

The intrinsic temperature effect of the Raman spectra of graphite

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The Raman spectra of ion-implanted highly oriented pyrolytic graphite (HOPG) are reported, in which an additional mode at 1083 cm^{-1} and three doublet structures in the positions of ~ 1350 , ~ 2450 , and $\sim 2710\text{ cm}^{-1}$ are revealed. Noticeable frequency shifts are observed for all the Raman bands between the spectra excited with different laser powers, which are interpreted as the pure temperature effect and a downshift in the C–C stretching frequency induced by the thermal expansion. Moreover, the pure temperature effect $(d\omega/dT)_V$ without anharmonic contribution is achieved in pristine HOPG. The results suggest that the pure temperature effect without anharmonic contribution plays an important role in the frequency shifts with temperature. © 1999 American Institute of Physics. [S0003-6951(99)01313-3]

The Raman spectra of graphite materials, such as graphite^{1,2} and carbon fibers,³ are known to reflect their structural features very sensitively, and the relation between spectra and structures has been well discussed.^{4–6} It is well known that graphite materials have a strong temperature effect (e.g., carbon nanotubes⁷) and that the Raman peaks will downshift while increasing the temperature of the samples. The variation of Raman peaks of graphite materials excited with different wavelengths has also been studied widely.⁸ The change of phonon frequency with temperature and excitation wavelength may present some difficulties in the analysis of spectra, and it is necessary to investigate, in detail, the spectra behavior dominated by the temperature. The volume and temperature effect dominate the change of phonon frequency with temperature;⁹ however, the volume effect induced by the thermal expansion cannot interpret the temperature dependence of the phonon frequency of diamond consistently.^{10,11} By extracting the pure volume dependence from the experimental result, the pure temperature effect has been found to play an important indirect role in the frequency shift of phonon.¹⁰ Because of much higher thermal conductivity, the temperature dependence of *highly oriented pyrolytic graphite* (HOPG) could not be observed previously; although, the graphite crystal is useful to investigate frequency shifts induced by the pure temperature effect because of its lower thermal expansion. However, we found that it is much easier to investigate the temperature dependence of Raman spectra when HOPG is implanted. A comparison of the temperature dependence of Raman spectra of pristine and ion-implanted HOPGs shows that the pure temperature effect still plays an important role in the shift of phonon frequency with temperature even when the anharmonic contribution is rather small.

The samples of HOPG are standard ones for achieving the atomic image of the graphite layer in a scanning tunneling microscope system (Park Scientific Instruments). Some of them have been implanted with carbon (¹²C) ions at ambient temperatures (CHOPG), with dose of 1.0

$\times 10^{14}$ ions/cm² at an accelerating voltage of 100 keV. The ion beam was normally directed to the graphite *c* face. The Raman spectra of the pristine and ion-implanted HOPGs are excited with 514.5 nm of an Ar⁺ laser (the laser power arrived at our samples is in the range 2–100 mW), and was recorded by the Dilor Super Labram in backscattering geometry at room temperature. This Raman system consists of a microscope with 100× objective lens (numerical aperture = 0.9), which allows a spatial resolution of less than 2 μm .

It is well known that except for the E_{2g} mode at $1582(G)\text{ cm}^{-1}$ in the Raman spectra of graphite,¹² there are two additional extra first-order lines at ~ 1360 and 1620 cm^{-1} for ion-implanted HOPG and microcrystalline graphite. These extra first-order lines have been interpreted as fundamentals corresponding to the high density of phonon states,^{5,13,14} and are usually designated as *D* and *D'* modes. In the region of higher-order Raman spectra, five distinct lines at ~ 2440 , $\sim 2720(2D)$, $\sim 2930(D+G)$, $\sim 3240(2D')$, and $\sim 4320(2D+G)\text{ cm}^{-1}$ are exhibited in the pristine and ion-implanted HOPGs.^{2,4–6,8,15} The inset of Fig. 1 shows the first- and second-order Raman bands of CHOPG excited with 15 mW. When compared to the reported Raman spectra of the ion-implanted HOPG,^{5,15–17} it was found that there exists a Raman band at 1083 cm^{-1} apparently (marked as *T* for convenience), which is not observed in HOPG. It is considered to be fundamental that is attributed to the features in the density of states. Moreover, there are three doublets at 1349 and 1368 cm^{-1} in the position of $\sim 1360(D)\text{ cm}^{-1}$, at 2687 and 2726 cm^{-1} in the position of overtone of *D* mode at $\sim 2730(2D)\text{ cm}^{-1}$, and at 2440 and 2458 cm^{-1} in the position of $\sim 2450\text{ cm}^{-1}$. Here, the doublet of 1349 and 1367 cm^{-1} was designated as D_1 and D_2 , and its overtone at 2687 and 2726 cm^{-1} as $2D_1$ and $2D_2$, respectively. We also designated the doublet in the position of $\sim 2450\text{ cm}^{-1}$ as $T+D_1$ and $T+D_2$ from the frequency match of these combination modes. This assignment is consistent with that of $\sim 2450\text{ cm}^{-1}$ in the graphite from the frequency match and λ dependence.⁸ For pristine HOPG, although the *D* doublet and *T* mode are forbidden because of the selection rule, the doublets of ~ 2450 and $\sim 2720\text{ cm}^{-1}$

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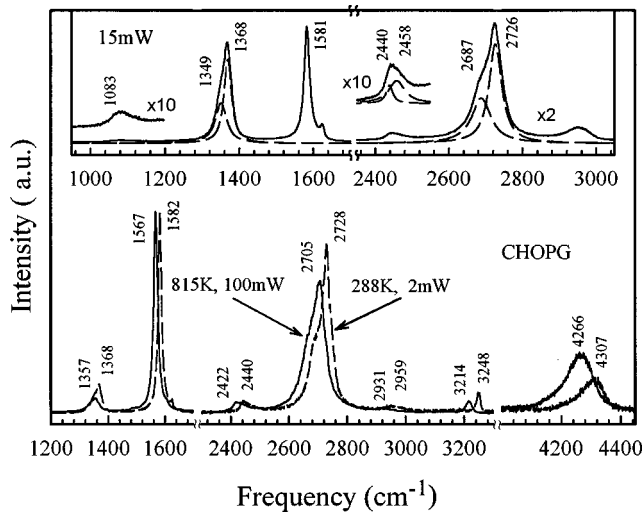


FIG. 1. Raman spectra of CHOPG excited with 514.5 nm while the laser power of the sample increased to 100 mW (the solid lines) from 15 mW and then decreased to 2 mW (the dash lines). The inset shows the spectrum of CHOPG excited before laser annealing with 15 mW.

should be designed as $T+D_1$, $T+D_2$ modes and $2D_1$, $2D_2$ modes, respectively. For the D doublet, we assign its low-energy side D_1 as mainly coming from the K point and its high-energy side D_2 from the M point, and this assignment agrees with the calculation of the second-order Raman cross section by Al-Jishi and Dresselhaus.¹⁴

Figures 1 and 2 show, respectively, the Raman spectra of CHOPG and HOPG excited with 514.5 nm while the laser power of the sample is increased to 100 mW from 15 mW and then decreased to 2 mW. In the spectra of CHOPG excited with 100 and 2 mW, the relative intensity of the D mode to the G mode, which indicates the disorder of the samples has decreased about seven times from that excited with 15 mW (see the inset of Fig. 1). According to the Stokes-to-anti-Stokes intensity ratios⁷ of the G mode, the calculated temperatures of CHOPG and HOPG are, successively, 815 and 647 K when the laser power of the samples increases to 100 mW. Thus, CHOPG is annealed because of absorbing the laser energy; the degree of laser annealing is comparable to that at the temperature of 950 °C for 0.5 h.⁵

The calculated temperatures of CHOPG and HOPG were decreased from 815 and 647 K to 288 and 286 K when the laser power of the samples is decreased from 100 to 2 mW. In this processing, noticeable frequency shifts between the spectra excited with different laser powers are observed for all Raman bands of HOPG and CHOPG. It suggests that the frequency shifts of the Raman bands should be caused by the

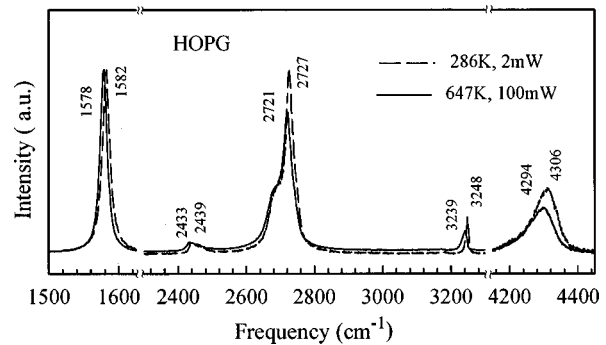


FIG. 2. Raman spectra of HOPG excited by 514.5 nm with laser power of 2 mW (the dash lines) and 100 mW (the solid lines) of the sample.

change of the sample temperature. Table I summarizes the frequencies of the Raman lines and the frequency shifts of the same Raman peaks between two spectra excited with different laser powers for CHOPG and HOPG. The temperature dependence of the higher-order bands follows that of the fundamentals and satisfies the summation rule. For example, the frequency shift of the $2D+G$ mode ($\sim 41 \text{ cm}^{-1}$) between two difference temperatures for CHOPG is the sum of that of the $2D$ mode ($\sim 23 \text{ cm}^{-1}$) and G mode ($\sim 15 \text{ cm}^{-1}$) or that of the $D+G$ mode ($\sim 29 \text{ cm}^{-1}$) and D mode ($\sim 11 \text{ cm}^{-1}$). This indicates that the temperature dependence of the Raman modes may be a powerful method for verifying and assigning the higher-order Raman modes of graphite materials. If we define the temperature coefficient χ of the G mode as the frequency shift of this mode when the temperature of the sample increases 1 K, then $\chi_{\text{CHOPG}} = 0.028 \text{ cm}^{-1}/\text{K}$ and $\chi_{\text{HOPG}} = 0.011 \text{ cm}^{-1}/\text{K}$, the temperature coefficients of CHOPG and HOPG are comparable to that of diamond.¹⁰

The change of phonon frequency with temperature is a manifestation of anharmonic terms in the lattice potential energy, in detail, is determined by the anharmonic potential constants, the phonon occupation number, and the thermal expansion of the crystal.⁹ In the common condition, the volume is always changed with the temperature of the sample. The measured frequency change at constant pressure can be written as¹⁰

$$\Delta\omega = \left[\frac{d\omega}{dT} \right]_V \Delta T + \left[\frac{d\omega}{dV} \right]_T \left[\frac{dV}{dT} \right]_P \Delta T = \chi_T \Delta T + \chi_V \Delta T,$$

where the former terms describe the pure temperature effect

TABLE I. The Raman peaks of HOPG and CHOPG excited by 514.5 nm with different laser power. The temperature labeled under ω is the calculated temperature of the sample. $\delta\omega$ is the Raman shifts of the same Raman peaks between two Raman spectra with different laser power.

Assignment	D_1	D_2	G	D'	$T+D_1$	$T+D_2$	$2D_1$	$2D_2$	$D+G$	$2D'$	$2D+G$
HOPG $\omega_{647 \text{ K}}/\text{cm}^{-1}$			1578		2433	2452	2680	2720	3239	4294	
HOPG $\omega_{286 \text{ K}}/\text{cm}^{-1}$			1582		2439	2458	2687	2727	3248	4306	
$\delta\omega/\text{cm}^{-1}$			4		6	6	7	7	9	12	
CHOPG $\omega_{815 \text{ K}}/\text{cm}^{-1}$	1339	1357	1567	1606	2422	2443	2668	2705	2930	3214	4266
CHOPG $\omega_{288 \text{ K}}/\text{cm}^{-1}$	1350	1368	1582	1623	2440	2460	2689	2728	2959	3248	4307
$\delta\omega/\text{cm}^{-1}$	11	11	15	17	18	17	21	23	29	34	41

and the latter the pure volume effect. The volume dependence of frequency can be calculated using the Grüneisen constant model:^{9,10}

$$\omega(T) = \omega(0) \exp \left[-3\gamma \int_0^T \alpha(T) dT \right],$$

where $\alpha(T)$ is the thermal expansion coefficient. According to the thermal expansion coefficient, the pure volume effect induced by the change of temperature can be estimated. The temperature dependence of HOPG could not be observed before mainly because of its high thermal conductivity and low thermal expansion coefficient (see Ref. 18). However, the sample will absorb laser energy and expand easily because of its lower thermal conductivity, which is caused by the shorter crystal planar domain size³ when there exist defects and impurity such as in the CHOPG. It then shows a stronger temperature dependence.

For pristine HOPG, the average value of the thermal expansion coefficient in the graphite layer plane is less than $-30 \times 10^{-8} \text{ K}^{-1}$ in the range of 300–850 K. It is very small compared to that of graphite in the direction of the c axis ($\sim 2740 \times 10^{-8} \text{ K}^{-1}$) and that of diamond ($\sim 900 \times 10^{-8} \text{ K}^{-1}$).^{16,18} The thermal expansion of graphite crystal mainly occurs along the c axis and has a small affect on the frequency of the “in-plane” mode. Our calculated frequency shift of the G mode according to the thermal expansion coefficient¹⁸ in the range of 300–850 K is negative ($\sim -0.001 \pm 0.0003 \text{ cm}^{-1}/\text{K}$) and smaller than the observed value. Therefore, the pure temperature effect, but not the pure volume effect, determined the temperature coefficient χ of the G mode of the pristine HOPG. Thus, we have $\chi_T = (d\omega/dT)_V = 0.011 \text{ cm}^{-1}/\text{K}$. However, the anharmonic contribution is rather small, since the calculated temperature of the sample (up to 850 K) is sufficiently below the Debye temperature of the graphite layer (2500 K).¹⁹ Also, it can be confirmed by the unchanged full width at half maximum (FWHM) of the G mode at different temperatures (from Figs. 1 and 2, one has $\text{FWHM}_{\text{HOPG}} = 12 \text{ cm}^{-1}$ and $\text{FWHM}_{\text{CHOPG}} = 17 \text{ cm}^{-1}$), since FWHMs are sensitively changed with temperature because of the anharmonic effects in samples such as diamond, silicon, and germanium.^{10,20} Therefore, frequency shifts of pristine HOPG are mainly attributed to the pure temperature effect without an anharmonic contribution. The difference of the temperature coefficients between the pristine and ion-implanted HOPGs is that the ion-implanted HOPG has a pure volume effect because of the finite crystal planar domain size caused by defects and impurity. The shorter the crystal planar domain size is, the easier the crystal planar domain expands with temperature, and the more notable the temperature effect becomes. When the pure temperature effect is excluded, the temperature coefficient induced by the pure volume effect is $\chi_V = (d\omega/dV)_T (dV/dT)_P = 0.017 \text{ cm}^{-1}/\text{K}$. The fact that the pure temperature coefficient without the anharmonic contri-

bution is comparable to the pure volume coefficient will be studied further. To completely interpret the experimental results, it is necessary to extend the existing models.

In conclusion, we have measured the Raman spectra of pristine and ion-implanted HOPGs, and observed a band at 1083 cm^{-1} , which does not exist in the HOPG, and three doublet structures in the position of the D mode, $\sim 2450 \text{ cm}^{-1}$ and the $2D$ mode in the spectra of the ion-implanted HOPG. The strong temperature effect of those samples and laser-annealing phenomenon of the ion-implanted HOPG caused by the different powers of the excited laser is observed. Noticeable frequency shifts of disorder graphite such as CHOPG are interpreted as the nonanharmonic pure temperature effect and a downshift in the C–C stretching frequency induced by the thermal expansion. The frequency shifts of pristine HOPG are attributed to the pure temperature effect without an anharmonic contribution. The results suggest that the pure temperature effect without an anharmonic contribution plays an important role in the frequency shifts with temperature.

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