

# **The Effects of Post-Deposition Annealing Conditions on Structure and Created Defects in Zn<sub>0.90</sub>Co<sub>0.10</sub>O Thin Films Deposited on Si(100) Substrate**

Musa Mutlu Can\*,<sup>1</sup>, Tezer Fırat<sup>2</sup>, S. Ismat Shah<sup>3</sup>, Feray Bakan<sup>1</sup> and Ahmet Oral<sup>1</sup>

<sup>1</sup>Faculty of Engineering and Natural Sciences, Sabancı University, Nanotechnology Research and Application Center (SUNUM), Sabancı University, Tuzla, 34956, İstanbul, TURKEY

<sup>2</sup>Department of Physics Engineering, Hacettepe University, 06800, Beytepe, Ankara, TURKEY

<sup>3</sup>Department of Material Science and Engineering, Department of Physics and Astronomy, University of Delaware, 19716, Newark, DE, USA

## **Abstract**

We analyze the effect of post-deposition annealing conditions on both the structure and the created defects in Zn<sub>0.90</sub>Co<sub>0.10</sub>O thin films deposited on the Si (100) substrates by RF magnetron sputtering technique using home-made targets. We concentrated on understanding the homogeneity of substituted Co<sup>+2</sup> ions and the annealing effects on the amount of defects in the ZnO lattice. Orientations of thin films are found to be in the [0002] direction with a surface roughness changing from 67±2 nm to 25.8±0.6 nm by annealing. The Co<sup>+2</sup> ion substitutions, changing from

7.5±0.3 % to 8.8±0.3 %, cause to form Zn–O–Co bonds instead of Zn–O–Zn and split the Co2p energy level to Co2p<sub>1/2</sub> and Co2p<sub>3/2</sub> with 15.67±0.06 eV energy difference. In addition, the defects in the lattice were revealed from the correlations between Zn–O–Co bonds and intensity of Raman peak at around 691 cm<sup>-1</sup>. Furthermore, the asymmetry changes of O1s peak positions in X-ray Photoelectron Spectra (XPS) were also found to be in accordance with the Raman results.

**PACS:** 63.20.kp, 63.50.-x, 75.50.Pp, 78.30.Fs

**Key Words:** Defects, Zinc Oxide, Magneto-optic materials, Semiconducting II-VI materials

**\*Corresponding Author:**

Phone: +90 (533) 929 0718, Fax: +90 (216) 483 9550

e-mail: musamutlucan@gmail.com

## Introduction

ZnO is one of the most widely investigated oxide semiconductors, because of room temperature magnetic applications[1-3]. Numerous theoretical and experimental studies have been performed on transition metal doped ZnO to understand the mechanisms of ferromagnetism[4-13]. However, the origins of magnetic behavior of transition metal doped ZnO structure [4-13] are still not well understood. There are three main suggestions for the magnetic behavior in doped ZnO. The first one is the *p-d* hybridization of orbitals due to holes in the lattice [5,6]. The second is the *s-d* hybridization in the n-type semiconductor [7]. Finally, the third potential mechanism is the formation of transition metal clusters [6,8,10,14] or the secondary phases in the ZnO lattice [14,15]. These results have actually increased the debate on the magnetic properties of ZnO, rather than giving a definite answer. Nowadays, another suggestion is focused on shallow donor/acceptor levels originating from the defects in the ZnO crystal[16,17]. The recent findings have shown the importance of defects, in addition to transition atoms in lattice, on ferromagnetic ordering [18-22]. Coey *et. al* emphasize the magnetic formation without magnetic ions in both  $d^0$  systems and other oxides with crystal defects [22]. Moreover, the point defects also determine the electrical and optical properties of ZnO thin films [23-28]. The point defect density of ZnO is studied for the optical performance [29], photo electrode application for the solar cells [30], carrier relaxation dynamics [31], gas sensing [32] and fluorescent properties for biomedical applications [33]. The defects are seen as the main control mechanism of physical properties of ZnO. Sol gel [34], molecular beam epitaxy (MBE) [35], pulse laser deposition (PLD) [36], metal-organic chemical vapor deposition (MOCVD) [37] and RF magnetron sputtering [38] techniques are widely

used to grow ZnO thin films. The amount of defects in a thin film can be controlled by changing the specific parameters used in the deposition technique. The main control parameters are the gases and their partial pressures used in the sputter deposition, as well as post-deposition annealing temperature and conditions [34-38].

Most of the studies are concentrated around “Zn-rich” defects, the oxygen vacancies and interstitial Zn atoms, due to their lower enthalpy of formation in the ZnO lattice[39]. The annealing temperature and deposition/post-deposition atmosphere are seen as the main parameters [23,26,28,40] to form and control the point defects in the lattice. There have been quite a few systematic analyses on defect formation and relation of these defects with dopant atoms, such as transition metals or non-magnetic elements, in the lattice. In addition to the effects of transition metals substituting for host anion atoms in lattice, the point defects are also effective on the physical properties, such as ferromagnetic behavior [41,42], optical transitions [25-27] and electrical properties [26] due to formation of shallow energy levels.

In this study, we have investigated the optimum growth and annealing conditions of the RF magnetron sputtered  $Zn_{0.90}Co_{0.10}O$  thin films, deposited on Si (100) substrates. This work is focused on obtaining homogeneously distributed Co dopant atoms and point defects in the  $Zn_{0.90}Co_{0.10}O$  thin films by controlling growth and post-deposition annealing conditions. Another aim of this work is to assist the future studies on point defects to control physical properties of ZnO.

## Experimental

We performed the  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$  deposition in a RF magnetron sputtering system equipped with 2" Sputter guns. The thin films were deposited from homemade  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$  targets. The synthesis process of the homemade targets were described in a previous study [43,44]. The targets also exhibited 0.7–1.1% tungsten contamination, which is generated from the vial and the balls of the mechanical miller during the synthesis process [43].

10x10 mm Si(100) single crystal samples were used as substrates after cleaning in acetone/alcohol and they were attached to the specimen holder by silver paste. The depositions were performed in Argon (70 %)-Oxygen (30 %) plasma for 60 minutes at 100W RF power under 10 mTorr pressure. During the depositions, the sample holder temperature was kept at  $420\pm 1^\circ\text{C}$ . This specific gas concentration was found to be the optimal condition of pure ZnO growth in our earlier work [26], where we varied the partial pressures from 0:100 to 50:50 percent. Furthermore, this concentration is found to be optimal to eliminate the formation of metallic Zn clusters and obtain large grain sizes with the preferred orientations.

In order to create defects in the lattice, three different post-deposition annealing conditions were employed. One type of samples was deposited without post-deposition annealing, and the others were deposited with post-deposition annealing under vacuum (in pressure range of  $5\times 10^{-7}$  and  $1\times 10^{-6}$  Torr) and under 1 mTorr of  $\text{O}_2$  atmosphere.

The structural analyses were performed by X-ray diffraction (XRD). The XRD patterns were obtained in the  $2\theta$  ranges of  $15 - 80^\circ$  employing a Rigaku Dmax B model diffractometer by using Cu-K $\alpha$  radiation source with a scanning speed of  $0.02^\circ/\text{minute}$ . Chemical analyses of the films were performed by Oxford Instruments PentaFET-6900 model energy dispersive X-ray spectrometer (EDS) under 5 kV acceleration voltages.

The surface morphology of the films was examined by JEOL/JMS-7400F model scanning electron microscopy (SEM) under 3 kV potential.

XPS spectra were obtained in a VG ESCALAB 220i-XL equipped with Al-K $\alpha$  monochromatic X-ray radiation source and SSI detector with  $\sim 0.1$  eV resolution. All measurements with XPS were done under  $\sim 1 \times 10^{-9}$  Torr pressure. The analyses were done by fixing C 1s binding energy level at 284.6 eV.

The room-temperature micro-Raman measurements were taken in the backscattering geometry using a Renishaw inVia Reflex Model Raman spectrometer. The Ar-ion laser with a 514 nm wavelength, applying 1 % of total power, was used by focusing into  $\sim 2$   $\mu\text{m}$  diameter on the surface. The measurements were recorded in  $100-1500\text{cm}^{-1}$  and in  $550-750\text{cm}^{-1}$  range.

Atomic Force Microscope (AFM) data were acquired in tapping mode with an AFM from NanoMagnetics Instruments Ltd. using NCHAu-D cantilevers with sharp tips,  $k \sim 40$  N/m and  $f_0 \sim 300$  kHz.

## Results and Discussion

The XRD patterns were measured in wide  $2\theta$  range from  $15^\circ$  to  $80^\circ$  to detect the existence of all the possible crystal phases, in addition to ZnO. The peak positions of Si(100) substrate are also demonstrated in Figure 1, in addition to the XRD peaks of the ZnO thin films. The spectra plotted in logarithmic scale to identify the extra peaks. It was found that there are three main peaks in the spectra at around  $30.32^\circ$ ,  $33.84^\circ$  and  $72.02^\circ$ . These peaks were in agreement with the planes of (1010), (0002) and (0004) of the hexagonal ZnO (ICDD PDF # is 00-036-1451), respectively. The dominant peak was observed for the (0002) plane, showing the preferred growth direction. No peaks from metallic Co or oxide state of Co was observed, which can be correlated to the clustering of the Co atoms in the ZnO lattice.

The XRD patterns were not sufficient to draw out information about the amount of Co and other impurity atoms in ZnO. The concentration of Co and the other contaminant atoms in the films were measured from the EDS spectra. The EDS data, shown in Table 1, are the results of the mean values of five different regions of the sample. All the data, shown in Table 1, are normalized by the total number of atoms in the lattice; Zn, Co, W and O. The average concentration of tungsten atoms in the films was found to be  $0.9\pm 0.1\%$ . The Co distributions on the surface of the  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$  thin films were found to be  $8.2\pm 0.3\%$ . The homogeneity in each thin film did not vary considerably. As it was mentioned in the Experimental Section, the tungsten impurities were suspected to come from the manufacturing process of the target.

The cross-sectional measurements were performed using SEM to determine the thickness of the films that were grown from  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$  targets. The results are summarized in Table 1. The SEM image of the thin film deposited without the post-

deposition annealing is given in Figure 2a. Morphologically, the only change observed is the surface roughness, measured by SEM [45] and AFM, at different post-deposition annealing conditions. The SEM and AFM images of the thin films without the post-deposition are shown in Fig. 2b and Fig. 2c, respectively. The AFM images were in agreement with the SEM data. The AFM images were used to measure the surface roughness. The measured roughness shows that the post-deposition annealing procedure decreases the surface roughness. The surface roughness, calculated from AFM images, were  $67\pm 2\text{nm}$ ,  $37.2\pm 0.5\text{nm}$  and  $25.8\pm 0.6\text{nm}$  for the non-post-deposition annealing, annealing under vacuum and annealing under  $\text{O}_2$  conditions, respectively. The main reason of decline in roughness originates from the enhanced grains by annealed in vacuum atmosphere and oxygen[46-49]. Annealing at  $400^\circ\text{C}$  seems to supply sufficient energy to surface atoms to diffuse into the surface vacancies or defects [48]. The smaller surface roughness at thin film annealed in an oxygen environment also reveals larger grain size than the others due to an adequate amount of oxygen atoms in environment.

After proving the existence of Co atoms in films, their positions in the lattice were determined by the XPS spectra. The spectra of the thin films are presented in Figure 3. The energy levels of Zn, Co and O were clearly observed in the spectra. The post-deposition annealing conditions, doped Co atoms or W impurities did not change the position of the energy levels of Zn  $2p_{1/2}$  and Zn  $2p_{3/2}$ , which are 1020.41 eV and 1043.48 eV, respectively. The data shown are the mean values of all thin films. The energy difference between Zn  $2p_{1/2}$  and Zn  $2p_{3/2}$  was calculated to be  $23.07\pm 0.02$  eV, which was in agreement with the literature [50].

The Co 2p and O 1s XPS peaks were investigated in detail to understand the positions of Co atoms and O vacancies in lattice, respectively [51-55]. The Co 2p



peak energy splits into two singlets as shown in Figure 4a-4c. As seen from figure, the energy split,  $15.67 \pm 0.06$  eV, between Co  $2p_{3/2}$  and Co  $2p_{1/2}$  states is the same for all the films. Furthermore, the energy shift of the Co  $2p_{1/2}$  peak, with respect to the metallic state of Cobalt (778.1-778.3 eV [50]), is found to be  $780.05 \pm 0.04$  eV. We interpret this as the Cobalt atoms have substituted  $Zn^{+2}$  ions as  $Co^{+2}$ , as mentioned in previous studies [7,50].

The XPS is a surface sensitive tool and can only give information about 20 nm depths from the surface. However, if the surface of the film is not too different than the rest and is not effected by other factors, the XPS data can be taken as representative of the film itself. Furthermore the XPS may also provide general information about the point defects density in thin films. The effects of the post-deposition annealing condition on the defects were also investigated by analyzing O 1s peaks in XPS data. The Oxygen 1s peak observed in XPS is composed of 3 closely spaced energy levels:  $O_a$ ,  $O_b$  and  $O_c$ . The analyses were done for spectra taken under identical conditions and the defect density was related to the change at the ratios of relative intensities in O 1s energy level. The O 1s energy levels in Figure 4 were fitted to three curves; mixture of Gaussian and Lorentzian functions. The calculated average values of the peak positions are at around  $529.6 \pm 0.1$  eV ( $O_a$ ),  $530.5 \pm 0.1$  eV ( $O_b$ ) and  $531.6 \pm 0.1$  eV ( $O_c$ ) as presented in Table 2.

$O_a$ ,  $O_b$  and  $O_c$  peak positions are originated from the  $O^{-2}$  ions surrounded by Zn atoms, from defects either having or originating  $O^{-2}$  deficiency in lattice and from chemisorbed, dissociated oxygen or OH species on the surface as  $H_2O$  molecules or weakly bonded  $CO_3$  molecules, respectively [51,52]. The post-deposition annealing conditions did not shift the energy level. Nevertheless, a change in relative intensities of the normalized areas of  $A_a$  (the area of  $O_a$  peak),  $A_b$  (the area of  $O_b$  peak) and  $A_c$

(the area of  $O_c$  peak) were observed at different annealing conditions. In the analysis,  $A_a/(A_a+A_b)$  and  $A_b/(A_a+A_b)$  ratios were investigated, relating to  $A_a$  and  $A_b$  to the amount of  $O^{2-}$  cation in the lattice. The results of the calculations were shown in Table 2. With post-deposition annealing, the intensity in  $A_b/(A_a+A_b)$  ratios decreased while that in  $A_a/(A_a+A_b)$  ratios increased. This suggests that the post-deposition annealing causes lower defect density due to  $O^{2-}$  deficiency in the main ZnO lattice. The changes in ratios is demonstrated in Table 2.

The possible defects in the lattice due to Cobalt substitution and post-deposition annealing were also analyzed using Raman spectra as shown in Figure 5. The measurements were taken in 100 to 1500  $cm^{-1}$  and 550 to 750  $cm^{-1}$  Raman shift range as shown in Figure 5a and in Figure 5b, respectively. In addition to the Raman peaks of Silicon substrate at 298  $cm^{-1}$  [56], 520  $cm^{-1}$  [57] and 618  $cm^{-1}$  [56,57], six more modes (a broad peak between 200-280  $cm^{-1}$ , 437  $cm^{-1}$ , another broad peak between 630-760  $cm^{-1}$ , 942  $cm^{-1}$  and 986  $cm^{-1}$ ) were obtained in the Raman spectra. Two of these broad peaks, the peak in between 200 – 280  $cm^{-1}$  and the peak at around 437  $cm^{-1}$ , are attributed to the ZnO vibration modes [56]. Furthermore, the broad peaks around 942  $cm^{-1}$  and 986  $cm^{-1}$  were observed as the second order vibrations of ZnO crystal [57]. The last Raman mode was at 691  $cm^{-1}$  as shown on Figure 5b. This mode was related to the disordered Zn–O–Co vibrations [58]. The analysis was extended by repeating the measurements in between 550 and 750  $cm^{-1}$  for 300 s integration time to make the peaks more visible. A specific enhancement in intensity depending on post-deposition annealing was observed.

The study of Sudakar *et al.* emphasized the disappearance of Zn–O–Co vibrations by the forming oxygen vacancies at around Co atoms in the lattice and the consequences were observed by the decreased Raman intensity [58], which was in

agreement with our observations, as shown in Figure 5b. The decrease in this peak intensity in Raman spectrum is attributed to the decrease in the concentration of oxygen dependent defects in the lattice. The lowest intensity was observed in the film deposited without post-deposition annealing that means the highest defects according to the others.

## **Conclusions**

In this study the  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$  thin films were grown by using RF Sputtering with home-made  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$  targets. It was attempted to dope 10 % Co atoms in ZnO films by using  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$  target; however, only  $8.2\pm 0.3$  % Co atoms were evenly distributed as determined from the results of surface analysis. The Co atoms were observed to be substituting the Zn atoms in lattice, and this also decreased the band gap at around 0.34eV, according to the XPS spectra. In addition, the concentrations of tungsten impurities in thin films were found to be in between  $0.5\pm 0.1\%$  and  $1.1\pm 0.2\%$  and these impurities located as oxidized states. In addition to the expected structure, the defects were also formed in the lattice, which was found from the asymmetry of O1s peak positions and from the intensity decrease of Raman mode at around  $691\text{cm}^{-1}$ .

## **Acknowledgments**

We acknowledge the financial support of The Scientific and Technological Research Council of Turkey (TUBİTAK), BİDEB program.

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## Figure Captions

**Figure 1.** XRD patterns of the films grown from  $Zn_{0.90}Co_{0.10}O$  target without post-deposition annealing, post-deposition annealing under vacuum atmosphere and post-deposition annealing under 1Torr  $O_2$  atmosphere.

Figure 2. The SEM micrographs of (a) cross sectional thickness and (b) surface morphology, and (c) AFM image of  $Zn_{0.9}Co_{0.1}O$  films without post-deposition annealing.

**Figure 3.** XPS spectra of the films grown from  $Zn_{0.90}Co_{0.10}O$  target without the post-deposition annealing, post-deposition annealing under vacuum atmosphere and post-deposition annealing under 1Torr  $O_2$  atmosphere.

**Figure 4.** XPS spectra of (a), (b), (c) the Co 2p (in binding energy range of 770 and 815eV) and (d), (e) and (f) O 1s (in binding energy range of 524 and 537eV) energy levels for the films deposited by  $Zn_{0.90}Co_{0.10}O$  target without post-deposition annealing, post-deposition annealing under vacuum and post-deposition annealing under 1Torr  $O_2$  atmosphere, respectively.

**Figure 5.** The Raman spectra of thin films grown without post-deposition annealing, post-deposition annealing under vacuum and post-deposition annealing under 1Torr  $O_2$  atmosphere (a) in the full range and (b) in the interval of 550 to 750  $cm^{-1}$ .

**Table Captions:**

**Table 1.** EDS data of thin films.

**Table 2.** Fitted curves of O1s peak positions for thin films deposited from  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$  target.

**Table 1.** EDS data of Zn<sub>0.90</sub>Co<sub>0.10</sub>O thin films.

<b>Post-Deposition Annealing Conditions</b>	<b>Normalized atomic ratio of Zn percentage (%)</b>	<b>Normalized atomic ratio of Co percentage (%)</b>	<b>Normalized atomic ratio of W percentage (%)</b>	<b>Thickness (nm)</b>
Without post annealing	41.1±0.5	8.8±0.2	0.9±0.1	962±4
Under Vacuum (in pressure range of 5x10 <sup>-7</sup> and 1x10 <sup>-6</sup> Torr)	41.5±1.7	7.5±0.3	1.1±0.2	707±1
Under 1 Torr O <sub>2</sub>	42.1±1.2	8.3±0.2	0.7±0.1	853±5

**Table 2.** Fitted curves of O1s peak positions for thin films deposited from Zn<sub>0.90</sub>Co<sub>0.10</sub>O target.

<b>Post-Deposition Annealing Conditions</b>	<b>O<sub>a</sub> (eV)</b>	<b>O<sub>b</sub> (eV)</b>	<b>O<sub>c</sub> (eV)</b>	<b>(A<sub>a</sub>/A<sub>a</sub>+A<sub>b</sub>) x 100</b>	<b>(A<sub>b</sub>/A<sub>a</sub>+A<sub>b</sub>) x 100</b>
Without post annealing	530.0±0.1	530.8±0.1	532.1±0.1	56	44
Under vacuum (in pressure range of 5x10 <sup>-7</sup> and 1x10 <sup>-6</sup> Torr)	529.3±0.1	530.3±0.1	531.4±0.1	71	29
Under 1Torr O <sub>2</sub>	529.4±0.1	530.3±0.1	531.4±0.1	72	28