XAFS study on the temperature-dependent occupation sites of Co codopants in (Co, Cu)-codoped ZnO films

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Abstract. Elemental codoping has been an effective way to regulate the structural and electronic properties of semiconductors. By using x-ray diffraction and x-ray absorption fine structure spectroscopy, we investigate the local structure and spatial occupations of Co dopants in Cu-doped ZnO thin films prepared by pulsed-laser deposition method. It is revealed that the Co dopants are substantially incorporated into ZnO matrix when the deposition temperature is increased up to 650 °C, although the preferential orientation of ZnO film is changed. The results provide experimental guidance in the synthesis of the co-doped ZnO based dilute magnetic semiconductors.

1. Introduction
Zinc oxide (ZnO) semiconductor has drawn intense scientific interest because of its potential application in photoelectronics, blue/UV light luminescence, and spintronics [1-3]. Until now, the most effective method to improve the properties of ZnO is to introduce impurity atoms [2, 4]. Doping of magnetic atoms into the ZnO lattice could achieve ferromagnetism for spintronic devices [5]. As a promising candidate for practical use, high mobility of electrons and enough carrier density are demanded, which could be resolved by codoping of another dopant into the single-doped materials [6]. Although a great number of studies have been performed to investigate the single- or co-doped ZnO systems, the relationship between the atomic occupation and electronic structure of the dopants in the ZnO matrix is still unclear.

The processes of the crystal formation are sensitive to the environmental conditions of samples preparation. For example, Chakraborti et al. have studied the effect of substrate temperature on the properties and structure of the (Co, Cu):ZnO thin films deposited on sapphire c-plane by pulsed-laser
deposition (PLD). The magnetization of ZnO thin films prepared at 500 °C decreased evidently compared with that of the films fabricated at 600 °C, which would be attributed to the formation of Cu nanoclusters in the ZnO lattice [6]. Our group has reported that the growth orientation of ZnO and the dopant occupation sites would be changed by varying the substrate temperature [7]. All of these studies have clearly implied that the atomic occupation, electronic properties, and crystal structure of doped ZnO systems can be affected by the growth temperature. In order to rationally control the structure and functional properties of ZnO-based semiconductors, it would be excited to seeking a comprehensive knowledge on the atomic and electronic interactions of the co-dopants in ZnO thin films under different growth temperatures.

In this study, a series of (Co, Cu)-co-doped ZnO thin films have been prepared with the same composition under different substrate temperatures by pulsed-laser deposition method. The x-ray absorption fine structure (XAFS) spectroscopy and x-ray diffraction (XRD) were used to probe the local structure and spatial occupations of Co dopants in the (Co, Cu)-codoped ZnO thin films. These results broad our understanding on the modulation of co-dopants for modifying the atomic and electronic properties of ZnO-based thin films.

2. Experimental Section
The Zn$_{0.93}$Co$_{0.05}$Cu$_{0.02}$O thin films were prepared on Si (100) substrates by pulsed laser deposition (PLD) (248 nm wavelength, 5 Hz repetition frequency) under various substrate temperatures (RT, 200, 400 and 650 °C). The Zn$_{0.93}$Co$_{0.05}$Cu$_{0.02}$O targets were synthesized by modified solid-state reaction method and the detailed procedures were described in our previous work [8]. The target and substrate were kept rotation during the experiment process. The structural properties of the (Co, Cu)-codoped ZnO thin films were characterized by X-ray Diffractometer. The Co K-edge XAFS spectra were used to ascertain the local structure around the Co ions performed in the fluorescence mode at the U7C beamline in the National Synchrotron Radiation Laboratory (NSRL), China.

3. Results and discussion

![Figure 1. XRD patterns of (Co, Cu)-codoped ZnO films grown at different temperatures and the pristine ZnO deposited at 650 °C as comparison.](image-url)
Figure 1 shows the XRD patterns of (Co, Cu)-codoped ZnO thin films deposited at different substrate temperatures. To highlight the dopant-related weak peaks, the peak intensity is shown at a logarithmic scale. The (201) diffraction peak of wurtzite ZnO located at 69° is predominant for the films grown at $T_s \leq 400$ °C. As the substrate temperature up to 400 °C, there are two additional peaks corresponding to the (002) and (004) planes of ZnO abruptly arising. Finally, the (201) peak vanishes entirely for the film deposited at 650 °C. These results indicate that the crystalline orientation of the codoped ZnO films transforms from the [201] direction at low substrate temperature to the c-axial orientation when the temperature is up to 400 °C. Furthermore, a low intensity peak corresponding to metallic Cu appears at ca. 43° for the films grown at $T_s \geq 400$ °C. The characteristic peaks of second phases related to Co or Cu do not emerge for all the films grown at various substrate temperatures.

Figure 2. (a) Co K-edge EXAFS oscillation functions $\chi(k)$ and (b) FT spectra of $k^3\chi(k)$ of Zn$_{0.93}$Co$_{0.05}$Cu$_{0.02}$O thin films deposited at different temperatures of RT, 200 °C, 400 °C, and 650 °C, and the pristine ZnO deposited at 650 °C and Co foil for references.

In order to clarify the atomic structures of the doped ions in the thin films, the extended x-ray absorption fine structure (EXAFS) technique is used to detect the local structures of Co dopants in ZnO lattice prepared at various substrate temperatures. The EXAFS oscillation $\chi(k)$ functions and the Fourier transform (FT) curves of the $k^3$-weighted $\chi(k)$ at Co K-edges for the films grown at different substrate temperatures are plotted in Figure 2. In the FT spectra for the samples, two strong peaks corresponding to the first-nearest Co–O and the second-nearest Co–Zn neighbors are located at around 1.55 and 2.88 Å, respectively [9]. For all the (Co, Cu) codoped ZnO thin films, there is no peak corresponding to the first-nearest Co–Co coordination of Co metal appears in the FT curve [10], which indicates that the Co ions are still substituted for the Zn sites in the ZnO matrix.

Summarizing above XRD and XAFS results, we conclude that temperature plays an important role on the interrelations between the atomic occupation of (Co, Cu) dopants and ZnO crystal orientations. Additionally, because the ionization energy of Co (17.3 eV) is lower than that of Zn (17.9 eV) and the
solubility of Co in ZnO is relatively large, Co ions could be successfully incorporated into the ZnO lattice and substituted for the Zn sites [11]. In contrast, the ionization energy of Cu (20.3 eV) is larger than that of Zn. The Cu atoms are energetically inert to be oxidized and substituted for the Zn sites. Consequently, the Co dopants are precipitated out as metallic species even under the relatively mild growth environment of low growth temperature [7]. Although the transformation of ZnO matrix preferential orientation would affect the dopants interactions and electronic exchange, the low concentration of Cu could not afford stronger electrostatic forces and enough electrons to reduce the Co ions. Therefore, the Co atoms were substituted into ZnO matrix for the samples prepared at all substrate temperatures.

4. Conclusion

The Zn$_{0.93}$Co$_{0.05}$Cu$_{0.02}$O thin films were prepared by PLD on Si (100) substrate at different substrate temperatures. The XRD results suggest that the orientation of the codoped ZnO films was changed and the Cu dopants were easily separated from the ZnO matrix with increasing the substrate temperature. In-depth analysis of the Co K-edge EXAFS data shows that the Co atoms were substituted into ZnO matrix for the samples prepared at all substrate temperatures. The results provide some hints for understanding the interaction between the dopant ions and the ZnO lattice in the transition metal-doped ZnO thin films fabricated at different substrate temperatures.

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