Structural and magnetic properties of annealed ZnO–Co digital alloys

D. W. KIM, W. J. CHO*
Nano-Device Research Center, Korea Institute of Science and Technology, 39-1, Haweolgog-dong, Seongbuk-Gu, Seoul 136-791, Korea
E-mail: wooncho@kist.re.kr

T. W. KIM
Advanced Semiconductor Research Center, Division of Electrical and Computer Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

Diluted magnetic semiconductor (DMS) materials, which can utilize both the spin and charge properties of carriers, have attracted attention because the combination of two degrees of freedom holds promise for potential applications in spintronic devices [1, 2]. Among the various 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 studied [3–6]. However, until now, the highest ferromagnetic transition temperature (T_c) obtained from III–V $Ga_{1-x}Mn_xAs$ DMS thin films has been 110 K [7]; thus, various studies on increasing the T_c of DMS materials have driven considerable efforts with the aim of realizing spintronic devices operating at higher temperature. Among several candidate DMS materials with a high T_c, $(Zn_{1-x}Co_x)O$ DMSs are of current interest because they are theoretically expected to have high T_c values, as a consequence of the large energy gap and effective mass of $(Zn_{1-x}Co_x)O$ [8, 9]. Since there are inherent problems due to possible existence of excess Co and CoO, the direct formation of $(Zn_{1-x}Co_x)O$ films is very difficult. Thus, an alternative growth method of the $(Zn_{1-x}Co_x)O$ films necessary for improving the crystallinity of films, and the improvement of the crystallinity of the films is very important in enhancing the value of T_c. Even though few works concerning the formation and the magnetic properties of the $(Zn_{1-x}Co_x)O$ films on sapphire substrates were performed [10, 11], studies on the formation and the magnetic properties of the $(Zn_{1-x}Co_x)O$ films on Si substrates have not been performed yet. 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.

This letter reports the effects of thermal annealing on the structural and optical properties of ZnO–Co digital alloys grown on *p*-Si (100) substrates by using the radio-frequency magnetron sputtering method. X-ray diffraction (XRD) measurement were performed to investigate the crystallization of the as-grown and the annealed ZnO–Co digital alloys, and superconducting quantum interference device (SQUID) measurements were performed to characterize their magnetic properties.

Polycrystalline stoichiometric ZnO–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 (100) orientation used in this experiment was $1 \times 10^{15}\ cm^{-3}$. 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 ZnO–Co digital alloy growth, the surfaces of the ZnO and Co targets were polished by Ar^+ sputtering. The ZnO–Co deposition was done at a system pressure of 0.021 Torr. The sputtering radio-frequency (rf) powers ($rf = 13.26$ MHz) for the ZnO target was 100 W, and that for the Co target was 60 W. The flow-rate ratio of Ar to O_2 was 2, and the growth rates of the ZnO and the Co thin films were approximately 1.17 and 1.22 nm/min, respectively. The typical thicknesses of the ZnO and the Co thin films were approximately 5 and 5 nm, respectively. The thermal annealing process was performed in a nitrogen atmosphere with a tungsten-halogen lamp as the thermal source. The thermal annealing process was carried out for 2, 5, and 8 min at 900 °C.

The XRD measurements were performed using a Rigaku D/Max-B diffractometer (RINT 2000) with Cu K_α radiation. Magnetic measurements were performed by using SQUID magnetometer (Quantum design MPMS-5S) with a magnetic field applied parallel to the film plane.

The as-grown ZnO and Co films had mirror-like surfaces without any indication of pinholes, which was confirmed by using Normarski optical microscopy and scanning electron microscopy measurements. A bright-field transmission electron microscopy image showed that 10 periods of ZnO–Co digital alloys were formed and that there are some defects, dislocations,

*Author to whom all correspondence should be addressed.

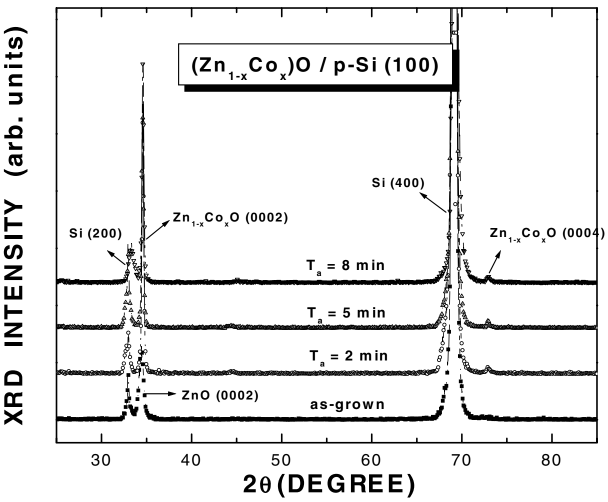

Figure 1 X-ray diffraction patterns of the (a) as-grown and the ZnO–Co digital alloys annealed at 900 °C for (a) 2, (b) 5, and (c) 8 min.

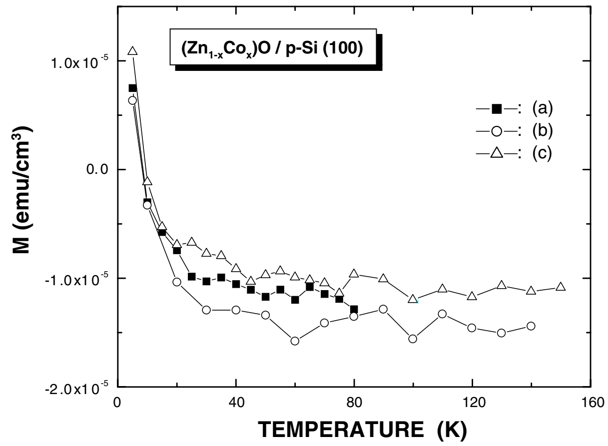

Figure 2 Magnetization curves as a function of the temperature for the ZnO–Co digital alloys annealed at 900 °C for (a) 2, (b) 5, and (c) 8 min.

or stacking faults at the ZnO–Co heterointerface. However, each ZnO–Co layer had a relatively sharp interfacial abruptness.

The XRD patterns for the (a) as-grown and the (b) annealed ZnO–Co digital alloys grown on p-Si (100) substrates are shown in Fig. 1. The (0002) $K_{\alpha 1}$ diffraction peak corresponding to the ZnO (0001) film for the as-grown ZnO–Co digital alloys, together with the (002) and the (004) diffraction peaks related to the Si (100) substrates, are clearly observed. The intensities of the (0002) and the (0004) $K_{\alpha 1}$ diffraction peaks related to the (0001) film for the annealed ZnO/Si digital alloys increase with increasing annealing time, and the full width at half-maximum of the (0002) $(Zn_{1-x}Co_x)O$ diffraction peak for the annealed ZnO/Si digital alloys than that for the as-grown samples. The diffraction peaks related to the Co and CoO single crystals for the annealed ZnO/Si digital alloys are not shown in Fig. 1. The XRD results for ZnO–Co digital alloys grown on the Si (100) substrates indicate that the annealed ZnO–Co digital alloys have a strong c-axis orientation and that the $(Zn_{1-x}Co_x)O$ film is formed by thermal treatment.

The magnetization curves as a function of the temperature for ZnO–Co digital alloys annealed for (a) 2, (b) 5, and (c) 8 min are shown in Fig. 2. While the as-grown ZnO–Co digital alloys do not show any magnetic properties, the annealed ZnO–Co digital alloys indicate paramagnetic characteristics [10]. The nonmagnetic properties of the as-grown ZnO–Co digital alloys are attributed to the existence of the CoO thin film phase with an amorphous state resulting from the oxidation of the Co, which is confirmed by the XRD results. However, when the ZnO–Co digital alloys are annealed, since $(Zn_{0.89}Co_{0.11})O$ thin films are formed due to substitution of Zn atoms for Co atoms resulting from the thermal diffusion of Co atoms into ZnO thin films by thermal treatment, the annealed ZnO–Co digital alloys contains paramagnetic properties.

In summary, XRD data showed that the $(Zn_{1-x}Co_x)O$ thin films formed on p-Si (100) substrates by using a magnetron-sputtering method and subsequent annealing were preferentially oriented in the (0001) direction. The magnetization curves as a function of the temperature for the annealed ZnO/Si digital alloys showed that the $(Zn_{0.89}Co_{0.11})O$ thin films have paramagnetic properties, the $(Zn_{0.89}Co_{0.11})O$ thin films formed from the ZnO–Co digital alloys due to thermal treatment. The present observation suggests the feasibility of the formation of the ferromagnetic $(Zn_{0.89}Co_{0.11})O$ thin films utilizing annealed ZnO–Co digital alloys. With careful growth of ZnO–Co digital alloys on p-Si substrate, it should be possible to produce $(Zn_{1-x}Co_x)O$ DMS epitaxial layers with high T_c. Furthermore, high-quality $(Zn_{1-x}Co_x)O$ DMS epilayers hold promise for applications in spintronic devices operating at high temperature.

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