Structural and magnetic properties of Ge$_{0.7}$Mn$_{0.3}$ thin films

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Ge$_{0.7}$Mn$_{0.3}$ thin films were fabricated on Al$_2$O$_3$ (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.

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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$_x$As [1] and Ga$_{1-x}$Mn$_x$As [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$_x$Mn$_{1-x}$ [10,11,13], Ge$_2$Mn$_x$ [14], Ge$_y$Mn$_z$ [15], Ge$_3$Mn$_4$ [16], and amorphous states [17,18], where their phase transition temperatures varied with Mn concentrations. Years later, it was revealed that the Ge$_1$–Mn$_{1-x}$ thin films can be ferromagnetically ordered due to the formation of Ge$_{1-x}$Mn$_x$ clusters with a transition temperature of 296 K [12,14,19]. In addition, it was reported that Ge$_{0.7}$Mn$_{0.3}$ had two transition temperatures: the antiferromagnetic–ferromagnetic transition at 150 K and the ferromagnetic–paramagnetic transition at 285 K [9,20]. Janjet et al. [15] showed that the locally separated Ge$_x$Mn$_{1-x}$ phase was formed on (Ge,Mn) epilayers 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 ($T_C$).

2. Experimental procedure

Ge$_{0.7}$Mn$_{0.3}$ thin films were fabricated on glass and Al$_2$O$_3$ (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 $8.9 \times 10^{-3}$ Pa. Before the deposition, Ar gas was introduced. During the deposition, the working pressure of...
4.1 × 10⁻¹ Pa was maintained. Ge₀.₇Mn₀.₃ thin films were grown at the substrate temperature range of 30–500 °C. In order to characterize the structure of the Ge₀.₇Mn₀.₃ thin films, we performed X-ray diffraction (XRD, Regaku, monochromatic CuKα radiation (λ = 1.5405 Å), 30 kV, and 30 mA) experiments. The thickness and surface morphology of Ge₀.₇Mn₀.₃ films were obtained by scanning electron microscopy (SEM, JEOL, JSM-7401F) with an operating voltage of 10 kV. The thickness of the Ge₀.₇Mn₀.₃ 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⁺ source measurements were carried out to investigate the stoichiometry and the interface quality. The Ge₀.₇Mn₀.₃ 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 range 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 Ge₀.₇Mn₀.₃ thin films, the chemical binding states of Mn and Ge ions were analyzed with a photoelectron spectroscopy (XPS, Surface system Korea, Theta probe) 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 Ge₀.₇Mn₀.₃ thin films grown at the substrate temperature range of 30–500 °C. Below the Tc of 300 °C, the Ge₀.₇Mn₀.₃/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 Ge₀.₇Mn₀.₃ thin films on glass substrates is lower than 400 °C. For the Al₂O₃ (0001) substrates, the polycrystalline structure was observed at growth temperatures of 400 and 500 °C.

To check the grains of Ge₀.₇Mn₀.₃ thin films, we observed the SEM images for the Ge₀.₇Mn₀.₃ thin films on Al₂O₃ (0001) substrates. Fig. 2 shows a representative plan-view SEM images of the Ge₀.₇Mn₀.₃ thin films on Al₂O₃ (0001) substrates grown at the substrate temperature range of 30–500 °C. Below the crystallization temperature, the Ge₀.₇Mn₀.₃ 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) 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 Ge₀.₇Mn₀.₃ thin films grown at the substrate temperatures of 400 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 Ge₀.₇Mn₀.₃ thin film grown at 500 °C compared to that of the Ge₀.₇Mn₀.₃ 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 Ge₀.₇Mn₀.₃ thin film. Fig. 3 shows DSC curve of the Ge₀.₇Mn₀.₃/Al₂O₃ (0001) films grown at 30 °C. The peak around 100 °C is attributed to the evaporation of H₂O caused by the difference between a reference sample (Al₂O₃ powder) and the Ge₀.₇Mn₀.₃/Al₂O₃ (0001) thin film. The anomalous peak at Tg = 360 °C is observed, which 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 (Tc = 400 °C), a weak ferromagnetic hysteresis curve like a superparamagnetic hysteresis curve with the saturated magnetizations is emerged because the Ge₀.₇Mn₀.₃ thin film is in a mixed state of amorphous and polycrystalline structures. In particular, we observed that the Ge₀.₇Mn₀.₃ thin film grown at 500 °C exhibited ferromagnetic hysteresis loops up to the observation temperature of about 350 K, indicating that the Ge₀.₇Mn₀.₃ 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 Ge₀.₇Mn₀.₃ thin films increases with the Tc except the Ge₀.₇Mn₀.₃ thin film grown at 500 °C due to the smaller grain size than the Ge₀.₇Mn₀.₃ thin film grown at 400 °C. Especially, the transition temperature of samples increases with the growth temperature. The Curie temperature of Ge₀.₇Mn₀.₃ 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 Ge₀.₇Mn₀.₃ thin films exhibited a Curie temperature above room temperature, in which the Ge₀.₇Mn₀.₃ thin films at Tc = 400 °C showed the Curie temperature near 300 K. For the case of the Ge₀.₇Mn₀.₃ thin films at Tc = 500 °C, we could not evaluate the Curie temperature due to the measurement limit of the SQUID.
magnetometer. We guess that the Curie temperature at $T_G = 500 \, ^\circ C$ would be higher than 400 K. Although the Ge$_{0.7}$Mn$_{0.3}$ thin film grown at $T_G = 500 \, ^\circ C$ has smaller grain size than the Ge$_{0.7}$Mn$_{0.3}$ thin film at $T_G = 400 \, ^\circ C$, the Curie temperature of the Ge$_{0.7}$Mn$_{0.3}$ thin film grown at 500 $^\circ C$ is higher than that grown at 400 $^\circ C$. We suggest that this is due to the difference in crystallinity between two Ge$_{0.7}$Mn$_{0.3}$ thin films. A ferromagnetic property can be greatly influenced by lattice strain. We also observed that the Ge$_{0.7}$Mn$_{0.3}$ thin film grown at 400 $^\circ C$ had the similar magnetic property to the Ge$_2$Mn$_5$ thin film. In this case, we can infer that the Ge$_{0.7}$Mn$_{0.3}$ film grown at 400 $^\circ C$ has an amorphous structure with small Ge$_2$Mn$_5$ crystalline nanoparticles [14]. From the structural and magnetic properties of the Ge$_{0.7}$Mn$_{0.3}$ thin films, we suggest that the increase in Curie temperature originates from the change of the crystallinities from the mixed structure of the amorphous and polycrystalline phase to polycrystalline structure.

For the chemical analysis, we observed the chemical binding states of the Ge$_{0.7}$Mn$_{0.3}$ thin films using X-ray photoelectron spectroscopy.
metal 2p3/2 is observed above 638.8 eV. Generally, the binding energy of Mn 2p3/2 is located above 641.1 eV the XPS peak of Mn 2p1/2 appears at 653 eV. The XPS peak of Mn metal 2p3/2 is observed above 638.8 eV.

Fig. 5 shows the chemical binding states of Mn 2p as a function of the binding energy. The XPS peak of Mn 2p3/2 is located above 641.1 eV the XPS peak of Mn 2p1/2 appears at 653 eV. The XPS peak of Mn metal 2p3/2 is observed above 638.8 eV.

4. Conclusions

The Ge0.7Mn0.3 thin films were fabricated on glass and Al2O3 (0001) substrates by a RF magnetron sputtering system. The Ge0.7Mn0.3/glass thin films grown below 300 °C exhibited the amorphous structures. The polycrystalline structures were obtained at the growth temperatures of 400 and 500 °C. We precisely estimated the crystallization temperature to be about 360 °C, which well supports the XRD results. At the growth temperature of 400 °C, the Ge0.7Mn0.3 showed the superparamagnetic characteristics with saturated magnetization. On the other hand, the Ge0.7Mn0.3 thin film grown at 500 °C exhibited a ferromagnetic hysteresis loop with the high Curie temperature. We suggest that the increase in Curie temperature originate from the change of the crystallinities from the mixed structure of the amorphous and polycrystalline phase to polycrystalline structure.

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References