CHAPTER 7

EVOLUTION OF STRUCTURE, MORPHOLOGY, GROWTH AND CHEMICAL COMPOSITION OF CARBON NANOSTRUCTURES AS A FUNCTION OF TIME OF PRE-ETCHING GROWN BY RF-PECVD

7.1 INTRODUCTION

After the discovery of fullerenes by Kroto and Smalley in the year 1985 [112], research on allotropes of carbon has became a wider area to understand the formation of many carbon nanostructure configurations and their potential applications. Among these allotropes of carbon, fullerenes and nanotubes have closed surfaces due to the participation of pentagon rings [113]. On the other hand, nanographites are characterized by the stacking of finite flat graphene sheets having open edges. It has been pointed out that the electronic properties of nanographites are greatly influenced by their edge shapes apart from quantum size effects and surface effects [114, 69].

These graphite sheets and carbon nanostructures may have potential applications, such as serving as catalyst support [115,116], electrode materials for lithium ion batteries [117], and electronic conducting fillers for conducting polymer composites [118-120], due to their remarkable surface area as well as special characteristics of flexibility and electricity, high thermal resistance and high chemical stability and lightweight [121]. In addition, this quasi-two-dimensional nanostructured material may serve as the building block for other promising carbon nano materials. For instance, nanotube like carbon scrolls have been formed from exfoliated graphite nanosheets via a scrolling mechanism [122]. Most nanostructures derive their configurations from topological defects in graphene sheets, and they energetically need to eliminate the dangling bonds by folding in on
themselves [102], carbon nanohorns are a new type of horn-shaped aggregate of single graphene sheets [80].

In some early studies [74, 123, 75], carbon nanosheets and carbon nanorods were produced with low yields accompanying other carbon allotropy such as CNT. Also, petal-like carbon nanosheets in a macroscopic quantity by an arc discharge reaction [82], and expanded graphite nanosheets were produced from various graphite interaction compounds submitted to the a brutal thermal shock [124-127].

However, there is a lack of well-separated, positional grown carbon nanostructures particularly in the case of micro electronic device fabrication. There are certain methods like micro wave plasma enhanced chemical vapor deposition and hot filament chemical vapor deposition methods [128-130] were reported for the growth of individual carbon nanostructures, but these methods, however, required high temperatures.

RF-PECVD is probably the most suitable carbon nanostructure growth method because it is relatively simple and has a high reliability than other methods. RF-PECVD used here, offers the variation of growth parameters like gas composition, substrate temperature, RF-power and the pressure of the reactions respectively. The theme of work is the evolution of growth, structural, morphological and elemental composition of the grown carbon nanostructures as a function of time of pre-etching. In this chapter, we report the growth of individual spherical carbon nanosheet-like structures and carbon nanorod like structures synthesized by RF-PECVD. In addition, we reported the growth of novel morphological individual nano shell-like structures, which were not reported yet, under the same growth conditions. The growth mode of this nano-shell like structure is still under investigation.
7.2 EXPERIMENTAL DETAILS

PE-CVD is a good tool for the production of carbon nanotubes and carbon nanostructures. It provides an excellent control of various parameters e.g., substrate temperature, gas ratio and RF-power etc. The chamber is an open-end type at both the ends with an internal diameter of 290 mm and cylindrical length of 400 mm. RF-electrode carrying RF-power of 13.56 MHz and gas is assembled in the top plate of the chamber. The bottom part of the top plate is provided with grooves and a perforated sheet for uniform gas distribution. Three Si (100) substrates of 10 mm × 10 mm were simply cleaned by sonicating in ethanol for several minutes and then dried in air. We used e-beam Physical Vapor Deposition (PVD) technique equipped with well digital thickness monitor for the deposition of iron thin films on Si substrates.

The three Si (100) substrates were transformed into e-beam PVD chamber to coat 10 nm thick iron films. We fixed the evaporation rate of the iron at 0.1 Å/sec, chamber pressure at 10^{-6} mbar in the room temperature. The samples were then kept in an evacuated vessel under primary vacuum. Then we transformed each sample into the RF-PECVD chamber for heating process to activate the catalyst films. We conducted three pre-etching reactions, in sequence, in which one experiment casted for 30 minutes, one was for 60 minutes and the third for 120 minutes. In addition, in each experiment of pre-etching reaction substrate temperature, RF-power and argon flow rate were maintained at 700 °C, 500 W and 60 secm respectively. The pretreated samples were characterized by AFM fixed in tapping mode to identify the changes in morphology, size and density of the catalyst films before they transformed into the RF-PECVD chamber for the synthesis process.

For growth of carbon nanostructures, we conducted three sequential experiments for all the three different pre-etching samples. While synthesizing , in all the three experiments, the substrate temperature, RF-power and time of deposition were kept at 700 °C, 500 W and 20 minutes respectively. The flow rates
of argon and methane were fixed at 20 sccm and 80 sccm respectively. Flow rates of argon and methane were maintained by mass flow controllers equipped with the chamber of RF-PECVD.

FE-SEM equipped with EDS investigated morphology, size and elemental analysis of carbon nanostructure samples. We used Raman spectroscopy for the structural analysis and identification of defects in the samples.

7.3 RESULTS AND DISCUSSION

Figure 7.1 represents the FE-SEM images of carbon nanostructures grown after three different pre-etching reactions. From figure 7.1 (a), it is observed that less density of the nucleation is seen in the 30 minutes pre-etching sample after PECVD process. It was also observed that most of the grown carbon nanostructures are islands in shape covered with amorphous carbon. The measured size of the carbon nanostructures is roughly around 300 to 350 nm. Whereas, comparatively high growth of carbon nanostructures was seen in the sample after 60 minutes pre-etching shown in figure 7.1 (b). Maximum area of the sample occupies near two-dimensional rod shaped carbon nanostructures with high lengths and low diameter compared to the carbon nanostructures grown after 30 minutes pre-etching sample. The measured length of the grown carbon nanostructures is around 200 nm and the diameter of the grown carbon nanostructures is around 100 nm respectively. It is also identified that the density, growth and orientation of the grown carbon nanostructures increases from 30 minutes to 60 minutes pre etching. Nevertheless, agglomerated growth of the carbon nanostructures is observed after 120 minutes pre-etching as shown from figure 7.1 (c).

The growth almost appears as foam covered with carbon that is more amorphous. The effect of pre-treatment on morphology, size and density of the catalyst films is described by the help of the data obtained from the AFM studies conducted in the tapping mode.
Fig. 7.1 FE-SEM images of carbon nanostructures grown on Si (100) substrates coated with 10 nm thick Fe-thin films (a) after 30 minutes pre-etching, (b) after 60 minutes pre-etching and (c) after 120 minutes respectively.

Figure 7.2 represents the AFM images of the Fe-catalyst films grown on Si substrates after pre-etching. From figure 7.2 (a), it is identified that there is no individual granules formation of the catalyst film seen after 30 minutes pre-treatment except very few irregular islands of catalyst film observed in the sample with a size of roughly about 250 to 300 nm.
Fig. 7.2 AFM images with corresponding line profiles of Fe-thin films deposited on Si (100) substrates with a thickness of 10 nm (a) after 30 minutes pre-etching, (b) after 60 minutes pre-treatment and (c) after 120 minutes respectively.

Whereas from figure 7.2 (b), the sample studied after 60 minutes pre-treatment under the same conditions of other parameters, a good activation behavior of the catalyst film is observed. It is seen that the catalyst film breaks into individual and small granules of size roughly about 100 nm in diameter. It can be explained in two ways; due to long time of pre-etching, density of high energetic Ar$^+$ ions and electrons in the plasma operates with a high frequency of (13.56 MHz) increases.
Mass of the electrons is very less compared to the heavy argon atoms and Ar\(^+\) ions. Therefore, this lighter electron attains high energy levels more easily than the heavier species and causes the secondary electrons.

Hence, it causes the bombardment of more number of Ar\(^+\) ions and electrons with high flux density, which in turn helps to increase the rate of etching and efficiency of the etching reaction. On the other side, due to long time pre-etching, there must be an increase of the substrate temperature because of long time etching process of high and concentrated ionic atmosphere. Nevertheless more dense and agglomerated type of granules growth were seen from the 120 pre-etching sample, as shown by figure 7.2 (c), it is identified that there is an increase in the size of the granules compared to the 60 minutes pre-etching sample, measured size of the granules is roughly about 200 nm. It is explained that, the time of reaction is double that of the previous reaction and hence, the above-mentioned two processes of the reaction effects the film even more time. Therefore, longer pre-treatment time brought about coalescence of the particles due to Ostwald ripening that resulted in the formation of the heavier granules. Perhaps, in this case, even though the time of pre-etching is so long (120 minutes), the size of the granule is less compared to the 30 minutes that represents that the granules in the 30 minutes sample are occupied with continuous layer like morphology.

In this work, we are trying to bring out the interrogation of the change in morphology, size, density, growth and crystalline nature of the grown carbon nano structures as a function of pre etching time. During the progression of this work to observe the above-mentioned changes, we have performed the high magnification scanning of the samples using FE-SEM. Figure 7.3 shows the high magnification FE-SEM images of the all the three samples.
Fig. 7.3 High magnification FE-SEM images of the carbon nanostructures grown on Si (100) substrates coated with Fe-film with a thickness of 10 nm (a) after 30 minutes pre-etching, (b) after 60 minutes pre-etching and (c) after 120 minutes pre-etching respectively.

It is believed that nanostructures grow by the decomposition of the carbonaceous gas on the surface of a catalyst granule. The carbon dissolves in the catalyst, diffuses through it, and exits to form the carbon nanostructure. In the case of the 30 minutes pre-etching sample the catalyst granules breaks into irregular island shaped structures as shown in figure 7.2 (a). The carbon nucleation takes place across the whole surface of the catalyst granule and hence resembles the shape, one can clearly see that from high magnification FE-SEM image shown in figure 7.3 (a). The presence of less dense island like carbon nanostructures other than the spherical structures is due to the uneven breaking of catalyst film during 30 minutes pre-etching. Whereas two-dimensional rod shaped carbon nanostructures were clearly observed from figure 7.3 (b) taken by high magnification mode of FE-SEM. The shape proportionate to the shape of the catalyst granule shown in figure 7.2 (b). Nevertheless, carbon foam like growth is observed in figure 7.3 (c) taken for 120 minutes pre-etching reveals the corrugation behavior of the catalyst granules.
observed from figure 7.2 (c). However, the change in the shape is most probably related to the dissolution, precipitation, and the saturation of the carbon into Fe. The less diameter growth of the two-dimensional rod shaped carbon structures (from figure 7.3 (b)) caused by the nucleation of the carbon nanostructures from sharp edged, less diameter catalyst granules as shown in figure 7.2 (b). Basically, there is a need of more number of carbon radicals to attain the saturation state and to extrude from the surface of the catalyst granule having large size.

Whereas the carbon nanostructures nucleates from the sharp edged granules precipitates and extrudes easily from the surface of the catalyst. This in turn supports the improvement in the length of the carbon nanostructures. Formation of large sized carbon nanostructures with poor growth behavior is observed from 30 minutes and 120 minutes pre etching sample. This is probably because the large catalyst granules serves like continuous catalyst thin film during the carbon nanostructures growth and as a result, produces a growth of large sized structures like that of the continuous film. This supports the linear growth behavior of the carbon nanostructures with catalyst granule size. Generally, the formation of more dense carbon nanostructures in long time pre-etching samples is due to the presence of dense catalyst granules.

A shell shaped carbon nanostructure is found during the ultra high magnification FE-SEM imaging in a particular region of the 60 minutes pre-etching sample after PE-CVD process is shown in figure 7.4. The grown carbon nanostructures appeared like a nanoshell shaped structures with a length of 100 nm and the diameter roughly about 70 to 80 nm. These carbon nanostructures are newly observed and their growth mode is yet to be understood.
Fig. 7.4 Ultra high magnification FE-SEM image of the novel shaped carbon nanostructures imaged from particular area of the 60 minutes pre-etching sample after RF-PECVD process.

To understand the effect of pre-etching on the chemical composition of the grown carbon nanostructures, we have performed EDS studies along with the high magnification FE-SEM experiments conducted for all the three samples (shown in figure 7.3). Probably high magnification is to avoid the low-resolution effect in the feedback and to maintain the weak sensitivity to the light elements. Figure 7.5 shows the EDS graphs of carbon nanostructures grown on Si substrate after three different pre-etching reactions.
Fig. 7.5 (a), (b) and (c) EDS graphs of Fe-catalyzed carbon nanostructures grown on Si (100) with catalyst thickness of 10 nm, pre-etching times of 30, 60 and 120 minutes respectively.

Table 7.1 (a), (b) and (c) shows the chemical composition of the carbon nanostructures grown on Si substrate after 30, 60 and 120 minutes pre-etching reactions respectively. From table 7.1 (b) one can clearly see the presence of high atomic and weight percentages of carbon that is observed from the 60 minutes pre-etching sample compared to the remaining two cases. It is known that the carbon nanostructures growth strongly depends on the formation of catalyst granule and enough granulation of catalyst film results in enhancement of carbon nanostructures growth [131]. This is because; carbon diffusion across metal particles is a rate-limiting step [132]. Carbon atoms formed by decomposition of hydro carbon gas such has methane used in the study dissolves into the metal particle. When super saturation of carbon in the metal occurs, the carbon atoms extruded from the particles and growth of the structures occurs. In the case of fine sized catalyst
granules after 60 minutes pre-etching, saturation process occurs very quickly than the other two cases. Insufficient or wider size formation of catalyst granule causes in saturation and slow precipitation of the carbon radical on the catalyst surface. This in turn causes the presence of amorphous carbon, excess of oxygen and iron content in the grown carbon nanostructures. From results shown in the tables 7.1 (a) and (c), one can clearly see the presence of more oxygen content after low and high pre-etching samples. Whereas, zero oxygen content is observed from 60 minutes pre-etching sample. This shows us the formation of oxidation content in the samples grown after less and long time pre-etching process.

Table 7.1 Elemental data of carbon nanostructures grown after 30 minutes pre-etching reaction.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
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<tbody>
<tr>
<td>C-K</td>
<td>06.52</td>
<td>13.62</td>
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<tr>
<td>O-K</td>
<td>05.35</td>
<td>08.38</td>
</tr>
<tr>
<td>Si-K</td>
<td>86.58</td>
<td>77.30</td>
</tr>
<tr>
<td>Fe-k</td>
<td>01.55</td>
<td>00.70</td>
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</table>

Table 7.2 Elemental data of carbon nanostructures grown after 60 minutes pre-etching reaction.

<table>
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<th>Element</th>
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</tr>
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<tr>
<td>C-K</td>
<td>92.69</td>
<td>98.04</td>
</tr>
<tr>
<td>Fe-K</td>
<td>05.98</td>
<td>01.36</td>
</tr>
<tr>
<td>Si-K</td>
<td>01.33</td>
<td>00.60</td>
</tr>
</tbody>
</table>
Table 7.3 Elemental data of carbon nanostructures grown after 120 minutes pre-etching reaction.

<table>
<thead>
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<th>Element</th>
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</tr>
</thead>
<tbody>
<tr>
<td>C-K</td>
<td>10.64</td>
<td>21.93</td>
</tr>
<tr>
<td>O-K</td>
<td>05.22</td>
<td>08.08</td>
</tr>
<tr>
<td>Fe-K</td>
<td>09.08</td>
<td>03.83</td>
</tr>
<tr>
<td>Si-K</td>
<td>75.06</td>
<td>66.16</td>
</tr>
</tbody>
</table>

Even though we studied, the crystalline nature and morphology of the grown carbon nanostructures with FE-SEM equipped with EDS, since carbon is a Raman active element, Raman spectroscopy is the useful nondestructive method for the structural analysis of different carbon materials [133]. Raman spectra taken on carbon nanostructures as shown in figure 7.6 are similar to those observed for CNTs. Figure 7.6 shows Raman spectra of carbon nanostructures grown after different pre-etching reactions (same samples as shown in figure 7.1). All the samples show a peak at 1321 cm\(^{-1}\) 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 [2×D]. The peak at 1576 cm\(^{-1}\) (g-band) is attributed to the vibration of sp\(^2\)-bonded carbon atoms in a two dimensional hexagonal lattice [110, 111]. From figure 7.6, it is observed that the ratio of \(I_D/I_G\) value is less for the structures grown after 60 minutes pre-etching reaction compared to the structures grown after 30 minutes and 120 minutes pre-etching reactions. This represents the presence of well-crystallized graphitic carbon in the sample grown after 60 minutes pre-etching. It is referred that the alignment of the carbon nanostructures on Si substrates grown in RF-PECVD process results from the influence of the electric field created by plasma also known as sheath [134]. It is also known that the electric field in the sheath is always preferred to direct towards sharp edged or fine sized surface catalyst particles, this helps the carbon radical to settle in alignment fashion during the growth of carbon nanostructures. It leads to the carbon species that dissolves,
saturates and then precipitates as graphite, as much as faster in the case of fine catalyzed particles after 60 minutes pre-etching than the other two cases.

Fig. 7.6 (a), (b) and (c) Raman Spectroscopy graphs of Fe-catalyzed carbon nanostructures grown on Si (100) with a catalyst thickness of 10 nm, pre-etching times of (a) 60 minutes, (b) 30 minutes and (c) 120 minutes respectively.

7.4 CONCLUSIONS

The paper reports the effect of pre-etching duration on the growth, morphology, size and elemental composition of the grown carbon nanostructures. Observation of more dense, less diameter and sharp edged catalyst granules after 60 minutes pre-etching using AFM is due to the bombardment of more concentrated high energetic Ar$^+$ ions, electrons and also due to the increment in temperature. Whereas presence of agglomerated growth after 120 minutes pre-etching brought about the coalescence of the granules due to Ostwald ripening. Increase in the growth density of carbon nanostructures after 60 minutes pre-etching shows the proportionality behavior between the catalyst granules and the growth of the carbon nanostructures. Sufficient decrease in the diameter of the Fe-catalyzed carbon nanostructures after 60 minutes pre-etching resembles the size of the catalyst
granules after 60 minutes pre-etching. Improvement in the length of the carbon nanostructures after 60 minutes pre-etching attributed to the fact that the nanostructures nucleates from the sharp edged granules precipitates and extrudes easily from the surface of the catalyst, this in turn represents the rate limiting behavior of carbon growth on the catalyst surface. The change observed in the morphology of the carbon nanostructures from island to rod and to foam like shapes from 30 to 60 minutes and to 120 minutes reveals the fact of dissolution, precipitation and saturation of carbon on iron catalyst. The good correspondence in structural and elemental analysis of the grown carbon nanostructures from both EDS and Raman spectroscopy for 30 to 60 and to 120 minutes pre-etching is related to the fact that in the fine sized catalyst granules after 60 minutes pre-etching, saturation occurs very quickly than the other two cases. Insufficient or wider size formation of the catalyst granules causes instauration and slow precipitation of the carbon radical on the catalyst surface; this in turn causes the presence of amorphous carbon, excess of oxygen in the grown carbon nanostructures. Observation of more defective behavior of the grown carbon nanostructures from Raman spectroscopy after 30 minutes and 120 minutes pre-etching compared to the 60 minutes pre-etching, which we correlated to the presence of more number of impurities from EDS analysis. Which, also supports the fact that the influence of electric field created by the plasma also known as the sheath in case of 60 minutes pre-etching. In addition, we also reported the growth of the nanoshell-like carbon nanostructures of which the growth mode is yet to be analyzed.