Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp896-897

Impact of Surface Treatment of SiO_2/Si Substrate on Mechanically Exfoliated Graphene

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Introduction

The extraordinary high field effect mobility values of both electron and hole have been reported on graphene films made by mechanical exfoliation of bulk graphite [1]. Although large-size monolayer graphene layers are demanded for precisely characterizing graphene properties in terms of handling and electrode attachment, the size of graphene transferred on SiO_2/Si substrate is still limited. To obtain a number of large-size graphene flakes on SiO_2, it is known that O_2-plasma treatment is efficient [2]. As the graphene FET mobility is concerned, the data on the SiO_2/Si substrate scatters considerably among many reports, and is limited to the typical value of ~10,000 cm^2/Vs [3]. This value is quite smaller than that of suspended one [1], which is explained by the scattering centers located at the SiO_2/graphene interface.

In this paper, we have paid attention to the possibility to achieve both the large size of graphene flakes and high mobility by O_2-plasma surface treatment.

Experiment

Graphene was transferred on HF-dipped and de-ionized water (DIW) -rinsed SiO_2 from Kish graphite by the mechanical exfoliation. Various SiO_2 surfaces were prepared by changing plasma gas and duration, as listed in **Table 1**.

The contact angle was measured to investigate the surface wettability. Then, the effects of the interaction between graphene and SiO_2 were also studied by the Raman spectra measurement. Finally, the transport properties were discussed for the graphene we have obtained in above-mentioned manner.

The ~1.5 μL droplets of DIW were contacted with the substrates and the static contact angles were measured from the photographic image of the droplets by θ/2 method. Moreover, microscopic Raman spectroscopy measurements were carried out with the 488 nm laser with a power of 0.5 mW at the sample position. The laser spot size at focus and the resolution of the wavenumber is ~600 nm for a ×100 objective lens and ~0.3 cm^{-1} for a 2400 gr/mm grating.

Table 1. Sample conditions.

	1	2	3	4	5
Gas	–	O_2/Ar	O_2/Ar	O_2/Ar	Ar
Flow rate [cc/min]	–	5/45	5/45	5/45	50
Time [s]	–	10 s	1 h	1 h	10 s
Transfer	ASAP	ASAP	ASAP	1 day later	ASAP

#1 is HF-dipped and DIW-rinsed SiO_2 (no plasma treatment). Graphene flakes were transferred on SiO_2 as soon as possible (ASAP) after the sample was taken out from the plasma chamber, except #4, where the sample was kept for one day after plasma treatment. RF power of 60 W was used.

Results and Discussion

Fig. 1 shows optical micrographs of graphene flakes on (a) HF-dipped SiO_2 (#1) and (b) O_2-plasma treated SiO_2 (#2). A clear difference can be seen between **Fig. 1(a)** and **(b)**. Larger graphene flakes with high density in **Fig. 1(b)**. The difference among those on SiO_2 in conditions #2, #3 and #5 were not so evident, while the result of #4 was similar to that of #1.

Fig. 2 shows the contact angles estimated from the images of DIW droplets on a highly oriented pyrolytic graphite (HOPG), HF-dipped SiO_2, and plasma treated SiO_2 (#2~#5). Graphite is known to be hydrophobic, while the contact angles of droplets on SiO_2 decreases from ~28° for #1 to nearly zero for #2, #3 and #5, indicating that the hydrophilic nature of the SiO_2 surface is enhanced by O_2-plasma treatment due to the increase in OH group density by removing the hydrocarbon contaminants on SiO_2 [4]. However, the contact angle increases to ~75° for #4. This is easily understandable in terms of re-adsorption of a huge amount of hydrocarbon contaminants on the SiO_2 surface.

In the Raman spectrum measurements, the laser was focused on the center position of graphene flake, because the peak position and FWHM were affected by the graphene edge. It should be noted that no

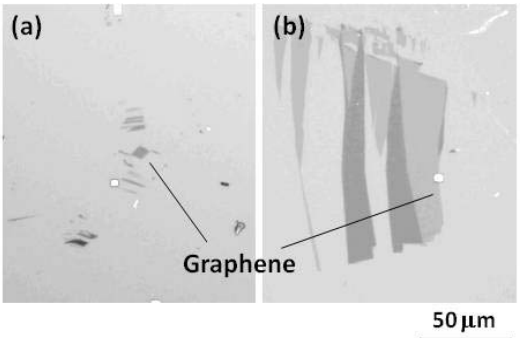

Fig. 1 Optical micrographs of graphene on (a) HF-dipped SiO_2 (#1) and (b) O_2-plasma treated SiO_2 (#2).

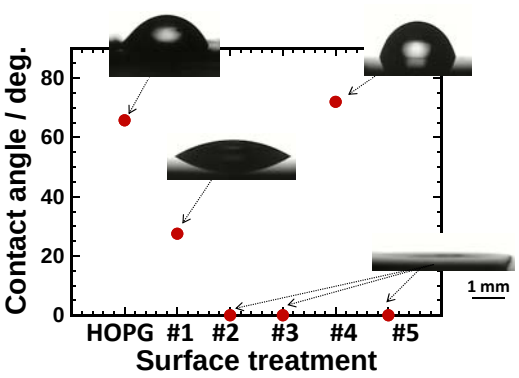

Fig. 2 Contact angles estimated from the images of DI water droplets on various substrates. The mean value of 5 set of measurements are shown.

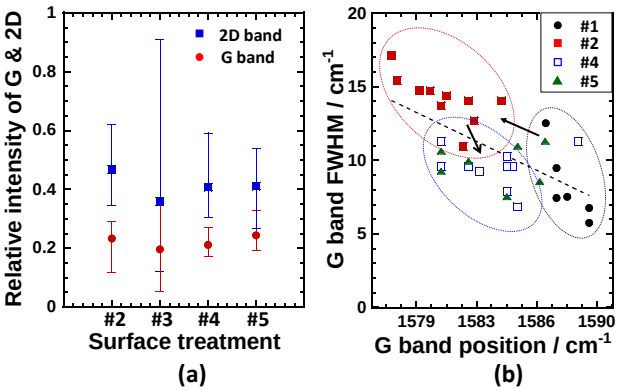

Fig. 3 (a) Intensities of G and 2D bands relative to those for HF-last SiO_2 and (b) G band FWHM vs. G band position for various surface treatments.

defect-related D band signal was observed in any surface treatment cases from #1 to #5. **Fig. 3(a)** shows normalized intensities of both G and 2D bands for various surface treatments relative to those for HF-dipped SiO_2. It is reported that Raman intensities of graphene on catalytic metals grown by CVD are considerably lower than those on SiO_2 due to the strong interaction between graphene and catalytic metals. The decrease in both G and 2D band intensities in **Fig. 3(a)** from those on HF-dipped SiO_2 strongly suggests that the interaction between graphene and SiO_2 is enhanced by the surface treatments.

In order to reveal the difference between O_2 and Ar plasma treatments, **Fig. 3(b)** shows the relationship between G-band peak position and FWHM of graphene on SiO_2 for #1, #2, #4 and #5 conditions. The FWHM for #1 (HF-dipped SiO_2) are statistically smallest at the highest G band position. While that for #2 shows a clear red-shift of G band and larger FWHM. The G band position and FWHM for the #4 (one day after O_2 treatment) move back slightly to #1, but not completely. In case of #5 (Ar plasma), the results were similar to #4. Therefore, the O_2 plasma treatment is likely to facilitate the interaction between graphene and SiO_2, compared with Ar plasma treatment. Since the large contact angle for #4 was observed, the less interaction between graphene and SiO_2 in Fig. 3(b).

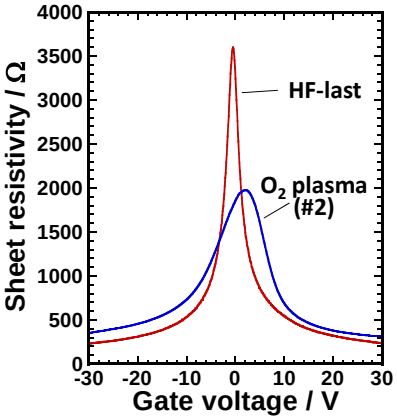

Fig. 4 Typical sheet resistivities vs V_g for the graphene FETs on HF-dipped SiO_2 and on O_2 plasma treated SiO_2.

Fig. 4 shows a comparison of typical relationship between sheet resistivity and gate voltage for the graphene on HF-dipped SiO_2 and on O_2-plasma treated SiO_2. These are the four-probe measurement results (no contact resistance contribution is included). It is clear that the peak of resistivity for graphene on HF-dipped SiO_2 is in most cases much sharper than that on O_2-plasma treated SiO_2. This fact implies that the mobility is considerably degraded by O_2-plasma treatment. It is likely that a large number of scattering centers are introduced by the O_2-plasma treatment.

Finally, let's consider the relationship between the adhesion of graphene on SiO_2 and mobility in detail. The red-shift of G band suggests that the O_2 plasma treatment might increase the interaction between them and that the number of local pinning centers modulating the phonon inherent in graphene. Therefore, it is quite reasonable that the mobility of graphene with the large size is on the whole degraded. The strong hydrophilic nature of the plasma-treated SiO_2 surface arises from the large OH group density. The interaction between graphene and SiO_2 might be a coupling of charged SiO_2 with non-uniform electron distribution in graphene polarized by OH^- on SiO_2, and furthermore might weaken a coupling between bottom graphene and upper graphene. This will work as new scattering centers.

Conclusions

The large size for graphene was achieved by the O_2 plasma treatment, while the mobility was degraded. The strong coupling interaction between graphene and SiO_2 suggested from the red-shift of the G band makes graphene far from the ideal suspended case. As far as graphene is transferred on O_2-plasma treated SiO_2, the large size and high mobility seems to be incompatible. Therefore, it is a critical issue for making the best of high potentiality of graphene to elucidate the graphene adhesion mechanism on SiO_2 and to find an appropriate surface treatment method.

AcknowledgementThe Kish graphite used in this study was generously provided by Dr. E. Toya of the Covalent Materials Co.**References** [1] K. I. Bolotin, et al., PRL, 2008, **101**, 096802.[2] X. Liang, et al., Nano lett. 2007, **7**, 3840.[3] K. Nagashio, et al., JJAP, 2010, **49**, 051304.[4] X. Zhang, et al., Electrochem. Solid-State Lett., 2004, **7**, G172.