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NANOTRIBOLOGICAL PROPERTIES OF EPITAXIAL GRAPHENE GROWN ON C-TERMINATED FACE OF SILICON CARBIDE SEMICONDUCTOR

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ABSTRACT

The frictional properties of mono-layer and multilayer epitaxial graphene grown on the C terminated face of SiC has been investigated by using atomic force microscopy measurements. Epitaxially grown graphene samples were characterized by Raman spectroscopy measurements. Atomic force microscopy has been employed in ambient conditions for friction measurements using pre-calibrated cantilevers. Both Raman spectroscopy and atomic force microscopy analysis showed that the number of defects, which increases consistent with increasing number of graphene layers, plays an important role on the tribological properties of epitaxial graphene.

Keywords: Friction, Nanotribology, Graphene, SiC, Atomic force microscopy

1. INTRODUCTION

The frictional characteristics of materials play an important role in many industrial applications. The developing technology has brought down the size of the devices and as a consequence applying liquid lubrication to overcome wear effects became almost impossible in most of the micro and nano-scale tools [1]. People have used a variety of liquid lubricants since ancient times to reduce the friction, wear and adhesion. The known assumptions about friction were only valid for macro scale until tribology comes out. At the atomic scale, understanding single asperities and real contact area is crucial to reveal the frictional properties of surfaces [2, 3].

Tribology describes the issues of friction wear and lubricity at nano, micro and macro-scale and yet one of the most interesting topics in today's research. Materials that exhibit different frictional properties between two interacting surfaces are used in tribological studies. One of the most suitable material is graphene which is a two-dimensional and semi-metallic material with a single atom thickness. Up to now, several studies of the tribological characteristics of epitaxially grown graphene were carried out only on the Si-face of SiC semiconductor. Increased friction coefficient of bi-layered graphene grown on the Si-face of SiC compared to mono-layer graphene grown on the Si-face of SiC was explained by excitation of photons by the mechanical energy of sliding tip over the graphene surfaces [4]. On the other hand, the friction coefficient of the graphenized surface grown on silicon terminated face of SiC was found to be 5 times lower than bare SiC surface. This has been explained by the low friction of a covalently bound graphitic interface layer between graphene and SiC substrate [5]. Further studies in ambient conditions using pristine and disordered graphene yielded that the friction coefficient of pristine graphene is remarkably lower than that of disordered graphene [6]. Another frictional characterization work was done on other 2D materials such as atomically thin sheets of exfoliated graphene, molybdenum disulfide, niobium diselenide and hexagonal boron nitride in ambient conditions [7]. The findings revealed that friction between the single atomic sheets and the atomic force microscope (AFM) probe is monotonically increased as the number of layers decreased for all samples.

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The motivation of this study is to compare the friction of multilayer with single layer graphene grown on the C-face surface of SiC. Some difficulties in the synthesis of graphene grown on the C-face SiC did not allow any tribological work to be done on this area. At the beginning of these difficulties, it is not easy to control the number of graphene layers formed on the C-rich surface while compared with the Si-face. Since the synthesizing graphene on the C-face under ultra-high vacuum (UHV) conditions is a fact and theoretical studies are still wondered, it was aimed to observe the frictional properties of graphene layers grown on the C-face SiC.

Epitaxial growth of graphene on SiC semiconductor under UHV conditions have two terminated sides. Both sides are suitable for the graphene formation because of its resemblance to SiC's crystal structure. By taking advantage of different vaporization temperature of Si and C atoms, mono and multi-layer graphene can be produced on both Si-face and C-face of SiC. The number of graphene layers formed on the C-face is much higher with respect to Si-face. Due to the vaporization temperature differences on C-face and Si-face of SiC, the number of layers of graphene can be controlled with the help of a technique called *capping* method [8]. J. Hass et.al experimentally show that multilayer grown on the C-face of SiC surface contains rotational stacking faults related to the epitaxial conditions at the graphene-SiC interface. As a result the multi-layer graphene grown the C-face of SiC does not grow as a simple AB stacked graphite film [9]. Due to the discrepancy in electronic, structural and sliding properties of graphene grown on C-face and Si-face, different frictional characteristics are expected.

Reducing friction and showing unexpected properties arouse attention to the investigation of graphene's tribological behavior. Investigating mechanically exfoliated mono and multi-layer graphene substrates, the layer dependence of frictional behavior was observed by AFM measurements. Reduction of layers amounted to a reduction in friction [7]. On the contrary, bilayer epitaxial graphene grown on Si-face showed lower friction compared to mono and multi-layer graphene [4].

2. EXPERIMENT

Commercially available substrates cut from n-type 6H-SiC wafers (Cree Company, North Caroline, USA) were first cleaned chemically using acetone and alcohol for 15 minutes in ultrasonic cleaner to remove the organic contaminants. After solvent cleaning, the native oxide layer on the surface of substrates were etched for 10 min. in a 6% HF solution. Epitaxial graphene layers are grown on the C-terminated face of a (4mm × 10mm) 6H-SiC crystal annealed at 1500°C for 20 min. in a UHV chamber with a base pressure of about 2×10^{-8} mbar. Prior to the graphene growth, SiC substrate degassed at 600°C over night and then the temperature is raised to 1100°C for about 10min. to remove the native oxide layer. During the growth experiment, the temperature of the annealed sample was measured remotely by using an optical pyrometer with 1°C resolution.

Si atoms evaporate at around 1350°C (figure 1a) whereas the C atoms evaporate at around 3000°C. This different evaporation temperatures allows the Si atoms evaporate before C atoms. However, as the growth rate of graphene sheets are altering on C and Si face of SiC due to higher interface energy on C-face compering to Si-face [10], capping method [8] was applied to the C-face of the SiC sample to control the growth rate of the graphene layers as shown on figure 1b.

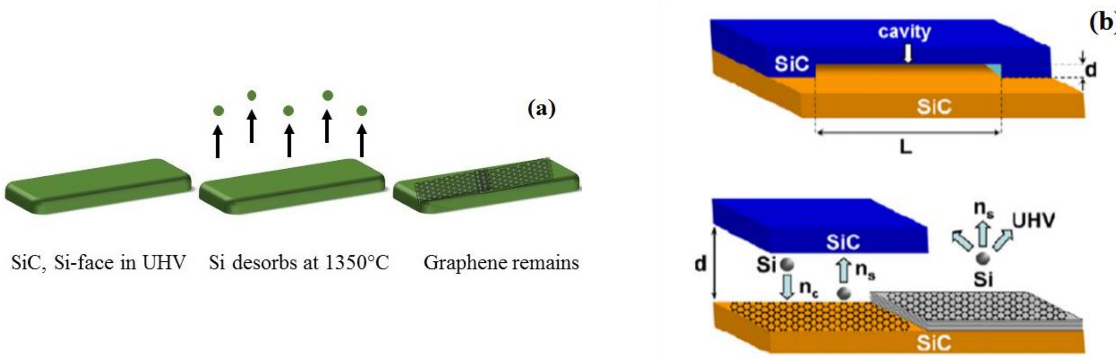

Figure1: **(a)** Evaporation of Si atoms on SiC surface, **(b)** Schematic view of capping method.

To apply the capping method another SiC substrate was placed on C face of SiC to create positive pressure on that face. The positive pressure slows down the evaporation of Si atom from the surface and thus the growth rate on both faces of the SiC can be controlled. Optimized parameters for growth of graphene layers on SiC surface are given on table 1.

Table 1: Optimum growth parameters for single and multilayer graphene on both faces of SiC

	Thermal Cleaning	Oxide Removal	Growth	Cooling down
Degree (°C)	600	1100	1500	600
Time (min)	Overnight	10	6	60

Princeton Instruments – Monovista Raman spectrometer was employed to ensure the mono and multi-layered graphene has been formed on the C-face of SiC sample. An Ar^+ ion laser with a 514 nm (2.41 eV) excitation source was used and all Raman signals were recorded in a spectral range between 1200 and 3000 cm^{-1} with a 600 groves/mm grating. The laser spot size is approximately 2 μm and laser was focused by x100 optical lenses. Each spectrum was analyzed using the TriVista software. Frictional properties of the grown graphene layers were measured using NanoMagnetics ambient AFM system operated in contact mode. The spring constant of the Nanosensors XY-PPPCONTR cantilever was obtained by engaging the AFM to dynamic mode and the spring constant of the cantilevers was determined as 0.1474 N/m.

3. RESULTS AND DISCUSSION

3.1. Raman Measurements

The existence of mono and multilayered graphene on the C-face of the SiC sample has been identified by Raman spectroscopy measurements. Raman Spectroscopy is a useful technique to obtain information about the vibrational phonon modes of molecules for identification and characterization. In addition, for layer characterization of graphene, Raman Spectroscopy measurements have crucial importance to identify the number and also the quality of graphene layers.

Basically graphene has three characteristic peaks for defining the structural properties of itself which are called D, G and 2D bands [10]. In the Raman spectrum shown in figures 2a and 2b graphene related 2D, G and D signals are well resolved together with SiC induced Raman signal. 2D, G and D bands corresponds to two-phonon, in-plane and defect induced vibrational modes of graphene, respectively. Relatively low 2D peak intensity shown in figure 2a indicates the mono-layer nature of graphene whereas high 2D peak intensity in figure 2b belongs to multi-layer epitaxial graphene. For mono-layer graphene the peak position of the 2D band was measured as 2687 cm^{-1} and for multi-layer graphene it was found to be 2692 cm^{-1}. The intensity of D band peak of multi-layer graphene has been determined to be greater than the one of mono-layer graphene. In order to quantitatively compare the amount of disorders in mono-layer with multi-layer graphene the corresponding I_D/I_G peak ratios were analyzed. The I_D/I_G for mono-layer graphene (0.2) was determent to be smaller than I_D/I_G ratio of multi-layer graphene (0.8). These obtained results manifest that multi-layer epitaxial graphene on the C-face surface of SiC contains larger amount of disorders compared to mono-layer graphene grown on the same surface of SiC [11, 12].

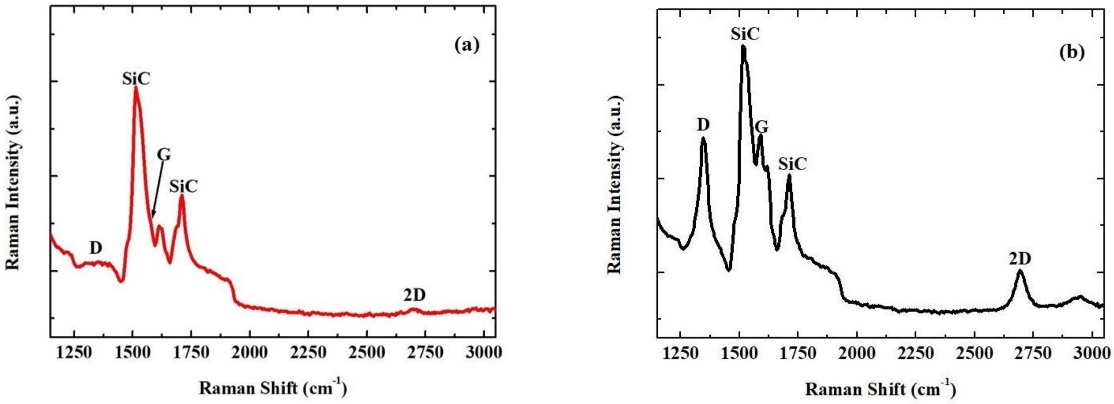

Figure 2: Raman spectra of **(a)** single and **(b)** multi-layer graphene

3.2. AFM Measurements

AFM is the most commonly used instrument in all scanning probe microscopes. After the invention of AFM, it is also extensively used by researchers to determine properties of materials such as surface topography, adhesion, friction, wear, lubricity of films and mechanical measurement [13, 14, 15], ranging from one micrometer to nanometer scale lubricant molecules or other semiconducting materials.

Friction measurements of mono and multi-layer graphene on C-face of SiC has been carried out by using ambient AFM. Initially, AFM cantilevers were calibrated by scanning the trapezoidal shaped test grating sample (figure 3a) which was mentioned in a great detail in the literature [16, 17]. In these studies it was shown that the dimensions of the cantilever is of crucial importance for the calibration of conventional AFM cantilevers. While the back and forth scanning (figure 3b) signals gave us the information about the lateral force measurements of the surface, the calibration constant of cantilever was used to convert these signals to nano Newton unit which describes the friction force on the surface. By means of AFM measurements we compared the surface friction properties of mono and multi-layer graphene grown on the C-face of SiC substrate.

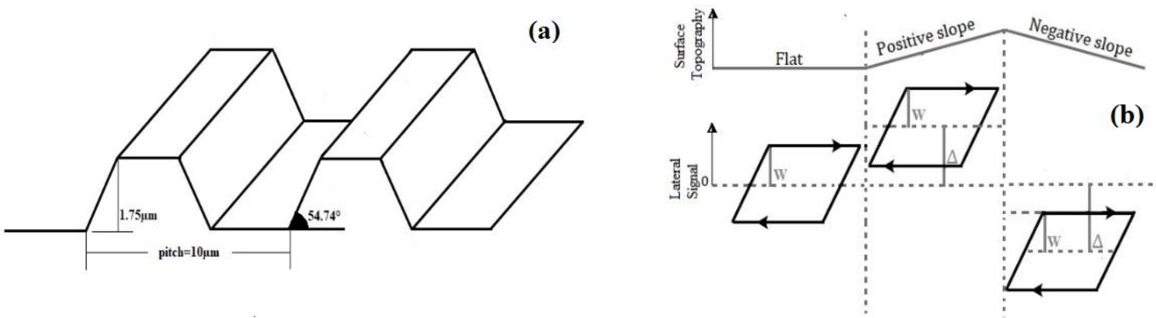

Figure 3. **(a)** Schematic friction loops (lateral signals for back and forth scans) for flat, positively sloped and negatively sloped surfaces at the same applied load. **(b)** Test grating sample for calibration of AFM cantilever (TGF11-MicroMasch [18].)

Frictional properties of mono and multi-layer graphene grown on C-face of SiC were measured by using NanoMagnetics ambient AFM system with contact mode. The spring constant of the Nanosensors XY-PPPCONTR cantilever that was used in our investigations has been obtained by employing dynamic mode of AFM and was found to be 0.1474 N/m. To find out the calibration factor and spring constant, the Sader method [17] has been applied. The lateral force calibration factor can be obtained from the voltage output of AFM that is in proportion to change in the horizontal position of the laser spot on the four-quadrant photodiode which is caused by the torsional twisting of cantilevers with an applied force on inclined surface of Si based test grating sample [16, 17, 19].

Friction force measurements were taken in two steps. As for the first step the calibration of cantilever was done for sensing the sample surface. In order to find the applied loads acting on the surface, certain set voltage values were determined and the obtained values has been used as the input for the AFM software. In the second step these voltages was used for characterizing mono and multilayer graphene on C-face of SiC surfaces to observe the applied load which varies from 10.0 nN to 25.0 nN with an increment of 5.0 nN (Figure 4). After these two steps, the lateral force signals were recorded while scanning the sample surface with respect to applied loads.

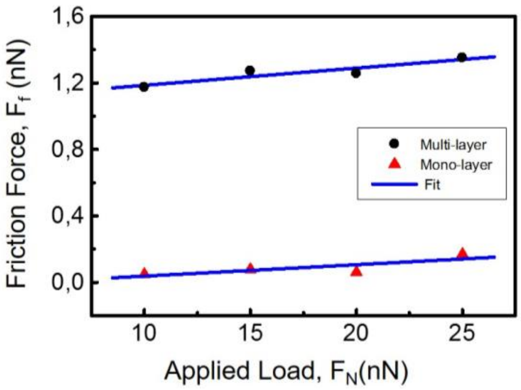

Figure 4. Friction force measurements of mono-layer (red triangles) and multi-layer (black dots) graphene grown on the C-face of SiC. The fitting equations for mono and multi-layered graphene are $F_f = -3 \times 10^{-2} + 7 \times 10^{-3} F_N$ and $F_f = 1.1 + 1 \times 10^{-2} F_N$, respectively.

As can be clearly seen in Figure 4, the friction forces are about in the range of 0.1-0.2 nN and 1.2-1.4 nN for mono-layer and multi-layer graphene samples, respectively. In other words, the friction force corresponding to multi-layered sample bigger than that of mono-layered one, this means that the multi-layer graphene displays more friction than mono-layer graphene. The coefficient of kinetic friction for mono-layer and multi-layer graphene was obtained as 7×10^{-3} and 1×10^{-2}, respectively. The observed difference in the coefficient of kinetic frictions between these two samples can be correlated with the amount of defects that were previously characterized by Raman spectroscopy measurements. We have already showed by Raman analyses that the defect concentration in multi-layer graphene is much higher than the one in mono-layer graphene. Our measurement clearly show that as the amount of defects increases in graphene the friction force also increases accordingly. Defect related increment of friction force in graphene is consistent with the studies carried out on different materials such as ZnO thin-films reported in literature [20, 21].

4. CONCLUSION

In summary, mono-layer and multi-layer graphene samples were grown on the C terminated face of SiC substrate by using high temperature UHV annealing process. Raman spectroscopy were conducted to determine the number of graphene layers and the amount of defects associated with these grown layers. Raman spectroscopy measurement show that the amount of defects in multi-layer graphene is greater than that of mono-layer graphene. Following Raman measurements the graphene layers were characterized by AFM in order to reveal their surface friction properties. The results of AFM measurements showed that the coefficient of friction for multilayer graphene is about two time greater than the one measured for mono-layer epitaxial graphene. The difference in friction coefficients were attributed to the amount of defects identified for both samples.

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