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Full Length Article

# Estimation of intrinsic work function of multilayer graphene by probing with electrostatic force microscopy

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ABSTRACT

In present study, electrostatic force microscopy (EFM) is used to estimate the intrinsic work function of few layer graphene (FLG) transferred on $SiO_2$ (300 nm)/Si (500 μm) substrate. This FLG has been prepared by using the mechanical exfoliation technique. In exfoliated FLG, adhesive residues are always left from scotch tape on its surface. These residues as well as $SiO_2$ substrate could modify the work function due to the formation of dipoles on the surface. Taking the effect of adhesive into account, FLG is pre-charged and then scanned with a tip biased with dc voltage. Intrinsic work function of FLG is determined and found to be $4.52 \pm 0.1$ eV.

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## 1. Introduction

Recently, graphene has attracted huge research interest due to its unique 2-dimensional structure exhibiting ballistic transport at submicron length scales [1] and extraordinary electronic [2], mechanical [3], optical [4], chemical [5] and thermal [6] properties. Since, graphene has all the atoms on its surface, interaction with environment plays a vital role [7] and can easily influence the intrinsic mobility as well as other electronic properties [8,9] such as surface potential, charge distribution and work function. Recently, by employing standard electrostatic force microscope (EFM) technique local electrostatic force on the graphene surface has been probed [8,10,11]. Work function of single layer graphene was reported to be $\sim 4.55 \pm 0.02$ eV [12] which is equivalent to that of graphite (~4.6 eV) [13] and found to be increasing as number of layers increase [14]. However, Panchal et al. reported that work function of bi-layer graphene ($\sim 4.44 \pm 0.02$ eV) is lower than that of single layer [12] which was grown through sublimation of Si-terminated face of an on-axis *4H*-SiC (0001) at 2000 °C. Graphene grown on SiC substrate was reported to possess different electronic properties compared to CVD-grown or mechanically exfoliated. Recently, the surface contact potential difference (CPD) between tip and FLG was also reported to increase as layer number increased [15] and found to be greatly influenced by the adsorbent on the surface of FLG [8] as well as FLG/substrate interface [16]. Therefore, it is necessary to measure the intrinsic surface potential of FLG accurately even if adhesive and adsorbent are present.

In present study, we aim to estimate the intrinsic CPD and work function of FLG prepared by scotch tape exfoliation method. In order to nullify the influence of residual adhesive, we have first pre-charged FLG surface and then scanned with biased tip. Variation in CPD of FLG, adhesive as well as $SiO_2$ substrate has been studied.We found that adopted methodology provides an excellent way to determine intrinsic work function of FLG and demonstrates that work function can be determined even if adsorbents are present on the surface of FLG.

## 2. Experimental details

FLGs were prepared by mechanical exfoliation method.Briefly, flakes of FLG were detached from HOPG (Highly oriented pyrolytic graphite) using adhesive tape (Scotch tape 3 M MAGIC TAPE 811 supplied by SPI). These flakes were cleaved repeatedly until thin layer of graphene was left on the tape and then transferred onto $SiO_2$ (300 nm)/Si (500 μm) substrate. Obtained FLGs were optically identified and probed with EFM. In order to carry out EFM measure-

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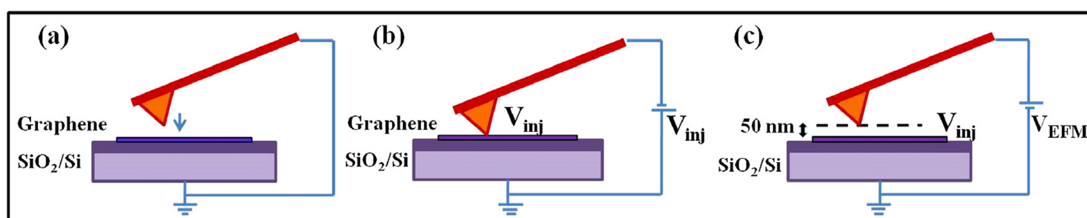


**Fig. 1.** (a–c) Schematic of the charge injection procedure and EFM measurement.

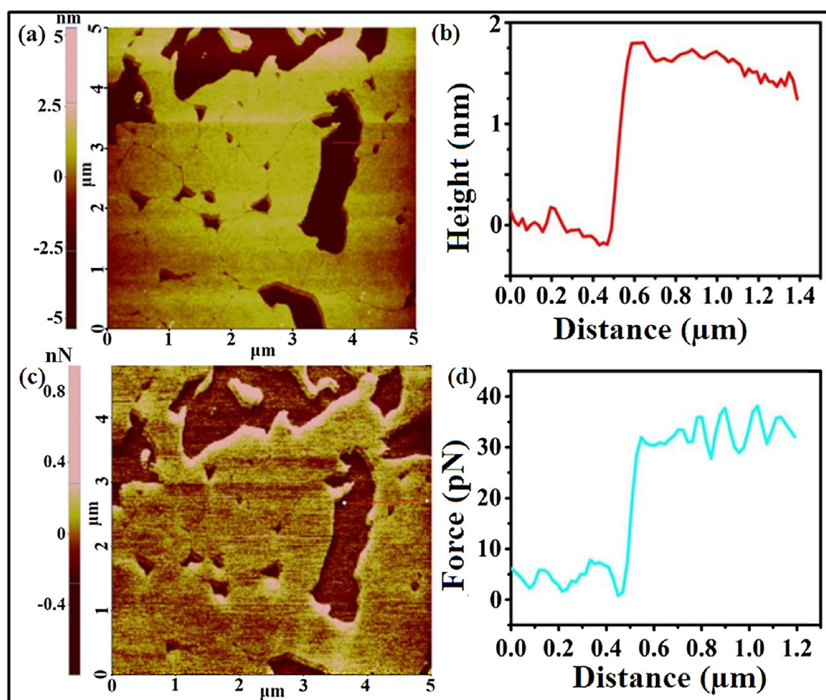


**Fig. 2.** (a) EFM topography image of FLG on $SiO_2$/Si substrate, (b) Height profile along line drawn on the topography image, (c) force image and (d) corresponding force profile.

ments, scanning probe microscope (Park, Model XE-100) with gold coated Si tip (NCSTAu) was used where resonance frequency and set point of the conductive tip were kept at 137 kHz and 21.04 nm, respectively. In order to pre-charge the FLG, charge injection was performed by following the procedure as reported earlier [9]. In the process, image of FLG was taken with the grounded tip in contact mode and then tip was brought into contact with FLG as shown in Fig. 1(b). Thereafter, a bias $V_{inj}$ (−1.5 V) was applied to the tip for 4 min followed by retraction of tip to 50 nm. FLG got charged in such a way that charge resides on its surface whereas in case of insulating $SiO_2$ or adhesive, charge resides in the interior. A dc bias was applied to the tip and then force, amplitude and phase images were recorded at different tip-bias-voltage ($V_{EFM}$) in range 3 V to −3 V as shown in Fig. 1(c). By controlling the tip bias, electrostatic force caused due to difference in the Fermi energy of tip and FLG, was nullified and local surface potential contact difference (LCPD) was mapped out. This procedure was applied to FLG, pristine as well as $SiO_2$/Si substrate affected by adhesive residues left from scotch tape.

## 3. Results and discussion

Typical EFM topography and force image of FLG transferred on $SiO_2$ (300 nm)/Si (500 μm) substrate are shown in Fig. 2(a) and (c), respectively. The line profile on topography image is drawn and plotted in Fig. 2b to estimate the thickness of graphene layer. The height difference between $SiO_2$ substrate and graphene layer represents the thickness of FLG and determined to be ∼1.75 nm. Since, during force imaging tip was lifted up to 50 nm, it is presumed that electrostatic force dominated while vander Waals force was minimized. The force imaging was performed keeping tip bias at −0.5 Vas show in Fig. 2(c). In the figure, equipotential areas can be distinguished as darker region corresponds to $SiO_2$/Si substrate and brighter one to FLG. At the edge, bright contrast reveals that the surface potential is low. This might have happened due to altered C=C bonds either by folded wrinkle or by the attachment of functional groups at this site [17]. It further reveals that at this site, work function was locally increased. An increase in electrostatic force as well as corresponding reduction in surface potential at the edges and corner sites might be due to defects, adsorbents or large amount of unsaturated bonds. It is well known fact that the local work function of graphene layers increases as concentration of unsaturated bonds or vacancy increases [18]. Furthermore, charge exchange at graphene/$SiO_2$ interface has been reported to influence the CPD resulting from the screening of interlayer coupling [17,19]. Previously, it was reported that Dirac point, where electron and hole conduction meet, significantly influenced with surface characteristic and dielectric constant of the substrate. It was reported that surface characteristic (untreated or functionalized) of $SiO_2$ lead to effective p-or n-type doping in graphene [20]. Since, in present case FLG was first pre-charged and then scanned with biased tip. Thin layered $SiO_2$ might increase the probability of leakage of the charge from graphene to $SiO_2$/Si substrates. As consequence, CPD as well as work function might vary. Therefore, work function of FLG

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