Effect of Ag nanoparticles on wafer-scale quasi-free-standing graphene characterization by surface enhanced Raman spectroscopy

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Keywords: quasi-free-standing graphene, SiC, H intercalation, Raman spectra

Abstract
Quasi-free-standing graphene (QFSG) obtained by H intercalation on SiC (0001) substrate paves a new way for widening the applications in microelectronics field. In this work, the direct and efficient characterization of wafer-scale quasi-free-standing graphene on SiC was presented by Ag-assisting Raman spectroscopy. The Si–H peak existing at the interface between graphene and substrate was tested unambiguously. The effects of Ag distribution and particle size on Raman enhancement were clarified both theoretically and experimentally. It was found that relative larger Ag particles at aggregation area were accompanied with the better enhancement. Moreover, Raman mapping with Ag assisting was executed on QFSG obtained under different growth conditions and the corresponding QFSG coverages were evaluated effectively. The optimum H intercalation temperature was determined to be around 1000 °C with the coverage being 73%. This study would supply a new approach for uniform and wafer-scale QFSG fabrication.

Introduction

Graphene obtained by thermal decomposition of SiC has been proven to be a promising method for micro-nano electronic devices application [1–5]. The morphology of graphene grown on SiC (0001) face is well-ordered and accompanied with better quality. The technology is also much more controllable compared with that of graphene grown on SiC (000−1) face [6, 7]. By using in situ Low-energy electron diffraction (LEED), Ni et al reported the formation of a (6√3×6√3) R30° buffer layer between graphene and the SiC substrate during the C atom reconstruction process [8, 9]. This structure has been proven to be electrically insulating and deteriorated the electronic properties of graphene to a large extent. Therefore, it is essential to decouple the buffer layer effect for the following electronic applications [10, 11].

In general, the buffer layer could be decoupled by adding outer molecules and atoms, such as H2, H2O, Pb and Li [10–14]. Amongst all of these means, H intercalation is easily realized and makes little effect on micro and nano devices, thus widely used in preparing QFSG [11]. By introducing active H atoms, the Si dangling bonds can be saturated and Si–H bonds are formed, meanwhile the original buffer layer beneath graphene is transformed into graphene leading to bilayer graphene on top of the SiC substrate. At present, Raman spectroscopy [15–17] and X-ray photoelectron spectroscopy (XPS) [18–20] are common methods for the QFSG characterization. Raman spectroscopy is a quite indirect way since the QFSG is assessed by strain comparison through the 2D peak shift or layer variation through the 2D peak broadening. Meanwhile, the laser spot of Raman spectroscopy is inevitable to be focused on the step edge rather than terrace area [21]. Considering the generally accepted growth mechanism for graphene on SiC, the nucleation sites occur on the step edge area prior to terrace, resulting in non-uniform graphene layer distribution on SiC substrate [22, 23]. From this viewpoint, the Raman spectroscopy might provide a biased result to a certain extent. When it comes to XPS measurement, it
is a time-consuming process and the sample couldn’t be tested in the whole wafer scale restricted by the chamber size. Developing a new method for charactering the QFSG is in impressing need.

Seyller et al gave out a direct Si-H stretch mode characterization by the p-polarization through the attenuated total reflection mode of Fourier transform infrared absorption spectroscopy (FTIR-ATR), which showed existence of the Si-H bonds (2131 cm\(^{-1}\)) linking to the SiC substrate beneath the QFSG [24]. Kunc et al studied the Si-H bands variation under different growth conditions in the same method [25]. Surface enhanced Raman spectroscopy (SERS) has been proven to be an efficiently method to get enhanced signals and improve the sensitivity of spectrometer [26, 27]. In contrast to FTIR, SERS can give out the essential information to study the properties of graphene simultaneously. Ferralis et al tested the QFSG directly by SERS with Au nanoparticles, where the Si-H peak at 2132 cm\(^{-1}\) appeared in the Raman spectrum. They also uncovered the interfacial properties under different QFSG treatment procedures by the variation of Si-H peaks intensities in SERS spectra [28]. In addition, Kazakova et al reported the intrinsic property of Si-H bond thoroughly and the variation for all graphene characteristic peaks in Raman spectra after H intercalated into the in situ growing epitaxial graphene [29]. Despite that the SERS is an effectively method to show the undiscovered information through common Raman spectroscopy, the enhancement relies on the size of metal particles strongly and the particles also exhibited a random distribution thus affecting the reproducibility of signals. Hence these relationships in the QFSG estimation need to be clarified. Furthermore, it is essential to study the QFSG coverage ratio by varying with the H intercalation technique because uniform graphene with large scale is the optimal platform in complex and integrated device fabrication.

In this paper, the Ag assisting SERS measurement was presented to characterize the QFSG. The effects of Ag dimension and distribution on Raman enhancement were investigated. Furthermore, QFSG samples grown under different H intercalation conditions were analyzed and the relationship between QFSG coverage and growth condition was discussed.

Experimental section

The 2-inch on axis (the miscut angle tolerances within ±0.20°) SiC (0001) substrate wafer was used in this work. The Si-terminated face of the substrate was processed by chemical mechanical polishing (CMP) with atomic scale steps. Afterwards, the wafer was cleaned by standard RCA method to remove chemical contaminants. Before graphene growth, the SiC substrate was etched in H\(_2\) flow at 1600 °C for 20 min. Then the substrate was annealed at 1600 °C for an hour under Ar atmosphere (grade 5.0). During the annealing process, the pressure of growth chamber was kept at 900 mbar [30]. After growth, H\(_2\) was introduced into the growth chamber at 900 °C ~ 1100 °C to achieve the H intercalation for obtaining QFSG. The SERS measurement was carried out at room temperature, where the Ag particles were placed on the sample surface and dry Ar gas flow was used to control the distribution.

The Raman spectra of QFSG were collected by a HR800 Raman spectrometer system from Horiba Jobin Yvon with 532 nm excitation laser. The 100× objective was used with a 600 diffraction grating. The step of Raman mapping was 0.5 µm. All the Raman spectra were tested for three times to lessen accidental error. The morphology of Ag particle was observed by Scanning electron microscopy (SEM, Hitachi S-4800) and the x-ray diffraction (XRD, Bruker D8) was utilized to distinguish the crystal structure of Ag particles.

Result and discussion

Firstly, the Raman spectra were collected respectively on in situ grown graphene and QFSG obtained by H intercalation, where averagely distributed 9 sites on the 10 mm × 10 mm square were chosen and the typical spectra was shown in figure 1. Before Raman characterization, the optical microscopy was used to confirm the area to be measured was on the SiC terrace as far as possible. It is observed in figure 1(a) that the characteristic G and 2D peaks originally at the positions of 1605 cm\(^{-1}\) and 2731 cm\(^{-1}\) shifted to the lower wavenumbers at 1585 cm\(^{-1}\) and 2695 cm\(^{-1}\) respectively after H intercalation. Figure 1(b) shows the enlarged 2D peak variation. After H intercalation, the FWHM of 2D peak increased from 37 cm\(^{-1}\) to 52 cm\(^{-1}\), which stood for bilayer graphene according to the equation of FWHM(2D) = \(\frac{45}{N} \times 0.88\) cm\(^{-1}\) (N represented the number of graphene layer) [16]. Based on these results, we can draw the conclusion that the strong mutual effect between the substrate and graphene had been weakened and one more graphene layer was formed after the present H intercalation processing.

By contrasting the QFSG Raman spectra before and after SERS in figure 2, an obvious peak appeared at the position of 2131 cm\(^{-1}\) ascribed to the Si-H bond apart from the original peaks [24], which showed the success of hydrogenation on the SiC(0001) surface underneath the QFSG undoubtedly. Raman spectroscopy measurement is based on the energy inelastic scattering. The usual method can only collect the in-plane stretch
mode of chemical bonds, while Si-H bonds are perpendicular to the surface. After present SERS treatment, the near-field plasmonic effect in the vicinity of Ag particles was introduced into the surface, thus the Si-H stretch mode was excited and could be collected from the QFSG sample. It is also need to point out that the absorbance wavelength of Ag metal particles occurs at around 400 nm. Compared with that of Au particles, of which the absorbance wavelength is around 500 nm, the surface enhanced effect with Ag assisting could take place with the 488 nm, 532 nm and 633 nm excitation lasers.

It was notable that the intensities of all the characteristic peaks of graphene were also enhanced, including the D, G and 2D peaks. Meanwhile, the second order peaks of SiC substrate at 1520 cm\(^{-1}\) and 1713 cm\(^{-1}\) exhibited the same tendency. It is presumable that the electric field enhancement could also make effect at the lower SiC substrate besides the upper graphene and interface.

In view of the inevitable random deposition of Ag particle, it is necessary to study the SERS effect in different Ag distribution areas. White arrow in figure 3(a) shows the mapping route from an Ag single particle to the latter aggregation area, and typical spectra are shown in figure 3(c), named from S1 to S6. Raman spectra collected in single particle area (S1 and S2) shows the same peak character and free of Si-H response. In contrast, the Si-H bond begins to get observed in S3, indicating enhancement appears. At the terminal of Ag particle aggregation area in the S6 spectra, the intensity of Si-H bond goes lower. To verify this phenomenon, other Ag aggregation areas were chosen and tested. The white arrow in figure 3(b) gives the typical mapping path across the Ag aggregation area. Figure 3(d) shows the obtained Raman spectra, where the Si-H peaks appears in all the six spectra. Compared with the spectra shown in figure 3(c), we can confirm that the Ag aggregation part (figure 3(d)) was accompanied with stronger surface enhancement effect.
For this near-field enhancement occurred at nanoscale features, the classic local model and nonlocal model have been widely used for explanation [31–33]. In the local model, the dielectric function can be described as

\[ \varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \]  

where \( \omega \) is the applied electromagnetic field frequency, \( \varepsilon_\infty \) stands for the infinite frequency, \( \gamma \) and \( \omega_p \) represent the metal damping and plasma frequency, respectively. When taking the electron-electron repulsion effect into account, the nonlocal model is developed. The transversal mode \( \varepsilon_T(\omega) \) is in line with the local model, while dielectric function at longitudinal direction is illustrated as

\[ \varepsilon_L(k, \omega) = \varepsilon_\infty - \frac{\omega_p^2}{k^2 + i\gamma\omega - \beta^2|k|^2} \]  

where \( k \) is the propagation vector and \( \beta \) represents the nonlocal parameter. Results by numerical analysis in figure 3(e) showed that the electric field excited by the metal particles did not distribute uniformly at the whole scale. At the edge of the metal, it was accompanied with higher electric field intensity compared with other areas. In the present work, the edge of Ag particles merged thus larger plasmonic near-field at the Ag particles aggregation area was formed, resulting in stronger Raman enhancement.

The SERS effect was measured employing Ag particles in different diameters to further verify the relationship between particle size and enhancement effect. Figures 4(a) and (b) exhibit the SEM images of Ag particles in different diameters under the same magnification. For the first kind of Ag particles, the average diameter was
∼50 nm. For comparison, the second kind of Ag particles were prepared with mean diameter of ∼500 nm. Both two kinds of Ag particles had rough surface which was essential for the surface electronic field simulation. The XRD spectrum in figure 4(c) illustrates that Ag particles used in this work are in pure phase with good crystallization quality and belong to 3C crystallographic symmetry. The blue and red lines in figure 4(d) represent the Raman spectra collected on the QFSG samples deposited with different Ag particles (50 nm and 500 nm in diameter). It was observable that all graphene peaks were enhanced simultaneously and the Si-H peak was effectively activated. The peak intensities when utilizing large Ag particles (500 nm) were much higher than that of smaller Ag particles. The detailed analysis of the peaks is summarized in table 1. Here, the enhancement factor F was calculated by getting the ratio of the peak intensity before and after Ag particle deposition (F = I_{after}/I_{before}). The D, G and 2D peaks of graphene were accompanied with different enhancement factors owing to the difference of corresponding scattering process. For Ag particles with the diameter of 50 nm, the biggest F value was found for D peak being 3.72. Nevertheless, the biggest F value (14.21) appeared at 2D peak position for the larger Ag particles. Particularly, the Si-H peak intensity with large Ag particles (500 nm in diameter) was 8.09 times as high as that of small Ag particles (50 nm in diameter).

### Table 1. The enhancement effect analysis for different characteristic peaks.

| Peaks | Pristine Intensity | Pristine Factor | D_{Ag}(50 nm)^a | D_{Ag}(500 nm)^a |
|-------|-------------------|----------------|----------------|----------------|
| D     | 254               |               | 945            | 2450           | 3.72 | 9.65 |
| G     | 925               |               | 1750           | 4050           | 1.89 | 4.38 |
| 2D    | 190               |               | 600            | 2700           | 3.16 | 14.21 |
| Si-H  | 0                 |               | 115            | 930            | /    | /    |

^a D_{Ag} means the diameter of Ag particles.

Figure 4. (a) and (b) are SEM images for Ag particles in different diameters, (c) XRD spectrum of Ag particles, and Raman spectra of Ag particles in different diameters.
Apart from the integration electric field effect, the intensity of the SERS signal for 2 dimensional materials is believed to be related to the Ag intrinsic feature. The intensity of the Raman enhancement can be expressed as the following equation [33].

$$\frac{\Delta I_{\text{SERS}}}{I_0} = \frac{3}{28} \sigma Q^2(\omega) Q^2(\omega_S) \left(\frac{a}{h}\right)^{10}$$

where $\Delta I_{\text{SERS}}$ is the intensity variation caused by SERS effect, $I_0$ is the pristine Raman signal, $a$ represents the particle radius, $h$ is deemed as the distance between particle center and graphene, $\sigma$ stands for feature of cross sectional area and $Q(\omega) = \frac{[\alpha_{np}(\omega)]}{4\pi a^3}$ stands for the Mie enhancement. Herein, $\alpha_{np}(\omega)$ is the polarizability of approximately spherical particles. As for the same enhancement system of QFSG with Ag particles, it can be roughly estimated that Raman enhancement is proportional to the tenth power of the ratio of particle radius and distance. In this work, $h$ was deemed to be the distance between particle center and bottom graphene, which was evaluated by adding particle radius and bilayer graphene thickness ($\sim 0.67$ nm) approximately. For Ag particle with smaller radius ($a = \sim 25$ nm), the value of $\frac{a}{h}$ was calculated to be 0.97, while for the large Ag particles ($a = \sim 250$ nm), the ratio was calculated to be 1.00. In view of the tenth power of $\frac{a}{h}$, the Raman enhancement factor of bigger Ag particles is about 1.35 times as high as that of the smaller Ag particles. Meanwhile, the particle radius $a$ also makes effect in the $Q(\omega)$ thus resulting in the exact magnification of enhancement factor for the larger particles varied from 2.32 to 8.09 compared with the small particles. Notably, the enhancement factor ($\sim 10$) in this work was relative lower than reported results ($\sim 14$) [32, 33]. It was assumed that in this epitaxial bilayer QFSG structure, the graphene-particle center distance $h$ was quite bigger than that of the monolayer graphene. In addition, the SiC substrate is lacking in interference enhanced Raman scattering which existed in Si/SiO$_2$ substrate.

The coverage of 2 inch wafer-scale QFSG prepared under different temperature conditions was estimated utilizing the Ag particles with the dimension of 500 nm in diameter. Noticing the Ag distribution could make

Figure 5. Raman mapping of QFSG in $5 \mu m \times 5 \mu m$ area under (a) $900^\circ C$, (b) $1000^\circ C$ and (c) $1100^\circ C$. 

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effect on the validity of Si-H bonds, the estimated regions were firstly verified to be the Ag aggregation areas before testing. Figure 5 shows the typical mapping results of QFSG in 5 μm × 5 μm region. It could be seen that the Si-H peak, representing in red color, appeared at all three samples, which meant the H atoms have been added to the in situ graphene evidently. The exact ratios of the Si-H peak response were obtained and calculated to be 67%, 73% and 60% for samples prepared at 900 °C, 1000 °C and 1100 °C, respectively, which clearly indicated that H was intercalated differently under the corresponding condition. Moreover, these results gave out an unambiguous enlightenment that H2 could not be decomposed completely at lower temperatures (<900 °C) while the H atoms might get released at higher temperatures (>1100 °C). To get fully covered QFSG, the annealing temperature should be selected around 1000 °C. The optimal annealing condition is worthy of discussion in the future work.

Conclusion

In summary, a direct and effective approach to assess the QFSG was presented. Through this enhanced Raman spectra assisted with Ag particles, the interface condition between graphene and substrate could be confirmed straightly. The relative larger Ag particles (500 nm in diameter) at aggregation area were found to possess the best enhancement effect. Meanwhile, the QFSG coverage was analyzed accurately and corresponding H intercalation conditions could be adjusted efficiently. It is believed that the Ag-assisting Raman spectroscopy method would make great effect on homogeneous and wafer-scale epitaxial graphene fabrication, which is beneficial for widening the application of graphene in microelectronics field.

Acknowledgments

This work was supported by funding SD2018BP002 from Shandong Provincial Key Laboratory of Biophysics, Foundation 31513020404-1 and National Key R&D Program of China 2018YFB0406703.

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