RESEARCH ARTICLE

Study of Thermal Conductivity in Two-dimensional Bi₂Te₃ from Micro-Raman Spectroscopy

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Abstract: Background: Topological insulator (TI), Bi₂Te₃ is a new class of quantum materials. Having ultralow dissipation surface states, TIs hold great promise toward different potential applications. Micro-Raman spectroscopy is a conventional and non-destructive technique, which has been widely used to characterize the structural and electronic properties of thermoelectric materials.

Objective: The objective of this study is to review power dependent and temperature dependent Raman spectra of Bi₂Te₃ nanoflakes on SiO₂/Si substrate to estimate the temperature coefficient and thermal conductivity of these flakes for possible application of this material in thermoelectrics.

Method: Bi₂Te₃ flakes of different thicknesses were mechanically exfoliated from high-quality bulk Bi₂Te₃ crystal using Scotch tape on 300 nm SiO₂/ Si substrates. The power dependent and temperature dependent Raman spectra were acquired with the help of HORIBA LabRAM confocal micro-Raman system in a backscattering geometry.

Results: The observed power dependent and temperature dependent Raman spectra of Bi₂Te₃ nanoflakes follow the same trend as discussed in various pieces of literature. From temperature coefficient and power coefficient values, the in-plane thermal conductivity has been estimated, which is found to be in the order of 10⁸ W/m·K. The enhancement in the thermal conductivity suggests that the underlying substrate significantly affects the heat dissipation of the Bi₂Te₃ flake based on the coupling strength with Bi₂Te₃.

Conclusion: This work provides a good platform to understand the role of the substrate on the thermal conductivity of exfoliated Bi₂Te₃ nanoflakes and this study can be extended to other substrates.

Keywords: Topological insulators, thermal conductivity, temperature coefficient, power coefficient, micro-Raman, figure of merit.

1. INTRODUCTION

Topological insulators (TIs) such as Bi₂Te₃, Bi₂Se₃ and Sb₂Te₃ are the new class of the quantum materials, which exhibit an insulating bulk gap and gapless Dirac surface states topologically protected under time reversal symmetry [1-3]. Having ultralow dissipation surface states, TIs hold great promise toward different potential applications including field effect transistors [4], magnetic field sensors [5, 6], and thermoelectricity [7, 8]. Thermoelectric materials can be used in the direct conversion of waste heat into electricity and this is one of the potential technologies for clean and reliable energy harvesting [9]. Typically, thermoelectric efficiency of any material is evaluated by dimension free figure of merit ($ZT$) at temperature $T$, defined as $ZT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is electrical conductivity, and $\kappa$ is thermal conductivity [10]. To increase the figure of merit ($ZT$), these three factors, namely the simultaneous increase in electrical conductivity, increasing thermoelectric power, and decreasing thermal conductivity, need to be controlled [11]. Therefore, recent investigations focus on reducing the dimensionality of these materials into the nanoscale regime to minimize the thermal conductivity and to achieve high figure of merit ($ZT$) [12]. In order to control the thermal conductivity of the typical materials, it is very necessary to understand the phonon dynamics of the materials, especially phonon-phonon and electron-phonon interactions [13]. Micro-Raman spectroscopy is a conventional and non-destructive technique, which has been widely used to characterize the structural and electronic properties of thermoelectric materials [14-17]. However, there are very few reports available regarding the study of thermometry using micro-Raman spectroscopy [18, 19]. Moreover, the effect of...
substrate on the thermal conductivity of TI has not been reported yet.

In the present work, we report power-dependent Raman study at room temperature and temperature-dependent Raman study in the range of 153 K to 303 K of two different mechanically exfoliated Bi$_2$Te$_3$ nano flakes. These studies are very important for a comprehensive understanding of anharmonic lattice vibrations, thermal expansion, and thermal conductivity [20-22]. From the power dependent and temperature dependent Raman spectra, we have calculated the temperature coefficients as well as the thermal conductivity of Bi$_2$Te$_3$ nanoflakes. Finally, the role of underlying SiO$_2$/Si substrate on the thermal conductivity of exfoliated Bi$_2$Te$_3$ nano flakes has been discussed.

2. MATERIALS AND METHOD

Bi$_2$Te$_3$ flakes of different thicknesses (20 nm and 60 nm) were mechanically exfoliated from high-quality bulk Bi$_2$Te$_3$ crystal (2D Semiconductors, USA) using scotch tape on 300 nm SiO$_2$/Si substrates. LV100ND- Nikon Microscope was used to identify and taking optical images of exfoliated Bi$_2$Te$_3$ flakes. The thickness of the Bi$_2$Te$_3$ flakes was measured using an atomic force microscope (Park NX-10 AFM) in non-contact mode.

The Raman spectra were collected on different Bi$_2$Te$_3$ nanoflakes with the help of HORIBA LabRAM confocal micro-Raman system in a backscattering geometry using a spectrometer equipped with a liquid-nitrogen-cooled CCD camera. A laser (632 nm) with spot size ~1 μm and tunable optical power from ~0.06 mW to 5.2 mW was used as the excitation source. The power dependent and temperature dependent Raman spectra were acquired in the frequency range from 100 cm$^{-1}$ to 160 cm$^{-1}$ with a spectral resolution of 1 cm$^{-1}$. Every Raman data were collected using integration time of 10s, acquisitions of 10 and 1800 grating. For room temperature (RT) Raman measurements, 100X objective was used while long working distance 50X objective was used for temperature dependent Raman measurements.

3. RESULTS AND DISCUSSION

Topological insulator, Bi$_2$Te$_3$ crystallizes in the rhombohedral crystal structure with space group $D_{3d}^5$ (R$ar{3}m$) and there are five atoms in its unit cell [18]. Bi$_2$Te$_3$ crystal forms by stacking five-atom layers along the z direction, which is known as a quintuple layer (QL) as shown in Fig. 1, with a thickness of about 0.96 nm [18]. The atomic arrangement of Bi$_2$Te$_3$ crystal shows that the Bi atom is sandwiched between two Te atoms, with the Te(2) atom acting as an inversion centre. Because of the centrosymmetric nature, the crystal structure gives rise to mutually independent Raman active modes. The strong covalent forces hold atoms together within a single QL, while the weak van der Waals’ force works between QLs. The bulk crystals of Bi$_2$Te$_3$ can be easily mechanically exfoliated due to weak van der Waals’ force in out of the plane direction. Although exfoliated samples keep the same composition and structure as the bulk crystals, but phonon dynamics change, when its thickness is reduced to nanoscale level [14, 15].

In the present investigation, mechanically exfoliated Bi$_2$Te$_3$ flakes were transferred on 300 nm SiO$_2$/Si substrate. Fig. 2(a) shows the optical image of two Bi$_2$Te$_3$ nanoflakes (denoted as Flakes 1 & Flakes 2). One can observe that the lateral dimensions of the flakes are in the range of 5 μm to 10 μm, which are large enough to perform further experiments. The high-resolution AFM images of the mechanically exfoliated Bi$_2$Te$_3$ flakes and their height profiles are presented in Fig. 2(b,c). From the AFM images, it is observed that the surface of exfoliated flakes is smooth and uniform in most of the regions. These regions of the Bi$_2$Te$_3$ flakes have been used to perform Raman measurements. The thicknesses of the Bi$_2$Te$_3$ flakes (Flakes 1 & Flakes 2) have been calculated from the AFM height profiles, which are found to be 20 nm and 60 nm, respectively, as shown in Figs. 2b & 2c.

In order to investigate the thermoelectric properties of the exfoliated Bi$_2$Te$_3$ flakes, micro-Raman spectroscopy has been performed using 632 nm laser. Fig. 3(a, b) shows power
Study of Thermal Conductivity

Fig. (2). (a) is the optical image of Bi$_2$Te$_3$ flakes of thicknesses of 20 nm (Flake1) & 60 nm (Flake2) respectively and (b) & (c) are their AFM images and height profiles respectively. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Fig. (3). (a) and (b) are the Power dependent micro-Raman spectra of 20 nm and 60 nm thicker Bi$_2$Te$_3$ flakes respectively. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

dependent Raman spectra of the 20 nm and 60 nm Bi$_2$Te$_3$ flakes at room temperature. As seen in Fig. 3(a,b), two prominent characteristics of Raman modes $E^2_g$ and $A^2_{1g}$ have been observed at \( \sim 102 \text{ cm}^{-1} \) and \( \sim 135 \text{ cm}^{-1} \) respectively for both of the flakes similar to that reported in the literature [17, 23]. With an increase in laser power, red shift as well as increase in peak intensity is observed in both of the Raman peaks. These changes are mainly due to variation in the local temperature of the sample’s surface because of an increase in the laser power from 0.4 mW to 2.6 mW [24, 25]. However, the protocol has been taken in selecting the above powers to avoid any burning of the flakes during the measurements. Power coefficients of the Raman modes ($E^2_g$ and $A^2_{1g}$) of Bi$_2$Te$_3$ flakes with different thicknesses have been calculated through the linear fitting of power dependence peak shift. The power-dependent peak positions in the linear and low-power range, which is governed by

\[
\Delta \omega = \omega(P_2) - \omega(P_1) = \chi_P(P_2 - P_1) = \chi_P \Delta P
\]

Therefore,

\[
\chi_P = \frac{\Delta \omega}{\Delta P}
\]  

Here \( \chi_P \) is the slope of power dependence in the linear region which is known as the first-order power-dependent coefficient and \( P \) is the laser power [26].

The values of the power coefficients are listed below in Table 1, which are found to be very low. We believe that such a low power coefficient is due to the substrate effect, similar to that reported in Su et al. for black phosphorus layers [27]. The power coefficient values reported in their work are lesser as compared to those of suspended samples by a factor of \( \sim 2.2 \) for all of the Raman modes [27].

Fig. 4 (a,b) shows temperature dependent Raman spectra of 20 nm and 60 nm Bi$_2$Te$_3$ flakes respectively, in the temperature ranges 153 K to 303 K. The characteristics Raman modes $E^2_g$ and $A^2_{1g}$ have been observed similar to power-dependent Raman spectra. As the temperature increases, both of the Raman modes get red shifted and broadened for both the flakes. The change in the Raman peak position with respect to temperature is governed by anharmonic terms in the lattice potential energy, which is determined by the anharmonic potential constants, the phonon occupation number, and the thermal expansion of the crystal [11, 28]. In addition, the decay of zone centre optical phonon into acoustic and
optical phonons leads to broadening of the Raman peaks with an increase in temperature [24]. The variation in the Raman peak position of the normal modes with temperature is mainly due to the contribution from thermal expansion or volume contribution and from the temperature contribution that results from anharmonicity. The phonon frequency $\omega$ can be expressed as a function of volume and temperature as follows [29]:

$$
\left(\frac{\partial \ln \omega}{\partial T}\right)_p = \left(\frac{\partial \ln V}{\partial T}\right)_p \left(\frac{\partial \ln \omega}{\partial \ln V}\right)_T + \left(\frac{\partial \ln \omega}{\partial T}\right)_V
$$

$$
= -\frac{\gamma}{k} \left(\frac{\partial \ln \omega}{\partial p}\right)_T + \left(\frac{\partial \ln \omega}{\partial T}\right)_V
$$

(2)

Where, $\gamma \approx \left(\frac{\partial \ln \nu}{\partial T}\right)_p$ and $k \approx -\left(\frac{\partial \ln V}{\partial p}\right)_T$ are the volume thermal coefficient and isothermal volume compressibility. The first term of the right-hand side of the equation represents the volume contribution at a constant temperature, and the second term represents the temperature contribution at constant volume. Hence anharmonic (pure-temperature) contribution can be determined from the values of $\gamma$, $k$, and isobaric temperature and isothermal pressure derivative of phonon frequency of the normal modes.

Fig. 5 (a-d) presents the plots of Raman peak shift and FWHM versus temperature of $E_g^2$ and $A_{1g}^2$ modes for different thicknesses. As temperature increases, all the peaks clearly show the linear shift to lower wave numbers and the FWHM also increases almost linearly with temperature. The temperature dependence of $E_g^2$ and $A_{1g}^2$ Raman modes is given by the following relation [11]:

$$
\omega(T) = \omega_0 + \alpha_1 T + \alpha_2 T^2
$$

(3)

Where $\omega_0$ is the frequency of $E_g^2$ and $A_{1g}^2$ modes for temperature $T$ at 0 K, $\alpha_1$ and $\alpha_2$ are the first-order and second-order temperature coefficients. The second-order term of temperature coefficient is expected to appear only at the high temperature values, which is beyond the scope of the present discussion. Using equation (3), the calculated first order temperature coefficients of $E_g^2$ and $A_{1g}^2$ modes of Bi$_2$Te$_3$ flakes for thicknesses 20 nm and 60 nm are listed in Table I. All the temperature coefficient values are found in the order of $10^{-2}$ cm$^2$/K. The values of first order temperature coefficients for 20 nm Bi$_2$Te$_3$ flake are less than those of 60 nm flake of both $E_g^2$ and $A_{1g}^2$ modes. Therefore, reducing the thickness directly affects the temperature coefficient values of Bi$_2$Te$_3$ flakes.

Finally, using first order temperature coefficient and power coefficient, we can calculate the thermal conductivity of Bi$_2$Te$_3$ flakes. The thermal conductivity can be estimated approximately using the formula below, which has been developed for 2D materials [30],

$$
\kappa = \alpha_1 \left(\frac{1}{2\pi h}\right)\chi_p^{-1}
$$

(4)

Where, $\kappa$ is thermal conductivity, $h$ is the thickness of the 2D film of the material, $\alpha_1$ is the first-order temperature coefficient and $\chi_p$ is the first-order power-dependent coefficient of particular Raman modes. Using equation (4), the calculated in-plane thermal conductivity of Bi$_2$Te$_3$ flakes for thicknesses 20 nm and 60 nm are listed in Table I. These values of thermal conductivities are higher than the reported thermal conductivity of Bi$_2$Te$_3$Se TI thin films [31]. High
thermal conductivity suggests that the supporting substrate plays a more sensitive role rather than just as a medium, i.e. the interfacial charges might significantly affect the thermal conductivity [27]. This higher thermal conductivity at the supported region can also explain the smaller temperature rise under high laser power. Therefore, it is concluded that substrate can significantly affect the heat dissipation of the Bi2Te3 flake. Recently, Ong et al. have also reported a theoretical study on the substrate effect of the thermal conductivity of graphene. The authors also found that both the reduction and the increment of thermal conductivity can be induced by the substrate, depending on the coupling condition [32]. Moreover, the thermal conductivity value of Bi2Te3 flake with the thickness of 20 nm is found to be higher than that for 60 nm flake as the substrate effect is more dominant for lower thickness flake.

The above results confirm that there is a direct effect of supported substrate, SiO2/Si, on the thermal conductivity value of Bi2Te3 nanoflakes. Therefore to calculate the actual thermal conductivity value of Bi2Te3 nanoflakes, free standing flakes would be ideal, which is our future direction.

**CONCLUSION**

In conclusion, we have successfully synthesized 2D Bi2Te3 TI nanoflakes down to 20 nm thickness using a mechanical exfoliation technique. Temperature dependent Raman study in the temperature range 153 K to 303 K and power dependent Raman study at room temperature have been carried out on the exfoliated nanoflakes in a confocal geometry. The temperature dependence of the peak position and line width of phonon modes A1g and E2g modes have been analyzed to determine the temperature coefficient, which is found to be in the order of 10^{-2} cm^{-1}/K. Using temperature coefficient and power coefficient values, in plane thermal conductivity has been estimated, which is in the order of 10^2 W/m-K on SiO2/Si supported substrate. The thermal conductivity value of Bi2Te3 flake with thickness of 20 nm is found to be higher than that of Bi2Te3 flake with thickness of 60 nm due to the substrate dominant effect for lower thickness flake. The effect of substrate on thermal conductivity has been explained in detail. This work provides a good platform to understand the role of a substrate on the thermal

**Table 1. Comparison of power coefficients, first order temperature coefficients, and in plane thermal conductivity of Bi2Te3 flakes of different thicknesses (20 nm & 60 nm).**

<table>
<thead>
<tr>
<th>Thickness – Raman Mode</th>
<th>Power Coefficient (cm^{-1}/mW)</th>
<th>Temperature Coefficient (cm^{-1}/K)</th>
<th>Thermal Conductivity (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 nm-E2g</td>
<td>-0.23</td>
<td>-0.0125</td>
<td>~ 432</td>
</tr>
<tr>
<td>20 nm-A1g</td>
<td>-0.38</td>
<td>-0.0134</td>
<td>---</td>
</tr>
<tr>
<td>60 nm-E2g</td>
<td>-0.31</td>
<td>-0.0149</td>
<td>~ 127</td>
</tr>
<tr>
<td>60 nm-A1g</td>
<td>-0.30</td>
<td>-0.0173</td>
<td>---</td>
</tr>
</tbody>
</table>

Fig. (5). (a) and (b) The peak position vs. Temperature and FWHM vs. Temperature of E2g and A1g Raman active modes respectively for 20 nm. Similarly (c) and (d) for 60 nm. (A higher resolution / colour version of this figure is available in the electronic copy of the article).
conductivity of exfoliated Bi$_2$Te$_3$ nanoflakes and this study can be extended to other substrates.

**LIST OF ABBREVIATIONS**

AFM = Atomic Force Microscopy  
FWHM = Full Width at Half Maximum  
OM = Optical Micrograph  
QL = Quintuple Layer  
TIs = Topological Insulators  
$ZT$ = Figure of Merit

**CONSENT FOR PUBLICATION**

None.

**AVAILABILITY OF DATA AND MATERIALS**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

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Study of Thermal Conductivity


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