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Net-like ferromagnetic MnSb film deposited on porous silicon substrates

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Abstract

MnSb films were deposited on porous silicon substrates by physical vapor deposition (PVD) technique. Modulation effects due to the substrate on microstructure and magnetic properties of the MnSb films were studied by scanning electron microscope (SEM), X-ray diffraction (XRD) and measurements of hysteresis loops. SEM images of the MnSb films indicate that net-like structures were obtained because of the special morphology of the substrates. The net-like MnSb films exhibit some novel magnetic properties different from the unpatterned referenced samples. For example, in the case of net-like morphology, the coercive field is as low as 60 Oe.

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1. Introduction

The fabrication of patterned submicro- /nano-sized ferromagnetic elements has attracted significant attention due to their remarkable properties and varied industrial applications [1–5]. As has been reported, there are several different procedures that can be adopted to prepare patterned magnetic element, e.g. various lithographic techniques [3], using modulated substrates [5,6] and chemical self-assembly method [7]. The reduced dimensions and patterned structure of the magnetic materials have strong effects on the fundamental magnetic properties [3–5]. Sun and Akinaga [5] deposited the cobalt films on the anisotropic noodle-like porous silicon substrates. They found that the coercivity of the cobalt films is enhanced as compared to the unpatterned Co films because of a modulation effect due to the substrate. On the other hand, submicrometric structures of amorphous Fe_xSi_{1-x} prepared by electron beam lithography exhibited the softest magnetic behavior with coercive field values as low as 9 Oe [3].

Different patterned structures of magnetic materials will result in various novel magnetic properties. When the magnetic element is patterned as an interconnected net-like structure, soft magnetic behavior will be expected for such a system due to the smaller demagnetizing field within the net-like structure. In this work, to obtain magnetic arrays with low coercivity, net-like MnSb ferromagnetic films were deposited on porous silicon substrates due to the modulation effect of the substrates. The MnSb film was selected mainly because it has a high Curie temperature (314 °C) and a high saturation magnetization ($4\pi M_s = 9.5$ kOe) [8]. These properties of MnSb make it a very promising candidate in the magneto-optical applications.

2. Experiment

The porous silicon (PS) substrates were made in darkness by electrochemical etching of boron-doped Si wafers with a resistivity of 1–10 Ω cm in a 12% hydrofluoric

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acid (HF) solution under a current density of 12 mA/cm^2 for 60 min. After etching, the samples were rinsed with de-ionized water and then immersed in ethanol for several minutes before drying by N_2. The MnSb films were grown directly on PS substrates by physical vapor deposition (PVD) technique. The deposition was carried out in a horizontal furnace. High-purity Mn (99.8%) and Sb (99.99%) were used as source materials. The source temperatures of Sb and Mn were kept at 450 and 850 °C during the deposition, respectively. During deposition of the films, the PS substrates were held at 250 °C, and the pressure of quartz tube was 4×10^{-9} bar. The deposition process was kept for 2 h with a deposition rate of about 300 nm/h.

For X-ray diffraction (XRD) measurements, X'Pert Pro MPD diffractometer was used with a Cu Kα source in a θ–2θ mode. Scanning electron microscopy (SEM) analysis was performed with a Hitachi-S4100. The magnetic hysteresis loops of the films were measured by an alternative gradient magnetometer (AGM) at room temperature.

3. Results and discussion

The morphology of the PS substrates was characterized by SEM before deposition of MnSb films. Due to the etching of HF, a net-like porous surface of the PS substrate was formed, as shown in Fig. 1. As can be seen, the net-like porous surface is maze-like, containing densely distributed pores and walls. The pores are found to have average diameter of hundreds of nanometers and walls have an average thickness of as the same order to the diameter of the pores. The depth of the pores can be varied depending on the time scale of electrochemical process. In the present work, the pores were about 10 μm deep.

Fig. 2 presents both plane view and cross-section SEM images after deposition of a 1-μm-thick MnSb film on the PS substrate. One can see from Fig. 2 that the MnSb film deposited only on the wall of the PS substrate, and inside of pores was void. The MnSb film exhibits the same net-like morphology as the PS substrate due to modulation effects of the substrate. The net-like MnSb film is well interconnected with the dimension of submicrometer.

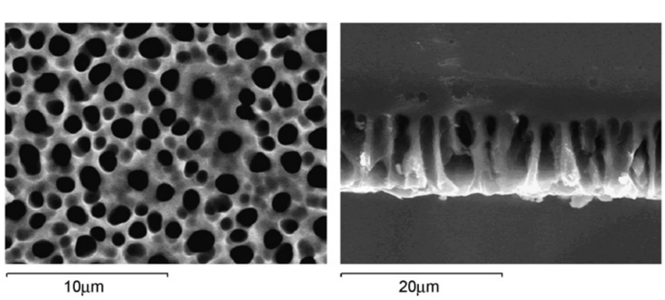

Fig. 1. Plane view and cross-section SEM images of the PS substrates prior to deposition of the MnSb films.

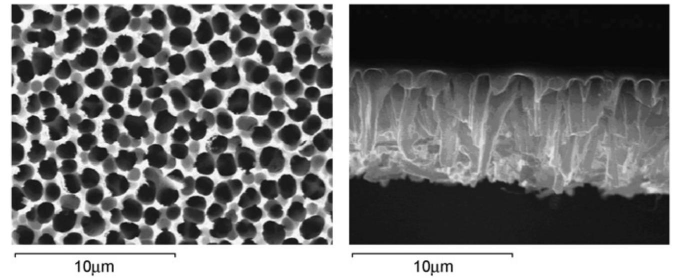

Fig. 2. Plane view and cross-section SEM images after deposition of a 1-μm-thick MnSb film on the PS substrate.

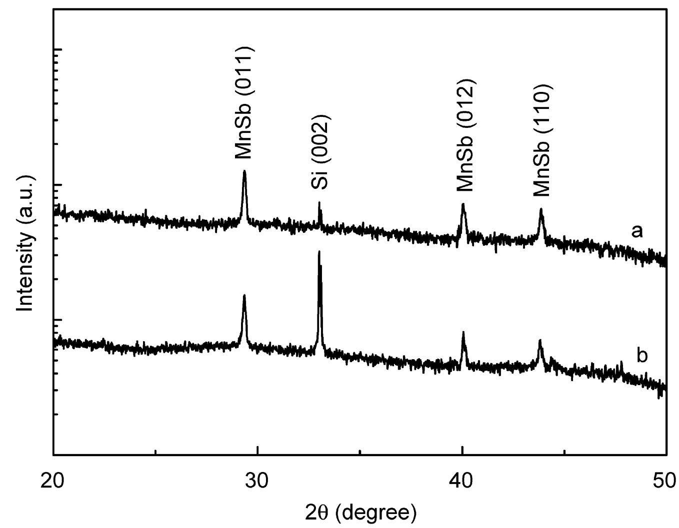

Fig. 3. XRD patterns of (a) the net-like MnSb film on the PS substrate and (b) the referenced film on the single-crystal Si.

To obtain structural information, a 1-μm-thick net-like MnSb film grown as above was examined by XRD in a normal θ–2θ configuration. The corresponding XRD pattern is presented in Fig. 3 with each Bragg peak assigned its identification and Miller indices. Obviously, the hexagonal NiAs structure MnSb phase is uniquely formed through the solid-phase reaction of Mn and Sb in both films. Three MnSb reflection peaks with proportionable intensity are observed in Fig. 3, indicating polycrystalline characteristics of the MnSb film. Due to its porous feature, the surface of the PS substrate is easily oxidized into silicon oxide. Hence, it is reasonable that the polycrystalline MnSb was formed on the surface of amorphous silicon oxide. Additionally, besides the expected MnSb diffraction peaks, one can clearly observe the normally forbidden Si (0 0 2) reflection at 33.02°, which is considered to be resulting from harmonics in the X-ray beam and/or multiple scattering [9]. The XRD pattern of a referenced MnSb film deposited on a smooth single-crystal Si substrate with the same growth conditions is also presented in Fig. 3, revealing a similar polycrystalline characteristic as for the net-like MnSb film on porous silicon substrate.

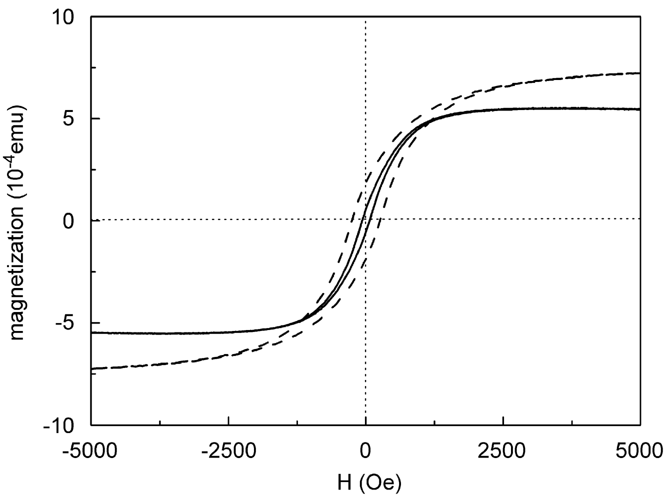

Fig. 4. Magnetic hysteresis loop of the net-like MnSb film on the PS substrate (solid line) and the referenced MnSb film (dash line) with magnetic field applied parallel to the film surface.

To investigate the magnetic properties of the net-like MnSb film, magnetic hysteresis loop of the MnSb film was measured by AGM by applying the magnetic field parallel to the film surface at room temperature, and the corresponding result is given as solid line in Fig. 4. In order to further clarify the net-like structure effects on magnetic properties, the magnetic hystersis loop of the referenced MnSb film on the single-crystal Si substrate is presented as a dash line in Fig. 4. The magnetizations in Fig. 4 are not normalized, since the amount of MnSb material on the PS substrate is hard to evaluate. Hence, the values of saturation magnetization, M_s is not comparable. Here, the most interesting is the difference in the coercivity for both samples as indicated in Fig. 4. The coercive field for the net-like MnSb film and the referenced sample are determined to be ~60 and 239 Oe, respectively. The coercivity of 239 Oe for the referenced MnSb film is in good agreement with the value of 257 Oe for the epitaxial MnSb film on GaAs substrates reported by Low et al. [8]. Obviously, the coercivity of the net-like MnSb film is much smaller than that of the unpatterned counterpart. SEM images have revealed that the present MnSb films are made up of net-like morphology due to the modulation of the PS substrate, with typical dimensions of submicrometer grid width and ~1 μm diameter of net pore. The net-like MnSb film can be regarded as many magnetic loops. When the magnetic field is applied parallel to the surface of the samples, the smaller demagnetizing field is obtained within the loop structure as close magnetic lines are formed.

It has been reported that the lateral dimensions decrease below 1 μm, a hardening of the magnetic material is observed because of the high valve of the demagnetizing field, so that the coercive and saturation field of the structures increase by at least one order of magnitude with respect to the unpatterned material [10]. This result could be an undesirable effect to fabricate certain devices. It turns out that in the case of net-like morphology, the coercive field is as low as 60 Oe because of the special structure. It would be an effective method to use this ferromagnetic element into some devices that need soft ferromagnetic material, such as inductance material and so on.

Besides the smaller coercivity, the net-like MnSb film exhibits lower squareness ($M_r/M_s = 0.28$, M_r, remanent magnetization, M_s, saturation magnetization) compared to the referenced MnSb sample ($M_r/M_s = 0.37$). It should be noted that the referenced MnSb film is also polycrystalline as revealed by its XRD pattern. Therefore, the effects of the crystalline orientation on the squareness can be excluded. It suggests that the different magnetic interaction mode resulting from the net-like structure can play an important role for the decreasing squareness within the net-like MnSb film. Further investigation is required to comprehend the results profoundly.

The porous silicon substrates with different pore depths from 5 to 20 μm were prepared by varying the electrochemical etching times. The magnetic properties of the MnSb films deposited on these different porous silicon substrates are similar. Such results are reasonable, since the MnSb film is deposited only on the wall of the porous silicon substrate as revealed in Fig. 2. Additionally, the pore diameter of porous silicon substrates can be adjusted within a narrow range (±20%) under our experimental conditions. Thus, the microstructure of porous silicon has little effect on the magnetic properties of the samples in the present work.

4. Conclusion

In summary, the net-like MnSb films, with typical dimensions of sub micrometer grid width and ~1 μm diameter of net-pore, have been prepared by PVD due to the modulation of the porous silicon substrate. Such net-like structure of the MnSb film resulted in some novel magnetic properties. The coercive field (~60 Oe) of the net-like MnSb film is much lower than that of the referenced smooth MnSb film. Additionally, the net-like MnSb film exhibited the lower squareness in the *M–H* loops.

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