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Growth of MnSb Thin Films on CdTe Substrates by Hot-Wall Epitaxy

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Ferromagnetic MnSb thin films were grown on CdTe (110) substrates for the first time by hot-wall epitaxy (HWE) technique using polycrystalline powders of MnSb as an evaporation source. The crystal orientation of these thin films was determined by X-ray diffractometry (XRD). The chemical composition of the films was determined by means of electron-probe microanalysis (EPMA) and by electron spectroscopy for chemical analysis (ESCA) depth profiling. Polar magnetooptical Kerr rotation spectra were measured in the 1.2 eV to 4 eV photon energy range.

KEYWORDS: CdTe, MnSb, epitaxial film, hot wall epitaxy, polar magnetooptical Kerr spectrum

In the last few years, hybrid structures consisting of magnetic thin films and semiconductor substrates have been attracting much interest as candidate materials for new device applications.[1] For this purpose, manganese pnictides such as MnAs and MnSb epitaxially grown on GaAs have been investigated.[2] These pnictides are known to crystallize in NiAs-type structure and be ferromagnetic at room temperature. Their magnetic and magnetooptical properties have been studied from the fundamental as well as applications points of view.[3-5] Magnetooptical spectra from polycrystalline MnSb materials were described by Buschow *et al.*[6] In bulk single crystals of MnSb large Kerr rotation at short wavelength was observed as reported by Tosaka *et al.* and Sato *et al.*[7,8] Magnetooptical effects of MnAs were measured in the spectral range of 1.3 eV to 2.6 eV by Stoffel and Schneider[9] and in the spectral range of 1.2 eV to 5.3 eV by Ikekame *et al.*[10]

In most of the previous studies on growth of manganese pnictide films III-V compounds were used as substarate materials. No film growth experiments involving use of II-VI compounds as substrate materials have been described in the litterature. Due to their applications in optoelectronics, integrated optics, thin film solar cells and semimagnetic semiconductors (SMS), II-VI compound semiconductors are of interest . Among these compound semiconductors, cadmium telluride (CdTe) is an attractive candidate for device applications because of its many useful characteristics: 1) It has an optimum band gap of 1.5 eV for solar energy conversion,[11,12] 2) combined with mercury, $Hg_{1-x}Cd_xTe$ it has great potential for applications in photonic detectors for wavelengths much longer than those obtainable with the III-VI semiconductors,[13-15] 3) combined with manganese, as $Cd_{1-x}Mn_xTe$, it is a semimagnetic semiconductor showing a giant Faraday effect caused by the exchange interaction between band carriers and localized magnetic moments of Mn^{2+} ions,[16] 4) it is the only one II-VI compound semiconductor in which homojunctions can be fabricated because it can be made in both n and p types, 5) the carrier concentration of CdTe can be changed easily by appropriate doping, which is promising for controlling carrier-induced magnetic interaction between ferromagnetic layers through RKKY interaction if CdTe is used as a spacer material in semiconductor/ferromagnetic hybrids and 6) HWE growth technology of CdTe has been well established. In addition, the lattice mismatch between MnSb and CdTe is much smaller than that between MnSb and GaAs, since the lattice spacing d_{220} of CdTe is 2.28 Å, which is much closer to d_{102} of MnSb than d_{100} of GaAs. The growth of high quality MnSb magnetic thin films on CdTe, combined with the above-mentioned useful characteristics of the substrate material, may lead to fabrication of new functional devices.

Crystal growth of MnSb films was performed in a conventional HWE system. The growth apparatus and the characterization methods are described in detail elsewhere.[17] The CdTe substrates were p-type doped single crystals, grown by the vertical Bridgman method |oriented to within ±0.5°, in the [110] direction|. They were p-type with a bulk-carrier density of 2×10^{15} cm^{-3}. This value was determined by Hall effect, C/V, and I/V techniques. The (110)-oriented surfaces were prepared by mechanical polishing of the single crystal with 0.3-μm aluminum oxide. The crystal was subsequently rinsed with deionized water, and then cleaned with trichloroethylene, acetone, and methanol in an ultrasonic cleaner. Finally, prior to insertion into the HWE chamber, the surface was etched with a solution of bromine in methanol (2 % in volume) to remove the uppermost layer.[18] The substrate was set in the HWE system on a molybdenum holder using indium contacts. The chamber was then evacuated to a pressure of 10^{-7} Torr, at which thermal cleaning of the substrate was carried out at 450 °C for 10 minutes. After the cleaning the substrate was cooled down to an appropriate temperature for MnSb thin films growth.

The MnSb evaporation sources were prepared as follows: polycrystalline MnSb was synthesized from elemental Mn and Sb by normal freezing technique, the details of which are described elsewhere.[19] The conditions for HWE growth of the MnSb thin films were as follows: 1) Source temperature, 700 °C; 2) substrate temperature, 300 °C to 400°C; 3) growth rate maintained at 0.1

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Å/s to 0.4 Å/s depending on the substrate temperature. At high temperature the grown films reevaporate resulting in film thinning; 4) typical growth time, 3 h, at which the film thickness was 1000–4000 Å.

These films were characterized as follows: structural properties were studied by X-ray diffractometry (XRD) using a Rigaku RAD-IIc diffractometer (Cu Kα-line). Compositions were determined by means of electron probe microanalysis (EPMA) using a JEOL JXA-8900R microanalyzer and by electron spectrometry for chemical analysis (ESCA) using a Shimadzu 8500 ESCA-SAM system. Polar magnetooptical Kerr rotation spectra were measured at room temperature for photon energies from 1.2 eV to 4 eV using a specially designed Kerr spectrometer developed in our laboratory.[20]

Typical XRD patterns of MnSb thin films grown by HWE on CdTe(110) surfaces at various substrate temperatures are shown in Figs. 1(b) and 1(c). In Fig. 1(a) an XRD pattern of a CdTe substrate is shown for comparison. At a substrate temperature of 300°C, the diffraction pattern of the film (Fig. 1(b)) shows a diffraction line which can be assigned to reflections from (20.1) planes from a hexagonal NiAs structure. A MnSb (10.2) diffraction line is believed to be buried in the foot of the CdTe (220) line. An indication of the (10.1) line of MnSb is also observed. As shown in Fig. 1(c), the film prepared at a substrate temperature of 320°C exhibits three distinct diffraction lines which can be assigned to reflections from (10.1), (10.2) and (20.1) planes from a MnSb thin film. The most prominent reflection comes from (10.2) MnSb planes. The intensity of the diffraction line corresponding to the (10.2) MnSb planes is comparable to the intensity of reflection from the (220) planes from the CdTe substrate. The difference in the angular positions, in 2θ values, between the (220) CdTe diffraction line and the (10.2) MnSb diffraction line is, from the literature, 0.83°.[21,22] In our experiment, the difference obtained in the angular positions in these two lines is smaller, 0.66°.

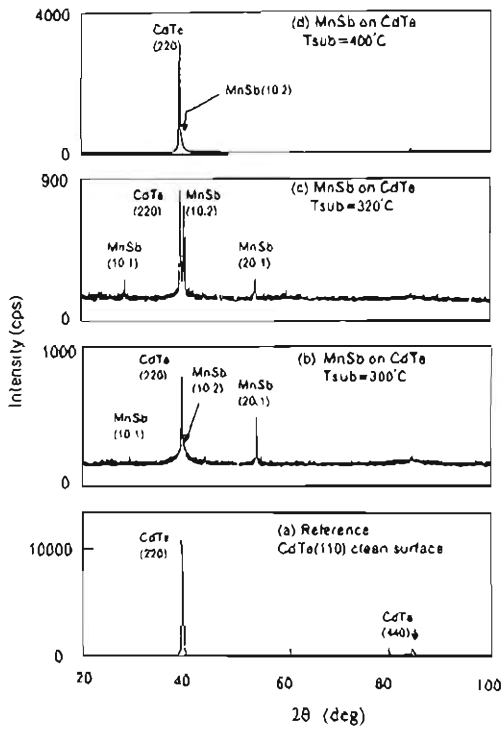

Fig. 1. Intensities of XRD lines vs 2θ from clean CdTe(110) substrate (a) and from MnSb thin films grown by HWE at substrate temperatures of 300°C (b), 320°C (c) and, 400°C (d).

For the film prepared at a substrate temperature of 400 °C, only one strong line assigned to the (220) diffraction of the CdTe substrate is observed in the XRD pattern as shown in Fig. 1(d). The MnSb (10.2) reflection is believed to be buried in the higher angle foot of the CdTe line, although it is not clearly resolved. This is because at high substrate temperatures the film thickness is much reduced due to the reevaporation of the MnSb, to as small as 1000 Å. By careful experimentation it is found that the MnSb (10.2) reflection is located at 39.75°, i.e., 0.87° higher than the position of the CdTe (220) line. The difference is close to the literature value of 0.83°. Other XRD lines were not observed.

From the results of the XRD studies described above, it is concluded that the orientation preference varies from (20.1) to (10.2) with increasing substrate temperature from 300 to 400°C. No prominent change in lattice constants with substrate temperature was observed in spite of the distinct change in the orientation preference.

The EPMA result indicates an Sb-rich composition for the films grown at substrate temperatures equal to or lower than 320°C and a stoichiometric composition within the experimental error (~3 at%) for all the films grown at higher substrate temperatures. The chemical composition of the thin films vs depth was analyzed by ESCA depth profiling. The X-ray excitation source used was a Mg-anode Kα-line and the sputtering gas was Ar^+ at 2 keV energy. The rate of sputtering was estimated as approximately 50 Å/min. The ESCA lines analyzed were Cd 3d, Te $3d_{3/2}$, Sb 3d and Mn $2p_{3/2}$. Figures 2 and 3 show plots of peak intensity vs sputtering time of ESCA depth profiling performed on the MnSb thin films grown at substrate temperatures of 320°C and 400°C.

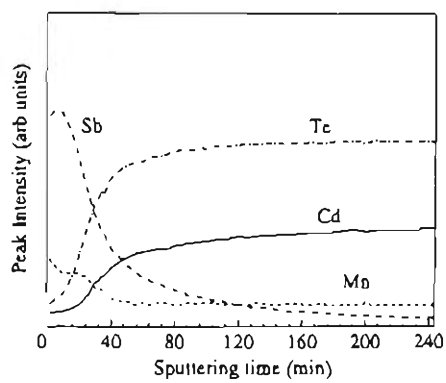

Fig. 2. Plot of peak intensity vs sputtering time of ESCA depth profiling performed on MnSb thin film grown at 320°C.

Table I. ESCA depth profile analysis.

Substrate Temperature °C	Sb at% Surface	Mn at% Surface	Cd at% Bulk	Te at% Bulk
320	70	30	44	56
400	49	51	44	56

respectively. Quantitative chemical analysis (within an experimental error of 10% for ESCA) of the surface and the bulk composition was performed using corresponding atomic sensitivity factors (ASFs) for each of the elements of which the concentration was determined. The calculated values are given in Table I. The values in Table I show that a stoichiometric composition is obtained in the film grown at a relatively high substrate temperature. In both films a quite marked interface is observed between the MnSb film and the CdTe substrate. The small tail observed for Sb in the plot of the depth profile in Fig. 2 is considered to be an artifact of the measurement, i.e. due to intermixing during the sputtering process. The interface is reached after 40 min of Ar^+ sputtering for the film grown at 320°C and after half of that time for the film grown at 400°C indicating that the sticking coefficient of Mn and Sb, consequently the film thickness, decreases with increasing temperature.

A polar magnetooptical Kerr effect was detected only in the sample prepared at 400°C. Figure 4 shows a polar magnetooptical Kerr rotation spectrum measured under a magnetic field of 1.7 T for a MnSb thin film grown on CdTe(110) at a substrate temperature of 400°C. The Kerr rotation steadily increases from $\theta_K = 0.08°$ at 1.4 eV until it reaches a maximum, $\theta_K = 0.09°$ at 1.7 eV. Above 1.7 eV a second region with decreasing θ_K exists up to a minimum at a photon energy of 2.87 eV. Above 2.87 eV there is a second increase in rotation until 3.6 eV where a second maximum, of less intensity, $\theta_K = 0.036°$ is obtained. Above this photon energy the Kerr rotation curve decreases continuously until it reaches zero at 4.1 eV. This type of inverted S curve with two maxima, within the same photon energy range, is observed also in the Kerr rotation spectra for MnSb bulk single crystals[9] and in MnSb thin films on GaAs (100) substrates grown by HWE.[7] The absolute value of maximum Kerr rotation is relatively small compared to the Kerr rotation value of a MnSb film on GaAs (100), which may be due to strong in-plane magnetic anisotropy, which leads to incomplete magnetic saturation in polar Kerr rotation. Detailed magnetic measurement is necessary.

In summary, MnSb thin films were grown on CdTe(110) substrates using an evaporation source of polycrystalline MnSb by HWE. For a substrate temperature of 400°C, preferential orientation of the MnSb (10 2) plane parallel to the (220) plane of the CdTe substrate was determined from the XRD spectrum. Only in the film prepared at 400°C was polar magnetooptical Kerr rotation detected. The chemical composition of the MnSb films grown at 400°C, determined by EPMA and by ESCA depth profiling, was stoichiometric. The ESCA depth profiles of the films indicate the presence of a well-defined interface between the films and the CdTe substrate. These results are quite useful for constructing well-defined MnSb/CdTe multilayers or superlattices, which should open up possibilities for realization of promising semiconductor/magnetic hybrids.

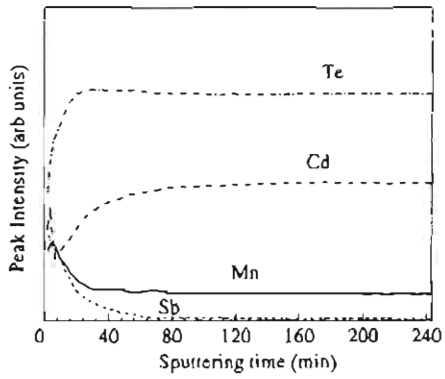

Fig. 3 Plot of peak intensity vs sputtering time of ESCA depth profiling performed on MnSb thin film grown at 400°C.

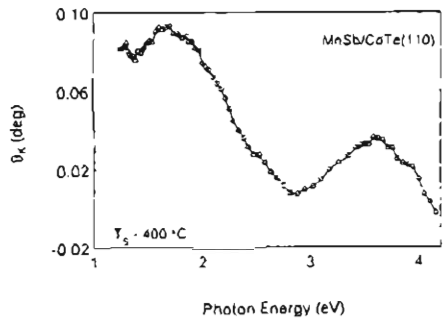

Fig. 4 Polar magnetooptical Kerr rotation spectrum of a MnSb thin film grown on CdTe(110) at a substrate temperature of 400°C.

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