Growth and electronic and magnetic properties of α-FeSe films on GaAs (001) substrates

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FeSe films have been grown on GaAs (001) substrates by low-pressure metal organic vapor deposition at different temperatures. X-ray diffraction analysis indicated that the FeSe films grown at substrate temperatures (T_s) between 220 and 340 °C were preferentially oriented with tetragonal structure. It was not possible to deposit films at T_s above 400 °C. The atomic molar ratios of Se/Fe increased with increasing the flow rate of $H_2Se/Fe(CO)_5$ and the growth temperature. The electronic property results showed that the conductive type of FeSe could be adjusted by controlling the growth temperature. The coercivity of FeSe decreased with increasing the growth temperature from 220 to 300 °C due to the improvement of crystal quality. © *2007 American Vacuum Society.* [DOI: 10.1116/1.2435374]

I. INTRODUCTION

Hybrid structures utilizing both ferromagnetic and semiconductor layers have been attractive because of the interest in potential applications for spintronic devices.[1–5] Potential applications of such ferromagnet-semiconductor combined structures have driven considerable efforts to fabricate novel spintronic devices.[6,7] For preparation of these devices, high quality ferromagnetic thin films are necessary. Among ferromagnetic thin films, Fe and MnAs have been widely investigated, because they could be easily grown on GaAs substrates.[8–10] As a new ferromagnetic material, FeSe films have attracted much attention because they are expected to be utilized as an interlayer for semiconductor/ferromagnetic metal heterostructure and could also be prepared on GaAs substrate.[11] The growth of FeSe thin film has been studied since the 1990s. Several methods have been attempted to prepare the iron selenide thin films: molecular beam epitaxy,[11,12] milling pure elemental powders of iron and selenium,[13–15] and selenization of evaporated iron thin films.[16] Takemura *et al.*[11,12] reported that the FeSe film prepared by the selenization of Fe film using molecular beam epitaxy consists of two phases with their coercive forces of about 300 and 2200 Oe. The structural evolution of a binary alloy with nominal composition $Fe_{25}Se_{75}$ prepared by ball milling was investigated as a function of milling time.[14] Most of Fe–Se compounds were prepared by two-step method, first fabricating Fe and second selenization.[11,16] The samples fabricated by selenization technique usually have many different phases and bad quality of crystal. In our previous work,[17,18] highly oriented single phase FeSe thin film fabricated by metal organic chemical vapor deposition has been reported and the conductive properties of FeSe have been studied.

However, no system study has been done on the growth and properties of high quality FeSe films, especially by low-pressure metal organic chemical vapor deposition. Therefore, it is a focus problem how to prepare high quality FeSe films.

In this article, we report the results on α-FeSe films grown on GaAs (001) substrates by low-pressure metal organic chemical vapor deposition (LP-MOCVD). The effects of the growth parameters [such as flow rate ratio of $H_2Se/Fe(CO)_5$ and growth temperature] on the crystal quality and electronic and magnetic properties of FeSe films have been investigated.

II. EXPERIMENT

FeSe thin films were prepared on GaAs substrates by LP-MOCVD system with a horizontal rectangular quartz reactor. The ironpentacarbonyl [$Fe(CO)_5$] carried by hydrogen was used as Fe source. The source was kept at 10 °C during deposition and the vapor pressure of $Fe(CO)_5$ was 13.5 Torr at 10 °C. The hydrogen selenide (H_2Se) diluted by high purity hydrogen (10% H_2Se) was selected as source material

TABLE I. Typical growth conditions for FeSe thin film grown on (001) GaAs substrates.

	I	II
Reactor pressure	150 Torr	150 Torr
Substrate temperature	260 °C	220–340 °C
$H_2/Fe(CO)_5$ bubbler flow	3 ml/min	3 ml/min
H_2/H_2Se gas flow	9–18 ml/min	18 ml/min
Total H_2 gas flow	1.5 l/min	1.5 l/min

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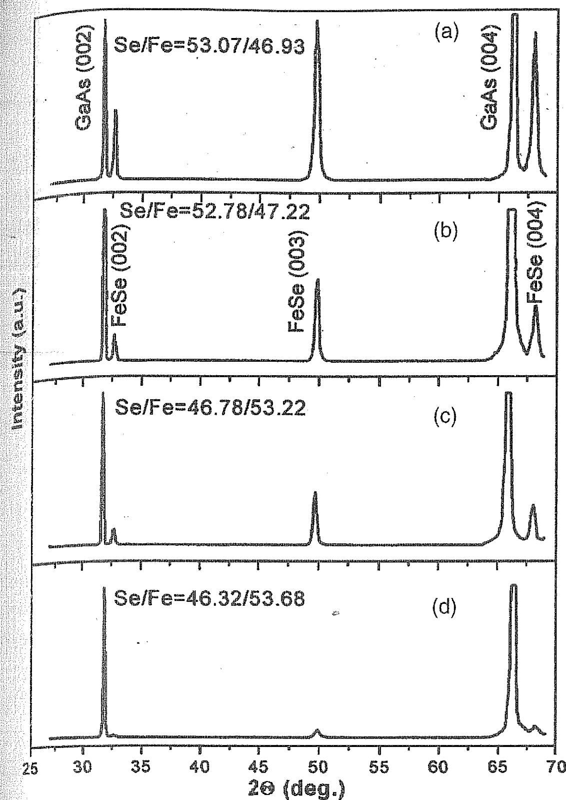

FIG. 1. XRD spectra of the FeSe thin film grown on GaAs (001) substrate at 260 °C with different flow rates of $H_2Se/Fe(CO)_5$: (a) 18/3, (b) 15/3, (c) 12/3, and (d) 9/3.

Se. The GaAs substrates were semi-insulating with (001) orientation. Before loading, they were cleaned by trichloroethylene, acetone, and ethanol for 5 min in an ultrasonic bath and etched in a sulfuric peroxide solution ($3H_2SO_4+1H_2O_2+1H_2O$) for 5 min at 20 °C. Subsequently, the substrate was boiled in hydrochloric acid for 5 min, followed by a de-ionized water rinse. The typical growth condition was shown in Table I.

The samples obtained were characterized with x-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). Magnetic properties were also investigated using vibrating sample magnetometry (VSM).

III. RESULTS AND DISCUSSIONS

FeSe films were grown on GaAs (001) substrates at different conditions (shown in Table I) with the thickness of 200 nm. A Ringaku O/max-RA x-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=0.154\ 178$ nm) was used to make θ-2θ scans to evaluate the crystalline quality and study the structure properties of the FeSe film. Figure 1 shows the XRD spectra of the FeSe prepared on GaAs substrate by LP-MOCVD with different flow rate ratios of $H_2Se/Fe(CO)_5$ from 9/3 to 18/3. All samples exhibit preferential orientation with c plane perpendicular to the substrate surface. Besides the diffraction peaks of GaAs substrate at 31.68° and 68.06°, diffraction peaks at $2\theta\approx 33°$, 50°, and 68° of the samples were observed. According to early reports, Fe–Se

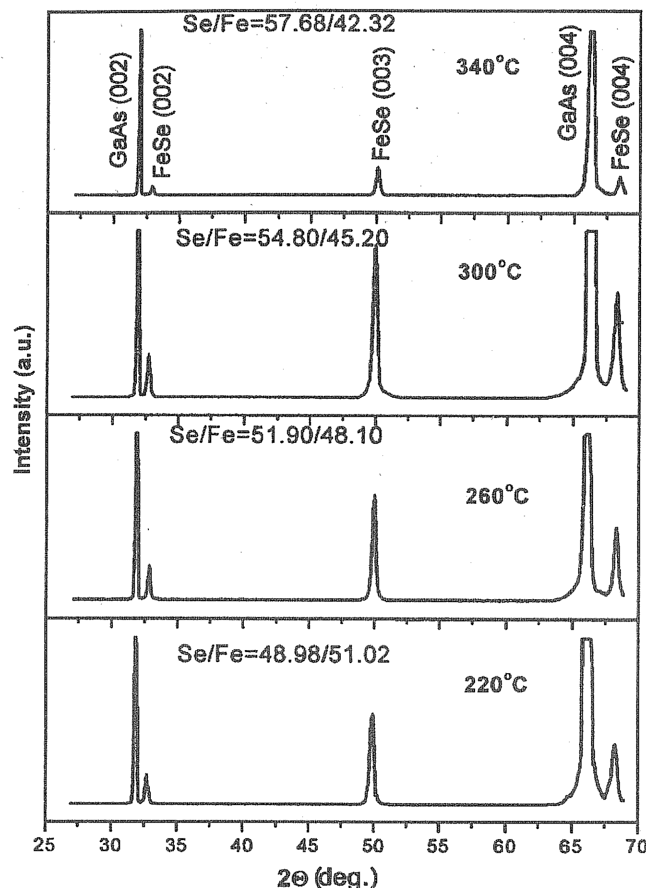

FIG. 2. XRD spectra of the FeSe thin film grown on GaAs (001) substrate with flow rate of $H_2Se/Fe(CO)_5$ at 18/3 at different growth temperatures.

system has two homogeneous and stable phases at room temperature: α-FeSe (isotropic with PbO structure, B10) with lattice parameters $a=0.3765$ nm and $c=0.5518$ nm and $FeSe_2$ (isotropic with FeS_2 marcasite structure) with lattice

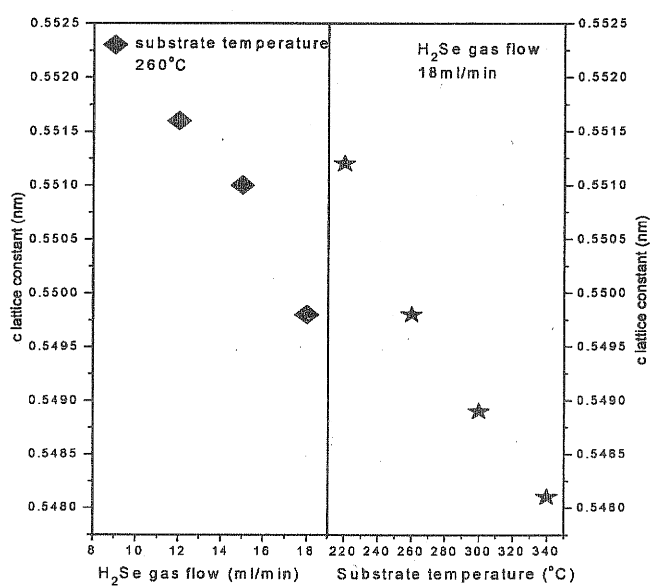

FIG. 3. c lattice constant of FeSe films vs growth temperature and flow rate of $H_2Se/Fe(CO)_5$.

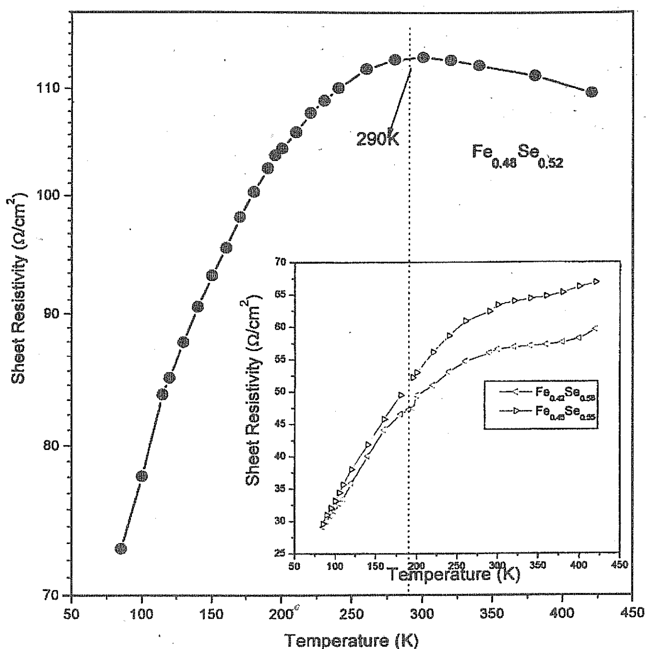

FIG. 4. Temperature-dependent resistivity curve of FeSe thin film prepared on GaAs (001) substrate at 260 °C with the flow rate of $H_2Se/Fe(CO)_5$ at 18/3. The inset shows the temperature-dependent resistivity curves of FeSe thin films prepared at 300 and 340 °C.

parameters a=0.3575 nm, b=0.4791 nm, and c=0.5715 nm. Therefore, the diffraction peaks at $2\theta \approx 33°$, 50°, and 68° can be associated with the diffraction from (002), (003), and (004) planes of the α-FeSe with tetragonal structure. The appearance of only (001) diffraction peaks indicates that the samples have a single phase and were preferentially oriented. Meanwhile, it can be found that the intensity of diffraction peaks increased with the increase of the flow ratio of $H_2Se/Fe(CO)_5$. At the flow rate ratio of $H_2Se/Fe(CO)_5$ below 9/3, Fe diffraction peak can be found in the XRD pattern. In order to study the effect of growth temperature (T_g) on crystallinity, we prepared FeSe films at T_g ranging from 220 to 340 °C, keeping the flow ratio of $H_2Se/Fe(CO)_5$ at 18/3. Figure 2 shows the XRD spectra of four samples grown at 220, 260, 300, and 340 °C, respectively. In this figure, it can be seen that the sample prepared at 300 °C has the strongest intensity of the diffraction peaks. Because with increasing the growth temperature from 220 to 300 °C, the sample crystalline quality was improved. However, with further increasing the growth temperature, the FeSe is difficult to deposit and the FeSe deposition did not occur at above 400 °C. The atomic molar ratios of Se/Fe of the samples prepared at different conditions were calculated by an EDS as shown in Figs. 1 and 2, indicating that the atomic molar ratios of Se/Fe increased with increasing the flow rate of $H_2Se/Fe(CO)_5$ and the growth temperature. The c-axis lattice constant of the FeSe film can be obtained from the

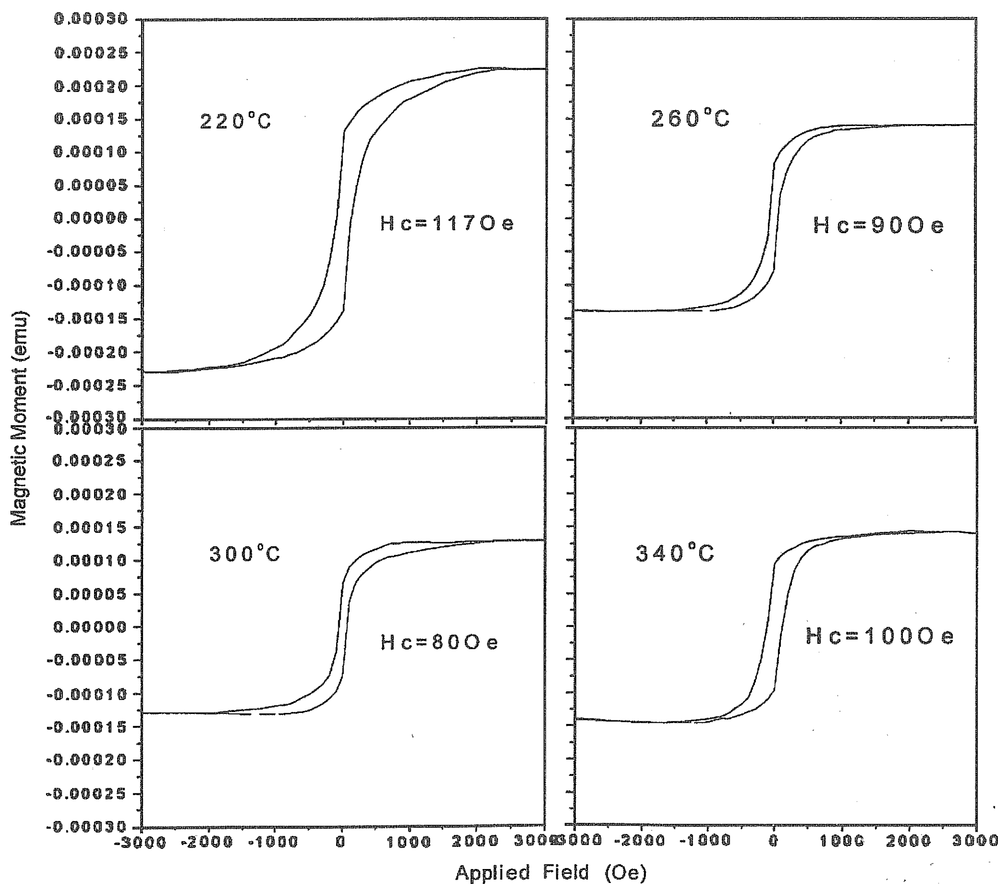

FIG. 5. Magnetization curves for the film prepared at different temperatures. The applied magnetic field was perpendicular to the surface of the film.

diffraction angle by the formula: $2d \sin \theta = n\lambda$. From the experimentally measured positions of (002), (003), and (004) diffraction peaks in Figs. 1 and 2, we have calculated the c-axis lattice constant, just as shown in Fig. 3. From this figure, it could be found that the c lattice constants of the samples prepared at 260 °C with different H_2Se gas flows decrease with the increase of H_2Se gas flows. Meanwhile, the samples grown on different temperatures with fixed H_2Se gas flow (18 ml/min) showed the decrease of c lattice constants with increasing the growth temperature. The stress effect may be responsible for the change of c lattice constant. But this stress effect affects all the samples similarly and should be ruled out. This slight change of perpendicular component of lattice constant in Fig. 3 could be attributed to the change of the atomic molar ratios of Se/Fe related to the flow rate of $H_2Se/Fe(CO)_5$ and the growth temperature. With increasing the atomic molar ratios of Se/Fe related to the flow rate of $H_2Se/Fe(CO)_5$ or the growth temperature, many Fe vacancies occurred and caused the decrease of c lattice constant.

Temperature-dependent resistivity curves of FeSe thin film prepared at 260 °C with the H_2Se gas flow of 18 ml/min were also determined from the Hall effect measurements, as shown in Fig. 4. In this figure, the resistivity curves as a function of temperature show a typical metallic behavior at cool state, while a semiconducting behavior at high temperature. Meanwhile, in Fig. 4, the resistivity curves show the peak at ~290 K. This result well accorded with Ref. 19. This critical behavior in the temperature-dependent resistivity characteristics is commonly observed at the temperature region around the T_C of ferromagnetic semiconductors, and this phenomenon is ascribed to the scattering of carriers by the magnetic spin fluctuation via exchange interactions. We also investigated the samples prepared at 300 and 340 °C with 18 ml/min H_2Se gas flow, as shown in the inset of Fig. 4.

For both samples, the resistivity curves as a function of temperature show a typical metallic behavior at the entire temperature range. This result is much different from that of the sample prepared at 260 °C. Therefore, it is determined by growth temperature whether FeSe is a metal or semiconductor, and we could adjust the conductive type of FeSe by controlling the growth temperature. However, the origin of this different behavior is not clear for FeSe and further work would concentrate on this phenomenon.

VSM measurements showed that the FeSe thin film is ferromagnetic at room temperature, as shown in Fig. 5. The applied magnetic field was perpendicular to the surface of the film. In this figure, it can be found that the sample prepared at 220 °C has the biggest saturation magnetization, but 260, 300, and 340 °C grown samples have the similar results. Lower growth temperature and Fe clusters in FeSe prepared at 220 °C may be responsible for this trend. By increasing the temperature from 220 to 300 °C, the coercivity (H_c) decreased, as the higher growth temperature could improve the crystal quality. However, the coercivity increased when the temperature increased from 300 to 340 °C, because it is difficult to deposit the FeSe films and the crystal quality became poor at the temperature above 300 °C. This is in good agreement with the results of the XRD measurements.

IV. CONCLUSION

High quality α-FeSe thin film has been prepared on GaAs (001) substrates by LP-MOCVD. The composition ratio of Fe/Se in FeSe film is strongly dependent on the flow rate of $H_2Se/Fe(CO)_5$ and the growth temperature. The typical hysteresis loops indicated that all FeSe films are ferromagnetic at room temperature and have a single ferromagnetic phase. Meanwhile, the critical behavior in the temperature-dependent resistivity characteristics is observed around 290 K for the sample prepared at 260 °C with flow rate of $H_2Se/Fe(CO)_5$ at 18/3 and we could adjust the conductive type of FeSe by controlling the growth temperature.

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