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High oriented FeSe thin film on GaAs(1 0 0) substrate prepared by low-pressure metalorganic chemical vapor deposition

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Abstract

High oriented FeSe thin films have been grown on GaAs(1 0 0) substrate at temperature 320°C using low-pressure metalorganic chemical vapor deposition equipment. X-ray diffraction analysis showed that high oriented FeSe thin films with the tetragonal structure were obtained. Atomic molar ratio of Fe/Se is about 1:1 by the measurement of energy dispersive spectrometer in SEM and both of Fe 2p and Se 3d binding energy were obtained by X-ray photoelectron spectroscopy. Moreover, images of atomic force microscopy reveal a surface morphology consisting of about 130 nm uniform granular film.

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Keywords: LP-MOCVD; FeSe thin film; Unitary orientation

1. Introduction

The interplay between spin and charge in semiconductors is of considerable contemporary interest for both fundamental physics and device applications. In particular, hybrid ferromagnet/semiconductor systems have elicited attention in the context of ''spintronic'' semiconductor applications that rely on spin injection from a ferromagnetic (or paramagnetic) material into a semiconductor [1–3]. Magnetic materials of interest in such heterostructures include II–VI-based paramagnetic semiconductors (e.g., ZnMnSe [4]) and III–V-based ferromagnetic semiconductors (e.g., GaMnAs [5]), as well as metallic/semimetallic ferromagnets (e.g., Fe [6], MnAs [7], FeSe [8]). Among various investigated materials, Fe/ZnSe and FeSe/ZnSe systems are attracting interests because they are not only with the ferromagnetic/semiconductor structure, but also can be grown on GaAs substrate [9,10]. Characterizations of bulk crystals of FeSe have been reported with Fe_3Se_4 and Fe_7Se_8 structures [11,12]. Furthermore, FeSe is preferably replaced by selenization technique [8,13,14], the selenization was performed with supplying a Se beam to the Fe films on GaAs

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substrate. But FeSe thin films have not been studied much, which especially prepared by MOCVD method. In this letter, we report that unitary orientation FeSe thin films were prepared on GaAs (1 0 0) substrate by low-pressure metalorganic chemical vapor deposition (LP-MOCVD) equipment. The composition, crystal structure and surface morphology of the FeSe films were investigated.

2. Experimental procedure

Samples studied were grown on GaAs substrate by LP-MOCVD equipment at substrate temperature 320°C with a growth pressure fixed at 150 Torr. Ironpentacarbonyl ($Fe(CO)_5$) and hydrogen selenide (H_2Se) were used as the precursors. The gas flow rates of $Fe(CO)_5$ and H_2Se were fixed at 7.5 and 3 ml/min, respectively. High purity hydrogen was used as carrier gas to carry the reactants into the reaction chamber with a horizontal rectangular quartz reactor and the total gas flow rate was kept at 2 l/min. The GaAs substrate was semi-insulating with (1 0 0) orientation. The substrate was cleaned in trichloroethylene, acetone and ethanol for 5 min in an ultrasonic bath, respectively. Subsequently, etched in a sulfuric peroxide solution ($3H_2SO_4$:$1H_2O_2$:$1H_2O$) for 5 min at 40°C, then boiled in hydrochloric acid for 3 min. Before growth, the substrate was annealed at 600°C in hydrogen ambient for 10 min, which is demonstrated to be an effective method to remove the oxide layer and residual surface contaminants. Sample grew in the reaction chamber for 30 min, and the thickness was about 200 nm.

The structure properties of the obtained sample were characterized by X-ray diffraction (XRD) equipment with CuK_a line ($\lambda = 1.5418$ Å). The atomic molar ratios of Fe and Se in the thin film were measured by energy dispersive spectrometer (EDS) based on the scanning electron microscopy (SEM) and composition and chemical bond configuration of FeSe film were measured by X-ray photoelectron spectroscopy (XPS). Surface morphology of the sample was measured by atomic force microscope (AFM).

3. Results and discussion

In order to investigate structural properties of the FeSe thin film, the XRD of $\theta - 2\theta$ scans was performed. Fig. 1 shows the XRD patterns of the as-grown sample. Beside the diffraction peaks of the GaAs substrate at $2\theta = 31.68°$ and 66.06°, three peaks appear at $2\theta = 32.31°$, 49.42° and 67.72°, which indicates that the samples are tetragonal FeSe according Ref. [14] and is correspond to (0 0 2), (0 0 3) and (0 0 4) diffractions of the FeSe samples. This appearance of only (0 0 l) diffraction peak indicates that the samples have better oriented crystal. The relationship between lattice constant of the investigated film and Miller exponent is given by using the classical formula:

$$d = \frac{\lambda}{2}\frac{[h^2 + k^2 + l^2]^{1/2}}{\sin\theta},$$

where h, k, l are the Miller exponent of crystal plane, λ is the X-ray wavelength($\lambda = 1.5418$ Å), and θ is the angle corresponding to the (hkl) peak. From the experimentally measured positions of the (0 0 2), (0 0 3), (0 0 4) peaks we have determined the lattice constant $c = 5.54$ Å, which was in agreement with the data published by other author [15]. According to Ref. [16], Fe–Se phases are two homogeneous and stable phases, α-FeSe and $FeSe_2$, and a variety of structures (the so-called γ structures), which are isotypic with an NiAs structure—B8 and they are usually obtained from

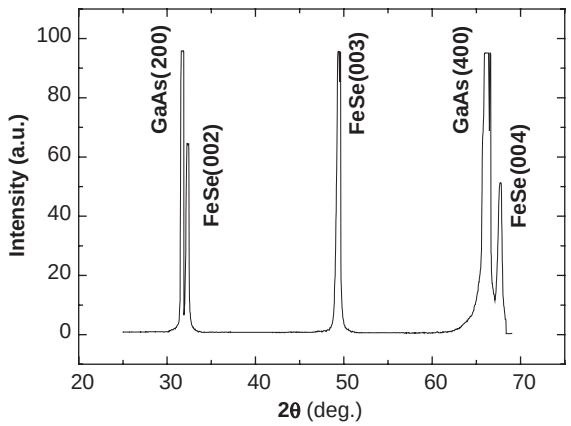

Fig. 1. X-ray diffraction patterns of the as-grown FeSe thin film.

the two previous phases by heating at high temperatures. At room temperature, the stable phases are the α-FeSe phase, whose structure is tetragonal (isotypic with a PbO structure, B10) with lattice parameters $a = 3.77$ Å, $c = 5.53$ Å, and the $FeSe_2$ phase, whose structure is orthorhombic (isotypic with FeS_2 marcasite structure) with lattice parameters $a = 4.801$ Å, $b = 5.726$ Å, $c = 3.582$ Å. Therefore, we obtained FeSe with the tetragonal structure according with above depiction. The above XRD results revealed that highly oriented tetragonal structure FeSe thin films were obtained.

The EDS in the SEM is used to investigate the elemental composition of the as-grown FeSe epilayer. Fig. 2 depicts the EDS results on the composition of the as-prepared film. From Fig. 2 we can see that the sample consists of Fe, Se, As and Ga element, thereinto As and Ga elements are from GaAs substrate, and Fe and Se elements are from growth film. Detailed result of Fe and Se element content is listed in Table 1, which shows

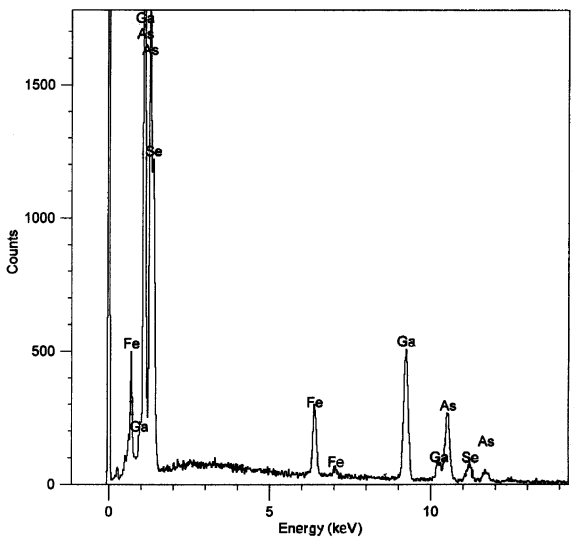

Fig. 2. The EDS spectrum of the as-grown sample.

Table 1
Result of EDS

Element	Weight (%)	Atomic (%)
Fe	40.81	49.36
Se	59.19	50.64

that atomic molar ratio of Fe/Se is 49.36/50.64, and is nearly 1:1. This result is consistent with X-ray diffraction analysis, i.e. the sample phase is FeSe.

The composition and chemical bond configuration of FeSe film were study by measurement of XPS spectrum. The Fe 2p spectrum and Se 3d spectrum of sample are shown in Fig. 3. The binding energy of the Fe $2p_{3/2}$ peak corresponds to iron selenide, as shown in Fig. 3(a). The Fe $2p_{3/2}$ peak appears at approximately 711.0 eV. This result accorded with Ref. [17]. Moreover, the Se 3d peak is fitted one peak with Gaussian-like shapes, as shown in Fig. 3(b). The peak situated at 55.7 eV can be attributed to FeSe [18]. Moreover, we found not corresponding peak of Fe–O or Se–O binding energy. Hence, XPS and highly oriented

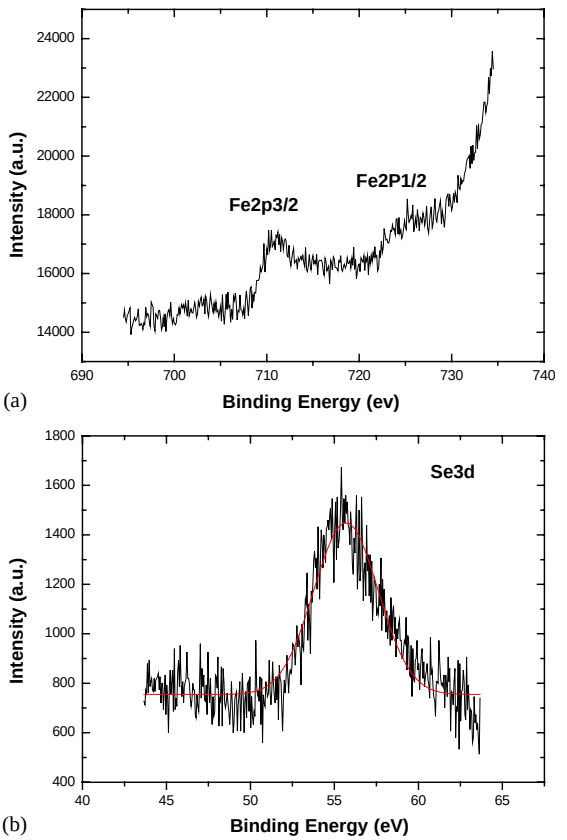

Fig. 3. XPS spectra of (a) Fe 2p and (b) Se 3d binding energy of FeSe thin film.

XRD indicated that no other phase or composition was obtained.

Mean grain size of the FeSe thin film was estimated using AFM. Fig. 4 shows a two-dimensional and a three-dimensional image of the FeSe thin film. As can be seen, the images show that the film has a granular structure. The mean size of granular structure was approximate to

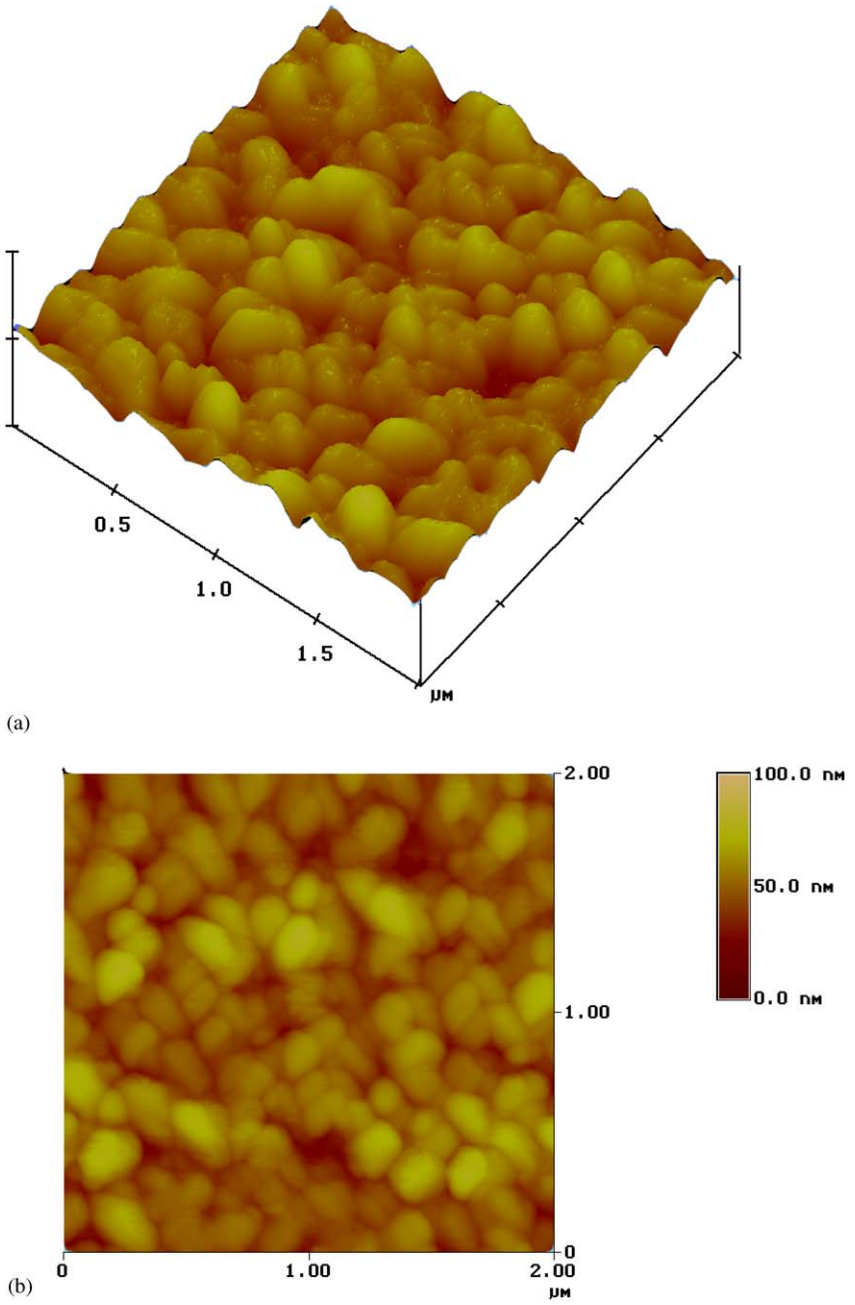

Fig. 4. Atomic force microscopy images for FeSe thin film prepared by LP-MOCVD (a) two-dimensional image and (b) three-dimensional image.

130 nm. In addition, a smooth, dense, uniform, and no cracking or voids FeSe thin film can be observed at the measured area. Above result indicate that sample with granular structure and relative smooth surface was obtained.

4. Conclusions

High-quality FeSe thin film is prepared on GaAs(1 0 0) substrate using the LP-MOCVD equipment. XRD and EDS in SEM analysis shows that the sample is (001) unitary orientated FeSe phase of tetragonal structure and atomic molar ratio of Fe/SE is about 1:1. Binding energy of both Fe 2p and Se 3d were obtained by XPS. Moreover, AFM reveals a surface morphology consisting of about 130 nm uniform granular film.

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