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Effect of thermal annealing on the structural and the optical properties of $(Zn_{1-x}Co_x)O$ thin films grown on p-Si (1 0 0) substrates

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Potential applications of spintronic devices utilizing diluted magnetic semiconductor (DMS) systems have driven extensive efforts to grow various kinds of materials [1]. DMS materials, which can utilize both the spin and charge properties of carriers, have become particularly attractive because of their promising applications in spintronic devices [2, 3]. Among various kinds for DMS materials, $Ga_{1-x}Mn_xAs$ and $In_{1-x}Mn_xAs$ DMS thin films grown on GaAs substrates have been the most extensively structures [4–10]. However, until now, the highest ferromagnetic transition temperature (T_c) obtained from III–V DMS thin films has been 110 K [11]; thus, various studies concerning increasing the T_c of DMS materials have instigated considerable efforts with the aim of realizing spintronic devices operating at higher temperature. Among several candidate materials with a high T_c, II–VI $(Zn_{1-x}Co_x)O$ DMSs with wide energy gaps are of current interest because they are theoretically expected to have high T_c values [12, 13]. However, relatively little work has been done on group II–VI DMS thin films in comparison with group III–V DMSs thin films because of the delicate problems encountered in the growth technique. Since the structural and the optical properties of the DMSs significantly affect their magnetic properties, which are of viral importance in the fabrication of high efficiency devices, studies of the physical properties of DMSs are indispensable when attempting to understand the performance of spintronic devices based on DMSs. Even though very few studies concerning the physical properties of $(Zn_{1-x}Co_x)O$ thin films have been reported [14–16], all of the $(Zn_{1-x}Co_x)O$ thin films were grown on sapphire substrates [14, 15]. Since Si substrates with large areas and good qualities are relatively cheap and extensively available in comparison with sapphires, Si technologies offer the potential applications for fabricating spintronic devices. However, studies on the formation and characterization of $(Zn_{1-x}Co_x)O$ thin films on Si substrates have not yet been reported. Thermal treatment is also necessary for the fabrication of high-quality spintronic devices utilizing $(Zn_{1-x}Co_x)O$ DMSs [17]; therefore, studies of the annealing effects on the structural and the optical properties will also play a very important role in enhancing device efficiency.

This letter reports the effects of thermal annealing on the structural and the optical properties of $(Zn_{1-x}Co_x)O$ thin films grown on p-Si (1 0 0) substrates by using the radio-frequency (rf) magnetron sputtering method and by subsequently thermal treatment. Even through our main purpose for the growth of $(Zn_{1-x}Co_x)O$ thin films was an investigation looking for physical evidence for the achievement of the high ferromagnetic T_c of $(Zn_{1-x}Co_x)O$ films as a consequence of the large energy gap and effective mass of ZnO, only preliminary structural and optical results from the samples are presented in this paper. X-ray diffraction (XRD) measurements were performed to investigate the crystallization of the ZnO thin films, and photoluminescence (PL) measurements were carried out in order to investigate the optical properties of the ZnO thin film.

Polycrystalline stoichiometric ZnO and Co with purities of 99.999% were used as source target materials and were precleaned by repeated sublimation. The carrier concentration of the B-doped p-Si substrates with (1 0 0) orientations used in this experiment was approximately 1×10^{15} cm^{-3}. The substrates were degreased in trichloroethylene (TCE), rinsed in de-ionized water, etched in a mixture of HF and H_2O (1:1) at room temperature for 5 min, and rinsed in TCE again. After the Si wafers had been cleaned chemically, they were mounted onto a susceptor in a growth chamber. After the chamber had been evacuated to 8×10^{-7} Torr, the deposition was done at a substrate temperature of 600 °C. Ar gas with a purity of 99.999% was used as the sputtering gas. Prior to $(Zn_{1-x}Co_x)O$ growth, the surface of the ZnO and the Co targets were polished by Ar^+ sputtering. The $(Zn_{1-x}Co_x)O$ deposition was done at a system pressure of 0.018 Torr. The sputtering radio-frequency power (rf = 13.26 MHz) for the ZnO target was 100, and those for the Co were 60, 90, 120, and 150 W. The flow-rate ratio of Ar to O_2 was 2, and the growth rate of the $(Zn_{1-x}Co_x)O$ thin film was approximately 1.15 nm/min. The thermal process was performed in a nitrogen atmosphere with a tungsten-halogen lamp as the thermal source. The

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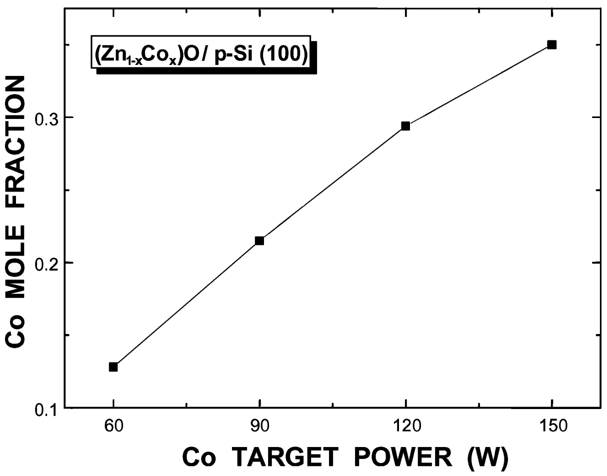

Figure 1 Co mole fraction as a function of the Co target power for the $(Zn_{1-x}Co_x)O$ thin films grown on *p*-Si (1 0 0) substrates.

thermal annealing process was carried out for 5 min at 900 °C. The XRD measurements were performed using a Rigaku D/Max-B diffractometer with Cu K_α radiation. The PL measurements were carried out using a 75-cm monochromator equipped with RCA 31034 photomultiplier tube. The excitation source was the 3250-Å line of a He–Cd laser, and the sample temperature was controlled between 10 and 300 K by using a He displex system.

The as-grown ZnO films had mirror-like surfaces without any indication of pinholes, which was confirmed by using Normarski optical microscopy and scanning electron microscopy measurements. Fig. 1 shows Co mole fraction as a function of the Co target power for the $(Zn_{1-x}Co_x)O$ thin films grown on p-Si (1 0 0) substrates. The Co mole fraction in the $(Zn_{1-x}Co_x)O$ thin film increases by increasing the Co target power. When the rf power for the Co target becomes 150 W, the Co mole fraction in the $(Zn_{1-x}Co_x)O$ thin films is 0.35.

Fig. 2 shows the XRD patterns for the (a) as-grown and the (b) annealed $(Zn_{1-x}Co_x)O$ films with various Co mole fractions of 0.128, 0.215, 0.294, and 0.35 grown on p-Si (1 0 0) substrates. The (0 0 0 2) and the (0 0 0 4) $K_{\alpha 1}$ diffraction peaks corresponding to the $(Zn_{1-x}Co_x)O$ (0 0 0 1) film, together with the (0 0 2) and the (0 0 4) diffraction peaks related to the Si (1 0 0) substrates, are only observed on the as-grown $(Zn_{1-x}Co_x)O$ films. The intensity of the XRD pattern related to the $(Zn_{1-x}Co_x)O$ film for the annealed $(Zn_{1-x}Co_x)O/Si$ heterostructure increases with increasing annealing temperature, and the full width at half-maximum for the (0 0 0 2) $(Zn_{1-x}Co_x)O$ diffraction peak for the annealed $(Zn_{1-x}Co_x)O/Si$ heterostructures decreases due to enhancement of crystallinity of the $(Zn_{1-x}Co_x)O$ thin film. When the Co mole fraction becomes 0.35, the peaks corresponding to the $Zn_{0.65}Co_{0.35}O$ (0 0 0 1) films are vanished. Furthermore, the (1 1 1) $K_{\alpha 1}$ diffraction peak related to the CoO (1 1 1) film is slightly observed at the annealed $(Zn_{0.35}Co_{0.65})O$ film. Even though the $(Zn_{1-x}Co_x)O$ films were formed through the substitution of Zn atoms for Co atoms, the CoO films were formed due to the excess existence of O_2 gas during the sputtering. The amount of the CoO film increases with increasing the rf power for the Co target, and the increase of the CoO film deteriorates the crystallinity of the $(Zn_{1-x}Co_x)O$ films due to interrupt of the thermal energy transfer of the Co atoms into the Zn atoms resulting from acting the CoO thin film as the blocking screen. The XRD patters for the as-grown and the annealed $(Zn_{1-x}Co_x)O$ thin films grown on the Si (1 0 0) substrates indicate that the as-grown and the annealed $(Zn_{1-x}Co_x)O$ films have a strong *c*-axis orientation and that the crystallinity of the $(Zn_{1-x}Co_x)O$ film is improved by annealing.

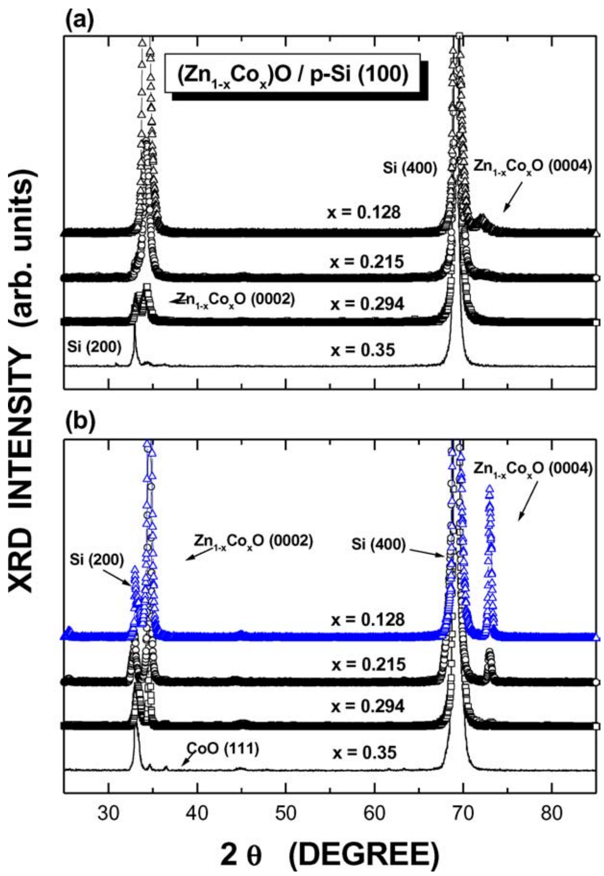

Figure 2 X-ray diffraction patterns of the (a) as-grown and the (b) annealed $(Zn_{1-x}Co_x)O$ thin films with various Co mole fractions grown on *p*-Si (1 0 0) substrates.

Fig. 3 shows PL spectra at 10 K for the (a) as-grown and the (b) annealed $(Zn_{1-x}Co_x)O/Si$ (1 0 0) heterostructures. One dominant PL peak was observed at 380 nm for the as-grown and the annealed $(Zn_{1-x}Co_x)O/Si$ (1 0 0) heterostructures. The peak at 380 nm is attributed to the band edge transition [18]. The intensity of the luminescence peak decreases with increasing Co mole fraction, indicative of the deterioration of the crystallinity of the $(Zn_{1-x}Co_x)O$ film.

In summary, the results of XRD measurements showed that the $(Zn_{1-x}Co_x)O$ thin films grown on p-Si (1 0 0) substrates by using the magnetron-sputtering method were preferentially oriented in the (0 0 0 1) direction. XRD patterns showed that the crystallinity of the $(Zn_{1-x}Co_x)O$ thin films grown on the Si substrates was improved by thermal treatment. PL spectra after annealing showed luminescence peaks related to the band edge transitions. Even though some

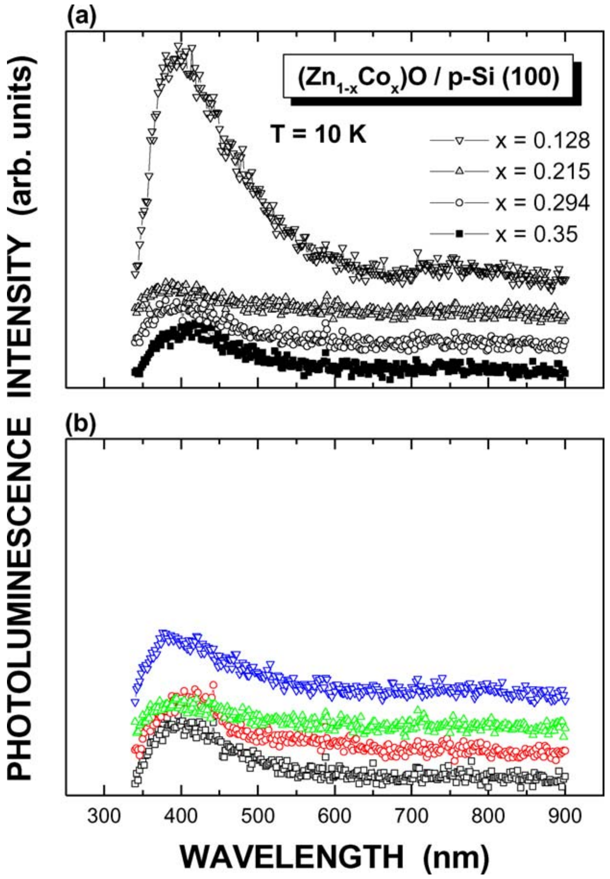

Figure 3 Photoluminescence spectra of the (a) as-grown and the (b) annealed (Zn$_{1-x}$Co$_x$)O thin films with various Co mole fractions grown on *p*-Si (1 0 0) substrates.

detailed investigations on the magnetic properties of the (Zn$_{1-x}$Co$_x$)O films remain to be clarified, these observations can help improve understanding of the effect of thermal annealing on the structural and optical of (Zn$_{1-x}$Co$_x$)O thin films grown on Si substrates.

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