys. Lett.* **20** 928

[8] Liu X C, Shi E W, Chen Z Z, Zhang H W, Zhang T and Song L X 2007 *Chin. Phys.* **16** 1770

[9] Hao W C, Li J J, Xu H Z, Wang J O and Wang T M 2011 *Prog. Nat. Sci.* **21** 31

[10] Gu G X, Xiang G, Luo J, Ren H T, Lan M, He D W and Zhang X 2012 *J. Appl. Phys.* **112** 023913

[11] Rai R C, Guminiak M, Wilser S, Cai B and Nakarmi M L 2012 *J. Appl. Phys.* **111** 073511

[12] Liu Y P, Ying M J, Mei Z X, Li J Q, Du X L and Kuznetsov A Y 2011 *Chin. Phys. B* **20** 066104

[13] Bahsi Z B and Oral A Y 2007 *Opt. Mater.* **29** 672

[14] Lee J B, Le H J, Seo S H and Park J S 2001 *Thin Solid Films* **398–399** 641

[15] Öztas M and Bedir M 2008 *Thin Solid Films* **516** 1703

[16] Major S, Kumar S, Bhatnagar M and Chopra K L 1986 *Appl. Phys. Lett.* **40** 394

[17] Puchert M K, Hartmann A, Lamb R N and Martin J W 1996 *J. Mater. Res.* **11** 2463

[18] Chen M, Wang X, Yu Y H, Pei Z L, Bai X D, Sun C, Huang R F and Wen L S 2000 *Appl. Surf. Sci.* **158** 134

[19] Cebulla R, Weridt R and Ellmer K 1998 *J. Appl. Phys.* **83** 1087

[20] Fan J C C and Goodenough J B 1977 *J. Appl. Phys.* **48** 3524

[21] Tauc J, Grigorovici R and Vancu A 1966 *Phys. Status Solidi* **15** 627