CHAPTER 4

LOW TEMPERATURE GROWTH OF CARBON NANOSTRUCTURES BY RF-PECVD

4.1 INTRODUCTION

Since the discovery of CNTs [77], these carbon nanostructures have attracted extensive attention due to their novel properties and potential applications such as high performing nanomaterials, high efficiency energy storage devices, coldfield emitters and their use in composite materials [78]. Many methods have been used for fabrication of carbon nanostructures, including arc discharge [79], pulsed laser deposition [80], thermal chemical vapor deposition [76], direct current [81], hot filament chemical vapor deposition and microwave chemical vapor deposition [82], 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. Consequently, one of the major hindrances in commercializing carbon nanostructure based applications is the high temperature for synthesis. In the RF-PECVD method, due to the radio frequency high (13.56 MHz) field the gases are ionized into electrons and ions. The lighter electrons are quickly accelerated to high energy levels compared to the heavier ions [83]. The high-energy electrons collide with the gas molecules resulting in dissociation and generation of reactive chemical species and the initiation of chemical reaction [84]. Consequently, the RF-PECVD offers us a technique to synthesize carbon-based nanostructures at significantly low temperatures compared to other techniques. It also allows us to accurately control source gas composition, pressure, flow rate and strength of applied RF power; factors which can influence the growth and morphology of carbon nanostructures [85]. This chapter deals about the low temperature synthesis of carbon
nanostructures and describes about the factors that influence the growth of carbon nanostructures.

4.2 EXPERIMENTAL DETAILS

The carbon nanostructures were grown by RF-PECVD, which offers control of various parameters as detailed previously [85]. In brief, the RF-electrode for the deposition chamber is a water-cooled electrode that carries RF power and gas. It is known that by adjusting the chamber pressure, the RF power, the RF voltage phase and the coil current we can control the plasma-coupling mode of the RF-PECVD. Based on these parameters we can generate either a capacitatively or an inductively coupled plasma. Though the complete elimination of the capacitative component ideally requires a Faraday’s shield, in this work we have been able to generate high-density inductively coupled plasma at low pressures [81].

A resistively heated stage was located 10 cm beneath the RF electrode. The temperature measurement and control is by means of digital PID controller with “K” type thermocouple. Inlet and outlet valves with swage lock type fittings are provided to feed the gas into the chamber during the process. The silicon (100) wafer was taken and thoroughly cleaned with acetone, distilled water, and then dried in air. The silicon substrate was transferred into the RF-PECVD chamber and the chamber pumped down to a vacuum of 10^{-5} mbar. The vacuum was created by using a rotary vane pump and an oil diffusion pump. Argon plasma was created inside the chamber using power from the RF source working at 13.56 MHz and 150W. Argon plasma at a pressure of 3×10^{-3} mbar was used to pre-treat the wafer. After 15 minutes of pretreatment, methane gas was passed into the chamber. Separate mass flow controllers were used for methane and argon gases. The flow rates of methane and argon were fixed at 16.4 sccm and 14 sccm, respectively. The process was carried out for 20 minutes at a substrate temperature of (< 300 °C). The morphology of carbon nanostructures was investigated by AFM and SEM. Elemental analysis of the samples was carried out by EDS equipped with SEM.
4.3 RESULTS AND DISCUSSION

It has been known that use of inductively coupled plasma in RF-PECVD tends to favor the growth of carbon nanostructures over carbon nanotubes, especially two-dimensional nanosheet-like structures. This has predominantly been attributed to the plasma density of the inductively coupled plasma process, which provides higher concentration of activated carbon species and produces a larger electric field, which in turn enhances the field-induced surface species migration. It has been noted that the plasma density of the inductive plasma is 10 times higher as compared to the capacitatively coupled plasma even though the gas pressure is lower as a result of the much higher fractional ionization rate [86]. Carbon nanosheets have been deposited under a variety of conditions without the need for any specific catalysts or preference to a particular substrate. Despite the ease of fabrication of carbon nanosheets, it has proved impossible to synthesize carbon nanosheets at temperatures less than 600 °C [81]. This work presents the synthesis of carbon nanosheets along with other carbon nanostructures at a significantly lower synthesis temperature.

Figure 4.1 shows SEM images of various carbon nanostructures grown on the silicon substrate. The images show the formation of irregular two-dimensional nanosheet-like structures on the substrate. Though the grown nanostructures were not uniform in shape and size, it was observed that along with the carbon nanosheets there is also a growth of one-dimensional carbon nanostructures. Typical nanosheets measure 1–2 μm in length and are seen growing parallel to the substrate surface. It was also observed that the edges of the nanosheet appear to grow vertically as can be deduced from the relative brightness in the image. The thickness of the edges is estimated to be around 100 nm, and the edges appear to have a graphene layer-like morphology. It has been noted that, in the growth of carbon nanosheets, the sheet size generally decreases with an increase in methane concentration due to the formation of large number of nucleation sites [81].
Further, the substrate temperature is known to play a very important role in the growth of carbon nanosheets. Typically, nanosheets are found as dense, free-standing structures at higher temperatures. Our samples show a predominant horizontal growth of irregular nanosheets. This may be attributed to the low synthesis temperature, which leads to reduced nucleation and growth. Though, the exact growth dynamics of the nanosheet structure is still under research, it is believed that that higher methane concentrations and substrate temperatures offer more carbon species or the driving force for nanosheet growth. The reduction in one or both of these factors as in our case leads to the formation of a horizontal nanosheet. As mentioned earlier, it can be inferred from the SEM images that the edges of the nanosheet appear to show some sort of vertical growth, and it can be concluded that upon change in reaction parameter the growth mode may favor horizontal or vertical deposition. It is also understood that, when coating thin films, the availability of the carbon species and the interactions between carbon-carbon species and carbon-silicon play vital roles in deciding the morphology and the growth mode of the thin film. It has also been proposed that the high flux of high-energy electrons and ion bombardment associated with the inductively coupled RF plasma would yield growth along the strongly bonded planes of the graphene sheet-like structures [81]. The process of growth is explained based on the fact that in inductively coupled plasmas the primary coupling force is the RF magnetic field. Hence, the induced electric field in the plasma region is usually non-conservative. This property, which is the primary distinction between inductively coupled plasma and capacitatively coupled plasma, has a conservative, irrotational electrical field that allows the charged particles to gain time average energy from the field without collisions. This allows the carbon to grow in a crystalline, but defective graphitic structure leading to formation of nanosheets. This can be confirmed by XRD of the nanosheet samples, as discussed in detail in [87]. The XRD shows typical reflections of (002), (004) and (101), confirming the defective graphitic structure of the nanosheets. Though the nanosheets were reliably synthesized at low temperatures, along with the nanosheets there are one-dimensional spherical nanoparticles having diameter around 140 nm.
Fig. 4.1 (a) & (b) SEM images of different type of carbon nanostructures grown on Si substrate in RF-PECVD process. (c) SEM image of spherical carbon nanostructures with diameters ranging between 76 – 140 nm. It also shows that the length of the carbon nanosheet-like structure is around 1μm. (d) SEM image of carbon nanosheet-like structures with length roughly around 0.5 – 1μm.

Figure 4.2 shows the AFM images of the carbon nanostructures grown using the inductively coupled RF-PECVD plasma. It can be seen that the nanoparticles grow around the nanosheet structures. This may be caused due to a marginal capacitative component of the plasma [86] or could be the presence of other amorphous carbon impurities.
Fig. 4.2 (a) & (b) AFM images of carbon nanostructures grown on Si substrate.

Figure 4.3 shows the AFM line profiles of carbon nanostructures. The nanoparticles are measured to be around 125 nm, which is in good correspondence to the SEM images.
Fig. 4.3 (a) & (b) AFM images of carbon nanostructures with line profiles. The diameters were seen to be 110 nm and 150 nm, respectively.

The image in figure 4.4 shows a novel morphology of carbon nanostructures found on the silicon substrate and its line profile. A nanoellipse-like structure is visible, which resembles a seed. These structures were concentrated on a particular region of the wafer. These carbon nanostructures are newly found, and their growth mode is yet to be understood. These nanostructures measure approximately 115 nm in diameter. The nonselective nature and flexible growth conditions of nanosheet growth give carbon nanosheets great potential for a number of applications.
Fig. 4.4 AFM image with corresponding line profile showing diameter of the nano ellipse to be around 115 nm.

It is well known that the surface morphology of the carbon nanostructures is important with respect to tribological applications. The three-dimensional AFM images shown in figure 4.5 show the growth of the nanosheets and the height histograms of the samples. The measured height histograms of the samples are roughly around 0.130 nm consistently, this represents that the carbon nanosheet-like structures grown on the Si substrates are having better smooth surfaces.

Fig. 4.5 (a) & (b) Three-dimensional AFM images of carbon nanostructure.

Figure 4.6 shows the EDS analysis for carbon nanostructures. A small peak indicating the presence of carbon can be seen in the presence of the more dominant
substrate peak. Table 4.1 shows the elemental data of carbon nanostructures present in sample.

Fig. 4.6 EDS analysis of the carbon nanostructures grown on silicon.

Table 4.1 Elemental data of carbon nanostructures present in the sample.

<table>
<thead>
<tr>
<th>Element Line</th>
<th>Net Counts</th>
<th>Weight %</th>
<th>Atom %</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-K</td>
<td>62</td>
<td>3.80</td>
<td>06.04</td>
<td>C</td>
</tr>
<tr>
<td>O-K</td>
<td>0</td>
<td>55.97</td>
<td>62.64</td>
<td></td>
</tr>
<tr>
<td>Si-K</td>
<td>32584</td>
<td>40.23</td>
<td>31.32</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.00</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
4.4 CONCLUSIONS

A variety of carbon nanostructures including nanosheet-like structures and nanoparticles were synthesized at a very low synthesis temperature. The morphology of the nanosheets and their growth mode were discussed. The reduction in synthesis temperature was found to affect the growth direction of the nanosheet and favor the growth of nanoparticles and other nanostructures along with carbon nanosheets. The inductive coupled plasma of the RF-PECVD proved to be a powerful method for the synthesis of carbon nanostructures at low temperatures (< 300 °C). Also reported were the presence of novel, elliptical carbon nanostructures concentrated on one corner of the substrate. Also, the good uniformity of nanosheets as indicated by the RMS roughness histograms indicated that carbon nanosheets may find potential tribological applications as thin film coatings.