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Structural and electrical characterizations of single tetragonal FeSe on Si substrate

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Abstract

(0 0 1)-Oriented FeSe thin films were successfully fabricated by metal organic chemical vapor deposition on Si substrate with large thermal mismatch. X-ray diffraction and X-ray photoelectron spectroscopy measurements indicate that the films are of single tetragonal phase FeSe. Hysteresis loop indicates that the FeSe structure is ferromagnetic at room temperature with coercive force of 260 Oe. The FeSe films show p-type conduction with carrier concentration of $10^{21}\,cm^{-3}$, and the anomalous Hall effect was discussed.

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1. Introduction

The combination of magnetic and semiconducting materials, such as Fe/ZnSe/GaAs [1] or MnAs/GaAs [2], etc., leads to new pathways in the development of semiconductor devices utilizing the spin of the carriers [3–5]. Reliable operation of the devices demands high Curie temperatures of the ferromagnetic materials. Iron selenides are excellent candidate materials for spin-based electronics, because FeSe is a ferromagnetic material with Curie's temperature higher than 300 K, and it can be grown on technologically important semiconductor substrates such as GaAs [6]. Nowadays, some magnetoresistance effects of the system Fe/ZnSe have been systematically studied [7,8]. Compared with Fe, FeSe shows much larger coercive force. Therefore, FeSe can be used as the ferromagnetic layer together with Fe in magnetic tunneling junction devices with ferromagnetic/semiconductor/ferromagnetic sandwich structure.

In this paper, single tetragonal FeSe thin films were successfully fabricated on Si substrate. The structural and electrical properties were studied in detail.

2. Experiments

Iron selenide thin films were grown on high-resistance n-type Si(1 0 0) substrates by low-pressure metal organic chemical vapor deposition (LP-MOCVD) at 260 °C, where the chamber pressure was fixed at about 2×10^4 Pa. Due to the large lattice mismatch and thermal mismatch between the FeSe film and silicon, the FeSe films tend to delaminate from the silicon substrate after cooling down from growth temperature to room temperature. Fortunately, it was found that low growth temperature and large H_2Se flow rate benefit the firmness and integrality of the FeSe films. Here, iron pentacarbonyl ($Fe(CO)_5$) and H_2Se were used as precursors, flow rates of which were fixed at 3.4×10^{-6} and

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1.5×10^{-4} mol/min by separate mass-flow controllers, respectively. High-purity hydrogen (99.999%) was used as carrier gas with total flow rate of 1.9 l/min. To minimize pre-reaction, the precursors were separated until approaching the substrate. The growth was performed for 30 min.

A rotating anode X-ray diffractometer with CuKα radiation of 0.154 nm was employed to characterize the structure of the FeSe thin films. The electronic states of Fe and Se ions in the films were investigated by X-ray photoelectron spectroscopy (XPS). Electrical properties were measured by a 7707 Hall measurement system (made by Lake Shore) in Van der Pauw configuration working at magnetic field of 0.9 T. The hysteresis loop measurement of the films was performed on a vibrating sample magnetometer (VSM).

3. Results and discussions

Fig. 1 shows the X-ray diffraction (XRD) patterns of the thin films. Besides the peak at about 69.3° from (4 0 0) Si substrate, three peaks located at about 32.53°, 49.70° and 68.17° can be observed, which is in accordance with 0 0 2, 0 0 3 and 0 0 4 peaks of tetragonal FeSe, or 2 0 2, 3 0 3 and 4 0 4 peaks of monoclinic Fe_3Se_4. Because the diffraction peaks of the two phases are generally too close (e.g., $d_{002} = 0.27590$ nm for tetragonal FeSe and $d_{202} = 0.27496$ nm for monoclinic Fe_3Se_4), they cannot be distinguished from the θ–2θ scan. Therefore, identifying of structure for the samples needs further criterions.

As known, Fe in FeSe is bivalent. However, Fe element in Fe_3Se_4 includes Fe^{3+} content. To affirm the electronic states of Fe ions in the thin films, XPS measurements were performed. Fig. 2 shows typical XPS spectra of the samples. For the original sample, binding energy band of Fe $2p_{3/2}$ is located at about 710 eV, which is in accordance with Fe^{3+} ions. Correspondingly, band of Se centered at 55.26 eV, which comes from Se^0. As it is well known, XPS is a surface analysis technology, the information offered by which comes from only several-nanometer thickness near sample surface. In order to obtain the electric states of the elements from the inside of sample, Ar ion ablation was performed before further XPS measurements. After ablating about 40-nm thickness, the band of Fe $2p_{3/2}$ shifts to 707 eV, which indicates that the inside iron is bivalent. Also, the band of Se shifts to 54.65 eV, the position of Se^{2-}. The inside Fe/Se ratio is about 1. Therefore, it can be concluded that the sample is single tetragonal FeSe by considering the XRD data. Fe^{3+} and Se^0 at surface should be caused by the oxidation from atmosphere.

Fig. 3 shows the hysteresis loop of one of the FeSe samples in the case that the applied magnetic field is parallel to the surface of FeSe films. As seen in the figure, the FeSe thin film shows ferromagnetic behavior at room temperature. The coercive force (H_c) is about 260 Oe for the in-plane case.

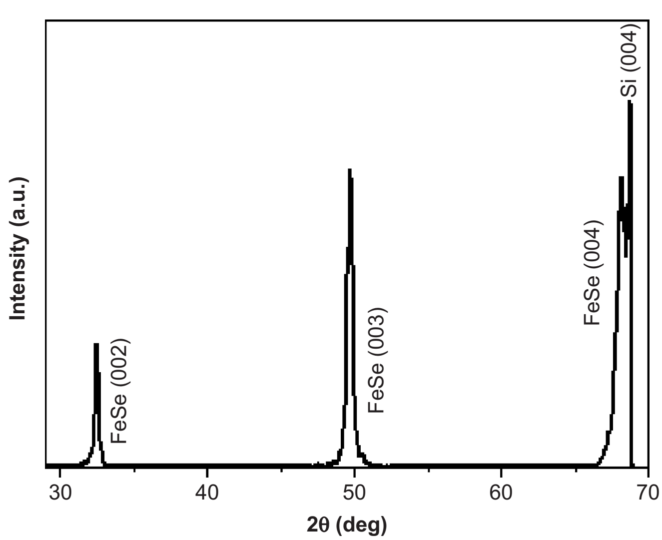

Fig. 1. X-ray diffraction spectrum of the FeSe thin film.

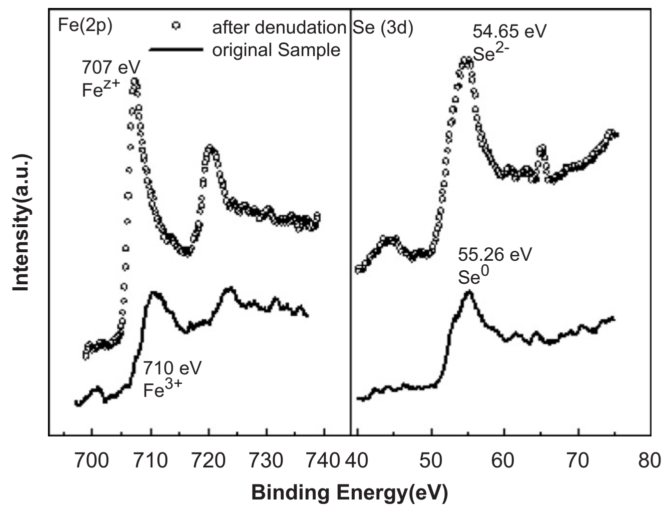

Fig. 2. A typical XPS spectra of the sample. The left part is for Fe (2p) and the right part is for Se (3d). The solid lines are the signals from the surface, while the dotted curves are the signals after the removal of 40 nm surface layer.

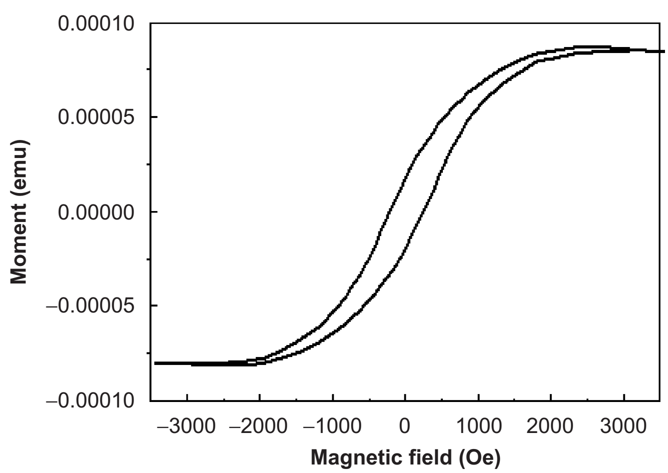

Fig. 3. Room temperature M–H curves of the FeSe thin film measured by VSM with the in-plane magnetic field.

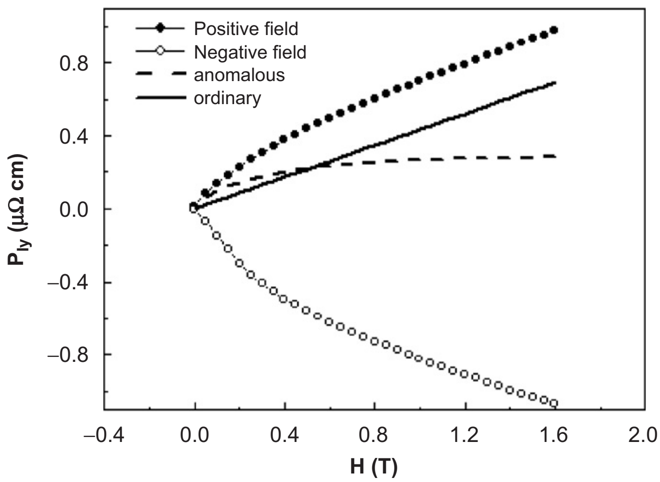

Fig. 4. The magnetic field dependence of the Hall resistivity of the FeSe thin films. The solid points and hollow circle denote the Hall resistivity data at positive and negative fields, respectively. The solid and the dashed lines denote the decomposition of the Hall resistivity at positive field into its ordinary and anomalous components, respectively.

To understand the carrier information of FeSe, Hall measurements were performed. The FeSe films show p-type conduction with hole concentration of $10^{21}\,\mathrm{cm}^{-3}$ and Hall mobility is about 0.4 at room temperature. Because the Si substrate used here is of n-type with resistivity of MΩ order, its conduction effect can be ignored.

However, anomalous Hall effect (AHE) should be taken into account for ferromagnetic materials during Hall measurements [9]. The Hall resistivity in a magnetic field is given by

$$\rho_{xy} = R_\mathrm{H} B + R_\mathrm{A} \mu_0 M, \quad (1)$$

where R_H is the ordinary Hall coefficient, B is the magnetic induction, R_A is the "anomalous" or extraordinary Hall coefficient, μ_0 is the permeability of vacuum, and M is the sample magnetization. Experimental studies of ferromagnets indicate that the AHE in many systems is well described by the following empirical expression:

$$R_\mathrm{A} \sim a[\rho_{xx}(B, T)]^{\gamma}, \quad (2)$$

where a is a constant, ρ_{xx} is the resistivity of samples, T is the temperature, and the exponent γ is determined by the dominant scattering mechanism, with values ranging from 1 to 2 [10]. For the present sample, the resistivity ρ_{xx} is about $2.5 \times 10^{-3}\,\Omega\,\mathrm{cm}$, which does not almost vary with external field. According to Eqs. (1) and (2), the variation of ρ_{xy} with magnetic field is dominated by the ordinary Hall effect after the magnetization saturates. In this case, Hall measurements can offer credible conduction-type results.

Fig. 4 shows the dependence of Hall resistivity ρ_{xy} on external field. The ρ_{xy} shows clear nonlinear magnetic field dependence at low fields, and varies linearly with a positive slope as the magnetic field increases up to 0.6 T. It can be fitted to a superposition of the ordinary and anomalous parts as shown in the figure. After the magnetization saturates, the linear evolvement of the ρ_{xy} indicates that the Hall resistivity variation is dominated by the ordinary part. The positive slope of ρ_{xy} at high field indicates that the p-type result is credible in this case. According to the ordinary/anomalous ratio larger than 1:1, we can also accept the errors of mobility and carrier concentration after the magnetic field reaches 0.6 T.

4. Conclusions

Single tetragonal FeSe thin films were fabricated on high-resistance n-type Si(1 0 0) substrates using LP-MOCVD. The FeSe films are ferromagnetic at room temperature and show p-type conduction with carrier concentration of $10^{21}\,\mathrm{cm}^{-3}$. Hall resistivity measurements at magnetic fields between 0 and 1.6 T show that the Hall resistivity varies linearly with magnetic field when the magnetic field increases beyond 0.6 T. It indicates that the p-type result is credible at high field, although there exist errors smaller than one order in the carrier concentration and Hall mobility resulted from AHE.

Acknowledgments

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