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Ferromagnetic MnSb Films Consisting of Nanorods and Nanoleaves*

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Abstract: Ferromagnetic MnSb films were synthesized on Si wafers by physical vapor deposition. X-ray diffraction revealed that the films primarily consisted of MnSb alloy. Nanorods and nanoleaves were observed in the MnSb films by field-emission scanning electron microscopy. These nanorods had an average diameter of 20nm and a length of up to hundreds of nanometers. The nanoleaves had a width and thickness of about 100 and 20nm, respectively. Magnetic hysteresis loops were measured by an alternative gradient magnetometer, and the loops showed strong geometrical anisotropy.

Key words: ferromagnetic; MnSb; nanorods and nanoleaves; physical vapor deposition
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1 Introduction

In recent years, there has been an increased interest in the incorporation of ferromagnetic materials into semiconductors because it offers a unique opportunity for a new generation of multifunctional devices that utilize conventional charged-based microelectronics with the addition of the spin degree of freedom[1~4]. Such coupling of electron charge and spin has led to interesting applications such as "spin field effect transistors"[5], "spin valves"[1], and "spin qubits"[6]. Ferromagnetic manganese antimonide (MnSb) has a NiAs-type structure with lattice constants of $a = 0.4128$nm and $c = 0.5789$nm[9], and its Curie temperature is reported to be 314℃[10]. Theoretical calculations[7] predict that MnSb with a zincblende (ZB) structure will show half-metallic ferromagnetism. In a half-metallic system, there is only one electronic spin direction at the Fermi energy, and therefore such a system has many unique properties and is an ideal component for spintronic devices[4]. MnSb merits special attention because of its numerous applications, such as thermomagnetic writing, erasable magnetic holography, magneto-optic readout using laser beams, and many others[8]. A great number of deposition processes[11~16], including molecular beam epitaxy (MBE), direct current sputtering, and hot wall epitaxy, have been reported for preparing MnSb films. On the other hand, currently there is considerable scientific and technological interest in magnetic nanostructures from theoretical, experimental, and device perspectives, since they show many novel properties that enable high integration densities. The final goal for ultrahigh magnetic storage applications is the fabrication of only one magnetic domain in one single nanostructure; this could then be used as one magnetic binary digit with two possible magnetization orientations corresponding to a "0" or a "1"[17]. Low *et al*. have reported MnSb films consisting of small and densely packed rectangular grains with diameters in the range of 170~1000nm[12], while Mizuguch and co-workers have reported the fabrication of nanoscale MnSb dots[14]. So far, no MnSb film consisting of other nanostructures has been

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reported yet. In this letter, we present MnSb films consisting of nanorods and nanoleaves on Si substrates synthesized by physical vapor deposition (PVD) in the absence of any metallic catalyzer.

2 Experiments

The MnSb films on Si substrates were prepared in a PVD system, using Mn and Sb metals as source materials. The growth chamber is a horizontal quartz tube, about 30mm in diameter. Firstly, cleaned Mn metal was placed in a quartz boat located at the center of the quartz tube. The Si substrates were rinsed successively by tetrachloromethane, acetone, ethanol, and de-ionized water in ultrasonic baths, and finally blown dry with nitrogen gas. Then the substrates were introduced into the quartz tube. The growth tube was evacuated to a pressure of 0.4mPa, and then after the quartz boat was heated to a temperature of 850℃, the Mn was evaporated and the deposition was initiated. During the growth of Mn, the substrate temperature was kept at a constant of 400℃. The Mn films were deposited for 2h. Then, the Sb films were deposited on the Mn/Si substrates in the same system with a clean quartz tube. The Sb source temperature was controlled at 450℃, and the substrate temperature was about 200℃. The Sb films were deposited for 1h. Finally, the samples were annealed at 350℃ for 20min under N_2 atmosphere, and the black-gray MnSb/Si films were obtained. The surface morphology of the MnSb films was observed by field-emission scanning electron microscopy (SEM). The structures of the films were measured by X-ray diffraction (XRD).

3 Result and discussion

Figures 1 (a) and (b) show the typical surface morphology of the MnSb film observed by field-emission SEM with different magnifications. It can be seen from Fig. 1 (a) that the MnSb film consists of the nanorods and nanoleaves. As shown in Fig. 1 (a), there is good uniformity in both the overall structure of the nanorods and nanoleaves and the individual elements. It can be determined from Fig. 1 (b) that the nanorods have a diameter and length of approximately 20nm and hundreds of nanometers, respectively. The nanoleaves have a width and thickness of about 100 and 20nm, respectively. The nanostructures occupied about 50% of the whole film.

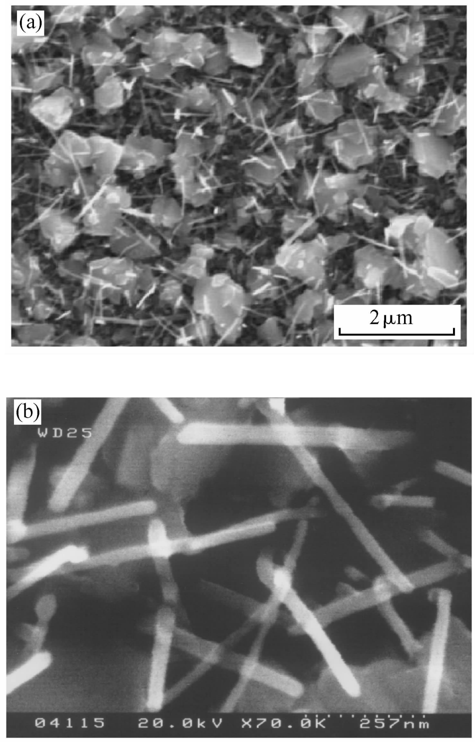


Fig. 1 Field-emission SEM photographs of MnSb film with different magnifications

A characteristic XRD pattern of the MnSb film is shown in Fig. 2. The two peaks at 29.46° and 40.08° are due to (011) and (012) reflections of MnSb, respectively, indicating that the primary MnSb phase was formed through the solid phase reaction of Mn and Sb in the films. Besides the MnSb phase, the diffraction peaks from Sb_2O_3 and Mn_3O_4 were also observed in the present spectrum, implying that the Mn and Sb did not react

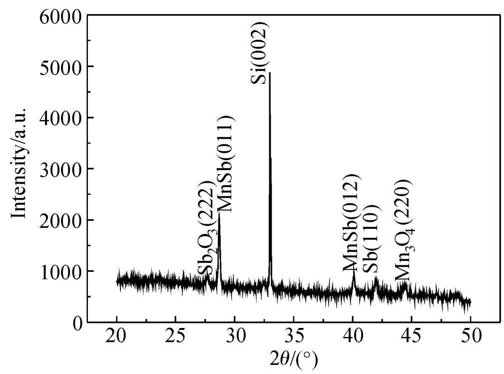
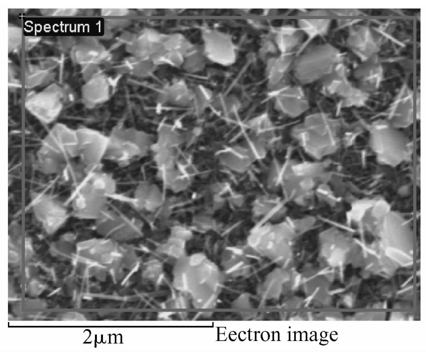


Fig. 2 A typical X-ray diffraction pattern of the MnSb film

completely. Additionally, the peak at 33.08° is assigned to the normally forbidden Si (002) diffraction, which was induced by crystal defects.

To check up the composition of the nanorods and nanoleaves, energy dispersive X-ray spectroscopy (EDS) measurements were carried out for the present sample. The corresponding results are shown in Table 1. The scanning area is also shown in Table 1, and it basically occupies the whole area of Fig. 1(a). It can be seen that the content of Mn is slightly higher than that of Sb in the film. Based on the XRD and EDS results, especially the stronger MnSb XRD peaks, the nanostructures are considered to be composed of the MnSb phase. There is high content of Si in the measuring result just because the film consists of isolated nanostructures and it cannot cover the substrate completely. The electron beam with high energy (the accelerated voltage was 14.28keV) broke down the film and diffused in the substrate, exciting the characteristic X-ray of Si. Additionally, the oxygen content was found to be 11.57%, which was contained in Mn and Sb oxide as indicated in the XRD pattern, due to oxidized silicon on the Si substrates and the adsorbed oxygen on the film.

Table 1　Results of energy dispersive X-ray spectroscopy of the film

Element	Weight %	Atomic %	Scanning area
O	5.91	11.57	
Si	71.12	79.41	
Mn	9.88	5.64	
Sb	13.09	3.37	
Totals	100.00	100	

Magnetic hysteresis loops of the film were measured by an alternative gradient magnetometer (AGM) at room temperature. The loops with H parallel ($H_{//}$) and H perpendicular ($H_{\perp}$) to the plane for the MnSb film are shown in Fig. 3, from which it can be concluded that the film is ferromagnetic. Since Mn is antiferromagnetic and Sb is non-ferromagnetic, the observed ferromagnetism probably originated from the MnSb phase. The magnetic hysteresis loops showed strong geometrical anisotropy. In the case in which H was parallel to the plane, the magnetization reached saturation at a low value of 1.5kOe, while in the case in which H was perpendicular to the plane, the magnetization hadn't yet reached saturation at a high value (about 15kOe). This means that the easy axis of the MnSb film is parallel to the plane. The hysteresis loops of this film with $H_{//}$ and $H_{\perp}$ to the plane are very similar to the results reported by Chen *et al*.[10].

To get the detailed parameters, the $H_{//}$ magnetic hysteresis loop is replotted in the inset of Fig. 3. The value of the saturation magnetization, the ratio between remanent magnetization and saturation magnetization (M_r/M_s) and the coercivity (H_c) is 5.80emu/cm^3, 0.1073 and 53Oe, respectively. It can be found that the saturation

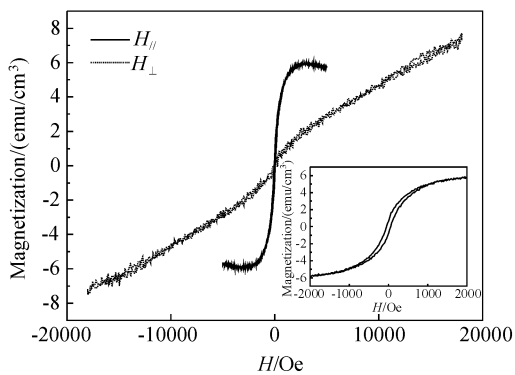


Fig. 3　Magnetic hysteresis loops of the MnSb film with magnetic field H perpendicular and parallel to the film plane, respectively

magnetization and remanent magnetization of this nanostructure film are smaller than those of other MnSb films[10]. There are two factors that may have an effect on the magnetization. The present film was prepared by PVD and the grains are isolated, and thus the bulk of the film cannot be calculated accurately. Secondly, the film is composed of several phases, and besides the magnetic MnSb phase, there are some nonmagnetic phases in the film. Both factors will result in lower values of magnetization.

4 Summary

In summary, MnSb films on Si were grown via a PVD method and then annealed. The MnSb films consisted of the nanorods and nanoleaves. The films were shown to be ferromagnetic at room temperature. The magnetization hysteresis loops showed obvious geometrical anisotropy.

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由纳米棒和纳米叶组成的铁磁性的 MnSb 薄膜*

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摘要：提供了一种利用物理蒸发沉积技术在单晶硅上生长纳米尺度的 MnSb 薄膜的方法. X 射线衍射分析表明薄膜的主要成分是 MnSb 合金. 场发射扫描电镜观察到薄膜是由纳米尺寸的棒状物和叶状物组成. 纳米棒的平均直径为 20nm，长度在几百纳米范围内. 纳米叶的厚度大约为 20nm，宽度为 100nm 左右. 用可变梯度磁力计测量了薄膜的磁滞回线，结果显示薄膜有很强的几何各向异性.

关键词：铁磁性；MnSb；纳米棒和纳米叶；物理气相沉积

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