Temperature dependence of Raman spectra of graphene on copper foil substrate

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Received: 27 October 2015 / Accepted: 17 December 2015 © Springer Science+Business Media New York 2015

Abstract We investigate the temperature dependence of the phonon frequencies of the G and 2D modes in the Raman spectra of monolayer graphene grown on copper foil by chemical vapor deposition. The Raman spectroscopy is carried out under a 532.16 nm laser excitation over the temperature range from 150 to 390 K. Both the G and 2D modes exhibit significant red shift as temperature increases, and the extracted values of temperature coefficients of G and 2D modes are $-0.101$ and $-0.180 \text{ cm}^{-1} \text{ K}^{-1}$, respectively, different from that of graphene on SiO$_2$ substrate. The obtained results shed light on the anharmonic property of graphene, the complex interfacial interactions between graphene and the underlying copper foil substrate as temperature changes, and also proposes a new routine to estimate the thermal expansion coefficient of graphene on copper substrate rather than on SiO$_2$ and SiN substrates. Furthermore, our work is instructive to study the similar temperature dependent mechanical properties, and the interfacial interactions between the other emerging two dimensional materials and their underlying substrates by temperature dependent Raman scatterings.

1 Introduction

Graphene, with its unique band structure and fascinating combination of extraordinary mechanical, thermal, optical, chemical, and electronic properties distinct from that of its bulk counterpart, has attracted enormous attention in scientific and industrial communities [1–7]. The chemical vapor deposition (CVD) technique for growing graphene on copper foils using hydrocarbon gas or solid carbon source, until now, has been the most convenient, reliable, and low cost way to produce large-scale, high-quality, and predominately monolayer graphene films [8]. The CVD approach is attractive because it permits fabrication over large areas and extends the applicability of graphene to arbitrary substrates [9], such as polyethylene terephthalate (PET), SiO$_2$, glass, or others, which is a requirement for applications of graphene-based devices. The quality of graphene is significantly influenced by the roughness and polycrystalline characteristics of the underlying copper foil substrate, which should be characterized and evaluated [10]. Testing directly on graphene/Cu is simple and charming, as there is little chemical contamination and mechanical damage due to no complex transfer process of graphene to other substrates that may have a significant effect on the testing results.

Raman spectroscopy has been demonstrated to be an ideal nondestructive diagnostic technique to indirectly characterize the vibrational, structural, and electronic properties of carbon-based materials [11–13]. Raman spectroscopy has been widely used for quick identification and inspection of monolayer, bilayer, and few-layer graphene, and evaluation of its physical properties, such as density of defects [14], amount of stress [12, 15], thermal conductivity [16, 17], and charge doping [18]. Ferrari et al. [11] first allowed for unambiguous, high-throughput, non-destructive identification of graphene layers by Raman spectroscopy. Eckmann

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et al. [14] presented a detailed analysis of the Raman spectrum of graphene containing different types of defects, and Zandiatashbar et al. [19] established a relationship between the type and density of defects and the mechanical properties of graphene by Raman spectroscopy. The Raman spectrum of graphene on flexible substrates under uniaxial tensile strain was measured, and the G and 2D modes exhibit significant red shift while the G band splits into two distinct \((G^+, G^-)\) features because of the strain-induced breaking of the crystal symmetry [12]. In addition, temperature is an important factor affecting the properties of graphene. Calizo et al. [20] investigated the temperature dependence of the G mode frequency in the Raman spectra of graphene on a SiO\(_2\)/Si substrate ranging from \(-190\) to \(100\) °C, and the coefficients of the G mode are \(-0.016\) cm\(^{-1}\)/°C for the single layer and \(-0.015\) cm\(^{-1}\)/°C for the bilayer systems, respectively. The thermal expansion coefficient (TEC) is an important thermal and mechanical performance parameter of graphene, which could be estimated by Raman frequency analysis. TEC of single-layer graphene on a SiO\(_2\) substrate was estimated with the temperature-dependent Raman frequencies in the temperature range from \(200\) to \(400\) K [21], and Raman scattering of monolayer graphene supported on silicon nitride over an extended temperature range were performed [22]. The native strain can be unambiguously determined by Raman frequency analysis notwithstanding the interface from the coexisting charge-doping effects, and native tensile strain was relieved by thermal annealing at a temperature as low as \(100\) °C and converted to compressive strain by annealing at higher temperatures [18]. There is also a large physisorption strain in CVD of graphene on copper substrates [23].

Despite aforementioned extensive studies, the temperature dependence of Raman spectra of graphene on copper foil substrate, an important factor in testing, has not been reported yet. In this paper, we investigate the temperature dependence of the phonon frequencies of the G and 2D modes in the Raman spectra of monolayer graphene grown on a copper foil substrate by CVD, which is very important for further understanding of thermal expansion, thermal conductivity, and the complex interactions between graphene and the underlying copper foil substrate under different temperatures. Furthermore, we estimated the TEC, and performed defects analysis of graphene by temperature dependent Raman frequencies.

2 Experiment

2.1 Sample preparation

The sample is synthesized using CVD method on polycrystalline copper foil with a thickness of \(25\) μm and a roughness of \(20\) nm as the substrate. Firstly, the copper foil surface is cleaned by hydrogen reduction mixed with Ar, and annealed at the process temperature of \(980\) °C in a quartz tube within \(20\) min. Next, diluted CH\(_4\) is introduced into the CVD system for several hours for graphene growth. Finally, the CVD system is slowly cooled to \(700\) °C and then quickly cooled to room temperature, and the cooling rate could be used to control the thickness of graphene films. The pressure is maintained at \(800\) Torr during the whole process.

After the CVD process, graphene almost completely covers the surface of the underlying copper foil. Figure 1a, b show the synthesized graphene/copper film and its corresponding SEM image, respectively. The copper boundaries which can be obviously seen underneath graphene in the SEM image, which are also the right sites where the boundaries of graphene form.

![Fig. 1](a) Synthesized graphene/copper foil; b SEM image of part enlargement of (a)
2.2 Experimental method

The Raman spectra (HORIBA Jobin Yvon HR800) of the sample are obtained with a 532.16 nm visible laser light excitation and collected in the backscattering configuration, and its frequency scanning resolution is 0.4 cm\(^{-1}\) with exposure time of 10 s. The spectra are recorded with an 1800 grooves/mm grating. We have used a microscope (50\(\times\), 0.6 N.A.) objective to focus the excitation laser beam on the target spot of the samples, and the size of the laser spot is about 3 \(\mu\)m keeping the laser power below 2.5 mW to avoid sample damage or laser induced heating. The sample is located in the cuvette, and its ambient temperature is controlled ranging from 150 to 390 K with an accuracy of 0.1 K by a cold–hot cell operated using a liquid nitrogen source.

3 Results and discussion

The temperature dependent Raman spectra mainly involving G and 2D modes of graphene grown on a copper foil substrate from 150 to 390 K are illustrated in Fig. 2a. The bottom Raman spectrum displays the phonon bands of CVD graphene transferred from the copper foil onto the SiO\(_2\) substrate at room temperature of 300 K as a reference.

It is noticeable from Fig. 2a that the spectra are noisy because of relatively strong luminescence from the copper foil [23], which shows significant discrepancies with the theoretical curves of free-standing graphene [24] and the experimental data of graphene on SiO\(_2\)/Si [20] and SiN [22] substrates. The temperature dependent Raman spectra are shown in Fig. 2b corresponding with Fig. 2a after subtracting the luminescence background from copper foil and filtering noise. Both G band 2D modes can be used to monitor the number of layers, and the peak-intensity ratio of the 2D to G after subtracting luminescence from copper foil decreases with increasing layers of graphene. According to the value of \(I_{2D}/I_G > 1.0\) from Fig. 2b, it is verified that all the Raman frequencies features are consistent with that of monolayer graphene grown on copper foil. Occasionally, the D and D\(^\prime\) modes appear in the spectrum, which indicates that there are some defects in the graphene samples [14].

Another appreciable feature is the G peak at 1587.33 cm\(^{-1}\), which corresponds to the E\(_{2g}\) mode (zone-center optical [12]), and the 2D peak at 2686.46 cm\(^{-1}\) (two-phonon zone-edge optical [12]) at room temperature of 300 K, which is slightly shifted compared to the intrinsic G peak value of 1581.6 cm\(^{-1}\) expected for charge- and strain-free graphene [18], suggesting some doping and

Fig. 2 a Raman spectra of graphene on copper foil substrate in the temperature range of 150–390 K, and of monolayer graphene on SiO\(_2\) at room temperature of 300 K; b Raman spectra for the luminescence background from copper foil is subtracted corresponding with (a); c splitting of G and 2D modes into indistinct subbands (G\(^-\), G\(^+\), 2D\(^-\), and 2D\(^+\))
strain in our samples. On some test points, the G mode splits into two distinct subbands \((G^+, G^-)\) or the 2D mode splits into two distinct subbands \((2D^+, 2D^-)\) because of the thermal strain-induced symmetry breaking \([12, 15]\), as shown in Fig. 2c.

Furthermore, both G and 2D modes exhibit significant red shift because of phonon softening \([12]\) upon temperature increasing. When temperature varies, two effects \([21]\) contribute to the Raman frequency shift: the temperature dependence of the phonon frequencies and the modification of the dispersion due to the strain caused by TEC mismatch between graphene and the underlying copper foil substrate. The former is an intrinsic property of graphene while the latter comes from the complex interplay between graphene and the underlying copper foil over the examined temperature range \([19, 20]\). Even at room temperature, it can be found that graphene grown by CVD on a copper foil substrate is subject to non-uniform physisorption strains, as reported by a previous study \([23]\).

The temperature dependence of G and 2D peaks in Raman spectra are shown in Fig. 3a, b, respectively. Every data point represents the mean value of seven measured points with standard deviation, and the mean values of the two subbands are used when the mode is split into two subbands (as shown in Fig. 2c). The dotted-dash line is a linear fitting of the data.

It can be seen from Fig. 3 that the 2D mode exhibits red shift more than the G mode as temperature increases, which implies that the 2D mode is very sensitive to strain. This is because the double resonance processes are sensitive to the changes in the electronic band structure that are induced by strain \([18]\). On the contrary, the G mode is an optical phonon with zero vector which is very sensitive to carrier density \([18]\) instead of strain. In this experiment, the strain changes more than carrier density over the examined temperature range from 150 to 390 K.

The temperature dependence of the G mode frequency shift in graphene on copper foil can be represented by the relationship \(\omega_G = \omega_0 + \chi_G T\), where \(\omega_0\) is the frequency of the G mode when temperature \(T\) is extrapolated to 0 K and \(\chi_G\) is the temperature coefficient defining the slope of dependence. The extracted negative value is \(\chi_G = -0.101 \text{ cm}^{-1} \text{ K}^{-1}\) which differs from values for monolayer graphene deposited on SiO\(_2\) \((-0.016\) and \(-0.05 \text{ cm}^{-1} \text{ K}^{-1}\)) \([20, 21]\) and SiN substrates \((-0.023 \text{ cm}^{-1} \text{ K}^{-1}\)) \([22]\). We also obtain that the temperature coefficient value changes less to be \(-0.089 \text{ cm}^{-1} \text{ K}^{-1}\) while decreasing temperature from 390 to 150 K as shown in Fig. 3a, which means that there is strong adhesion between graphene and the underlying copper substrate, and the temperature dependency is almost revisable in the temperature range from 150 to 390 K.

The thermal contribution to the Raman frequency shift of the G mode has three parts, the thermal expansion, the anharmonic effect, and thermal strain, which can be expressed as \([21]\)

\[
\Delta \omega_G(T) = \Delta \omega_G^E(T) + \Delta \omega_G^A(T) + \Delta \omega_G^S(T)
\]

(1)

\(\Delta \omega_G^E(T)\) and \(\Delta \omega_G^A(T)\) indicate the thermal expansion of the lattice and an anharmonic effect of free-standing graphene, respectively. Most importantly, \(\Delta \omega_G^S(T)\) is the effect of the strain \(\varepsilon(T)\) caused by the TEC mismatch between graphene and the substrate, and can be expressed as \([21]\)

\[
\Delta \omega_G^S(T) = \beta \varepsilon(T) = \beta \int_{T_0}^T (\alpha_{\text{Sub}}(T) - \alpha_{\text{Graphene}}(T)) dT
\]

(2)

where \(\beta\) is the biaxial strain coefficient of the G band, which has been estimated to be \(-70 \pm 3 \text{ cm}^{-1}\%\) at room temperature \([25]\), and \(\alpha_{\text{Sub}}(T)\) and \(\alpha_{\text{Graphene}}(T)\) are the
temperature dependent TECs of the substrate and graphene, respectively.

Figure 4 shows the temperature dependent frequency shift of the Raman G mode as a function of temperature, and the temperature dependent frequency shift of the G mode caused by the TEC mismatch between graphene and the substrate after eliminating the effects of $\Delta \omega_G^S(T)$ and $\Delta \omega_G^A(T)$ according to the theoretical curve on free-standing graphene [24]. It can be found from Fig. 4 that the thermal expansion and anharmonic effects contribute to the frequency shift of the G mode far less than the thermal strain does.

The TEC of copper foil is larger than that of SiO$_2$, such as its G mode’s frequency shifts more than that of the latter under the same temperature range as Fig. 4. In other words, we would extract temperature dependent TEC of monolayer graphene if the precise values of Eq. (2), $b$, and $a_{\text{Copper}}(T)$ have been obtained. As negative TEC of graphene on SiO$_2$ substrate is estimated [21], TEC of graphene could also be extracted by temperature dependent Raman frequencies of graphene on a copper foil substrate, which will be another routine to estimate the TEC of graphene rather than graphene on SiO$_2$ and SiN substrates.

Similarly, the temperature dependence of the 2D mode frequency shift can be linearly interpolated. The proportionality of $\omega_{\text{2D}} = -0.180 \text{ cm}^{-1} \text{ K}^{-1}$ ($-0.165 \text{ cm}^{-1} \text{ K}^{-1}$ while decreasing temperature). It would also be valuable to exploit other Raman signals such as the 2D mode as an alternative to the G mode to study the complex interfacial interactions between graphene and the underlying substrate and extract some properties of graphene.

Furthermore, we can also obtain the relationship between biaxial strain and strain-induced G and 2D band shifts as shown in Fig. 5 according to Eq. (2) and Fig. 4.

From Fig. 5, we find that both G and 2D bands show blue shifts when graphene is compressed while they show red shifts when graphene is stretched, which is consistent with previous studies [12, 26, 27]. The shift rates are found to be $-83.14 \text{ cm}^{-1} \text{ K}^{-1}$ for G band, and $-119.93 \text{ cm}^{-1} \text{ K}^{-1}$ for 2D band respectively, which means 2D mode is more sensitive to strain than G mode. The shifts rates due to biaxial strain are also different from that of graphene undergoing uniaxial strain state [26, 27].

Defects, such as edges, grain boundaries, vacancies, and implanted atoms, are inevitable in the graphene sheet either because of the production process [28] or the operating condition [29]. The presence of defects gives rise to other two features at around 1350 cm$^{-1}$ (D mode) and 1615 cm$^{-1}$ (D’ mode). The D’ mode appears just as a small shoulder of the G mode, and the intensity of D’ mode is relatively small compared to the D mode [14]. The intensity ratios of $I_{D}/I_{G}$, $I_{2D}/I_{G}$, and $I_{2D}/I_{D}$, are usually used to probe the nature and distribution of defects [14, 19, 30, 31]. In our 49 Raman spectra over the temperature range from 150 to 390 K, there are only five spectra which contain the D and D’ modes besides of the G and 2D modes, which implies our graphene sample has few defects. Furthermore,
the mean ratio value of $I_D/I_G$ of the five Raman spectra is 3.52 with a standard deviation of 1.18, which indicates boundary-like defects [14].

4 Conclusions

In conclusion, we report the first experimental investigation of the temperature dependence of the Raman spectra of monolayer graphene grown by the CVD technique on a copper foil substrate. Over the temperature range from 150 to 390 K, both the G and 2D modes’ frequencies show red shift as the temperature increases, and the extracted temperature coefficients of G and 2D modes are $-0.101$ and $-0.180 \text{ cm}^{-1} \text{K}^{-1}$, respectively, which are very different from values reported previously for monolayer graphene deposited on SiO$_2$ and SiN mainly because of the larger TEC mismatch between graphene and underlying copper foil. Our results shed light on complex strain state at the interface between graphene and the underlying copper foil substrate as temperature changes, and also propose a new routine to estimate the TEC of graphene on copper substrate rather than on SiO$_2$ and SiN substrates. Our work is also instructive to study the similar temperature dependent mechanical properties, and the interfacial interactions between the other emerging two dimensional materials and their underlying substrates by temperature dependent Raman scatterings.

Acknowledgments  This work is supported by Basic Research (973) from Ministry of Science and Technology with Contract Number of 2011CB309504. Authors are also grateful to the Analytical and Testing Center, Huazhong University of Science and Technology for technical assistances.

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