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Research articles

Enhanced magneto-transport and thermoelectric properties of MnP nanorod thin films grown on Si (1 0 0)

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ABSTRACT

The MnP thin films were grown on Si (1 0 0) substrates at 300 and 400 °C using molecular beam epitaxy (MBE). The films crystallize in an orthorhombic structure. FE-SEM images indicated that both films are composed of vertically aligned MnP nanorods. However, the density of the nanorods in the film grown at 400 °C is higher than that grown at 300 °C, leading to a considerable decrease of resistivity in this sample. Both films showed a ferromagnetic behavior, but the Curie temperature increased from 275 K for the film grown at 300 °C to 325 K for the film grown at 400 °C. Anomalous Hall effect (AHE) and negative magneto-resistance (MR) were observed in the films. While both films exhibited a metallic behavior, a higher thermoelectric power factor (PF) was achieved for the film grown at 400 °C.

1. Introduction

MnP has been known as a complex magnetic material with an antiferromagnetic helical alignment below 47 K, the ferromagnetic behavior between 47 and 291 K, and paramagnetism at higher temperatures [1–8]. The crystallographic structure of MnP is orthorhombic, with lattice constants of a = 5.916 Å, b = 3.173 Å, and c = 5.260 Å, which is distorted from the NiAs-type hexagonal crystal structure [8–11]. MnP has been reported to show the catalytic and magnetocaloric properties [10,12]. Therefore, creation of MnP thin films might have great potential for the spintronics applications.

The MnP nanowhiskers with ferromagnetic behavior up to room temperature were reported by Bouravleuv et al. [13] Choi et al. observed a ferromagnetic ordering in a MnP thin film grown on GaAs substrate and explained that the change of the transition temperature between the FM and helicoidal magnetic states (T_N) from 47 to 100 K could be caused by strain due to lattice mismatch between the epitaxial MnP film and GaAs substrate [14]. The changes of T_N and T_C also were observed in polycrystalline MnP and nanostructure embedded in GaP epilayers [15–19]. In addition to its attractive magnetic properties, MnP was known as a superconductive material [20]. Cheng et al. discovered a superconductivity on the border of long-range magnetic order in the itinerant-electron helimagnet MnP upon the application of a high pressure.

In this work, we fabricated MnP nanorod thin films on Si (1 0 0) substrate by MBE and investigated the influence of growth temperature on the thermoelectric and transport properties of the films. The close-packed structure of nanorods in the film grown at 400 °C results in a significant decrease in resistivity as compared to the film grown at 300 °C. The larger hysteresis in the Hall resistance vs. magnetic field was also observed for the film grown at 400 °C. The reduction of resistivity is likely a cause for increasing the Power Factor (PF) in the film grown at 400 °C.

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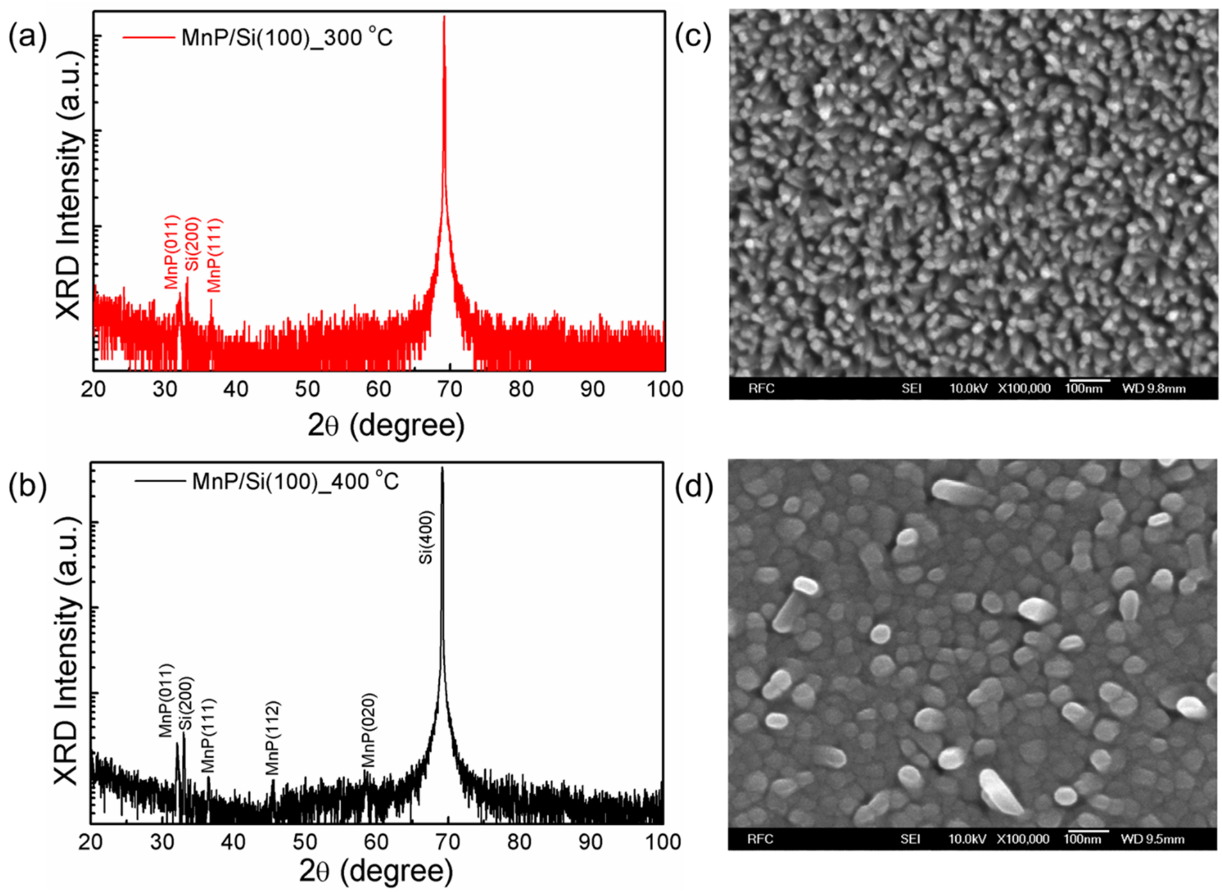

Fig. 1. (a, b) θ-2θ XRD patterns, (c, d) SEM surface images of MnP thin films grown at 300 °C and 400 °C, respectively.

2. Experiment

The MnP thin films were fabricated on Si (1 0 0) substrate by using MBE. The substrates were chemically cleaned by rinsing in the methanol for 20 min before loading into the growth chamber and heated up to 600 °C for 30 min to remove impurities and oxidized layer. The substrate temperature was cooled down to 300 or 400 °C for two times of growth. Base pressure in growth chamber before growing is 10^{-9} Torr. The phosphorus pressure of 3.5×10^{-6} torr and the Mn-deposition rate of 0.2 Å/s were maintained during the growth process. The thickness of the film was determined to be ~1000 Å. All samples were cooled down to room temperature before being removed from the vacuum chamber. The growth of the film was monitored by using *in-situ* reflection high-energy electron diffraction (RHEED). After the growth, the crystal structure of the films was characterized by X-ray diffraction (XRD). Surface morphology and the composition were characterized by field emission scanning electron microscope (FE-SEM). Transport property measurement system (TPMS) was used to characterize the electrical resistivity (ρ), the Seebeck coefficient (S), magnetoresistance, and the Hall effect (R_H).

3. Results and discussion

The XRD patterns as shown in Fig. 1 (a, b) indicated an orthorhombic crystal structure in both films. From the XRD data, the lattice parameters of the orthorhombic MnP thin film grown at 400 °C were determined to be a = 5.839 Å, b = 3.164 Å, and c = 5.301 Å. By comparing the lattice parameters of this film with those of bulk MnP, compress strain along a and b axes of the MnP thin film on Si (1 0 0) is determined. FE-SEM images as shown in Fig. 1(c, d) indicated that MnP nanorods can be grown on Si (1 0 0) at 300 and 400 °C using MBE. Furthermore, all nanorods were vertically grown on the substrate surface and the size of nanorods increased in the film grown at 400 °C as compared to the film grown at 300 °C. FE-SEM images confirmed the formation of a close-packed structure at 400 °C.

Magnetic properties of the MnP nanorod thin films are presented in

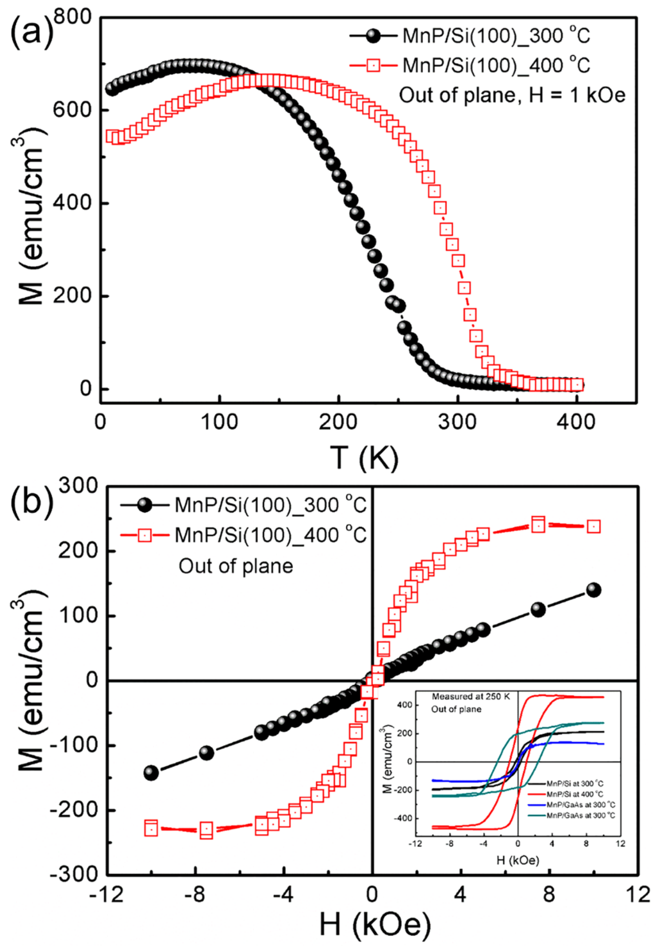

Fig. 2. (a, b) The temperature dependent field cooled (FC) magnetization curve measured with 1 kOe out of plane magnetic field applied to the film and (b) hysteresis loops at 300 K of MnP nanorod thin films grown on Si (1 0 0) substrates at 300 and 400 °C. Inset is hysteresis loops of MnP thin films grown on Si (1 0 0) and GaAs substrates at 300 and 400 °C.

Fig. 2. The temperature dependence of field cooled (FC) magnetization with an applied out of plane magnetic field of 1 kOe to the film (as shown in Fig. 2(a)) indicated a ferromagnetic behavior in both films. The shape of the M − T curve of the film is similar to that of bulk MnP. Relative to the bulk MnP, the Curie temperature (T_C) decreased to 275 K in the film grown at 300 °C, while it increased to 325 K in the film grown at 400 °C. The Curie temperature in nano-structured materials is strongly dependent on the size of particles. For the small size of particles, the Curie temperature drastically decreases as the fluctuations of electron spins become more prominent. In the MnP film grown at 400 °C, the size of nanorods increases as compared to the MnP film grown at 300 °C. So that, the closely packed structure was created. This could be a possible reason for the increase of the Curie temperature in the film grown at 400 °C. Magnetic field vs. out of plane magnetization (MH) plots at 300 K are shown in Fig. 2(b). At 300 K, the ferromagnetic behavior of the film grown at 400 °C is still observed, while it disappeared in the film grown at 300 °C. We note that, in this measurement, the external magnetic field was out of the plane to the film, so the coercivity in the easy axis direction is small. The inset of Fig. 2 (b) showed the magnetic field dependent out of plane magnetizations at 250 K of the MnP films grown at 300 and 400 °C on Si(1 0 0) and GaAs substrates, respectively. The saturation magnetization and coercivity of the MnP film grown at 400 °C are higher than those of the film grown at 300 °C. The results indicated that 400 °C is an optimal growth temperature for achieving the high magnetic properties of a MnP thin film.

Electrical transport under magnetic field for MnP nanorod thin films are present in Fig. 3. The anomalous Hall effect (AHE) which is the result of asymmetric scattering in the presence of the intrinsic magnetization was observed in both the films. Note that, Hall resistivity is expressed as $\rho_{xy} = R_o\mu_0 H + R_s\mu_0 M$, where M is the perpendicular component of the magnetization, R_o is the ordinary Hall coefficient, and R_S is contribution from the AHE [20–22]. So, the presence of the AHE hysteresis loops strongly suggest a ferromagnetic ordering. Here, as shown in Fig. 3(a, b) a strong anomalous Hall effect was observed in the temperature range of 50 to 250 K. These results indicate a ferromagnetic ordering in MnP nanorod thin films on Si (1 0 0) substrate. The disappearance of hysteresis loop in the R_H-H plots at 300 K indirectly confirm that T_C of MnP nanorod films is around room temperature. Magnetoresistances (MR) vs. magnetic field of MnP nanorod thin films were shown in Fig. 3 (c, d). The negative MR, which is induced by the decrease in the scattering centers of a sample when magnetic field increased, was observed in both the thin films. In the film grown at 300 °C, negative MR was observed at below 300 K and butterfly shape of MR appears at below 200 K. In the film grown at 400 °C, the negative MR was changed to positive MR below 50 K and butterfly shape appears at 100 K. The modification from negative to positive MR corresponds to the decrease in magnetic moment of the MnP thin film on lowering the temperature. The maximal MR of the film grown at 300 °C is 1% at 20 K, while it is 2% at 100 K for the film grown at 400 °C.

Temperature-dependent resistivities (R-T curves) for the MnP nanorod thin films are presented in Fig. 4 (a). The increase of resistivity with increasing temperature in both films demonstrated a metallic behavior. However, at above 150 K, the slope of the R-T curves decreased and then mostly saturated at temperatures higher than the T_C. The electrical resistivity of a ferromagnetic material was mainly contributed by the scattering of conduction electrons with lattice vibrations (phonons scattering) and magnetic spin system (spin waves scattering). So, the reduced slopes of the R-T curves above 150 K are attributed to the reduced spin waves scattering due to the reduced magnetization. A saturation trend in resistivity was observed above the T_C, where the magnetic transition occurs in the film. As compared to the film grown at 300 °C, the strong reduction of resistivity in the film grown at 400 °C

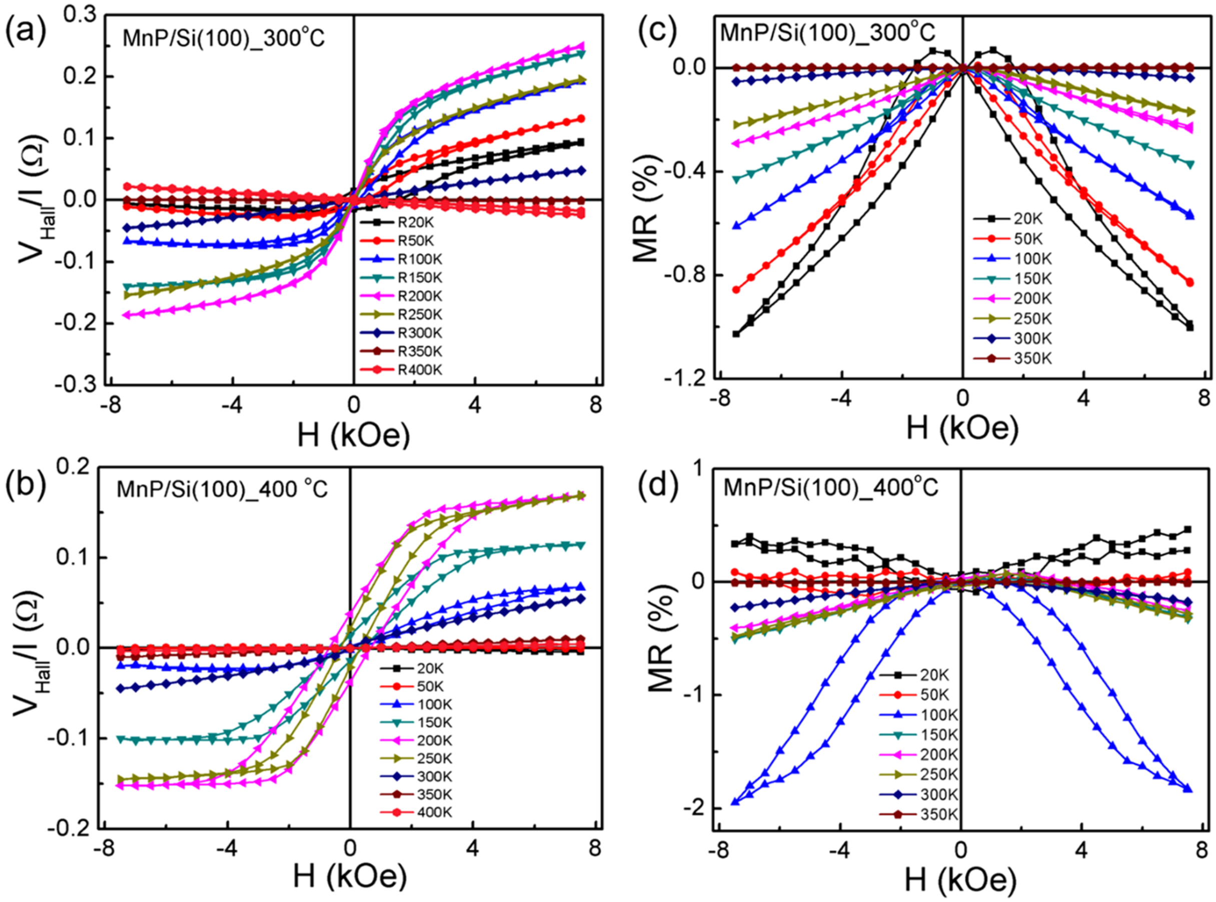

Fig. 3. (a) R_H versus the external magnetic field *(H),* (c, d) Magnetoresistance (MR) versus H at selected temperature of MnP thin films grown at 300 °C and 400 °C, respectively.

can be explained by the decrease of conduction electrons scattering when the distance between nanorods decreased. The thermoelectric power factor (PF = S^2/ρ, where S is Seebeck coefficient as shown in the inset of Fig. 4 (b), ρ is the resistivity), which characterizes for converting heat energy to electrical energy, is shown in Fig. 4 (b). The PF values increased with increasing temperature for both films. Above 290 K, the PF value of the film grown at 400 °C increased rapidly, and the maximum PF value of this film is three orders of magnitude higher than that of the film grown at 300 °C.

4. Conclusions

The MnP nanorod thin films with an orthorhombic structure have been grown on Si (1 0 0) substrates at 300 and 400 °C by using MBE. Size of nanorods increased so that the close-packed structure of MnP nanorods was constituted at 400 °C. The anomalous Hall effect and negative magnetoresistance confirmed a ferromagnetic ordering. The increase of T_C in the MnP film grown at 400 °C is attributed to the increase in size of the MnP nonorods. Both films showed a metallic behavior. The decrease of resistivity originated at the decrease of conduction electrons scattering when the distance between nanorods decreased due to the close-packed structure is a major cause of the high-power factor above 300 K in the MnP film grown at 400 °C.

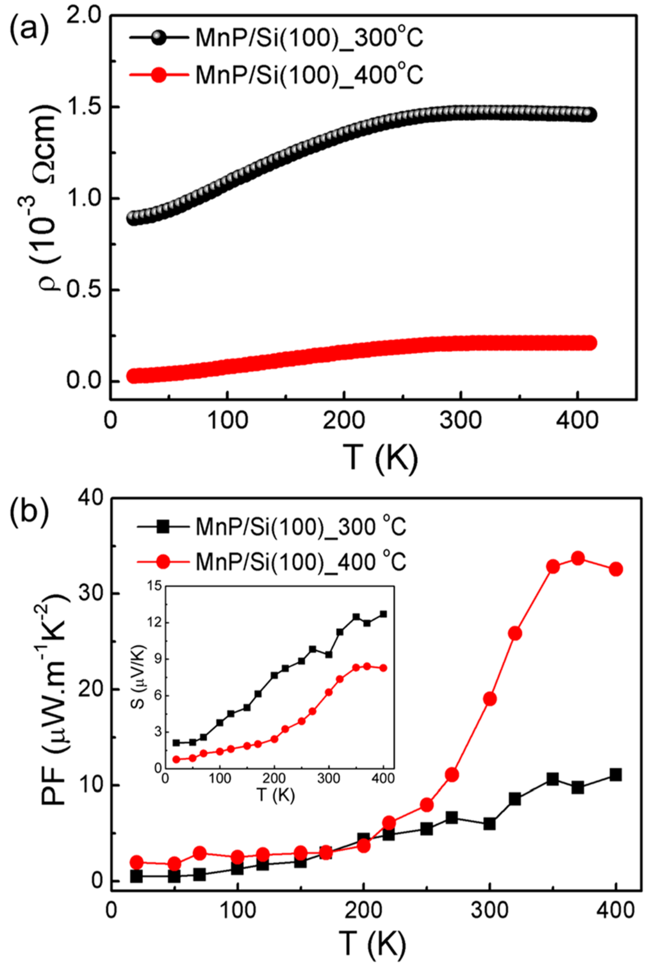

Fig. 4. (a) Temperature dependent resistivity and (b) thermoelectric power factor of MnP thin films grown at 300 °C and 400 °C. Inset of (b) is Seebeck coefficient of MnP films.

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