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Ferromagnetic FeSe: Structural, electrical, and magnetic properties

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FeSe thin films were grown on GaAs (001) substrates using low-pressure metalorganic chemical vapor deposition. X-ray diffraction analysis showed that FeSe thin films were in tetragonal structure with (002) orientation. It was found that the FeSe thin films were ferromagnetic above room temperature, revealing a maximum saturation magnetization about 590 emu/cc along the in-plane magnetic easy axis. The Hall measurement indicated that the as grown FeSe thin films was of *p*-type conduction with hole concentration of as high as $10^{20} \sim 10^{21}$ cm^{-3}. The magnetic circular dichroism spectrum was employed to study the electronic structure. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2159561]

Recently, the field of spintronics has attracted considerable attention because it offers unique opportunities for a new generation of multifunctional devices utilizing conventional charge-based microelectronics with the addition of the spin degree of freedom.[1] The combination of electron charge and spin has led to many interesting applications such as spin-polarized field effect transistor,[2] spin-valve transistor,[3] and spin-filter/aligner[4] based on ferromagnet/semiconductor heterostructures. For preparation of these devices, high-quality ferromagnetic thin films are necessary. The epitaxial growth of high-quality ferromagnetic materials on semiconductors is one of the key factors to make these devices. Many ferromagnetic thin films with Curie temperature (T_c) higher than 300 K including Fe,[5] MnAs,[6] MnSb,[7] and so on, have been grown on GaAs substrates. FeSe is another novel magnetic material[8] with Curie temperature above room temperature that can be epitaxially grown on GaAs substrate. Characterization of bulk crystals of Fe_3Se_4 and Fe_7Se_8 structures[9,10] shows Curie temperatures about 314 and 455 K, respectively. There are few reports on the magnetic properties of the FeSe thin films. Takemura and co-workers[8,11] reported the saturation magnetization of 120 emu/cc for FeSe thin films prepared by selenization of the Fe films on GaAs substrate. Little about the basic properties of FeSe are currently known. There is still confusion as to whether FeSe is a metal or semiconductor since the as-grown FeSe usually shows low resistivity. The only experimental data about the band gap of FeSe that we can get is about 0.14 eV,[12] which is based on the thermal activation energy evaluated from temperature-dependent resistivity measurement. FeSe is also mentioned with the band-gap energy of about 3.0 eV by Luo and Furdyna in a review article.[13]

In this letter, we will present the structural, electrical, and magnetic properties of FeSe films grown by low-pressure metalorganic chemical vapor deposition (LP-MOCVD). It is found that FeSe thin films are ferromagnetic above room temperature. The electric properties are studied by the Hall measurement and temperature-dependent resistivity. Magnetic circular dichroism is also employed to study the electronic structure.

FeSe samples with thickness about 200 nm are grown on semi-insulating GaAs (001) substrate by MOCVD. Ironpentacarbonyl [$Fe(CO)_5$] and hydrogen selenide (H_2Se) are employed as the precursors. The details of the sample preparation can be found elsewhere.[14] Structures and crystalline quality of the obtained FeSe thin films are analyzed by x-ray diffraction (XRD) on a Rigaku O/max-RA x-ray system in θ-2θ configuration. Magnetic characteristics are studied using a vibrating sample magnetometer (VSM) (Lake Shore Company) at room temperature. The electrical properties and Hall data are measured using four probes with Van der Pauw geometry.

Figure 1 shows the XRD patterns of the as-grown

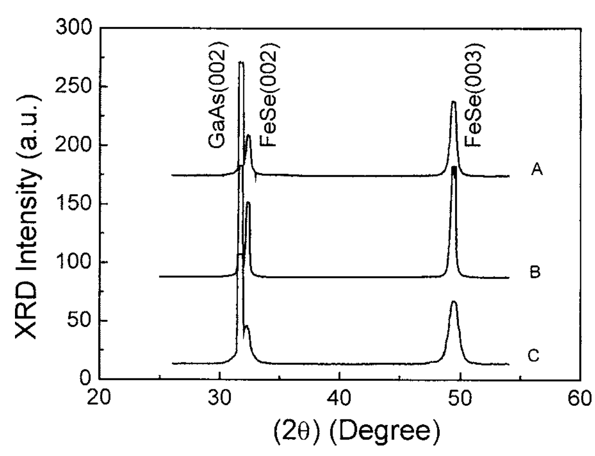

FIG. 1. XRD patterns of the as-grown FeSe samples at 250 °C (sample A), 320 °C (sample B), and 350 °C (sample C).

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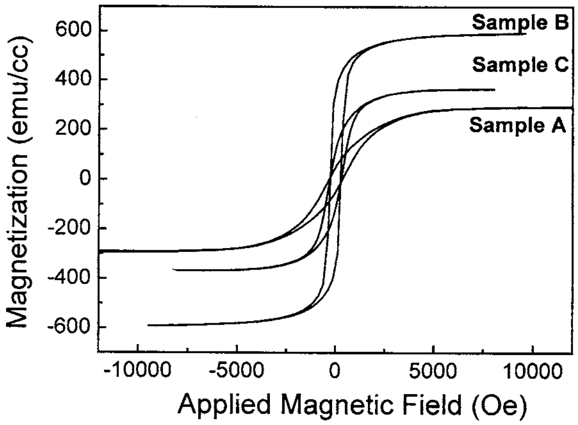

FIG. 2. M-H curves of samples A, B, and C measured by VSM at room temperature. The external magnetic field H was parallel to the GaAs ⟨100⟩ direction.

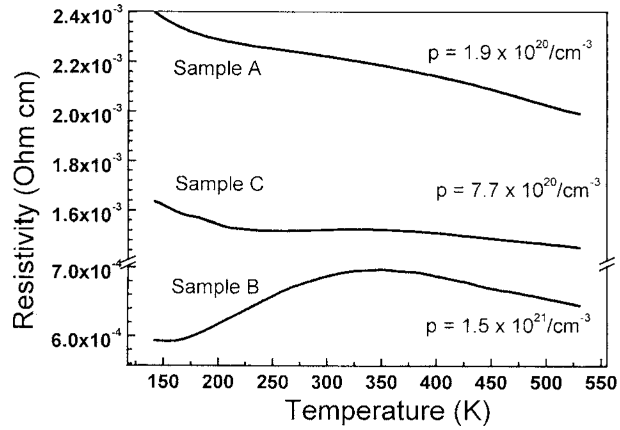

FIG. 3. Temperature-dependent resistivity for sample A, B, and C as indicated.

samples with substrate temperature T_S at 250, 320, and 350 °C, marked as A, B, and C, respectively. For all samples, in addition to the diffraction peak of GaAs (002), two diffraction peaks at $2\theta = 32.31°$ and 49.42° are in good agreement with (002) and (003) diffraction peaks of the tetragonal α-FeSe phase [JCPDS Card: 03-0533]. This appearance of only (00l) diffraction peaks indicates that the samples have good crystal quality and preferential crystal orientation perpendicular to the GaAs (001) plane. However, the FeSe thin films show polycrystalline structure despite of their uniform crystal orientation. The full widths at half-maximum (FWHMs) of the (002) diffraction peaks are 0.66° for sample A, 0.26° for sample B and 0.39° for sample C, which shows the optimized growth temperature of about 320 °C.

Figure 2(a) presents the M-H curves of samples A, B, and C measured by the VSM at room temperature. An external magnetic field H is applied parallel to the GaAs ⟨100⟩ direction. For the in-plane magnetizations, the FeSe films are found to be isotropic. We can see that the FeSe thin films are ferromagnetic and the Curie temperature T_C should be higher than room temperature, which is consistent with previous experiments.[11] The saturation magnetizations (M_s) of samples A, B, and C are 293, 590, and 366 emu/cc, respectively, and seem to be very sensitive to growth parameters such as substrate temperature. The coercivity (H_c) and the ratio between the remnant magnetization and saturation magnetization (M_r/M_s) of samples A, B, and C are listed in Table I. By simple comparison, it can be seen that sample B has the lowest H_c but the highest M_s and M_r/M_s ratio among the three samples. This is in agreement with the XRD observation that sample B has the narrowest FWHM value. According to Scherrer's formula, the grain size of sample B will be much larger than the other two samples. Since the ferromagnetic coupling is strongly dependent on the exchange interaction between neighboring magnetic ions, decrease of the grain size (or domain) can even change a system from a ferromagnetic state to a paramagnetic state. Thus, samples with larger grains will present a larger M_s at low magnetic field. Similarly, a smaller H_c value will also be expected in samples with larger grains due to the easier magnetization inversion for larger magnetic domains. Here, the M_s (590 emu/cc) of our FeSe thin film is much larger than previous literature reported highest value of 120 emu/cc,[11] which indicates the significantly improved crystal quality.

TABLE I. Magnetic properties of FeSe thin films at room temperature.

Sample	T_S (°C)	M_s (emu/cc)	M_r (emu/cc)	H_c (Oe)	M_r/M_s
A	250	293	46	342	0.16
B	320	590	348	263	0.59
C	350	366	116	294	0.32

Temperature-dependent resistivity of different FeSe samples is also studied, as shown in Fig. 3. The carrier concentration was measured by Hall experiment using normal four-probe geometry at room temperature. The resistivity is found to range from 10^{-3} to 10^{-4} Ω cm and the FeSe films show p-type conduction with hole concentration of $10^{20}-10^{21}$ cm^{-3} at room temperature. Since the anomalous Hall effect may be dominant in magnetic materials, the exact carrier concentration can only be determined at low temperature at very high magnetic field. The interesting thing here is the different behavior of the resistivity against temperature for samples with different carrier concentration. For sample A, which has the lowest carrier concentration, the resistivity *increases* with the decrease of temperature, showing the behavior of an insulator. For sample B, which has the highest hole concentration, the resistivity *decreases* with the decrease of temperature when T is lower than 350 K, demonstrating metallic behavior. There is a metal-insulator transition occurring in FeSe when the carrier concentration is higher than a critical value, which is same to the phase transition observed in heavily doped semiconductors or recently in ferromagnetic semiconductor GaMnAs.[15]

The absorption spectrum (not shown here) shows a slow increase from about 1.0 up to 2.5 eV in the measured range from 0.4 to 3.2 eV, which may come from the absorption components with convolution of both the interband transition and the intra-ion d-d transition of the transition from the electronic band to the d-band of Fe^{2+}. Further considering of the high density of carriers about 10^{21} cm^{-3} in the as-grown FeSe thin films, we cannot observe sharp structures in the absorption spectrum for the accurate determination of the band structure. A magneto-optical effect, which is the result of the sp-d exchange interaction, provides characteristic insight into the electronic band structure of magnetic materials. In this letter, we present magnetic circular dichroism (MCD) spectra of the well-oriented polycrystalline FeSe films grown

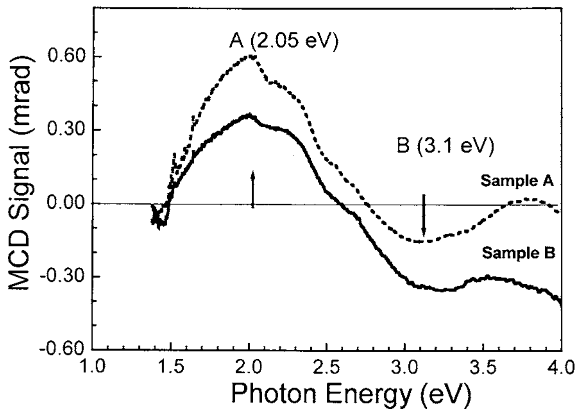

FIG. 4. MCD spectra of sample A and B at room temperature.

on GaAs. The MCD spectra were measured at room temperature with magnetic field of 200 G using monochromatic light from a Xe lamp in a spectral range from 250 to 900 nm. The polarization states of the incoming light are modulated between σ^- and σ^+ at 50 KHz by a photoelastic modulator. The reflected beam is detected by a photomultiplier tube and a lock-in amplifier.

Figure 4 shows MCD spectra of samples A and B at room temperature. The general features are a broad positive peak at about 2.05 eV together with a negative peak at about 3.1 eV. It suggests that electronic transitions with respect to these two corresponding structures include initial or final states belonging energy bands with different spin polarization. However, lack of spin-polarized energy-band calculation and further experiment, more detailed information on the origin of these structures is not available at present. Similar to the positive MCD signal for the Mn^{2+}/Mn^{3+} *d*-band-related transitions in GaMnAs and MnAs systems,[16,17] the positive peak at about 2.05 eV could originate from the Fe^{2+} 3*d*-band-related transitions. The negative peak at about 3.1 eV is believed to come from the band-to-band transition of FeSe due to the antiferromagnetic *p-d* exchange interaction. Here, we still do not know whether the ferromagnetic coupling is coming from the double-exchange interaction or hole-mediated exchange interaction. However one thing we find is that the saturation magnetization is higher in samples with higher hole concentration. The origin of the high density holes in the samples are still not clear, though the hole density is found to depend on the growth parameters. We think the change of the hole density originates from the nonstoichiometry in FeSe. Further theoretical and experimental work will help to identify the origin of the holes and the role of the holes in mediating the ferromagnetic coupling.

In conclusion, FeSe thin films with tetragonal structure are grown on GaAs (001) substrate by LP-MOCVD. The maximum saturation magnetization of the FeSe thin films is as high as 590 emu/cc at room temperature. The magnetic measurement shows that the FeSe films are along the in-plane magnetic easy axis. It is also found that the growth parameters could strongly influence the electrical and magnetic properties of FeSe. Success in fabricating FeSe brings new material candidate for the room-temperature application of spintronic devices.

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