Phonon propagation in isotope diamond thin films studied by pump-probe laser reflectivity measurement

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1. Introduction

Diamond is widely used in industry because of its many excellent properties, such as the highest hardness, stiffness, and thermal conductivity. The highest thermal conductivity makes it suitable for heatsinks in electronics devices, especially in integrated circuits. The highest stiffness allows us to develop high-frequency acoustic-wave resonator devices. The elasticity also relates to interatomic potentials and is widely used for validating density-functional-theory calculations for predicting physical properties.

Natural diamond consists of 98.9% ^{12}C and 1.1% ^{13}C. Anthony *et al.* [1] reported that thermal conductivity of diamond was enhanced by nearly 50% at room temperature by decreasing the ^{13}C ratio to 0.1%; this is a surprising result because the thermal conductivity of diamond could be enhancement only by removing 1% impurity of ^{12}C. Vogelgesang *et al.* [2] indicated that the bulk modulus of pure ^{13}C diamond is higher than that of pure ^{12}C diamond by 0.18%.

However, details of the isotope effect on the phonon properties of diamond remain unclear due to the difficulties in measuring elastic stiffness and thermal conductivity of diamond thin films. Recent progresses in the chemical vapor deposition (CVD) technique have allowed fabrication of high-purity diamond thin films with controlling the isotope ratio. However, the time for phonon propagation inside the diamond thin films is too short (~100 ps) to be measured with conventional methods. An advanced ultrafast ultrasonic experimental method is then required for accurate determination of the phonon behavior in diamond thin films. In this study, we evaluate the elastic constant and thermal diffusivity along the film thickness direction using the pump-probe ultrafast light pulse method.

2. Methodology

We used picosecond ultrasound technique to detect the Brillouin oscillation inside the isotope diamond thin films. Picosecond ultrasound is a pump-probe technique. The probe light is backward diffracted by the acoustic wave which is induced by the pump light. The diffracted light interferes with the surface reflected probe light. The total reflectivity of the probe light changes periodically. Such phenomenon is so-called Brillouin oscillation. With the calculation of backward diffraction and Brillouin frequency, the out-of-plane sound velocity can be determined. The out-of-plane elastic constant can also be determined via $C_{11}=\rho v^2$.

The out-of-plane thermal conductivity is also evaluated by the reflectivity change of the probe light, because it is proportional to the surface temperature according to the photo thermal effect. We simulated the surface temperature change after the transient heating by the pump light pulse and determined the thermal conductivity by comparing the measured and simulated reflectivity change. Our simulated model consists of 10-nm Pt top surface, 3000 nm diamond thin film, and 0.5 mm diamond substrate, which are same as the experiment. We changed only the thermal conductivity of the diamond thin-film layer, remaining all other parameters unchanged. In the simulation of the surface-temperature change, we start from the heat equation

$$\frac{\partial T(t,z)}{\partial t}=\frac{\kappa}{\rho C}\frac{\partial^2 T(t,z)}{\partial z^2}=\alpha\frac{\partial^2 T(t,z)}{\partial z^2} \tag{1}$$

After applying Fourier transformation for time, used two boundary conditions:

1. The heat is supplied by the pump light pulse:

$$f_1^{(in)}(t)=-k_1\frac{\partial T}{\partial z}=pH(t)e^{-at} \tag{2}$$

where k_1 denotes the thermal conductivity of the Pt thin film. p is the power of the pump light pulse. H(t) is the step function, a is the pulse with.

2. The back surface of the substrate is adiabatic.

$$f^{(out)}(t)=-k_3\frac{\partial T}{\partial z}=0 \tag{3}$$

where k_3 denotes the thermal conductivity of the substrate.

The surface temperature was then calculated by the inverse Fourier transform method. Fig. 1

shows examples of calculations. Our calculation indicates that the surface temperature drops fast with the increment of the thermal conductivity of the diamond layer.

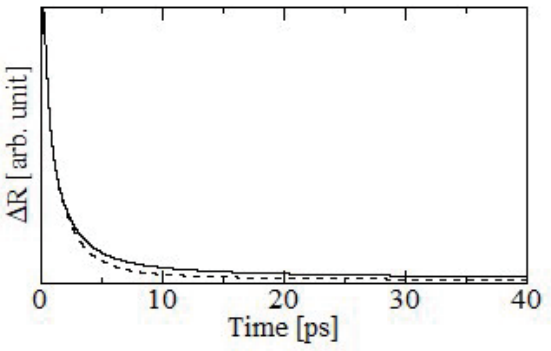

Fig. 1 The simulation result for the surface temperature change. The solid and dashed lines are calculations for thermal conductivity of diamond thin film of 1000W/mK and 4000W/mK, respectively.

3. Experiment

We measured three epitaxial [100] single layer isotope diamond specimens with 0%, 50%, and 100% ^{13}C. We use Ti-Sapphire pulse laser with 140 fs duration and 80 MHz repetition rate. The wavelength of the pump and the probe light pulses are 800 nm and 400 nm, respectively.

Fig. 2 shows the as-measured Brillouin-oscillation signal measured for 100% ^{13}C diamond thin film. We subtracted the background of attenuation (Fig. 3). Then obtain the time-frequency analysis by using FFT in many short time segment to distinguish the interface of the diamond thin film and the substrate (Fig. 4).

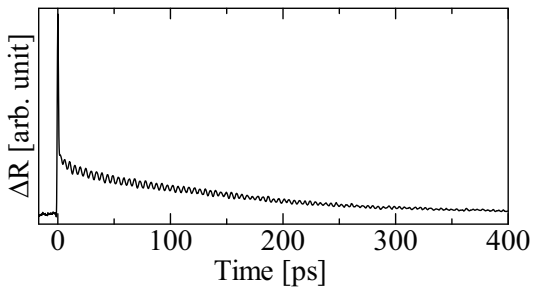

Fig. 2 The typical measured reflectivity change of the probe light versus propagating time of the ultrasound.

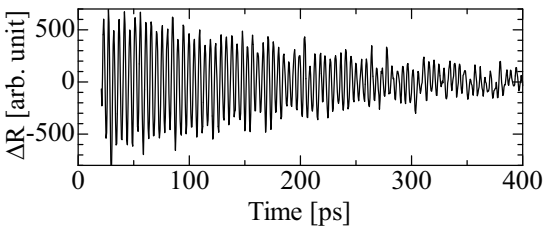

Fig. 3 The baseline-subtracted Brillouin oscillation signal of Fig. 2.

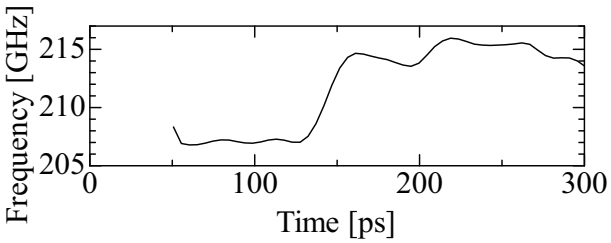

Fig. 4 Time frequency analysis of Brillouin oscillation for 100%^{13}C diamond-film specimen.

4. Result & Discussion

We succeeded in measuring the out-of-plane elastic constant (C_{11}) of single layer diamond thin films with 0% 50% and 100%. The result shows in Fig. 4. The elastic constant of ^{13}C is higher than that of ^{12}C by 0.6%. Through the figure, 50% ^{13}C possesses the highest elastic constant, which is higher than that of ^{12}C by 0.12%. Theoretically, we speculate that the elasticity of isotope diamond increases with the ^{13}C ratio because impurity diamond consists of ^{12}C and ^{13}C so that the elasticity should be between the two. Furthermore, previous theory, in Ref. [2] expects that the elastic constant increases with the ^{13}C ratio. Thus, the existing theory fails to explain this observation and its clarification is also a purpose of my research.

We also compared the thermal conductivity of the three specimens. The 50% ^{13}C shows significantly low thermal conductivity compared with pure ^{12}C or ^{13}C diamond. It is reasonable because the more the impurity of isotope, the more the phonon scattering inside the material, and the lower the thermal conductivity. The thermal conductivity of ^{12}C shows slightly higher than that of ^{13}C. It also fits our expectation well. Pure ^{12}C and ^{13}C roughly possess the same heat capacity and the phonon mean free path. According to the phonon kinetic theory, the thermal conductivity proportional to the velocity of phonon. The acoustic wave we obtained in Brillouin frequency shows that the speed of wave in ^{12}C is faster than that in ^{13}C. We can expect that the thermal conductivity of ^{12}C is also higher than that of ^{13}C.

Acknowledgment

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References

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