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Structural and magnetic properties of $Ge_{0.7}Mn_{0.3}$ thin films

Sung-Kyu Kim [a], Jong Yeog Son [b,*], Young-Han Shin [b], Moon-Ho Jo [b], S. Park [c], Tae Eun Hong [d], K.J. Yee [e]

[a] National Center for Nanomaterials Technology, POSTECH, Pohang 790-784, Korea, & Research Center for Dielectric and Advanced Matter Physics (RCDAMP), Pusan National University, Busan 609-735, Republic of Korea
[b] Department of Materials Science and Engineering, POSTECH, Pohang 790-784, Republic of Korea
[c] Department of Physics, Pusan National University, Busan 609-735, Republic of Korea
[d] Busan Center, Korea Basic Science Institute, Busan 609-735, Republic of Korea
[e] Department of Physics, Chungnam National University, Daejeon 305-764, Republic of Korea

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ABSTRACT

$Ge_{0.7}Mn_{0.3}$ thin films were fabricated on Al_2O_3 (0001) and glass substrates at growth temperatures ranging from room temperature to 500 °C by a radio frequency magnetron sputtering. We found that the $Ge_{0.7}Mn_{0.3}$ thin films showed a polycrystalline-to-amorphous transition at about 360 °C, and the ferromagnetic transition temperature of each thin film depends on its structure — crystalline or amorphous states. Particularly, the $Ge_{0.7}Mn_{0.3}$ thin films showed room temperature ferromagnetism when they were fabricated at temperatures above the crystallization temperature.

1. Introduction

Diluted magnetic semiconductors (DMS) have been widely investigated for spintronic applications such as spin valves and spin transistors. The ferromagnetism and spin transport characteristics of DMS have been demonstrated by the optical or electrical manipulation experiments of electron spin states for several DMS systems [1–8]. After the discovery of spontaneous ferromagnetic ordering in $In_{1-x}Mn_xAs$ [1] and $Ga_{1-x}Mn_xAs$ [2], many researchers have reported ferromagnetism in metal-doped III–V and II–VI semiconductors [3–6]. However, the physical origin of ferromagnetism in the metal-doped semiconductors has been under debate because ferromagnetism arises not only from the substitution of diluted ferromagnetic elements but also from the formation of ferromagnetic metal clusters. In order to preclude the possible ferromagnetism due to metal cluster formations, many researchers explored DMS with non-ferromagnetic metals such as Mn, Cr, and Cu [3,4,7,8].

Meanwhile, metal-doped group IV semiconductors also have been studied by several research groups that have a possibility to generate room temperature ferromagnetism for spintronic applications. Park et al. reported that ferromagnetic behaviors ($T_C = 116$ K) were observed in Mn-doped Ge epitaxial layers at the Mn content of $x = 0.035$, and the ferromagnetism possibly depended on the Mn concentration at temperatures above room temperature by theoretical calculations [8,12]. Single crystals of Mn-doped Ge exhibited the ferromagnetic ordering at 285 K [9–11]. However, it was found that the origin of the ferromagnetism in Mn-doped Ge arose from the secondary phases, such as Ge_8Mn_{11} [10,11,13], Ge_3Mn_5 [14], Ge_2Mn [15], $GeMn_3$ [16], and amorphous states [17,18], where their phase transition temperatures varied with Mn concentrations. Years later, it was revealed that the $Ge_{1-x}Mn_x$ thin films can be ferromagnetically ordered due to the formation of Ge_3Mn_5 clusters with a transition temperature of 296 K [12,14,19]. In addition, it was reported that Ge_8Mn_{11} had two transition temperatures: the antiferromagnetic–ferromagnetic transition at 150 K and the ferromagnetic–paramagnetic transition at 285 K [9,20]. Jamet et al. [15] showed that the locally separated Ge_2Mn phase was formed on (Ge,Mn) epitaxial layers with the ferromagnetic–paramagnetic transition above 400 K.

In this work, we report ferromagnetism of $Ge_{0.7}Mn_{0.3}$ thin films with a ferromagnetic transition temperature of above 350 K and the relationship between crystalline structure and ferromagnetism of the $Ge_{0.7}Mn_{0.3}$ thin films grown at various growth temperatures (T_G).

2. Experimental procedure

$Ge_{0.7}Mn_{0.3}$ thin films were fabricated on glass and Al_2O_3 (0001) substrates by a radio frequency (RF) magnetron sputtering system. A $Ge_{0.7}Mn_{0.3}$ single target was prepared by a slow-cooling crystal growth method in Ar ambiance. A sputtering chamber was evacuated by a turbo pump and base pressure was below 8.9×10^{-4} Pa. Before the deposition, Ar gas was introduced. During the deposition, the working pressure of

* Corresponding author. Tel./fax: +82 54 279 5409/82 54 279 2399.
E-mail address: sonjyson@postech.ac.kr (J.Y. Son).

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4.1×10^{-1} Pa was maintained. $Ge_{0.7}Mn_{0.3}$ thin films were grown at the substrate temperature range of 30–500 °C. In order to characterize the structure of the $Ge_{0.7}Mn_{0.3}$ thin films, we performed X-ray diffraction (XRD, Regaku, monochromic CuKα radiation (λ = 1.5405 Å), 30 kV, and 30 mA) experiments. The thickness and surface morphology of $Ge_{0.7}Mn_{0.3}$ films were obtained by scanning electron microscopy (SEM, JEOL, JSM-7401F) with an operating voltage of 10 kV. The thickness of the $Ge_{0.7}Mn_{0.3}$ thin films was ranged from 170 to 200 nm. Secondary ion mass spectroscopy (SIMS, CAMECA, IMS6f) with a source current of 20 nA and O^{2+} source measurements were carried out to investigate the stoichiometry and the interface quality. The $Ge_{0.7}Mn_{0.3}$ thin films showed uniform Ge and Mn concentrations from the surface to the interface between the thin film and the substrate. The thermodynamic effect was observed by differential scanning calorimeter (DSC, MAC Science, DSC-3100). Magnetic properties were measured with a superconducting quantum interference device (SQUID, Quantum Design, XL-5) magnetometer. For the measurement of magnetization as a function of temperature, an applied magnetic field of 0.1 T was used in the temperature ranging from 10 to 350 K with an interval of 5 K. To measure magnetic hysteresis loops, we applied magnetic field in the range of −0.6–0.6 T with an interval of 0.025 T. To understand the origin of ferromagnetism in the $Ge_{0.7}Mn_{0.3}$ thin films, the chemical binding states of Mn and Ge ions were analyzed with a chamber base pressure of approximately 1×10^{-10} Torr and X-ray photoelectron spectroscopy (XPS, Surface system Korea, Theta probe) using Al Kα radiation ($h\nu$ = 1486.6 eV, 150 W, a spot diameter of 0.5 mm) at take-off angle of 90°. The spectra were normalized for the C (1s) peak at 284.6 eV. The curve fitting of the spectra was generated by subtraction of a Shirley background, followed by decomposition calculations using Gaussian–Lorentzian mixed functions.

3. Results and discussion

First, we measured the XRD patterns for the whole set of samples to characterize their structures. Fig. 1 shows XRD patterns for the $Ge_{0.7}Mn_{0.3}$ thin films grown at the substrate temperature range of 30–500 °C. Below the T_G of 300 °C, the $Ge_{0.7}Mn_{0.3}$/glass thin films have amorphous structures because the broad peaks in the XRD patterns are located at the 2θ range of 20°–30° as shown in Fig. 1(a). On the other hand, polycrystalline structures were observed for growth temperatures of 400 and 500 °C, indicating that the crystallization temperature of $Ge_{0.7}Mn_{0.3}$ thin films on glass substrates is lower than 400 °C. For the Al_2O_3 (0001) substrates, the polycrystalline structure was observed at growth temperatures of 400 and 500 °C.

To check the grains of $Ge_{0.7}Mn_{0.3}$ thin films, we observed the SEM images for the $Ge_{0.7}Mn_{0.3}$ thin films on Al_2O_3 (0001) substrates. Fig. 2 shows a representative plan-view SEM images of the $Ge_{0.7}Mn_{0.3}$ thin films on Al_2O_3 (0001) substrates grown at the substrate temperature range of 30–500 °C. Below the crystallization temperature, the $Ge_{0.7}Mn_{0.3}$ thin films show fine grains. Above the crystallization temperature, big circular grains with size of about 100 nm were observed, which supports that the full width at half maximum (FWHM) of the (111) peaks decreases with the increase of the substrate temperature in Fig. 1. The $Ge_{0.7}Mn_{0.3}$ thin films grown at the substrate temperatures of 400 °C and 500 °C show that the grain size gets smaller with the increase in the substrate temperature above the crystallization temperature because the additional energy is consumed for increasing the crystallinity of the polycrystalline $Ge_{0.7}Mn_{0.3}$ thin film grown at 500 °C compared to that of the $Ge_{0.7}Mn_{0.3}$ thin film with the mixed structure of amorphous and polycrystalline phases grown at 400 °C.

For the precise determination of the crystallization temperature, we measured DSC data for the $Ge_{0.7}Mn_{0.3}$ thin film. Fig. 3 shows DSC curve of the $Ge_{0.7}Mn_{0.3}/Al_2O_3$ (0001) films grown at 30 °C. The peak around 100 °C is attributed to the evaporation of H_2O caused by the difference between a reference sample (Al_2O_3 powder) and the $Ge_{0.7}Mn_{0.3}/Al_2O_3$ (0001) thin film. The anomalous peak at T_1 = 360 °C is observed, which

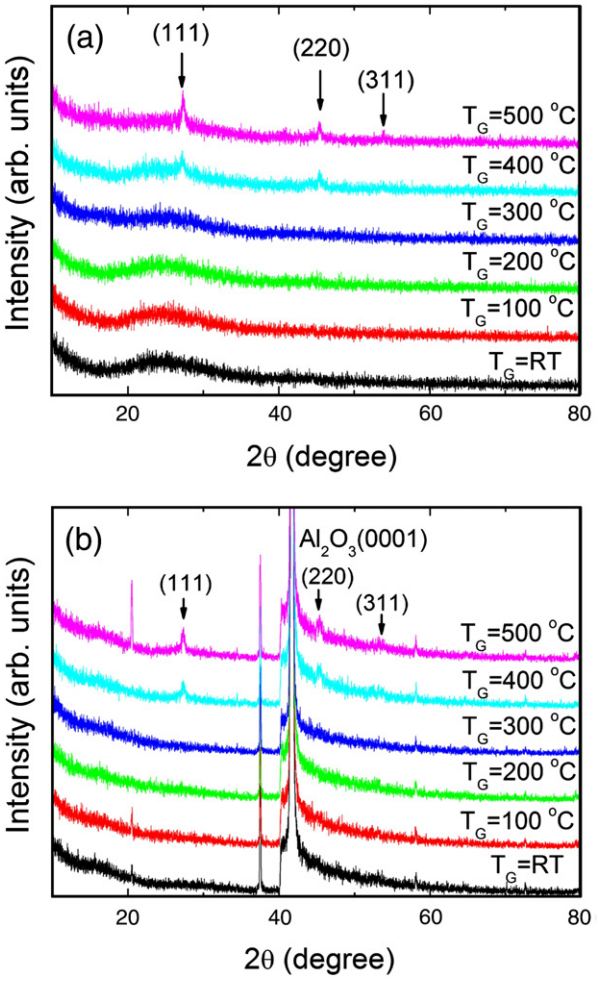

Fig. 1. XRD patterns of (a) $Ge_{0.7}Mn_{0.3}$/glass and (b) $Ge_{0.7}Mn_{0.3}/Al_2O_3$ (0001) films grown at various temperatures. The circles indicate Al_2O_3(0001) substrate peaks.

is the transition temperature from a pure amorphous state to a polycrystalline state. Therefore, we could estimate the crystallization temperature of about 360 °C, which well supports with the XRD results.

Fig. 4(a) shows magnetic field dependence of magnetization (*M*–*H*) curves of the samples at 300 K. Up to the growth temperature of 300 °C, there are small changes in magnetization. Above the crystallization temperature (T_G = 400 °C), a weak ferromagnetic hysteresis curve like a superparamagnetic hysteresis curve with the saturated magnetizations is emerged because the $Ge_{0.7}Mn_{0.3}$ thin film is in a mixed state of amorphous and polycrystalline structures. In particular, we observed that the $Ge_{0.7}Mn_{0.3}$ thin film grown at 500 °C exhibited ferromagnetic hysteresis loops up to the observation temperature of about 350 K, indicating that the $Ge_{0.7}Mn_{0.3}$ thin film grown at 500 °C has a higher ferromagnetic transition temperature above 350 K.

Fig. 4(b) shows the temperature dependence of the magnetization (*M*–*T*) measured at 0.1 T. Magnetization of $Ge_{0.7}Mn_{0.3}$ thin films increases with the T_G except the $Ge_{0.7}Mn_{0.3}$ thin film grown at 500 °C due to the smaller grain size than the $Ge_{0.7}Mn_{0.3}$ thin film grown at 400 °C. Especially, the transition temperature of samples increases with the growth temperature. The Curie temperature of $Ge_{0.7}Mn_{0.3}$ thin films grown at 30, 100, 200, and 300 °C was measured at 48, 50, 70, and 106 K, respectively [Fig. 4(b)]. Above the crystallization temperature, the $Ge_{0.7}Mn_{0.3}$ thin films exhibited a Curie temperature above room temperature, in which the $Ge_{0.7}Mn_{0.3}$ thin films at T_G = 400 °C showed the Curie temperature near 300 K. For the case of the $Ge_{0.7}Mn_{0.3}$ thin films at T_G = 500 °C, we could not evaluate the Curie temperature due to the measurement limit of the SQUID