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Defect Generation in Mono-layer Graphene in O_2-PDA and FGA

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Abstract

Either post deposition annealing (PDA) or forming gas annealing (FGA) is to improve the top-gate dielectric devices. However, it would degrade the grapheme because of possible reactions of graphene. This paper discusses the defect generation in mono-layer graphene under both O_2-PDA and FGA.

1. Introduction

Graphene has emerged as a promising material for various practical device applications. To make graphene applicable for practical devices and circuits, the top-gated graphene device is much more required, compared to back-gated devices. However, it is quite tough to form a high-quality or uniform top gate dielectric stack on graphene because of no dangling bonds on two-dimensional material. In addition, although the post-deposition O_2 annealing (O_2-PDA) or forming gas annealing (FGA) is needed to achieve high quality dielectric films, in the meanwhile it may degrade graphene quality owing to a possible reaction between graphene and O_2 or H_2 molecules. Prior to the formation of top-gate dielectric, it is of significant importance to understand the characteristics of graphene without top-gate dielectric under such ambient annealing. The thermal treatment for conventional gate dielectrics usually needs around 600ºC, which also restricts the PDA process for graphene. This paper reports how the defects are generated in mono-layer grapheme (MLG) against O_2 and Ar/H_2 at elevated temperatures. Defects were estimated by microscopic Raman measurement and atomic force microscopy (AFM).

2. Experimental

MLG was transferred onto a 90-nm-thick SiO_2/p^+-Si substrate by the micromechanical cleavage of Kish graphite. Prior to graphene transfer, SiO_2/Si substrates were annealing at 1000ºC for 5 minutes in 100% O_2 flow. Graphene flakes were annealed in 100% O_2 or Ar/H_2 (5%), respectively, for 30 minutes as a function of annealing temperature in a home-made tube furnace. The number of graphene layers were detected by optical contrast and further verified by Raman spectra. Before and after annealing, Raman spectroscopy measurements of graphene layers were performed with λ =488 nm Ar laser (Horiba HR800) with a power of ~ 0.5 mW at the sample position, which was set to prevent potential damage to graphene during the measurement. The laser spot size at focus and the resolution of the wavenumber were ~1 μm dia. and ~0.3 cm^{-1}, respectively.

3. Results and Discussion

Fig. 1 shows typical results of mono-layer graphene in the Raman measurement as a function of annealing temperature in O_2. The D band peak obviously increases with the increase of annealing temperature. To improve the accuracy, the semi-log scales were used to estimate the D and G peak maginitude. Additionally, both G and 2D bands have a blue-shift after an O_2 annealing, which can be clearly seen in Fig. 1.

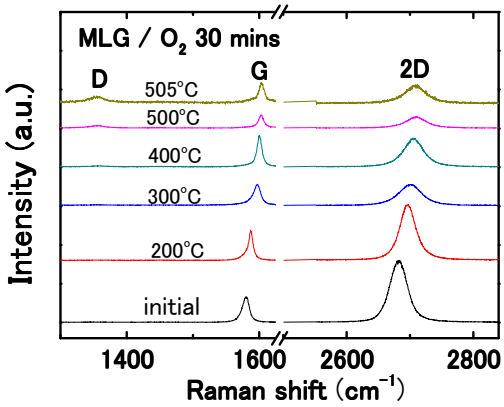

Fig.1 Typical Raman spectra of mono-layer graphene for several kinds of annealing temperature in O_2.

The Raman intensity of D band over G band, I_D /I_G, as a function of temperature is summarized in Fig.2. It is obviously observed that two kinds of defect generation processes are overlapped in MLG. It appears a special corner-point of 400ºC in defects generation process along the temperature, as denoted in Fig.2. Below the corner-point the defects generation in O_2 annealing is quite insensitive to the temperatures.

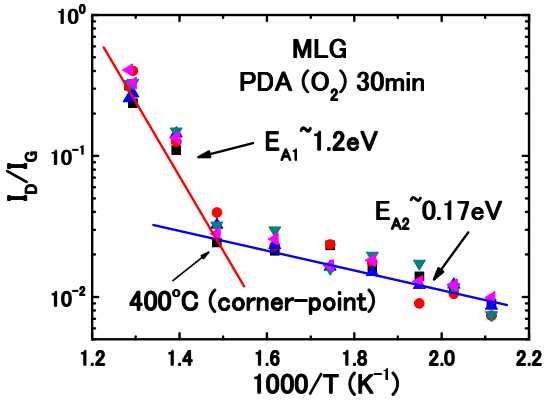

Fig.2 I_D/I_G as a function of 1/T in O_2 annealing. Two kinds of activation energies are clearly observed.

More interestingly, the defects generation is prominent above the corner-point. The results indicate that two independent activation processes are involved in the degradation process, whick can be described as follows,

$$I_D/I_G = A_1 \exp\left(-\frac{E_{A1}}{k_B T}\right) + A_2 \exp\left(-\frac{E_{A2}}{k_B T}\right) \quad (1)$$

where A_1, A_2 are constants, E_{A1} and E_{A2} are activation energy (E_A) above and below the corner-point, respectively. In case of MLG, E_{A1} and E_{A2} are estimated to be 1.2eV and 0.17eV, repectively, from the fitting. E_{A2} in the temperature range below the corner-point is negligibly small, possibly resulting from the thermal mismatch between graphene and SiO_2/Si substrate. Above the corner-point E_A of 1.2eV should be much more concerned, which is correspoing to the oxygen effect in the annealing.

In the O_2-PDA, the defect generation is dominated by the chemical reaction between graphene and O_2 at elevated temperatures, especially above the corner-point. As a matter of fact, the etching "pits" are detected after O_2 annealing as shown in Fig. 3 [1]. Therefore, it is quite natural that E_{A1} of 1.2V should be related to the C-O bond breaking, very similar to the theorectical expetation of 1.5eV in graphene oxide [2]. This fact is quite suggestive of the G-O bond formation in O_2-PDA.

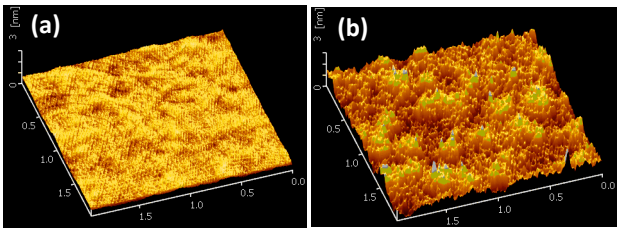

Fig.3 3-dimensional AFM image of MLG before (a) and after (b) an O_2 annealing at 500°C for 30 minutes. RMS is 0.1nm for the former and ~0.3nm for the latter, respectively.

Fig.4 shows temperature evolution of I_D/I_G of MLG in FGA for 30 mintutes. Below 450°C, I_D/I_G is very small and almost keeps unchanged. E_A above 400°C in FGA is only 0.28eV, which is quite different from PDA in O_2, in case E_{A1} is 1.2eV. It is interestingly pointed out that E_A (0.3eV)

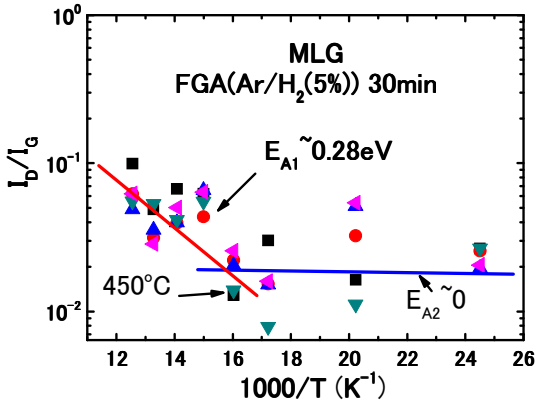

Fig.4 I_D/I_G as a function of 1/T in the Ar/H_2 (5%) annealing. Two regions are also observed.

in FGA above the corner-point is similar to E_{A2} (0.17) in O_2-PDA below the corner-point, though whether the defects are also generated by thermal mismatch expansion in case of FGA or not obviously needs further investigations.

Indeed, we observed prominent differences in Raman spectra between O_2-PDA and FGA treated graphene. The Raman spectra of MLG at 500°C for both O_2-PDA and FGA are compred in Fig.5. It appears that D band is broadened and the "baseline" is also enhanced in FGA, marked by the red dash in Fig.5(a). Furthermore, though the G band near the center is still sharp, its tails seem to extend to some extent, as shown in Fig.5(a). This phenomenon is similar to that observed in disordered carbon[3] and CVD graphene heated in vacuum [4]. The band spectral broadenings indicates that a structure disorder occurs in MLG after FGA [4, 5], which may result from the heating effect and/or the small amount reactions between graphene and remaining H_2, or O_2 and H_2O underneath graphene. It is worth noting that the heating effect also exists, though the reaction between graphene and O_2 dominates the defect generation above the corner-point in case of O_2-PDA.

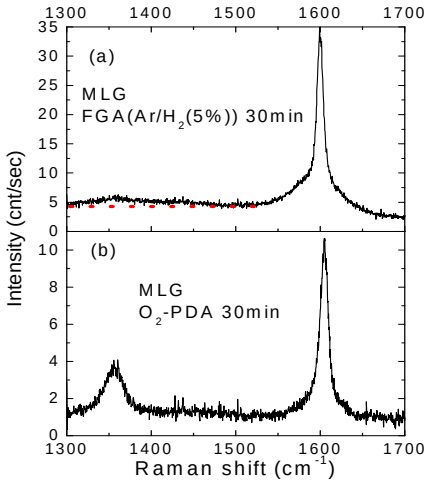

Fig.5 Raman spectra of MLG at 500°C for both (a) FGA and (b) O_2–PDA .

4. Conclusions

The defect generation in MLG in both O_2–PDA and FGA was investigated. Two kinds of activation energies are observed. Above the corner-point, E_A for O_2-PDA is 1.2eV while ~0.3eV for FGA. The present results point out more importantly that the thermal treatment in O_2 even below 400°C for the top-gate graphene device integration may affect the graphene characteristics.

Acknowledgement

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References

[1] L. Liu *et al.*, *Nano Lett.*, **8**, 1965 (2008).[2] R. Lahaye *et al.*, *PRB*,**79**, 125435 (2009).[3] A. C. Ferrari *et al.*, *PRB*, **61**,14095 (2000) .[4] S. Suzuki *et al.*, *JPCC*, **117**, 22123 (2013). [5] D. C.Elias *et al.*, *Science.* **323**, 610 (2009).