Chapter 1

INTRODUCTION

1.1 Carbon

While carbon lies in the same periodic group as silicon and germanium, carbon possesses very different chemical properties. Carbon has a unique property, in that its outer shells electrons can hybridize in three ways producing sp$^3$, sp$^2$ and sp$^1$ type bonds. Diamond, being tetrahedral in structure, has strong sp$^3$-type bonds. Graphite, on the other hand, is a crystalline form of sp$^2$ bonded carbon with a planar-type trigonal structure and has much weaker bonds between the graphite sheets. A range of carbon materials exist, the properties of which depend not only on the sp$^3$/sp$^2$ bonding ratio but also on the crystallite size. For example, evaporated carbon (a-C) and glassy carbon are primarily sp$^2$ bonded, with glassy carbon consisting of graphite-like ribbons. Tetrahedral amorphous carbon (ta-C) is an amorphous form of mainly sp$^3$ bonded material. ta-C is sometimes known as amorphous diamond. Diamondlike carbon (DLC) has a mixture of sp$^2$ and sp$^3$ type bonds, and has similar structural and electrical properties as diamond. Another form of sp$^3$ bonded carbon structure is nanocrystalline diamond. Like graphite, crystal size determines the properties of the sp$^3$ bonded carbon.

Various sp$^3$ structures will be studied here. Diamond, with its large band gap and high thermal conductivity, is the subject of most interest due to its possibility of being produced as electronic devices. Another form of sp$^3$ carbon is the much studied carbon nitride C$_3$N$_4$. This material has been predicted as having a hardness comparable to diamond. C$_3$N$_4$ is also metastable and so, a proper study on the various forms of (CN)$_x$ is essential to the understanding of the C$_3$N$_4$ structure. A third form of sp$^3$ structure to be studied here is the formation of nanocrystalline diamond through Ostwald ripening.

1.1.1 Diamond

The different types of bondings lead to very different properties in the various forms of carbon. Table 1.1 lists the differences in some of the properties found in sp$^2$ and sp$^3$ structures, together with those Si and Ge of the same chemical group as carbon. Diamond is the hardest known mate-
<table>
<thead>
<tr>
<th>Property</th>
<th>Graphite</th>
<th>Diamond</th>
<th>Silicon</th>
<th>Germanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>2.46</td>
<td>6.71</td>
<td>3.57</td>
<td>5.43</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.26</td>
<td>3.52</td>
<td>2.33</td>
<td>5.32</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>-0.04</td>
<td>5.47</td>
<td>1.11</td>
<td>0.67</td>
</tr>
<tr>
<td>Debye temperature (K)</td>
<td>2500</td>
<td>950</td>
<td>1860</td>
<td>645</td>
</tr>
<tr>
<td>Thermal conductivity (W/cm.K)</td>
<td>30</td>
<td>0.06</td>
<td>25</td>
<td>1.24</td>
</tr>
<tr>
<td>Electron mobility (10(^{13}) cm²/V.s)</td>
<td>20</td>
<td>0.1</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Hole mobility (10(^{13}) cm²/V.s)</td>
<td>15</td>
<td>0.09</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>3</td>
<td>5</td>
<td>5.58</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Table 1.1: Some properties of carbon, silicon (Si) and germanium (Ge) taken at room temperature.

Due to its other extreme properties (see Table 1.1), diamond also has a high potential for use in electronic, optical and mechanical devices. Diamond is commonly used as cutting/polishing medium due to its hardness and strength. Ultra-thin and ultra-strong diamond windows have been produced for many uses due to its transparency, strength and high thermal conductivity. By itself, diamond is a poor electrical conductor due to the large band gap between the valence and conduction bands. However, diamond, being in the same group as Si and Ge, offers the possibilities of semiconducting devices. Boron has been proven to be a substitutional p-type dopant in diamond with an acceptor level of 0.37eV above the diamond valence band. On the other hand, N-type doping has yet to be truly achieved. To produce a diamond based electronic component, controlled doping of diamond is essential.

The conventional method of diffusion of dopants is too slow in diamond to be considered for practical doping method. Ion implantation is a better choice due to its ability for precise dopant concentration and spatial control and the ability to overcome the strength of the superhard matrix. However, ion implantation into diamond causes much damage to the sp³ bonds. Diamond being metastable (graphite is the stable form of carbon), even at room temperature, graphitizes or amorphizes easily when the bonds are damaged or broken. However, this damage can be annealed out, if the annealing temperature and the damage level are kept below a critical value. It is of interest, therefore, to study on a microstructural scale the transformation from diamond to graphite/amorphous carbon.

Normal ion implantation energies are in the 10’s and 100’s keV range. Within this range, the damage can be severe and graphitization will occur if the dosage used is high. Please note that from here onwards, graphitization is the term used for the formation of planes of aromatic carbon in
hexagonal rings and not for the stacking of planes in the c-axis in the formation of graphite which requires high annealing temperature (2000°C). However, if a higher energy range is used, ie in the MeV range, the doped or end-of-range damage region will be buried under a relatively undamaged diamond cap. The damage in the cap region will almost fully recrystallize on annealing. Thus the MeV ion implantation method provides a method of producing deeply buried doped layers in diamond for electronic devices. Techniques have been developed to allow the diamond cap layer to be lifted off and the end-of-range and cap regions can be studied in detail, thus elucidating the structural changes induced by MeV implantation.

1.1.2 Carbon Nitride

Another sp³ structure that is of current interest is C₃N₄. The main attraction to this elusive material is its hardness which had been predicted to be comparable to that of diamond. Many methods have been used to synthesize this material and it is found that carbon nitride is metastable and can exists in various structures. Therefore, carbon in sp³ and sp² form can be found simultaneously in the films. The common observation is that the deposited (CN)ₓ films are spatially inhomogeneous. Evidence of such structures can only be found on average at a micron scale.

1.1.3 Nanocrystalline Diamond

Annealing of quartz or sapphire implanted with high doses of carbon results in the formation of precipitates or nanoclusters of carbon. This is based on Ostwald ripening theory. High energy implantation is required such that the carbon ions are buried under high pressure due to the top matrix layer. High doses of carbon have to be implanted into the matrix in order for there to be a sufficiently large carbon concentration which will lead to precipitation of the nanoclusters upon annealing. This method has been used successfully on many other types of ions, for example Si and Ni. Because the clusters are of the nano scale, microanalysis studies are important. Because carbon can bond either in sp² or sp³ forms, there is a competition between the formation of graphitic and diamond nanoclusters, which will be investigated here.

1.2 Aim of Thesis

This thesis addresses three materials fabrication issues, which are all connected with the sp²-sp³ relationship in carbon. All three cases involve spatial inhomogeneity on the sub-micron scale. There is a need to study on atomic scale the properties of irradiated diamond to understand its microstructure as influenced by irradiation as no such previously known studies has performed. Due to the inhomogeneity nature of (CN)ₓ films, atomic level studies on the films will help characterize the carbon properties better. Formation of nanocrystalline diamond in a matrix will of
course also require microanalysis studies on the structures of the formed nanoclusters, whether the nanoclusters formed will be sp² or sp³ bonded.

To summarize, the aims of this thesis are to investigate the following:

- the properties and behaviour of ion irradiated type IIa diamond on a micron scale with a view to understand better the defect structures and their behaviour which will be crucial in optimizing the doping of diamond by ion implantation
- the possibility of creation of ion tracks due to ion irradiation and the possibility of such tracks taking part in electrical conductivity
- the possibility of using the lift-off technique instead of the conventional ion-beam thinning method (which tends to produce surface structural defects) to produce thin films for TEM analysis
- the structural properties of \((\text{CN})_x\) films and the composition variation of C:N with varying irradiation conditions to optimize the probability of achieving a higher percentage of N content
- the properties of carbon implanted quartz and the possibility of the growth of nano-crystalline diamond when annealed

In the following chapters, the various types of analysis and their respective results on each of the carbon material mentioned previously will be presented fully. A detailed discussion on each technique will also be presented. Investigation of the irradiated diamond is presented in Chapter 2. Main techniques used in this study are electron spin resonance (ESR), Raman, transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). In Chapter 3, the detailed analysis of \((\text{CN})_x\) using methods such as rutherford backscattering spectroscopy RBS, Auger spectroscopy (AES), Raman, TEM and EELS will be presented. Results from the study of formation of carbon nanoclusters in quartz will be presented in Chapter 4. A correlation and/or discrepancy between the results obtained using the various methods will also be discussed in both the chapters. A general overview or conclusion of these two materials will then be given in Chapter 5. The results from studies on the carbon irradiated quartz and the possibility of the formation of diamond nanoclusters will be presented. A microstructural study of Ti/diamond abraded systems in the view of influences on growth of CVD diamond films by Ti is presented in Appendix A. The microstructural behaviour of single-crystalline and polycrystalline diamond under similar irradiation conditions will be compared and some previously studied results on CVD diamond films will also be presented in Appendix A. Some of the results obtained will be presented in each chapter, while most of the remaining results, especially the diffraction patterns and the fitted spectra will be presented in the Appendix B.

Much less would have been achieved without the technical assistances that were given by various
people even though all the collected data were analyzed by myself. Firstly, implantation of 320keV ions into the diamond windows were performed with the help of Prof Rafi Kalish at Technion, Israel. The ESR measurements were performed by Chris Noble of University of Monash while the AES measurements were performed by Dr Steven Johnson of RMIT. The Raman spectra were all collected under the supervision of Dr Kerry Nugent. The deposition of the (CN)$_x$ films could not have been achieved without the help of Dr Val Gurarie. High energy implantation of the He$^{++}$ particles into diamond together with the collection of RBS and PIXE data using the Pelletron nuclear microprobe accelerator were performed with assistance from Dr Andrew Saint and Mr Roland Syzmanski. I am also grateful to Julius Orwa for his contribution of C irradiated quartz samples for the study of nano-crystalline diamond.
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