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다결정 $Ge_{1-x}Mn_x$ 박막에서 Ge_3Mn_5 상의 형성과 특성

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다결정 $Ge_{1-x}Mn_x$ 박막의 자기적 상들에 관한 연구가 이루어졌다. Molecular beam epitaxy(MBE) 장비를 이용해 400 °C에서 $Ge_{1-x}Mn_x$ 박막을 성장시켰다. $Ge_{1-x}Mn_x$ 박막의 캐리어 유형은 P타입 이였고, 전기 비저항 값은 4.0×10^{-2}~1.5×10^{-4} ohm-cm이었다. 자기적인 특성과 미세구조의 분석에 기초하여 $Ge_{1-x}Mn_x/SiO_2/Si(100)$ 박막에 310 K 이내의 큐리에온도를 지닌 강자성의 Ge_3Mn_5 상이 형성되었음을 알 수 있었다. 게다가, Ge_3Mn_5 상이 형성된 $Ge_{1-x}Mn_x$ 박막은 20 K, 9 T의 자기장에서 약 9 %의 음의 자기저항을 보였다.

주제어 : 자성반도체, 스핀트로닉스 재료, Ge-Mn 금속간 화합물, 자기저항

Formation of Ferromagnetic Ge_3Mn_5 Phase in MBE-grown Polycrystalline $Ge_{1-x}Mn_x$ Thin Films

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Magnetic phases of polycrystalline $Ge_{1-x}Mn_x$ thin films were studied. The $Ge_{1-x}Mn_x$ thin films were grown at 400 °C by using a molecular beam epitaxy. The $Ge_{1-x}Mn_x$ thin films were p-type and electrical resistivities were 4.0×10^{-2}~1.5×10^{-4} ohm-cm. Based on the analysis of magnetic characteristics and microstructures, it was concluded that the ferromagnetic phase formed on the $Ge_{1-x}Mn_x/SiO_2/Si(100)$ thin films was Ge_3Mn_5 phase which has about 310 K of Curie temperature. Moreover, the $Ge_{1-x}Mn_x$ thin film which had Ge_3Mn_5 phase showed the negative magnetoresistance to be about 9 % at 20 K when the magnetic field of 9 T was applied.

Keywords : spintronic materials, Ge-Mn compounds, magnetoresistance, magnetic phase

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I. Introduction

Recently, IV-group, $Ge_{1-x}Mn_x$ Diluted Magnetic Semiconductor (hereafter referred to as DMS) has been reported [1]. This introduced interests to the DMS fields converged by III-V or II-VI groups [2-4]. However, low Curie temperatures (T_C) have not risen yet. So, many scientists have been studying to find various kinds of methods in which the T_C can increase. Among them, now, we are taking interest in intermetallic compounds. There are many intermetallic compound phases that have magnetic properties in Ge-Mn system. It has been investigated that some intermetallic compounds, such as Ge_3Mn_5, Ge_8Mn_{11}, $GeMn_{3.4}$ and Ge_2Mn_5, have ferromagnetic properties at near room temperature. Especially, Ge_3Mn_5 have the hexagonal Si_3Mn_5 type of structure, strong ferromagnetism about 150 emu/cm^3 at 5 K and relatively low T_C around room temperature about 296 K~320 K. Ge_8Mn_{11} has the orthorhombic structure, 274 K of relative low T_C, and spin flopping transition at near 140 K. On the other hand, Ge_4Mn, which does not exist in the Ge-Mn phase diagram, have ferromagnetic properties up to 340 K [5-10].

In this study, $Ge_{1-x}Mn_x$ thin films were grown on Si(100) wafer using a Molecular Beam Epitaxy (hereafter referred to as MBE). Then, formation conditions of the Ge_3Mn_5 on the $Ge_{1-x}Mn_x$ thin films was studied and their spin electronic properties were analyzed in order to study the potential of spin injection materials.

II. Experimental

$Ge_{1-x}Mn_x$ thin films were grown on Si(100) wafer using MBE. Native oxide layer on Si(100) wafer was not removed intentionally in order to provide nucleation sites for various phases seen in the Ge-Mn phase diagram. Working pressure was maintained greater than 10^{-8} torr. Growth rate was ~100 Å/min and final thickness of film was about 5,000 Å. Substrate temperature was controlled at 400 °C. Mn concentration on $Ge_{1-x}Mn_x$ thin films was $0 < x < 0.9$. Composition of $Ge_{1-x}Mn_x$ thin films was analyzed using the Energy Dispersive X-ray Spectroscopy (EDS) and thickness was measured by using alpha-step ET5000 (Kosaka Laboratory Ltd.). Hall effect measurement was done by applying the van der Pauw configuration in a magnetic field up to 0.5 T to examine the type and concentration of carriers at room temperature. Electrical resistivity at room temperature was measured by a standard four-probe. Structural analysis was carried out using X-ray Diffractometer (XRD). Magnetization behaviors were measured by using the vibrating sample magnetometer (VSM) and the superconducting quantum interference device (SQUID) magnetometer. The temperature denpendence of resistivity and magnetic field dependence of magnetoresistacne were studied by means of a physical properties measurement system (PPMS) with external applied magnetic field up to 9 T.

III. Results and Discussion

Electrical resistivities of $Ge_{1-x}Mn_x$ thin films were measured at room temperature. The electrical resistivities of $Ge_{1-x}Mn_x$ thin films were 4×10^{-2}~5×10^{-4} ohm-cm, and decreasd with increasing Mn concentration. Hall effect measurement showed $Ge_{1-x}Mn_x$ thin films had p-type major carriers. Some of $Ge_{1-x}Mn_x$ thin films followed anomalous Hall phenomena. Carrier concentration was estimated to be 10^{18}~10^{21}/cm^3 and increasd with Mn at%.

Fig. 1 shows XRD patterns of $Ge_{1-x}Mn_x$ thin films grown at 400 °C. In the XRD patterns, it was confirmed that $Ge_{1-x}Mn_x$ thin films were poly crystals. Moreover, in case of 28 at% grown samples at 400 °C, high magnetization values were detected at room temperature (as reported by us in Ref.7) and all peaks were indexed by Ge_3Mn_5 phase without any other extra magnetic phases like single crystal. In the XRD patterns, it was detected that samples having 31 and 34 % of increased Mn contents had peaks of Ge_3Mn_5 with unknown intermetallic compounds, in which the intensity of Ge_3Mn_5 slightly decreased.

In order to understand the details of magnetic behaviors of $Ge_{1-x}Mn_x$ thin films which have Ge_3Mn_5 phases, magnetization characteristics were measured at low tem-

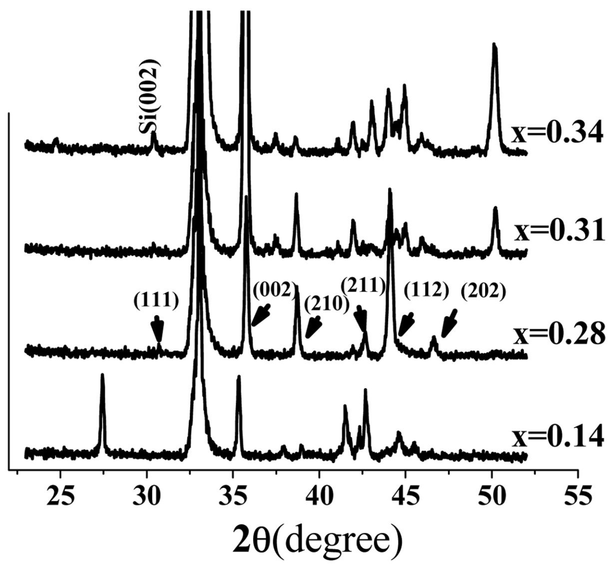

Fig. 1. XRD patterns of $Ge_{1-x}Mn_x$ thin films grown at 400 °C, diffraction peaks indicated by arrows are those Ge_3Mn_5 phase.

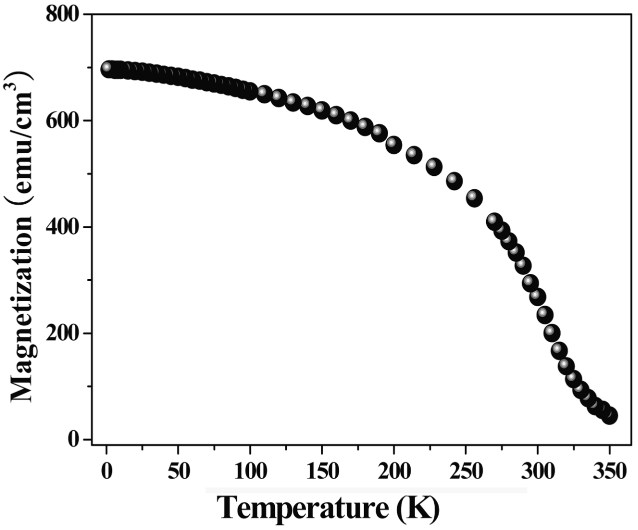

Fig. 2. Temperature dependence of the magnetization for the $Ge_{0.72}Mn_{0.28}$ film grown at 400 °C using SQUID. Applied field was 2 T.

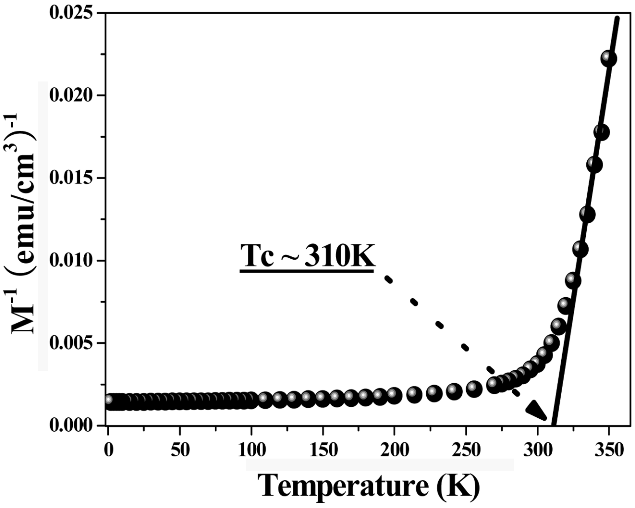

Fig. 4. Temperature dependence of the inverse magnetization for $Ge_{0.72}Mn_{0.28}$ film at grown 400 °C. Applied field was 2 T. The solid line represents the fit of the Curie-Weiss law to the high temperature data.

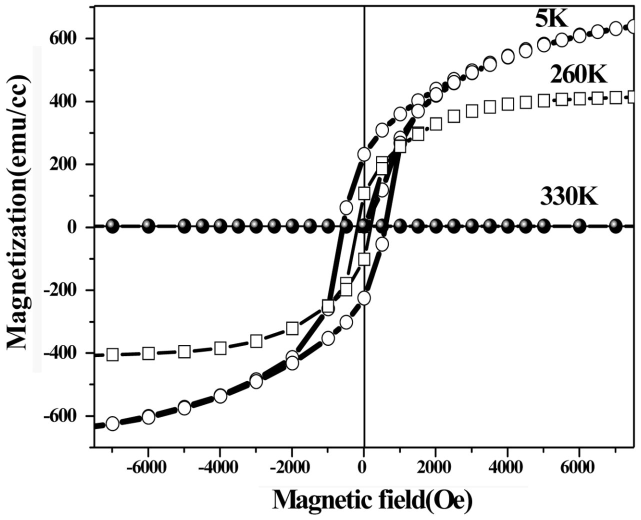

Fig. 3. Magnetization hysteresis loops of $Ge_{0.72}Mn_{0.28}$ film grown at 400 °C using SQUID.

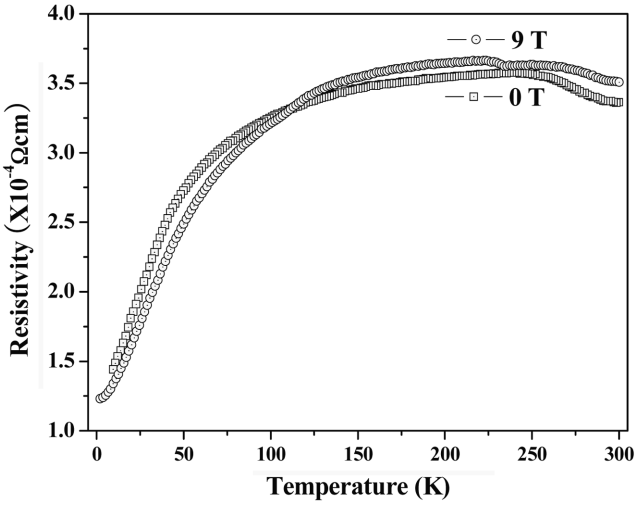

Fig. 5. Transport data for $Ge_{0.72}Mn_{0.28}$ film at grown 400 °C: Resistance vs. temperature for 0 T and 9 T.

perature by using a SQUID. Fig. 2 shows temperature dependence of the magnetization for the $Ge_{0.72}Mn_{0.28}$ film grown at 400 °C with the magnetic field of 2 T is applied parallel to the film surface. The results of SQUID analysis implied that there was only one strong ferromagnetic phase, which has far bigger magnetization value than other phases in $Ge_{1-x}Mn_x$ system. Also, T_C of the ferromagnetic phase was above room temperature. The M-H curves in Fig. 3, also display hysteresis loops at temperatures below 330 K. However, the M-H curve at 330 K shows paramagnetic behavior. It could be ferromagnetic Ge_3Mn_5 phases transformed to paramagnetic phases.

The Curie temperature was estimated from a Curie-Weiss fit to the data as the magnetization approaches to zero. As Shown in Fig. 4, it was confirmed that $Ge_{0.72}Mn_{0.28}$ thin film exhibited ferromagnetic behavior with around 310 K of T_C.

We carefully measured the change of resistance that depends on temperature and magnetoresistance for the $Ge_{0.72}Mn_{0.28}$ thin film. Fig. 5 shows a temperature dependence of ressistance curves without and with applied magnetic field of 9 T. The resistance decreased in the range of low temperature (T < 110 K), while the resistance increased in the range of high temperature (T > 110 K)

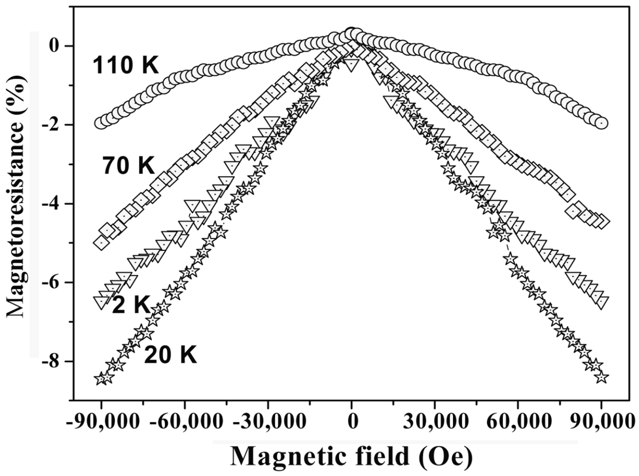

Fig. 6. Transport data for $Ge_{0.72}Mn_{0.28}$ film at grown 400 °C: Plots of magnetoresistance vs. magnetic field at different temperatures.

with applied field. In addition, at temperatures in the range of 0 < T < 250 K, the resistance increases with increasing of temperature, which is indicating metallic behavior. However at higher temperatures (T > 250 K) the resistance decreased like a behavior of semiconductors.

Magneto-transport measurements were performed with the current perpendicular to the applied field (± 9 T) at temperatures from 2 to 110 K. Significant magnetoresistance (*MR*) is observed as shown in Fig. 6. It shows negative magnetoresistance (*MR*) at temperatures below 110 K of $Ge_{0.72}Mn_{0.28}$ thin film. When we applied field at each temperture, MR curves look like symmetry and the magnitude of MR ratio decreased as temperture increased. The negative MR reaches to ~9 % at 20 K. This behavior is similar to the nano scale ferromagnetic cluster/semiconductor systetm such as MnAs feromangetic cluster/GaAs and Ge_8Mn_{11} cluster/$Ge_{1-x}Mn_x$ matrix [9, 11]. Therefore, the origin of negative MR in $Ge_{0.72}Mn_{0.28}$ film at grown 400 °C could be explained by the spin dependent scattering of carriers by the ferromagntic Ge_3Mn_5 cluster, where the scattering probality decrease as the direction of the magnetization of cluster aligns with increasing external magnetic field.

In conlusion, we have grown and investigated mangetic and electrical propeties of $Ge_{1-x}Mn_x$ thin films with the formation of Ge_3Mn_5 magnetic phase. The XRD measurement reveals the formation of Ge_3Mn_5 phase in $Ge_{0.72}Mn_{0.28}$ film at grown 400 °C without any extra phases. Magnetic measurement reveals that the $Ge_{0.72}Mn_{0.28}$ films show ferromangetic properties at room temperature, which is atributed to the formation of Ge_3Mn_5 phase in the film. The Curie temperature of $Ge_{0.72}Mn_{0.28}$ thin film was determined around 310 K. The $Ge_{0.72}Mn_{0.28}$ thin film shows negative magnetoresistance (*MR*) at temperatures below 110 K. The negative MR at low temperature was observed due to the spin-dependent scattering of carriers by Ge_3Mn_5 clusters.

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