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Magnetic properties of Mn-implanted n-type Ge

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Abstract

Mn^+ ions were implanted into n-type Ge(1 1 1) single crystal at room temperature at an energy of 100 keV with a dose of $3 \times 10^{16}\,cm^{-2}$. Subsequent annealing was performed on the samples at 400 °C and 600 °C in a flowing nitrogen atmosphere. The magnetic properties of the samples have been investigated by alternating gradient magnetometer at room temperature. The compositional properties of the annealed samples were studied by Auger electron spectroscopy and the structural properties were analyzed by X-ray diffraction measurements. Magnetization measurements reveal room-temperature ferromagnetism for the annealed samples. The magnetic analysis supported by compositional and structural properties indicates that forming the diluted magnetic semiconductor (DMS) Mn_xGe_{1-x} after annealing may account for the ferromagnetic behavior in the annealed samples.

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1. Introduction

Diluted magnetic semiconductors (DMSs) combine the electronic transport properties of semiconductors and the memory characters of magnetic materials and are important in the development of spin-controlled electronic devices and integrated magnetic device applications. Nowadays, the investigation of DMSs has received a great deal of attention. The most extensively studied and most thoroughly understood materials of DMSs are $A_{1-x}^{II}\,Mn_xB^{VI}$ and $A_{1-x}^{III}\,Mn_xB^{V}$, in which Mn replaces a fraction of group II or III sublattices randomly [1–3]. However, Si- or

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Ge-based DMSs will be more practical for applications since present semiconductor technology may be used [4–6].

It is predicted theoretically that the Curie temperature T_c of the diluted magnetic semiconductor (DMS) Mn_xGe_{1-x} may reach 400 K [7]. Park et al. [6] reported on the epitaxial growth of Mn_xGe_{1-x} by molecular beam epitaxy (MBE), in which the Curie temperature is found to increase linearly with manganese (Mn) concentration from 25 to 116 K. Sunglae Cho et al. reported the ferromagnetism in highly Mn-doped (up to 6%) Ge single crystals with $T_c = 285$ K [8]. Franco D'Orazio et al. [9] reported the magnetic properties of Mn-implanted Ge in which a hysteresis appeared just below room temperature. A hybrid structure Ge:Mn was reported to show ferromagnetic properties and magnetoresistance phenomena near room temperature, attributed to Mn-rich ferromagnetic clusters [10].

In this paper, the samples were prepared by implantation of Mn^+ ions into n-type Ge(1 1 1) single crystal at room temperature and subsequent annealing. The annealed samples show ferromagnetism at room temperature.

2. Material preparation

The samples investigated in this paper were obtained by implantation of Mn^+ ions into Ge substrate and subsequent annealing. The substrate is (1 1 1)-oriented n-type Ge single crystal. The Ge substrate was chemically cleaned using a standard HF/H_2O etchant and H_2O_2/H_2O rinse before sample growth. Then, the Ge substrate was inserted into the growth chamber where the vacuum was $< 1 \times 10^{-5}$ Pa. The implantation was performed using an energy of 100 keV and a dose of $3 \times 10^{16}\,cm^{-2}$, while the temperature of the substrate during the process was kept at room temperature. Following implantation, parts of the as-implanted sample were annealed at 400 °C and 600 °C in a flowing nitrogen atmosphere. During the annealing process, the sample surface was in contact with a polished germanium wafer so as to prevent Mn from evaporating from the sample surface.

3. Results and discussion

The magnetic properties of the samples were measured on a Model 2900 MicroMag™ Alternating Gradient Magnetometer (AGM) at room temperature. The results of magnetization measurements reveal room-temperature ferromagnetism in the annealed samples while no ferromagnetism can be observed in the as-implanted sample. Fig. 1 shows the magnetic hysteresis loops at room temperature for the sample annealed at 400 °C and the sample annealed at 600 °C. The magnetization curves were obtained with the applied field parallel to the sample surface. The diamagnetic background of the Ge substrate was subtracted from the data. The coercivity H_c and saturation magnetization M_s of the sample annealed at 400 °C are about 408 Oe and 5.62×10^{-5} emu, respectively. The H_c and M_s of the sample annealed at 600 °C are about 114 Oe and 7.98×10^{-6} emu, respectively. The H_c and M_s of the sample annealed at 600 °C are smaller than those of the sample annealed at 400 °C.

Pure Ge does not have a net magnetic moment, resulting in diamagnetism with a molar susceptibility of $-11.6 \times 10^{-6}\,cm^3\,mol^{-1}$ [11]. Metallic Mn is antiferromagnetic, with a Neel temperature of 100 K. In addition, nearly all of the possible Mn-based binary and ternary oxides are antiferromagnetic. Only Mn_3O_4 is ferromagnetic with a T_c of 42 K [12]. In Mn nitrides, which might be caused by the annealing process, Mn_4N is ferromagnetic with T_c above room temperature [13]. In the Mn–Ge phases, Mn_5Ge_3 and $Mn_{11}Ge_8$ are ferromagnetic intermetallic compounds with T_c near room temperature [14,15]. Furthermore, the DMS Mn_xGe_{1-x} is ferromagnetic and has a large variation of T_c from 25 to 285 K depending on the different growth conditions.

The compositional and structural properties of the samples were analyzed in order to understand what phases could account for the ferromagnetic behavior in the annealed samples. The compositional properties of the annealed samples were examined by Auger electron spectroscopy (AES). Fig. 2 is the AES spectra at the sample surfaces, which show the existence of manganese, germanium, carbon and oxygen. The reason for the

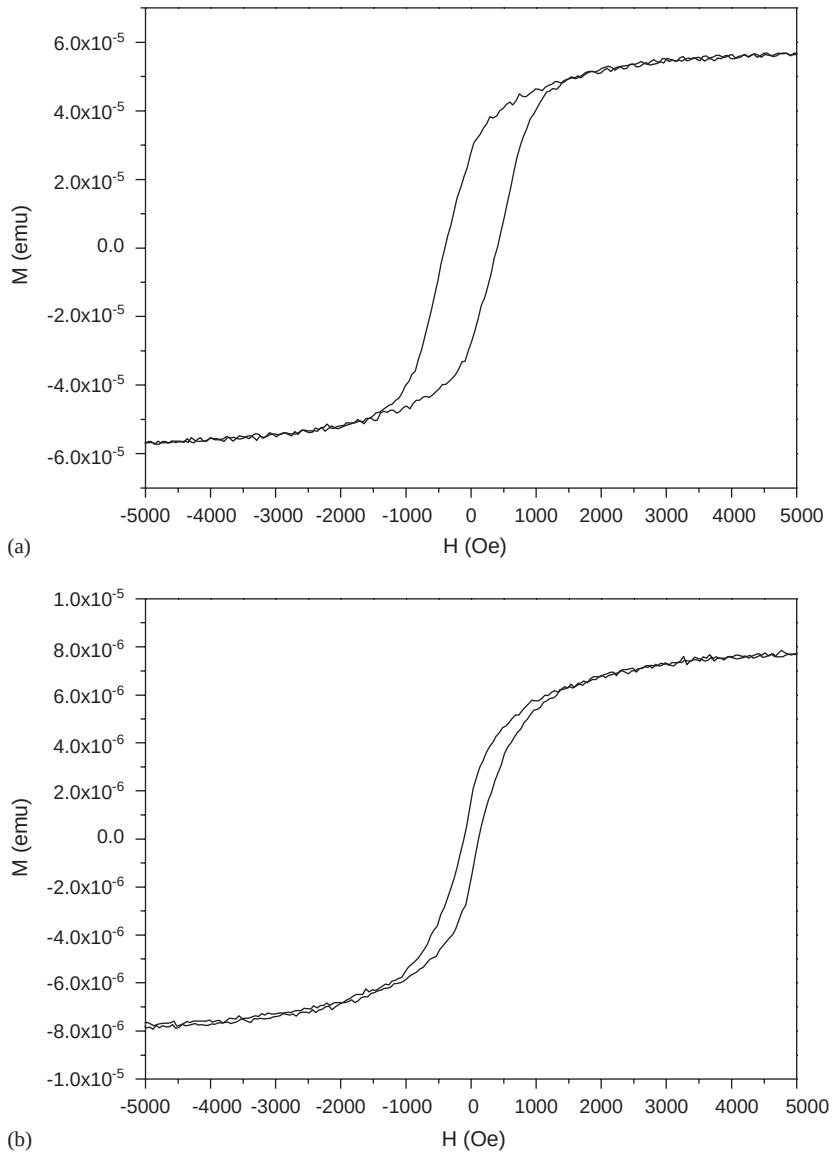

Fig. 1. The hysteresis loops of the samples examined by AGM at room temperature: (a) the sample annealed at 400 °C; (b) the sample annealed at 600 °C.

existence of carbon is that the sample surfaces were contaminated after the samples were taken out of the growth chamber. The element oxygen is introduced by oxidation of manganese after the samples were removed from the growth chamber. No signal of nitrogen is observed based on the kinetic energy of nitrogen, which precludes the formation of Mn nitrides during the annealing process. It is highly likely that Mn_3O_4 might be formed at the sample surfaces, but it cannot account for room-temperature ferromagnetism due to its rather low T_c (42 K). It can also be seen from Fig. 2 that the Mn peak intensity of the sample annealed at 600 °C is stronger than that of

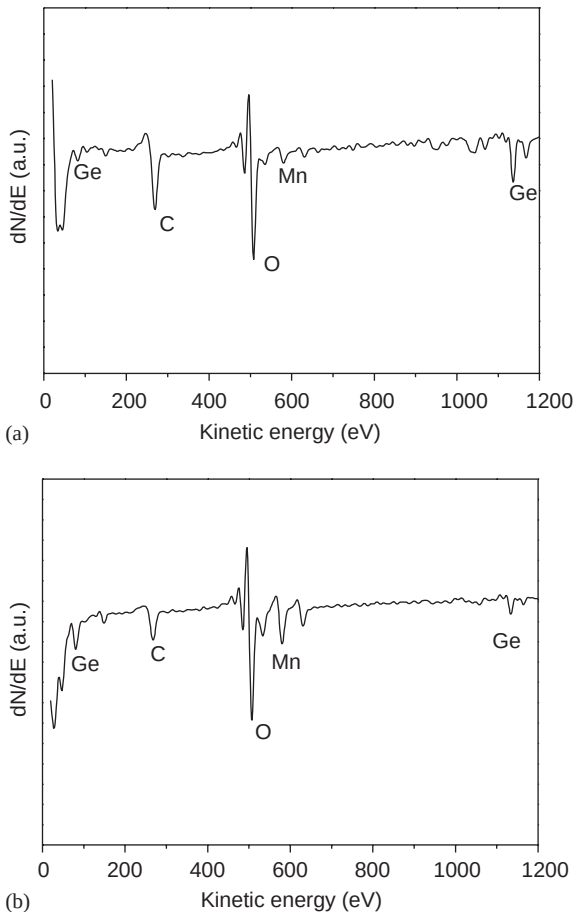

Fig. 2. AES spectra at the sample surfaces: (a) the sample annealed at 400 °C; (b) the sample annealed at 600 °C.

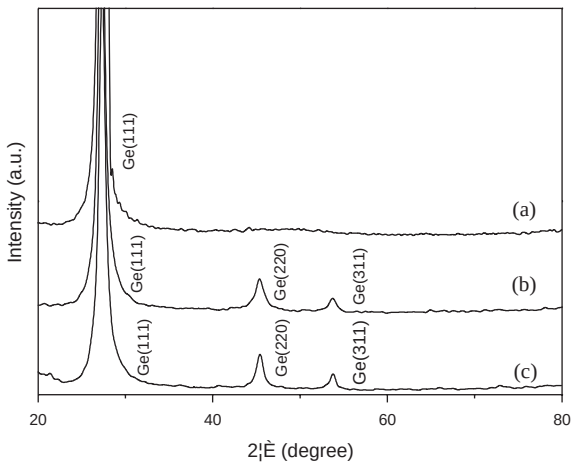

Fig. 3. XRD spectra of the samples: (a) as-implanted sample; (b) the sample annealed at 400 °C; and (c) the sample annealed at 600 °C.

the sample annealed at 400 °C. The Mn dose is identical for all the samples. Thus, increasing the annealing temperature from 400 to 600 °C causes the out diffusion of Mn toward the surface.

The structural properties of the samples were studied by X-ray diffraction measurements. XRD patterns of the samples were measured with a Rigaku diffractometer using Cu Kα radiation for structural analyses. The wide range XRD (20–80°) patterns are shown in Fig. 3. In the as-implanted sample, only the Ge(1 1 1) peak is observed. The diffraction peaks of Ge(2 2 0) and (3 1 1) appear in the annealed samples. The results show that the crystal structure of the as-implanted sample is destroyed by the heavy manganese ions being implanted and becomes amorphous. After the annealing process, the crystal structure of the as-implanted sample was restored and polycrystalline germanium was formed due to the incorporation of a lot of manganese ions. No additional diffraction peak can be observed except germanium. There are two possible causes accounting for the phenomenon. One is that the ferromagnetic secondary phases were formed in the annealed samples, but the sizes of the secondary phases were too small to be detected by the XRD measurements. The other is that the DMS Mn_xGe_{1-x} was formed in the annealed samples, in which Mn was located in the position of Ge crystal lattice.

The Mn dose in this study was above the solid solubility limit of Mn in Ge. It is possible to form the Mn-related ferromagnetic secondary phases with T_c near or above room temperature in the annealed samples. It should be noticed that increasing the annealing temperature can cause the further growth of ferromagnetic secondary phases and result in the increase of the hysteretic behavior [9]. The ferromagnetic behavior in the sample annealed at 600 °C should be stronger than that in the sample annealed at 400 °C. However, increasing the annealing temperature from 400 to 600 °C resulted in the reduction of H_c and M_s. So, the ferromagnetic origin of the annealed samples

cannot be attributed to the Mn-related ferromagnetic secondary phases. According to theory [7], the magnetic order in Mn_xGe_{1-x} strongly depends on the Mn site locations due to the RKKY-like interaction between the localized Mn ions. The T_c of Mn_xGe_{1-x} could be up to 400 K for Mn atoms located in a certain case. The annealing process may affect the Mn site locations in the sample and the magnetic properties of the sample. Therefore, the sample annealed at a different temperature will show different magnetic properties. In this study, ferromagnetism in the sample annealed at 600 °C is weaker than that in the sample annealed at 400 °C. It suggests that the annealing process at 400 °C is more favorable to ferromagnetism than the annealing process at 600 °C. So, it is believable that the DMS Mn_xGe_{1-x} was formed after annealing and may be responsible for the ferromagnetism in the annealed samples.

4. Summary

The samples were prepared by implantation of Mn^+ ions into n-type Ge(1 1 1) single crystal at room temperature and subsequent annealing. The annealed samples show ferromagnetism at room temperature. The origin of the ferromagnetism is discussed. The diluted magnetic semiconductor Mn_xGe_{1-x} was formed after annealing and may be responsible for the ferromagnetism in the annealed samples.

Acknowledgements

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