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Growth and Morphological changes of Two-dimensional Carbon nanostructures with time of Deposition by Radio Frequency Plasma Enhanced Chemical vapor deposition

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Abstract - In this work, we report the growth of different types of two-dimensional(2D) carbon nanostructures and their change in the morphology, growth and size on Si substrate with deposition time. The 2D carbon nanostructure were grown in the presence of Argon plasma with Methane as a carbon source without any special pre-treatment of the substrate using Radio Frequency Plasma Enhanced Chemical Vapor Deposition (RF-PECVD). Field Emission Scanning Electron Microscopy (FE-SEM) and Atomic Force Microscopy (AFM) were proven the grown carbon nanostructures were hexagonal Islands, rod shaped and white patches like structures. We identified the changes in the diameters of the grown nanostructures from 35-130 nm with deposition times 30 to 120 minutes. The surface roughness of the samples was reported by the 3D analysis of AFM. The presence of D and G peaks was identified by Raman Spectroscopy. Raman spectroscopy showed that the ratio of I(D)/I(G) increases with increasing deposition time.

Keywords – Radio Frequency Plasma Enhanced Chemical Vapor Deposition (RF-PECVD), hexagonal islands, rod - shaped structures, white patches like structures, I(D)/I(G).

INTRODUCTION

Carbon nanostructures with varying morphological configurations have sought the attention of the researchers in recent times. The foundation for their interest lies in the potential applications of these nanostructures from innovative electronics to structural elements. The presence of such properties in these structures is due to the specialized orientation of sp2 bonded carbon and the behavior of their electronic structure [1]. Among these allotropies of carbon, carbon nanosheet is a special type of two-dimensional nanostructure [2]. It preserves the graphene layers as relatively isolated structure with strong anisotropy in physical properties [3,4]. Single graphene layer has a hexagonal symmetry with two atoms per unit cell. Carbon atoms have four valence orbitals, three of them build the sp2 bonds which give rigidity to the structure and the other orbital gives rise to the valence and conduction bands [5]. Graphite is the stakes of graphene; it exhibits the ferromagnetic and super conducting fluctuation behaviors due to its unconventional electronic structure of edge-inherited non-bonding states [6, 7]. It is said that an isolated graphene has the convenient property of the electronic states near the Fermi level. By symmetry, the lower and upper bands touches at the corners of the hexagonal Brillion Zone that tend to the formation of zero density of states at the Fermi level. This results in linear rise of energy and it behaves as the zero-gap semiconductor that modifies significantly the screening of coulomb interaction [8].

These two-dimensional carbon nanostructures have attracted extensive attention such as high performing nanomaterials, high efficiency energy storage devices, cold field emitters and in composite materials [9]. Many methods have been used for fabrication of carbon nanostructures, including arc discharge [10], pulsed laser deposition [11], thermal chemical vapor deposition [12], direct current [13], hot filament chemical vapor deposition and microwave chemical vapor deposition [14], most of which are operated at high temperatures around 1000 °C. Such high temperatures are not suitable for working, especially with respect to electronics where most components are highly temperature sensitive. Also, in all these methods, carbon nanosheets and different types of two–dimensional carbon nanostructures existed as byproducts during the synthesis of carbon nanotubes. Carbon nanostructures obtained by these methods have mixed structures. Efforts were taken to synthesize individual grown carbon nanostructures over Si (100) substrates without catalyst or any special pre-treatment of the substrate using RF-PECVD. In this work, we report the growth of different types of two-dimensional carbon nanostructures on Si (100) substrates in the presence of Argon plasma with Methane as a carbon source. The variation in morphology and growth of the carbon nanostructures with time of deposition is also studied.

II. EXPERIMENTAL DETAILS

The RF-PECVD chamber is an open-end type chamber covered with water-cooled lines. Length and diameter of the chamber is 400 mm and 290 mm respectively. The two-electrodes are inserted parallel to the length of the chamber. The upper-electrode carries RF-power and gas into the deposition chamber. Sample holder cum heater works as a lower electrode, the temperature of the sample is controlled by means of a digital PID controller with "K"-type thermocouple attached to the lower electrode. The two electrodes are separated by a distance of 8 cm enabling the RF–Unit to generate a power of 500 W with the frequency of 13.56 MHz Two mass flow controllers handle the inlet of Methane and Argon gas into the deposition chamber.

SUBSTARTE PREPARATION

Si (100) wafers were used as substrates for the deposition of carbon nanostructures. These substrates were cut into1 cm x 1cm pieces and were sonicated in ethanol and acetone, and air-dried. The substrates were subsequently placed inside the chamber and the chamber was pumped down to a pressure of 1 x 10-5 mbar with the help of oil diffusion pump and rotary pump. Substrates were etched for 15 minutes using Argon plasma generated at 500 W RF power and a constant Argon gas flow rate of 20 sccm.

Variation in Time of Deposition

The reaction involved variation in the time of deposition while all the other parameters such as Methane composition (30%), substrate temperature (550 °C) and RF-power (500 W) were kept constant throughout the reaction. Reactions were carried out for 30, 60 and 120 minutes respectively.

III. RESULTS AND DISCUSSIONS

Effect of Time of Deposition

We can observe from fig. 1 that the orientation, grain size and corrugation behavior of the nanostructures increase with increasing deposition time. From figure 1(a), one can see the formation of amorphous soot when the deposition time is 30 minutes. The grown carbon nanostructures are densely packed islands covering the substrate without gaps. The diameter of the grown carbon nanostructures is roughly around 35 to 40 nm, it is determined by the graphs drawn for the particle size distribution shown in the inset of figure 1(a). As the time of deposition increases to 60 minutes as seen in figure 1(b), the formation of more clustered, elongated size, rod shaped nanostructures of carbon is observed at some sites on the substrate with a diameter of roughly around 65 to 75 nm. It is represented by the graphs drawn for the particle size distribution shown in the inset of figure 1(b). The green colored circles represent the growth of rod-shaped carbon nanostructures with elongation in length. The elongation of the nanostructures in the sample deposited for 60 minutes could be attributed to the increase in distribution of carbon with increasing deposition time. When the deposition time reaches 120 minutes, it can be observed that there is the formation of corrugated structures with high density over silicon substrate (from figure 1 (c)).

The amorphous carbon nanostructures grown in the 30 minutes sample are relatively smooth, isolated and parallel to the substrate surface. As the deposition time increases the growth of nanostructures switches from parallel to nearly vertical and occupies different orientations, few of them appear to be horizontal rod shaped like structures and few of them appear to be bulged island like structures with more sizes. As the deposition continues beyond 60 minutes, they become more corrugated and bunched together reside in a range of orientations relative to the substrate, some have folded up, to different degrees, with their own weights. As the time of deposition reaches 120 minutes and above, the range of orientations becomes increasingly random as the carbon nanostructure become more massive. From figure 1(c), one can clearly see the corrugation behavior of grown carbon nanostructures. The diameter of the grown carbon nanostructures is roughly around 100 to 130 nm; it is represented by the graphs drawn for the particle size distribution shown in the inset of figure 1(c). It can also be identified from figure 1(c) at the top white colored patches at the tip of the corrugated nanostructures with less diameter is represented by the green colored circles.

The vertical growth of carbon nanostructures reaches a point where the diameter of the structures decreases. This is due to the presence of low and uneven distribution of thermal energy across the graphene layers, after reaching a certain height. The deposition of carbon radicals that supports the crystalline growth of the carbon nanostructure decreases and the carbon radicals that favor the defective nature of carbon nanostructure increases and it has been proven by the Raman spectroscopy analysis of the samples included in the further part of this work. It is also due to the bombardment of high energetic Argon plasma with high frequency at these heights. It is also believed that as additional graphene layers are added to the structure, the long-range inter-atomic forces become stronger resulting in the collapse of nanostructures closer to each other [15].

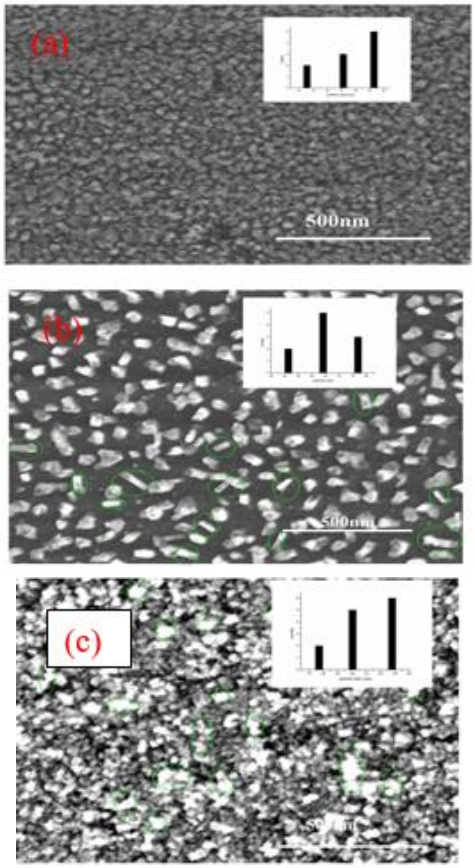

Fig. 1. FE-SEM images of carbon nanostructures grown at three different time depositions on Si substrates:(a)30 minutes;(b)60 minutes;(c)120 minutes. The other deposition conditions are 30% Methane, RF- power (500W) and Temperature 550 °C.

Figure 2 shows the three dimensional AFM images of carbon nanostructures grown at three different time depositions. The 3D images represent an increasing order of size, change in orientation, shape and density of the carbon nanostructures with increase in time of deposition.

Even though the structural nature and morphology of the grown carbon nanostructures were studied by FE-SEM and AFM, it has been said that Raman spectroscopy is the best technique to study and analyze the carbon nanostructures since carbon is a Raman active element. It may provide more effective information about crystallography and morphology of the carbon nanostructures [16]. Raman spectra taken on carbon nanostructures as shown in fig.3 are similar to those observed for carbon nanotubes.

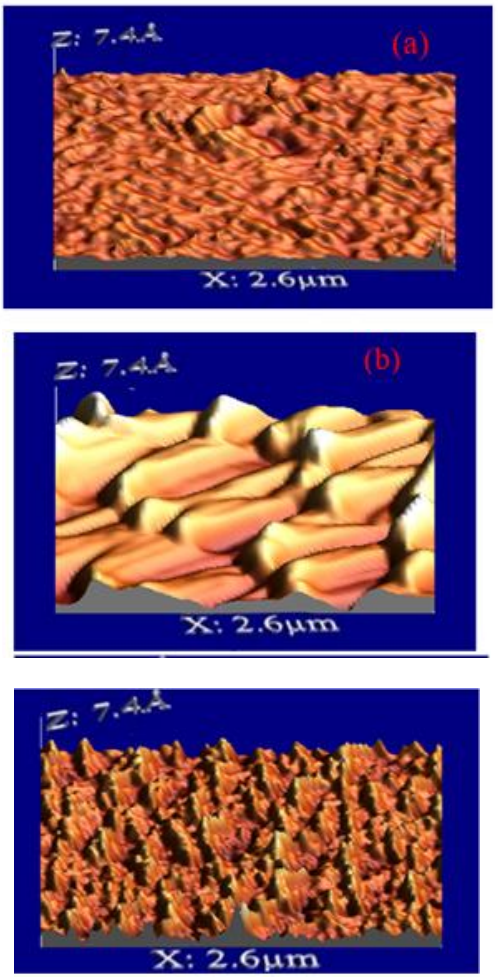

Fig. 2 AFM 3D images of carbon nanostructures grown at three different times of depositions: (a) 30, (b) 60, and (c) 120 minutes respectively.

Fig. 3 shows the Raman spectra taken from nanostructures grown at different time depositions. All the samples show a peak at 1321cm-1 in the D-band (Defects) which is associated with vibrations of carbon atoms with dangling bonds in plane terminations of the disordered graphite. The peak at 2639 cm-1 is an overtone of the disordered graphite [2xD]. The peak at 1576 cm-1 (g-band) is attributed to the vibration of sp2 bonded carbon atoms in a two- dimensional hexagonal lattice [17, 18].

It is identified that the intensity variation of the D and G (Graphite) peaks (D)/I(G) increases with reaction time. This indicates a more nanocrystalline structures and the presence of large number of defects of the nanostructures. The defects may include vacancies and strained hexagonal/non-hexagonal

(pentagon or heptagon) distortions. This leads to the non-uniformity, corrugation and twisting of carbon nanostructures shown in the FE-SEM images. The small peak at 2912 cm-1 is attributed to the combinations of the D and G bands.

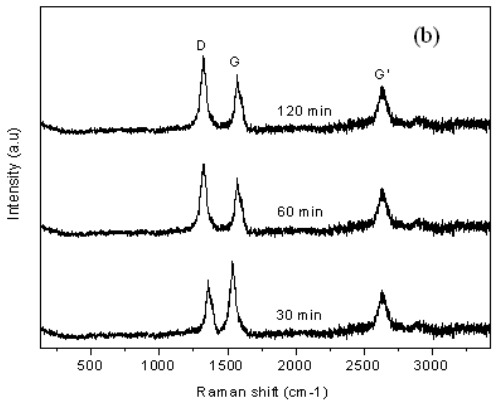

Fig.3 Raman spectroscopy of carbon nanostructures grown at different deposition times respectively.

IV. CONCLUSIONS

We reported the growth of hexagon ice lands-like carbon nanostructures and rod-shaped nanostructures with the variation in deposition time. Change in the size, morphology and orientation of the carbon structures were observed with increasing time of deposition. It was also observed that while the time of deposition increases more corrugation nature of carbon nanostructures were seen. White patches like carbon features have been seen at the tip of carbon nanostructures after 120 minutes growth, which represents the presence of defective carbon species after the growth at certain height due to the presence of low and uneven thermal energy. The observed variations in the diameter of the structures are roughly around 35-130 nm as the time of deposition increases from 30 to 120 minutes. RF-PECD has proven to be the prominent technique to grow the different types of carbon nanostructures with varying parameters for different applications.

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