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Synthesis of multilayer graphene by filtered cathodic vacuum arc technique

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***Abstract*—Filtered cathodic vacuum arc technique has been used to deposit amorphous carbon films of varying thickness on catalytic nickel thin film grown on SiO_2/Si substrates. Subsequently these a-C films were annealed in vacuum at 650 ºC. Raman spectroscopy together with optical microscopy and scanning electron microscopy has revealed multilayer graphene formation.**

***Index Terms*— Graphene, Filtered cathodic vacuum arc, Raman spectroscopy, Optical microscopy, Scanning electron microscopy.**

I. INTRODUCTION

Two-dimensional graphene has specially attracted a lot of attention because of its unique properties such as high carrier mobility, the quantum Hall effect at room temperature, high transmission of white light, high elasticity, high surface area etc. Thus, there has been much effort to synthesize single and multilayer graphene by a number of methods. Mechanical exfoliation [1] of graphene layers using scotch tape is so far the most popular technique but the major issues with this method are poor reproducibility and non-compatibility with device fabrication. There were also reports describing the use of chemical methods to grow graphene layers [2] but these methods require multiple steps and wide variety of resources which may not be compatible with device fabrication. Another method based on electrochemical expansion of graphite electrode has been used for synthesizing graphene layers, but only few layer graphene can be grown by this method [3]. For the synthesis of large area graphene layers, chemical vapor deposition and epitaxial growth on SiC substrates are commonly preferred methods [4, 5] but, graphene layers grown by these methods exhibit large number of defects. Ji et al. [6] have reported the effect of gaseous environment of argon and hydrogen on the formation of graphene from amorphous carbon (a-C) films deposited by sputtering technique on copper substrates. They have reported that the graphene is formed only in presence of hydrogen gas which suggests that gaseous hydrocarbons and / or their intermediates yield graphene on copper through the reaction of hydrogen gas and the a-C films. Zheng et al. [7] have reported metal catalyzed crystallization of amorphous carbon films (2.5-40 nm thick) deposited by electron beam evaporation to graphene by thermal annealing at 650-950 ºC under argon flow at a pressure of 1.7 Torr. Recently synthesis of homogeneous graphene layer on silicon substrates with nickel film annealed at 800 ºC in nitrogen atmosphere [8] and in vacuum condition [9] by arc plasma deposition and arc discharge in He and H_2 gas combination at relatively high pressure [10] has been reported.

We report a new and simple filtered cathodic vacuum arc (FCVA) technique for the synthesis of large area graphene at low annealing temperature. The results of a systematic study of FCVA deposition of amorphous carbon (a-C) films and conversion of graphene on silicon substrates are presented in this article. The FCVA technique has advantage of high energy of depositing ions and degree of ionization than that of conventional evaporation, electron beam evaporation and sputtering techniques. It has precise control of thickness and thus highly reproducible and attractive method for the production of graphene layers under high vacuum conditions. The quality and structure of graphene layers can further be controlled by the thickness of a-C films.

II. EXPERIMENTAL DETAILS

Figure 1 shows the fabrication steps to synthesize multilayer graphene. The silicon <100> n-type substrates of resistivity 0.001-0.005 ohm cm is covered with thermally grown SiO_2 layer of ~ 0.4 μm thickness and capped with ~ 0.3 μm thick nickel film. Nickel thin film was deposited by D.C. magnetron sputtering technique using 99.99 % pure 50 mm dia. nickel target. Argon gas of high purity 99.999% was used to maintain a chamber pressure of $\sim 10^{-2}$ mbar. Prior to deposition, the sputter chamber was evacuated to a base pressure of $\sim 10^{-8}$ mbar using turbo molecular and rotary pump. The a-C films of three different thicknesses of about 10, 18 and 38 nm were then deposited by FCVA technique using 56 A arc current at a pressure of $\sim 10^{-5}$ mbar. The base pressure achieved in the FCVA system was $\sim 10^{-6}$ mbar. The a-C films were deposited sequentially for 5 sec and then cooled for 50 sec. The process was repeated until the required thickness was obtained. Pulse type of cathodic vacuum arc can control the thickness of thin film by controlling the number of pulse. The growth rate obtained was ~1 nm/sec. The deposition system consists of a water cooled cathode and anode, plasma guiding

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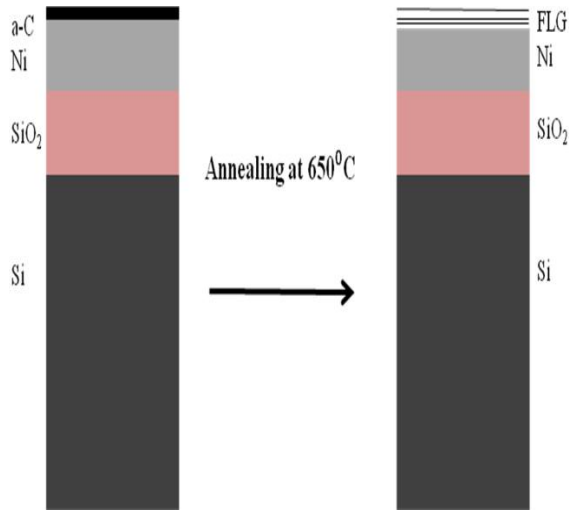

FIG. 1 Fabrication steps for synthesizing multilayer graphene.

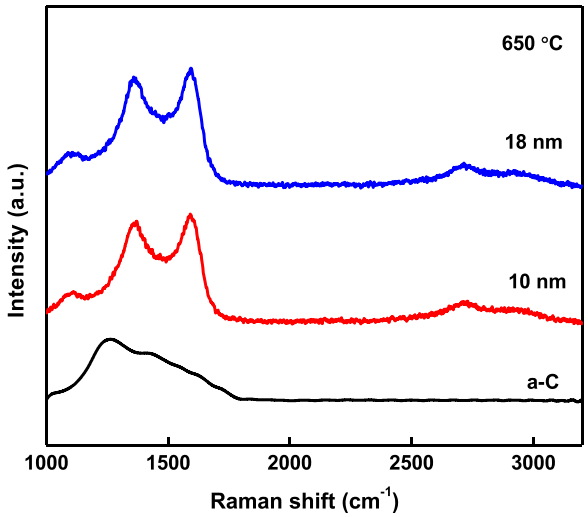

FIG. 2 Raman spectra of a-C/Ni/SiO_2/Si samples annealed at 650 ºC with thickness of a-C films of 10 nm and 18 nm.

duct and magnetic coil. The FCVA technique is based on striking the arc between two graphite electrodes (50 mm dia. graphite cathode and a retractable graphite rod of 7 mm dia. with purity 99.999 %). An arc spot produces neural macro particles which cause several problems such as rough surface, pin hole and micro cracks in the films. A linear magnetic filter has been used to remove the macro particles generated during the arc and a magnetic field of ~350 G was achieved inside the duct. Other details of the system are given somewhere else [11-13]. The a-C/Ni/SiO_2/Si samples were taken out after deposition and then heated inside the vacuum furnace at 650 ºC for 10 minutes at a pressure of ~10^{-3} Torr which was obtained by rotary pump. The heating rate for achieving the desired temperature was ~25 ºC/min. The vacuum furnace was then switched off and allowed to cool naturally. Multilayer graphene (few layer graphene, FLG) was then obtained on the surface of samples shown in Fig. 1. Graphene was transferred by dipping the sample in $FeCl_3$ aqueous solution which acts as a nickel etchant and finally floating it in the deionized water. Further, it was rinsed in acetone and sonification was made in isopropyl alcohol. It was then lifted on SiO_2/Si wafer or on quartz substrates and allowed to dry. Raman spectra was taken by a Reninshaw spectrophotometer (micro- Raman model inVia Reflex) with 514 nm laser excitation and notch filter cutting at ~50 cm^{-1} at room temperature at ~5 mW incident power. The transmittance was carried out by Perkin Elmer spectrophotometer (Lambda 950) in the range 400-1000 nm. The graphene microstructure was examined by optical microscope (Zeiss model Axiolab A) having polarized light facility. The SEM of graphene layers was observed in JEOL-JSM-7500 F SEM equipment. The thickness of a-C films were determined by a surface profilometer (Talystep- Taylor and Hobson).

III. RESULTS & DISCUSSIONS

Raman spectroscopy is considered as one of the most reliable, non-destructive and fast characterization technique to detect graphene [4, 14, 15]. Fig. 2 shows the Raman spectra of a-C/Ni/SiO_2/Si samples with a-C films of different thicknesses (10 and 18 nm) annealed at 650 ºC for 10 min in vacuum. The a-C films deposited at room temperature without any annealing show a broad peak from 1100-1700 cm^{-1} indicating amorphous nature of the sample. The samples having 10 nm and 18 nm thickness annealed at 650ºC show the characteristics graphene fingerprints of D (1357-1371 cm^{-1}), G (1591-1594 cm^{-1}) and 2D (2715 cm^{-1}) peaks whereas the carbon film of 38 nm thickness does not show the 2D peak but shows only a D peak at ~1380 cm^{-1} and G peak at ~1590 cm^{-1} whose Raman spectra is not shown in the figure. The most notable features is the appearance of 2D peak, whose position and shape revealed the formation of multilayer graphene [14, 15] while D peak is always related to the disorder [16]. The presence of well defined G, D and 2D features in the present study reveals the formation of graphene layers. The G peak is due to the doubly degenerate zone centre E_{2g} vibrational mode, D band is related to defects and the 2D peak is due to a second-order of the D peak which originates via a participation of two phonons with opposite wave vectors leading to momentum conservation [4, 14] From Raman spectra by determining the I_D/I_G, I_{2D}/I_G ratio and full width of half maximum of 2D peak ($FWHM_{2D}$), one can infer the quality of the graphene layers [4,14-16.] The I_D/I_G, I_{2D}/I_G and $FWHM_{2D}$ evaluated for different thickness of a-C films are summarized in Table 1. Hao et al. [15] while probing number of layers and stacking order of few layer graphene (FLG) by

TABLE 1. Parameters evaluated from Raman measurements

Thickness of a-C films / Properties	10 nm	18 nm
I_D/I_G	0.93	0.94
I_{2D}/I_G	0.39	0.38
$FWHM_{2D}$ (cm^{-1})	192.2	199.9

Raman spectroscopy have reported typical values of $FWHM_{2D}$ of five layers graphene as 66.1±1.4 cm^{-1}.The values of I_{2D}/I_G < 1 together with FWHM > 192 cm^{-1} in the present study indicate multilayer graphene. Annealing temperature [7] may also play an important role in the optimization of such study. Graphene formation and the quality of graphene were reported to be relatively independent of annealing time up to 60 min. For longer annealing times, the areas with graphene are notably reduced and for annealing times > 5 hours, no carbon or graphene are detected by Raman [7]. In a recent study [17] we have reported that 750 ºC seems to be the optimum temperature of annealing for conversion of a-C films into graphene. Further work is being carried out with the reduced thickness of a-C films of 3-6 nm and subsequently annealed at 750 and 800 ºC before reporting the number of layers and exact optimum temperature of annealing.

The formation of graphene on nickel was explained on diffusion and segregation process [7, 18]. First carbon atoms are diffused into the nickel lattice at high temperature and form solid solutions. While cooling, the segregation of carbon atoms to surface leads to the formation of the graphene layers [7, 18]. Annealing temperature is an important factor that affects the segregation of carbon atoms and the quality of graphene layers. This is the important difference between our "limited source" and chemical vapor deposition (CVD) processes, where the carbon source is virtually limited and controlling the number of layers depends on the tight control over a number of deposition parameters. Fig. 3 shows the transmittance spectra of a-C films transferred on quartz substrate in the wavelength range from 350 nm to 1000 nm. It

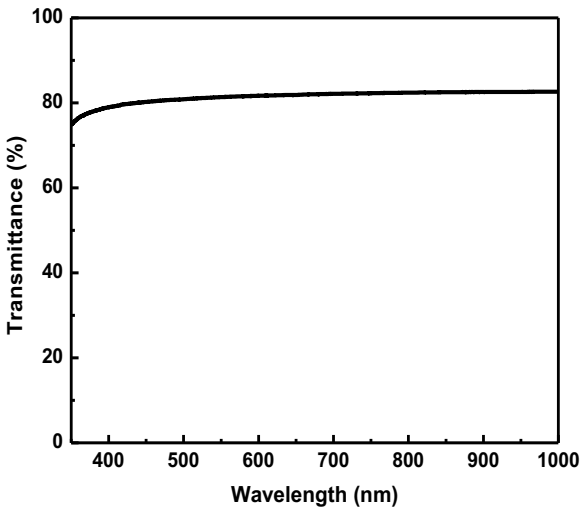

FIG. 3 Transmittance spectra of graphene sample of 10 nm thickness.

is evident from the curve that the value of optical transmittance of graphene transferred on quartz substrate is 80-82 %. The values of sheet resistance of these graphene layers are found to be ~15 kΩ / square. Optical method offers the potential for rapid and nondestructive characterization of large area graphene material [19, 20]. In the monochromatic light source, white light allows rapidly sorting out graphene range of thickness regions because graphene with different range of thickness can exhibit different colors that can easily be appreciated by the naked eye [21]. Fig. 4 shows the optical micrograph obtained from graphene - nanosheets transferred on SiO_2 / Si substrate which was synthesized by annealing the a-C films (10 nm thick) at 650 ºC. From the micrograph, one

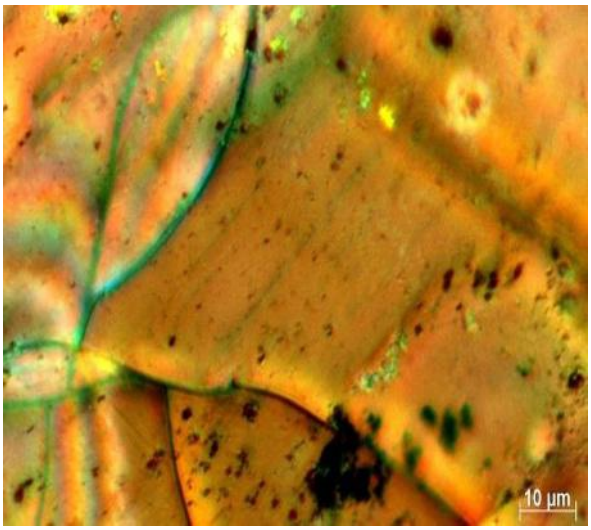

FIG. 4 Optical image of multilayer graphene of 10 nm thickness transferred on SiO_2/ Si substrate.

can see that the graphene sheet is not lying flat on the substrate, and as a result, it is giving different reflections of colors. In the whole scan area, cracks are due to the mismatch in the coefficients of thermal expansion of graphene and substrate, and it is not due to grain boundaries. The black spot appeared in Fig. 4 could be of amorphous carbon or solvent residue present on the surface. The optical microscopy study reveals that the graphene obtained in the present work consists of multilayer. Fig. 5 shows the typical SEM micrograph of multilayer graphene on SiO_2/Si substrate which was sysnthesized by annealing the a-C film at 650 ºC. It is evident

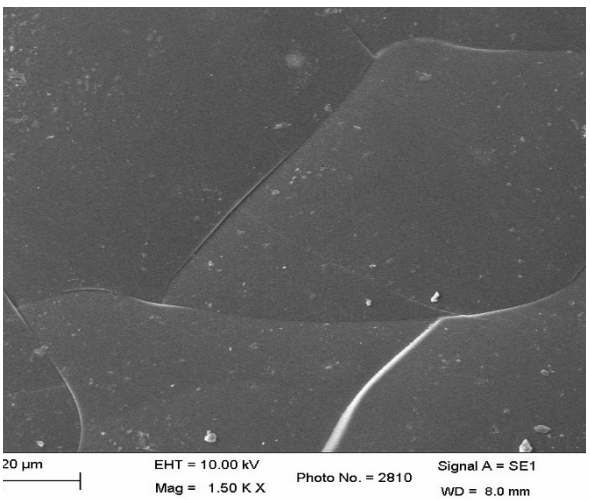

FIG. 5 Typical SEM micrograph of multilayer graphene of 10 nm thickness transferred on SiO_2/ Si substrate.

from the micrograph that graphene films are uniform but there are wrinkles formations due to the polycrystalline nature of nickel film at very high temperature. Some particles shown on the surface of geraphene are also observed. These particles may be the residual etchant that might remain there during the transfer process. In brief, the ability to tune the number of layers by the deposited a-C film (i.e., limited source) presents a unique method toward controlled assembly and synthesis of graphene on large area and presents an important advantage as compared to CVD process where the carbon source is unlimited.

IV. CONCLUSIONS

A simple and novel filtered cathodic vacuum arc technique has been used to deposit a-C films on catalytic nickel thin film grown on SiO_2/Si substrates and subsequently converted these films into large area graphene by post annealing the sample in vacuum at 650 ºC. Raman spectroscopic study of a-C films has revealed the formation of multilayer graphene with optical transmittance of 80-82 % and sheet resistance of ~15 kΩ /square. The temperature of annealing has been reduced to 650 ºC in contrast to the existing temperature of annealing (≥800 ºC) cited in the literature [7-9]. It has been observed that the quality and graphene layers can be controlled by the thickness of a-C films. In future, lowering the thickness of a-C films on nickel and copper catalysis substrate and the effect of gaseous environment will be explored to prepare few layer graphene.

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