Characterization of FeSe thin films prepared on GaAs substrate by selenization technique

Y. Takemura, H. Suto, N. Honda, and K. Kakuno

Division of Electrical and Computer Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya, Yokohama 240, Japan

K. Saito

Department of Electronics and Information Sciences, Teikyo University of Science and Technology, 2525 Yatsuzawa, Uenohara, Yamanashi 409-01, Japan

FeSe thin films were prepared on GaAs(100) substrate by the selenization of Fe films using molecular-beam epitaxy. FeSe compound thin films were obtained at a substrate temperature above 380 °C. From the depth profiles of Fe and Se in the selenized film measured by Auger electron spectroscopy, it was confirmed that an FeSe layer with a constant ratio of Fe/Se was formed. The measured composition ratio of Fe/Se in the film was 1/3. It was different from the composition in Fe_3Se_4 or Fe_7Se_8 , which is a stable bulk FeSe compound. From the measured $M-H$ curve, it was found that the obtained FeSe film consisted of two phases with different magnetic properties.

© 1997 American Institute of Physics. [S0021-8979(97)31508-4]

I. INTRODUCTION

Magnetic semiconductors including Mn-related materials and semiconductor/magnetic metal hybrid structures have recently attracted much attention as new magnetic materials and their applications for electronic devices. Among them, Fe/ZnSe and FeSe/ZnSe systems are interesting because their thin films can be grown on a GaAs substrate.¹⁻³ In this article fabrication and characterization of FeSe thin films are reported. FeSe thin films are expected to be utilized as an interlayer for semiconductor/ferromagnetic metal heterostructures, or as a new magnetic material. Characterizations of bulk crystals of FeSe have been reported with Fe_3Se_4 and Fe_7Se_8 structures,^{4,5} but FeSe thin films have not been studied much. The lattice structure of bulk Fe_3Se_4 and Fe_7Se_8 is NiAs type with ordered Fe vacancies. The origin of the ferromagnetism of these materials is attributed to this ordered arrangement of Fe vacancies similar to the case of Fe_7Se_8 pyrrhotite. Curie temperatures of Fe_3Se_4 and Fe_7Se_8 are 314 and 455 K, respectively. Because of their lattice structures, they have a strong magneto-crystalline anisotropy along the c axis.

II. EXPERIMENTS

FeSe thin films were prepared on GaAs substrate by the selenization technique. A semiinsulating nondoped GaAs(100) substrate was used. Before the deposition of the Fe film, the substrate was chemically etched in a solution of $3\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ at 60 °C for 1.5 min, followed by successive rinses of acetone and methanol. The Fe thin film deposited on GaAs substrates by vacuum evaporation or sputtering was selenized in a molecular-beam-epitaxy (MBE) chamber as shown in Fig. 1. Conventional MBE equipment with solid sources was used. A typical thickness of the Fe films was 235 nm. The selenization was performed by supplying a Se beam from a K cell at substrate temperatures ranging from 260 to 530 °C for 1–4 h. The Se beam pressure was varied from 2×10^{-8} to 8×10^{-8} Torr.

The thickness and depth profiles of Fe and Se of the selenized films were evaluated in order to confirm the formation of FeSe. Auger electron spectroscopy (AES) was used for the measurement of the depth profiles. Electron dispersive x-ray spectroscopy (EDX) was used to determine the Fe/Se ratio in the films. As for magnetic properties of the films, $M-H$ curves were measured with a vibrating sample magnetometer (VSM) at room temperature.

III. RESULTS AND DISCUSSION

The thickness of the selenized films was measured. Because the vapor pressure of Se is as high as 0.1 Torr at 250 °C, the Se atom itself is not deposited on the Fe films by supplying a Se beam to the Fe films on GaAs substrate at substrate temperatures above 250 °C. The increase of the Fe film thickness by the selenization process is only caused by the formation of an FeSe compound. Figure 2 shows the total thickness of the films selenized for 1 h with Se beam pressure of 2×10^{-8} Torr at the various substrate temperatures. The total thickness is defined as described in Fig. 1. As the thickness of the Fe film before the selenization is 235 nm, selenization of the Fe does not proceed below the substrate temperature of 320 °C. It indicates that the substrate temperature is not high enough for the diffusion of Se atoms and reaction of Fe and Se. Above 380 °C the film thickness in-

FIG. 1. Schematic diagrams of the selenization process of Fe film on GaAs(100) substrate to prepare FeSe thin film in the molecular-beam-epitaxy equipment.

FIG. 2. Total thickness of the films selenized for 1 h with Se beam pressure of 2×10^{-8} Torr at substrate temperatures of 260–530 °C. The thickness of the Fe film before the selenization is 235 nm. Arrows indicate the calculated values assuming the formation of NiAs-type Fe_3Se_4 or Fe_7Se_8 .

creases, which can be understood by the formation of FeSe compound. The complex dependence of the total thickness on the substrate temperature is explained by the selenization rate and the reevaporation of Se atoms. The selenization rate is considered to increase with an increase in substrate temperature. It is because the selenization process consists of the diffusion of Se atoms and the chemical reaction of Fe and Se. On the other hand, with increasing substrate temperature the number of the reevaporated Se atoms increases, which results in a decrease of the selenization rate.

As for bulk FeSe compounds, Fe_3Se_4 and Fe_7Se_8 with a NiAs-type structure are stable. In Fig. 2 the calculated values of the total thickness are also indicated. In the calculation it is assumed that the whole Fe layer is selenized and that NiAs-type Fe_3Se_4 or Fe_7Se_8 are formed. The lattice parameters of $a = 0.354$ nm, $c = 0.558$ nm for Fe_3Se_4 , and $a = 0.362$ nm, $c = 0.589$ nm for Fe_7Se_8 are used, respectively.^{4,5} Thicknesses of the obtained films are not so different from the calculated values, but the structure of the films can not be determined from the figure.

Figure 3 shows the depth profiles of Fe and Se of the selenized film measured by AES. The sample was selenized at a substrate temperature of 380 °C with a Se beam pressure of 4×10^{-8} Torr for 4 h. The total thickness of the film was 250 nm. As shown in the figure, the profile pattern consists of two regions: region (a) and region (b). They correspond to the regions from the surface to the depth of 100 nm and from the depth of 100 nm to the substrate, respectively. In region (a) signals from Fe and Se are detected and it indicates that the whole Fe layer is selenized. The intensities of signals of Fe and Se are constant, which indicates that the layer consists of FeSe compound with a constant composition ratio of Fe/Se. If the layer consists of FeSe alloylike structure, the intensity of the AES signal of Se should decrease with increasing depth from the surface. The measured value of the composition rate of Fe/Se in this sample from the EDX measurement was 1/3. The result indicates that FeSe layer in region (a) is a Se-rich structure comparable to Fe_3Se_4 or Fe_7Se_8 .

FIG. 3. Depth profiles of Fe and Se measured from the selenized film of 250 nm thickness by Auger electron spectroscopy. Selenization was performed for 4 h with Se beam pressure of 4×10^{-8} Torr at the substrate temperature of 380 °C.

In region (b) the signal intensities of Fe and Se decrease toward the interface of the film/GaAs substrate. Since a signal from Se is observed near the interface, it is found that the whole Fe layer is selenized. The decreases of the signal intensities of Fe and Se are caused by the diffusion of Ga from GaAs substrate. In order to avoid the diffusion of Ga atoms, the duration of the selenization process should be reduced.

The measured $M-H$ curve of an FeSe film of 600 nm thickness is shown in Fig. 4. The sample was selenized at a substrate temperature of 460 °C with a Se beam pressure of 2×10^{-8} Torr for 1 h. The external magnetic field H was applied along the GaAs [011] axis (in plain of the film). The saturation magnetization M_S and remnant magnetization of the film are 120 and 41 emu/cm³, respectively. The obtained M_S is larger than the reported value of M_S in bulk Fe_7Se_8 (65 emu/cm³ at 290 K).⁴ The $M-H$ curve indicates that the sample consists of two phases with their coercive forces of about 300 and 2200 Oe. As for bulk Fe_3Se_4 and Fe_7Se_8 of NiAs-type structures, it has been reported that the c -axis

FIG. 4. $M-H$ curve measured on the selenized film of 600 nm thickness with a vibrating sample magnetometer. Selenization was performed for 1 h with Se beam pressure of 2×10^{-8} Torr at a substrate temperature of 460 °C. The external magnetic field H was applied along GaAs [011] axis (in plain of the film).

direction is magnetically hard and that the in-plane direction, perpendicular to the c axis, is magnetically soft. The double phase structure observed in the $M-H$ characteristic of the sample is presumably attributed to the mixed structures, for example, regions (a) and (b), as obtained in the AES profile, or to the mixed crystal orientation of the film. Although the reflection high-energy electron diffraction (RHEED) pattern of the sample indicates that the film is polycrystalline, the crystal orientation has not been determined.

IV. CONCLUSION

FeSe thin films were prepared on GaAs(100) substrate by the selenization technique. After the selenization process the thickness of the film increased, which corresponded to the formation of FeSe compound. By AES depth analysis it was confirmed that the Fe layer was selenized and that a FeSe layer with a constant ratio of Fe/Se was formed. The composition ratio of Fe/Se in FeSe film was measured to be 1/3 by the EDX measurement. Since bulk FeSe, Fe₃Se₄, and Fe₇Se₈ have been reported to be stable compounds, there is a possibility that a different crystal structure of FeSe thin film

was obtained from the selenization process. From the measured $M-H$ curve the obtained FeSe film consisted of two phases with different coercive forces. These results indicate that the obtained FeSe thin films have different structural and magnetic properties from bulk FeSe compounds.

ACKNOWLEDGMENTS

The authors would like to acknowledge Professor M. Konagai at the Tokyo Institute of Technology for the EDX measurement and Professor M. Naoe and Dr. N. Matsushita at the Tokyo Institute of Technology for the VSM measurement.

¹B. T. Jonker, J. J. Krebs, G. A. Prinz, and S. B. Qadri, *J. Cryst. Growth* **81**, 524 (1987).

²K. Park, L. Salamanca-Riba, and B. T. Jonker, 40th MMM Conference 1995, paper CQ-03.

³T. Abe, T. Kondo, Y. Shigeno, H. Munekata, J. Abe, H. Ikekame, and K. Sato, in Spring Meeting Jpn. Soc. Appl. Phys., 1996, paper 29a-W-7.

⁴T. Kamimura, K. Kamigaki, T. Hirose, and K. Sato, *J. Phys. Soc. Jpn.* **22**, 1235 (1967).

⁵A. F. Andresen, *Acta Chem. Scand.* **22**, 827 (1968).