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Crystallographic and magneto-optical studies of nanoscaled MnSb dots grown on GaAs

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MnSb ultrathin films with the nominal thickness of 0–1.40 nm were grown on sulfur passivated GaAs substrates by molecular beam epitaxy. Atomic force microscopy analysis showed that MnSb formed nanosize clusters on the substrate, and the coalescence of the clusters occurred at the nominal thickness between 0.70 and 1.05 nm. The intensity of the polar magnetic circular dichroism of MnSb clusters suddenly increased when the nominal thickness reached the critical value of 1.05 nm. The coalescence among the dots can be correlated with the sharp increase of the magnetic circular dichroism intensity. © *2000 American Institute of Physics.* [S0003-6951(00)01013-5]

Hybrid structures of nanoscaled manganese compounds and semiconductors are expected to exhibit interesting properties because of their various magnetic characters, or specific electronic structures at the interface between ferromagnetic materials and semiconductors.[1–7] We have reported upon the preliminary results of the cluster formation of manganese pnictides on GaAs substrates by using sulfur passivation technique.[8,9] It is well known that GaAs substrates terminated by VI-element atoms like sulfur or selenium have low surface energy, and several studies of forming nanocrystal of III–V compound semiconductors on the substrates have been reported.[10,11] This method is superior in terms that the sefl-assembled growth of metallic clusters on semiconductors can be easily performed. Although magneto-optical properties of manganese compounds have been extensively investigated,[12–16] no magneto-optical study on the nanoscaled ferromagnetic dots has been reported so far. In this letter, we show the formation and magneto-optical properties of nanoscaled MnSb dots grown on sulfur passivated GaAs substrates.

The samples were grown on semi-insulating GaAs (001) epi-ready substrates by a conventional molecular beam epitaxy (MBE) technique. To terminate the surface of GaAs substrates by sulfur, the substrate was dipped into an $(NH_4)_2S_x$ solution for 1h, then rinsed by pure water. After the thermal cleaning at 400–500 °C in ultrahigh vacuum, the reflection high energy electron diffraction from the surface showed the (1×1) pattern. The (1×1) streaky pattern remained unchanged at the growth temperature of 250 °C. The flux ratio of Sb/Mn was set at 4–5. The wedge-like MnSb film with the nominal thickness from 0 to 1.05 nm was fabricated using a linear shutter equipped in the growth chamber at 250 °C. Here, the nominal thickness means the thickness in case MnSb forms a uniform thin film.[17] It was verified that no contamination such as oxygen was detected before the deposition of MnSb by *in situ* Auger analyzer equipped with the growth chamber.

The surface morphology of samples was evaluated by *ex situ* atomic force microscopy (AFM) using the tapping mode. Four samples with a nominal thicknesses of 0, 0.35, 0.70, and 1.05 nm were investigated. Figure 1(a) shows the AFM image of the sample with a nominal thickness of 0.70 nm. The density of dots (the number of dots in an unit area) increased gradually from 0 to 0.70 nm, and almost saturated for more than 0.70 nm. The average densities of dots at 0.35, 0.70, and 1.05 nm were estimated from the AFM images to be about 6.3×10^{10}, 9.3×10^{10}, and 9.4×10^{10} cm^{-2}, respectively. No significant change of the average dot diameter (about 20–30 nm) was observed in the whole range of these nominal thicknesses. The average height of the dots was estimated by a cross-sectional analysis on each sample, as shown in Fig. 1(b). With increase of the nominal thickness, the average height increased gradually (from 2.2 to 2.5 nm). The increase in the average height is, however, much smaller than that in the amount of deposited atoms.

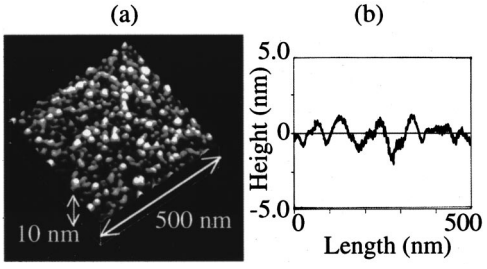

FIG. 1. (a) Atomic force microscopy image of MnSb dots grown at 250 °C. The nominal thickness is 0.7 nm. Clusters of MnSb self-arranged on GaAs have the density (the number of dots in a unit area) of about 9.0×10^{10} cm^{-2} and an average height of 2.0–3.0 nm. (b) The images of cross-sectional analysis on MnSb dots grown at 250 °C with a nominal thickness of 0.70 nm.

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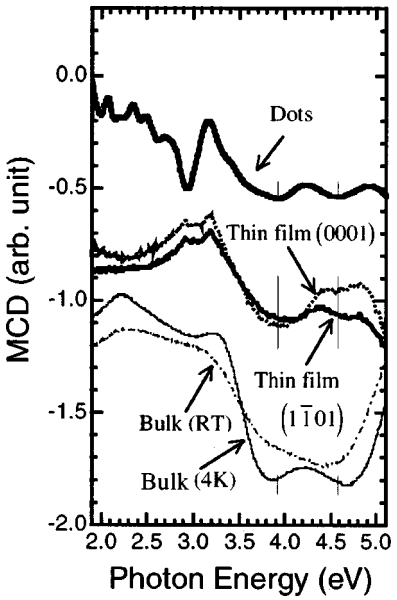

FIG. 2. MCD spectrum of MnSb dots (1.05 nm) is shown by a thick solid line. The magneto-optical signal of the GaAs substrate is subtracted from the MCD spectrum. For comparison, MCD spectra of (1101) and (0001) MnSb thin films (the thickness is 5 nm) obtained by the MBE growth on (001) and (111)B GaAs substrates are shown by solid and dotted lines, respectively. Measurements of dots and thin films were performed at room temperature (RT). MCD spectra of (1101) bulk MnSb measured at 4 K and RT are shown by solid and dotted lines, respectively (Ref. 14). Two bump structures observed at around 4.0 and 4.5 eV are indicated by vertical lines.

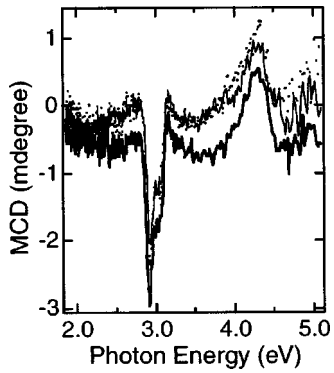

FIG. 3. The raw MCD spectra of MnSb granular films with various nominal thicknesses. The spectra of 0.35, 0.70, and 1.05 nm are shown in dotted, thin solid, and thick solid lines, respectively. Measurements were performed at RT. Sudden enlargement of spectrum is observed when the thickness exceeds 0.70 nm. It is noted that the additional structure observed at around 3.0 eV in the spectra arises from the existence of E_1 and E_0' peaks of the GaAs substrate.[19]

Assuming that each dot has a truncated cone-like shape as seen in AFM images, it is estimated that the coalescence among neighboring dots will start between the nominal thickness of 0.70 and 1.05 nm. This critical thickness can be calculated by the size of dots and the nominal thickness of MnSb. Over the critical thickness, the vertical growth will start. This estimation supports that the average density does not increase above 1.05 nm when the dots are grown at 250 °C.

To investigate the magneto-optical properties of MnSb dots, polar magnetic circular dichroism (MCD) measurements in a visible wavelength region were performed. For the measurements, we prepared another set of samples which were capped by Sb to prevent the oxidation. It was shown from our previous study that the oxidation of the surface of MnSb on GaAs (001) becomes active above 270 °C in the atmospheric condition, so it is considered that oxidation does not seriously occur.[18] However, this Sb cap layer was grown to make double sure of the MCD measurements. The thickness of the Sb cap layer was 10 nm, and the growth temperature was kept at 50 °C. In this letter, MCD θ is defined as follows:

$$\theta = \frac{180}{\pi}\left(\frac{R_+ - R_-}{R_+ + R_-}\right), \tag{1}$$

where R_+ and R_- express the reflectivities for σ_+ and σ_- lights, respectively. MCD spectra were measured using the monochromatic light from a Xe lamp in the wavelength ranging from 250 to 500 nm in the magnetic field of 1.88 T. A CD contribution was subtracted by reversing the magnetic field. The MCD signals from granular samples were very weak, so the signals were accumulated several times to improve the signal-to-noise ratio, and obtained the spectra by the smoothing procedure. Figure 2 shows the MCD spectrum of MnSb dots with the nominal thickness of 1.05 nm grown at 250 °C. For comparison, epitaxial (1101) and (0001) MnSb thin films (the thickness is 5 nm) grown on GaAs (001) and (111) substrates, and the epitaxial (1101) MnSb film (150 nm) are also shown. Two bump structures at around 4.0 and 4.5 eV were observed in the spectrum of the granular film. The structures commonly appear in all spectra. Our previous study revealed that the MCD spectrum of MnSb shows the crystal-orientation dependence.[14] When the incident light is normal to (1101) MnSb thin film, the spectrum measured at room temperature shows the bump structures at around 4.0 and 4.5 eV, and these relative intensities are almost identical. On the other hand, in the spectrum of the (0001) MnSb thin film the bump structure at around 4.5 eV becomes weak. Since the intensities of these two bumps are almost identical in the spectrum of the granular film, MnSb dots are supposed to grow in the same orientation with the MnSb (1101) epitaxial film, indicating that the preferential orientation occurs even though the surface is covered with sulfur. As shown in this figure, these bump structures are not seen clearly at room temperature in the spectrum of the bulk MnSb, although they become observable at low temperature (4 K). This fact may indicate that a broadening of the energy band structure in ultrathin films and the granular film is rather small even at room temperature. It is noted that the additional structure observed at around 3.0 eV in the spectra of ultrathin films and the granular film is due to the existence of E_1 and E_0' peaks of GaAs.[19]

Figure 3 shows MCD spectra of samples with nominal thicknesses of 0.35, 0.70, and 1.05 nm. The MCD θ intensity increases clearly when the nominal thickness exceeds 0.70 nm. It is thought that a magnetic *critical thickness* exists between 0.70 and 1.05 nm. The room-temperature saturation magnetization values of these samples measured by superconducting quantum interference device magnetometer also showed the sudden increase between 0.70 and 1.05 nm. The value of a sample with the nominal thickness of 1.05 nm is about three times as large as that of 0.70 nm. That of 0.35 nm is as large as that of 0.7 nm. Therefore, the increase of

MCD intensity is attributed to the increase of the saturation magnetization. Although the formation of a magnetic dead layer at the heterointerface is thought to be a plausible candidate as a reason for the increase of the saturation magnetization at first glance,[20–22] the following experimental observations indicate that the critical thickness below which the magnetization seems to be dead is not explained only by the magnetic dead layer at the interface:

(1) the change of the average height of dots is so small that the ratio of the dead layer thickness to the height of dots is considered not to depend on the nominal thickness;

(2) the cross-sectional transmission electron microscopy images (not shown in the present letter) has revealed that the interface between MnSb dots and GaAs substrate is very abrupt, and no intermixing occurs. One or two monolayers of sulfur are thought to prevent the chemical reaction at the interface.

The coalescence among dots may increase the saturation magnetization followed by the increase of the MCD intensity. The similar effect of the coalescence has been reported very recently in Fe/Cu ultrathin films.[23] The detailed chemical investigation of the heterointerface is in progress.

In conclusion, we have studied crystallographic and magneto-optical properties of MnSb dots grown on sulfur passivated GaAs (001) substrates. When the dots were grown at 250 °C, the density of dots increased with increase of the nominal thickness and saturated above 0.70 nm, while the average size of dots remained almost unchanged in the nominal thickness ranging from 0.30 to 1.05 nm. MnSb dots are thought to have the preferential orientation of MnSb (1101) judging from the MCD spectra. The MCD intensity of the dots with the nominal thickness of 1.05 nm showed the sudden increase, and the coalescence among the dots which occurs around 0.70–1.05 nm can be correlated with the sudden increase.

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