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Electrostatic deposition of graphene

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Abstract

Loose graphene sheets, one to a few atomic layers thick, are often observed on freshly cleaved HOPG surfaces. A straightforward technique using electrostatic attraction is demonstrated to transfer these graphene sheets to a selected substrate. Sheets from one to 22 layers thick have been transferred by this method. One sheet after initial deposition is measured by atomic force microscopy to be only an atomic layer thick (∼0.35 nm). A few weeks later, this height is seen to increase to ∼0.8 nm. Raman spectroscopy of a single layer sheet shows the emergence of an intense D band which dramatically decreases as the number of layers in the sheet increase. The intense D band in monolayer graphene is attributed to the graphene conforming to the roughness of the substrate. The disruption of the C–C bonds within the single graphene layer could also contribute to this intense D band as evidenced by the emergence of a new band at 1620 cm^{-1}.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, graphene (graphite sheets that are one-atom thick layers of sp^2 bonded carbon) has attracted a tremendous amount of attention [1]. The structure and the physical properties of graphene have been theoretically studied over several decades, as this 2D structure provided the building block for the formation of 3D graphite, 1D nanotubes, and 0D bucky balls [2]. Graphene is predicted to have remarkable properties such as large thermal conductivity comparable to the in-plane value of graphite, superior mechanical properties and excellent electronic transport properties [3]. The charge carriers in graphene are predicted to have zero effective mass and the transport properties are expected to be governed by the relativistic Dirac equation rather than the Schrödinger equation [4, 5]. Mechanical cleavage has been widely used to separate a few layers of graphene from highly oriented pyrolytic graphite (HOPG). Ribbons and terraces with step edges of graphene have been obtained by peeling off the surface layers of HOPG using scotch tape [6]. Alternative methods such as exfoliation [7] and epitaxial growth on single-crystal silicon carbide substrates [8] have produced multi-layer graphene sheets, but not single layer sheets. Recently, Stankovich *et al* developed a technique to make large amounts of single layer graphene sheets embedded in a polymer matrix [9]. All of these methods are tedious and labour-intensive. Furthermore, none of these methods address how to place the graphene sheets in a desired location, which is of great importance in constructing electrical experiments and assembling heterogeneous electronic systems. In this paper we discuss an electrostatic approach to deposit sheets of graphene on a given substrate.

2. Background

This deposition method was motivated by the observation with scanning tunnelling microscopy that there are numerous small sheets of graphene, of from one to several layers, on the surface of freshly cleaved HOPG. The sheets are loosely bound to the bulk graphite and can be removed from the surface rather easily by applying an electrostatic field (from an STM tip).

Graphene pieces on two different HOPG surfaces are shown in figure 1. The STM was operated in constant current mode and the bias voltage applied to the tip was 0.11 V. Shown in figure 1(a) are triangular graphene sheets, once and twice folded. The area of the STM picture is ∼200 nm × 200 nm. In figure 1(b) a graphene ribbon, ∼50 nm wide and more than

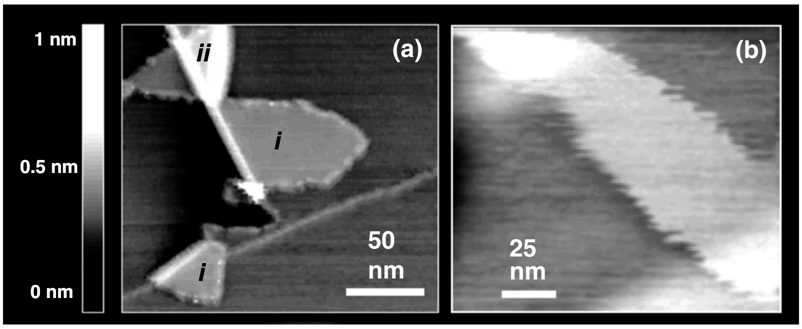

Figure 1. Scanning tunnelling microscope images of (a) single (i) and double (ii) folded graphene and (b) a graphene ribbon on the HOPG.

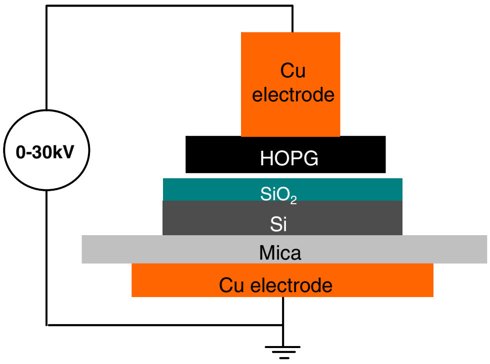

Figure 2. Schematic of the experimental set-up for electrostatic deposition of graphene sheets.

500 nm long, is seen on the HOPG surface. These sheets are found to be loosely bound to the bulk graphite and therefore can be easily removed by an electrostatic attractive force. Most notably, only the thinnest layers should be removed for the lowest voltages. For larger voltages, all layers up to a given thickness are removed. Therefore, a sheet of a desired thickness, say n layers thick, can be removed by first applying a voltage that only removes sheets with up to $n - 1$ layers on a dummy substrate, followed by the application of the appropriate voltage for n layers on the target substrate.

3. Experimental details

First one side of the HOPG sample was cleaved using the scotch tape technique to obtain a clean surface [6]. Then, the other side of the sample was glued to a copper electrode with silver epoxy. As shown in figure 2, this electrode was connected to the positive terminal of a high voltage source (0–30 kV and 0–10 mA, ER series, Glassman High Voltage, Inc.). The second electrode is a 3 mm thick copper plate connected to the ground terminal of the power supply. A 0.1 mm thick mica sheet was placed on top of the grounded copper plate. Note that the mica sheet blocks DC current for conducting substrates and also reduces the possibility of voltage breakdown. The substrate is then placed over the mica sheet as shown in figure 2. Substrates tested in our experiments are: (i) 300 nm thick SiO$_2$ layer on a silicon substrate (500 μm thick) and (ii) a 1 mm glass microscope slide.

Deposition was observed to occur for applied potentials between 1 and 13 kV. For the applied voltage V_{ap} in the range 3 kV $< V_{\mathrm{ap}} <$ 5 kV mostly single to three layer thick graphene sheets are deposited. For 5 kV $< V_{\mathrm{ap}} <$ 8 kV sheets from 3 to 7 layers are deposited. For $V_{\mathrm{ap}} >$ 10 kV sheets of 10 layers and greater are deposited. Also, the number of sheets is found to increase with the increasing applied voltage.

After cleaving, the HOPG surface exhibits a number of micron-sized graphene structures as seen in figure 1. An applied voltage causes the surfaces to become oppositely charged with the lightest and thinnest sheets of graphene being most easily attracted to the substrate. The HOPG sample attached to the copper electrode was brought into contact with the substrate for ~5 s, resulting in the transfer of graphene from the HOPG to the substrate. The graphene sheets were studied using optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and micro Raman spectroscopy.

4. Results

Figure 3 shows a few graphene sheets that were deposited on the Si/SiO$_2$ substrate using an applied voltage of 5 kV. The darker regions in the optical image in figure 3(a) correspond to graphene and the lightest regions correspond to the SiO$_2$ surface. Graphene sheets under 60 nm thickness have variable transmittance, with the single layer thick sheets being nearly transparent. Close-ups (the dashed square in figure 3(a)) taken with a Zeiss 35 VP Supra SEM reveal additional graphene sheets in figure 3(b). The contrast variations in the image are due to the conductivity differences between the higher conductivity graphene and the lower conductivity SiO$_2$. Graphene sheets can be seen to overlap each other. The image and height profile in figure 3(c) was taken with a CP Veeco AFM. The profile along the dotted line shows that the height of the sheet is only ~0.35 nm; that is, the thickness of a single graphene layer. The maximum height in the profile is ~0.8 nm which is due to the folding of this single layer into a double layer. It should be noted that the measured step height between the graphene and SiO$_2$ can differ from the actual step height due to differences in interaction of the AFM tip with the graphene and the SiO$_2$. This difference is negligible since the images were taken in contact mode. The step height of this monolayer on SiO$_2$ was observed to change over time, as is reported below.

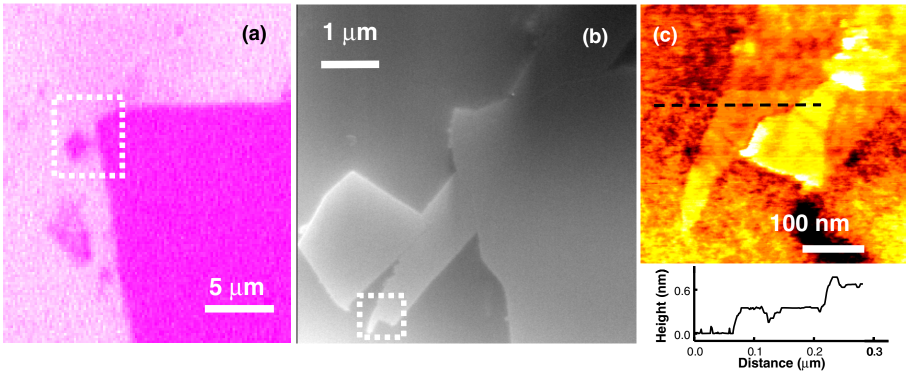

Figure 3. Optical (a), SEM (b) and AFM (c) images of a graphene sheet produced by electrostatic transfer. In the optical image the monolayer graphene sheet within the dashed box is nearly transparent. A SEM image of the region depicted by the dashed box in (a) is shown in (b). The dashed box in (b) corresponds to the AFM image and the line scan shown in (c). The height profile shows that this sheet is only one monolayer thick.

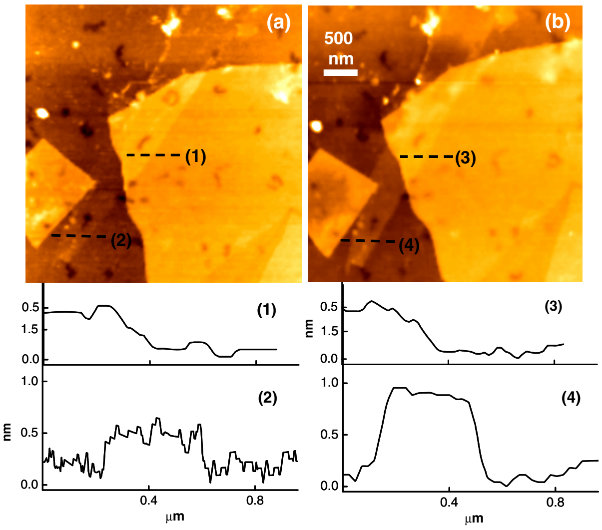

Figure 4. Height differences of the graphene (a) 1 day after deposition and (b) 45 days later after leaving it in a laboratory environment. The AFM height profiles (1)–(4) correspond to dashed lines (1)–(4), respectively, in (a) and (b). In either (a) or (b) the nearly square sheet on the left is 5 monolayers thick, while the large sheet on the right is 7 layers thick.

Figure 4 shows the same graphene sheet shortly after deposition and 45 days later after leaving it in a standard laboratory environment. Note that this sheet lies partly on the thicker graphene sheet and partly on the SiO_2 substrate. The dashed lines (1) and (2) again show that the freshly deposited monolayer in figure 4(a) is only ~0.35 nm thick. After a period of 45 days, the scan along dashed line (3) in figure 4(b) shows that the single graphene layer is still 0.35 nm thick relative to the thicker graphene sheet. However, the scan along dashed line (4) in figure 4(b) shows that the graphene height is now ~0.8 nm above the substrate surface. It is interesting to note that previous studies using the earlier deposition methods reported monolayer graphene heights of ~0.8 nm thickness. With our method, the step height appears to relax over time to ~0.8 nm from an initial thickness of ~0.35 nm. Perhaps, the strong electrostatic force pulling the graphene layer to the substrate accounts for the initial height. The increase of the height over time may be due to charge neutralization which enables the layer to return to an equilibrium height due to van der Waals forces alone. The moisture creeping into the space between the substrate and the graphene could also play a role in the increase in height. Interestingly, the height of the part of the sheet that is on top of the thick graphene sheets remains constant at ~0.35 nm even after 45 days. This implies that the interaction between the SiO_2 substrate and the graphene sheet is weaker than the interaction between the HOPG piece and the graphene sheet.

The ability to obtain graphene sheets of various thicknesses provides a unique way to pattern graphene for physical studies. As an example of one study enabled by this fabrication method, we have observed changes in the Raman spectra due to the proximity of the sheets to the SiO_2 substrate. Figure 5 shows the Raman spectra of graphene samples with varying numbers of layers on Si/SiO_2 substrate taken in the backscattered geometry from a Renishaw Micro Raman spectrometer under the excitation wavelength of 638 nm. Guided by the previously studied AFM images, the graphene sheets were located in the Raman micrograph for spectroscopic studies. The number of layers quoted for each sample corresponds to the step height measured in the AFM divided by the nominal thickness of 0.35 nm. Each spectrum shows clear signatures at ~1335 cm^{-1} (D band), ~1580 cm^{-1} (G band) and ~2660 cm^{-1} (G′ band) specific for sp^2 carbon structures with inherent disorders and defects. Interestingly, the single layer of graphene shows the most intense D band and a single G′ band. The intense D band can be explained as due to the disorder of the otherwise perfect graphene sheet attempting to conform to the roughness of the substrate. As the number of layers increase, (1) the intensity of the D band diminishes and the G′ band splits into two branches; (2) the intensity of the G band increases; and (3) the G band downshifts considerably (up to ~9 cm^{-1} for 22 layers). It should be emphasized that our monolayer graphene sheets have shown the largest ratio of D band to G band intensity reported to date. This stems from the fact that the use of high voltage causes higher conformity of the graphene layer with the roughness of the substrate, causing more disorder of the sp^2 structure. Another interesting feature in the Raman spectrum of the monolayer graphene

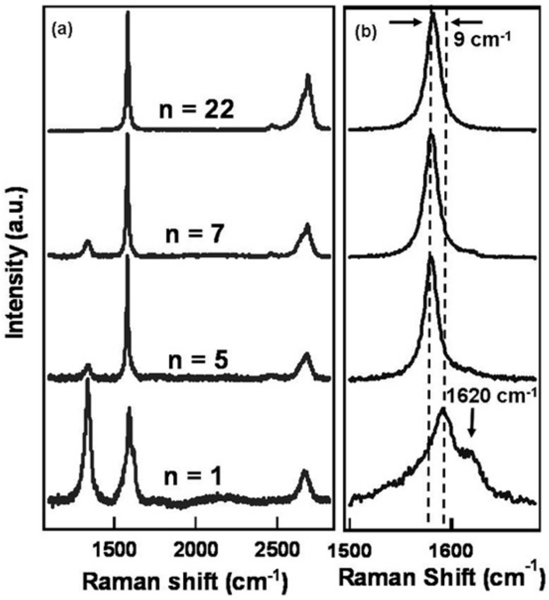

Figure 5. Raman spectra of graphene sheets with varying numbers of sheets (a). The details of the shifting of the G band (b).

sheet is the presence of a new peak at ∼1620 cm^{-1}. This band has been observed previously in vapour grown carbon fibres [10], and more recently in nitrogen-doped SWNTs [11]. This 1620 cm^{-1} feature has been identified with a maximum in the phonon density of states associated with midzone phonons. The presence of defects (like broken C–C bonds) within the single graphene layer could also contribute to the intense D band. As n increases, the number of defects due to missing C atoms or broken C–C bonds becomes a smaller fraction of the total number of carbon bonds present in the sample, which leads to an increasingly intense G band.

5. Conclusions

Since graphene shows unusual and interesting properties, the positioning of graphene on a suitable substrate at a selected location is important both for studying the fundamental properties of graphene and developing graphene-based devices. Electrostatic deposition of graphene provides a convenient alternative to the popular method of mechanical cleaving of HOPG, with the added benefit of selective deposition. This technique enables the number of layers deposited to be controlled. As demonstrated by the Raman experiments, the ability to place various numbers of layers on a surface, provides a useful tool for examining the physics of surfaces and interfaces. Varying the thickness of graphene from 22 to 1 layers upshifts the G band and increases the intensity of the D band. Also the G′ band can be seen to be split into two bands for graphene of multiple layers, while for monolayer graphene there is only a single G′ peak [12, 13].

Acknowledgments

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