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Growth of FeSe on general substrates by metal-organic chemical vapor deposition and the application in magnet tunnel junction devices

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Abstract

Single-phase tetragonal FeSe films were grown on *c*-plane sapphire, SiO_2, GaAs (100) and Si (100) substrates by low-pressure metal-organic chemical vapor deposition method. X-ray diffraction analysis shows that all the FeSe thin films on different substrates are of (00l) orientation. Spin-dependent magnet tunnel junction with Fe/ZnSe/FeSe structure were fabricated, and the tunneling magnetic resistance ratio decreased with increasing the thickness of ZnSe layer in the range of 10–20 nm.

Keywords: Metal-organic chemical vapor deposition; FeSe films; Magnet tunnel junction

1. Introduction

The Fe–Se compounds, such as FeSe, $FeSe_2$, Fe_3Se_4 and Fe_7Se_8, etc. [1–4], are important family of Se-based materials. Fe–Se compound attracts more and more attention because most of them show ferromagnetism. They are expected to be utilized as interlayer for semiconductor/ferromagnetic metal heterostructures, or as promising magnetic material. Selenization of iron thin films is an usual route to fabricate Fe–Se compounds thin films. However, it usually obtains non-oriented thin films, even mixtures of more than two Fe–Se compounds [5–8]. The unsatisfactory crystal quality limits the study on Fe–Se compounds within composition analysis and structure characterization, and accordingly restricts the research on optical, electrical properties. It hampers the improvements of research on Fe–Se compounds. Fortunately, we found that low-pressure metal organic chemical vapor deposition (LP-MOCVD) seems very suitable for fabricating FeSe thin films, an important Fe–Se compound with Curie's temperature higher than 300 K [9]. By rotating an angle of 45°, the mismatch between (100) ZnSe substrate and (00l) tetragonal FeSe could be reduced to 6%. It offers a possibility for epitaxial growth between the two compounds. Compared with Fe, FeSe has much larger coercive force. Therefore, FeSe can be used as the ferromagnetic layer together with Fe in magnetic tunneling junction (MTJ) devices with ferromagnetic/semiconductor/ferromagnetic sandwich structure.

In the present work, tetragonal FeSe thin films with (00l) orientation were grown on *c*-plane sapphire, silica, GaAs and silicon substrates. A tunnel magnetoresistance (TMR) ratio of 5.5% was observed on a MTJ with Fe/ZnSe/FeSe structure at room temperature.

2. Experiments

The samples were grown on *c*-plane sapphire, SiO_2, semi-insulating GaAs (100) and high resistant n-type Si (100) substrates by LP-MOCVD with a horizontal rectangular quartz reactor. The chamber pressure was fixed at about 2×10^4 Pa. Before being put into the growth chamber, the substrates were cleaned by ultrasonic bathing with a sequence of acetone and ethanol for 5 min, respectively, and then were chemically polished with respective routes. In addition, Si substrate was bathed in HF

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solution (5%) to get rid of the oxide layer. Iron pentacarbonyl ($Fe(CO)_5$) and H_2Se were used as precursors, flow rates of which were fixed in the range of $(2.1–4.1)\times10^{-6}$ mol/min and $(5.0–15.0)\times10^{-5}$ mol/min by mass-flow controllers, respectively. The iron pentacarbonyl source was kept at 10 °C during the deposition. High purity hydrogen (99.999%) was used as carrier gas with total flow rate of 1.9 l/min.

From X-ray diffraction patterns and scanning electron microscope images for the surface morphology, it was found that 350 °C is the optimized growth temperature for the FeSe growth on *c*-plane sapphire and SiO_2 substrate. However, this temperature seems too high for nucleation of FeSe on Si and GaAs substrate because the films cannot be grown with good orientation. Therefore, reducing growth temperature was performed to accelerate the nucleation on Si and GaAs substrates and FeSe with good (001) orientation were obtained at 260 °C on Si and GaAs substrates. On the other hand, due to the lack of thermal energy at low substrate temperature, the pyrolysis of H_2Se was suppressed. Therefore, increasing H_2Se flow rate benefits the integrality of the FeSe films at low growth temperature.

Structures of the thin films are analyzed by rotating anode X-ray diffraction (XRD) with CuKα radiation of 0.154 nm on a Rigaku O/max-RA X-ray system in θ–2θ configuration. As for magnetic properties of the films, the Magnetization dependance on magnetic field strength (*M–H* curves) were measured with a vibrating sample magnetometer (VSM) at room temperature. The electrical properties and magnetoresistance were measured by a 7707 Hall measurement system.

3. Results and discussions

Fig. 1 shows the XRD patterns of the samples on *c*-plane sapphire, SiO_2, semi-insulating GaAs and high resistant n-type Si substrates, respectively. For all the samples, besides the diffraction peaks from substrates, three peaks located at about 32.53°, 49.70° and 68.17° can be observed, which are in good agreement with 002, 003 and 004 diffraction peaks of tetragonal α-FeSe. The oriented growth of FeSe thin films means that

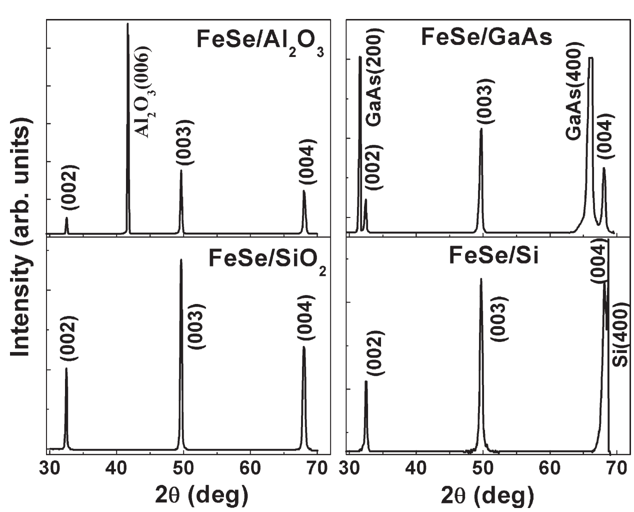

Fig. 1. X-ray diffraction patterns of the FeSe thin films grown on *c*-plane sapphire, SiO_2, GaAs and Si, respectively.

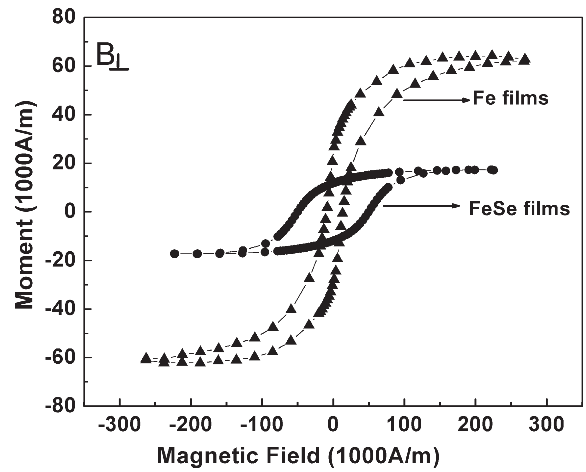

Fig. 2. Room temperature *M-H* curves of the FeSe and Fe thin films measured by VSM. The magnetic field is perpendicular to the samples surface.

MOCVD is more suitable to grow α-FeSe than other techniques, such as selenization of Fe thin film. Further more, the (00l) oriented FeSe film can be easily grown by changing growth parameters in a certain scale, although the substrates used are of different structures, even non-crystal. It indicated that (00l) oriented growth might be the essential characteristic of α-FeSe. In other material systems, such as ZnO thin film, the oriented growth characteristic is usually observed.

To get understanding of the carrier information of FeSe, electrical measurements were performed. The FeSe films show *p*-type conduction with hole concentration of 10^{20}–10^{21} cm^{-3}, and the resistivity in the range of 10^{-3} Ωcm at room temperature. Compared with most ferromagnetic metals, the resistivity of FeSe is more close to that of semiconductors, which can weaken the interface charge accumulation caused by conduction mismatch.

Previously, we have found that the in-plane hysteresis loop has lower coercivity (Hc) and higher saturation magnetizations (M_S) than that of out-of-plane for Se-rich FeSe film [10]. According to this result, the magnet field should be set in parallel configuration to obtain good magnetoresistance ratio and operation at smaller magnet filed in the application of MTJ with FeSe electrode [11,12]. However, due to the difficulty in placing the samples parallel to the field, the samples are set perpendicular to the applied field. In this work, it is enough for showing the prospects of FeSe in MTJs.

Fig. 2 shows the room-temperature magnetization curves for the FeSe/GaAs and Fe/ZnSe(20 nm)/GaAs samples in the case that the applied magnetic field is perpendicular to film surface. As seen, the FeSe and Fe thin films show ferromagnetic behaviors at room temperature. The M_S and the remnant magnetizations (M_r) are 63,260 A/m and 23,420 A/m for Fe films, and 17,150 A/m and 11,590 A/m for FeSe films, respectively. The coercive force (H_c) values are about 10,300 A/m for Fe films and 51,000 A/m for FeSe films, respectively. Significantly, the FeSe thin film has much larger coercive force than has the Fe thin film. It offers possibility for constructing FeSe/semiconductor/Fe MTJ devices.

Mixed ferromagnetic/semiconductor heterostructures gain an increasing interest due to their potentialities for spintronic applications as spin injectors and spin analyzers for polarized currents into semiconductors [13]. The use of a semiconductor barrier in heterostructure with ferromagnetic metal electrodes describes an important type of magnetic tunnel junctions. Here we use wide gap II-VI semiconductor ZnSe for the barrier layer in the Fe/ZnSe/FeSe MTJs. The Fe/ ZnSe system has been well studied by some groups [14,15]. In these reports, no reduction of Fe magnetic moment at the Fe/ZnSe interface was found and Fe/ZnSe (001) was considered as an example of a very low reactivity interface system. Compared to the tunnel junction with oxides barrier layer, ZnSe layer can efficaciously prevent the incorporation of oxygen into the interfacial Fe or FeSe layer. Also, a certain conduction of ZnSe layer can decrease the resistance of the tunneling junction, and allow thick barrier layer to prevent pinhole forming. In addition, the optimal growth temperature of ZnSe is about 300 °C, which is close to the growth temperature of the two ferromagnetic layers. The low growth temperatures of the junction can restrain the diffusion between the interfaces of the Fe/ZnSe/FeSe heterostructures.

A series of MTJs with various barrier thicknesses were grown via LP-MOCVD on the GaAs substrates separated by two masking steps. An 80-nm-thick FeSe layer was first grown on a GaAs substrate at 280 °C as the bottom ferromagnetic electrode.

Then a 5–24 nm-thick ZnSe tunnel barrier layer were deposited on the FeSe layer at 300 °C. Finally, an 80 nm-thick Fe top electrode was subsequently deposited at 300 °C. To protect the Fe layer from oxidation, an Au layer was deposited on the top electrode. The junction area is $(2.5\pm0.2)\times(2.5\pm0.2)$ mm^2.

Room temperature Photoluminescence (PL) spectra of ZnSe (100 nm)/FeSe/GaAs was measured (not shown here). Only one PL peak centered at 2.69 eV is observed, which is very close to the band-edge emission peak of bulk ZnSe (2.70 eV). In another word, the ZnSe thin film grown on FeSe layer maintains the bandgap close to bulk ZnSe. It assures that the ZnSe grown on FeSe can be used as the barrier layer in MTJs.

Fig. 3 shows the typical TMR curves measured at room temperature for the Fe/ZnSe/FeSe MTJ samples on GaAs substrate with $d_{ZnSe}=11$, 15 and 19 nm. The injection current is 5 μA. The magnetic field is perpendicular to the surface of the MTJ. The positive bias voltage V was added to the FeSe electrode. The TMR ratio is defined as $(R_{ap}-R_p)/R_p$, where R_{ap} and R_p are the resistance for the antiparallel (ap) and parallel (p) alignments of the magnetizations. The samples with $d_{ZnSe}=11$, 15 and 19 nm exhibited the TMR effect with TMR ratios of 5.5%, 4% and 1.8% at room temperature, respectively. For the samples with $d_{ZnSe}=5$ nm and 24 nm, no TMR effect was observed during the measurement. The fabrication condition resulted that the junction areas were larger than that reported in most references, which increases the probability of pinhole on thinner ZnSe layer. Therefore, the absence of TMR can be understood for the sample with small d_{ZnSe}. For the sample with $d_{ZnSe}=24$ nm, it is believed that the spin of the most carriers has conversed before the tunneling completes.

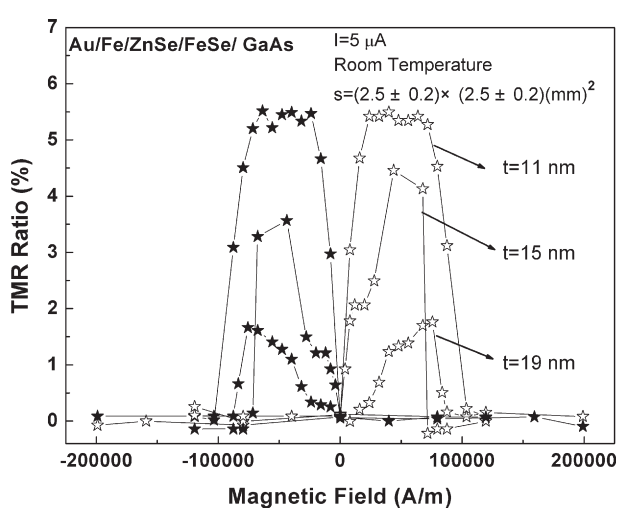

Fig. 3. Room temperature TMR curves of Fe/ZnSe/FeSe MTJs with $d_{ZnSe}=11$, 15 and 19 nm, respectively.

4. Conclusions

In conclusion, single-phase α-FeSe thin films were fabricated on general substrates by LP-MOCVD method. The good orientation of the samples indicates that MOCVD is a suitable method to grow α-FeSe thin films. Growths on different substrates indicate that (00l)-orientation is the essential characteristic of α-FeSe. Due to the resistivity close to semiconductor, FeSe is more suitable to construct MTJ devices than other ferromagnetic materials. A simple Fe/ZnSe/FeSe junction was fabricated and a TMR ratio up to 5.5% was observed at room temperature, which indicates α-FeSe is a promising ferromagnetic material for MTJ devices.

Acknowledgments

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