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AFM characterization of Multilayered Graphene film used as Hydrogen Sensor

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***Abstract*—**Graphene, the crystalline allotrope of Carbon has phenomenal electrical properties and hence a number of application prospects. Multi-Layered Graphene (MLG) has tremendous application prospects as gas sensors. Thermal CVD performed at atmospheric pressure is a very simple and affordable synthesis technique for growing MLG. In this project we characterized Thermal-CVD grown MLG films with the Atomic Force Microscope (AFM) to determine the optimal growth condition by measuring surface roughness and thickness. The results were verified by both contact and close-contact mode of imaging. It was also determined that increased surface roughness creates additional sites for Hydrogen adsorption. The results agree with other Hydrogen sensor data.

Keywords—AFM, CVD, Graphene, SiO_2

I. INTRODUCTION

Graphene is a crystalline allotrope of carbon and described as a one-atom thick layer of graphite. It is the thinnest and strongest known material in the universe.[1] Graphene can sustain current densities six orders of magnitude higher than that of copper, shows record thermal conductivity and stiffness, is impermeable to gases, and reconciles such conflicting qualities as brittleness and ductility. [1] Kosuke Nagashio, et al found that carrier mobility in the monolayer was significantly larger than in the multilayer and the carrier transport in the monolayer was also extremely sensitive to charged impurity density. [2] It has been demonstrated that planar substrates were the most suitable for the nucleation and the growth of multi-layer graphene. [3] Substantial amount of research have been performed on deposition of graphene on SiO_2/Si substrate, although the layer number dependence is still unclear. [4] Masa Ishigami, et al reported atomic structure nanoscale morphology of graphene on SiO_2 using the atomic resolution Scanning Tunneling Microscopy (STM) in 2007. [5] In another article on the STM characterization of grapheme deposited on SiO_2 film showed graphene to be slightly smoother than the supporting SiO_2 substrate. Other substrates including [6] Si3N4/Si substrate has also be used for growing graphene. The scanning electron microscopy (SEM) has been used to examine the microstructure and mechanical properties of the graphene on Si_3N_4 composites. [7] It is worth noting that the growth of graphene using Plasma Enhanced Chemical Vapor Deposition (PECVD), one of the popular methods for synthesizing single layered Graphene needs high temperature (950 ℃). [8] However, there are recent reports of growing multi layered Graphene (MLG) in atmospheric conditions using thermal Chemical Vapor Deposition (CVD).[9] This inexpensive and elegant method of synthesizing Graphene is a condition favorable for the application of Graphene as a device. Our current project is to characterize the MLG samples with regard to the growth parameters with the primary focus on its Hydrogen sensing ability..

II. EXPERIMENTAL

MLG was synthesized by performing CVD at atmospheric conditions. The precursor gases were Methane (CH_4) mixed with Hydrogen (H_2) with Copper (Cu) catalyst. Nitrogen was used as the carrier gas primarily to prevent oxidation of the MLG. After annealing a copper coated Si/SiO_2 wafer with a mixture of N_2 and H_2 the CH_4 was introduced. MLG is synthesized when 15 sccm of CH_4 reacts with 5 sccm of H_2 in presence of 300 sccm of N_2 at 1000℃

Four samples of graphene deposition were characterized with the AFM. SA1 is the SiO_2/Si substrate (present, i.e.; thermally grown SiO_2). SA2 is the sample of graphene thermal CVD grown on SiO_2/Si substrate for 8 minutes. SA3 is the sample of graphene on SiO_2/Si substrate using the method of thermal CVD for 15 minutes. SA4 is the sample of graphene on SiO_2/Si substrate (SA3) after being used for hydrogen sensing. The Hydrogen sensing data would be included in a separate article.

III. RESULTS AND DISCUSSIONS

The roughness and thickness measurements of the samples

As the table 1 below, all the samples are scanned five times in the close contact (tapping) mode using AFM. The Roughness and thickness of all samples are measured in the close contact at the size of 3μm×3μm. It shows that the SA3 has the both the maximum roughness and thickness among all the samples. While the SA4 sample shows a significant reduction to both the roughness and thickness data. All the roughness and thickness data were measured by doing an average measurement at 5 different dissimilar spots on the sample. All the thickness data were calculated with reference to the substrate SA1.

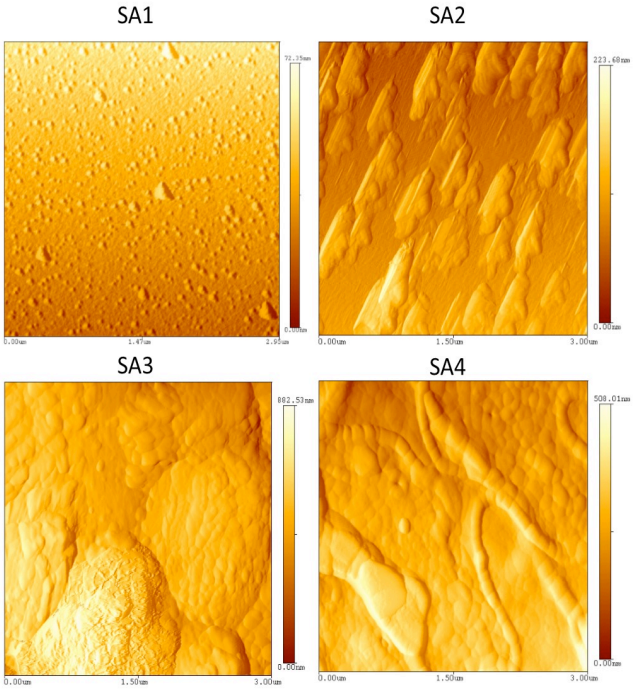
Table 1. The Roughness and thickness of each sample (n=5) are obtained in the closed contact mode. The roughness is measured in the size of 3μm×3μm, the thickness is measured in the size of 20μm×20μm.

Sample	SA1	SA2	SA3	SA4
Roughness (nm)	31.02±30.50	84.83±34.33	255.10±118.00	103.60±66.90
Thickness (nm)	137.34	467.32	3467.96	2111.96

The differences of micrographs of all graphene samples

All AFM images are captured in [(X:Y=3:3)μm] dimension with the scan rate of 0.5 Hz in the close contact mode. The sample SA1 has flat background with tiny mounts with the diameter of nearly 0.1 um. In SA2 and SA3 graphene was grown on the Si/SiO_2 substrates. However, higher growth of graphene was found on the thermal CVD SiO_2/Si substrate. The SA3 sample, which is multi-layer graphene on thermal CVD grown SiO_2 /Si substrate is scanned in the present study. It is worth mentioning here that the sample SA4 (Fig1) has much more smooth surface with lower thickness of graphene after the hydrogen sensing. This is due to hydrogen passivation of the defects on the surface of graphene and more compact film. The probable bonding of Hydrogen with the available dangling bonds on the graphene surface (leading to Hydrogen adsorption) can be observed on figure-1 –SA4 as long chain-like features on the graphene surface.

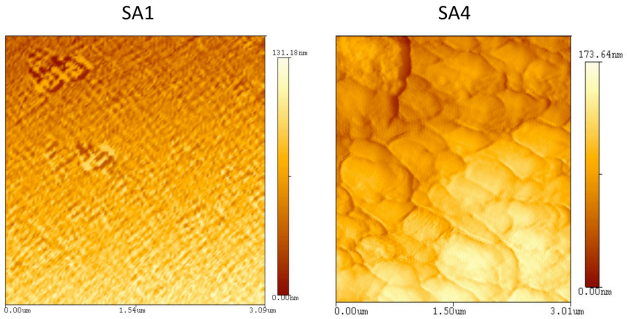
Figure 1. The micrographs of SA1, SA2, SA3 and SA4 obtained in the close contact mode. Size: 3μm×3μm.



The micrographs of SA1 and SA4 obtained in the contact mode.

To further compare the differences between the SA1 and SA4, the contact mode AFM images of SA1 and SA4 were captured in [(X:Y=3:3)μm] dimension with the scan rate of 0.5 Hz. The roughness of them is 36.24 ±10.42 nm and 60.71 ±27.40 nm, relatively. It is the similar to the result we got in the close contact mode.

Figure 2. The AFM contact micrograph of SA1 and SA4. Size: 3μm×3μm.



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V. DISCUSSIONS

We have characterized graphene grown by thermal CVD in different conditions and also the ability of the MLG films to perform as Hydrogen sensors. Our measurements demonstrate that as the deposition time increase more layers of graphene get deposited making the film surface more rough. This is beneficial for Hydrogen sensing as it creates more adsorption sites for Hydrogen. We have verified this hypothesis by observing the decrease in roughness of the graphene surface after hydrogen adsorption. The similarity of the close and contact mode micrographs demonstrate that hydrogen has been adsorbed on the MLG surface.

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