CHAPTER 5

MAGNETIC PROPERTIES OF CARBON NANOSHEETS

5 INTRODUCTION

Carbon allotropes show a variety of magnetic properties ranging from diamagnetism [88] to ferromagnetism [89] and exhibit magnetic susceptibility in the range of $\chi = (10^{-4} - 10^{-7})$ emu/g, which indicates a diamagnetic nature. Exceptions to this include a variety of carbon nanostructures, such as amorphous carbon, activated carbon fibres, single-wall carbon nanohorns, nanoscale carbon tori and charred anthracenes [90]. Although the origin of this type of anomalous low magnetisation (compared to typical ferromagnetic materials) of organic materials has been assumed to be the result of magnetic impurities, recent studies have indicated that some organic materials exhibit low magnetisation as an intrinsic property due to a number of factors, such as the ferromagnetic interaction of spins [91] or the presence of defects [89]. Recently, soft X-ray dichroism experiments have proved beyond doubt that carbon’s ability to order magnetically is not related to the presence of the impurities in the sample [92]. In other reported cases, the carbon-based materials contain less than 0.1% iron, whereas the measured magnetisation values exceed the value expected from impurities by several times, even when it is assumed that all iron present is ferromagnetic. Absence of a correlation between magnetic properties and impurity content was found in a number of carbon nanostructures, including highly oriented pyrolytic graphite [89], suggesting an intrinsic ferromagnetic signal.

Magnetisation values more than an order of magnitude larger than the expected saturated magnetisation due to any possible transition metal impurity were reported for activated mesocarbon micro beads composed of micro graphite crystallites, glassy carbon, carbon nanoparticles and carbon nanofoam [93].
Carbon nanosheets are 2-D graphite structures, characterized by their nanoscale thickness (few nm) and open geometry (open non-connected edges leading to the presence of edge inherited non-bonding states), are an allotrope of carbon which has attracted significant attention since its discovery [81]. Carbon nanosheets have been synthesized using RF-PECVD reliably on a variety of substrates and under a wide range of reaction parameters. Carbon nanosheets have shown potential applications in fuel cells, protective coatings and microelectronic technologies. While the magnetic properties of other carbon allotropes, such as fullerenes, nanohorns, nanotubes and nanofibres, have been widely studied, the properties of the 2-D nanosheet remain unexplored. It is known that the use of inductively coupled plasma in RF-PECVD tends to favor the growth of carbon nanosheets over CNTs. This has 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 that, in turn, enhances the field-induced surface species migration [94].

The present chapter discusses about the growth of carbon nanosheet-like structures on silicon substrates at varying reaction times. The structural and magnetic properties of the nanosheets are explored, with emphasis on the latter. The exhibited magnetisation is discussed based on the structural characteristics, intrinsic properties and defect formation.

2 EXPERIMENTAL PROCEDURE

In brief, the RF electrode for the deposition chamber contained the input valves for the feedstock and reaction gases. By adjusting the chamber pressure, RF power, RF voltage phase and coil current, the plasma-coupling mode of the RF-PECVD can be controlled. Inductively coupled plasma was preferred for the experiment as it favors the growth of carbon nanosheets. A resistively heated stage was located 10 cm beneath the RF electrode.
The temperature was measured and controlled by a digital PID controller with a “K” type thermocouple. Inlet and outlet valves with swage-lock fittings were provided to feed the gas into the chamber during the process.

The silicon substrates (1 × 1 cm) were cleaned using acetone, distilled water in an ultrasonic bath, and then dried in a vacuum. The silicon substrates were then transferred into the RF-PECVD chamber and the chamber was pumped down to a vacuum of 10⁻⁵ mbar. Argon plasma was created inside the chamber using power from the RF source working at 13.56 MHz and 150 W. Argon plasma at a pressure of 3 × 10⁻³ mbar and a substrate temperature of 200 °C was used to pre-treat the wafer to outgas the impurities in the substrates. After 15 minutes of pre-treatment, 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 15 and 12.2 sccm, respectively. The process was carried out for 30, 60 and 120 minutes at a stable substrate temperature of 350 °C. Morphology of the nanosheet samples was observed using an AFM. All images were taken in contact mode using silicon cantilevers with force constants of 0.02 – 0.77 Nm⁻¹ and tip heights 10 – 15 μm. FE-SEM was used to study the growth and topographic features of carbon nanosheets. The phase purity of the nanosheet samples was analyzed using a Panalytical XRD. XRD was carried out in grazing angle geometry, with the incident beam fixed at ω = 1.8° (30 minutes sample), 2.0° (60 minutes sample) and 2.2° (120 minutes sample) while the detector was scanned. These incident angles were found to best attenuate diffraction from the substrate. Field-dependent magnetisation of the nanosheet samples was studied using a VSM. The sample masses were calculated by measuring the samples before and after analysis using a high precision weighing machine. Raman spectroscopy was used to explore the hybridization states of the sample exhibiting ferromagnetism. The impurity content in the samples was analyzed using an Oxford EDS and AAS with a hollow cathode lamp. In AAS, absorbance measurements were made at the Cu principle line at 325 nm and at an alternative 328 nm.
The band pass was set to 0.8 nm and the lamp current at 3 mA. The air flow rate was 2 l min\(^{-1}\) and the acetylene flow rate was 0.8 l min\(^{-1}\).

5.3 RESULTS AND DISCUSSION

AFM images of the samples for deposition times of 30, 60 and 120 minutes are shown in figures 5.1 (a-c), respectively.

Fig. 5.1 (a-c) AFM images of the samples for deposition times 30, 60 and 120 minutes respectively. Diameter of the sheets is roughly around 100 to 120 nm, and length is about 2 µm.

The images show the formation of irregular two-dimensional nanosheet-like structures on the substrate. Though the grown nanosheets were not uniform in shape and size, it was observed that the nanosheets had predominantly grown parallel to the substrate. Typical nanosheets measured 500 nm in length. Furthermore, the AFM images show the presence of cracks or deformations in the surface of the carbon nanosheets. In addition, the density of defects per unit area increased with
increasing deposition time. It was also observed that the edges of the nanosheets appeared to grow vertically at the edges, as can be deduced from the relative brightness in the SEM images (figures 5.2 (a-c)).

Fig. 5.2 (a-c) FE-SEM images of the samples for deposition times 30, 60 and 120 minutes respectively. Diameter of the sheets is roughly around 100 to 120 nm and length is about 2 μm.

Grazing angle XRD spectra of the carbon nanosheet samples are shown in figure 5.3. The characteristic peak (2θ) observed at ~ 22.45° can be assigned to the (002) reflection of graphite [95]. The substrate peak can be observed at 2θ ~ 55.86°, which corresponds to the (311) phase of crystalline silicon [96]. Furthermore, it can also be observed that there is an increase in the intensity C (002) peak with increasing deposition time as a result of increased carbon content in the film. Peak narrowing was also noticeable with increasing deposition time, indicating that the graphite formed in the later stages tended to be crystalline in nature. This increase in crystallinity with time can be attributed to the increase in
long-range inter atomic forces between the carbon atoms already deposited on the substrate and the upcoming carbon radicals causes more number of carbon radicals to draw towards already deposited carbon leading to an increase in the vertical periodic arrangement in the new nanosheets and resulting in a more crystalline phase compared to the shorter deposition times.

![Graph of XRD spectra](image)

Fig. 5.3 The grazing angle XRD spectra of the carbon nanosheet samples. The characteristic peak ($2\theta$) observed at $\sim 22.45^\circ$ can be assigned to the (002) reflection of graphite. The substrate peak can be observed at $2\theta \sim 55.86^\circ$, which corresponds to the (311) phase of crystalline silicon.

The VSM was calibrated using a nickel sphere and gadolinium oxide powder, and the resolution of the VSM was established to be about $1 \times 10^{-7}$ emu. Figure 5.4 shows the magnetisation curves of the nanosheet samples at 300 K. Data analysis was done after subtracting the substrate and holder offset. The carbon nanosheet samples with deposition times of 30 and 60 minutes exhibited conventional diamagnetic behavior common to most carbon allotropes. On the other hand, the sample with a deposition time of 120 minutes exhibited ferromagnetic behavior, as can be seen in the hysteresis loop. This indicated that carbon nanosheets exhibit ferromagnetism, as is the case for amorphous carbon prepared by pyrolysis.
The magnetisation of carbon nanosheet samples, measured at a field of 10 kOe, was 0.36 G. Furthermore, the sample mass for the 120 minutes deposition was calculated to be 0.004 g.

![Graph showing magnetic hysteresis spectra](image)

Fig. 5.4 Magnetic hysteresis spectra for carbon nanosheets with deposition times of (a) 30 minutes (b) 60 minutes and (c) 120 minutes.

The amount of ferromagnetic mass in the sample is unknown and, hence, the magnetisation of the sample cannot be quantified with respect to its mass or volume. As mentioned previously, the ferromagnetic properties of carbon-based materials are assumed to be due to the presence of impurities; therefore, it is essential to verify that the samples are free of all impurities. EDS was used to analyze the composition of the samples containing carbon nanosheets. Figures 5.5 (a-c) shows the EDS curve of all three-carbon nanosheet samples and the clear presence of silicon and carbon (with varying intensity). The impurity content of the samples was also verified using atomic absorption spectroscopy and the results are
tabulated in table 5.1. The nickel and chromium content of the sample was 15 ppm, while the iron content was less than 10 ppm.

![Graphs showing EDS analysis of carbon nanosheet like structures grown at three different time depositions (a) 30, (b) 60, (c) 120 minutes.]

Fig. 5.5 EDS analysis of carbon nanosheet like structures grown at three different time depositions (a) 30, (b) 60, (c) 120 minutes.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt%) – 30 min</td>
<td>&lt;0.001%</td>
<td>0.002%</td>
<td>0.003%</td>
</tr>
<tr>
<td>Content (wt%) – 60 min</td>
<td>&lt;0.001%</td>
<td>0.003%</td>
<td>0.004%</td>
</tr>
<tr>
<td>Content (wt%) – 120 min</td>
<td>&lt;0.002%</td>
<td>0.002%</td>
<td>0.004%</td>
</tr>
</tbody>
</table>

Table 5.1 Impurity analysis by AAS.

This presence of impurities could have arisen from the use of stainless steel tweezers for handling the samples. Concerning the influence of impurities on the magnetisation of the sample, is it known that the magnetisation of Fe – Cr or Fe – Ni alloys or CrO₂ is much smaller than that of pure iron. Even if the content of the
sample were assumed to be pure iron, the magnetisation contribution of the impurities can be calculated to be $\sim 0.017$ G, while the magnetisation of the sample indicates a saturation magnetisation of $0.36$ G, which is far greater than that attributable to the presence of impurities in the sample. Also, as can be seen for impurity data from the AAS results, the 60 minutes sample displayed a higher content of magnetic impurities compared to the 120 minutes sample and yet exhibited clear diamagnetism. This indicates that the magnetism exhibited by the 120 minutes sample is not due to the presence of impurities. It is obvious that AAS and EDS may not be ideal methods for characterizations of carbon-based magnetism, especially since it cannot resolve the hydrogen content of the sample, where the presence of hydrogen has been shown to influence the magnetic properties of carbon-based materials [97]. Nonetheless, in this case, the magnetisation exhibited by the carbon nanosheets was sufficient to indicate the existence of some intrinsic magnetic order. Thus, an alternative explanation for the source of magnetism in carbon allotropes was required. Other theories for the origin of magnetism in carbon include the presence of defects in the structure and magnetism induced by spin-polarized charge transfer [97, 98]. The presence of defects in carbon materials may be estimated using Raman spectroscopy. Thus, the nanosheet samples were characterized by Raman spectrometer. Figure 5.6 shows the Raman spectra of the 30, 60 and 120 minutes samples. It is known that the Raman spectrum of diamond ($sp^3$ hybridization) exhibits a sharp peak at 1322 cm$^{-1}$ and graphite shows a sharp peak at 1588 cm$^{-1}$ ($sp^2$ hybridization) [75]. These are designated the D and G peak, respectively [99].

Note that in the 120 minutes sample, the $I_G/I_D$ ratio is significantly higher than expected from nanosheet-like carbon structures [81]. The 30 and 60 minutes sample show Raman spectra typical of carbon nanosheets with low graphitization and a ratio almost equal to 1, similar to those exhibited by diamond-like carbon films. In contrast, the 120 minutes sample exhibits very high graphitization compared to the samples, with a ratio equal to 2.7. This increase in graphitization ($I_G$) is known to lead to an increase in edge-inherited non-bonding $\pi$ electronic
states (edge states) in addition to the \( \pi \) and \( \pi^* \) bands [93, 100]. This, in turn, leads to an increase in non-bonded \( \pi \) electrons, which are a major source of magnetism in materials.

Fig. 5.6 Raman spectroscopy of carbon nanostructures grown at three different time depositions (a) 30, (b) 60, (c) 120 minutes.

Furthermore, the increase in disorder leading to \( sp^2 \) hybridization of carbon is the origin of dangling bonds, which have an intrinsic magnetic moment [100]. Hence, it can be postulated that these defects are the source of the magnetism exhibited by the sample. It is possible that the sample may contain a small quantity of hydrogen, given the fact that the synthesis procedure involves the break-up of methane molecules. During this process, it is possible that either smaller
hydrocarbons or hydrogen itself will be trapped in the carbon structures. The presence of such adsorbed or trapped hydrogen molecules may also result in magnetism. Further research is currently underway to estimate the presence and influence of hydrogen in the sample.

54 CONCLUSIONS

Carbon nanosheets have been fabricated using RF-PECVD and their structural and magnetic properties studied. AFM, SEM and XRD were used to characterize the formation and nature of carbon nanosheets. VSM analysis of the samples indicated that the sample with a 120 minutes deposition time exhibited ferromagnetism at room temperature. The influence of trace impurities was eliminated by EDS analysis. Further analysis by Raman spectroscopy on the ferromagnetic sample indicated that the magnetism may arise from an increase in number of non-bonded π electrons due to increased graphitization and defect density. As the synthesis procedure of carbon nanosheets is reliable and repeatable, this process could be used to reliably fabricate magnetic carbon nanostructures.