Cross-Plane Thermal Conductivity and Thermal Boundary Resistance in CuFeSe₂ Thin Films

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ABSTRACT
In semiconductor industry, heat dissipation is always a key factor for the high-density integrated circuits. In this work, a series of high-quality CuFeSe₂ thin films with various thicknesses ranged from 200 to 800 nm were prepared for the study of film thermal conductivity and thermal boundary resistance between film and substrate. The thermal resistances of both thin film and interface boundary decrease linearly with increasing temperature at 100-350 K. The room-temperature thermal boundary resistance was estimated around 3.1×10⁻⁸ K-m²/W, which is about the same magnitude as that of 200 nm film. In the meantime, the thinner film with better crystallization was characterized by X-ray diffraction and electrical resistivity. The correlations among thermal conductivity, crystallization and film thickness were reflected in the series of thin films. The thermal conductivity of conducting electrons calculated from resistivity data and Wiedemann-Franz law only contributes about 3% of total thermal conductivity. This consequence explains the thermal conductivity of CuFeSe₂ thin film is mostly dependent on lattice crystallization and film thickness.

Introduction
CufSe₂ is a type I-III-VI₂ semiconductor, which is considered to be the small band gap photovoltaic material with a direct band gap of 0.16 eV. It has a tetragonal structure (space group P42c) with lattice constants a=5.53 Å and c=11.04 Å. This work, a series of high-quality CuFeSe₂ thin films with various thicknesses ranged from 200 to 800 nm were prepared and studied for film thermal conductivity and thermal boundary resistance between film and substrate. These films were fabricated by pulse laser deposition (PLD) on silicon substrates, and their structure and crystallinity were determined by X-ray diffraction pattern. The temperature dependence of cross-plan thermal conductivities of thin films were measured using the differential 3ω technique. In order to obtain the thermal boundary resistance between film and substrate, thermal resistance versus film thickness is plotted and fitted to a curve, and the intercept at zero thickness is defined as the thermal boundary resistance. After the subtraction of boundary thermal resistance, the intrinsic thermal conductivity of each thin film is obtained.

Fig. 1 (a) The X-ray diffraction pattern for various thickness films. The planes of (100), (200) and (300) are clearly observed in 200 and 400 nm thick films. The mark * represents the peak of Cu₂Se substrate. The mark + represents the minor phase Cu₄Se₂ (111) peak in 600 and 800 nm thick films. The tetragonal structure of CuFeSe₂ was shown in right. (b) The (100) plane diffraction peak of different thickness CuFeSe₂ Sample. The thinner sample has the better crystallization. (c) The rocking curve profile for 200, 600, and 800 nm samples. The 200 nm sample has the better preferred orientation than thicker samples.

Fig. 2 The temperature dependence of electrical resistivity of 200, 600 and 800 nm films. All thin films show the semiconductor-like behavior. Inset shows the temperature dependence of activation energy. The activation energy were estimated by the formula \( R=R_0 \exp(E_a/kT) \). The calculated activation energy of CuFeSe₂ thin films is 0.16 eV for 200 nm and ~0.1 eV for 600 and 800 nm sample.

Fig. 3 The temperature dependence of thermal boundary resistance \( \theta_{BD} \). Inset: The thickness dependence of thermal resistance and polynomial fitting. The intercept \( T_0 \) indicates the temperature drop across the boundary interface. The Schematic represents the configuration of sample preparation.

Fig. 4 Temperature dependence of thermal conductivity of CuFeSe₂ thin films of 200, 400, 600, and 800 nm films. The inset (a) shows the thickness dependence of thermal conductivity at 300 K. The inset (b) shows the contributions of thermal conductivities of lattice phonons and conducting electrons calculated from electrical resistivity.

Summary
The thermal conductivity of highly crystalline CuFeSe₂ thin film deposited on silicon oxide substrate was studied. The temperature dependence of thermal boundary resistance was extracted, and the exact thermal conductivity of thin film was obtained after the correction of thermal boundary. The thicker films have lower thermal conductivity due to their poor crystallinity. The main contribution of thermal conductivity in 200 nm film was mainly coming from lattice phonons, and only 3% was contributed by conducting electrons. This result explained the quality of crystallization can dramatically affect the value of thermal conductivity.

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