

The Effects of Heat Treatment on Room Temperature Ferromagnetism in a Digitally Co Doped ZnO Thin Film

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The effects of heat treatment on room temperature ferromagnetism of Co-doped ZnO were investigated with a (ZnO 20Å/Co x Å)₂₀ multilayer structure where $x = 1.5, 3, 4.3, 6$ and 9 Å. As the thickness of the Co sub-layer increased, the ZnO/Co multilayer changed its magnetic state from diamagnetism at Co 1.5 Å and 3 Å to weak ferromagnetism at Co 4.3 Å and strong ferromagnetism at Co 6 Å and 9 Å. The heat treatment, in a vacuum at 400°C, changed the diamagnetic property into a ferromagnetic one, resulting in room temperature ferromagnetism for all Co sub-layer thicknesses. The improvement in ferromagnetism could be ascribed to the exchange coupling between dispersed Co atoms through XRD, optical transmittance and TEM analysis.

Keywords: cobalt, zinc oxide, dilute magnetic semiconductor, multilayer, doping, ferromagnetism

1. INTRODUCTION

Zinc Oxide (ZnO) is a *II-VI* semiconductor material with a wide direct bandgap of 3.37 eV and has been studied widely because its promising applications, for example in, transparent conducting electrodes, gas sensors, varistors, piezoelectric devices and solar cells, etc. Since Dietl *et al.*^[1] theoretically predicted the ferromagnetism of ZnO with a dilute quantity of a transition element, ZnO DMS (dilute magnetic semiconductor) has become one of the challenging materials for spintronics. So far, several theoretical models have been proposed to understand the ferromagnetism in ZnO DMS, besides the hole mediated indirect exchange mechanism proposed by Dietl *et al.*,^[1] BMP (bound magnetic polaron) model^[2] was proposed to explain the ferromagnetism. According to the BMP model, donor electrons in an impurity band participate in the exchange mechanism. The traditional ferromagnetic exchange models such as ruderman-kittel-kasuya-yosida (RKKY) and the double exchange model are still valid explanations of the ferromagnetism of highly doped ZnO DMS. Secondary phase or dopant precipitation/cluster is known to be responsible for the ferromagnetism at very high doping levels.

However, there have been continuing controversies regarding the ferromagnetism in ZnO. These controversies are partly due to the low reproducibility in ZnO DMS sample preparation and the difficulty in identifying the state of ferromagnetic dopants in ZnO thin films. The former is related to the control of defects (vacancy, interstitial or substitutional) in the films and the latter is related to the homogeneity of the films. Therefore, the control of a uniform defect state over the whole thin film is critical in gaining an understanding of the origin of ferromagnetism in ZnO DMS and for manufacturing ZnO DMS applications.

In this study, we used a multilayer structure with which we could control precisely the amount of doping element as well as the dopant profile in the film. In a ZnO/Co multilayer structure, the amount of Co dopant can be tuned by adjusting the Co sub-layer thickness and the Co profile in the film can be controlled by varying the ZnO sub-layer thickness or by heat treatment after deposition. The Co sub-layer thickness and heat treatment were chosen as effective control parameters in the present study, and the effects of each parameter on the ferromagnetism in ZnO/Co multilayer are discussed.

2. EXPERIMENTAL PROCEDURE

ZnO/Co multilayer structures were fabricated by magnetron sputtering on to a borosilicate glass or silicon substrates.

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A RF power source was used for ZnO deposition and a DC power source for Co deposition. It is common to use an Al 2 wt. % doped ZnO target for stable electrical conductivity in a ZnO thin film but in this experiment, an undoped ZnO target was used to eliminate third element effects on the magnetic properties of ZnO thin film. The working pressure was 5 mTorr and input power was fixed at 400 W for both RF and DC power. The deposition temperature was 100°C. Co and ZnO sub-layers were deposited alternately 20 times to obtain a (ZnO 20 Å/Co x Å)₂₀ multilayer structure; the top surface of the multilayer structure was covered with ZnO 20 Å. The nominal thickness of the Co sub-layers were 1.5, 3, 4.3, 6, 9 Å and the final film thickness ranged from 440 Å to 600 Å as measured by a surface profiler. The Co contents corresponding to the nominal Co sub-layer thickness was calculated to be 13.6, 23.9, 31.0, 38.6, 48.5 at. % using a density of 8.9 g/cm³ for Co and 5.6 g/cm³ for ZnO. Annealing was performed at 400°C in a vacuum of 6×10^{-6} Torr for 1 hour. For both as-deposited and annealed samples, the electrical and optical properties were measured by Hall measurement and UV-Vis spectrometer, respectively. Also, the magnetic property was observed by VSM (vibrating sample magnetometer). Finally the microstructure was measured by XRD (x-ray diffraction) and TEM (transmission electron microscopy). Borosilicate substrates were used for transparency and Hall measurements, while (100) silicon substrates were used for magnetic property and microstructure analysis.

3. RESULTS AND DISCUSSION

3.1 The effects of Co concentration

The magnetization of the as-deposited ZnO/Co multilayers were measured using VSM at room temperature and are shown in Fig. 1. For the multilayer with thin Co sub-layers

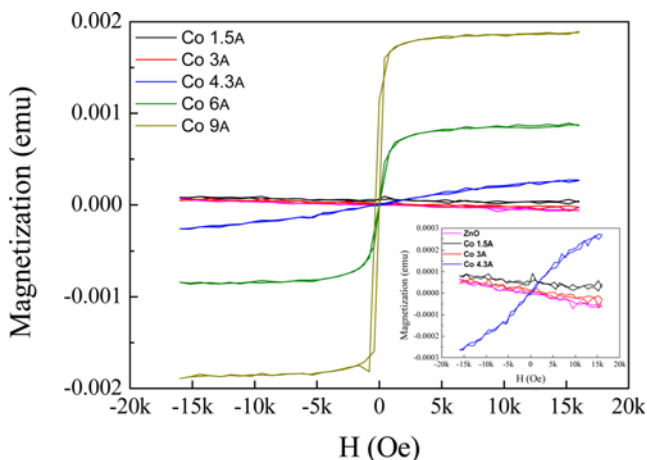


Fig. 1. Room temperature magnetization curves for as-deposited (ZnO 20 Å/Co x Å)₂₀ multilayer where $x = 1.5, 3, 4.3, 6, 9$ Å. The inset shows close-up comparison of Co 1.5, 3, 4.3 Å and pure ZnO magnetization.

of 1.5 Å and 3 Å thickness, diamagnetism was observed, that is, the multilayer was magnetized in the opposite direction to the applied magnetic field (inset in Fig. 1). As the Co sub-layer thickness increased, the ZnO/Co multilayer changed its magnetic property from diamagnetism to ferromagnetism. In the case of Co sub-layer thicknesses of 6 Å and 9 Å, ferromagnetic behavior was observed and the saturated magnetization value increased with Co sub-layer thickness. In order to investigate the origin of the diamagnetism in the multilayer with thin Co sub-layer, a ZnO single layer sample was prepared 420 Å thick which corresponded to the total ZnO thickness in the multilayer structure. Undoped ZnO was reported to show a sequential transition from ferromagnetism to paramagnetism and diamagnetism with increasing film thickness.^[3] The 420 Å thick ZnO single layer was found to have diamagnetism and as shown in the inset in Fig. 1, M-H curves of the ZnO single layer and multilayer are strongly correlated. This result implies that 1.5 Å and 3 Å Co sub-layers have a negligible ferromagnetic contribution to the total magnetization of the multilayer and the ZnO sub-layer was mostly responsible for the diamagnetic nature of the M-H curve.

Based on previous reports,^[1,2,4] the role of the Co atom as a source of ferromagnetism in ZnO can be summarized as follows. The Co atoms can segregate to form a ferromagnetic secondary phase as an extrinsic ferromagnetic source. In this case, the Co doped ZnO can be regarded as a mixture of a ferromagnetic Co metal cluster and semiconductor ZnO, where the ferromagnetism originates from Co clusters. Non-segregated Co atoms can occupy solid-solution sites in the ZnO being either ferromagnetic coupled or magnetically isolated. In case of magnetic isolation, the magnetization directions of the Co atoms become randomly distributed, resulting in paramagnetism. When charge carriers, either electron or hole, mediate the exchange coupling of spin states between Co atoms, the magnetization of Co atoms can be ordered to result in a ferromagnetic semiconductor. Therefore, it is critical to investigate the existence of the Co second phase so as to clarify the origin of ferromagnetism in Co-doped ZnO. The microstructure of the ZnO/Co multilayer was analyzed using XRD and the results are shown in Fig. 2. All samples were step-scanned from 20° to 80° in 0.02° steps and the peak position was calibrated with respect to the Si substrate peak. It should be noted that multilayer repetition was increased to make the total multilayer thickness 1500 Å for XRD analysis, since no peak was observed for (ZnO 20 Å/Co x Å)₂₀ samples due to their low thickness. As shown in Fig. 2, only ZnO and Co related peaks were observed in addition to the Si substrate and SiO₂ peaks. ZnO peaks were found to be around $2\theta = 33^\circ$, which corresponds to the hcp (002) plane with 4% tensile strain in the c-axis. The Co peak was found at $2\theta = 44.2^\circ$ to 44.7° , which corresponds to Co fcc (111) $2\theta = 44.3^\circ$, Co hcp (002) $2\theta = 44.8^\circ$, and Co₃O₄

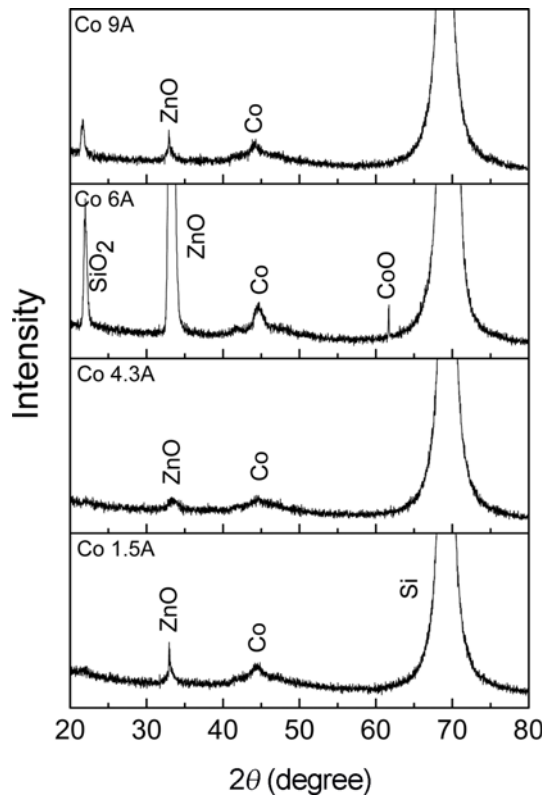


Fig. 2. XRD patterns for as-deposited $(\text{ZnO } 20 \text{ \AA}/\text{Co } x \text{ \AA})_{60}$ multilayer where $x = 1.5, 4.3, 6, 9 \text{ \AA}$.

(400) $2\theta = 44.8^\circ$. Since these peak positions are close to each other and the Co sub-layer was only one or two monolayers thick, the peak could not be indexed clearly. In addition, the multilayer's characteristic superlattice peak at low angles ($2\theta < 10^\circ$) were not observed, which indicated that the interface between sub-layers was not atomically sharp. Therefore, the monolayer thick Co sub-layer may not be continuous but rather be regarded as a solid solution or nanocrystals embedded in the ZnO matrix.^[4]

The Co^{2+} ion has a very similar size to the Zn^{2+} and is known to have a large solubility in the ZnO lattice.^[5] Straumal *et al.*^[5] showed that the maximum Co solubility of 40 at. % in ZnO thin films depends on the grain size of the ZnO. Jang *et al.*^[6] also proposed complete Co diffusion into the ZnO matrix at a deposition temperature of 100°C . Due to this large solubility and an elevated deposition temperature of 100°C , intermixing at the interface between the ZnO and Co sub-layers could occur. This is important especially for the low Co sub-layer thickness. When the diffused Co^{2+} ions substitute for Zn^{2+} ions, the characteristic absorption peaks become apparent in the optical transmission spectra.^[7] These absorption peaks have been reported in several researches^[8,9] and regarded as an evidence for the Co^{2+} substitution for Zn^{2+} sites in the ZnO lattice. Absorption peaks at wavelengths of 665 nm, 618 nm and 571 nm correspond to

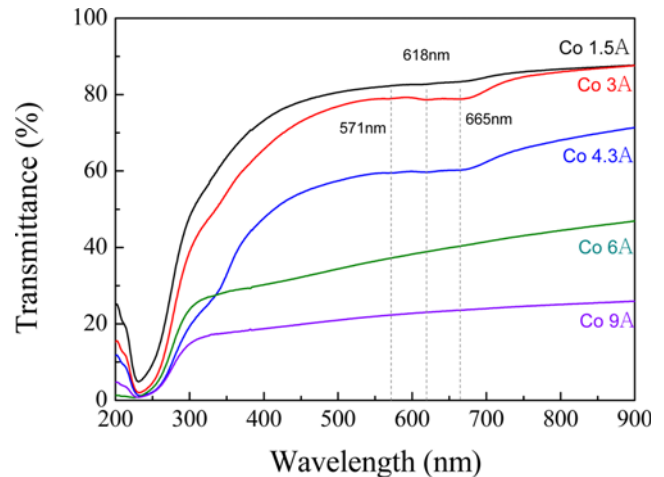


Fig. 3. UV-Vis transmission of as-deposited $(\text{ZnO } 20 \text{ \AA}/\text{Co } x \text{ \AA})_{20}$ multilayer where $x = 1.5, 3, 4.3, 6, 9 \text{ \AA}$. The vertical lines indicate the characteristic absorption peak positions.

${}^4A_2 \rightarrow {}^2E(G)$, ${}^4A_2 \rightarrow {}^4T_1(P)$ and ${}^4A_2 \rightarrow {}^2A_1(G)$, respectively.^[9] Figure 3 shows the optical transmission measured by a UV-Vis spectrometer. The characteristic absorption peaks were observed for the Co 1.5 Å, 3 Å and 4.3 Å sub-layers, which all indicated that Co atoms had diffused into the ZnO sub-layer and substituted into Zn sites. As for the multilayer with Co 6 Å and 9 Å, the noticeable characteristic absorption peaks were not observed. This is partly due to the overall transmittance performance decrease from 80% to 20% as the thickness of the Co sub-layer increased from 1.5 Å to 9 Å. In the case of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ alloy structure, this degradation in transmittance can be ascribed to the increased dissolution of Co into ZnO.^[8]

3.2 The effects of heat treatment

As-deposited samples were annealed at 400°C in a vacuum for 1 hour. The magnetization behavior of the annealed multilayer was observed as shown in Fig. 4. In contrast to the as-deposited state, all samples showed room temperature ferromagnetism. Multilayers with 1.5 Å and 3 Å thick Co sub-layers, which were diamagnetic in their as-deposited state, showed ferromagnetic behavior (the inset of Fig. 4). The weak ferromagnetism of the multilayer with Co 4.3 Å thick strengthened to show saturated magnetization after the annealing process. The magnetization saturation value was found to increase after annealing and the increment was larger for the thinner Co sub-layers. The transition from diamagnetism to ferromagnetism at thin Co sub-layer samples could be ascribed to two reasons; firstly, the segregation of Co atoms to form ferromagnetic Co metal clusters and secondly, the exchange coupling of isolated Co atoms or Co nanocrystals to show ferromagnetic ordering by charge carriers. XRD measurements showed that the peak position for the ZnO shifted slightly to a lower diffraction angle while

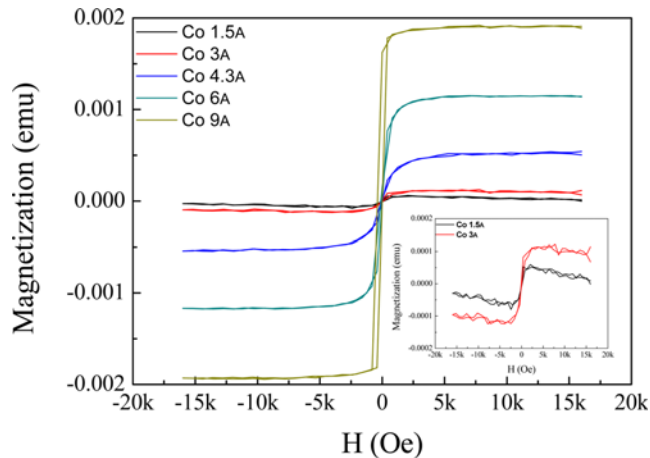


Fig. 4. Room temperature magnetization curves for $(\text{ZnO } 20 \text{ \AA}/\text{Co } x \text{ \AA})_{20}$ multilayer where $x = 1.5, 3, 4.3, 6, 9 \text{ \AA}$ after vacuum annealing at 400°C . Inset: magnetization of Co 1.5, 3 \AA .

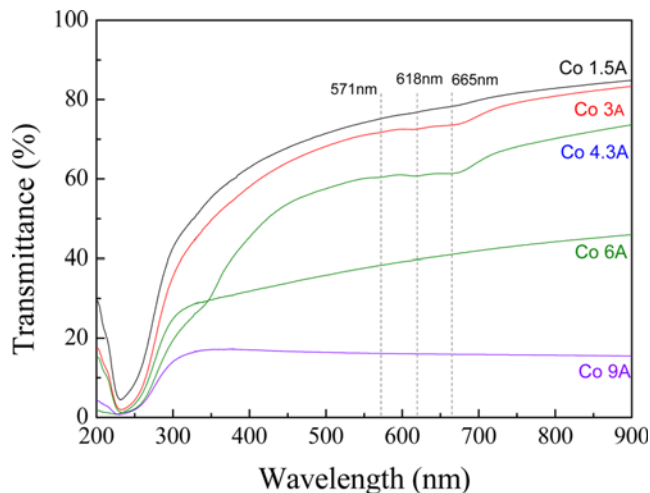


Fig. 5. UV-Vis transmission of $(\text{ZnO } 20 \text{ \AA}/\text{Co } x \text{ \AA})_{20}$ multilayer where $x = 1.5, 3, 4.3, 6, 9 \text{ \AA}$ after vacuum annealing at 400°C . The vertical lines indicate the characteristic absorption peak positions.

the Co peaks remained in almost the same position after the annealing process (not shown here). Due to low peak intensities, it was hard to conclude from the XRD measurement whether Co segregation took place through the annealing process. However, as shown in Fig. 5, the characteristic absorption peaks remained at the same position for the Co 1.5 \AA , 3 \AA and 4.3 \AA sub-layers and the intensity appeared to slightly increase. Inferred from these observations, Co atoms of thin Co sub-layers appear not to segregate through the annealing process but remain as substitutes for Zn sites or nanocrystals embedded in the ZnO matrix. In order to investigate the microstructure in detail, TEM analysis was performed and the high resolution TEM images for the Co 1.5 \AA sub-layer are shown in Fig. 6. HRTEM lattice images were indexed as ZnO (011) and Co (011) for the as-depos-

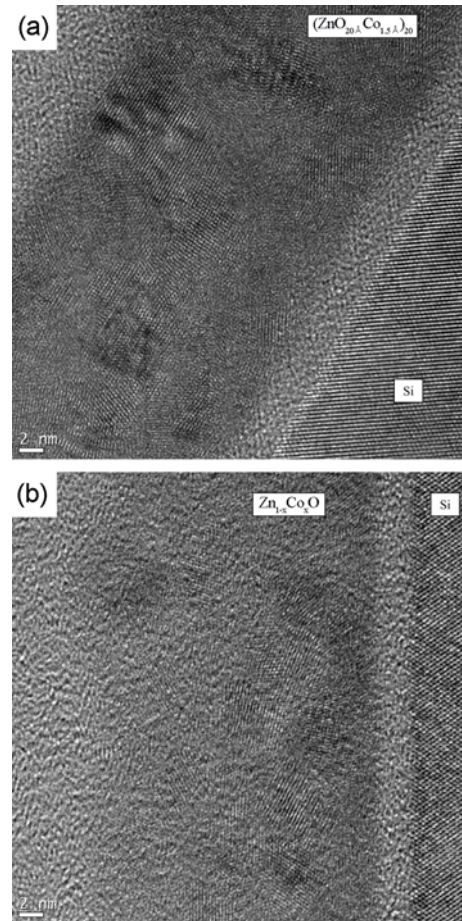


Fig. 6. High resolution TEM lattice image of $(\text{ZnO } 20 \text{ \AA}/\text{Co } 1.5 \text{ \AA})_{20}$ (a) as-deposited state (b) vacuum-annealed at 400°C , 1 hr.

ited sample and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ for the annealed sample. This result confirms that ferromagnetic Co metal clusters were not formed by the annealing process and that the transition from paramagnetism to ferromagnetism by annealing could be attributed to exchange coupling between dispersed Co atoms.

The origin of occurrence of exchange coupling through annealing was not clear, however the defects in the ZnO sub-layer may be increased following the annealing process as reported by Xie *et al.*^[10] The charge carriers induced by increased defects could mediate indirect exchange coupling between Co atoms and result in room temperature ferromagnetism.

4. CONCLUSIONS

Room temperature ferromagnetism of Co-doped ZnO was investigated with a $(\text{ZnO } 20 \text{ \AA}/\text{Co } x \text{ \AA})_{20}$ multilayer structure where $x = 1.5, 3, 4.3, 6$ and 9 \AA . In the as-deposited state, the transition from diamagnetism to ferromagnetism was observed with increasing Co sub-layer thickness. The vacuum anneal-

ing process resulted in the enhancement of ferromagnetism for all Co sub-layer thicknesses. Since substantial Co cluster formation was not observed before and after annealing, for the thin Co sub-layer, Co atoms appear to be magnetically isolated in the as-deposited state and became ferromagnetic exchange coupled after vacuum annealing. The annealing process could increase the defects in ZnO, and charge carriers induced by defects might mediate the indirect exchange coupling.

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