Zn$_{1-x}$Co$_x$O film valence by photoelectron spectroscopy

Yingzi Peng$^{1,2}$, Dexuan Huo$^1$ and Liping Zhu$^2$

$^1$ Department of Physics, School of Science, Hangzhou Dianzi University, Hangzhou 310018, P.R.China
$^2$ State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, P.R.China

E-mail: yingzip@hdu.edu.cn

Abstract. The Co-doped ZnO film was fabricated using a pulsed laser deposition method on a C-sapphire substrate. The structural properties of the Co-doped ZnO film and the chemical states of elements have been studied in this paper. The XRD and HRTEM characterization results show that it is wurtzite structure with the C-axis of the film aligned with that of the substrate without obvious precipitation. Furthermore the experimental results probably reveal the occupation of Co ions at Zn sites in the host lattice. The oxygen ions are lying in metal oxide, which are due to O - Zn(Co) bonds, though a few oxygen deficiencies and oxygen vacancies were also detected. Co ions have replaced part of Zn sites in the host lattice, resulting in Co - O bonds and no obvious precipitate was detected in the film under our experimental conditions. The substituted Co ions are in the 2$^+$ oxidation state. The electronic-structure parameters $\Delta$, $U$ are also induced.

1. Introduction

Diluted magnetic semiconductors (DMSs) are semiconductors with some magnetic ions as impurities in the host lattice. Generally, DMSs are synthesized by semiconductors doped with 3d transition metal ions while their semiconductor properties are maintained. The discoveries of InMnAs and GaMnAs in the 1990s re-activated research in magnetic semiconductors [1] and stimulated the development of a new field called spintronics. Since then, how to develop new DMSs with higher Curie temperatures became a common concern. Dietl theoretically predicted that the Curie temperatures of DMSs, such as ZnO and GaN based compounds, could be raised to room temperature within a mean-field picture [2]. After that, ZnO doped with 3$d$ transition metals has become a hot topic for research [3-5]. Though many experimental results have been reported on Co-doped ZnO, there are controversies on the reports of ZnO-based DMSs studies, such as the inconsistency of results reported by different groups and confused explanations of the magnetic behaviors. Therefore, recently it has received much attention to explore the physical mechanisms underlying ZnO-based DMSs [6]. Among these, the studies on valence or chemical states of materials were attracted much interests [7-9]. For example, D. Seghier et al. studied a deep electron trap in ZnO and Co-doped ZnO epilayers and suggested a

1 Corresponding author: Yingzi Peng, yinzip@hdu.edu.cn

Published under licence by IOP Publishing Ltd
correlation between the observed ferromagnetism in these materials and the oxygen vacancy [10]. Ref [11] reported the ferromagnetism ordering of the materials could be switched between “on” and “off” by introducing or removing, respectively, the oxygen vacancies in Co-doped ZnO.

In our previous papers, the observation of room temperature $M-H$ loops of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films were already reported [12-14]. This work is following our previous reports on ZnO based diluted magnetic semiconductors, in which Co-doped ZnO thin films were synthesized using a dual-beam pulsed-laser-deposition method. This paper addresses chemical states of the films prepared using a single beam pulsed-laser-deposition (PLD) method by photoelectron spectroscopy, which can provide useful chemical-state information and relatively straightforward interpretation of spectra. In this paper, very sophisticated computer curve fitting routines will be used.

2. Experiment

The Co-doped ZnO film was fabricated by a pulsed laser deposition method from a ceramic target on a C-plane sapphire substrate. A pulsed KrF excimer laser (Lamba physic) was used as a light source. The laser was set to operate at a repetition rate of 10 Hz, laser energy around 110 mJ. A single crystal sapphire substrate was used to support the crystal growth of the thin film. The substrate was put on the substrate holder at a distance of 50 mm from the target. The film was formed at 650 °C in ambient pressure around $5 \times 10^{-5}$Torr. The target for PLD was prepared by a self-assembly ceramic technique using ZnO and Co powders following the procedure of mixing, compacting and calcining. The Co contents of targets are 5 at%.

The specimen was analyzed by X-ray diffraction (XRD) to identify the crystal structures and orientation of the films. X-ray photoelectron spectroscopy (XPS) was performed to determine element chemical states of the components. Detailed lattice structures and possible precipitates were obtained by a high-resolution transition electron microscopy (HRTEM).

3. Results and discussions

The Co-doped ZnO film was examined by XRD. Figure 1 shows the XRD pattern of the specimen on the sapphire substrate. The graph shows a clear XRD pattern, that is, besides the peak corresponding to the (0006) of substrate, only diffraction peaks corresponding to the (0002) and (0004) planes of the Co-doped ZnO film can be clearly observed. Note that presenting in the logarithm scale, besides the peaks corresponding to $\lambda_{\text{Cu}1}$, the peaks of (0002) for the film and the (0006) for the substrate corresponding to $\lambda_{\text{Cu}2}$ and $\lambda_{\text{Cu}β}$ were also detected, indicating high orientation growth of the film. No peak of other phases were detected. Consequently, it is a wurtzite structure with the C-axis of the film aligned with that of the substrate. The (0002) peak of the film is close to that of ZnO, probably implying that part of Zn sites in the host lattice were replaced by Co ions. The inset shows the rocking curve around (0002) peak of the specimen. The value of full-width at half maximum (FWHM) of the peaks is around 0.2°. Based on the results, the dispersion of the orientation is relatively small and the film is expected to grow along a preferred direction.
In order to study the details of the crystal structures, HRTEM of the Co-doped ZnO film was characterized. Figure 2 presents the HRTEM cross-section image and the selected area electron diffraction pattern of the film. The film lattice is shown in Figure 2(a), showing a very clear lattice. Figure 2(b) shows a selected area electron diffraction pattern of the film. It can be seen that it is a wurtzite structure without obvious precipitation. HRTEM for substrate and interface were also characterized (not shown here), showing that the C-axis of the film aligned with that of the substrate, which are similar to our previous results. These results seem to coincide with the results of XRD. According to our experimental results, no obvious precipitate was detected. These results probably reveal a suggestion of the occupation of Co ions at Zn sites in the host lattice.

Figure 2. HRTEM image of the Co-doped ZnO thin film (a) and its corresponding selected area electron diffraction pattern (b).
XPS was used to characterize the chemical states of components for the films. XPS spectra of the Co-doped ZnO film were taken in the range till 1100 eV, as shown in Figure 3. Peaks corresponding to Zn, Co and O is observed in the figure. The XPS spectrum of C 1s is also shown in this figure, as the binding energy of C 1s is usually used as an internal reference in the spectrum [15]. The spectra corresponding to O 1s core level, Zn 2p core level and Co 2p core level of the Co-doped ZnO specimen are calibrated by 284.6 eV binding energy of C 1s as the internal reference spectra. Then element atom ratio can be obtained by the spectra. Under our experimental conditions, the atom ratio of Co:Zn is about 1:10, which is much larger than that prepared in target. And the atom ratio of Zn:O is about 1:0.9, indicating that there is some oxygen vacancies in the specimen.

The Zn 2p spectrum is shown in Figure 4. A single Gaussian was nicely fit and the peak appeared at 1021.7 eV, which is lying within the standard reference value of Zn in ZnO. It can be identified as Zn 2p\(3/2\) peak [16]. The binding energy value suggests that Zn atoms are in +2 oxidation state. However, based on this binding energy value, it is hard to rule out the possibility of the presence of Zn interstitial defects completely, as the differences of the binding energy mentioned above are so small [16].

The binding energy of O 1s is given in Figure 5. The O1s peak is observed to reveal a shoulder at higher binding energy. The asymmetry nature of the curve reflects the variation of oxidation number of oxygen. By fitting the peak with gaussians, the O1s can be separated into two peaks, the lower energy peak and the higher energy peak. The lower energy peak located at 530.2 eV (Peak 1) is in agreement with the binding energy for O 1s of 528.1 - 531.05 eV for a metal oxide [16], which may be attributed to oxide ions in ZnO or CoO in our case. Here, it is attributed to O – Zn(Co) bonds from the wurtzite structure of Zn\(^{2+}\) ion of the Co-doped ZnO. While the higher energy peak, located at 531.2 eV (Peak 2), corresponds to the oxygen deficient region within the ZnO matrix, that is, it can be assigned to O - H bonds resulting from exposure to air and surface contamination which is due to the chemisorbed oxygen of the surface hydroxyl, absorbed H\(_2\)O and so on. The presence of the higher energy peak coincides with the results of wide survey scan.
Figure 6 reveals the Co $2p$ XPS spectrum for Co-doped ZnO thin film in the upper panel. By fitting
the peak with Gaussians (some components of Lorentzian), the spectra could be deconvoluted into
four peaks P1, P2, P3 and P4. The peaks P1 located at 780.9 eV, corresponding to the binding energy
of Co - O bond and can be assigned to Co $2p3/2$ core level. It is further notable that no apparent peak
occurred around 778 eV , indicating that no apparent Co - Co bonding exists in the film. Namely, the
observed Co $2p3/2$ peak position is quite different from that of the Co metal and also away from other
cobaltic oxide [16]. The peak P3 around 796.4 eV, can be assigned to Co $2p1/2$ core level. The
difference between the peaks for Co $2p3/2$ and Co $2p1/2$ is close to 15.5 eV, which coincides with that
of the value of CoO (around 15 eV) [16]. Hence it is reasonable to suggest that Co$^{2+}$ incorporate into
wurtzite lattice at the Zn$^{2+}$ sites, without forming obvious impurity phase like metallic Co.

As we know, photoelectrons were ejected while XPS is processing. When the outgoing
photoelectron simultaneously interacts with a valence electron and excites it or shakes it up to a higher
energy level, the energy of the core electron is then reduced slightly giving a satellite structure. Satellite structure is also named as shaking up resonance transition. This perturbation gives rise to
some discrete energy-loss phenomena [15] which are related to electronic structures. Hence under our
experimental conditions, it is reasonable to assign the peaks P2 and P4, observed around 786.2 eV and
802.3 eV, respectively, to the satellite structures of Co $2p3/2$ and Co $2p1/2$, which are related to the
$d$-band metal Co due to the interaction between the core hole and the valence electrons O $2p$ resulting
in a change in the potential seen by the valence electrons upon the creation of the core hole. Namely,
the satellite peaks reflect the excitation of a valance-band electron from an occupied state to an
unoccupied state. Here, in order to analyze the photoemission spectra, the line spectra have been
broadened by Gaussians and Lorentzians (mostly Gaussians). The former represents the instrumental
broadening and finite bandwidth effects, and the latter relates to the lifetime broadening that increases
with binding energies. The relative intensity and energy of the satellite to the main peak are carefully
determined. The relationship between the relative binding energies and the ionization cross-section is
schematically shown in the lower panel of Figure 6. It can be seen that strong satellite structures were
obtained in this study. Furthermore, the strong and well defined satellite peaks reflect the fact that the
substituted Co ions are in the $2+$ oxidation states, and the interaction between cobalt and oxygen is
strong, which will be discussed in details as follows.
All these experimental results probably supply us a reasonable picture of the chemical states for the specimen. In short, the oxygen ions are lying in metal oxide, which are due to O - Zn(Co) bonds, though there are a few oxygen deficiencies and oxygen vacancies. Co ions have replaced part of Zn sites in the host lattice, resulting in Co - O bondings and no obvious precipitate was detected in the film. The substituted Co ions are in the 2+ oxidation state. More electronic-structure parameters can be induced as follows:

Our experimental results show that Co-doped ZnO thin film has a wurstite-type lattice, that is, the thin film has a similar band structure to that of ZnO. Here, it is reasonable to consider that $E_F$, locates in the center of the bandgap, and the relative position of Fermi level and the top of the valence band, $E_F - E_v$ for Zn$_{1-x}$Co$_x$O is that $E_F - E_v \approx 1.6$ eV, similar to that of ZnO [17]. In the film, Co atoms substitute Zn-sites, hence there is a tetrahedral crystal field applied on the Co ions. The Co-doped ZnO system can be regarded as the case of Co$^{2+}$ ($d^7$) in a tetrahedral field of ZnO. The exchange interaction between the $p$ band in the valence band and the $d$ electrons is mainly derived from the $p$-$d$ hybridization. Especially at the $\Gamma$ point, the top of the valence band is constructed purely from the anion $p$ orbitals that can only hybridize with the $d$ orbitals of $t_2$ symmetry [18].

In DMSs, two fundamental interaction mechanisms are considered: the direct Coulomb exchange and the kinetic exchange. It is known that the final state of $d$ electrons is determined by the competition of crystal field splitting energy and intro-atomic exchange energy [19]. Kinetic exchange, i.e., the hybridization of the band states with localized ionic $d$ orbitals, may be viewed as a second-order perturbation effect involving virtual transition of an electron between the band states and ionic orbitals [20]. The exchange interaction between the $s(p)$ electrons in the conduction band and the $d$ electrons of the Co$^{2+}$ is derived from the direct exchange. To reveal the 3$d$-3$d$ Coulomb interaction and the 3$d$-anion hybridization, the electronic-structure parameters $\Delta$, $U$ are important, where $\Delta$, the multiplet-averaged charge-transfer energy between the ligand and the transition-metal atom, is defined as the difference between the multiplet-averaged energies of the $d^n$ and $d^{n+1}L^1$ configurations at the transition-metal atom, where $d^n$ denotes $n$-electron occupancy at the transition-metal site in the
presence of fully filled ligand levels, and \( L \) denotes a hole in an anion \( p \) orbital. Therefore, 
\[
\Delta = E^{\alpha}(d^{n+1}L^1) - E^{\alpha}(d^n). \quad U, \]
the multiplet-averaged Coulomb interaction, is defined by
\[
U \equiv E(d^{n+1}) + E(d^{n+1}) - 2E(d^n)[21].
\]
Based on the above expressions and the peak positions from Figure 6, relative electronic-structure parameters for Co\(^{2+}\) in Co-doped ZnO can be suggested as follows, \( \Delta \) about 5.3 eV, \( U \) about 4.9 eV. Based on the devised electronic-structure parameters for Co\(^{2+}\) in Co-doped ZnO, the exchange interaction in the Zn\(_{1-x}\)Co\(_x\)O thin films could be estimated, which will be discussed in our outcoming papers.

4. Conclusions
This paper addresses chemical states of the films prepared using pulsed-laser-deposition method by photoelectron spectroscopy. Our present experimental results show that it is wurtzite structure with the C-axis of the film aligned with that of the substrate without obvious precipitation. The oxygen ions are lying in metal oxide, which are due to O - Zn(Co) bonds, though there are a few oxygen deficiencies and oxygen vacancies. Co ions have replaced part of Zn sites in the host lattice, resulting in Co - O bonds. The substituted Co ions are in the 2+ oxidation state. The electronic-structure parameters \( \Delta, U \) are also induced.

Acknowledgment
The authors thank Innovation Research Team for Spintronic Materials and Devices of Zhejiang Province. The work has also been supported by fund from State Key Lab of Silicon Materials, Zhejiang University (Grant No. SKL2008-5).

References
[1] Ohno H, Shen A, Matsukura F, Oiwa A, Endo A, Katsumoto S and Iye Y 1996 Appl. Phys. Lett. 69 363
[2] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 Science 287 1019
[3] Wang J X, Sun X W, Yang Y, Huang H, Lee Y C, Tan O K and Vayssieres L 2006 Nanotechnology 17 4995
[4] Ramón T Z, Jamil E and Claude L C 2008 Appl. Phys. Lett. 93 233119
[5] Nakahara K, Takasu H, Fons P, Iwata K, Yamada A, Matsubara K, Hunger R and Niki S 2001 J. Cryst. Growth 227-228 923
[6] Hsu H S, Huang J C A and Huang Y H 2006 Appl. Phys. Lett. 88 242507
[7] Das J, Pradhan S K, Sahu D R, Mishra D K, Sarangi S N, Nayak B B, Verma S and Roul B K 2010 Physica B 405 2492.
[8] Xu X Y and Cao C B 2010 Journal of Alloys and Compounds 501 265
[9] Zhou S Q, Potzger K, Xu Q Y, Talut G, Lorenz M, Skorupa W, Helm M, Fassbender J, Grundmann M and Schmidt H 2009 Vacuum 83 S13
[10] Seghier D and Gislason H P 2009 Physica B 404 4800
[11] Singhal R K, Arvind S, Xing Y T, Sudhish K, Dolia S N, Deshpanded U P, Shripathid T and Elisa B S 2010 Journal of Alloys and Compounds 496 324
[12] Peng YZ, Liew T, Chong T C, An C W and Song W D 2006 Appl. Phys. Lett. 88 192110
[13] Peng YZ, Liew T, Song W D and Chong T C 2009 *Chinese Physics B* **18** 5501
[14] Peng YZ, Liew T, Ye Z Z and Zhang Y Y 2007 *Chinese Science Bulletin* **52** 2742
[15] John F Watts 1990 *An introduction to surface analysis by electron spectroscopy* (Oxford University Press, Royal Microscopical Society, UK)
[16] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1995 *Handbook of X-ray Photoelectron Spectroscopy* (Physical Electronics, USA)
[17] Ley L, Pollak R A, McFeely F R, Kowalczyz S P and Shirley D A 1974 *Physical Review B* **9** 600
[18] Mizokawa T and Fujimori A 1997 *Physical Review B* **56** 6669
[19] Bhide V G and Rajoria D S and Mössbauer 1972 *Physical Review B* **6** 1021
[20] Blinowski J and Kacman P 1992 *Physical Review B* **46** 12298
[21] T. Mizokawa, T. Nambu, A. Fujimori, T. Fukumura and M. Kawasaki 2002 *Physical Review B* **65** 085209.