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Graphene Oxide Thin Films: A Simple Profilometer for Film Thickness Measurement

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Abstract*— Graphene oxide (GO) films are a few hundred nanometers thick semi-transparent films which have recently become commercially available. GO, used to make the films, is the oxidized form of graphene which can be visualized as a graphene sheet with its basal plane decorated by oxygen-containing groups. GO, produced using the Hummers method, is hydrophilic, solution processable, and an insulator. GO can also be treated to be converted into reduced Graphene Oxide (rGO), which is conductive. The GO can be deposited onto a substrate such as FTO, ITO and glass, to create films. The resulting graphene oxide film measured by a simple profilometer based upon a commercial strain gauge force transducer is described. It has been used on polymer film coated substrates to determine film thicknesses on the order of 20 mn. Measured film thicknesses agree with gravimetrically determined values to within 20 nm and also suitable to potential applications.

***Key words*: Hummers'method, Graphene oxide thin film, spin coating, profilometer**

I. INTRODUCTION

Graphene oxide (GO) have recently emerged as a new carbon - based nanoscale material that also provides an alternative path to graphene [1]. The solubility of graphene oxide in water and other solvents allows it to be uniformly deposited onto wide ranging substrates in the form of thin films or networks, which makes it potentially useful for microelectronics [2] .Graphene oxide is an insulator but controlled oxidation provides tunability of the electronic and mechanical properties including the possibility of accessing zero- band gap graphene via complete removal of the C− O bonds. The structure of GO is often simplistically assumed to be a graphene sheet bonded to oxygen in the form of carboxyl, hydroxyl or epoxy groups [3].

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There are several different ways to create graphene films. Mechanical exfoliation[4] (the "scotch-tape method") can be used to pull sheets of graphene off of graphite using tape, or chemical vapor deposition (CVD)[5, 6] to grow graphene on metal. However, mechanical exfoliation is only useful for isolating small quantities of graphene, and CVD is expensive, requiring capital equipment and expertise in wet chemistry to transfer graphene film on an insulator. In contrast, abundant chemicals are used to oxidize graphite to make GO and for this reason the production of GO films is relatively inexpensive. Further, the transparency and thickness of GO thin films can be adjusted continuously to be used in a broad range of applications.

GO films, which can be used for nonvolatile memory, may expand the current applications of memory technology because it maintains its properties even when only one or a few atomic layers thick. GO-based memory would also have mechanical flexibility, a clear advantage over the current generation of nonvolatile memory sources such as dynamic random access memory (DRAM) and flash memory. It has been demonstrated that even after 1,000 flexes, the bipolar resistive switching of the graphene oxide-based memory device was not degraded [7].

II. EXPERIMENTAL

A. Sample preparation

For synthesis of GO we have selected well known method Hummers Method [8] from graphite flakes as described in our previous work [9]. Homogenous graphene oxide aqueous suspension with a concentration of 0.05grams of GO was suspended in 20ml Water of and 20ml of Ethylene Glycol in two different beakers. Then after the solutions sonicated by probe type sonicator for 2 hrs for uniform aqueous solution.2grams of PVP(Polyvinyl Pyrrolidone) was added to the aqueous solution and stirred at 80^0C for 5hours. The GO suspension was then spin coated at 6000 rpm for 30 s with a spin coating apparatus[10-14] (HOLMARC Spin coater-model: HO-TH-05) on clean fluorine doped tin oxide (FTO), indium tin oxide (ITO) substrates and glass slides, which were first washed with acetone, ethanol and deionized water for 10 min successively under the assistance of ultrasonication. The GO thin films were obtained after drying at room temperature for 24 hrs as shown in Fig.1.

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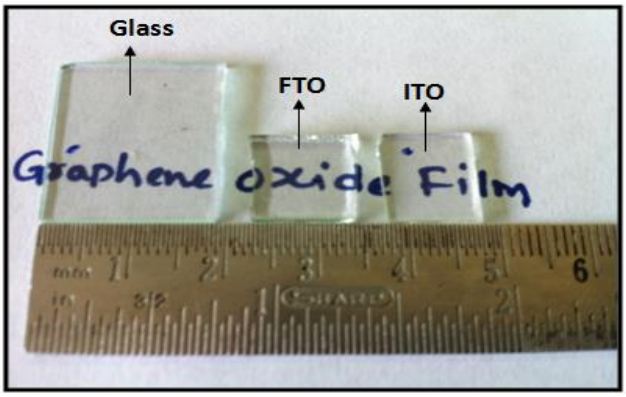

Fig.1. Graphene oxide thin films with different substrates (a) Glass, (b) FTO, (c) ITO.

III. CHARACTERIZATIONS

Morphological studies were carried out by using field emission scanning electron microscope (FESEM) (Model Zeiss Ultra 55). X-ray diffraction (XRD) patterns were recorded from 10 to 40° using Cu Kα as the x-ray source (λ=1.54 Å); Bruker's AXS Model D8 Advance System was used to carry out the XRD experiments. XRD studies were carried out to understand the crystallinity and phase of the samples, respectively. The thicknesses of the prepared films were characterized by profilometer (Dektak 8000 profilometer).

IV. RESULT AND DISCUSSION

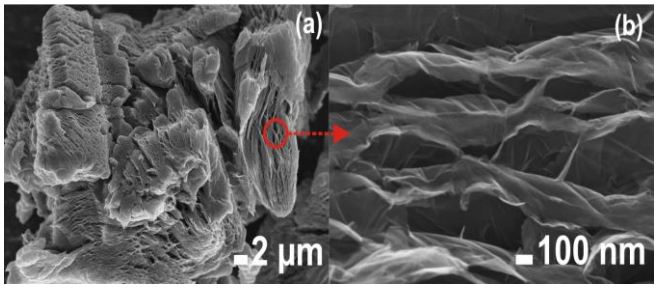

Fig.2.Field emission scanning electron micrographs of GO (a) protracted view of GO, (b) Stretched GO

Field emission scanning electron micrographs of GO are shown in Fig 1(a & b) and also we can observe that stretched areas in protracted view and close view GO. In close view stretched graphene sheets observed this indicated by orange cloured.

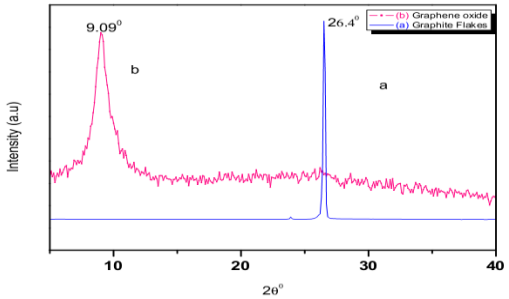

Fig.3. XRD pattern of (a) Graphite flakes and (b) GO

Fig.3 shows the XRD patterns of graphite flakes, and graphene oxide. Graphite flakes exhibits a strong and sharp peak at 26.4^0 in Fig.2(a), indicating a higher ordered structure, that corresponds to a basal spacing d_{002} = 0.334nm. The pattern of graphene oxide, on the other hand, exhibits a 001 reflection at 9.09^0 corresponding to a basal spacing of d_{001} = 0.961 nm.The interlayer spacing of GO was calculated to be 0.961 nm according to the diffraction peak at 2Θ =90.9º. This value is higher than interlayer spacing of graphite flakes (d-spacing= 0.334nm, 2Θ =26.4°), due to the presence of oxygenated functional groups and intercalated water molecules.

GO Thin film was prepared by dispersing GO in two different solvents namely Ethylene glycol and Water. Films were prepared by varying the rpm while spin coating the solution on glass substrate. The thickness of the thin film was measured by Profilometer. The average thickness of ethylene glycol used thin film was obtained as 73.6nm, 37.4nm, 22.3nm, 20.5nm, 15.5nm and 13nm at 2000, 3000, 4000, 5000, 6000 and 7000 rpm respectively (table-1). The average thickness of water used thin film was obtained as 346nm, 98.6nm, 56.3nm, 45nm, 31.6nm, 19.8nm at 2000, 3000,4000, 5000, 6000 and 7000rpm respectively (table-2).

Table.1. Thickness of GO glass film- Ethylene glycol

S.NO	*GO Film-Ethylene glycol Rpm (30 Sec)*	*Left (A0)*	*Middle (A0)*	*Right (A0)*	*Avg (A0)*	*Avg (nm)*
1	GO-E 2000	178	1235	795	736	73.6
2	GO-E 3000	316	357	449	374	37.4
3	GO-E 4000	305	162	204	223	22.3
4	GO-E 5000	125	258	206	205	20.5
5	GO-E 6000	192	170	105	155	15.5
6	GO-E 7000	115	170	105	130	13

Table-2: Thickness Results of GO glass film-Water

S.NO	*GO Film-Water Rpm (30 Sec)*	*Left (A^0)*	*Middle (A^0)*	*Right (A^0)*	*Avg (A^0)*	*Avg (nm)*
1	GO-W 2000	3044	4539	2798	3460.3	346
2	GO-W 3000	187	1705	1066	986	98.6
3	GO-W 4000	429	592	668	563	56.3
4	GO-W 5000	679	204	467	450	45.0
5	GO-W 6000	368	388	192	316	31.6
6	GO-W 7000	182	219	193	198	19.8

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It is observed that as the rpm increases the thickness of the thin film reduces in both the cases as shown in the Fig.4. Thus high rpm is preferable to obtain very thin film. Ethylene glycol used thin films are having less thickness when compared to the thin films obtained by using water. Thus we conclude that fine GO thin films can be obtained at high rpm spin coating using ethylene glycol solvent.

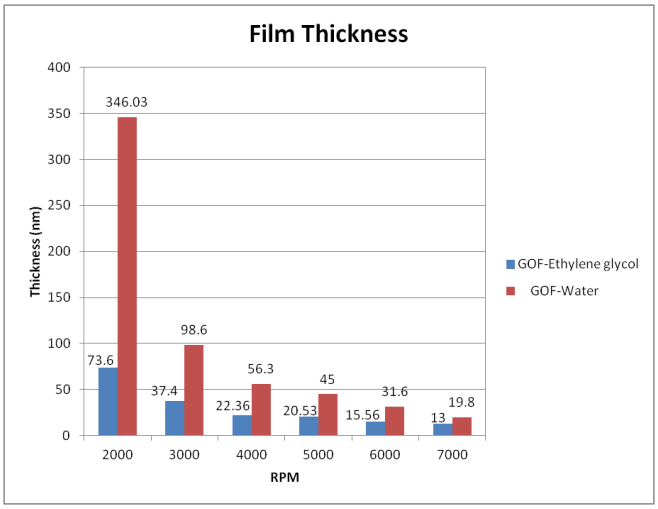

Fig.4.Rpm Vs Thickness

Based on the observations of Glass substrate thin films, ITO and FTO substrates based thin films were prepared. As fine GO thin film was obtained at 6000rpm, the same parameters are maintained to get thin film using ITO and FTO substrates and the thickness is 12nm and 14nm respectively which is less than that of glass 15.5nm.

Table-3: Thickness of various Substrates GO film

S.NO.	*Substrate for GO film*	*RPM*	*Avg. Thickness(A°)*	*Avg. Thickness(nm)*
1	Glass	6000	155	15.5
2	FTO	6000	140	14
3	ITO	6000	120	12

V. CONCLUSION

We have fruitfully made GO thin films by using different substrates with the help of spin coater. We observed an inverse relation between the thickness of the thin film and the rpm used at spin coating, which means the increase in rpm reduces the thickness of the GO film. In addition to rpm, changes in solvent and substrate also vary the thickness of GO film. Ethylene glycol and ITO are the suitable solvent and substrate respectively for obtaining very thin films. Thus we optimized effective parameters during the making of GO thin films such as RPM, concentration of PVP in different solvents for making GO thin films.

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