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Phase Transformations in the Mn–Ge System and in Ge_xMn_{1-x} Diluted Semiconductors

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Results of an X-ray diffraction study as well as magnetic and electrical measurements of the solid-state reactions in Ge/Mn polycrystalline films of an 80/20 atomic composition have been presented. It has been shown that the ferromagnetic Mn_5Ge_3 phase is formed first on the Ge/Mn interface after annealing at ~120°C. The further increase in the annealing temperature to 300°C leads to the beginning of the synthesis of the $Mn_{11}Ge_8$ phase, which becomes dominating at 400°C. The existence of new structural transitions in the Mn–Ge system in the region of ~120 and ~300°C has been predicted on the basis of the presented results and results obtained earlier when studying solid-state reactions in different film structures. The supposition about the general chemical mechanisms of the synthesis of the Mn_5Ge_3 and $Mn_{11}Ge_8$ phases during the solid-state reactions in the Ge/Mn films of the 80/20 atomic composition and the phase separation in Ge_xMn_{1-x} ($x > 0.95$) diluted semiconductors has been substantiated.

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INTRODUCTION

Ferromagnetic diluted semiconductors have been intensively studied in recent years. However, the nature of ferromagnetism in diluted semiconductors does not find an unambiguous fundamental explanation. One of the explanations of ferromagnetism in diluted semiconductors at room temperature is the formation of magnetic precipitates arising as a result of phase separation [1, 2]. Particular attention is paid to Ge_xMn_{1-x} diluted semiconductors, which have the Curie temperature above room temperature depending on the conditions of the preparation and annealing. In particular, the ferromagnetism of Ge_xMn_{1-x} films can be explained by the spinodal decomposition of the Ge_xMn_{1-x} homogeneous solid solution and the formation of the ferromagnetic precipitates Mn_5Ge_3 ($T_C = 304$ K) [3, 4], $Mn_{11}Ge_8$ ($T_C \sim 275$ K) [5, 6], Ge_2Mn ($T_C < 400$ K) [7], and Ge_2Mn_5 ($T_C = 304$ K) [5]. However, it is difficult to experimentally determine the components of the phase separation using modern techniques [1]. The diagram of the Mn–Ge phase equilibrium is constantly being refined. There were recent reports about the synthesis of new Mn–Ge phases in the phase systems with the Curie temperature above room temperature: Ge_3Mn ($T_C \sim 400$ K) [8], $MnGe_4$ ($T_C = 340$ K) [9], Ge_3Mn ($T_C \sim 300$ K) [10], and unknown phases with the composition $Ge_{0.7}Mn_{0.3}$ ($T_C > 400$ K) [11] and $Mn_{0.75}Ge_{0.25}$ ($T_C > 300$ K) [12]. It is important to note that ferromagnetic precipitates are formed as a result of low-temperature spinodal decomposition. Scenarios and mechanisms of the chemical interaction of Mn with Ge remain poorly studied. Studies of the characteristics of the solid-state reactions of Mn with Ge may provide important information for the analysis of the formation of the magnetic phases based on Mn.

In this work, we study the formation of phases in Ge/Mn film samples having a high Ge content with increasing annealing temperature to 450°C. The formation of the phase sequence Ge/Mn $\longrightarrow$ (~120°C) Mn_5Ge_3 $\longrightarrow$ (~300°C) $Mn_{11}Ge_8$ is demonstrated. The magnetic characteristics of the reaction products are presented and the possibility of the formation of Mn_5Ge_3 and $Mn_{11}Ge_8$ phases during the phase separation in Ge_xMn_{1-x} diluted semiconductors is discussed.

SAMPLES AND EXPERIMENTAL TECHNIQUE

The initial Ge/Mn film structures were obtained by the successive thermal deposition of Mn and Ge layers on glass substrates in a vacuum of 10^{-6} Torr. Substrates

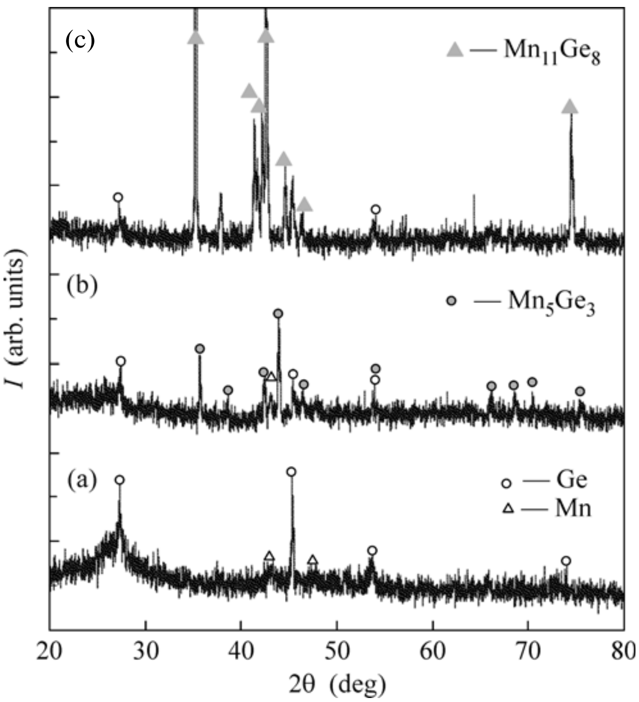

Fig. 1. Diffraction patterns of the 80Ge/20Mn film system for (a) the initial sample and sample after annealing at (b) 250 and (c) 400°C.

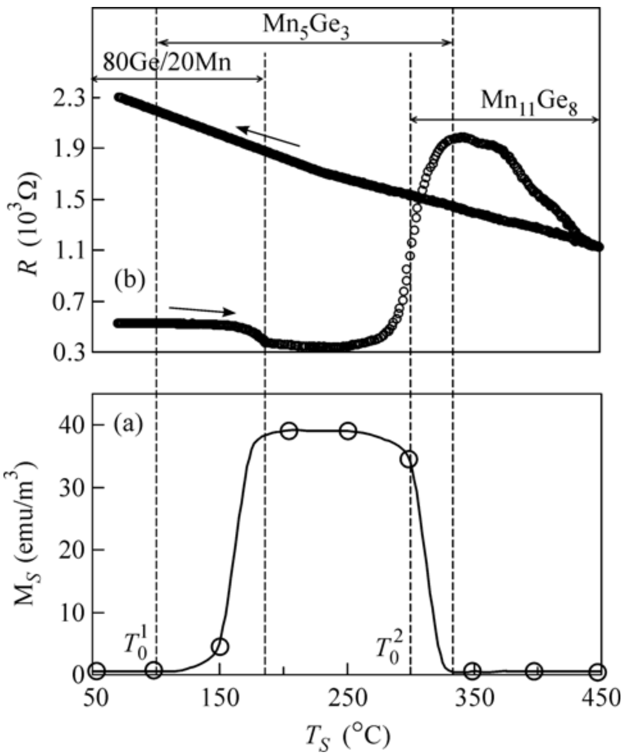

Fig. 2. (a) Saturation magnetization $M_S(T_S)$ and (b) electric resistivity $R(T_S)$ of the 80Ge/20Mn bilayer film system versus the annealing temperature. Vertical dashed lines mark the beginning and termination of the synthesis of the Mn_5Ge_3 and $Mn_{11}Ge_8$ phases. The temperature ranges of the existence of the 80Ge/20Mn film system, as well as the Mn_5Ge_3 and $Mn_{11}Ge_8$ phases, are shown on top.

were degassed at 350°C with the subsequent deposition of Mn layers at a temperature of 200°C. The upper Ge layers were deposited at room temperature in order to avoid the reaction between Ge and Mn during deposition. The Ge/Mn samples were subjected to thermal annealing in the temperature range from 50 to 450°C with a step of 50°C and exposure at each temperature for 30 min. Samples with an 80Ge : 20Mn (hereinafter 80Ge/20Mn) atomic ratio and a total thickness of 1.5 μm were used in the experiments. The saturation magnetization M_S was measured with an MPMS-XL SQUID magnetometer (Quantum Design) in a magnetic field of up to 5 kOe. The formed phases were identified with a DRON-4-07 diffractometer (Cu K_α radiation). X-ray fluorescence analysis was used to determine the thickness of the Ge and Mn layers. The electrical resistivity was measured by the conventional four-probe method. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

The diffraction patterns of the initial 80Ge/20Mn films (Fig. 1a) contained weak reflections from α-Mn and Ge. Reflections from Mn disappeared and reflections of the ferromagnetic Mn_5Ge_3 phase appeared after annealing at 150°C (Fig. 1b). This phase became the main phase after annealing at 250°C. With the annealing temperature increasing above 250°C, reflections of the Mn_5Ge_3 phase disappeared and new $Mn_{11}Ge_8$ peaks appeared, which became dominating after annealing at 400°C (Fig. 1c). Additional weak reflections, which were attributed to the GeO_2, MnO, and MnO_2 phases, were also present in the diffraction patterns after annealing at 400°C. These results demonstrate the formation of the phase sequence 80Ge/20Mn ⟶ Mn_5Ge_3 ⟶ $Mn_{11}Ge_8$ during heating to 400°C.

Figure 2a shows the dependence of the magnetization of the 80Ge/20Mn films on the annealing temperature, which indicates the existence of two critical temperatures T_0^1 ~ 120°C and T_0^2 ~ 300°C. The initial 80Ge/20Mn samples remained nonmagnetic with the annealing temperature increasing to 120°C. After annealing at 120°C, the magnetic measurements demonstrated the presence of a slight magnetization in the samples, which increased strongly after annealing at 250°C. The appearance of the magnetization at 120°C and its strong increase at 250°C indicate the mixing of the Ge and Mn layers and the solid-state synthesis of the ferromagnetic phase with the initiation temperature T_0^1 ~ 120°C. The decrease in the magnetization during annealing above 300°C and its com-

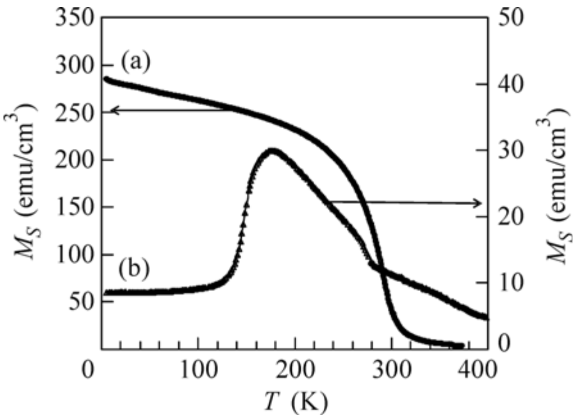

Fig. 3. Temperature dependences of the saturation magnetization $M_S(T)$ measured in a magnetic field of 5 kOe for the 80Ge/20Mn film system after annealing at (a) 250 and (b) 400°C.

plete disappearance above 400°C are related to the formation of the nonferromagnetic phase with the initiation temperature T_0^2 ~ 300°C. These results agree with the X-ray data demonstrating the successive formation of the Mn_5Ge_3 ferromagnetic phase and the $Mn_{11}Ge_8$ nonmagnetic phase at the temperatures of T_0^1 ~ 120°C and T_0^2 ~ 300°C, respectively.

Figure 2b shows the dependence of the electrical resistivity $R(T_S)$ of samples on the annealing temperature. With increasing temperature, the resistivity of the 80Ge/20Mn films increases slightly and starts to decrease sharply above 120°C. This indicates that there are no changes on the Ge/Mn interface up to 120°C. The start of the strong mixing of the Ge and Mn layers and the formation of Mn_5Ge_3 occur above 120°C. With the further increase in the temperature, the smooth behavior of $R(T_S)$ changes at 300°C. The resistivity increases strongly owing to the synthesis of $Mn_{11}Ge_8$, which is terminated at 450°C. The inverse course of the resistivity shows that the $Mn_{11}Ge_8$ phase is a semiconductor. The temperature dependence of the electrical resistivity indicates that the initiation temperatures of the Mn_5Ge_3 and $Mn_{11}Ge_8$ phases are T_0^1 ~ 120°C and T_0^2 ~ 300°C, respectively.

The temperature dependences of the saturation magnetization $M_S(T)$ shown in Fig. 3 completely confirm the successive formation of the Mn_5Ge_3 and $Mn_{11}Ge_8$ phases in the 80Ge/20Mn films after annealing at 250 and 400°C, respectively. The shape of the $M_S(T)$ dependence after annealing at 250°C (Fig. 3a) shows the presence of only one phase in the sample with the Curie temperature T_C ~ 300 K inherent in the Mn_5Ge_3 phase [3, 4]. A feature of the $Mn_{11}Ge_8$ phase is the presence of ferromagnetic order in the temperature range of 150–275 K [13]. Figure 3b presents the temperature dependence $M_S(T)$ of the saturation magnetization after annealing at 450°C. Its course is characteristic of the $Mn_{11}Ge_8$ phase both in the bulk [13] and in the film [6] samples.

It is well known that the solid-state reactions in thin films occur at low temperatures. With increasing annealing temperature, only one (first) phase is formed. The further increase in the temperature leads to the formation of a phase sequence. At present, there are no conventional substantiations of the formation of the first phase, phase sequence, and their initiation temperatures, although some models were proposed (see [14, 15] and references therein).

It was shown in [16–19] that many low-temperature reactions in bilayer films start at the minimum temperature T_K of the structural solid-state transformation in this binary system ($T_0 = T_K$). In particular, the equality $T_0 = T_K$ is fulfilled for eutectic transformations [16], during the order/disorder phase transition [17], for the martensitic transformations [18], and for the eutectoid decay [19]. On the basis of the aforesaid, we suppose the existence of two low-temperature solid-state transitions in the Ge-rich region of the Mn–Ge system. The first transformation starts at the temperature of ~120°C. It is related to the transformation in the Mn_5Ge_3 phase. The second exists above 300°C and is related to the transformation in the $Mn_{11}Ge_8$ alloy.

It is known that an increase in the annealing temperature is accompanied by the spinodal decomposition of the majority of diluted magnetic semiconductors, which can explain the appearance of ferromagnetic order at room temperature. For the Mn–Ge system after annealing above 120°C, Mn_5Ge_3 precipitates prevail in the $Mn_{1-x}Ge_x$ films with a high Ge content ($x > 0.95$) [3]. The studies of the structural and magnetic properties of the $Mn_{1-x}Ge_x$ films showed that the Mn-rich clusters embedded in the Ge matrix already start to form at a substrate temperature of 60°C. However, the Mn atoms chemically interact with the Ge atoms only above 120°C and form nanosized precipitates of the intermetallic Mn_5Ge_3 phase [4]. The experimental coincidence of the initiation temperatures of the Mn_5Ge_3 phase implies the general chemical mechanisms during the solid-state reactions and phase separation in the Ge–Mn films. Above 120°C, strong chemical interactions between Mn and Ge lead to the formation of the first Mn_5Ge_3 phase independently of whether the Mn and Ge atoms are in the solid solution or in the bilayer film systems. The second transformation, which occurs above 300°C, is related to the transformation in the $Mn_{11}Ge_8$ alloy. According to [5], the $Mn_{11}Ge_8$ phase in the $Mn_{1-x}Ge_x$ samples grows at a higher temperature (>300°C) than the Mn_5Ge_3 phase. The close initiation temperatures of the $Mn_{11}Ge_8$ phase in the 80Ge/20Mn films and $Mn_{1-x}Ge_x$ solid solutions imply the general chemical mechanisms and scenarios of their formation. Since the Ge content in the Mn_5Ge_3 phase is somewhat lower than that in the $Mn_{11}Ge_8$ phase, it is reasonable to suppose that the formation of the $Mn_{11}Ge_8$ phase in both cases is possible according to the solid-state reaction $Mn_5Ge_3 + Ge \longrightarrow Mn_{11}Ge_8$. This reaction in the 80Ge/20Mn films occurs between Mn_5Ge_3 crystallites and the residual Ge layer. The synthesis of the $Mn_{11}Ge_8$ phase in the $Mn_{1-x}Ge_x$ films occurs between the Mn_5Ge_3 precipitates and Ge atoms present in the solid solution. This agrees with [20], where it was shown that annealing initiates the transformation of Mn_5Ge_3 into the $Mn_{11}Ge_8$ phase. It is important to note that the low-temperature interactions between Mn and Fe [21] and Mn and Ga [22] were also observed earlier.

CONCLUSIONS

We have studied the phase transitions in polycrystalline Ge/Mn nanofilms with the 80Ge : 20Mn composition with an increase in the annealing temperature to 450°C. The Mn_5Ge_3 ferromagnetic phase and the $Mn_{11}Ge_8$ phase are successively formed at the temperatures of 120 and 300°C, respectively. The existence of two solid-state transitions at ~120 and ~300°C in the Mn–Ge system is supposed on the basis of the analysis of the solid-state reactions in the layered film structures. The results presented give an important contribution to the understanding of the low-temperature formation of the Mn_5Ge_3 and $Mn_{11}Ge_8$ phases, which can underlie ferromagnetism of $Mn_{1-x}Ge_x$ diluted semiconductors.

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