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Laser flash Raman spectroscopy method for characterizing thermal diffusivity of supported 2D nanomaterials

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ABSTRACT

2D nanomaterials have been attracting extensive research interests due to their superior properties and the accurate thermophysical characterization of 2D materials is very important for nanoscience and nanotechnology. This paper presents a transient "laser flash Raman spectroscopy" method for measuring the thermal diffusivity of 2D nanomaterials in the supported form without knowing the laser absorption coefficient. Square pulsed laser rather than continuous laser is used to heat the sample and the accumulated Raman signals are used to determine the time-averaged temperature rise of both the supported 2D material and the substrate. The laser absorption coefficient can be eliminated by comparing the temperature rises measured with different laser spot sizes and laser pulse durations. The method sensitivity is also analyzed by case studies for typical 2D nanomaterials. This method is useful for measuring the thermophysical properties of 2D materials in the most applicable forms and figuring out the difference between the supported and free-standing 2D material.

1. Introduction

Since the discovery of exfoliated graphene in 2004 [1], several kinds of 2D nanomaterials have been produced and continuously attracting extensive research interests due to their superior properties and promising applications in nanoscale electronics and electro-mechanical systems. As for the thermal science, the accurate thermophysical characterization of 2D materials is very important for both the applications and fundamental research. So far, some contact measurement methods have been used to determine the thermal conductivity of the most popular 2D material, namely graphene. These contact methods included the electrical self-heating method [2,3], the T-type method [4] and the suspended microdevice method [5–7], which were based on the temperature dependent electrical resistance of suspended sensors or graphene itself and had relatively high temperature resolutions. However, the electrical and thermal contact resistance can give rise to large errors. Moreover, the suspended micro/nano devices with electrodes are very difficult to fabricate and can be damaged during the electrical measuring process.

Besides the contact methods, a non-contact Raman spectroscopy technique has been used to determine the thermal conductivity of suspended 2D materials such as graphene [8–16], 2D molybdenum disulfide (MoS_2) [17,18], 2D tungsten disulfide (WS_2) [19] and 2D hexagonal boron nitride (h-BN) [20]. In these measurements, the 2D materials were suspended over holes or trenches and heated by continuous laser while the temperature at the laser spot was measured by the Raman band shifts based on the linear relationship between the Raman band shifts and temperature. However, the heat flux, i.e. the absorbed laser power, was either theoretically estimated or measured by a laser power meter with uncertainty [15], resulting in large errors in thermal conductivity characterization.

On the other hand, compared with the suspended 2D materials, the supported 2D materials were seldom measured due to the difficulty of eliminating the interfacial thermal resistance, although in most applications the 2D nanomaterial will be used in the supported form and the interfacial effects can give rise to thermophysical properties distinctly different from the suspended counterpart. Cai et al. [15] provided a Raman spectroscopy method for simultaneously determining the thermal conductivity of graphene and interfacial thermal conductance between graphene and the Au substrate by changing the laser spot radii and estimating the laser absorption coefficient. Cai et al. [15] assumed that the laser absorption of the supported graphene was twice of the suspended graphene and that the temperature rise of the Au substrate was negligible. The second assumption was validated by the fact that the maximum temperature rise in the Au substrate was estimated to be less than 4 K when the measured temperature rise of

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graphene was 114 K. Zdrojek et al. applied Cai et al.'s method in the thermal conductivity and interfacial thermal conductance measurements of 2D MoS_2 [21] and single-walled carbon nanotube thin films [22] supported on SiO_2/Si substrates. During the measurements, Zdrojek et al. [21,22] also checked from the Raman spectra that the temperature rise of the Si substrate was negligible while the maximum temperature rise of the supported 2D nanomaterial was about 100 K. Further, Judek et al. [23] improved the steady-state heat conduction model of supported 2D materials by considering the temperature rise of the SiO_2 substrate. Judek et al. [23] took the interfacial heat conduction as surface heat input to the substrate but neglected the laser power absorbed by the substrate. Judek et al. [23] simultaneously extracted the thermal conductivities and interfacial thermal conductance of graphene and MoS_2 supported on SiO_2 by numerically solving this improved steady-state model with an estimated laser absorption coefficient and changing the laser spot radii by changing the z positions of the objective lens. However, in the methods developed by Cai et al. [15] and Judek et al. [23], the laser absorption coefficient of the supported 2D material is a must-know value but can only be estimated rather than directly measured, which can cause large systematic errors.

Besides, the thermal diffusivity is another important thermal transport property but there is not yet any effective method for directly measuring the thermal diffusivity of supported 2D materials in the literature. This paper presents a transient "laser flash Raman spectroscopy" method for measuring the thermal diffusivity of 2D nanomaterials in the supported form without knowing laser absorption. A series of cycled square laser pulses rather than continuous laser is used to heat the sample and the accumulated Raman signals are used to determine the time-averaged temperature rises of both the supported 2D material and the substrate. The average temperature rises will change with different laser pulse durations and laser spot sizes and the laser absorption coefficient can be easily eliminated by a normalization technique. Actually, we previously applied this transient laser flash Raman spectroscopy method in measuring the thermal diffusivity of suspended multiwall carbon nanotubes with ~90 μm length and 8 nm diameters in vacuum [24] and presented the theory for applying this transient method in characterizing suspended circular 2D materials [25]. As for supported 2D materials, the transient heat conduction models with a general analysis of the substrate are much more sophisticated. Here, the transient heat conduction models coupling the supported 2D material and the substrate are analytically solved and the sensitivity of this method is analyzed by case studies for typical 2D nanomaterials.

2. Two-dimensional transient model and the solutions

2.1. Two-dimensional transient model coupling the temperatures of the supported material and the substrate

As shown in Fig. 1, a series of cycled square laser pulses is irradiated at the 2D nanomaterial supported on a substrate. The sample is heated during the laser pulse duration and fully cooled to the ambient temperature during the pulse interval. During every laser pulse, the incident laser is partly absorbed by the 2D material and partly transmitted onto the substrate, absorbed and reflected at the substrate surface. In general, there will be temperature rises in both the 2D material and the substrate and heat will be transferred between the 2D material and the substrate through interfacial thermal conductance. The interfacial heat flux is at least 5 orders larger than the heat loss through radiation or natural convection [15] and thus this supported material can be measured in atmospheric condition without considering heat loss to the environment. The time averaged temperature rises of both the 2D material and the substrate can be simultaneously measured from their Raman band shifts and will change with varying laser heating time. If the laser pulse duration is much longer than the relaxation time of the energy carrier of the test material, the heat conduction processes in the 2D material and the substrate are diffusive and can be expressed in cylindrical coordinates as Eqs. (1) and (2):

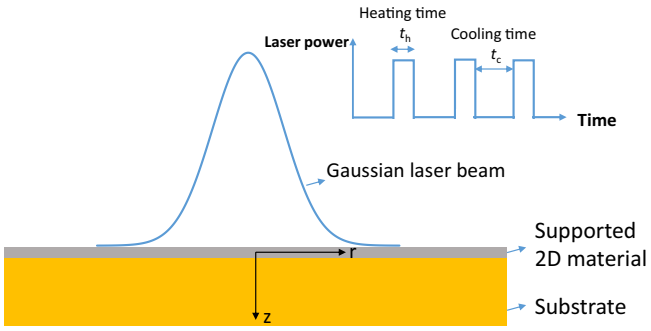

Fig. 1. Schematic of the supported 2D material and the square pulsed Gaussian laser.

$$\frac{\partial^2\theta_{sup}(r,t)}{\partial r^2}+\frac{1}{r}\frac{\partial\theta_{sup}(r,t)}{\partial r}+\frac{\eta_1 q_0\exp(-r^2/r_0^2)}{\lambda_{sup}d}-\frac{h(\theta_{sup}(r,t)-\theta_b(r,0,t))}{\lambda_{sup}d}=\frac{1}{\alpha_{sup}}\frac{\partial\theta_{sup}(r,t)}{\partial t}\qquad(0\leqslant r<\infty;\ 0\leqslant t\leqslant t_h),\tag{1}$$

$$\frac{\partial^2\theta_b(r,z,t)}{\partial r^2}+\frac{1}{r}\frac{\partial\theta_b(r,z,t)}{\partial r}+\frac{\partial^2\theta_b(r,z,t)}{\partial z^2}=\frac{1}{\alpha_b}\frac{\partial\theta_b(r,z,t)}{\partial t}\qquad(0\leqslant r<\infty,\ 0\leqslant z<\infty;\ 0\leqslant t\leqslant t_h),\tag{2}$$

where $\theta_{sup}(r, t)$ is the temperature rise of the supported 2D material at radius r and time t and $\theta_b(r, z, t)$ is the temperature rise of the substrate at position (r, z) and time t; q_0 is the laser power density at the beam center, r_0 is the laser spot radius where the laser power density attenuates to $1/e$ of q_0, η_1 is the effective laser absorption coefficient of the supported 2D material, and thus the total laser power absorbed by the 2D material is $Q=\eta_1 q_0\pi r_0^2$; λ_{sup} and d are respectively the thermal conductivity and thickness of the 2D material, h is the interfacial thermal conductance per unit area, and α_{sup} and α_b are respectively the thermal diffusivities of the supported 2D material and the substrate, t_h is the laser heating time.

Before the laser heating, the sample remains at the ambient temperature and the initial conditions are expressed as

$$\theta_{sup}(r,0)=\theta_b(r,z,0)=0.\tag{3}$$

At the boundary $r=0$, the axial symmetry condition gives

$$\frac{\partial\theta_{sup}}{\partial r}(0,t)=\frac{\partial\theta_b}{\partial r}(0,z,t)=0.\tag{4}$$

At the boundary $r=\infty$, the temperature rises are zero and the boundary conditions are expressed as

$$\theta_{sup}(\infty,t)=\theta_b(\infty,z,t)=0.\tag{5}$$

If the optical absorption depth of the substrate for the incident laser is much smaller than the thickness of the substrate, the laser heating effect for the substrate can be regarded to take place only at the substrate surface. In fact, laser exponentially attenuates in the substrate and the optical absorption depths of common substrates such as semiconductors like silicon or germanium and metals like gold or copper are no more than 100 nm for common green or blue laser [26]. On the other hand, the thickness of the substrate is usually about 1 mm and thus the surface heating assumption is