Temperature-dependent Raman investigation on suspended graphene: Contribution from thermal expansion coefficient mismatch between graphene and substrate

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Dedicated Raman investigation was performed on the graphene suspended on the round holes, compared with graphene supported on Si/SiO2 substrate, in the temperature range from 173 K to 673 K. We observed an unexpected result that the temperature-dependent Raman frequency shift of suspended graphene was similar as that of supported graphene. This evidenced that the strain caused by thermal expansion coefficient mismatch between graphene and substrate cannot be neglected from suspended graphene. We predicted that the unsupported graphene zone and its surrounding graphene that adhered to substrate should be considered as a whole while studying the thermodynamic properties of this suspended graphene, and thus a semi-quantitative factor was introduced to the estimate the contribution from substrate to the suspended graphene, explaining well this result. Our results suggest that the thermal expansion coefficient mismatch induced strain should be taken into consideration in the study of electronic and transport properties of suspended graphene devices, in which the self-heating effect cannot be eliminated during operation.

1. Introduction

Graphene, of two dimensional hexagonal lattice structure, has attracted considerable attention since its first observation in 2004 [1–3]. Owing to its unique structure, various distinct physical properties arise [4–7] and make it a promising candidate for electronic devices [7,8]. Recently, free-standing graphene (FG) received remarkable research interests, because it has exhibited better transport properties than substrate supported graphene (SSG) [4,5,9]. So various electronic devices, such as resonators, electromechanical switch devices, and transistors have been fabricated based on FG [10–12]. It is also reported that the graphene-based force and gas sensors have been fabricated, as the resistance of graphene is very sensitive to the changes of strain [13,14].

It is already reported that the transport properties or band structure can be modified by introducing strain to graphene sheet [15,16]. Due to the self-heating arising during the operation of graphene-based devices or the changes of ambient temperature, the strain emerges in graphene sheet as a result of the variation of lattice parameters. It has been demonstrated that the thermal expansion coefficient (TEC) of graphene is a key parameter that can modulate the electronic properties of graphene and the performance of graphene-based devices. Therefore, from the application point of view, it is crucial to investigate the TEC of FG as a function of temperature. In recent years, many experimental and theoretical works have been carried out to study the TEC of graphene (αgr). However, these results are still in controversy [17–23]. It was observed by different groups that the sign of TEC changed from negative to positive at different temperatures [17–19]. Mounet and Marzari dedicated a negative αgr based on density functional perturbation theory (DFPT) using a representative of the quasi-harmonic approximation [20]. Magnin et al. found both negative and positive αgr by employing atomistic Monte Carlo (MC) simulations with different potentials [21]. A negative αgr was observed by Yoon et al. using Raman spectroscopy in the range of 200–400 K [22]. Linas and coworkers predicted a positive αgr over room temperature [23]. It is noteworthy that the theoretical calculations were performed on the base of FG. However, most of the

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experimental studies were carried on SSG.

Raman spectroscopy is a powerful technique for investigating the structural and electronic properties of graphene, such as number of layers, stress and doping [24–28], and also Raman spectroscopy has been demonstrated to be a feasible tool to study the thermal behaviors of monolayer graphene [22,23,28–32]. However, all the previous researches were carried on the graphene adhered to substrates. Although some studies have tried to get an insight into the TEC of graphene using substrate corrections methods [22,23], direct Raman investigation on FG is rarely reported so far, to the best of our knowledge.

As we know, however, absolute FG cannot be achievable in the laboratory, which actually exists in the form of suspended graphene (SUG). In the SUG devices, the working or testing zone of the graphene sheet is free of confinement from substrate, while the other part of graphene is adhered to substrate. In this work, a SUG sample was prepared by transferring an exfoliated graphene flake to a Si/SiO₂ substrate with disk-like holes, and was employed as the substitution of FG. A complex Raman study was carried on SUG, compared with graphene on Si/SiO₂ substrate (SSG), in the temperature range from 173 K to 673 K. The Raman peaks for both SUG and SSG shifted linearly to lower frequency positions with increasing temperature. It is noteworthy that the frequency shifts of SUG are very close to that of SSG, which is contrary to our previous hypothesis. This suggests that the TEC mismatch between graphene and SiO₂ substrate play an important role in the frequency shift of SUG as well as SSG. These results indicate that the unsupported graphene zone and its surrounding graphene that adhere to substrate should be considered as a whole while studying the thermodynamic properties of SUG devices. Because the self-heating effect cannot be eliminated during the operation of suspended graphene devices, the strain consequently emerges due to TEC mismatch should be taken into consideration while studying the electronic and transport properties of devices. In addition, the temperature effect should be regarded as a factor when designing force and gas sensors, which are highly sensitive to the changes in the resistance of graphene.

2. Experimental

2.1. Sample preparation

To achieve SUG, a periodic pit array is firstly fabricated on SiO₂ (300 nm)/Si substrate by the UV lithography and reactive ion etching technology, having 5 μm in diameter and 500 nm in depth. Graphene flakes were mechanically exfoliated from natural graphite onto the pre-patterned SiO₂/Si substrate previously cleaned by oxygen plasma. The single layer graphene is roughly picked out by its purple color (typically on 300 nm thick SiO₂ substrate) from optical microscopy seen in Fig. 1(a), but still need further demonstration by Raman spectroscopy.

2.2. Raman spectroscopy

Raman spectra were collected using a confocal micro-Raman spectrometer (Horiba/Jobin Yvon HR 800). A solid state laser of 532 nm wavelength was used as the excitation source. The laser beam was focused using a 50× long-working distance objective with numeric aperture NA = 0.5, and the spot size was about 1.5 μm. To avoid the local-heating effect, the laser power was controlled to be less than 1 mW on the surface of the heating stage. The sample was placed inside a cryostat cell (Linkam, THMS 600), and the Raman spectra were measured in the temperature range from 173 to 673 K with an interval of 100 K, as shown in Fig. 1(b).

3. Results and discussion

Fig. 2 shows the room-temperature Raman spectra of SUG and SSG. One can see that both samples exhibit classic spectral features.
of monolayer graphene, of which the intensity ratio of 2D band to G band is over two. The two intense peaks at around 1580 and 2680 cm\(^{-1}\) are the G and 2D bands, respectively. Besides, two weak peaks at around 2450 and 3250 cm\(^{-1}\) are assigned as the T + D and 2D’ peaks, respectively [33,34]. It is worthy to note that the frequencies of Raman peaks of SUG are lower than their correspondences of SSG. The downshift of the Raman peaks for SUG compared with SSG was also observed in previous studies [29,30]. The higher Raman frequencies of SSG would be attributed to the confinement from substrate, although the graphene flake is just attached to the SiO\(_2\) surface by Van der Waals force.

Fig. 3 exhibits the Raman spectra of SUG at selected temperatures, which share the similar behaviors as those of SSG (are not shown here). As shown in Fig. 3, it is notable that all the Raman peaks shift to lower frequencies and broaden with increasing temperature. Moreover, the intensity of 2D peak decreases significantly compared with G band. Similar phenomenon has been reported as well in previous studies [29,30]. As reported in previous publications, the linearly shifts of Raman peaks are associated with thermal expansion of C–C bands [29–31]. Besides, the changes on bandwidth and intensity of 2D band are associated with oxygen induced hole-doping [28]. On the other hand, Apostolov et al. predicted that the electron-phonon coupling also plays an important role in the temperature dependence of G band [35]. As temperature is a homogeneous effect, the graphene lattice will expend or shrink along two axes at the same time with the same variation. As a result, the graphene lattice undertakes a biaxial strain while the lattice changes with temperature. In such a case, the point group remains at D\(_{3h}\), and the G mode does not split (see Fig. 3).

The Raman spectra of SUG and SSG are deconvoluted using Gaussian/Lorentzian mixed function and compared as a function of temperature. One can see that the G band for both SUG and SSG nearly linearly shifts to lower frequency with increasing temperature, as shown in Fig. 4. Following previous reports [28,31], the experimental data can be fitted using a linear function \(u_T = u_0 + \chi T\), where \(u_0\) and \(u_T\) are the peak frequency at 0 K and selected temperature points, and \(\chi\) is the slope of the fitting line. The fitting parameters for G and 2D bands are listed in Table 1. The frequency shift slope of G peak in SUG is \(-0.01496\) cm\(^{-1}\) K\(^{-1}\), while the frequency shift slope of SSG is \(-0.01517\) cm\(^{-1}\) K\(^{-1}\). The values of slope are in well agreement with previous reports. In contrary to our expectation, the difference of frequency slope between SUG and SSG is very small (0.00021 cm\(^{-1}\) K\(^{-1}\)). In order to understand this striking phenomenon, further analysis is performed. The temperature behavior of the frequency shift of G peak (\(\Delta u_G\)) is compared between SSG and SUG, after removing the Raman frequency of G peak at \(T_0 = 0\) K (\(\Delta u_G(T)\)). As shown in Fig. 5(a), the \(\Delta u_G\) of both SSG and SUG are much smaller than the \(\Delta u\) of free standing graphene and graphite obtained from DFT calculation. It has been demonstrated by the excellent agreement between theoretical calculation and experimental works that the temperature dependent Raman shift of graphite is determined by the anharmonicity of the C–C interaction [17,36]. The results in Fig. 5(a) imply that the anharmonic property is not the sole contribution to the Raman shift of SUG, although the zone under Raman measurement doesn’t attach to substrate.

We can also see in Fig. 5(a) that the \(\Delta u_G\) of SUG is very close to that of SSG, suggesting the substrate plays an important role in the thermodynamic behavior of free standing graphene suspended on holes. After subtracting \(\Delta u_G\) of SUG, the residual value of \(\Delta u_G\) of SSG is shown in Fig. 5(b). It can be seen in Fig. 5(b), the frequency difference gradually decreases from positive value to negative value. This suggested that the thermodynamic of SUG is slightly different from that of SSG. The origin of the discrepancy on frequency shift will be discussed in detail in following section.

It has been reported that the temperature-dependent Raman frequency shift of FG (\(\Delta u_{FG}(T)\)) is commonly attributed to the thermal expansion of the lattice (\(\Delta u_{L}(T)\)) and an anharmonic effect (\(\Delta u_{A}(T)\)) which changes the phonon self-energy [22]. The \(\Delta u_{FG}(T)\) can be expressed as

\[
\Delta u_{FG}(T) = \Delta u_{L}(T) + \Delta u_{A}(T)
\]

![Fig. 5(a)](image)

![Fig. 5(b)](image)

**Table 1**

<table>
<thead>
<tr>
<th>(\Delta u_{FG}) (cm(^{-1}))</th>
<th>(\Delta u_{L}) (cm(^{-1}) K(^{-1}))</th>
<th>(\Delta u_{A}) (cm(^{-1}))</th>
<th>(\Delta u_{A}) (cm(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FG</td>
<td>1587.6124</td>
<td>-0.01496</td>
<td>2675.53</td>
</tr>
<tr>
<td>SG</td>
<td>1589.1534</td>
<td>-0.01517</td>
<td>2677.92</td>
</tr>
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</table>
For the graphene pinned on substrates, the thermal behavior of Raman shift of G peak becomes more complex. When temperature varies, both usual thermal effects and strains induced by the TEC mismatch between the substrates and graphene must be taken into consideration. As a result, the frequency shifts of the Raman G band are tried and compared in order to find the most suitable form of \( a_{gr} \), as shown in Fig. 6. The TECs from Lindsay-Broido model \( a_{LB} \) and Mounet-Marzari model \( a_{M} \) are employed in Eq. (3), respectively, for integrating over temperature. Then, the frequency shifts of SSG in our work corrected by removing the substrate effect with \( a_{LB} \) and \( a_{M} \), respectively, are plotted in Fig. 7. As reported previously [22,23], the theoretical Raman frequency shift of free-standing graphene calculated by Bonini and coworkers [17] using density-functional theory (DFT) calculations under appropriate anharmonic expansions is adapted as reference. As shown in Fig. 7, large discrepancies between the results corrected with \( a_{LB} \) and \( a_{M} \) models and the DFT reference data are observed, which suggest a new form of \( a_{gr} \) should be evolved into our work for the substrate correction. And thus, the expression of \( \Delta \omega_{G}(T) \) Eq. (3) could be transformed as following

\[
\Delta \omega_{G}(T) = \beta \int_{T_0}^{T} \left[ a_{SiO_2}(T) - a_{gr}(T) \right] dT
\]

As shown in Fig. 6, \( a_{SiO_2} \) is already known, so that the

\[
\Delta \omega_{G}(a_{SiO_2}) = \beta \int_{T_0}^{T} a_{SiO_2}(T) dT - \beta \int_{T_0}^{T} a_{gr}(T) dT
\]
contribution from the TEC of SiO$_2$ can be obtained by integration. By adopting the DFT reference data as pure frequency shifts $\Delta \omega_{SiO_2}(T) - \Delta \omega_{SSG}(T)$ into our work, the temperature-dependent of $\alpha_{gr}(T)$ can be derive from Eqs. (2) and (4). The calculated $\alpha_{gr}(T)$ is nominated as $\alpha_{SG}(T)$, which can be expressed using a quadratic function $\alpha_{SG}(T) = -2.02363 + 0.00173T + 1.299 \times 10^3 T$. Different forms of $\alpha_{gr}$ have been obtained by using different semi-empirical potentials in Monte Carlo simulations [21]. The temperature behavior of $\alpha_{SG}(T)$ in our work is similar as those obtained by Teroff and LCBOP potentials. On the other hand, a linearly variable $\alpha_{SG}(T)$ obtained using Lindsay-Broido potential (black dots in Fig. 6) was employed to explain the temperature dependent Raman shifts of graphene on SiN/Si substrate [23]. As shown in Fig. 6, the sign of $\alpha_{SG}(T)$ changes from negative to positive at around 400 K, which is the same as that predicted in Yoon's work [22]. In addition, one can see that $\alpha_{SG}$ is around $-0.4 \times 10^{-6}$ K$^{-1}$ at room temperature, which is between the values those used in Yoon's $(-8.0 \times 10^{-6}$ K$^{-1}$) and Linas's $(1.55 \times 10^{-6}$ K$^{-1}$) works [22,23]. As shown in Fig. 7, the values of $\Delta \omega_S(T) - \Delta \omega_R(T)$ in our work show well agreement with DFT data after introducing the obtained $\alpha_{SG}(T)$ into the calculation of pure frequency shift.

On the other hand, there is still a certain discrepancy on frequency shift between SUG and SSG, as presented in Fig. 5(b). In order to explain this phenomenon, the preparation progress of SUG should be taken into consideration. In this work, only the graphene above the hole is unsupported, but most part of the SUG sheet is adhered to SiO$_2$ layer. Although there is no work directly reported the adhesive force from pinned graphene to the suspended graphene, the adhesive force from pinned graphene exclusively exists and has been predicted in the studies of the elastic properties and blister of suspended graphene [6,39]. Therefore, the contribution from the adhered graphene should be taken into consideration in the investigation of the temperature behavior of SUG. While temperature varies, the strains induced by the TEC mismatch between the substrates and graphene will be suppressed on graphene area that is pinned on SiO$_2$ area, performing the same as what did in SSG. Obviously, the graphene suspended over the hole is strongly connected with the pinned graphene area by strong covalent bonds interactions. While the temperature changing, the Raman frequency shift of the SUG is definitely modulated by the graphene section that is pinned on substrate. When evaluating the thermodynamic of SUG, the graphene sheet should be taken as a whole, including unsupported graphene over the hole and the graphene section pinned on substrate. As the graphene flake is continuous, the contribution from $\alpha_{gr}$ doesn't change in Eq. (4). Only the part related with $\alpha_{SG}$ needs to be revised because of holes on the substrate. Thus, the expression of $\Delta \omega_{SG}(T)$ for SUG could be written as following

$$\Delta \omega_{SG}^{\text{fl}}(T) = \beta \cdot R_{\text{rel}} \int_{T_0}^{T} \alpha_{SG}(T) dT - \beta \int_{T_0}^{T} \alpha_{gr}(T) dT$$

(5)

where $R_{\text{rel}}$ implies the relative contribution of SiO$_2$ substrate to SUG. Approximately, we tried to represent $R_{\text{rel}}$ using the area ratio of the SSG to the whole graphene flake. As shown in Fig. 1, the periodicity of the holes is 12 $\mu$m $\times$ 12 $\mu$m, while the diameter of the disc-like hole is 5 $\mu$m. Hence, the estimated the relative contribution from SiO$_2$ is $R_{\text{rel}} = 0.8636$ for the SUG in our work. Introducing the $\Delta \omega_{SG}^{\text{fl}}(T) - \Delta \omega_{SG}^{\text{fl}}(T)$ obtained from SSG (shown in Fig. 7) into Eq. (5), the contribution from SiO$_2$ into the frequency shift of SUG is deduced, and its ratio to that of SSG plotted in Fig. 8. One can see that except 473 K, the values of ratio are less than 1 at other temperature points. The abnormal at 473 K may be due to the errors in the measurements. The lattice symmetry and surface roughness of substrate may also effect the evaluation of centration of TEC mismatch in the Raman shift of graphene. As we know, the single crystal transition metal dichalcogenides (TMDs), such as MoS$_2$, WS$_2$, which have similar lattice symmetry and atomically flat surface as graphene. Therefore, cleaved single crystal TMDs would be good candidate of supporting substrates which could reduce the errors in future measurement. As indicated by the red line in Fig. 8, the average ratio is 0.8119 over the temperature range, which is very close to the calculated relative contribution factors $R_{\text{rel}}$. Our prediction that the unsupported and supported graphene areas should be considered as whole is reasonable. Of course, the adhesive graphene should affect the thermal expansion of SUG zone in a certain distance, so-called coherent length. Out of this length, the substrate contribution to SUG could be neglected. Additional experimental and theoretical works are needed to clarify the coherent length in SUG, which is outside the scope of this work.

The results shown in Fig. 8 imply that with temperature changing, the strain arise from SUG due to TEC mismatch as well as that did in SSG. This would be helpful for understanding the electronic and transport behaviors of SUG based devices. It has been reported that the resistance of graphene will be modulated by involving strain in graphene sheet [15,25]. As we know, self-heating or joule heating is a serious side effect which cannot be eliminated during the operation of graphene transistors [40]. In this case, with increasing temperature of the device, the strain will be suppressed in SUG by the TEC mismatch between graphene and substrate. The electronic and transport properties of SUG devices will be modulated as a result. In addition, the changes in the ambient temperature can also introduce the strain into the graphene, which should be taken into account during designing SUG devices, especially for high sensitivity force and gas sensors at low and high temperature conditions.

4. Conclusion

In this work, comprehensive Raman study was carried respectively on supported and suspended graphene in the temperature range from 173 K to 673 K. Like SSG, the temperature dependent of frequency shift of the SUG is significantly affected by the thermal expansion coefficient mismatch between graphene and substrate.
This phenomenon was well explained by a scheme that the un-supported graphene and its surrounding graphene adhered to substrate are considered as a whole. A semi-quantitative factor $R_{\text{rel}}$ obtained by the area ratio of the graphene adhered to substrate to the whole SUG, was introduced to estimating the relative contribution of substrate to SUG. Our results suggest that as well as SSG devices, the TEC mismatch induced strain plays an important role in the transport properties of SUG electronic devices. In addition, it implies that the changes in the ambient temperature should be taken into consideration while designing SUG-based force and gas sensors.

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References