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# Comparative studies of the structural and magnetic properties in Cu, Co codoped ZnO multilayer films sputtered on different substrates

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**Abstract** The $Zn_{0.959}Cu_{0.023}Co_{0.018}O$ multilayer films on silicon and polystyrene particles array were prepared using RF magnetron sputtering technique. The influences of the substrate on structural and magnetic properties of Cu, Co codoped ZnO multilayer films were investigated by X-ray diffraction, Scanning electron microscope, X-ray photoelectron spectroscopy, and vibrating sample magnetometer. The results indicated that all the samples were the wurtzite structure with hexagonal shapes of ZnO holding different degree of preferred orientation, the $Cu^{2+}$, $Cu^{+}$ and the $Co^{3+}$, $Co^{2+}$ ions would uniformly substitute into the $Zn^{2+}$ sites of ZnO lattice in the samples sputtered on the different substrates. All the samples showed room temperature ferromagnetism, the saturation magnetization and the coercivity of the samples sputtered on the different substrates changed due to the chemical states of the Cu and anisotropy energy of the samples.

## 1 Introduction

Transition-metals (TM) doped ZnO [1–9] is intensely investigated as a popular candidate for spintronics due to the room-temperature ferromagnetism it performs. The presence of 3*d* TM magnetic ions in these materials lead to an exchange interaction between itinerant *sp* band electrons or holes and the d electron spins localized at magnetic ions, resulting in interesting versatile magnetic-field induced functionalities. 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 [10–14]. However, most of the ZnO thin films samples in related literatures were mainly sputtered on two-dimensional crystal materials [15–17], and few studies of the ZnO thin films deposited on the ordered colloidal particles had been reported [18] The lattice mismatch and thermal expansion coefficient between the thin films and substrate will inevitably produce the residual stress at the interface, which will affect the structural and magnetic properties of the ZnO diluted magnetic semiconductor films material. In order to well understand the influence of the substrates(plane substrates and the curved surface substrates) on the structure and chemical valence of the elements in the samples, the change causes for the saturation magnetization and coercivity of samples on Si substrate and on polystyrene particles array, the structure and the magnetic properties have been studied in the paper. The obtained results are promising to contribute the development of the Cu, Co codoped ZnO multilayer films.

## 2 Experiment

Cu,Co codoped ZnO multilayer films have been sputtered on Si substrate and polystyrene particles array using RF magnetron sputtering technique. The polystyrene particles array substrates were prepared by self-assembly method and the preparation process was below: the substrates were ultrasonically cleaned in ammonia and peroxide solution,then

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rinsed with deionized water. The monodisperse polystyrene particles (Duke Scientific Corporation) with diameters of 500 nm were received as a 10 wt% stoste. The deposition chamber was evacuated by a turbomolecular pump to a base pressure of $2.0 \times 10^{-4}$ Pa. The sputtering was performed in an argon atmosphere. And working pressure during deposition was fixed at 2.0 Pa, RF power was 50 W. We prepared multilayer films by using alternately sputtering method. The sputtering rates of ZnO, CuO, Co targets had been measured before the sample preparation, the $Zn_{0.959}Cu_{0.023}Co_{0.018}O$ samples have been produced based on the sputtering rates. The $Zn_{0.959}Cu_{0.023}Co_{0.018}O$ multilayer films on silicon and polystyrene particles array were formed by $[ZnO(52\ nm)/Co(1.24\ nm)/CuO(0.98\ nm)]_{10}$ with the ZnO target, Co target and CuO target sputtering about different time(460, 42, 24 s) in one cycle and the sputtering power of the three targets are: 50, 50, 24.4 w. The crystal structures of the multilayer films were determined by using X-ray diffraction (XRD). The morphology were first checked by a field emission scanning electron microscopy (SEM). The chemical valence states of zinc, oxygen, cobalt and copper in the films were investigated by X-ray photoelectron spectroscopy (XPS) on ESCA LAB 220-XL photoelectron spectrometer (VG Scientific, USA). The magnetic properties at room temperature were measured by a vibrating sample magnetometer (VSM).

## 3 Results and discussions

Figure 1 shows the XRD patterns of Cu and Co codoped ZnO multilayer films fabricated by sputtering on Si substrate and polystyrene particles array. This show that both of the samples exhibit diffraction peaks located at the same positions (2θ = 34.4°) with those of ZnO, implying the doping does not change the wurtzite structure with hexagonal shapes of ZnO, and no diffraction peaks corresponding to metallic Co, Cu or other phases appear in both of the samples, this indicates that within the X-ray detection limits, all the Co, Cu codoped ZnO films are monophasic. No obvious shift of these peaks are observed, this is consistent with Vegard's law since the Co and Cu ionic radius is comparable to that of $Zn^{2+}$ (0.060 nm), and the concentration of Co and Cu in our films is much smaller than the solubility limit. The multilayer films sputtered on Si substrate (Fig. 1a) in the direction (0 0 2) have very high crystalline quality. After depositing on polystyrene particles (Fig. 1b), the orientation of the films display a randomness character. We speculate that substrate may be the factor to influence the orientation. For the substrate material is polystyrene, the lattice mismatch between ZnO and substrate can be neglected. The crystalline is not controlled by the interface strain energy but controlled by the interface energy. So the XRD pattern is more approach the standard pattern.

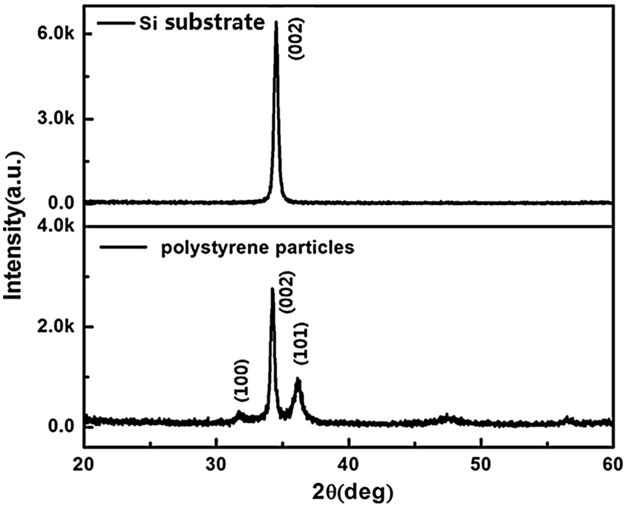

**Fig. 1** XRD patterns for the Cu, Co codoped ZnO multilayer films sputtered on different substrates

Figure 2a, b shows the SEM surface micrographs of the Cu and Co co-doped ZnO multilayer films prepared on Si substrate and polystyrene particles array. The surface morphologies are significantly different with the change of substrates. The surface of the multilayer films on Si substrate consists of many nonuniform spherical grains distributed on the flatter base. The images of the films prepared on polystyrene particles array are composed of nanostructure materials with nanosphere shapes. It is found that the surface appears flatter, and particle distributes uniformly and appears small. Furthermore, as shown in Fig. 2, Polystyrene nanoball is arranged orderly and closely, and the clearance between the ball is very obvious. That is, the film thickness is considered to far less than the ball diameter. It is rational to consider that the ZnO film is made up of many hemispherical membrane.

X-ray photoelectron spectroscopy (XPS) measurements were carried out to investigate the chemical bonding states. Figure 3a–f present the XPS survey spectra (0–1, 200 eV), the Cu 2p and Co2p XPS spectra of the Cu, Co codoped ZnO multilayer films prepared on Si substrate and polystyrene particles array, which shows all the peaks for no other elements except Zn, O, Cu, Co and C, the Gaussian was fitted to exactly locate peak positions. In the XPS spectrum (a),(d) the C1 s core level at approximately 284.6 eV corresponding to the alkyl chain (C–C) or absorbed carbon arises from the contamination from oil-diffusion pump. Figure 3b presents the XPS peaks of the Cu in the Cu, Co codoped ZnO multilayer films prepared on Si substrate. The Cu 2p3/2 and 2p1/2 peaks of the Cu, Co codoped ZnO films located at 933.4 and 953.0 eV are closed to the peaks of $Cu^{2+}$ 2p3/2 and $Cu^{2+}$ 2p1/2

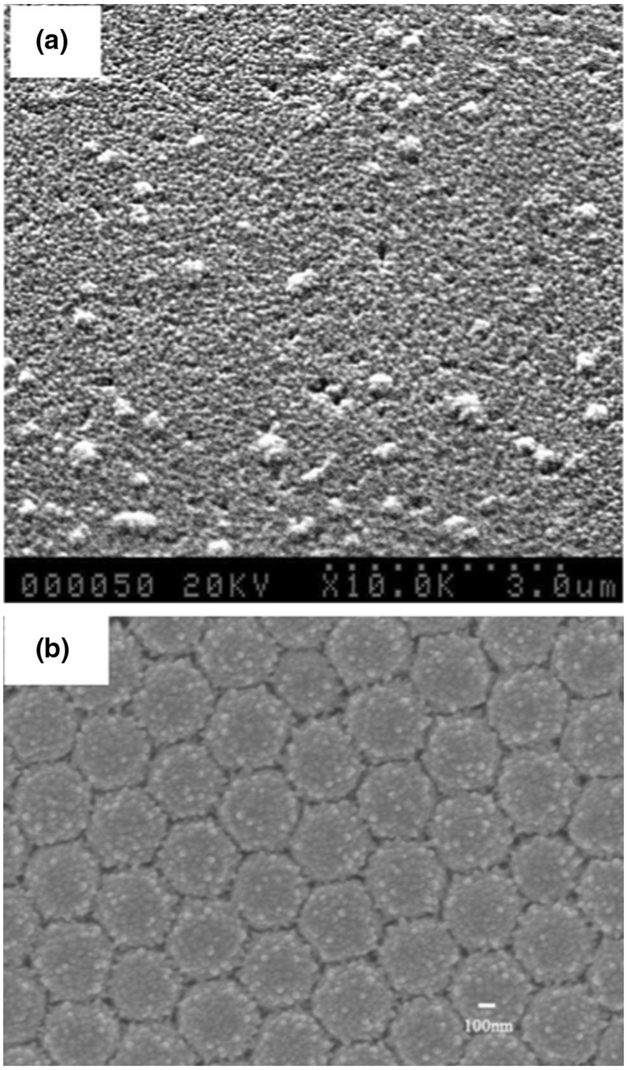

**Fig. 2** SEM images of the Cu, Co codoped ZnO multilayer films sputtered on different substrates: **a** Si substrate, **b** Polystyrene particles

respectively. From the results, it can be seen that the valence state of Cu in the samples could be assigned to +2. Figure 3d presents two peaks centered at 779.3–795.1 eV, corresponding to the Co 2p3/2 and Co2p1/2 respectively. The locations of these main peaks are close to that of the core-level XPS spectrum of Co2p ions in $Co_2O_3$ single crystal [19]. It can be concluded a trivalent state of cobalt in the samples, no other impurity phase are found. It indicates that the Co ion is substituted for Zn ion site in the ZnO lattice.

The Cu-2p XPS binding energy region of the Cu, Co codoped ZnO multilayer films prepared on polystyrene particles array is shown in Fig. 3e. Photoelectron peaks corresponding to the Cu 2p3/2 and 2p1/2 core levels were observed at 932.8 and 952.8 eV, the energy difference between the two peak is 20.0 eV, indicating that the Cu cations present +1 valence [20]. Figure 3f shows two peaks detected at the energy positions of 775–800 eV correspond to the Co $2p_{3/2}$ and $Co2p_{1/2}$ orbitals. Position of Co $2p_{3/2}$ peak (780.2 eV) is found similar to CoO, specific to Co–O bonding (780.1 eV) and much different from Co metal (778 eV) and $Co_2O_3$ (779 eV). These findings confirm that Co ions stay bivalent in ZnO lattice having a high-spin d state [21, 22], without forming impurity phases like metallic Co or $Co_2O_3$. The atomic ratio of Cu:Zn of sample measured by the results of XPS were about 0.024 for the two samples on Si substrate and on polystyrene particles array, virtually the same to the expected nominal composition. The valence states of Cu, Co for Cu and Co codoped ZnO multilayer films sputtering on Si substrate and polystyrene particles array were different and it indicates that the substrate has impacted on the valence states of elements for the samples.

Magnetic properties of Cu and Co codoped ZnO multilayer films were measured at room temperature using VSM, as shown in Fig. 4, and respectively to show the clear room temperature ferromagnetism. Though it is not clarified how oxygen vacancy and dopant concentration promote ferromagnetism, P-type carrier generated by Cu doping is considered to be a main fact or to induce RTFM [23]. According to the XRD and XPS analysis results, Our samples do not contain any second phase. Hence ferromagnetic ordering may be intrinsic and may not be due to any other magnetic phases or clusters. Weaker saturation magnetization were appeared for the films sputtering on polystyrene particles than that on Si substrate. $Cu^{1+}$and $Cu^{2+}$ cations are expected to possess $3d^{10}$ and $3d^9$ configurations, respectively. $Cu^{1+}(3d^{10})$ cations orbitals were filled, and much less doing any contribution for ferromagnetic. However, $Cu^{2+}$ ($3d^9$) cations provides one unpaired electron and induces FM [24]. $Co_3O_4$ and $Co_2O_3$ is of ferromagnetic property,but the CoO possess antiferromagnetism in nature. Therefore, characteristic chemical states of Cu element and Co element which are important in determining the ferromagnetism of our samples. $Cu^{2+}$ in the Cu, Co codoped ZnO multilayer films prepared on Si substrate was the main reason for the ferromagnetic enhancement.

It is noticed from inset of Fig. 4 that the coercivity is also higher for sputtering on polystyrene sphere than that of on Si substrate one. We speculated that it may be the following reasons. The magnetic exchange rely on the interaction between adjacent atoms of the electron orbital. Any change of the interaction between atoms position will also affect the electron orbital interaction relations. Our earlier studies have shown that stress of the sputtering on polystyrene sphere is greater than on the Si substrate [25]. Crystal anisotropy energy, which caused by stress, can be approximate calculated by using Equation:

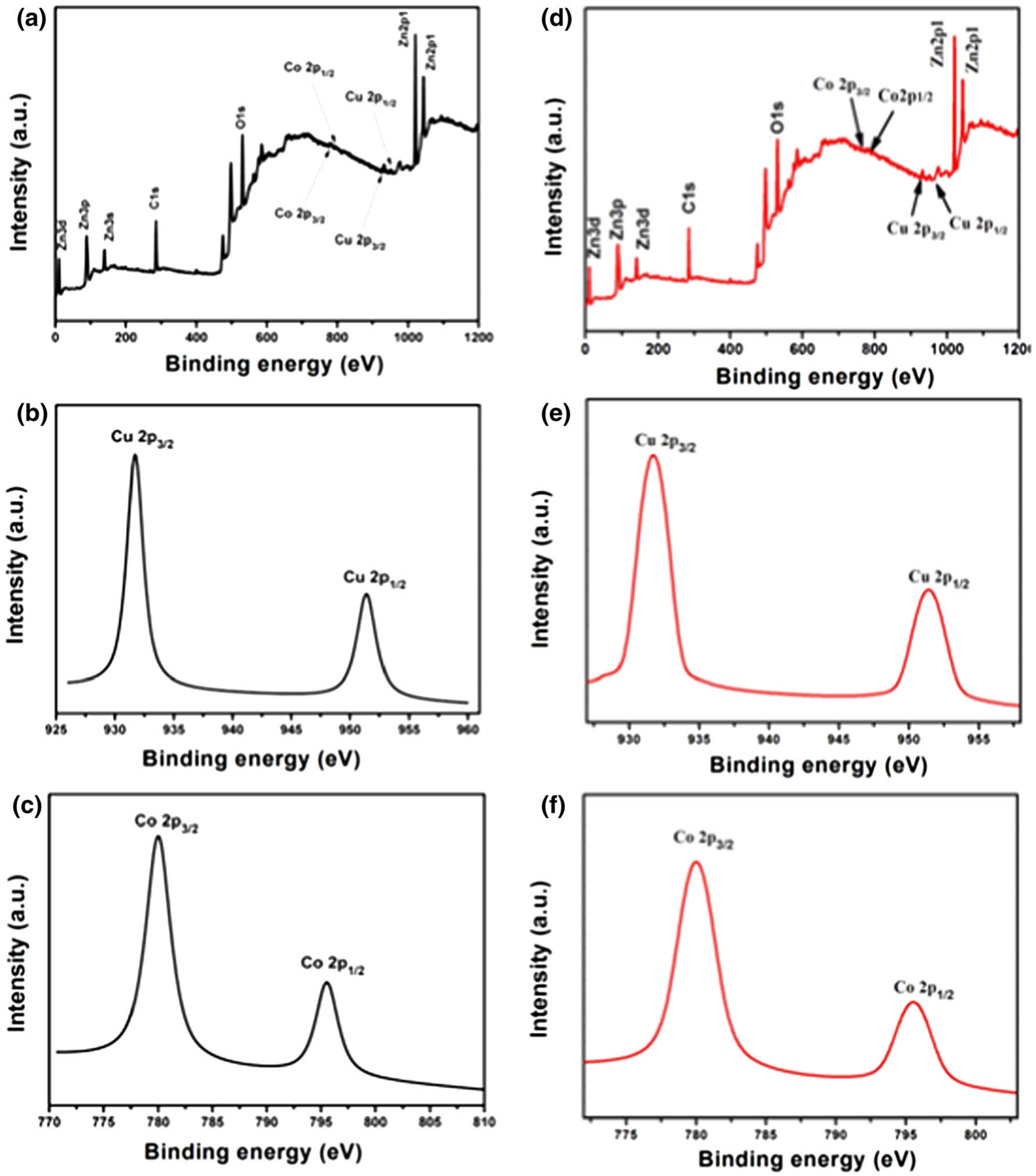

**Fig. 3** XPS spectra of the Cu, Co codoped ZnO multilayer films sputtered on different substrates: **a** Si substrate, **b** Si substrate, **c** Si substrate, **d** Polystyrene particles, **e** Polystyrene particles, **f** Polystyrene particles. The full-spectrum **a**, **d** and high-resolution scan of Cu2p **b**, **e** and Co2p **c**, **f**

$$E_{\sigma} = -\frac{3}{2}\bar{\lambda}\sigma\sin^{2}\theta$$

where $\bar{\lambda}$ is a constant, $\sigma$ is the stress of the sample, $\theta$ is the angle between stress and c shaft. The samples sputtering on polystyrene sphere possess more anisotropy energy than on Si substrate one. For the existence of anisotropy energy, work is done against the energy barrier when the magnetization along a preferred magnetization axis pivot in another. And coercivity as the deflection field for the stability, it is likely to change, as anisotropy energy change.

## 4 Conclusion

In summary, The $Zn_{0.959}Cu_{0.023}Co_{0.018}O$ multilayer films on silicon and polystyrene particles array were successfully synthesized using RF magnetron sputtering technique. The

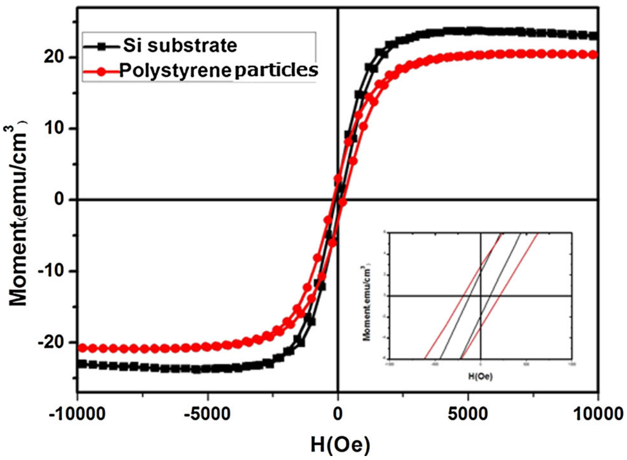

**Fig. 4** Room-temperature magnetization hysteresis curves of the Cu, Co codoped ZnO multilayer films sputtered on different substrates

influences of substrate on the structural and magnetic properties of samples were investigated in this paper. XRD measurements indicated that the films were of wurtzite structure without impurity phases. XPS results showed that the substrate had impacted on the valence states of elements for the samples. All the samples showed the clear room temperature ferromagnetism, and the valence state of Cu affected the saturation magnetization of the samples. The coercivity of the samples was affected by substrate, which was tightly linked to the change of anisotropy energy.

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