

Graphitization at Interface between Amorphous Carbon and Liquid Gallium for Fabricating Large Area Graphene Sheets

Jun-ichi Fujita^{1,2}, Ryuichi Ueki^{1,2}, Yousuke Miyazawa^{1,2}, and Toshinari Ichihashi³

¹PRESTO JST, Japan Science and Technology Co., Kawaguchi, Saitama 332-0012, Japan

²Institute of Applied Physics, University of Tsukuba, Tsukuba 305-8573, Japan

³NEC Nanoelectronics Laboratory, 34-Miyukiga-oka 305-8501, Japan

Abstract

We have found that liquid gallium exhibits as a good graphitizing catalyst for a large area graphene sheet. While gallium and carbon are known to be an insoluble system, however, we have found that the catalytic reaction occurs at a very narrow interfacial region between amorphous carbon and liquid gallium. Amorphous carbon film was transformed into graphite layer composed of a few layers of graphene sheet. These thin graphene film can be easily transferred into silicon substrate through the intermediation of PDMS rubber stamping.

Keyword: graphitization, Ga, catalyst, resistivity

Corresponding Author: Jun-ichi fujita, fujita@bk.tsukuba.ac.jp

1. Introduction

Since the discovery of the stable existence of graphene[1-3], which has characteristic structure of two dimensional carbon honeycomb network, many of amazing electronic property was discovered; quantum hale effect[4] that was explained well with Dirac fermions, tunable band gap[5,6] depending on the channel width, and a possible candidate for the spintronics devices combined with spin localization at the zigzag edge state[7-9]. Here the base material of the graphene was prepared by mechanical exfoliation from graphite crystal, but the effective size for the device fabrication process was limited in several micron meters. Thus large area graphene production process and ultimate control of the thickness to be a monolayer of graphene sheet, and it may be allowed for a few stack of graphene, will enormously contribute to the graphene electronics. One of possible candidate will be sublimation process on SiC (0001) hexagonal surface[10,11], where about 1800 °C of high temperature annealing sublimated Si atoms and remained excess carbon produced a few layers of graphene. Another conventional method of graphene growth technique is chemical vapor reaction/deposition on a metal crystal such as Ni, Co, and Cu. Such CVD technique can be easily extended to large area production[12-14], but it seems to contain some issue of controlling the defect and layer thickness.

In contrast, our idea of graphitization with liquid gallium is unique. Transition metal catalyst is commonly utilized for graphitization[15], where the carbon atom was easily dissolved into the catalyst and excess carbon at the growth point produced sheet and/or tubular graphite[16]. But, the carbon was insoluble into gallium from the view point of macro-scale reaction, thus non of phase diagram was available. However, we have found that liquid gallium acted as a superior catalyst for surface graphitization since it can uniformly cover a large area even if the target object has a three dimensional component, and the liquid gallium catalyzes amorphous carbon from the outermost surface.

From this view point, the success of large-area graphene production on a copper foil[14] seems to be originated in the same mechanism where catalytic reaction strongly restricted at the foil surface due to the insolubility of carbon into copper. We have previously reported that amorphous carbon pillars grown by focused ion beam induced chemical vapor deposition (FIB-CVD) technique[17,18], containing a certain amount of Ga that comes from as the ion species, were turned into multi-walled graphite tubes when a biasing voltage was instantly applied[19]. Here, the distinctive feature of the transformed pillar was gallium droplets coexistence with the graphite partition inside the graphitized tube, and the outside of the tube still remained as an amorphous carbon. Such reaction may also be understood by a thermal graphitization and tubulization induced with high temperature gallium vapor. However, some of experiment also suggested that carbon nanotube can be grown by gallium mixed carbon source, suggesting a viable catalytic properties of liquid gallium[20,21].

In this paper, we report the catalyzing manner of liquid gallium on a large area of amorphous carbon film in terms from TEM and EELS analysis.

2. Contact angle of gallium droplet on an amorphous carbon film

It would be generally understood that carbon doesn't dissolved into gallium, thus non of solubility diagram was available, however, near edge X-ray absorption fine structure (NEXAFS) obtained from an extremely shallow surface region of FIB-CVD diamond like carbon film suggested that there appeared a characteristic peak originated from a bonding of C-Ga at 400 °C[22]. Thus gallium and carbon can be combined in electric state from an atomic-scale view point even though the solubility would be almost negligible.

Therefore, the realization of the possible bonding state between gallium and carbon should change the surface interfacial energy of the amorphous carbon film, and thus the

contact angle of gallium droplet that supported on a carbon film should be changed, depending on the ambient temperature. The insolubility of carbon into liquid gallium suggested the large difference of the surface energy, thus the contact angle of gallium on amorphous carbon is very large exceeding 120 degrees, as shown in Fig. 1 (a). Tested carbon film was fabricated on SiO₂ substrate by laser ablation with 1064 nm of pulsed YAG laser, and the gallium droplet settled on the film was annealed in vacuum furnace at (b)200, (c)400 and (d)600 °C for 30 minutes. The increase of the annealing temperature decreased the contact angle of gallium droplet and showed nearly perfect wetting at 600 °C. Such a dramatic decrease of the contact angle indicates enormous increase in the adhesion tensor, suggesting the existence of a strong chemical bond at the interfacial surface.

3. Interfacial graphitization with gallium

Based on the wettability of gallium on amorphous carbon, we examined the graphitization of the amorphous carbon film that floated on gallium droplet. The experiment is very simple as follows. We utilized a formvar resin (SPI CHEM) dissolved with ethylene dichloride to obtain a template film of amorphous carbon film. A formvar film floated on water was scooped by aluminum washer so as to have about 2mm in diameter of the diaphragm, as shown in Fig. 2(a). Then the film was dried and coated about 10 nm thick amorphous carbon using laser ablation technique. Vacuum annealing of these specimens for 30 min at 700 °C, at a back pressure of approximately 10⁻⁴ Torr, decomposed the formvar film, but 10 nm thick of amorphous carbon film and the back side support of formvar remained as a negligible small residue as shown in Fig. 2(b). We confirmed this pre-heating at 700 °C without gallium never transformed the amorphous carbon film into a graphene.

Such amorphous carbon film was stamped on the gallium droplet so as to transform

the film on the gallium surface, as shown in Fig. 2(c). It should be noted that the amorphous carbon film remained intact even after annealing it at 1000 °C for 30 min. as shown in Fig. 2(d). The vapor pressure of gallium was relatively low being about 1×10^{-4} Torr at 1000 °C, thus the reduction of the gallium during reaction was small enough to keep contact on the catalyzing interface.

The high resolution transmission electron microscope (HRTEM) image of the graphitized film is shown in Fig. 3. The film was separated from liquid gallium by soaking it in hydrochloric acid, thus the film breaks into small fragments in liquid, but they tended to float and segregated on the water surface. Thus these fragments scooped in a Cu-mesh tended to crumple and contain many wrinkles and foldings. Thus the graphene stacking in a TEM image can be observed at the folding edge of the crumpled surface. Fig. 3(b) shows the typical TEM image of graphene stacking which is consisted of 4 layers of graphene, and the spacing was 0.34 nm.

Although the original amorphous carbon film had a thickness of approximately 15~20 nm, many of the folded parts that formed on one side of the amorphous carbon film comprised approximately 3 to 5 graphene sheets having a thickness of approximately 1~2 nm, and the other side of the amorphous carbon remained intact. Therefore, the graphene stacking positioned outside of the folding contributed the thicker interference of the incident TEM electron beam,

and the thick interference length can be projected as clear image as shown in Fig. 4 (a), where the left side of the space of vacuum generated a monotonic contrast of the image. In contrast, the graphene stacking unfolding inside, small bending radius of curvature of graphene produced weak contrast in the TEM image, as shown in (b). This implied that although liquid gallium covers a large area, the catalytic reaction was limited to the narrow interfacial region just above the liquid surface. We believe optimizing the reaction

condition can produce a large and true single graphene monolayer sheet.

Typical electron energy-loss spectroscopy (EELS) spectra of the graphitized film was shown in Figure 5(a). The π^* peak that originated in sp^2 bond and σ^* peak that comes from sp^3 bond were the characteristic feature of conventional graphite as shown in (b), but the disordering of carbon atom in amorphous and/or diamond like carbon (d) causes the broadening as well as chemical shift of the σ^* peak. From this view point, the π^* peak and the sharp rising edge at the lower energy side of the σ^* peak are characteristic feature for the graphitized film of this work. If we take the certain amount of remained amorphous carbon layer that still adhered backside of the graphene stack into account the peak broadening and tailing of σ^* like that of amorphous carbon(d), the EELS spectrum of this work can be basically understood to be the same of typical graphite.

This surface graphitized film can be easily transformed from the gallium surface to another substrate such as poly-dimethyl-siloxane (PDMS). Adhesion between graphene and PDMS is remarkably nice, thus a soft contact of PDMS with the floated film easily transfers the film onto the PDMS as shown in Fig. 6. While the liquid gallium still adhered the film after transferred onto the PDMS, soaking in diluted hydrochloric acid removed the gallium, keeping the original shape of the amorphous carbon film. These graphene film can transferred again onto conventional Si substrate. Typical Raman spectrum of the film is characterized by a strong D peak as well as clear G and 2D peaks, as shown in Fig. 7. However, we think the large intensity of the D peak comes from the amorphous carbon layer that still embedded beneath the graphene stacking, and the large 2D peak having almost the comparable intensity of the G peak supports the quality of the graphene sheets.

Based on these experimental results of the catalytic effect of liquid gallium, even though the macro solubility would be absent, however, liquid gallium exactly induced the surface graphitization of amorphous carbon film. The catalyzing mechanism between

gallium and carbon is still not clear though, experimental results suggested that the reaction occurred at the very narrow interfacial region, where a singular point of internal energy might allow non-equilibrium solubility of carbon and/or an intermediate product such as hydro-carbon may play an important role in this graphitization mechanism from the view point of the poor solubility of carbon. This liquid nature of gallium at the reaction temperature would be a great benefit that enables the surface graphitization even if the target material forms three dimensional shape, in addition this liquid manner can cover uniformly a large area of amorphous carbon film. We think this liquid gallium catalyst will be greatly useful for the future application for the CNT cables and the basis of graphene electronics.

Summary

We found that liquid gallium has a strong catalytic ability of graphitization, where not only amorphous carbon but CNT as well melted and were catalyzed with the liquid gallium at 700 °C. The graphitized layer was very thin, composed of about 4 to 10 graphene sheets, but the surrounding layer contains many defects and folding. Catalytic mechanism of gallium on amorphous carbon is still not clarified, but the liquid nature to be able to cover entirely the specimen surface, even though it may have a 3D structure, could be a large benefit to transform the surface into graphitic layer. This technique of liquid gallium catalyst for the surface graphitization will open a new approach to produce a large area graphene sheet for future graphene based electronic devices.

This work was supported by the PREST-JST, and the venture business laboratory funds from the University of Tsukuba.

References

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science*, 306(2004)666-669.
- [2] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth and S. Roth, *Nature* 446(2007)60-63.
- [3] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, *PANS* 102(2005)10451-10453.
- [4] K. S. Novoselov,¹ Z. Jiang,^{2,3} Y. Zhang,² S. V. Morozov,¹ H. L. Stormer,² U. Zeitler,⁴ J. C. Maan,⁴ G. S. Boebinger,³ P. Kim, A. K. Geim, *Science*, 315(2007)1379.
- [5] M. Y. Han, B. Ozyilmaz, Y. Zhang, P. Kim
Phys. Rev. Lett. 98 (2007) 206805.
- [6] S. D. Dalosto, and Z. H. Levine, *J. Phys. Chem. C*, 112 (2008)8196–8199.
- [7] M. Fujita, K. Wakabayashi, K. Nakada and K. Kusakabe,
J. Phys. Soc. Jpn. 65 (1996)1920-1923.
- [8] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus,
Phys. Rev. B 54 (1996) 17954.
- [9] E. W. Hill, A. K. Geim, K. Novoselov, F. Schedin and P. Blake
IEEE Trans. Magn. 42 (2006) 2694-2696
- [10] C. Virojanadara, M. Syväjarvi, R. Yakimova, L. I. Johansson, A. A. Zakharov, T. Balasubramanian, *Phys. Rev. B*, 78(2008)245403.
- [11] T. Seyller, K.V. Emtsev, K.-Y. Gao, F. Speck, L. Ley, A. Tadich, L. Broekman, J.D. Riley, R.C.G. Leckey, O. Rader, A. Varykhalov, A.M. Shikin
Surf. Sci. 600 (2006) 3906-3911.
- [12] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov,

- E. H. Conrad, P. N. First, and W. A. de Heer,
J. Phys. Chem. B 108(2004) 19912-19916.
- [13] J. Coraux, A. T N'Diaye, M. Engler, C. Busse, D. Wall, N. Buckanie,
F-J M. heringdorf, R.van Gastel, B. Poelsema, and T.Michely.
New J. Phys. 11 (2009) 023006.
- [14] Li X, Cai W, An J, Kim S, Nah J, Yang D, Piner R, Velamakanni A, Jung I, Tutuc E,
Banerjee SK, Colombo L, and Ruoff RS, Science, 324(2009)1312-1314.
- [15] T. de los Arcos, M. G. Garnier, J. W. Seo, P. Oelhafen, V. Thommen, and D. Mathys,
J. Phys. Chem. B 108 (2004) 7728-7734.
- [16] T. Ichihashi, J. Fujita, M. Masahiko, Y. Ochiai, Phys. Rev. Lett., 92, 215702(2004).
- [17] S. Matsui, T. Kaito, J. Fujita, M. Komuro, K. Kanda, and Y. Haruyama,
J.Vac. Sci. Technol. B 18(2000) 3181-3184.
- [18] J. Fujita, M. Ishida, T. Sakamoto, Y. Ochiai, T. Kaito, and S. Matsui,
J.Vac. Sci. Technol. B 19(2001)2834-2837.
- [19] J. Fujita, T. Ichihashi, S. Nakazawa, S. Okada, M. Ishida, Y. Ochiaic, T. Kaito,
and S. Matsui, Appl. Phys. Lett. 88 pp.093109-383111, (2006)
- [20] Y. Gao, Y. Bando, Nature 415(2002)599.
- [21] Z. W. Pan, S. Dai, and D. B. Beach, Apple. Phys. Lett. 82(2003)1947-1949.
- [22]A. Saikubo, K. Kanda, Y. Kato, J. Igaki, R. Kometani, and S. Matsui,
Jpn. J. Appl. Phys. 46 (2007) pp. 7512-7513.

Figure captions

Figure 1 Contact angle of gallium droplet strongly depended on the ambient temperature.

Figure 2 Photo image of (a) formvar film stretched on aluminum washer, (b) 15 nm thick of amorphous carbon film supported on aluminum washer is stable even after vacuum annealing at 700 °C, (c) amorphous carbon film stamped on liquid gallium surface, and (d) film still keeps the original shape even after annealing at 1000 °C on liquid gallium.

Figure 3 TEM image of (a) gallium treated amorphous film which was supported on copper mesh, (b)HR-TEM image of the graphene stack that observed at the film folding region.

Figure 4 Catalytic reaction induced at the gallium was strongly restricted at the interface region. Thus (a) the graphene stacking was positioned outer side of the folding can be seen clear contrast, in contrast, (b) graphene stacking that folded inner side tended to be projected as weak contrast.

Figure 5 shows the Typical EELS spectra of carbon based allotropes, (a) Ga induced graphene film, (b)graphite crystal, (c) C60, and (d) amorphous carbon film prepared by arc-discharge method.

Figure 6 (a) film is transferred on PDMS substrate adhered with liquid gallium, and (b) gallium can be removed by soaking in a diluted hydrochloric acid.

Figure 7 shows typical Raman spectrum of the film that transferred on a SiO₂ substrate.

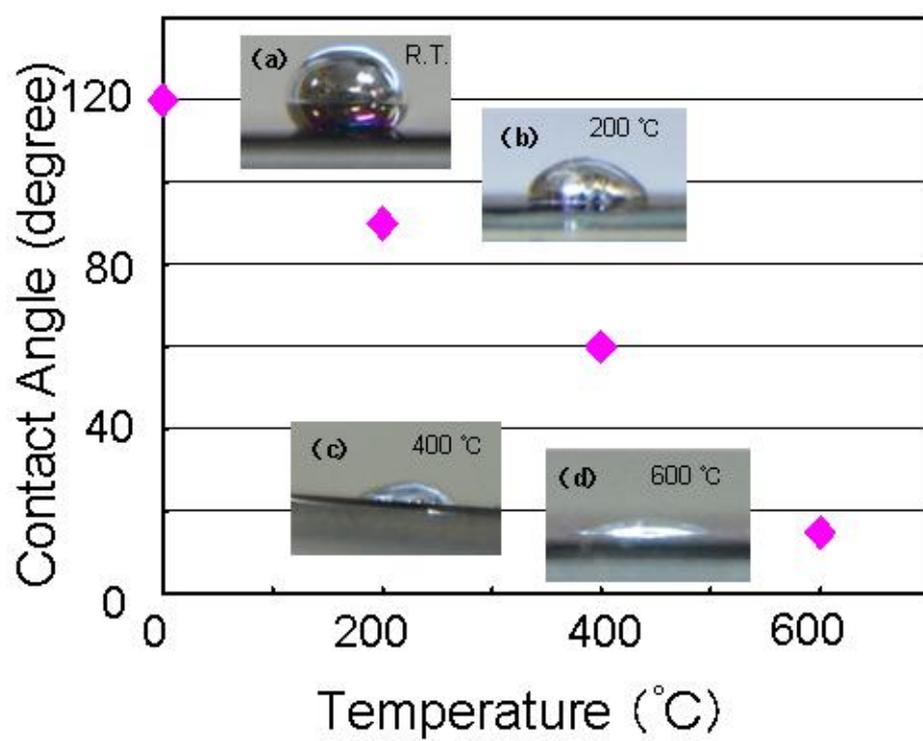


Figure 1

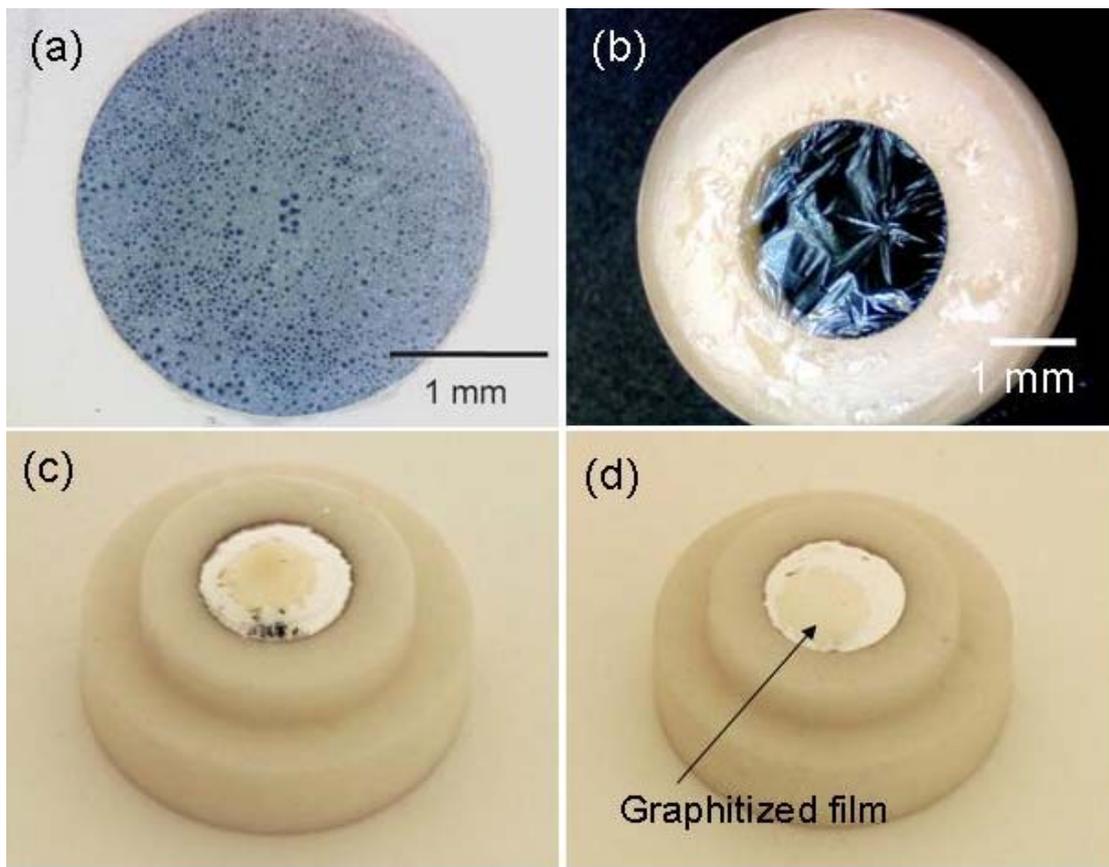


Figure 2

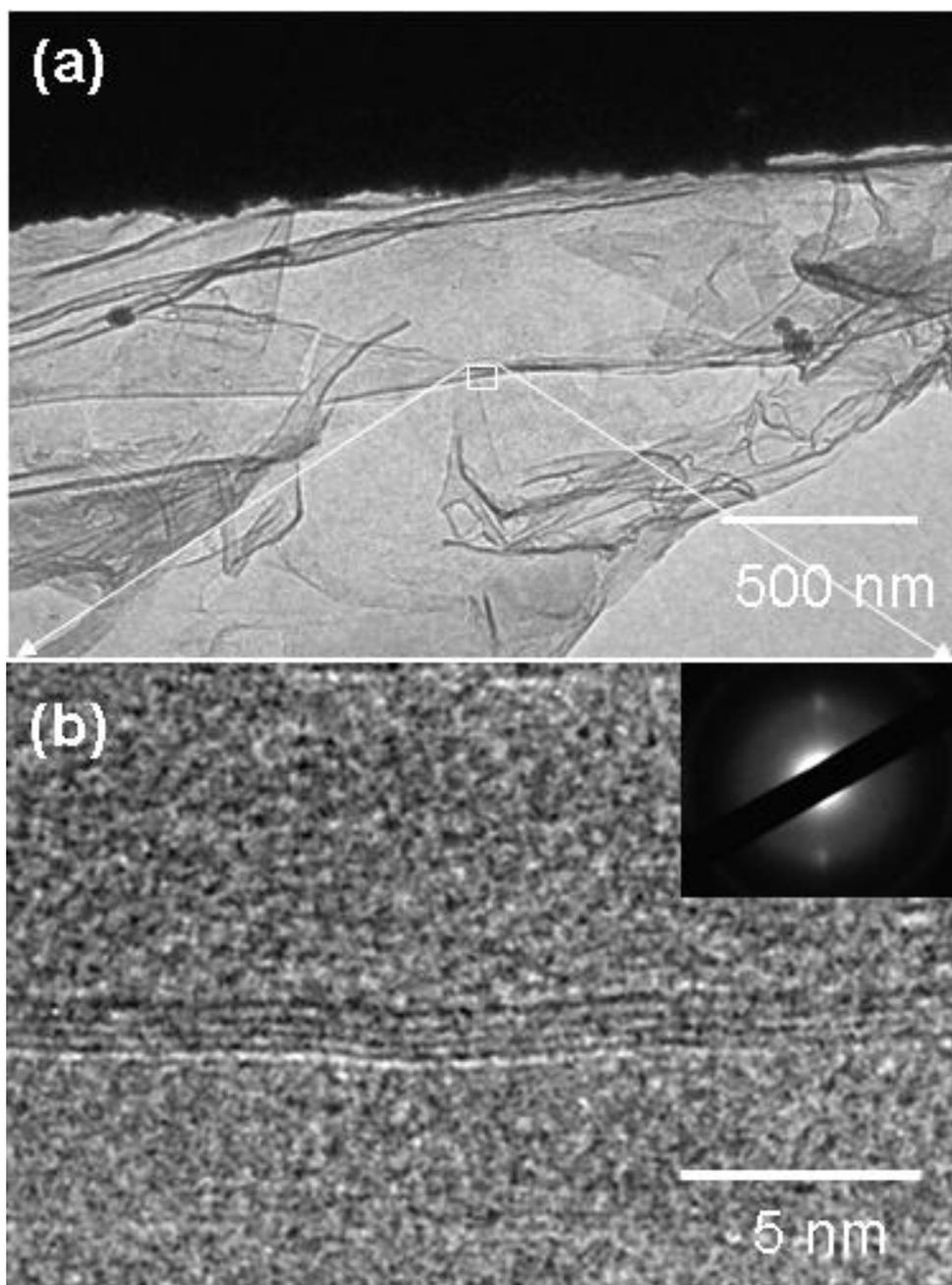


Figure 3

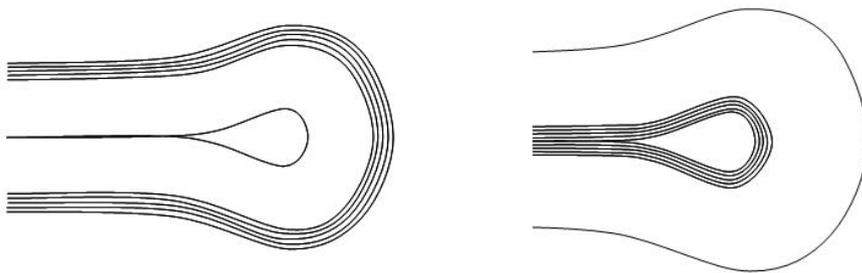
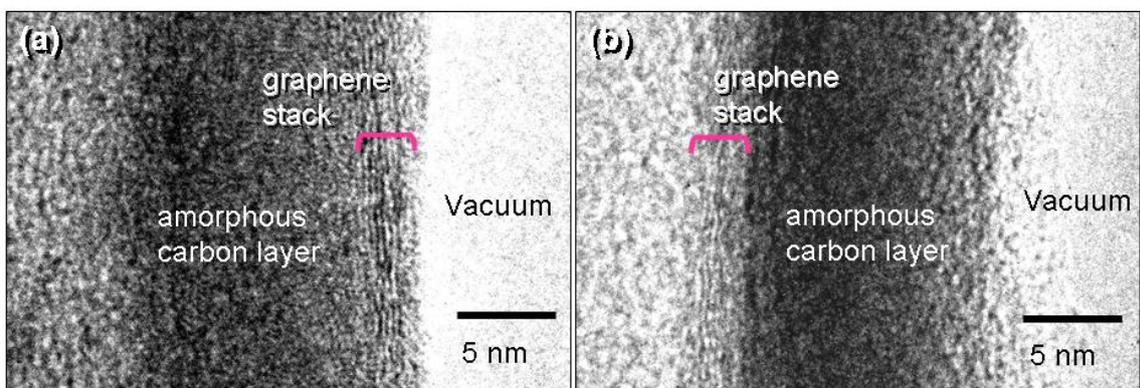


Figure 4

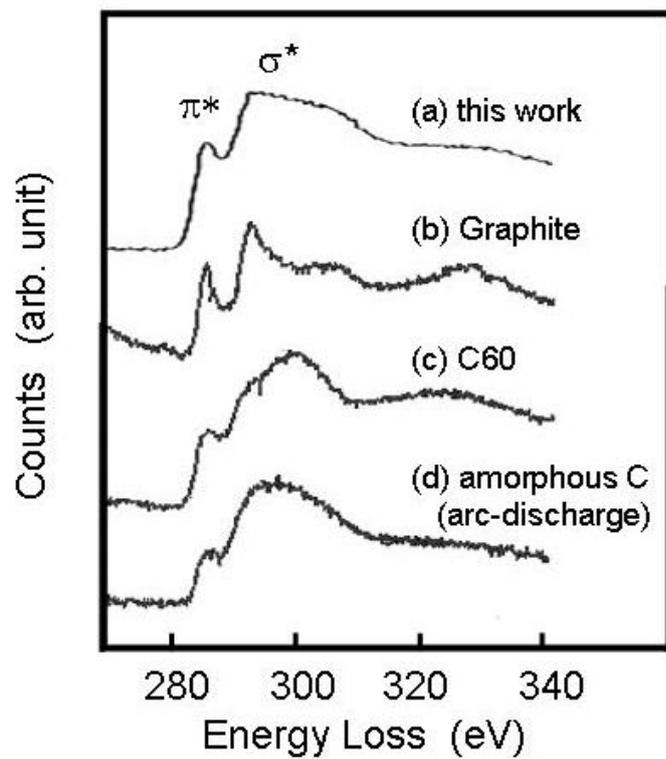


Figure 5

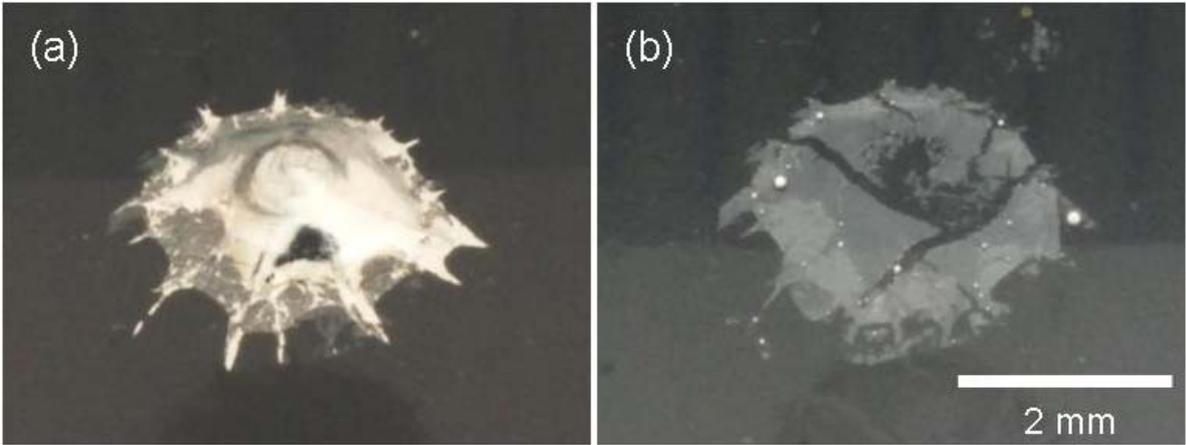


Figure 6

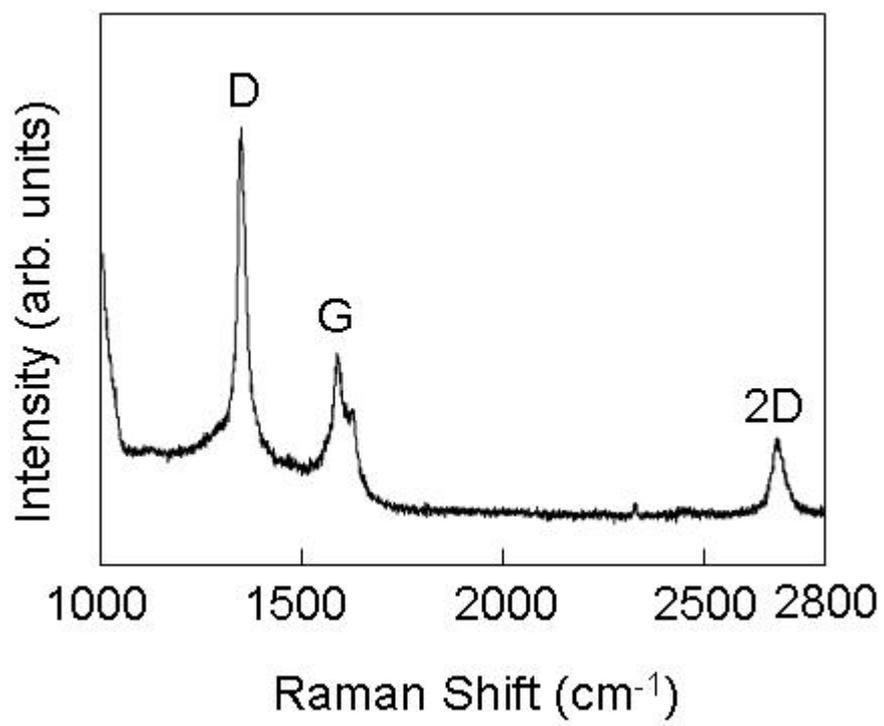


Figure 7