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Few layer graphene synthesis via SiC decomposition at low temperature and low vacuum

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Received 16 November 2015, revised 18 February 2016
Accepted for publication 22 February 2016
Published 21 March 2016

Abstract

Based on the large-scale availability and good electrical properties, the epitaxial graphene (EG) on SiC exhibits a big potential for future electronic devices. However, it is still necessary to work continuously on lowering the formation temperature and vacuum values of EG while improving the quality and increasing the lateral size to fabricate high-performance electronic devices at reduced processing costs. In this study, we investigated the effect of the presence of Mo plate and hydrogen atmosphere as well as the vacuum annealing durations on SiC decomposition. Our studies showed that the graphene layers can be produced at lower annealing temperatures (1200 °C) and vacuum values (10⁻⁴ Torr) in the presence of Mo plate and hydrogen. For high quality continuous graphene formation, Mo plate should be in contact with SiC. If there is a gap between Mo and SiC, non-wetting oxide droplets on few layer graphene (FLG) are recorded. Moreover, it is found that the morphology of these islands can be controlled by changing the annealing time and atmosphere conditions, and applying external disturbances such as vibration.

Keywords: graphene, SiC decomposition, low temperature, low vacuum, molybdenum, hydrogen annealing

(Some figures may appear in colour only in the online journal)
pressure to atmospheric pressure using Ar. Very recently Jin et al. [19] showed that the crystallinity of EG on SiC can be enhanced even at lower annealing temperatures by capping the substrate with a molybdenum plate during vacuum annealing. According to this study Mo-plate absorbs the Si atoms and facilitates an environment favorable for growing high-quality EG films. However, the ultra-high vacuum (UHV) system, used in that study, was not equipped with a high-temperature hydrogen etching apparatus capable of removing polishing scratches. So they could not perform hydrogen annealing. However, hydrogen annealing is critical in SiC technology. It is either performed at high temperatures (1500 °C) to remove polishing scratches of SiC [20] for high quality EG synthesis or performed at lower temperatures (1000 °C) to prepare epitaxially ideal SiO₂–SiC interface for MOSFET technology [21]. For the former, it was shown that when it is done at very high temperatures for long durations etch pits form on the surface and decreases the quality of EG formed on SiC [20]. And for the latter one, when temperature is around 1000 °C it was shown that surface carbon in the form of graphitic clusters are formed [22].

In this study, we investigated the effect of the presence of Mo, hydrogen and vacuum annealing durations on SiC decomposition and for the first time we showed graphene formation through low temperature hydrogen annealing of SiC in contact with Mo plate.

2. Experimental

6H–SiC single crystal wafers with optical polished faces were obtained from Intrinsic Semiconductor Corporation (acquired by CREE Inc.). In order to clean the surface of SiC, samples are washed with Piranha (H₂SO₄:H₂O₂, 3:1) solution for 10 min and rinsed with deionized water, then the samples are kept in hydrofluoric acid (HF) for 1 min and again rinsed with deionized water and dried. Clean SiC wafer is introduced into the high vacuum (HV, 10⁻⁶ Torr) system (Nanovak) (figure 1(a)) on a Mo plate, which is covered by another Mo plate on top (figure 1(b)). As can be seen from figure 1(b), a pair of high current vacuum feedthroughs is employed to flow current (around 100 A) through the Mo plates. As the current passes, Mo plates get hotter which in turn heats the SiC wafer. The temperature of the sample is measured using a thermocouple in contact with sample. In order to investigate the effect of hydrogen, in some experiments, H₂ is passed with a flow of 5 sccm (10⁻⁴ Torr).

Scanning electron microscopy (Nova NanoSEM 430, FEI) and atomic force microscopy (HP AFM, NanoMagnetics Instruments) are used to investigate the morphology of the surface. In order to confirm the formation of EG and evaluate its quality, Raman spectroscopy (alpha300 S, WITec) is used. X-ray photoelectron spectrometer (XPS, K-Alpha, Thermo Scientific) is also used to investigate the surface chemistry.

3. Results and discussion

The surface morphology of the two faces (up and down) of as-received SiC is given in figures 2(a) and (b). The micro scratches from polishing are visible on both faces. In all experiments C-face is positioned as down face and hence Si-face is up face. SEM and Raman spectroscopy studies show that the morphology of the structures formed on up and down surfaces of SiC substrate after treatment are different. While island-like structures are observed on up surface, graphene-like structure is formed on down surface. In order to understand the reason of different surface morphology formation, Si face is positioned also as down face, however, similarly the island formation is observed on up surface and graphene-like structure is formed on down surface. In order to understand the reason of different surface morphology formation, Si face is positioned also as down face, however, similarly the island formation is observed on up surface and graphene-like structure is obtained on down surface. Therefore, the difference is attributed to the position of SiC wafer and Mo plate. As shown in figure 1, the upper surface of SiC is not in contact with the Mo plate but down surface is in direct contact with Mo. Therefore, parallel to the study by Jin et al. [19], once again it is shown that, when SiC is in contact with Mo plate, Mo plate absorbs the Si evaporated from the SiC surface and the carbon atoms left on the surface self-organize to form graphene layers. Furthermore, it is found that when there is a gap between SiC and Mo, Mo evaporates and deposits on SiC from the Mo plate above the sample resulting in island formation.

3.1 Effect of hydrogen

In order to study the effect of hydrogen annealing, two sets of samples are prepared. In the first set, the samples are prepared by using two different hydrogen annealing durations (30 min and 100 min). And in the second set, (30 min and 100 min) hydrogen annealing is followed by 240 min vacuum annealing (figure 2).
SEM and Raman studies show that even only by hydrogen annealing, graphene is formed on down surface of SiC without requiring high vacuum values at 1200 °C (figures 2(d), (f) and 3(c), (d)). When 240 min vacuum annealed sample (figure 3(b)) is compared with the 30 min H2 and 240 min vacuum annealed sample (figure 3(e)), from SiC peak intensity, it is found that hydrogen annealing resulted in the formation of thinner graphene layers. However, hydrogen annealing duration should be also optimized. SiC peak intensity in Raman spectra indicates that 30 min hydrogen annealing results in formation of thinner graphene layer (figure 3(c)) compared to 100 min hydrogen annealing (figure 3(d)). Similar results are also obtained for the samples for which hydrogen annealing is followed by 240 min vacuum annealing. 30 min hydrogen and 240 min vacuum annealing results in a thinner graphene layer (figure 3(e)) than the one obtained by 100 min hydrogen and 240 min vacuum annealing (figure 3(f)). Since the best results (thinner graphene layers) are obtained through 30 min H2 annealing, this duration of hydrogen annealing is fixed for further studies.

3.2. Effect of vacuum annealing duration

In figure 4, Raman spectra of the samples, which annealed at 1200 °C in hydrogen for 30 min and vacuum for various durations (0, 30, 60, 240 min) are given. Since no SiC (substrate) signals are recorded from the up surfaces in Raman studies, carbon formed on up surface is always thought to be thicker than the one formed on down surface.

With respect to the morphology: once again island formation (figure 5) is observed on up surface (when there is no direct contact between sample and Mo); however, when sample and Mo are in contact, ordered graphene-like structures (figure 6) are recorded. To evaluate the order of carbon structures, ratios of $D$ peak intensity to $G$ peak intensity ($I_D/I_G$) are measured from Raman spectroscopy data for both surfaces (figure 5).

For up surface (Si-face, where there is a gap between SiC and Mo), if there is no vacuum annealing after hydrogen annealing the disorder degree of the carbon formed on the surface is the highest (figure 5(a)). When the hydrogen annealing is followed by 30 min vacuum annealing, the disorder decreases sharply and islands get larger in size (figure 5(b)). As the vacuum annealing duration increases to 60 min, the disorder slightly increases and the island size becomes smaller (figure 5(c)). Finally, increasing the vacuum annealing duration (to 240 min) results in further increase in disorder and decrease in island size (figure 5(d)).

For the down surfaces (C-face), where SiC and Mo are in contact, we show that graphene sheets can be produced even only through 30 min hydrogen annealing (figures 4(b) and 6(a)). And since SiC peaks are also observed, this layer is
thought to be thin. However, when 30 min hydrogen annealing is followed by 30 min vacuum annealing, SiC peaks disappear showing that a thicker carbon formed on the surface. Moreover, it is found that when the vacuum annealing duration is increased to 60 min, SiC peaks start to appear again and get pronounced even more with increasing annealing duration (240 min) while the disorder peak of carbon diminishes.

Raman spectroscopy is widely used to determine the number of graphene layers [23]. Normally when the number of graphene layers is very few, it is difficult to distinguish the G and D peaks in the spectra because their intensities are much smaller than those of the surrounding peaks from the SiC substrate. However, our Raman spectroscopy results (figure 3) show well defined D and G peaks together with SiC peaks with different intensities. Therefore, this reveals that the formed graphene is not single but few layer graphene (FLG). Moreover, our measurements show that the 2D peak can be fitted with a single Lorentzian, which is in agreement with literature [24]; and smallest value of FWHM for this peak is 60 cm$^{-1}$, which is obtained by only H$_2$ annealing. Then as the vacuum annealing duration is increased to 30 min and 60 min, the FWHM value increases to 77 cm$^{-1}$ and 84 cm$^{-1}$, respectively, and then decreases to 64 cm$^{-1}$ for even longer annealing duration (240 min). Moreover, SEM studies show that if there is no vacuum annealing (only H$_2$ annealing), the graphene structures are more continuous (figure 6). On the other hand early stages of vacuum annealing results in Swiss cheese structure (figures 6(b) and (c)). This may be because of large amount of Si escape beneath the surface (figure 7(c)).

As vacuum annealing duration is increased, graphene formed
on the surface gets more ordered, Si diffusion decreases, and therefore no more Si escape channels are produced, and more continuous graphene is achieved (figure 7(e)).

Based on our observations, we hypothesized the following process that is also explained schematically in figure 7. When the SiC and Mo plate are in contact as shown in figures 7(a) and (b), during 30 min of H2 annealing, Si atoms diffuse into the Mo plate leaving C atoms on the interface (figure 7(c)). The relatively free C atoms rearrange to form the graphene layer (figure 6(a)), which is very thin as evidenced by the SiC peaks observed in Raman spectra (figure 4(b)). When H2 annealing is followed by vacuum annealing (figure 7(d)), further SiC decomposition results in a thicker (as evidenced by the lack of SiC peaks in Raman Spectra) and less ordered (figure 6(b)) carbon. As vacuum annealing continues (figure 7(e)) the graphene like structures grow till a certain point at which the already formed C interface prevents further Si diffusion into Mo plate. This also decreases SiC decomposition
and thus further free C formation. At prolonged annealing times (figure 7(f)), the carbon reorganization and interface relaxation processes dominate the new free C formation at the interface. During this reorganization/relaxation processes, we observe disorder-order transition at the graphene like interface (figure 6(d)). This transition also results in a decrease in the thickness of the C interface (figure 7(f)) as evidenced by the enhancement of SiC peaks (figure 4(b)).

3.3. Effect of vibration

To study the effect of vibration on island formation and morphological evolution, an external disturbance is provided by a mechanical pump (50 Hz measured on the pump), placed inside the frame under the furnace. The effect of vibration on the structures formed for 30 min H₂ annealing with and without additional vacuum annealing is shown in figure 8. After 30 min H₂ annealing, the presence of vibration results in coarser agglomerated structures (figure 8(b)) compared to dispersed fine islands formed without vibration (figure 8(a)). Raman studies show that the coarse structure (figure 8(b)) is mostly amorphous (figure 8(c)). XPS results also reveal the presence of MoOₓ and SiOₓ peaks (figure 1(b)).

When 30 min H₂ annealing is followed by 240 min vacuum annealing in the presence of vibration, fine islands are observed on a smooth surface. Based on the SEM image (figure 8(f)) one can speculate that the wetting angles of these islands are approaching the non-wetting conditions. Raman studies show that smooth surface is FLG (figure 8(g)) and XPS studies showed the presence of oxides on the surface.

This process with the simultaneous application of external disturbances may provide self-organized structures with controlled size and morphology on FLG. Such systems may find applications in optoelectronics and by further tailoring these islands with organic molecules such as peptides and DNAs novel sensors can be designed.

4. Conclusions

We studied the effects of the presence of Mo plate, annealing duration and atmospheric conditions (e.g. hydrogen and vacuum) and the application of external disturbances such as vibration on the SiC decomposition process. Mo, when in contact with SiC, can decrease the decomposition temperature of SiC by absorbing Si, evaporating from the surface of SiC. We demonstrated for the first time that, when SiC wafer is in direct contact with Mo, the hydrogen annealing for 30 min at 1200 °C is enough to form ordered graphene on SiC without the need of high vacuum annealing.

When hydrogen annealing is followed by vacuum annealing, two processes compete with each other. The first one is the free carbon formation due to SiC decomposition.
with Si diffusing into Mo and the second one is the carbon reorganization at the interface forming graphene sheets. When the latter process dominates, the new C layer formation slows down by a self-limiting process. This feature makes the process very versatile to obtain high quality graphene with controlled thickness by adjusting the annealing time and temperature.

We also showed that, when Mo is placed above SiC wafer (without direct contact), Mo evaporates and deposits on SiC leading to the formation of oxide islands along with some carbon formation on the surface. Furthermore we demonstrated that the application of external vibrational disturbances resulted in nano to micro sized islands on high quality FLG. This capability enables us to develop novel material systems with versatile fabrication techniques leading to novel electronic applications.

Acknowledgments

The authors would like to thank Prof Dr Omer Tarik Ogurtani (METU), Dr Elif Balkas (CREE Inc.) and Prof Dr Zafer Durusoy (Novanov) for their valuable comments; Asst Prof Bulent Ozer (TOBB ETU) for vibration measurements; and Nanomagnetics Inst. for AFM studies. The Materials Characterization Facility of UNAM-Bilkent University provided access to SEM and spectrometers used in this study. This work was supported by TUBITAK (grant no 213M481).

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