

Effect of the Formation of Ambient Ice-like Water Ad-Layers at the Interface of Different Layer Graphene on SiO₂/Si and Si Substrates

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Abstract

Objectives: In this work, we probe the effect of ambient conditions on few layer and multi-layer graphene interfaces in Si and SiO₂/Si substrates. **Methods/Statistical Analysis:** Scanning probe microscopy techniques have been employed to study the topography of the few layer graphene and multi-layer graphene interfaces by Intermittent-Contact Atomic Force Microscopy (IC-AFM) and the changes in the surface gradient of electrical forces have been probed by electrical force microscopy. A study of different thickness of mechanically exfoliated graphene layers, with and without folds, deposited on SiO₂/Si and Si substrates is presented here. **Findings:** The number of ambient ice-like water ad-layers are determined by measurement of the heights of the graphene layers using IC-AFM, while as Electrical Force Microscopy (EFM) is used to determine the nature of the electrical interaction forces at the graphene interfaces on the different substrates. It is found that with increasing thickness of graphene on Si substrates, the electrostatic interaction increases on account of larger number of ambient ice-like water ad-layers formed. **Application/Improvements:** The electrical nature of Graphene interfaces on hydrophilic and hydrophobic substrates have an important role for the graphene-based devices operating under ambient.

Keywords: Ambient Ice-like Water ad-Layers (IWLs), Atomic Force Microscopy (AFM), Graphene, Interfaces

1. Introduction

Graphene, since the time of its first isolation¹, on account of diverse range of interesting electrical, thermal, optical and mechanical properties, has become one of the most important research materials to be considered for applications in a wide variety of fields. In this context, it is important to understand the behaviour of different layers of graphene on hydrophobic and hydrophilic substrates. There have been several techniques employed to visualize the

interfacial water ad-layers such as Atomic Force Microscopy (AFM)², Scanning Tunneling Microscopy (STM)³, and Raman spectroscopy⁴.

We have recently reported the interaction and dynamics of ambient water ad-layers on patterned Highly Oriented Pyrolytic Graphite (HOPG) surface using AFM voltage nanolithography, towards contributing to a slow etching reaction of the etch nanopatterns long after the lithography⁵. This has been attributed to the polarized ice-like water ad-layers having a stored electrostatic energy

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which gets dissipated slowly over time. We, further, made an analysis of the growth time and evolution of the ice-like water ad-layers on mechanically exfoliated Few Layer Graphene (FLG) and multi-layer graphene (MLG) transferred on hydrophobic Si and hydrophilic SiO₂/Si substrates⁶. In this work, we present the results of the effects of different layer graphene interfaces, without any folds and with folds, on the formation of Ice-like Water ad-Layers (IWLs).

2. Experimental

The Graphene flakes were obtained using the mechanical exfoliation technique using ZYB grade HOPG, with a mosaic spread of ~ 0.8 deg. The mechanically exfoliated graphene flakes were transferred to clean p-doped Si (100) and n-doped SiO₂/Si (100) substrates, as per the procedure reported in our earlier work⁶. FLG and MLG regions on Si and SiO₂/Si substrates were identified and analyzed with the help of an optical microscope (Olympus BX61, Japan) and a CP-II AFM (Veeco, USA). For the AFM voltage lithography process, contact mode AFM was used and a conducting tip (SCM-PIT with Pt/Ir coating, resonance frequency 60 kHz, and spring constant 1–5 N m⁻¹) was employed. An ambient humidity of 50% RH was maintained during the voltage lithography with the AFM kept in a controlled humidity chamber in a class 1000 clean room.

3. Results and Discussion

Figure 1 shows the intermittent-contact AFM (IC-AFM) topography image of mechanically exfoliated MLG on SiO₂ substrate. An average line profile (Figure 1) across a region depicted by the top rectangular box at point A, B and D, reveals the typical height of graphene layer with respect to SiO₂/Si substrate to be in the range of 3.58 – 9.92 nm. As MLG tends to be hydrophobic in nature² and SiO₂/Si is hydrophilic in nature, the ambient IWLs take much longer to form, typically in 21–45 hours, as reported in our earlier work⁶. Consequently, the EFM phase images of this surface, as shown in Figure 1 at +2V and -2V do not show opposite color contrast, pointing that the surface shows a capacitive-type interaction instead of coulombic-type interaction on account of the absence of formation of ambient IWLs. Accordingly, the EFM phase shift values, which represents a measure of electrostatic interaction for +2V and -2V are both positive in sign, as shown in Figure 1.

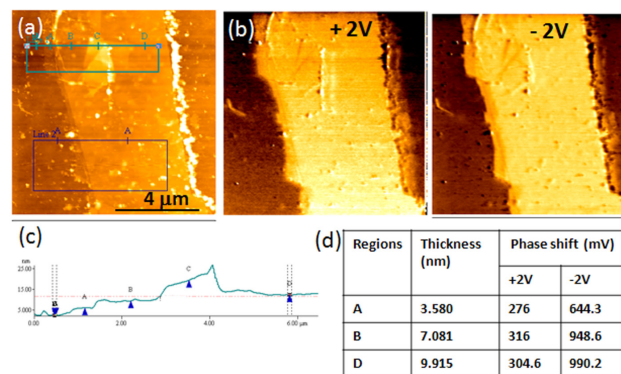


Figure 1. Multi-layer graphene on SiO₂ substrate: (a) IC-AFM topography image; (b) EFM images for +2V and -2V; (c) average line profile; and (d) table showing the thickness and phase shift values at A, B and D points marked in top rectangle marked in (a).

Ambient ice-like water ad-layers' formation was also analysed for mechanically exfoliated Few Layer Graphene (FLG) interfaces on hydrophobic Si substrates. Figure 2 shows the IC-AFM topography image of FLG of thickness 2.074 nm and 2.479 nm, at the points A and B marked across the average profile line (Figure 2) corresponding to 5 and 6 layer graphene, respectively, with one ice-like water ad-layer of height ~ 0.4 nm formed at the interface of FLG, which tends to be hydrophilic nature. EFM phase images of the FLG on Si substrate, in Figure 2 show a dark contrast for +2V and bright contrast for -2V, due the attractive electrostatic interaction and repulsive electrostatic interaction, respectively, at the surface. Accordingly, the phase shift, which is a measure of the type of electrostatic interaction, is negative for +2V and positive for -2V with the magnitude being higher for larger number of graphene layers, as shown in table in Figure 2.

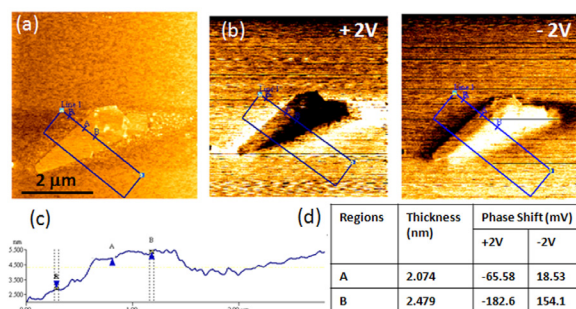


Figure 2. Few layer graphene on Si substrate: (a) IC-AFM topography image; (b) EFM images for +2V and -2V; (c) average line profile; and (d) table showing the thickness and phase shift values at A and B points marked in rectangle marked in (a).

Figure 3 shows the another FLG graphene flake on Si substrate of thickness 2.519 nm and 1.55 nm at points A and B across the average line profile, shown in Figure 3. The measurements at points A and B across the average line profile on the FLG flake, point to the formation of 3 IWLs to 2 IWLs at the interface of graphene and Si substrate. Accordingly, the EFM phase images of this FLG flake, as in Figure 3 shows a bright contrast for +2V and a dark contrast for -2V, pointing to repulsive interaction for positive bias and attractive interaction for negative bias, as against the FLG flake in Figure 2. This reversal in the electrostatic interaction is on account of the presence of larger number of polarized IWLs viz. 3 IWLs to 2 IWLs, at the interface of this FLG at the silicon substrate. The table in Figure 3 shows higher positive phase shift values of 254.9 mV and 273.7 mV for + 2V bias polarity, at points A and B, respectively, across the FLG flake due to larger number of IWLs at the interface. Upon bias reversal to -2V during EFM phase imaging, the corresponding negative phase shift values are also higher in magnitude for the same reason. This clearly brings out the significant contribution of the formed polarized ice-like water ad-layers on the electrical nature at the interface of graphene and the substrate.

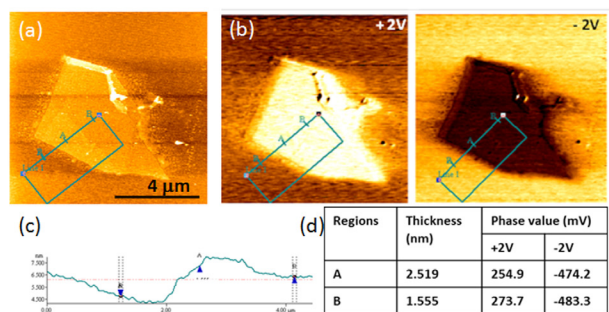


Figure 3. Few layer graphene on Si substrate: (a) IC-AFM topography image; (b) EFM images for +2V and -2V; (c) average line profile; and (d) table showing the thickness and phase shift values at A and B points marked in rectangle marked in (a).

We also studied the formation of ice-like water ad-layers in the different regions of isolated patterned FLG on Si, with a fold and without a fold at the graphene

surface on Si substrate as a function of time, as shown in Figure 4. Topography and EFM phase images were taken simultaneously and monitored with time for patterned FLG on Si substrate to investigate the effect of polarized ice-like water ad-layer. Graphene surface is charged as it shows coulombic behavior with the reversal of bias polarity.

For the region of patterned FLG without any folds (Figure 4), a monolayer of ice-like water ad-layer does not form immediately between the graphene and Si substrate but takes about ~4.9 hours to form, as the water affinity for hydrophilic FLG and hydrophobic Si substrate are dissimilar, as reported in our earlier work⁶. The presence of lithography defects created by the patterning of FLG using AFM induces quick formation of the IWLs at the interface. With time, initially there is an increase in the number of IWLs formed up to about 30 hours (Figure 4), however the number of IWL with time, get altered due to their meta-stable nature. The normalized changes in EFM phase shift viz. $\Delta\phi/\phi_0$, which are obtained from the EFM phase imaging of the region, do not show a clear trend up to ~ 30 hours (Figure 4).

In contrast, there is a bi-layer IWLs formed between the graphene and fold interface (Figure 4) for the patterned FLG on Si between 5- 23 hours, as seen in Figure 4, which remains stable over a longer period of time of ~ 80 hours. Accordingly, the normalized changes in EFM phase shift ($\Delta\phi/\phi_0$) up to ~ 24 hours show a reduction due to charge dissipation of water ad-layers with time and there after shows minimal fluctuation.

For both graphene interfaces with and without folds, upon nitrogen flushing, shows a removal of a bi-layer of IWLs.

4. Conclusions

This scanning probe microscopy study brings out the various effects of the formation of ambient ice-like water ad-layers in the interface region of different thickness of mechanically exfoliated few layer and multilayer graphene deposited Si and SiO₂/Si substrates. It is observed that with increasing thickness of graphene on Si substrates, the electrostatic interaction increases on account of the formation more number of ambient ice-like water ad-layers formed,

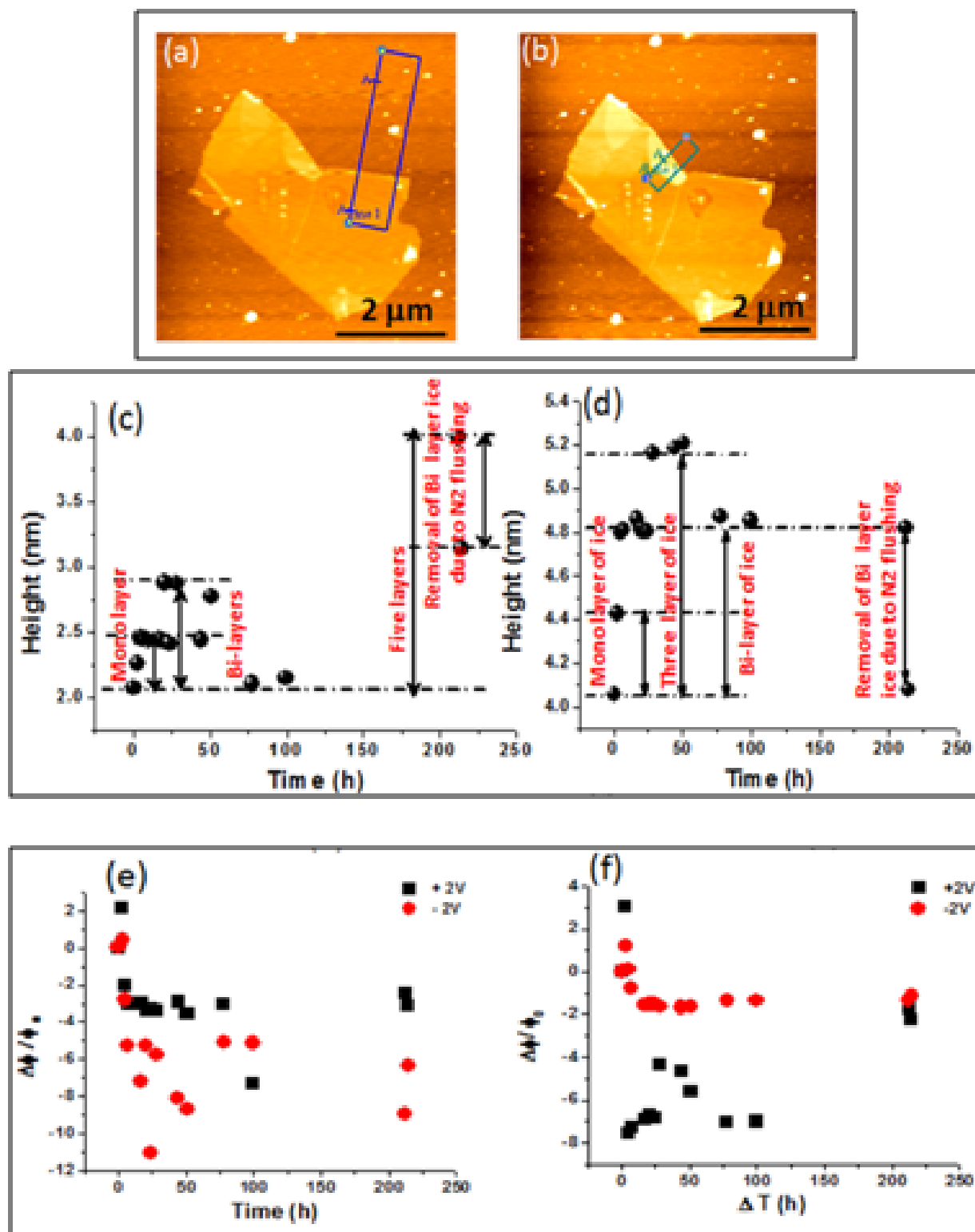


Figure 4. IC-AFM topography images: (a), (b) with rectangles marked in different regions on Few layer graphene on Si substrate; (c), (d) Plots of heights at different time intervals, (e) and (f) Plots of normalized changes in the EFM phase shift ($\Delta\phi/\phi_0 \times 100$), with time, measured for points marked in rectangles marked in (a) and (b).

as shown by the increase in the magnitude of the EFM phase shift values. This points to important consideration for the working of graphene based devices under ambient conditions.

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6. References

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