Cross-plane Seebeck coefficient and thermal conductivity of CuFeSe2 thin film

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Cross-Plane Seebeck Coefficient and Thermal Conductivity of $CuFeSe_2$ Thin Film

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Abstract. The $CuFeSe_2$ is a member of the I-III-VI_2 semiconductors, whereas it shows different physical properties from the chalcopyrite family, include the tetragonal structure, the small band gap ~0.16 eV and the weak magnetic behavior. Only a few articles focused on this material in recent years. The measurements of the Seebeck coefficient and thermal conductivity of the high quality $CuFeSe_2$ thin film could provide valuable information for its thermal application. In this report, a $CuFeSe_2$ thin film with thickness ~200 nm on SiO_2/Si substrate was prepared by pulse laser deposition (PLD). The highly crystallized film shows a preferred orientation (h 0 0) normal to the film surface. Two pairs of heater/sensor Au strips were thermally deposited on the thin film and substrate separately for thermal conductivity measurement using differential 3ω method. The Seebeck coefficient across the film plane was directly measured by two additional EMF probes below and above the film with temperature gradient generated by heater/sensor at frequency 2ω. The temperature dependence of thermal conductivity and Seebeck coefficient were measured in a wide temperature range from 150 to 300 K. The room-temperature thermal conductivity and Seebeck coefficient are obtained to be 3.5 W/m-K and -108 μV/K respectively.

Keywords: Cross-plane, Seebeck coefficient, 3 omega
PACS: 73.50.Lw 73.61.At

INTRODUCTION

The semimagnetic semiconductor $CuFeS_2$ of chalcopyrite structure has been well studied in past decades [1]. But there are limited information for the tetragonal structure compound $CuFeSe_2$ which were found in the study of $CuGa(In)_{1-x}Fe_xSe_2$ family [2]. Although $CuFeSe_2$ has interesting electrical behavior and magnetic properties, only a few articles focused on this compound in the recent years [1-6], thus the synthesis information on this compound was also limited in a few literatures. For example, the bulk crystal was fabricated by the solid-state reaction [3, 4]; the thin film samples were grown by selenization of a CuFe alloy precursor [5]. The nanocrystal samples were synthesized by solventothermal process [6].

In this paper, we introduce a new method for preparing the high quality $CuFeSe_2$ thin film samples by Pulsed Laser Deposition (PLD). A highly crystallized film of thickness 200 nm having the preferred orientation (h 0 0) normal to the film surface was prepared. The quality and the growth direction of the thin film were characterized by X-ray diffraction. For thermal property measurements, the differential 3ω method was applied to measure the cross-plane thermal power and thermal conductivity of the $CuFeSe_2$ thin film.

SAMPLE AND MEASUREMENT TECHNIQUE

The thin films were grown by Pulsed Laser Deposition (PLD), using the KrF excimer laser (Lambda Physik LPX Pro) with λ=248 nm. Deposition process was under high vacuum (10^{-5} torr) with laser pulse frequency 5 Hz and power density 5 J/cm^2. The distance between target and substrate was around 4.7 cm. The Si (1 0 0) substrate having 400 nm thickness SiO_2 insulation layer was heated to temperature 250 °C for better film growth condition. The target of PLD was prepared with element composition: Cu:Fe:Se = 1:1:2 sintered at 600–700 °C under vacuum. Target is one inch in diameter and 8 mm in thickness.

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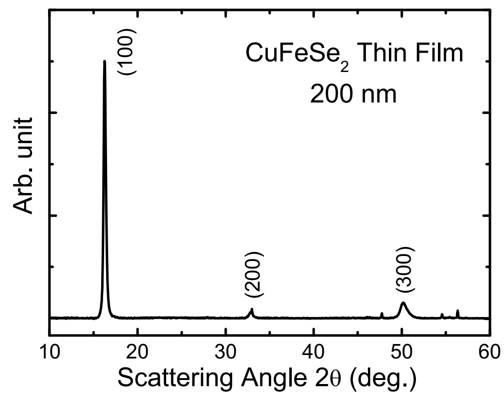

FIGURE 1. X-ray diffraction pattern of 200 nm $CuFeSe_2$ thin film with (h 0 0) preferred orientation.

Figure 1 shows the X-ray diffraction pattern for the $CuFeSe_2$ thin film growth by PLD. The growth direction of $CuFeSe_2$ thin film is along a-b plane, which was normal to the substrate surface.

For the cross-plane Seebeck coefficient and thermal conductivity measurement, the differential 3ω method [7,8] was employed. Two Au electrical leads for cross-plane thermal EMF measurement were deposited above and below the $CuFeSe_2$ thin film respectively. The flow chart of sample preparation was shown in the Figure 2(a). Step 1: The silicon substrate with 400 nm thermal growth SiO_2 insulation layer. Step 2: Deposited the bottom EMF probe for thermal EMF measurement. Step 3: Deposited a 100 nm SiO_2 insulation layer by Plasma Enhanced Chemical Vapor Deposition (PECVD) with an open window for the electrical contact of the previous EMF probe with later deposited $CuFeSe_2$ thin film. Step 4: Deposited a 200 nm $CuFeSe_2$ thin film. Step 5: Deposited another 100 nm SiO_2 insulation layer on $CuFeSe_2$ thin film with an open window for electrical contact of top electrode by PECVD. Step 6: Deposited the top EMF probe for thermal EMF measurement of the thin film sample. Step 7: Covered whole sample with 300 nm SiN_x insulation layer by PECVD. Step 8: Deposited the Au heater/sensor on the film specimen and reference substrate respectively. The completed sample for the 3ω measurement was shown in Figure 2(b).

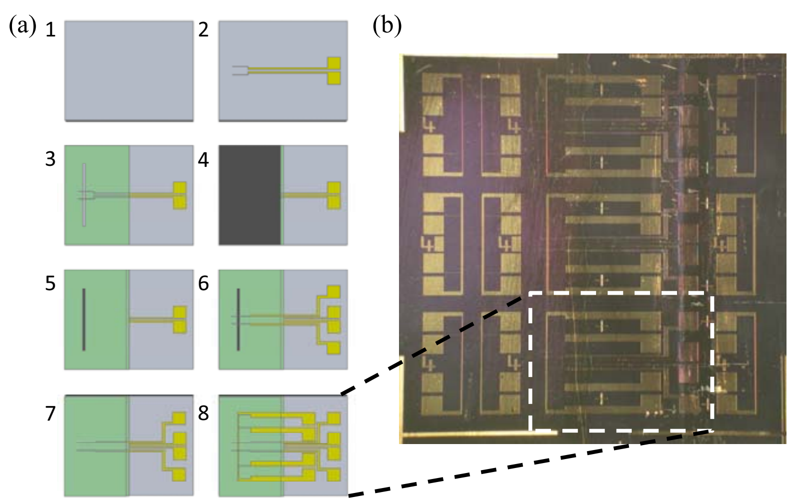

FIGURE 2. (a) Flow chart of sample preparation. (b) The photo diagram of the film specimen, and the reference at right side of the sample.

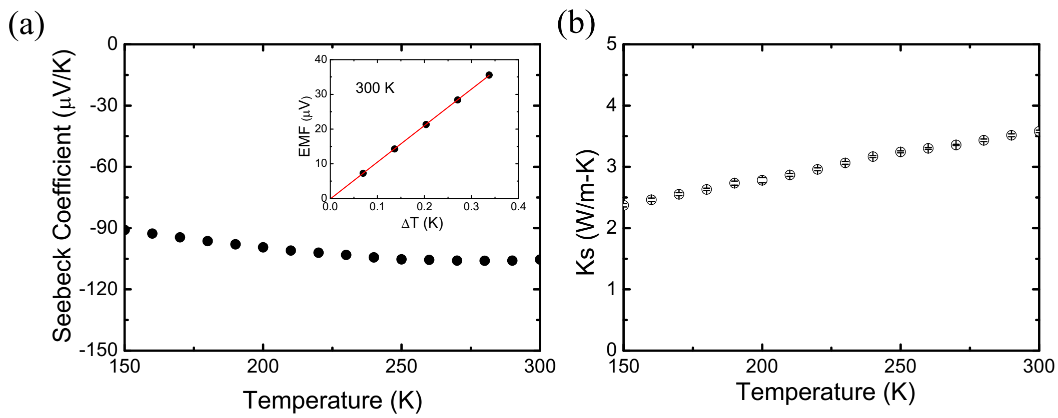

FIGURE 3. (a) The temperature dependence of cross-plane Seebeck coefficient. The inset shows the fitting result of the EMF verse temperature gradient. (b) Cross-plane thermal conductivity of 200 nm $CuFeSe_2$ thin film.

Using 3ω technique to measure the cross-plane Seebeck coefficient was demonstrated by B. Yang [9] in 2002. In their work, two sets of heater/sensor and EMF probe were deposited on two films with different thickness in order to obtain the cross-plane Seebeck coefficient by taking the difference of the temperature and the thermal EMF between the two films. In this report, two EMF probes were deposited above and below the film specimen, and the electrical contact is right under the 3ω heater/sensor with the rest of the electric lead protected by the SiO_2 insulation layer to reduce any possible thermal EMF noise in measurements. When the AC current was applied to the heater/sensor, the temperature gradient was generated across the $CuFeSe_2$ thin film at frequency 2ω. By measuring the 2ω signal between two EMF probes, the thermal EMF generated by temperature gradient was obtained. Furthermore the temperature gradient across the sample can be measured by the 3ω signals of sensors. The actual temperature gradient across the film is the 3ω signal difference between sensors on film and the reference. It is noticed that the reference part only composes the 300 nm SiN_x insulation layer. Owing to the thermal boundary resistance of the film specimen (includes interface between $SiN_x/CuFeSe_2$ and $CuFeSe_2/SiO_2$) and reference part (includes only the interface between SiN_x/SiO_2) cannot be totally subtracted, this can lead an underestimate of the magnitudes of thermal conductivity and Seebeck coefficient. But the magnitude of the thermal boundary resistance is relatively small, in normal condition is in the order of 10^{-8} K-m^2/W [10] which is corresponding to an equivalent temperature change ~ 0.01 K.

The temperature dependence of Seebeck coefficient measurement shows the $CuFeSe_2$ film is p-type and the Seebeck coefficient along a-b plane is from -90 to -108 μV/K as temperature increases from 150 to 300 K as shown in fig. 3(a). The cross-plane thermal conductivity is shown in fig. 3(b) which also shows the increase as temperature increase. Meanwhile the value of cross-plane thermal conductivity is calculated as 3.5 W/m-K at 300 K.

CONCLUSION

In this report, we demonstrated the PLD method to grow the highly preferred orientation $CuFeSe_2$ thin film on SiO_2/Si substrate, and the growth direction is along the a-b plane which is normal to the substrate surface. The 3ω method was applied to measure the cross-plane thin film thermal conductivity and Seebeck coefficient. The cross-plane Seebeck coefficient of $CuFeSe_2$ thin film is -108 μV/K, and the thermal conductivity is 3.5 W/m-K at room temperature. Both of these two properties slowly increase with temperature increase. Although the thermal boundary resistance of interfaces between films in this measurement has not been fully subtracted, since it is one older smaller than that of the film specimen, the data shown in this report still provide the valuable information of the $CuFeSe_2$ compound.

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