Experimental Study on Low-Temperature Thermal Conductivity of Silicon Carbide Using the TDTR Method: Postprint

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Abstract

Experimental studies on the thermal conductivity of semiconductor materials such as silicon carbide under low-temperature conditions are extremely scarce, and data are insufficient to meet the optimization requirements of theoretical models. Existing experimental measurements primarily rely on contact-based steady-state methods for thermal conductivity measurement, which suffer from large experimental errors and excessively high costs for low-temperature measurements. In this work, through the organic integration of conventional femtosecond laser pump-probe thermal reflectance method with a low-temperature system, we completed the measurement of the thermal conductivity of single-crystal silicon carbide and its temperature-dependent variation under low-temperature conditions of 4~300 K. The study reveals that the thermal conductivity of single-crystal silicon carbide exhibits a maximum value around 100 K; when the temperature is below 100 K, its thermal conductivity is positively correlated with temperature, whereas when the temperature is above 100 K, its thermal conductivity is negatively correlated with temperature. The deviation of the extremum point' s position from theoretical values may be attributed to factors such as sample electron concentration and defect distribution.

Full Text

Preamble

An Experimental Study on Thermal Conductivity of Silicon Carbide via the TDTR Method under Low Temperatures

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Abstract

Experimental investigations on the thermal conductivity of semiconductor materials such as silicon carbide under cryogenic conditions are extremely limited, resulting in scarce data that cannot satisfy the optimization requirements of theoretical models. Existing experimental measurements primarily rely on contact-based steady-state methods, which suffer from large experimental errors and prohibitive costs for low-temperature testing. This study integrates conventional femtosecond laser pump-probe time-domain thermoreflectance (TDTR) with a cryogenic system to measure the thermal conductivity of single-crystal silicon carbide across the temperature range of 4 K–300 K and characterize its temperature dependence. The results demonstrate that the thermal conductivity of single-crystal SiC exhibits a maximum value around 100 K, showing positive correlation with temperature below 100 K and negative correlation above 100 K. The deviation of the peak position from theoretical predictions may be attributed to factors such as sample electron concentration and defect distribution.

Keywords: time-domain thermoreflectance; cryogenic system; thermal conductivity; silicon carbide crystal

Introduction

Silicon carbide crystals exhibit excellent properties including high thermal conductivity, low thermal expansion coefficient, high hardness, and strong corrosion resistance. As one of the most promising non-metallic functional materials, SiC is widely used in high-temperature engine blades, high-temperature waste heat recovery heat exchangers, and represents an ideal material for cryogenic engineering under special operating conditions. The thermal performance of SiC under relevant operating conditions is a critical parameter for its application. Numerous scholars have investigated the thermal properties of SiC at room and high temperatures, yielding relatively abundant data. For instance, P. G.

Neudeck et al. measured the temperature dependence of SiC thermal conductivity from 300 K to 800 K using steady-state methods and predicted the relationship between thermal conductivity and temperature using various phonon scattering mechanism models [1]. Wu Qingren et al. employed the laser flash method to test the relationship between thermal conductivity and temperature for SiC materials from 300 K to 1300 K, noting an inverse relationship [2]. Su Guoping et al. utilized the 3 method to measure the thermal conductivity of anisotropic SiC crystals at room temperature [3].

In contrast, experimental data on the thermal properties of SiC at cryogenic temperatures remain relatively scarce, with limited research conducted due to experimental difficulties and application domains. Representative achievements include G. A. Slack' s investigation of the influence mechanism of nitrogen and oxygen impurity doping on SiC thermal conductivity, revealing that nitrogen impurities primarily affect phonon scattering by altering the stress field, while oxygen impurities influence phonon scattering through lattice defects [4]. Slack also studied the temperature dependence of thermal conductivity for pure SiC and SiC containing different impurities, demonstrating that heat conduction in SiC is dominated by phonons, with various impurities and grain boundaries causing phonon scattering that reduces thermal conductivity, an effect that becomes more pronounced at lower temperatures [5]. However, these low-temperature experiments predominantly employed steady-state contact methods, with the entire apparatus immersed in liquid helium/liquid nitrogen or ethanol-dry ice mixtures, where measurement accuracy is constrained by multiple factors including temperature control, heating power, heat dissipation, and temperature measurement precision [6].

Overall, research on thermal property measurements under cryogenic conditions remains limited, focusing primarily on thermal conductivity measurements of superconducting materials [7-13] using steady-state contact methods. This paper presents thermal conductivity measurements of SiC under atmospheric pressure from 4 K to 300 K using femtosecond laser pump-probe time-domain thermoreflectance (TDTR) combined with an Oxford Instruments liquid nitrogen/liquid helium cryogenic system. In this thermal property measurement system, the sample resides in a high-vacuum state, and effective experimental signals are obtained through non-contact optical thermoreflectance. The system offers high-precision temperature control with minimal influencing factors during measurement, significantly improving experimental accuracy compared to conventional contact methods.

Achieving and maintaining stable control of cryogenic experimental conditions is a key factor for low-temperature thermal property measurements. Conventional liquid immersion methods cannot achieve continuous temperature control, offering limited temperature sampling points that fail to meet the requirements for dense experimental sampling. This study employs Oxford Instruments' microvolume liquid nitrogen/liquid helium cooling coupled with electric heating and PID control to maintain stable temperature in an ultra-high vacuum sample

chamber, achieving temperature control precision of 0.1 K and ensuring accurate and continuous temperature-dependent measurements. Considering that helium, as a strategic reserve resource, has faced large-scale production restrictions and soaring prices, impacting cryogenic experimental research worldwide, low-temperature TDTR technology provides crucial technical support for cost control and popularization of low-temperature thermal property measurements.

1 Experimental Apparatus and Principle

1.1 Experimental System

The TDTR + Cryogenic experimental system primarily consists of two components: a femtosecond laser pump-probe thermoreflectance system (TDTR) and a cryogenic system, as shown in Figure 1 [Figure 1: see original paper].

(1) Femtosecond Laser Pump-Probe Thermoreflectance System

The TDTR measurement principle involves evaporating a ~100 nm metal film onto the sample surface as a sensing layer. A modulated pulsed laser heats the sensing layer to produce temperature rise, while a probe laser irradiates the heated surface. Within a certain temperature range, the reflectivity of the sensing layer is approximately linear with temperature, so the reflected probe light intensity varies with the surface temperature of the sensing layer. This temperature variation is a characteristic function of the sample structure and corresponding material thermal properties. By fitting the heat transport model with experimental measurement data, unknown thermal properties of the sample can be obtained.

The experimental system employs a Maitai BB Ti:sapphire laser with a wavelength of 800 nm, pulse width of 100 fs, repetition rate of 80 MHz, and power of 1.85 W. The laser is split into pump and probe beams by a polarizing beam splitter. The pump beam passes through a nonlinear bismuth borate (BIBO) crystal for frequency doubling, converting approximately 30% of the 800 nm laser to 400 nm wavelength. A long-wave filter removes the unconverted 800 nm light (eliminating its influence on the detection signal), and the beam is then modulated by an Electro-Optic Modulator into laser pulses with specific waveforms and frequencies to heat the sample surface sensing layer. The probe beam passes through a beam expander that enlarges the beam diameter by 2–3 times, then through a linear displacement stage (travel range of 600 mm, with double reflection achieving a maximum delay time difference of 8 ns between pump and probe beams), polarizing beam splitters, and other optics to maintain collinearity with the pump beam before being focused onto the sample sensing layer by a 10× objective lens. A photodetector senses the reflected probe light, and a lock-in amplifier extracts the effective thermoreflectance signal loaded with electro-optic modulation characteristics.

(2) Cryogenic System

The cryogenic system comprises seven main components: cryogenic chamber,

sample holder, transfer tube, cryogen storage dewar, gas flow pump, molecular pump, and temperature controller. The working principle is as follows: The cryogenic chamber and transfer tube are evacuated by a molecular pump to a vacuum level of ~10 Pa, with the pump continuously operating during experiments. The temperature controller is set to the desired temperature condition and placed in automatic control mode. The gas flow pump is activated, and liquid helium flows from the dewar through the transfer tube to the heat exchanger inside the cryogenic chamber for cooling. Vaporized helium gas is discharged through the transfer tube' s interlayer channel and gas flow pump. Liquid helium cooling is used for the 4 K–77 K range, while liquid nitrogen cooling is employed for temperatures above 77 K.

1.2 Sample Heat Transport Model

The effective signal collected by the lock-in amplifier in the femtosecond laser pump-probe thermoreflectance system is:

$$Z(\omega_0) = \frac{\beta Q_{\text{pump}} Q_{\text{probe}}}{T} H(\omega_0)$$

where is the thermo-optical reflection coefficient of the sensing layer, Q_{pump} and Q_{probe} are the energies of individual pump and probe laser pulses, T is the laser pulse interval, ω_0 is the modulation frequency, and H( ) is the sample' s response in the frequency domain to unit-energy pulse heating:

$$H(\omega) = \frac{1}{\pi R_{\text{pump}}^2} \int_0^\infty \exp\left(-\frac{r^2}{2R_{\text{pump}}^2}\right) \exp\left(-\frac{r^2}{2R_{\text{probe}}^2}\right) \frac{C}{D} r\, dr$$

where R_{pump} and R_{probe} are the laser spot radii of the pump and probe beams on the sample surface, and C and D are two sub-matrices of the sample transfer matrix containing thermal property information. Detailed derivations are available in previous literature [14, 15]. At a specific measurement frequency ω_0, assuming C and D are known, the simulated signal corresponding to the experimental measurement signal can be calculated through H( ) and $Z(\omega_0)$. By fitting C and D, the relevant thermal properties of the sample under investigation can be obtained.

The TDTR system is commonly used for measuring multilayer thin films and their interface thermal resistance. This study aims to test the thermal conductivity of SiC materials under cryogenic conditions. Sample preparation involves polishing the SiC surface, boiling in aqua regia to clean surface impurities, ultrasonic cleaning with acetone, ethanol, and ultrapure water, drying, and then evaporating a ~100 nm thick Al film as the sensing layer using electron beam evaporation (Al has high thermal conductivity, high reflectivity, shallow optical penetration depth—31 nm for 400 nm light and 35 nm for 800 nm light—and good adhesion to most materials). The structure is shown in Figure 2 [Figure

2: see original paper]. This test structure represents a heat transport model for a bilayer film.

2 Experimental Details

2.1 Sample Preparation

The test sample is a single-crystal SiC provided by a commercial supplier. Although direct measurement of the sample' s crystal structure was not performed in this work, basic properties can be determined through thermal conductivity measurements at room temperature. Fitting the amplitude signal yields a thermal conductivity of 478.6 W/(m · K), which is close to the 490 W/(m · K) value for 6H-type single-crystal SiC, leading to the conclusion that the tested sample is 6H-type.

2.2 Sensing Layer Thickness Measurement

The thickness of the sensing layer prepared by electron beam evaporation is an empirical value with low precision. However, the sensing layer thickness is a primary parameter in the heat transport equation with high sensitivity, necessitating improved accuracy. X-ray reflectometry was employed to measure the film thickness, revealing an Al film thickness of 100.24 nm with an error of ±2.5 nm and maximum roughness not exceeding 3 nm. Additionally, the picosecond acoustic method is a common, rapid, non-destructive, and accurate technique for measuring opaque thin film thickness. Since the TDTR system uses femtosecond laser detection of thermal reflectance signals, it possesses the capability for picosecond acoustic thickness measurement. In 2012, Hohensee et al. utilized the TDTR system for sensing layer thickness measurement [16]. This study explored thickness measurement through echo signals, with results shown in Figure 3 [Figure 3: see original paper]. The test employed a delay stage moving speed of 0.3 mm/s and sampling frequency of 10 points/s. With the speed of sound in aluminum being 6400 m/s, the TDTR test signal shows an echo time interval of 31.5 ps, yielding an Al film thickness of 100.1 nm, which agrees well with the X-ray reflectometry measurement.

2.3 Sensitivity Analysis

Sensitivity is a crucial parameter for any measurement method—the higher the experimental data' s sensitivity to the measured parameter, the more accurate the measurement results. In this experiment, the accuracy of measurement results is determined by the sensitivity of the lock-in amplifier' s collected signals to the fitted parameters. We adopted the sensitivity definition from Gundrum et al. [17]:

$$S_x = \frac{\partial \ln Y}{\partial \ln x}$$

where x is the parameter to be fitted, Y is the signal collected by the lock-in amplifier (representing amplitude, phase, or complex signals), and S_x is the sensitivity of the collected signal to parameter x. The logarithmic form eliminates the influence of signal intensity on sensitivity. This study conducted sensitivity analysis on amplitude signals. The Al/SiC sample heat transport model includes six physical parameters: thermal conductivity of Al film (k_{Al}), thermal conductivity of SiC (k_{SiC}), specific heat capacity of SiC ($C_{p,\mathrm{SiC}}$), specific heat capacity of Al film ($C_{p,\mathrm{Al}}$), Al film thickness (δ_{Al}), and interface thermal conductance between Al sensing layer and SiC substrate ($G_{\mathrm{Al/SiC}}$). The sensitivity of $G_{\mathrm{Al/SiC}}$ is very small across the entire delay time range; therefore, this analysis focuses on the remaining five parameters.

Figure 4 [Figure 4: see original paper] shows the sensitivity analysis results. Figure 4(a) presents the amplitude signal sensitivity when all five parameters are increased by 1% from their true values, while Figures 4(b)-4(f) show the sensitivity when each parameter is individually increased by 5%. As seen in Figure 4(a), $C_{p,\mathrm{Al}}$ and δ_{Al} exhibit the highest sensitivity to the amplitude signal throughout the delay time, indicating that these two parameters are most accurately measured by TDTR experiments. This also demonstrates that the accuracy of these two parameter values is the primary controlling factor for the accuracy of other unknown parameters during fitting. The sensitivity of k_{Al}, k_{SiC}, and $C_{p,\mathrm{SiC}}$ to the amplitude signal is approximately one order of magnitude lower than that of $C_{p,\mathrm{Al}}$ and δ_{Al}. Comparison of Figures 4(a)-4(c) reveals that $C_{p,\mathrm{Al}}$ and δ_{Al} have similar sensitivity patterns, decreasing with increasing delay time. Figures 4(d)-4(f) show that the sensitivity of k_{Al}, $C_{p,\mathrm{SiC}}$, and k_{SiC} are essentially of the same order of magnitude—approximately 10% of the sensitivity of $C_{p,\mathrm{Al}}$ and δ_{Al}. The sensitivity of k_{Al} remains essentially constant across the delay time range, while the sensitivity of k_{SiC} and $C_{p,\mathrm{SiC}}$ shows a slight increasing trend with delay time. This indicates that during data fitting in the TDTR system, the selected fitting time range and the accuracy of k_{Al} values under corresponding conditions have relatively minimal impact on the target measurement values.

2.4 Experimental Testing

The physical implementation of the TDTR + Cryogenic experimental system is shown in Figure 5 [Figure 5: see original paper]. The measured sample is installed in a high-vacuum cryogenic sample chamber, with the probe and pump beams from the conventional TDTR system reaching the sample surface sensing layer through optical windows. This study measured the thermal conductivity of SiC from 4 K to 300 K, testing three points at each temperature condition. Each point was repeatedly tested three times using modulation frequencies of 1 MHz, 3 MHz, and 5 MHz, with final results representing the average of multiple measurements.

The essence of TDTR system data processing involves obtaining unknown physical properties by fitting experimental measurement data with the theoretical heat transport equation. This requires that other relevant physical parameters

in the heat transport equation be accurately determined to ensure the accuracy of the unknown parameters. However, data for these parameters under cryogenic conditions are scarce, often requiring values from literature, empirical approximations, or theoretical predictions, making error quantification difficult. These errors inevitably propagate to target values such as SiC thermal conductivity, introducing uncertainty into experimental results. To qualitatively assess whether the TDTR method can satisfy measurement and analysis of the temperature-dependent thermal conductivity of SiC under cryogenic conditions, this study first compares experimental signals under different conditions (as the collected amplitude signal variations reflect changes in the entire sample structure' s physical parameters), avoiding the influence of uncertainties in parameter values within the heat transport equation at different temperatures. The amplitude signals collected by the TDTR system at various temperatures are shown in Figure 6 [Figure 6: see original paper], demonstrating that the sample surface' s thermal reflectance signals vary with time under different temperature conditions, indicating that the TDTR system can capture the comprehensive effects of sample property parameter variations. Specific numerical values are obtained through fitting the heat transport model with experimental signals.

3 Experimental Results Analysis and Discussion

The variation of SiC thermal conductivity with temperature from 4 K to 300 K is shown in Figure 7 [Figure 7: see original paper]. The experimental results demonstrate that the temperature dependence of SiC thermal conductivity measured in this work follows the same trend as the research results of David Morelli [19] and Glen A. Slack [5]. This is primarily because at high temperatures, more phonon modes are excited, increasing the number of heat-carrying phonons and their energy. At low temperatures, although fewer phonons are excited, the phonon mean free path increases, also contributing to enhanced thermal conductivity. The competition between these two mechanisms, combined with phonon scattering from material structural factors such as defects and grain boundaries, creates the trend shown in Figure 7.

While experimental data show good consistency in the high-temperature region, significant discrepancies exist in the low-temperature region, possibly arising from several aspects. First, sample purity and structural differences: although the intrinsic phonon mean free path increases at low temperatures, defects and impurities within different samples cause varying degrees of phonon scattering, leading to substantial differences among researchers' test results [20]. Second, although the TDTR method offers high-precision temperature control for cryogenic testing, inaccuracies in the values of Al film thermal conductivity and specific heat capacity, SiC specific heat capacity, and interface thermal conductance between SiC and Al at low temperatures all introduce errors into the target measurement values, with sensitivity increasing at lower temperatures, making experimental accuracy difficult to control. Other researchers using conventional contact methods such as steady-state techniques also have measurement and pro-

cessing errors from temperature gradients and heat loss, contributing to large discrepancies in low-temperature measurements.

The peak thermal conductivity of SiC measured in this work occurs at approximately 100 K, which differs significantly from Glen A. Slack' s experimental result showing a peak at ~50 K [5], but is close to David Morelli' s result with a peak at ~90 K [19]. Both deviate from the theoretical prediction of ~70 K [21]. This discrepancy may be caused by differences in electron concentration or other defects among various samples [22]. We note that A. J. Minnich et al.' s research indicates that at low temperatures, increased phonon mean free paths may exceed the probe laser spot diameter [23], potentially causing measured thermal conductivity values to be underestimated. However, comparison with experimental data from that literature [23] reveals that when the probe spot size increases from the minimum of 15 μm to the maximum of 60 μm, the corresponding thermal conductivity variation remains far smaller than the difference between our results and those reported by Glen A. Slack. Therefore, while this factor warrants further investigation and discussion, it should not be the primary reason for the significantly lower thermal conductivity values.

This work establishes a non-contact experimental system for characterizing material thermal properties under cryogenic conditions (TDTR + Cryogenic), achieving precise continuous temperature control from 4 K to 300 K and expanding the research capabilities of the original TDTR system. The study reveals that the thermal conductivity of the tested single-crystal SiC exhibits a maximum at 100 K, showing positive correlation with temperature below 100 K and negative correlation above 100 K. The factors influencing SiC thermal conductivity under cryogenic conditions are complex, with different researchers obtaining different values. Due to the complicated influencing factors in low-temperature thermal conductivity measurements, future research will focus on preparing test samples with ideal physical structures, employing appropriate experimental protocols and characterization methods to investigate the effects of various factors on thermal conductivity, and improving the sensitivity and value accuracy of corresponding physical parameters in the heat transport model.

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Note: Figure translations are in progress. See original paper for figures.