Chapter 3

Thermal evolution of defects in self ion irradiated Highly Oriented Pyrolytic Graphite

The investigation of the defect kinetics in 200 keV C$^+$ ion implanted highly oriented pyrolitic graphite (HOPG) is presented in this chapter. The thermal evolution of implantation induced defects is probed using three techniques sensitive at different depth levels. The dependence of the defect annealing on the implantation dose is brought out by implanting HOPG at two doses – $10^{14}$ & $10^{15}$ ions/cm$^2$, the higher one close to creating amorphisation near the projected range. The topography of the sample as seen by Atom force microscope (AFM) becomes highly ridged for higher dose implantation. The ridged surface is considered to be due to basal plane fragmentation followed by bending and curling of the surface sheets along the preferred/random directions depending on the damage produced. Defect recovery at near surface region has a small effect on surface topography with curvilinear ridges showing highly intricate network after annealing. The defect annealing mechanism at the near-surface region probed by Raman spectroscopy shows a fast and a slow process for both the doses; however difference among two doses lies in the recovery of the FWHM of the G-band. The slow positron beam spectroscopy shows vacancy recovery from 373 K and a clear movement of open volume defect towards surface by 623 K for lower dose sample. A particular defect type becomes visible in higher dose sample after annealing up to 523 K near the end of implantation range. This remains stable till 673 K showing a surface bound movement only at 723 K. Complete defect recovery also leads to a modified structure consisting of cross linking inter layer interstitial clusters at the projected range. This is brought to light by a lower than bulk S-parameter for the recovered region.
3.1 Introduction

Defect study in carbon allotropic materials is an area which has seen large amount of investigations owing to their importance to the industry and to the basic understanding of solids. Among the various carbon allotropes, graphite and diamond are often used as model materials and the inferences obtained from them are extended to their more exotic forms. For example graphite is a prototype for $sp^2$ hybridized group and for structures which show a layered nature. Graphite has been used extensively in the nuclear industry and is among the proposed materials for plasma facing wall of fusion reactors. This is because of its excellent high temperature properties (like high melting point and thermal shock resistance), low activity after neutron exposure and low Z [1]. This in turn has fuelled extensive research on defects in graphite to understand and control the after effects of radiation damage. Property changes like basal plane contraction, the $c$-axis expansion, the Wigner energy release, and the changes in electrical and thermal conductivity limit their long term use [2, 3]. Ion or electron beam induced structural transformations and phase transformations in graphitic materials are another area which drives the defect research industry. There has been demonstration of irradiation induced transformation of graphitic forms to diamond [4, 5], welding of Carbon nano-tubes with electron irradiation and formation of carbon onion structures [6]. The recent discovery of defect induced magnetism [7] and suggestions of doping/defect induced room temperature (RT) superconductivity in graphite [8, 9] has attracted the interest of basic physics fraternity as well. Ion beam based patterning of graphite surface is a major research area which seeks to understand and utilize the arrangement of defects on graphite surface as it is a common substrate for the growth of nanostructures and for various microscopic techniques [10, 11]. By extending the knowledge obtained about the
nature of defects on graphite surface, the electronic interaction of defects in 2D-graphene plane with electrons are now understood and are predicted to be magnetic [12].

In spite of all the effort over past five decades, the nature, formation, migration and interaction of even simple point defects like vacancies and interstitials in graphite remain sketchy. This is largely due to the highly anisotropic nature where different behaviour dominates parallel to the $c$-axis and that along the basal plane. Theoretical studies have predicted number of possible defect structures to explain the experimentally observed property changes and measured migration energies. To highlight one such discrepancy; the measured migration energy is $\sim 3.1$ eV for mono vacancies whereas the theoretically predicted value is $\sim 1.7$ eV [3]. The experimental investigations of defects in graphite has depended on Raman spectroscopy, Transmission electron microscopy (TEM), Scanning Tunnelling microscopy (STM), Atomic Force microscopy (AFM), Electron Paramagnetic Resonance, Ion Beam Analysis techniques like Rutherford back Scattering (RBS) and Channelling, Secondary Ion mass spectrometry and rarely on Hyperfine Interaction techniques. Many of these techniques are constrained by the fact that they are not directly defect related and depend on some property change with damage creation. Techniques like STM has been extremely successful in imaging mono vacancy structures on graphite surfaces, however difficulties arise in analysis due to probe-defect interactions or scan rate dependence etc. TEM studies on the other hand bring in sample preparation uncertainties as well as defect structure modification by the impinging electron beam. Hence there remains substantial uncertainty leaving space for further investigations using defect specific and non-interacting techniques.

Positron annihilation spectroscopy which is sensitive to vacancies or open volume regions in a material can be utilized to understand the atomic vacancy evolution in graphite effectively. This is achieved by self-probing of open volume defects by
positrons within its thermal diffusion length. In defect free graphite, the positron density distribution has a quasi two dimensional nature with the positron density being confined mostly to the inter-layer region. With the creation of vacancy type defects, this two dimensional confinement changes to specific trapping at the defect site. This results in variations in defect sensitive parameters like momentum distribution and positron lifetime [13, 14]. Hence, in the present investigation slow positron beam spectroscopy is utilized to understand the thermal evolution of vacancy like defects in graphite and thus try to bring out the dependence of thermally activated vacancy reactions on the type and density of defects produced. In the subsequent section we look at studies on different defect species in irradiated graphite and the understanding developed on the defect energetic in past six decades.

3.1.1 Literature Review

Ion implantation results in the deposition of the kinetic energy of the impinging ions on to the lattice and a cascade follows which results in the formation of lattice disorder and defect species like the Frenkel pair along the track of the implanted ion. At sufficiently high doses these disordered regions overlap and finally a non-crystalline or amorphous layer is formed [15]. This disorder can be recovered or relaxed by thermal annealing process. A large scatter in literature is observed in the proposed annealing processes, involved defect structures, their activation energies and temperatures of occurrence. Hence, some of the important studies are highlighted as shown in Table 1.
Table 1: Various annealing processes, defect structures involved, temperatures of occurrence and important remarks from literature. \( V, v \)- vacancy, \( I, i \)- interstitial, \( a \) – basal plane lattice vector, \( c \) – lattice perpendicular to basal plane, \( m \)-migration, 2D/3D \( \rightarrow \) dimension. Red and Black denote experimentally determined values. Green and Blue are from ab-initio/theoretical calculations. \( \alpha, \beta \) are un-equivalent sites in the unit cell.

<table>
<thead>
<tr>
<th>Process/Defect structures assigned by authors</th>
<th>Activation energy/ Temperature of occurrence/ Important Findings.</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>V migration</td>
<td>( E_{v,a}^m = 3.1 ) eV ( E_{v,c}^m &gt; 5.5 ) eV</td>
<td>[16,17]</td>
</tr>
<tr>
<td>I-V recombination</td>
<td>( E_{\text{barrier}} = 0.24 ) eV. Occurring till 1523 K</td>
<td></td>
</tr>
<tr>
<td>I release from traps, weakly bound I-groups</td>
<td>( E_{\text{binding}} = 1.2 – 1.7 ) eV.</td>
<td></td>
</tr>
<tr>
<td>( I_2 ) (dimer) = 2I</td>
<td>( E_{\text{activation}} &gt; 1.2 – 1.7 ) eV. Hence cannot be a player in Wigner Energy release</td>
<td></td>
</tr>
<tr>
<td>Wigner Energy Release</td>
<td>( 473 ) K, ( E_{\text{activation}} = 1.2 – 1.7 ) eV</td>
<td></td>
</tr>
<tr>
<td>I-group migration and coalescence – nucleation of I-loop</td>
<td>( E_{\text{activation}} = 1.17 ) eV.</td>
<td></td>
</tr>
<tr>
<td>( V_2 ) (di-vacancy)</td>
<td>Collapses to edge dislocation dipole or vacancy line.</td>
<td></td>
</tr>
<tr>
<td>I migration</td>
<td>( E_{l,a}^m = 0.45 ) eV</td>
<td>[18]</td>
</tr>
<tr>
<td>I binding to trap</td>
<td>( E_{\text{binding}} = 1.38 ) eV, 473 K release from trap followed by I-V recombination.</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>( E_{v,a}^m = 3.1 ) eV ( E_{v,c}^m &gt; 5.5 ) eV ( E_{\text{formation}} = 7 ) eV</td>
<td>[19-20]</td>
</tr>
<tr>
<td>I migration</td>
<td>( E_{l,a}^m &lt; 0.1 ) eV, ( E_{l,c}^m &gt; 5 ) eV ( E_{\text{formation}} = 7 ) eV</td>
<td></td>
</tr>
<tr>
<td>I-loop/V-loop disappearance</td>
<td>( E_{\text{activation}} &gt; 8 ) eV</td>
<td></td>
</tr>
<tr>
<td>I migration (followed by I-V recombination)</td>
<td>0.89 -1.0 eV, fast annealing second order process from 388 K</td>
<td>[21-31]</td>
</tr>
<tr>
<td>( I_2 ) migration (assisted ( I_2 ) – V recombination)</td>
<td>1.8 eV, slow annealing process</td>
<td></td>
</tr>
<tr>
<td>( V, I ) clustering/ Cluster migration</td>
<td>( E_{l,a}^m = 0.15 ) eV, &gt; 573 K. Responsible for 2D-regrowth</td>
<td>[15,32-36]</td>
</tr>
<tr>
<td>I migration</td>
<td></td>
<td></td>
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<tr>
<td>2D – re growth</td>
<td>1773-2573 K, 0.67 eV</td>
<td></td>
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<tr>
<td>3D – epitaxial re growth</td>
<td>&gt; 2573 K, 0.78 eV/1.2 eV</td>
<td></td>
</tr>
<tr>
<td>c-axis random re growth</td>
<td>1773-2573 K, 0.47 eV</td>
<td></td>
</tr>
<tr>
<td>I migration</td>
<td>$E_{I,a}^m = 0.39$ eV, &gt;220 K</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>$E_{V,a}^m = 3.1$ eV, &gt;1273 K</td>
<td></td>
</tr>
<tr>
<td>I-V recombination</td>
<td>$E_{\text{barrier}} = 0.5$ eV</td>
<td></td>
</tr>
<tr>
<td>I migration (followed by weak I-V pair and I-I pair formation in two annealing steps).</td>
<td>$E_{\text{activation}} = 0.027$ eV, 5-15 K &amp; $0.05$ eV, 15-45 K</td>
<td></td>
</tr>
<tr>
<td>I (migration-long range – dispersion of weak pairs).</td>
<td>0.09-0.11 eV, 45-65 K</td>
<td></td>
</tr>
<tr>
<td>I (migration-long range, trapped by stronger I-V and I-I pair)</td>
<td>65-85 K</td>
<td></td>
</tr>
<tr>
<td>I-V pair $\rightarrow$ I + V</td>
<td>0.27 eV, 85-125 K, at 100 K strong stored energy release peak &amp; 0.40 eV, 120-180 K</td>
<td></td>
</tr>
<tr>
<td>I+I $\rightarrow$ I$_2$ / I-I pair</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n^*I_2 \rightarrow (I_2)_n$</td>
<td>0.55 eV, 165-230 K &amp; 230-400 K</td>
<td></td>
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<tr>
<td>I$_2$ - 2V , I – V recombination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I$_2$)$_2$ $\rightarrow$2I$_2$ (rate limiting)</td>
<td>1.34 eV, 448-513 K</td>
<td></td>
</tr>
<tr>
<td>I$_2$ - 2V recombination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I$_2$+ (I$_2$)$_2$ $\rightarrow$ (I$_2$)$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I$_2$+ (I$_2$)$_3$ $\rightarrow$ (I$_2$)$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I$_2$)$_3$ $\rightarrow$3I$_2$ (rate limiting)</td>
<td>1.50 eV, 473-543 K</td>
<td></td>
</tr>
<tr>
<td>I$_2$ - 2V recombination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I$_2$+ (I$_2$)$_3$ $\rightarrow$ (I$_2$)$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I$_2$)$_4$ $\rightarrow$4I$_2$</td>
<td>1.78 eV, 533-593 K</td>
<td></td>
</tr>
<tr>
<td>I$_2$ - 2V recombination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I migration (Molecular Dynamics)</td>
<td>0.01 eV</td>
<td></td>
</tr>
<tr>
<td>V migration to cluster/loop formation</td>
<td>&gt; 1473-1573 K</td>
<td></td>
</tr>
<tr>
<td>Vacancy loop disappearance</td>
<td>&gt;1773 K</td>
<td></td>
</tr>
<tr>
<td>small I clusters $\rightarrow$ large I</td>
<td>373-773 K</td>
<td></td>
</tr>
<tr>
<td>Clusters</td>
<td>I clusters break down $\rightarrow$ I, followed by I-V recombination</td>
<td>873-1173 K</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------------------------------------------------</td>
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<tr>
<td>I-loop disappearance</td>
<td>1473 K</td>
<td></td>
</tr>
<tr>
<td>Twin formation and Amorphisation</td>
<td>0.03-0.3 eV</td>
<td></td>
</tr>
<tr>
<td>I migration (I-V recombination)</td>
<td>0.33 eV</td>
<td></td>
</tr>
<tr>
<td>I migration</td>
<td>2 eV</td>
<td></td>
</tr>
<tr>
<td>Disorder region growth (rate limiting factor is I migration)</td>
<td>0.014 eV</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>$&gt;1573$ K</td>
<td></td>
</tr>
<tr>
<td>$V_6$</td>
<td>Stable up to 1773 K</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>$&lt;873$ K</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>$&lt;673$ K</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>$&gt;348$ K, 0.9-1.0 eV</td>
<td></td>
</tr>
<tr>
<td>I migration</td>
<td>0.44 eV</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>1.6 eV</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>$E_{V,a}^m = 1$ eV $E_{V,c}^m = 4.7$ eV</td>
<td></td>
</tr>
<tr>
<td>I migration</td>
<td>$E_{V,a}^m &lt; 0.03$ eV $E_{I,c}^m = 3.9$ eV/2.3 eV (interstitialcy mechanism)</td>
<td></td>
</tr>
<tr>
<td>I migration</td>
<td>$&gt;1.4$ eV</td>
<td></td>
</tr>
<tr>
<td>Adatom migration</td>
<td>0.47 eV</td>
<td></td>
</tr>
<tr>
<td>Adatom migration</td>
<td>0.4 eV</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>1.3 eV</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>0.94 eV</td>
<td></td>
</tr>
<tr>
<td>$V \rightarrow V_2$ (5-8-5)</td>
<td>1.6 eV</td>
<td></td>
</tr>
<tr>
<td>$V_2 \rightarrow V_2$ (555-777)</td>
<td>5.74 eV</td>
<td></td>
</tr>
<tr>
<td>Adatom migration</td>
<td>0.4 eV</td>
<td></td>
</tr>
<tr>
<td>Migration Type</td>
<td>Energy (in eV)</td>
<td></td>
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<tr>
<td>----------------</td>
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<td></td>
</tr>
<tr>
<td>A (ground state, B-barrier state, C-metastable state)</td>
<td>1.2-1.7 (a-axis)</td>
<td></td>
</tr>
<tr>
<td>(A-B-A) migration</td>
<td>0.9 eV, 800K</td>
<td></td>
</tr>
<tr>
<td>(A-B-C) transition</td>
<td>0.5 eV (c-axis possible for irradiated HOPG)</td>
<td></td>
</tr>
<tr>
<td>(B-C-B) migration</td>
<td>0.7 eV (possible for irradiated HOPG)</td>
<td></td>
</tr>
<tr>
<td>(c-axis migration along B-C-B, aa-stacking)</td>
<td></td>
<td></td>
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<tr>
<td>Adatom migration</td>
<td>0.84 eV (a-axis)</td>
<td></td>
</tr>
<tr>
<td>I migration</td>
<td>1.27 eV (a-axis)</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>1.44 eV (a-axis), 0.99 eV (a-axis, on graphene)</td>
<td></td>
</tr>
<tr>
<td>V_{2} (inter planar) migration</td>
<td>3.2-3.5 eV</td>
<td></td>
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<tr>
<td>I-V pair recombination</td>
<td>1 eV (perfect graphite)/ 0.5 eV (sheared)</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>3.2-3.6 eV (inter conversion of various types or de trapping of V)</td>
<td></td>
</tr>
<tr>
<td>V \rightarrow V_{2} (5-8-5)</td>
<td>1.26eV(a-axis), 1.37 eV (a-axis, on graphene)</td>
<td></td>
</tr>
<tr>
<td>I migration(bridge)</td>
<td>2.17 eV</td>
<td></td>
</tr>
<tr>
<td>I migration(spiro)</td>
<td>0.42 eV(sub-surface – a-axis)</td>
<td></td>
</tr>
<tr>
<td>I(spiro) \rightarrow I(bridge)</td>
<td>0.53 eV (sub-surface – c-axis)</td>
<td></td>
</tr>
<tr>
<td>I-V_{1} \rightarrow I-V_{2}</td>
<td>0.9 eV</td>
<td></td>
</tr>
<tr>
<td>I-V_{1} recombination</td>
<td>&gt;350K</td>
<td></td>
</tr>
<tr>
<td>I (C-dumb bell structure) \rightarrow I (bridge)/I migration through this inter conversion</td>
<td>0.9 eV (c-axis migration)</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>1.7 eV</td>
<td></td>
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<tr>
<td>V_{2} migration (in-plane)</td>
<td>7 eV</td>
<td></td>
</tr>
<tr>
<td>Inter-planar V_{2} migration</td>
<td>2.8 eV (inter conversion of various types or de trapping of V)</td>
<td></td>
</tr>
<tr>
<td>I-V pair recombination barrier</td>
<td>1.4 eV</td>
<td></td>
</tr>
<tr>
<td>I (spirom) migration</td>
<td>0.9 eV</td>
<td></td>
</tr>
<tr>
<td>I_{2} \rightarrow I</td>
<td>~1eV</td>
<td></td>
</tr>
<tr>
<td>V_{2}^{3(\text{trans})} third neighbour planar divacancy in –transform migration</td>
<td>3 eV</td>
<td></td>
</tr>
<tr>
<td>V_{2}^{3(\text{trans})} \rightarrow V_{2} (planar)</td>
<td>2.8 eV</td>
<td></td>
</tr>
<tr>
<td>V migration</td>
<td>3.5 eV</td>
<td></td>
</tr>
</tbody>
</table>

Thus the vacancy migration barrier has values from 0.90 – 3.1 eV and activation from temperatures as low as 348 K to as high as 1473 K. Similarly the interstitial migration has values from 0.027 eV – 2.1 eV. The defect annealing mechanism is also complicated.
by large number of stable and meta stable structures possible for vacancies and interstitials. This is due to the property of C-atom to bind in different forms (sp to sp$^3$). There is also a difference in defect energetics near to surface and away from it influencing the experiments which are surface sensitive or bulk sensitive. The scatter is also due to different type of implantation conditions used like species and temperature. Yet certain generally accepted features can be brought out from the literature surveyed.

- It is now accepted that there is a recombination barrier between interstitial (I) and vacancy (V) and this stems from the existence of I-V meta stable state which has been experimentally shown [97]. It is also accepted that since Wigner energy peak at 473 K is due to I-V recombination, the meta stable state has a role in it.
- There is large evidence theoretically and some experimental proof that the migration barrier for vacancy along basal plane is not 3.1eV but much lower.
- Though there is no consensus on migration energy of interstitials, there is a wealth of evidence pointing to recovery taking place from temperatures as low as 10K. Hence if a higher migration barrier for I is correct, the observed low temperature recovery needs explanation.
- Once they are mobile, interstitials do cluster to form I$_2$ as they are more stable.
- V$_2$ (first nearest neighbour planar) is immobile with very high migration energy.

There seems to be evidence in favour of barrier for divacancy formation from aggregation of monovacancies. Hashimoto et.al [98] has seen through HRTEM three single vacancies in the nearest neighbour position, yet stable enough not to form higher clusters (di- or tri-).
- There is a mixed phase hybridization (sp$^2$-sp$^3$) developed due to bridging, bending and cross linking of the adjacent layers.
- Annealing mechanism has a dependence on the amount of damage produced.
In spite of a certain level of understanding as mentioned above, the basic methodology of defect recovery remains vague from the activation numbers mentioned above. A positron based study could clarify some of the discrepancies as they are vacancy specific and non-destructive.

There has been previous studies which have utilized positron lifetime technique to identify the nature of bulk defects formed by electron or neutron irradiation in graphite [13, 51-53]. But to our knowledge the only experiment which looked at the vacancy profile and its annealing in a depth resolved manner using positron beam was by Yang et.al. [99]. They used beam based positron lifetime and Doppler broadening spectroscopy to identify the defect structures produced by RT irradiation of HOPG samples with 70keV $^{12}$C$^+$ ions to a fluence of $10^{15}$ ions/cm$^2$ and to understand their thermal recovery. From depth resolved lifetime values (obtained by simple lifetime decomposition with no larger lifetimes) they had concluded that the major defect produced is of V$_6$ type with some V$_9$ clusters very near to the surface and V$_4$, V$_2$ & V$_1$ near the implantation range where V$_n$ represent n-vacancies clustered together. They found that when annealed to 373 K, all defects except V$_1$ had moved out and that by 473 K through I-V recombination even the single vacancies have been removed. They assumed that the larger clusters were formed due to the agglomeration of mono vacancies during the dynamics of irradiation. These results were correlated with the disappearance of ferromagnetic behaviour up to ~75% by 373 K and complete disappearance by 473 K. V$_1$, V$_4$ (some stable structures) and V$_6$ were found to have a net magnetic moment through spin averaged VASP calculations. They argued that for a particular vacancy concentration, the deformation field surrounding the vacancy was larger than the separation between the vacancies and that helps in local magnetic coupling with electrons transferred between two in-equivalent atom positions in 2D graphite. They
ruled out Hydrogen-Vacancy complexing in their samples through the observed positron lifetime. There was a discrepancy though in their Doppler broadening data which showed larger S-parameter (defect sensitive) even at 473 K and complete defect recovery only by 773 K where S-parameter values were lower than that in the un-implanted reference samples. This discrepancy was said to be due to complex defect structures with higher lifetimes, not visible in slow positron beam lifetime measurements though reflecting in S-parameter measurements. However it has to be pointed out here that the highest lifetime measured in graphitic samples was ~ 477 ps in glassy carbon [51].

There are other studies which used similar irradiation conditions as used in the present chapter. One such study utilised RBS in channelling mode on HOPG samples irradiated with 230 keV $^{12}$C$^+$ ions to a dose of $10^{15}$/cm$^2$. The recovery of the damaged region as a function of isochronal heat treatment was followed [36] and is given here in Fig. 1 (a) and (b). Fig. 1 (a) contains data from samples annealed up to 1373K for 20 minutes and Fig. 1(b) contains samples annealed up to 2573K. It can be seen that even for annealing temperatures at 573K there is a recovery from the surface region as well as a small epitaxial re-growth from the back interface. Major change at the projected range is observed only for annealing above 1373K as shown in Fig. 1 (b).

This results shows that the sample is highly disordered at the projected range but only to a lesser extent near the surface. The annealing taking place for temperatures up to 2573K was assumed to be due to migrating interstitials resident between the graphite planes. By making an Arrhenius plot of the re-grown interface in this temperature regime, the activation energy was deduced to be around 0.15eV and hence the assumption that the interstitials play a major role was justified. It was also found that in this regime, the growth is diffusion limited and as soon as the growth reaches the highly
Fig. 1: Back scatter yield from channelling study on samples irradiated with $10^{15} \mathrm{C}^+ \mathrm{ions/cm}^2$ and annealed between (a) 573-1373K and (b) annealed between 1373-2573K. Reproduced from [36].

In the disordered region, the kinetics becomes complicated and is not dominated only by diffusion or by epitaxial re-growth. For the epitaxial 3D growth occurring in temperatures above 2573K, the activation energy was found to be $\sim 1.2 \, \text{eV}$. Such a small value was explained by an epitaxial recovery mechanism with crystalline substrate (the
crystalline region below the damaged surface) providing the nucleation sites and/or due to the presence of oriented crystallites even in highly damaged top layer.

Annis et.al. [74] utilized 165 keV C$^+$ ion irradiation at various doses from $6 \times 10^{13}$ ions/cm$^2$ to $3 \times 10^{15}$ ions/cm$^2$ to understand the surface damage creation mechanism and identified two type of defect feature at higher doses – rectilinear ridges running across the HOPG surface and highly networked and curvilinear ridges. Since the energy and dose are similar to the present investigation, images from the study are reproduced here which shows both type of ridge structures mentioned above in Fig. 2 (a-c).

Fig.2: AFM images from two regions of sample irradiated to (a & b) $3 \times 10^{15}$ ions/cm$^2$ and (c) to $6 \times 10^{14}$ ions/cm$^2$ with 165 keV C$^+$ ions. (Reproduced from [74]).

Their study showed that for all the doses used, patches of ordered basal plane remained on the sample surface and that it maintained the crystallinity to give the corresponding Raman features. They argued a possibility of buried amorphous layer for
the highest dose implantation after comparison with a sample irradiated to same dose, at the same rate but with 35 keV ions. For lower dose sample (< $6 \times 10^{14}$ ions/cm$^2$) they observed patches of disordered as well as normal structures. Linear defects in $\langle 10\overline{1}0 \rangle$ direction which were associated to a line of eight vacancies were seen in the lower dose samples. Apart from this surface protrusion which is a few nano-meter high was also observed and was assigned to interstitial clusters below the surface layer and to fragmentation and rotation of basal plane. The latter was assumed to provide easy migration path for the interstitials across the c-axis. For higher doses, dendrite like cracks were seen and some of them were deeper than the implantation depth. This was explained to be due to heavy contraction near surface layer by fragmentation or by vacancy collapse resulting in large amount of stress. The stress is released by cracking along the crystal direction and/or along the weak spots like grain boundaries. For the highest dose they observed ridges or wrinkles on the surface where one set was rectilinear possibly along $\langle 10\overline{1}0 \rangle$ direction and the other curved. No twin boundaries were associated with these ridges though such identification had been done earlier [54,55]. Calculating the number of carbon atoms in the ridges and its surface coverage, they argued that migration energy of 0.44 eV would be required to carry interstitials (part of Frenkel pair) from the bulk to the surface. This as argued earlier was aided by the fragmentation of the basal plane leading to easy migration path. The carbon atoms thus reaching the surface could accumulate at the fragment intersections (stress centres) and the ridges grow. In the initial stage of irradiation fragmentations occurs along crystallographic directions and thus explain the linear ridges. As dose increase fragmentation becomes random and this could explain the curvilinear random ridges seen. Another possible mechanism that they proposed was basal plane slip like tectonic plate movement giving rise to observed ridges preferentially along the step edges.
High resolution TEM (HRTEM) studies on certain forms of graphite (graphene, CNT etc.) have helped in identifying & understanding the dynamics of some of the exotic defect species possible in graphite. Hashimoto et.al. [98] had showed the existence of pentagon-heptagon Stone Wales defect on a SWNT after electron irradiation. They had also identified up to three single vacancies lying next to one another showing that damaged region is more prone to further damage than the undamaged region and that there is a possible barrier for clustering to higher vacancies. While searching for adatoms on single walled CNT (SWNT) surface, they found three adatoms attached very close to a divacancy again giving evidence for I-V recombination barrier. The structure they assumed implied that the adatom migration energy is ~0.47 eV. Similar study by the same group [97] on double walled (DWNT) showed the existence of intimate I-V pair (one I with V or I with V₂ – it was not possible to distinguish between these two) after electron irradiation which was the first experimental identification of an inter-layer defect with partial sp³ character. At low temperatures (~93K) clustering of vacancies and interstitials were observed due to knock outs near an earlier defect which did not get enough time to recover. Very important observation is that even for higher temperature they did not find much movement by interstitials or vacancies showing that the interlayer migration has higher barrier than surface atoms. By counting the number of I-V pairs at different irradiation temperatures, the energy dynamics of this particular defect was given which is reproduced below in Fig 3. There is a steep decrease in the number of I-V pairs formed with increasing irradiation temperature; however, a plateau is seen to occur beyond 473 K which is indicated by a broken line. The start of this threshold has closeness to the Wigner energy peak at 473 K.
Fig.3: Number of intimate I-V pair counted for different irradiation temperature. (Reproduced from [97]).

By techniques which are sensitive at different depth levels a comprehensive know how on defect evolution can be built as given by the results above. Here channelling gives depth resolved information on the thermal evolution of interstitial (I) like defects, STM & AFM shows how surface structure develops through defects and TEM provides proof for specific nature of atomistic defects. In this scenario, the present study tries to throw more light into the annealing mechanism of vacancies using positron beam based Doppler broadening spectroscopic measurements on samples which are irradiated with $^{12}$C$^+$ ions of 200 keV energy along with Raman spectroscopy and AFM. Since Doppler broadening study is used, the defect structures at specific depths cannot be identified but the qualitative change with temperature will bring out the activation channels in the damage recovery and possible defect structures involved can be pointed out based on already existing activation energy data.
3.2 Experiments

Highly Oriented Pyrolytic Graphite Samples of SP-1 grades (equivalent to ZYA grade) were obtained from SPI supplies. This grade has very high crystalline order and exhibits properties close to single crystal graphite. The mosaic spread is as low as 0.4±0.1° and the lateral grain size is usually higher than 1µm and can be typically up to 3mm. All the samples were freshly cleaved before implantation and the surface would consist of steps of several atomic layers with height of single step ~ 0.34 nm. The density is 2.27 g/cc and the samples were of dimension 10x10x1 mm. The impurity levels in the sample are at 10 ppm ash or better [100].

3.2.1 Carbon Ion Implantation

Carbon ions (^{12}C^{+}) were implanted into the samples using a 1.7MV Tandetron accelerator at IGCAR, Kalpakkam, whose details are given elsewhere [101]. In the present study, HOPG samples were irradiated at room temperature with 200 keV C^{+} ions parallel to the c-axis to a fluence of 10^{14} and 10^{15} C^{+} ions/cm^{2}. A beam diameter of 10 mm was used to get uniform damage across the sample. The beam current was kept around 55 nA to avoid beam heating of the sample. The beam energy was selected so as to be equivalent to a damage creation by a 1MeV neutron as well as have the damaged region inside the optical skin depth of 514.5 nm laser light. If a non–relativistic head on collision of hard spheres is considered, the maximum energy that can be transferred to a primary knock on atom (PKA) (T_{max}) is given as

$$T_{max} = \frac{4MMpT_p}{(M+Mp)^2}$$  \hspace{1cm} (1)

where $M =12M_p$ mass of carbon nucleus and $M_p$ is the mass of neutron with energy $T_p$. This amounts to about 300keV energy for PKA created by 1MeV neutron. The
particular ion was also chosen to avoid any impurity based effect during defect evolution. Keeping in mind the optical skin depth (~ 50-70 nm), a lower but closer value to 300 keV i.e. 200 keV was chosen. This is the minimum energy possible for singly charged carbon ions in this accelerator. The higher dose was selected to achieve a highly disordered region close to amorphisation near to the projected range and a lower dose was selected to look at the variation in defect evolution with damage density and defect type.

3.2.2 Vacuum Annealing

The implanted samples were annealed in a vacuum better than 10^{-6} mbar using a vacuum system described in section 2.2.2. The samples were cumulatively annealed for 60 minutes to different temperatures from 373 K to 773 K in steps of 50K. They were also annealed at 973K and at 1273K for the same time. The furnace is pre-heated to the required temperature and is inserted over the quartz tube containing the sample once the required vacuum is achieved. After the prescribed time, furnace is removed and the tube is quenched into liquid nitrogen bath to speed up the temperature drop. For all temperatures, the rise time and the fall time between 373 K and ~0.95*final temperature is less than 300 s. Relaxation below 373 K was shown to be very slow and for temperatures like 473 K, the fastest relaxation process had a characteristic time constant of ~450 s [30, 31]. Hence the processes occurring during the rise and fall time could be ignored compared to that at the set temperature. The set temperature was attained within an accuracy of +5°C for all temperatures.
3.2.3 Slow Positron Beam Spectroscopy (SPBS)

Implanted and annealed samples were investigated with magnetically guided variable energy slow positron beam [102] in order to track the recovery of the damaged region of graphite surface with isochronal annealing and the role played by open volume defects in the process. The details of the slow positron beam as well as the defect characterisation methods are discussed in section 1.3.1 of chapter 1 and in section 2.2.3 of chapter 2. However for the sake of completion the parameters used for the present experiment are discussed here. The positron annihilation $\gamma$-spectrum from the sample was recorded using an high purity germanium detector having an energy resolution of 1.42 keV at 662 keV $\gamma$ line of Cs$^{137}$ with a shaping time of 6 $\mu$s in the spectroscopic amplifier. Around $3 \times 10^5$ counts were collected in the main peak (511±10 keV) at a count rate of 27 cps using this detector for annealing temperatures up to 473K. For higher temperatures, $\sim 8.5 \times 10^5$ counts were collected in the main peak at a count rate of 450 cps. This rise in count rate was due to the installation of a new 50 mCi source into the beam line.

The Doppler broadening of the 511 keV annihilation $\gamma$ ray is quantified, as described in 1.3.1, using a line shape parameter S and a wing parameter W (wing region of the peak is defined in this case as 513.5 to 518.5 keV and 503.5 to 508.5 keV). With the total counts in the main peak, central region and wing region, an error of $< \pm 0.002$ is expected for S parameter and an error of $< \pm 0.0004$ is expected on W parameter. VEPFIT [103] code is used to fit the experimental S vs Energy of positrons (E) data and give the fraction of positrons annihilating in various trapping centres as a function of depth as well as the S parameter corresponding to each trapping centre. It has to be specifically mentioned here that the positron beam direction was parallel to c-axis and the implantation depth of positrons given with each data is with respect to the c-axis.
Directionality is not important for the obtained S-parameter versus Energy spectrum for isotropic materials because of the three dimensional random diffusion of positrons post thermalisation. However in a layered structure like perfect graphite where there is a quasi 2D confinement and a pointed confinement at nearby defect sites, the obtained information is sensitive to lattice direction but with a resolution equivalent to positron diffusion length along the c-axis. When vacancies are created on the basal plane, the diffusion length reduces drastically to values equivalent to the inter-planar distance and hence the technique does become highly direction sensitive.

3.2.4 Positron lifetime spectroscopy

Unlike slow positron Doppler broadening spectroscopy, conventional positron lifetime spectroscopy gives quantitative information on the defect nature of the bulk of the sample. The lifetime of positrons inside the sample is proportional to the local electron density at the site of annihilation and hence variation induced in this by the formation of atomistic open volume defects can be quantified with characteristic lifetimes and their intensities. A brief theory of positron annihilation spectroscopy is covered in 1.3.1, though for sake of completion experimentally relevant points are discussed here. The experiment is carried out by placing a $^{22}$Na source encapsulated 1µm thick Nickel foil in between two identical samples in the sandwich geometry and by using a fast-fast positron lifetime setup. The obtained positron decay spectrum is fit to multiple exponential decay schemes using LT9 [104] program which takes care of Gaussian resolution functions and subtracts the self-annihilation events from the source.

In the present study, two HOPG samples of the same grade (SP-1) were used for sandwich mounting. Around $10^6$ counts were collected in the region of interest. The Gaussian resolution function and the contribution from source annihilations were found
using similar measurement on Silicon (100) single crystal. The data is fit to two components using LT9 and a variance close to 1 signals a very good fit.

### 3.2.5 Raman Spectroscopy

Raman spectroscopy is a powerful non-destructive technique to understand the symmetries and bonding nature of the solids. Through symmetry forbidden Raman lines and their intensities, it is also possible to understand degree of disorder of the system. Raman spectrum of various carbon forms provide specific signatures which makes it a most commonly used tool in the characterization of various allotropic and disordered forms of carbon like HOPG, diamond, glassy carbon, carbon fibres, carbon nanotubes, graphene, graphitic foams etc. [2, 105]. Raman spectroscopy is a powerful non-destructive tool in the case of ion implanted studies through the presence of crystallinity and defect specific modes such as the zone centre \((k=0)\) \(E_{2g2}\) allowed mode of frequency shift 1582 cm\(^{-1}\) (G) and through the disorder induced double resonant modes at around 1360 cm\(^{-1}\)(D) and 1620 cm\(^{-1}\)(D’). Three dimensional correlations of the two dimensional graphene planes can also be tracked using the overtone mode at 2720 cm\(^{-1}\) (G’). The dispersive behaviour of the D and G’ modes and the difference of the Stokes and anti-Stokes spectra are also used to understand the complexity of the double-resonant process.

As known, in Raman spectroscopy an intense beam of laser of frequency \(\omega_0\) is irradiated on to the sample. The scattered light consisting of the Rayleigh scattering part \((\omega_0)\) and the Raman scattered part \((\omega_0+\omega’\text{-Stokes} \ & \ \omega_0-\omega’\text{-anti_Stokes})\) is measured using a system consisting of light source, transmission optics and light counting system. As the intensity of stokes lines are greater than the anti-stokes ones, the characterization is usually carried out using the measurement of Stokes lines. Any measurement system consists of four major components (1) Excitation source (2) Sample illumination and
collection (3) wavelength selector and (4) Detection, acquisition and control system [106]. For the present measurements a Renishaw µ-Raman spectrometer was used, whose description is given elsewhere [107].

In the present measurement, a 50X objective lens at the microscope was used to illuminate the sample and the scattered light was accumulated normal to the sample in the backscattering geometry. The data was acquired for 120 s with a power of ~100 mW to have good signal to noise ratio. The spectral range was chosen from 100 cm$^{-1}$ to 4000 cm$^{-1}$. The spot size was ~ 2µm. The Raman shift in wave number was calibrated using 520.5 cm$^{-1}$ Raman line from Silicon single crystal. It should also be emphasized here that for a wavelength of 514.5 nm the optical skin depth is of the order of ~50 nm and hence, present Raman characterization would be looking at the tail of the implantation induced damage profile. The obtained spectrums was background corrected using linear fit at selected frequency ranges and the resultant spectrum was fit to multiple Lorentzians using PeakFit.

### 3.2.6 Atom Force Microscopy

The topography of the freshly cleaved pristine samples as well as that of implanted samples was mapped using NT-MDT Solver PRO atom force microscope. The measurement was done in the semi-contact mode using the standard silicon cantilever which is maintained at a constant force. The details of the instrument are given elsewhere [108].
3.3 Results

3.3.1. TRIM

The profile of vacancies produced by the implantation of 200 keV C\(^+\) ions parallel to the c-axis is shown in Fig.4. This was generated using the monte carlo simulation package TRIM [109]. The displacement energy (E\(_d\)) required to produce isolated Frenkel pair (I-V) is taken to be 34 keV [3]. This will decide the number of vacancies/interstitials produced per ion.

![Graph of vacancies and C atoms per Angstrom per ion vs depth](image)

Fig.4: Profile of damage produced and implanted C\(^+\) ions (200 keV) generated using TRIM [109]. The displacement energy was taken to be 34keV for implantation along \(c\)-axis.

The peak damage is predicted to be around ~350 nm deep and it is shown to extend till ~425 nm. The peak of the projected range (R\(_p\)) of the implanted C\(^+\) ions is around 375 nm. Elman et. al.[15] has shown that the theory which is generally used for non-crystalline solids is applicable to a certain extent to a crystalline and layered material like graphite. Though some caution is required when taking the values generated as
absolute quantities because an amorphous structure proportional to the material density is assumed in this code and hence, certain features like channelling is not taken into account. It also doesn’t allow for vacancy-interstitial recombination or structural relaxation to a new phase, since zero Kelvin calculations are performed. Hence, the damage predicted by TRIM is always overestimated [2].

The vacancies produced per ion ($Vpi$) is predicted to be 210 for the taken displacement energy. Since a 1 cm$^2$ beam was used, and as the damage extends till ~ 400 nm (as predicted by TRIM), the damage volume ($V_d$) can be taken as $4 \times 10^{-7}$ cm$^3$. The atomic density ($N$) of HOPG is ~ $1.25 \times 10^{23}$ atoms/cm$^3$. Therefore using relation

$$dpa \ (displacement \ per \ atom) = D = \frac{\varphi(Vpi)}{V_dN}$$

(2)

where $D$ is the total damage and $\varphi$ is the fluence; the damage produced in dpa can be calculated. Hence for the fluence used here, $10^{15}$ and $10^{14}$ C$^+$ ions/cm$^2$ the damage produced is 0.04 and 0.004 dpa respectively.

3.3.2. Pristine HOPG

Atom Force Microscopy

Topography of the freshly cleaved pristine HOPG sample measured using AFM in semi-contact mode is given in Fig. 5. The topography looks mostly featureless with sharp multiple step edges due to cleaving. Large patches of graphitic basal planes with sizes $>3\mu$m can be seen which coincides with the in-plane crystallite size of $>1\mu$m as suggested by the supplier [100].
Fig.5: AFM image of pristine freshly cleaved surface of HOPG taken at semi-contact mode. The topography is mostly featureless with sharp step edges due to cleaving.

**Positron Lifetime Spectroscopy**

Positron lifetime measurements on as received freshly cleaved samples (2 nos) of HOPG SP-1 grade resulted in a lifetime spectrum as shown in Fig.6. The fit data and the deduced lifetime components are also shown in the figure. The obtained values are tabulated in Table 2. The spectrum could be fit to two components after fixing the resolution function and source correction. The values are very close to that obtained by Iwata et.al. [51] for Pyrolytic graphite annealed at 3273K for 4 hours.

The obtained lifetimes could be interpreted in terms of two – state trapping model. If $\tau_f$ is the defect free lifetime, $\lambda_f$ the corresponding annihilation rate, $\kappa_1$ the specific trapping rate of a defect species, $\tau_2$ the defect lifetime of that species, $\lambda_d$ the corresponding annihilation rate then the bulk annihilation lifetime obtained by experiments would be

$$\tau_1 = \frac{1}{\kappa_1 + \lambda_f}$$  \hspace{1cm} (3)
where \( \tau_f = \frac{1}{\lambda_f}, \tau_2 = \frac{1}{\lambda_d} \). The specific trapping rate \( \kappa_1 \) is related to the obtained intensities as

\[
I_1 = 1 - \frac{\kappa_1}{(\kappa_1 + \lambda_f) - \lambda_d}
\]  \hspace{1cm} (4)

and

\[
I_2 = \frac{\kappa_1}{(\kappa_1 + \lambda_f) - \lambda_d}
\]  \hspace{1cm} (5)

Fig.6: Positron Lifetime spectra for pristine HOPG samples. Also shown are the fit line (solid red line), the lifetime components (blue dash dot dot and dash dot green line) and the source component (pink dashed). The residue of the fit is shown in the same time scale above.

combining these we can write \( \tau_1 \) as

\[
\frac{1}{\tau_1} = \frac{1}{\tau_f} + \left( \frac{1}{\tau_f} - \frac{1}{\tau_d} \right) \frac{I_2}{I_1}
\]  \hspace{1cm} (6)
Table 2: Positron Lifetime results for pristine HOPG samples. Probability for annihilation in trap is a measure of the crystalline quality [51].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$ (ps)</th>
<th>$I_1$ (%)</th>
<th>$\tau_2$ (ps)</th>
<th>$I_2$ (%)</th>
<th>$\tau_{\text{mean}}$ (ps)</th>
<th>$\tau_1$ (calculated) (ps)</th>
<th>Probability for annihilation in trap</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>160±2</td>
<td>54±1</td>
<td>344±3</td>
<td>46±1</td>
<td>245±5</td>
<td>158</td>
<td>0.24</td>
<td>1.12</td>
</tr>
</tbody>
</table>

The probability for annihilation in the trap ($P_d$) is given by,

$$P_d = \frac{\kappa_1}{\kappa_1 + \lambda_f}$$  \hspace{1cm} (7)

By assuming the bulk lifetime in highly oriented pyrolytic graphite as 210 ps [13], the calculated values of $\tau_1$ is very close to the experimentally observed value showing that the two state trapping model works well for the as received samples. Therefore the pristine sample contain defect free crystallites with random $a$-axis orientation. The intercrystallite surfaces act as effective trapping sites giving rise to the second component which is close to the surface state lifetime (350 ps) of HOPG [110]. The probability of annihilation is a measure of such trap sites i.e. of the area of the internal surfaces. Hence ~25% of the implanted positrons annihilate at these internal surfaces.

**Slow Positron Beam Spectroscopy**

S-parameter for the pristine samples shows a gradual decrease with increase in positron energy from a high S-value very near to the surface reaching the bulk S-parameter by 8keV as shown in Fig.7 (a). The high value at the surface is due to the phonon assisted positronium (Ps) formation and the relative Ps yield for 200 eV
positrons at 300K was shown to be as high as 16% [111]. They had also speculated that in HOPG, either the surface trap state is not present or the electrons sampled by the surface-bound positrons are very similar to those seen by interlayer positrons. They had calculated the energy at which the Ps yield falls off by half as 2.4 KeV. By fitting the S vs E data to a simple monolayer model using VEPFIT (description is given in 1.3.1), the diffusion length of positrons in graphite is found to be 209±11 nm, which is close to the value for Silicon (245 nm). The bulk positron lifetimes for both materials are also close (210 ps for HOPG and 220 ps for Silicon) and through the relation between diffusion length and bulk positron lifetime, the fit value looks good provided they have similar positron diffusion co-efficient at 300 K. This value is fixed for subsequent fits in irradiated samples for the defect free bulk layer. As there are no depth specific traps, the linearity of the S-W correlation plot as given in Fig.7 (b) is conserved. Hence, this can be used to look at defects at specific depths in irradiated samples. The error bar on S and W parameter are also provided in the S-W correlation plot, to identify the specific inflexion points when going from surface to bulk in irradiated samples beyond experimental errors. It has to be emphasized here that the position (S=1, W=1) correspond to bulk annihilations which encompasses both annihilations in defect-free bulk as well as in internal surfaces as shown by positron lifetime measurements. In the range of the present annealing temperatures, though no change is expected to the grain size as 2D grain growth starts for temperatures >1773 K and 3D ordering takes place only above 2573 K [32]. As the major contributor to the second lifetime does not show any change during the present annealing regime, changes appearing in the S-parameter can be interpreted independent of them.
Fig. 7: (a) S and W parameter variation with implanted positron energy for pristine HOPG sample. The mean implantation depth of positrons is also given in the top axis. The solid line through the S vs. E curve is the fit to the data considering a simple monolayer model using VEPFIT. (b) The linearity of S vs W correlation plot as positron goes deeper into the sample shows the absence of a third annihilation site other than bulk and surface of the sample. The arrow shows increasing positron energy. The scales of the axes are chosen to be constant throughout this chapter for better comparison with irradiated samples.
Raman Spectroscopy

The first and second order Raman spectrum of the pristine HOPG sample is shown in Fig.8 (a) and (b) respectively. Also shown are that obtained for irradiated samples which are up shifted in scale for clarity. The first order spectrum is fit to four Lorentzians for pristine HOPG sample. The major peak is the G-band at 1583 cm\(^{-1}\) which is the Raman active mode for sp\(^2\) carbon network. This mode is degenerate at the brillouin zone (BZ) centre (the in plane transverse optical (iTO) mode and the Longitudinal optical (LO) mode) with \(E_{2g2}\) symmetry. The degeneracy disappears for general points inside the BZ. The full width at half maximum (FWHM) of the fit Lorentzian to this peak is 13.93 cm\(^{-1}\). There is a very weak disorder peak at \(\sim 1361\) cm\(^{-1}\) (D) whose origin has been recently ascribed to double resonance through an elastic scattering process via defect [105]. Though it has a doublet structure it is not visible in this case due to very low intensity. The integrated intensity ratio \(I_D/I_G\) is as small as 0.00862 where as the peak intensity ratio of these two modes is only about 0.0019. Using the empirical relation put forward by by Tuinstra and Koening [112] connecting the in plane crystallite size \(L_a\) to the intensity ratio as

\[
L_a (nm) = \frac{4.4}{(I_D/I_G)} \quad (8)
\]

we get the in plane crystallite size to be around 510 nm and using the relation by Pimenta et.al [105] which utilizes the integrated intensity ratio and the energy of the excitation laser light (\(E\)) as

\[
L_a (nm) = \frac{560}{E^4} \frac{1}{(I_D/I_G)} \quad (9)
\]

the in plane crystallite size is around 1925 nm. As the two values differ, one of them could be used to get a qualitative (as both are empirical) picture during thermal evolution.
Fig. 8: (a) The first order Raman spectrum of pristine HOPG shows the double degenerate G band at ~ 1583 cm\(^{-1}\) (E\(_{2g}\) symmetry) from the zone centre which is active for sp\(^2\) carbon networks. Also shown are the Raman modes obtained for low dose and high dose samples for comparison which are up shifted for clarity. The defect induced double resonance Raman process generated D band at ~ 1360 cm\(^{-1}\) and D' band at ~ 1620 cm\(^{-1}\) and they can be seen emerging with the increase in dose. (b) The second order Raman spectrum for pristine HOPG and implanted samples are shown. The symmetry allowed G’ band along with the deconvoluted G’\(_{3DA}\) and G’\(_{3DB}\) Lorentzian peak positions are shown in them. For higher dose sample, there is also weak G’\(_{2D}\) peak at ~2707 cm\(^{-1}\) corresponding to 2D graphite. The feature around 2450 cm\(^{-1}\) corresponds to overtone of LO mode where as the feature at ~ 2950 cm\(^{-1}\) is defect induced D+G mode. The symbols are explained in detail in the text.
$L_a$ can also be looked upon as the phonon correlation length as defects/grain boundaries tend to change the lattice atom interaction. Thus considering $L_a$ as the average distance between in plane defects, Nakamura et al [21] has shown that the defect density ($N_d$) is related to the intensity ratio as

$$N_d = \text{constant} \times \left( \frac{I_D}{I_G} \right)^2$$

for lower irradiation doses. The other two weak Lorentzians observed for pristine HOPG are around 1496 cm$^{-1}$ and 1754 cm$^{-1}$. The latter is named M$^+$ mode and is assigned to be the overtone of the out of plane Transverse optical mode (oTO) where as the earlier one is close to 1450 cm$^{-1}$ LO mode [113].

The second order Raman spectrum of pristine HOPG shows the presence of symmetry allowed overtone of the defect induced D mode (i.e. $\sim 2*D$), though here conventional naming system is followed and is named as G’ band. It has a doublet structure and can be fit using two Lorentzians – G’$_{3DA}$ at 2686 cm$^{-1}$ and G’$_{3DB}$ at 2728 cm$^{-1}$. The relative intensity ratio of G’$_{3DB}$ to G’$_{3DA}$ is constant and for measured spectrum it was obtained to be about 2.4. The changes in the number of peaks in this band are a measure of the stacking order of the graphitic planes. For turbostratic graphite samples where there is no stacking order along $c$-axis this band is composed only of one Lorentzian around 2707 cm$^{-1}$ (G’$_{2D}$) and as the stacking order improves (on annealing) the band goes from one peak to two peak via three peak regime which shows combined existence of 2D as well as 3D structure in the system. The introduction of intercalants or interstitials by ion implantation in the interlayer region causes an expansion of the layer spacing from 3.35 Å up to 3.45 Å when the interaction between the layers is destroyed and a 2D graphitic structure form. Thus variation in the relative intensity ratio of G’$_{3DB}$ and G’$_{2D}$ with thermal treatment could be followed to understand interlayer species arrangement and the recovery of the stacking order in ion implanted samples. Another
weak feature in the pristine HOPG spectrum is around 2450 cm\(^{-1}\), whose origin has been assigned to the overtone of the LO mode [114].

The presence of the D-peak and the D’ peak (\(\sim 1620\) cm\(^{-1}\)), with intensity comparable to G-peak, differentiates the spectrum obtained for irradiated samples from that for pristine HOPG. Both the peaks have their origin in the double resonance process but are understood as inter-valley (for D mode) and intra-valley (for D’ mode) process involving electronic states at K and K’ points (for D mode) or those involving electronic states around the same K (or K’) point (for D’ mode) in the brillouin zone of graphite [113]. The D-peak shows a doublet structure with two peaks around 1347 cm\(^{-1}\) and 1367 cm\(^{-1}\) for the irradiated samples. The doublet nature becomes difficult to resolve for higher dose and is some time ascribed to the loss of 3D ordering i.e. increase in turbostraticity [115]. The FWHM of all the peaks show an increase with the dose. The peak position of G-band shows only a marginal change of < 2.5 cm\(^{-1}\) with irradiation. The irradiated samples also have a weak and broad peak around 1500 cm\(^{-1}\) characteristic of amorphous carbon with double bonding, though it has appreciable intensity only for higher dose sample. In the frequency shift range from 100cm\(^{-1}\) to 1200cm\(^{-1}\), a low intensity peak at \(\sim 1085 \text{cm}^{-1}\) (which is not seen in un-irradiated graphite) appears (not shown here). This is assigned to hydrogenated carbon with chains of alternate single and double bonds [116].

The second order spectrum of irradiated sample shows the defect induced peak D+G mode at \(\sim 2950\) cm\(^{-1}\) (absent for the pristine HOPG) which increases in intensity and broadness with dose. This feature is considered to be a combination of D and G modes. The 2*LO mode around 2450 cm\(^{-1}\) is not resolvable for higher dose sample. The G’ band shows broadening for lower dose sample and goes to a three peak regime.
(G'$_{3DB}$, G'$_{3DA}$ and G'$_{2D}$) for higher dose. Parameters deduced from Raman spectrum would be discussed for each dose in respective sections.

3.3.3. Low Dose implantation (10$^{14}$ C$^+$/cm$^2$)

Atom Force Microscopy

The changes in the topography of the sample with low dose carbon ion implantation and after the complete annealing cycle are given Fig.9 (a-d). The images are taken at two different positions on the sample. The AFM image shows that there are locations with flat patches of ordinary graphitic surface with sharp edges due to cleaving with no indication of any implantation induced disordering except for the smaller size of basal fragments compared to the pristine surface (Fig. 9(a)). Whereas at a different location of the same sample disordered protrusions are visible among patches of graphitic basal planes. The protrusions are ~20 nm high and ~a few 100 nm wide. The protrusions are too large to be due to sub-surface interstitial clusters as seen in other low dose irradiation [117], but are more likely to be the nucleation phase of the ridge structures as documented by Annis et.al. [74] (shown in Fig.2). Muto et.al. [118], using TEM studies of the ridge structure, argued that the ridges are curled graphitic planes due to $sp^3$ defects on a $sp^2$ matrix similar to the ones observed by Hiura et.al. [119], though the nucleation phase of this phenomenon is not very clear. The electronic transformation from $sp^2$ to $sp^3$ was invoked as the ridges formed within few seconds of irradiation. As seen here, the protrusions have a rather irregular structure and do seem to be along the edges of basal plane fragments. After the annealing cycle up to 1273 K, the topography looks similar to the pristine sample however with wavy nature at some locations. The regions where there are ridges or folding, remains after the annealing.
Fig. 9: AFM image of HOPG implanted with 200 keV $^{12}$C$^+$ with a dose of $10^{14}$ ions/cm$^2$ taken at two different regions. (a) The surface shows flat basal plane with sharp step-edges produced by cleaving similar to what was observed in un-implanted specimen (b) Another region on the same sample which shows small protrusions along the sharp step edges. The protrusions are ~ 20 nm high and ~ a few 100 nm wide. (c) and (d) Topography after going through the complete annealing cycle which again shows defect free regions as well as curls running through the surface.

Raman Spectroscopy

Raman spectrum of the sample irradiated to low dose was fit in three different regimes – 100 to 1200 cm$^{-1}$, 1200 to 1900 cm$^{-1}$ and 2350 to 3100 cm$^{-1}$. The measurements were taken at two different locations within the implanted zone and the maximum variation among different measurements is given as the error or deviation possible on the data points. The presence of a weak mode at ~ 1085 cm$^{-1}$ differentiates the first region from that in pristine graphite. The intensity of the peak was weak but yet was compared with another intense mode in the same region which was present in un-
irradiated graphite at 805 cm$^{-1}$. It shows an increase in relative intensity (with respect to 805 cm$^{-1}$) from ~0.30 (for 300 and 373 K) to 0.6 at 423 K. There after the peak does not show any change in relative intensity till 773K. The relative intensity shows a marginal reduction to 0.42 at 973 K and remains at a similar value for 1273K annealing. Since it has very less intensity and does not show appreciable change with annealing from 423K it will not be discussed here. The region from 1200-1900 cm$^{-1}$ is fit to 6 peaks, among which, four have appreciable intensity which are the D peak doublet, D’ and the G peak. The important parameters deduced from Lorentzian fit are shown in Fig. 10(a-b). It has been observed that FWHM of the G band is more responsive to amorphization and shows a sudden jump with very small rise in the intensity ratios [59]. Here FWHM of irradiated sample is higher than but close to the pristine value, which shows that the density of defects in the probe volume is small and that the sub-surface still maintains a high degree of crystalline nature. It can also be seen that the FWHM of the G band shows a tendency to recover with annealing. However, even after annealing up to 1273 K, FWHM remains higher than that for pristine sample. The intensity ratio of the D-peak with the G – peak on the other hand shows a rapid decline and reaches a minimum by 523 K, thereafter there is a small increase at 623 K which again undergoes a decrease. Here too, the D-peak remains in the spectrum and does not reach the condition of pristine sample even on annealing to 1273 K. The correlation length increases from ~10 nm to ~30 nm by the end of annealing cycle as shown in the Fig.10 (b). D’ intensity ratio also shows exactly the same trend as in D-peak (not shown here) but the increase at 623 K is much more pronounced. By taking the Raman spectrum along the graphite edge it was shown that the D-peak intensity shows a variation even with nature of the edge (zig-zag or armchair) whereas D’ intensity remained constant [105]. Hence the, difference in
amount of variation in D and D’ could be understood in terms of the influence of factors other than defects on the D-peak, like the region of the probed surface. The main point

![Graph](image)

Fig.10: (a) FWHM of the G band in the as-irradiated sample and its variation with annealing. The FWHM of the pristine sample is also shown as open star. (b) Annealing behaviour of the relative intensity ratio of D peak with the G peak (I_D/I_G) shown as black squares and phonon correlation length (L) shown as red circles calculated using the empirical relation in equation (8).

however is that both D and D’ peak shows a rapid decrease from 373 to 523 K which is similar to the fast process seen in other implantation studies [30,59.] The drop at the second instance from 623 K to 1273 K is slow compared to the first drop and it reflects a
complex process reported by [31]. The two processes are separated by an increase in the range of 523-623 K, which indicates an increase in the defect concentration in the sub-surface region. It has to be emphasized here that the defect can be any structural modification which can provide an elastic scattering centre in the double resonance process and need not necessarily be the ones created by irradiation. However its origin will be discussed later in the chapter. An additional broad and weak peak at 1500 cm$^{-1}$ has to be invoked to get a good chi-square for the fit. The intensity of the peak is very low and does not show any particular trend. This peak is usually attributed to be present in amorphous carbon and its weak presence shows that the damage in the probed depth is not close to amorphisation. The second order spectrum near the G$'$ band could only be fit with two peaks corresponding to 3D$_A$ and 3D$_B$ with frequency shift 2687 and 2727 cm$^{-1}$ respectively. These peaks showed marginal increase in their FWHM and remained as such during the entire annealing period. The intensity ratio between them I$_{3DB}$/I$_{3DA}$ fluctuates around 1.8 – 2.4 which is the expected value for these peaks. This shows that in the volume which is investigated by the laser light disordering along the c-axis is very small.

**Slow Positron beam spectroscopy**

The variation of S-parameter with implanted positron energy (E) for the low dose sample in the as irradiated state is shown in Fig 11(a). The variations in S vs. E after annealing for 60 min to different temperatures are also given. The data points are 5-point smoothened with fixed boundary condition and normalised with respect to the bulk value. A fit to the experimental points are obtained using VEPFIT [103] assuming a two layer model – a defected surface layer and an un-defected bulk. In the as implanted sample, the S-parameter shows a slow decrease from the surface maximum, to reach a
Fig. 11: (a) S parameter versus Positron beam energy (E) for the as implanted and isochronally (60 minutes) annealed samples. Only representative curves are shown for clarity. The top axis shows the mean implantation depth. The error bars are shown on the data for 523 K at equally spaced points. The data points are 5-point smoothened with fixed boundary. The line through the data points are fit using a two-layer model in VEPFIT [103]. With annealing, the S-parameter at the peak damaged area shows a decrease and interface between the damaged layer and the un-defected bulk shows a re-growth towards the surface. (b) The variation of the average of S-parameter till 2keV as a function of the annealing temperature is shown.
“flat” region extending from ~ 3 keV - 7 keV (i.e. ~ 100 - 400 nm) followed by a shoulder. Beyond this, the S-parameter shows a gradual decrease towards the bulk. The peak damaged region (identified as the “flat & shoulder” region) agrees well with the vacancy profile predicted by TRIM [109]. The damage is highest near the projected range with decreasing disorder towards the surface, which is evident from the closeness of the trend of the curve to that of the pristine sample near surface. The higher S-parameter at the surface is due to Ps formation as well as due to surface restructuring after irradiation with protrusions. In the sub-surface region (< 2 keV, 50 nm), the defects created by irradiation are not trapping positrons as efficiently as in the projected range and hence, they are able to escape to the surface giving a greater contribution from surface S-parameter. By thermal treatment of the sample at 373 K for 60 minutes, the “shoulder” or the interface between the defected layer and the pristine layer move towards the surface accompanied by a decrease in the S-parameter of the damaged region. At 423 K the curve looks same as that of 373 K, except for a pronounced lower S-parameter at the peak damage region with same boundary. For 473 K, the interface moves towards the surface with little change in S-parameter. The trend of decreasing S-parameter and increasing recovered region continues for isochronal treatments at higher temperatures and by 773 K there is a near complete (a small hump is seen very near to surface) removal of the defected (open volume) region. On annealing the sample further at 973 K and at 1273 K, the gradual decreasing trend in S-parameter observed for pristine sample is repeated. It is also noted that there is a decrease in the surface S-parameter (< 2keV/50nm) with annealing, the maximum change at 373 K, which gradually slows down at 523 K. There is a second large decrease beyond 523 K, after which the surface S-parameter remains more or less constant. To make this point clear, this variation is shown in Fig.11 (b), where average of S-parameter from 0 to 2 keV is
plotted as a function of annealing temperature. Another factor is the existence of definite flat region where S-parameter is more or less constant in the as irradiated sample and up to 423 K annealing. The flat region suggests that in spite of positron implantation profile broadening and positron diffusion after thermalisation, positrons are seeing similar open volume region in this depth range and the S-parameter is solely that of the damaged region from 100-300 nm and is free from diffusion related contribution from surface or bulk. It is also clear that there is a definite motion of open volume region towards the surface at 623 K.

The experimental S versus E data is fit using VEPFIT and the results are shown as a box profile in Fig. 12 (a). The S-parameter derived for the defected layer is now corrected for positron-diffusion after thermalisation. The width of the box represents the width of the defected region as seen by positrons. Fig.12 (b) shows the variation of derived S-parameter and width with thermal treatment. An ideal model for VEPFIT, could have been one with three layers instead of two as shown above, the additional layer representing the sub-surface defects. A three layer model, however produced unrealistic results with poor chi-square values. This is due to the difficulty in delineating the surface from the near or sub-surface region due to the large diffusion length of positrons in graphite. Hence even though a single value is given for the defected layer from surface, the value is more representative of the defected region 100 – 300 nm. The values are very close to that obtained in flat region of the S versus E curve (Fig.11(a), giving proof for the earlier argument that the S-parameter at flat region is a true representation of the defected layer. The data for 423 K could not be fit to good chi-square with fixed values of bulk diffusion length and physically significant width of damaged layer and hence not shown here. Though taking clue from the other fits it is
Fig. 12: (a) S parameter versus depth as derived from VEPFIT using a two layer model for as implanted and annealed samples. (b) The values of derived S-parameter and upper boundary of the defected layer with error bars.

clear that the S-parameter would be exactly same as that in the flat region i.e. same as that for 473 K and upper boundary of damaged layer would be close to that for 373 K, though the surface restructuring is pronounced in this case making the total width of the damaged region smaller. It was also difficult to fit the data for 773 K to two layers as the
small hump like feature is very close to the surface occurring at around ~ 50 nm (2 keV), and hence was only fit to bulk layer.

R-parameter which is defined as $\frac{S-S_{\text{bulk}}}{W-W_{\text{bulk}}}$ is free of the effect of concentration of defects [120] provided there is only one type of defect. For bulk measurements R parameter can be calculated correctly if there is homogeneous distribution of defects in the probe volume. In case of beam measurements, S-W correlation plot gives a similar qualitative picture as R-parameter calculated for specific positron energies will not be a correct indicator with a dependence on positron diffusion and possibility of trapping at other sites away from region of interest. R-parameter can then be considered as a slope in the S-W plot and a change in slope will point to a change in defect character and not concentration. The S-W correlation plot of the as-implanted sample is given in Fig. 13. The plot also contains the inflexion points of annealing at 373, 423 and 473 K. This is done to keep the clarity of the figure. Each temperature is identified by a different colour and different symbol. The pink arrow (with head and tail) passing through the yellow squares gives the direction of increasing energy, with arrow head at (S,W) of pristine sample close to (1,1). Yellow squares lying outside this arrow represent the damaged region in the as implanted state. Similar deviations for other temperatures are given. It is clear that the (S,W) co-ordinates corresponding to inflexion or deviation for annealing temperatures from 373 – 473 K lie on a line joining them to the bulk (S,W) value, where as the as irradiated sample lie outside this line. Thus, at 373 K there is a definite change in defect type, and for annealing up to 473 K, a change in concentration of this defect type is expected. For higher annealing temperatures the deviation from the straight line denoted by the pink arrow is too small or too close to the surface making such analysis difficult.
Fig. 13: S vs W parameter for as-irradiated (RT) and annealed sample (up to 473 K). The complete S-W correlation plot is given for as-irradiated sample with positron beam energy as running parameter. The pink arrow represents the increasing positron energy. For other temperatures, only the inflexion or deviation points are shown for clarity. Different temperatures are identified in the figure by different symbols and colours. The black line is an aid to the eye to identify that inflexion points of 373, 423 and 473 K lie on straight line joining them to the undefected bulk (S,W) co-ordinate.

Thus to summarize, the sub-surface S-parameter (≤ 50nm) shows a major drop at 373 K, with a maximum decrease at 623 K. Beyond this there is not much change in sub-surface S-parameter. The defected region S-parameter shows a decrease starting from 373 K with maximum drop at 423 K and at 523 K with a little change (factoring the statistical error) at 473 K. At 623 and 673 K, the defected region is close to surface signalling a migration of open volume region towards surface. The maximum recovery of the damaged region (in terms of width) happens at 523 K. Complete recovery takes place for annealing at temperatures more than 773 K. The S-W correlation plot gives a hint that there is a change in defect character at 373 K and from 423-473 K, change in S-parameter is due to change in concentration of the defects rather than a change in its type.
3.3.4. High Dose implantation (10^{15} \text{C}^+/\text{cm}^2)

**Atom Force Microscopy**

AFM images of the sample irradiated to $10^{15}$ \text{C}^+/\text{cm}^2 are given Fig.14 (a-c). The images taken after the annealing cycle is given from Fig. 14(d-e). The images are taken at different positions on the sample. The AFM image shows structures similar to the ones given in Fig.2, with ridges on the sample. The first image shows the existence of linear ridges running across the sample. The second image shows curvilinear ridges apart from the linear ones. The third image gives evidence of linear ridges going in opposite directions giving a square grid structure with oriented flat basal plane inside each grid. The ridges are of the order µm in length. These were considered to be associated with twin bands due to its development along crystallographic directions [54]. It was later assigned to the fragmentation of basal plane followed by adatom aggregation along the stress centres at the fragment interface [74]. These were also assigned to curls on graphite sheet due to sp^3 hybridisation and speculated its development along twin directions [118]. From XPS studies, there is evidence of mixed sp^2-sp^3 nature at least in the sub-surface (~3 nm) region giving credence [121] to the idea.

For the aggregation mechanism, an activation barrier of 0.47 eV [78] has to be crossed for surface migration. Such large scale ridge formation becomes hard unless the migration parallel and perpendicular to the basal plane becomes faster in the dynamics of irradiation and the migrating atoms avoid other possible traps. For low dose implantation also, µm level irregular protrusion were seen in Fig. 9 along the step edges and such structure becomes difficult to be explained by adatom aggregation mechanism alone as the entire irradiation lasts only for a short time. It is known that with increasing dose there is an enhanced fragmentation of basal plane leading to bending and cross linking of the planes with added stress along the fragment interface. This would lead to an
increased sp³ character of the graphite sheet and hence there will be an added curling of the surface sheets to relieve stress accumulated in the surface and sub-surface layers. Depending on the amount of irradiation dose the fragmentation can be along the weak centres like the grain boundaries, step edges etc. or along certain preferred orientation or at random sites. Thus low dose implantation leads to fragmentation along the already existing random step edges in the pristine sample with bending and curling leading to irregular µm level protrusions. Small amount of wrinkling, recovery and waviness is

Fig.14: AFM image of HOPG implanted with 200 keV $^{12}$C⁺ with a dose of $10^{15}$ ions/cm² taken at three different regions. (a) The surface shows oriented basal plane strips separated by linear ridges running across the sample in a roughly periodic manner (b) Another region on the same sample which shows curvilinear ridges. (c) Square grids with linear ridges running across in perpendicular directions. (d) Topography after the full annealing cycle. 3D plot shows an intricate network structure. Small change is observed by annealing with increase in cross networking and ridges could be seen running inside each grid as well. (e) Regions where only linear ridges are present remain even after annealing.
seen after annealing up to 1273 K, thus showing that point defect recovery at the surface does play a role during their subsequent evolution by annealing. At medium doses fragmentation and curling progress along certain preferred orientation [77] leading to linear ridges and at higher dose random directions start to fragment and curl leading to curvilinear ridges and wrinkling. Annealing treatment does not show appreciable change, however the curvilinear ridges exhibits a little more intricate structure showing an enhanced stress release by curling during vacancy recovery near surface. Such surface features are also an indication of large scale damage extending from the projected range up to the surface as is evident from slow positron results below showing the importance of sub surface disorder and their recovery on surface topography.

Raman Spectroscopy

Raman spectrum obtained at two different regions of the sample implanted to high dose is given in Fig.15 (a-c). Unlike in the case of low dose sample the measurement at two points did not always give the same parameters and this is represented as two sets of points in the graphs – solid squares and open circles. It shows that the sample sub-surface has highly disordered regions close to amorphisation which is represented by FWHM of G-band > 45 cm\(^{-1}\). There are also other less disordered regions with FWHM < 40 cm\(^{-1}\). These regions show different annealing behaviour for FWHM where the highly disordered region not showing any significant recovery till 973 K where as for regions with lower FWHM the recovery starts by 423 K. For latter, there is a fast drop beyond 423 K, a threshold region is seen between 573 K – 723 K and a slow decrease thereafter. In the case of the intensity ratio of D-peak with the G-band (Fig. 15(b)), both sets show a similar trend even though the values are different. There is fast decrease in the intensity ratio from 373 K itself with a slowing down near 573 K –
723 K beyond which there is a slow drop. The phonon correlation length calculated increases from ~ 2.5 nm to 25 nm by the end of annealing cycle as given in Fig. 15(c). As in the case of low dose sample, the FWHM and the intensity ratio does not reach the pristine values even after annealing to 1273 K. Apart from the these four peaks, the broad peak at 1500 cm$^{-1}$ has to be introduced to get a good fit. Here the integrated intensity ratio of 1500 cm$^{-1}$ peak with G-band remains constant throughout the annealing cycle at around 0.25±0.11, which is appreciable compared to other peaks in the region. Its presence shows high level of disordering close to amorphisation in the sub-surface/surface region, which is also corroborated by high FWHM of the G-band at some regions of the sample.

The second order spectrum from 2350 – 3100 cm$^{-1}$ was fit to 6 peaks. Three of them constituted the G’ band, one of them was the D+G band and the other two belonged to the band at 2450 cm$^{-1}$. The G’ band was now found to consist of a broad peak around 2704 cm$^{-1}$ with a standard deviation of 5 cm$^{-1}$. This is very close to the G’ peak assigned to turbostratic or 2D graphite. Hence the implantation dose is such that in the sub-surface region there is a loss of c-axis ordering. The intensity of this peak with respect to the more intense 3DB peak at ~ 2727 cm$^{-1}$ fluctuates around 0.2-0.6 and does not show any decreasing trend by annealing up to 1273 K. However the FWHM of both 3DA and 3DB peaks show an overall decreasing trend from values as high as 150 cm$^{-1}$ to 50 cm$^{-1}$. The intensity ratio between 3DB to 3DA is smaller than that obtained for low dose and pristine sample but shows a higher value of 1.8 - 2.2 for the final annealing temperature of 1273 K.
Fig. 15: (a) FWHM of the G band in the as-irradiated sample and its variation with annealing. (b) Annealing behaviour of the relative intensity ratio of D peak with the G peak (c) phonon correlation length calculated using the empirical relation in equation (8). Solid squares and open circles represent measurements at different positions on the implanted zone.

Slow Positron beam spectroscopy

The dependence of the defect annealing mechanism on the irradiation dose is brought out by the S vs. E curves for the sample irradiated to higher dose and its thermal evolution in comparison to that for low dose sample. The curves are given in Fig 16 (a). It should be mentioned that only representative temperatures are shown for clarity. The curves obtained for as irradiated sample and after annealing at 373 K was exactly the
same. The S parameter curves showed no difference between annealing temperatures 423 and 473 K. Similar trend was also seen at 573 K and 623 K. The observed defect annealing mechanism can be better conveyed through Fig. 16 (b-c) which plots the S-parameter at specific energies (5 keV & 2 keV) as a function of temperature where interesting features were seen, one representing a peak in S vs E curve and another a local minimum in the same curve. The as irradiated sample shows an increase in S-parameter from the surface to a high value between ~ 3 keV - 5 keV beyond which there is a drop to the bulk S – value in S vs E curve as given in Fig. 16 (a). The sub-surface (1-2 keV) shows a small recovery on annealing to 423 K. At 523 K two interesting features arise, one a local minimum around 2keV and another a peak at around 5 keV. The peak at 5 keV has lesser S-parameter compared to the as irradiated state and it decreases on further annealing to 573 K as also shown in Fig. 16 (b). The S-parameter at 5keV remains at around the same value on further annealing till 673 K, after which the peak in S vs E curve disappears (at 723 K) and the curve resembles that of the low dose sample at 523 K with a shoulder. There is a definite movement of the peak towards the surface, with a shoulder now appearing at lower energy as compared to the peak position. The S-value corresponding to the shoulder shows a decrease on annealing to 773 K and shows a complete disappearance by 973 K. Annealing at 1273 K takes the S-parameter near the projected range to values lower than bulk S-parameter. The small recovery seen near surface at 423 K becomes the local minimum at 523 K, and it shows further decrease only at 673 K as also shown in Fig. 16(c). With the appearance of the shoulder near surface, the local minimum disappears and the S-parameter of the region now represents this higher S-parameter which decreases on annealing to 973 K. There is not much change in sub-surface S-parameter on further annealing to 1273 K, however the surface S-parameter at 0 keV (i.e. 235 eV beam transport energy) shows a decrease at 1273 K.
from the earlier values. Unlike the low dose sample, here the back interface between the damaged and the pristine region shows a sluggish recovery for temperatures greater than but near 523 K, making a major shift only at 723 K.

Fig.16: (a) S parameter versus Positron beam energy (E) for the as implanted and isochronally (60 minutes) annealed samples. Only representative curves are shown for clarity. The top axis shows the mean implantation depth. The error bars are shown on the data for 523 K at equally spaced points. The data points are 5-point smoothened with fixed boundary. The line through the data points are fit using a two-layer model in VEPFIT [103]. (b) Variation of S-parameter at 5 keV (implantation depth ~ 232 nm) with temperature where a peak appears in Fig. 16 (a) after annealing up to 523 K. (c) S-parameter at 2 keV (implantation depth of 50 nm) with temperature where a local minimum appears in Fig. 16 (a) after annealing up to 423 K.
The data for as – irradiated sample is fit to a two layer model and for annealing treatments from 423-673 K a three layer model is used in VEPFIT to account for the local minimum. For annealing temperatures from 723 K, again a two layer approach gives the best fit. The results are shown as a box profile in Fig. 17. The recovery near surface which starts at around 423 K, grows towards the damaged region till 673 K and S-parameter of the region is even lower than the bulk value from 523 K onwards. The S-parameter of the damaged region represented here is free from diffusion related contributions and thus is higher than the experimental S-parameter at 5keV plotted in Fig. 16(b), but the trend remains same. This is true for S-parameter of the sub-surface region. The width of the damaged region decreases with annealing mostly due to the recovery at the surface before moving towards the surface.

![Graph showing S parameter versus depth](image)

**Fig. 17**: S parameter versus depth as derived from VEPFIT using a two layer model for as implanted and for thermal treatments at 723 K, 773K, 973 K & 1273 K. A three layer model is used for other temperatures.
The S-W correlation plot for as-irradiated sample is shown in Fig. 18(a), with
linear fits to three regions, showing three slopes near the inflexion point. Fig. 18(b)
shows the same curve along with S,W co-ordinates corresponding to the inflexion points
alone for annealing temperatures from 523 – 623 K. The details of the curve are given in
the figure caption. The key information from Fig. 18(a) is the presence of two separate
positron trapping regions, one near surface and the other at around 5keV represented by
intersecting straight lines. The near surface trap region could not be brought out by
VEPFIT but appeared as a separate minimum from 423 K. The S-parameter of damaged
layer got from VEPFIT represents the deeper trap which is evident from the closeness of
this to the value at intersection i.e. ~ 1.035. Annealing brings out its presence by a peak
around the region. The peak region appearing at 523,573 and 623 K lie along a straight
line through bulk S,W value. This shows over thermal treatment, the concentration of
this defect decreases till 623 K. From as irradiated state to 523 K, however the change of
slope is small and hence it is not possible to say conclusively whether there is an actual
change of defect type. In the as irradiated state, there will be different type of defects
because of high dose of implantation. It is possible that the particular defect type is
distinguishable when others are removed through thermal treatment as seen by the drop
of S-parameter near surface. Hence evidence is presented for the first time for spatially
separated defect types in as – irradiated state of HOPG which has different thermal
stabilities. The one which is dominant near surface starts to anneal out from 423 K itself.
The prominent defect near the projected range is stable up to 673 K, which most
probably disintegrates and moves towards the surface at later annealing temperatures.
Fig.18: (a) S vs W correlation plot for as–irradiated (RT) sample with positron beam energy as running parameter. The increasing positron energy is represented through different symbols as given here. Red squares for 0-1 keV, orange circles for 1.5-5 keV, green triangles from 5.5-8 keV, blue kites for 8-11 keV, and others for higher energies. Three straight lines are linear fits to three slopes near inflexion point, surface to ~ 2keV (green), 2.5-4.5keV (black) and 5 keV- 20 keV (red). The S,W coordinates corresponding to the intersection of straight lines are given near each crossing. (b) S-W correlation plot as in (a) but with inflexion points (alone) of other annealing temperatures identified by different symbols. The peak region in S-E curve is identified here. The violet arrow is an aid to eye showing a near straight line passing through S,W coordinates of the peak region of temperatures from 523-623 K to bulk S,W values. The olive green arrows connects one of the intersection points derived for as-irradiated state to the peak region of 523 K, showing small change of slope with respect to the violet arrow.
Hence to summarize, the as–irradiated sample shows two trapping sites for positrons, one dominant near surface and the other near projected range. The near surface defect starts annealing by 423 K; however the major change happens at 523 K (just beyond 473 K) creating a local minimum in S vs E curve. There is further decrease in near surface S-parameter with annealing up to 673 K, the layer S-parameter going below bulk value as derived from VEPFIT. The recovery up to 673 K mostly happens near surface decreasing the width of the damaged region as the back interface motion is slow till 673 K, showing a boundary motion to surface only at 723 K. The defect near projected range shows a decrease in concentration till 673 K, beyond which it most probably disintegrates or/and moves to surface. The defect thus accumulated near surface undergoes complete recovery by 973 K. However the S-parameter of the recovered region lies below the bulk S-value.

3.4 Discussion

Broadening of FWHM of the G-band has been related to vibration excitation lifetime near a defect [26, 64] or to C-C bond length/nature variation by irradiation. For the low dose sample, inside the Raman probe volume there is not much disorder along the c-axis as evidenced by the absence of any major parameter shift in the second order spectrum. However there are point defects as well as fragmentation of basal plane and nucleation of the ridge structures which would cause an increase in FWHM of the G-band due to the limited lifetime of phonons starting at the fragment interfaces or at point defects inside of the basal fragments. The amount of broadening is low in this case as seen from the values obtained. It is known that the 2D re-growth with a-axis alignment for pyrolytic graphite starts above 1873 K [36], hence no variation is expected in FWHM by annealing up to 1273 K, even when point-defects contributing to the broadening have
been removed. The relative intensity ratio on the other hand is related more to the in-plane defect density prior to clustering and hence shows a sharp drop during annealing from even 373 K signalling a fast defect recovery process in the sub-surface region inside each fragment. The subsequent slow drop beyond 623 K shows that a slow complex defect recovery process dominates. The non attainment of the pristine value for 1273 K also signals that the intensity ratio has its share from the fragment interfaces as edge of graphite sheets are also defect states that give rise to the D-peak. Hence, the intensity ratio would reach zero only beyond 1873 K when actual grain growth starts along a-axis and later along c-axis.

In the case of higher dose sample too the intensity ratio behaves in the exactly same way with decrease from the first annealing temperature. However, the intensity ratio is much higher now and the decrease is not as sharp as in the case of low dose sample. There are different intensity ratios obtained from different regions of the same sample, however both show similar two-slope decrease with a relatively faster drop followed by threshold around 573-623K, and a slow decrease. The difference in behaviour from low dose sample is evident from FWHM of G band, which is much higher than that of low dose sample. There are also different values obtained from different regions of the same sample showing inhomogeneous distribution of disorder and different annealing behaviour. It has been shown that there is a slow recovery when there is near amorphization by implantation [25]. Hence, in this case the little change in FWHM of G band till 973 K would point to highly disordered region, probably belonging to broken, bent and curled and cross linked sheets, which are responsible for ridged and cracked formations on the graphite surface. The 3D disorder along the c-axis which is shown by the presence of weak 2704 cm⁻¹ band, also require temperatures as high as 2573 K to be removed by recrystallisation along that direction. The presence of
ridged surface may also be responsible for peaks at 1500 and 1085 cm\(^{-1}\) going by their stability till 1273 K. Inter and intra planar defects or clusters which can affect the planarity of graphene sheets also contribute to FWHM rise by changing the bond nature and length. But these can recover at much lower temperature as and when the defects responsible are removed; hence FWHM of G-band from such regions show a decrease with annealing from about 423 K and shows a trend similar to the intensity ratio. Hence for both lower and higher dose sample there is a fast recovery process at low temperatures and then a slowing down across the similar temperature range from 473-723 K, followed by a slow decrease. The difference among them points to the complexity of the defect structure involved in the surface and the sub surface region.

The difference arising from the type and density of defects is also reflected in the annealing process as imaged by the open volume defect sensitive S-parameter. For the low dose there is recovery of the damaged region from the projected range and from the front surface from 373 K itself with a marked reduction in S-parameter. However the drop is significant beyond 473 K signalling the importance of some process which enhances the open volume defect or vacancy removal after this thermal barrier. There is also a movement towards surface from 623 K - 773 K, which is an extremely low temperature for all sorts of defect migration along the c-axis with the reported migration energies for c-axis diffusion. For higher dose sample however there is no recovery at the projected range till 673 K. Near surface recovery starts only at 423 K and the barrier at 473 K is significantly visible with large drop in S-parameter at the first temperature (523 K) beyond this point. The surface bound movement is from 723-773 K. For both low dose and high dose sample complete recovery is achieved by 973 K, but the structure to which recovery happens is different with higher dose sample giving a lower than bulk S-
parameter which was also reported by Yang et.al.[99], however no explanations were provided.

The 473 K annealing temperature which seems important here is linked to the Wigner energy release process and is attached to I-V recombination [50]. However the process which leads to recombination has many possible candidates. Many of the earlier studies has considered the possibility of I getting released from a trap whose binding energy is of the order of 1.3 eV, though the exact nature of trap was not identified [16-18]. Some others utilized the lower migration of I to account for I-V recombination at temperatures lower than 473 K and disassociation of I₂ clusters for recombination beyond 473 K [50]. Accumulation of I₂ and vacancy loop at temperatures lower than 573 K, disassociation and migration of I₂ above 573 K and migration of vacancies to form vacancy loop at 773 K are another set of processes speculated to explain the recovery process at temperatures which is much lower than the recrystallisation in 2D or 3D [61]. An intimate I-V pair which was first theoretically predicted and later experimentally seen [91, 97] is also held responsible for the sudden jump near 473 K. It was also shown theoretically that I-V pairs did not form in all cases and depended on the approach of I near a α-site (atom on top and bottom) or a β-site (hexagon centre top and bottom). I-V pair was shown to form only near β-site and no barrier was seen for recombination at α-site. I-V pair recombination barrier was also depended on its nearby structure – perfect, sheared or near-surface [84]. The vacancy is assumed to be immobile in many of these speculated processes and hence required a mobile I. Telling et.al. [89] also assumed structures like inter-planar divacancy to explain the observed immobility of otherwise mobile (~ 1.7 eV) vacancy and attached its existence to vacancy density. The slow recovery was always associated with I released from large clusters or dislocation loops of I type, and vacancy clustering to or collapsing to dislocation loop of V type.
The channelling result by Venkatesan et.al. [36] reflects (Fig.1) I movement and it can be seen that I is released near surface even at 573 K. It could be also assumed from the known migration energies that I migrates before a vacancy and hence the initial recovery at 423 K for higher dose sample could be due to I migrating to α-sites leading to I-V recombination without any barrier or to β-sites leading to I-V intimate pairs. When the 473 K barrier is overcome I migration followed by enhanced I-V recombination could explain the observed large reduction of S-parameter near surface. Theoreticians have predicted at least three type of interstitial positions-bridge, y lid and spiro- their stability depending on the existence of sheared graphitic order [93]. The defects, I and V which recovered from 423-523 K near surface also caused large increase in FWHM and defect peak intensity ratio in Raman spectrum. Hence those structures which could cause an interlayer bonding with basal plane buckling could be responsible here rather than simple bridge structures. Hence the migration of single I which cause interlayer bonding is thought to start from 423 K. The recovered vacancy defect may also be of larger type like the V₆ or V₉ as predicted by pulsed positron lifetime [13].

The lack of recovery at the end of range is due to alternate I and V structures which are more stable against migration or recombination. The S-W correlation plot (Fig. 18) gives evidence that the vacancy structure in the as irradiated state and that in 523 K annealed condition are different. It could be thermally produced by vacancy clustering. This is possible if the vacancy migration barrier is in the range as predicted by most of the theoretical studies i.e. 1-1.7 eV. The new structure formed should also be energetically more favourable than its isolated components. If any barrier for structure transformation is involved then that should be achievable in this thermal treatment. For example the first neighbour in-plane divacancy formation from migrating monovacancy has to undergo a barrier of at least 1.6 eV to collapse to 5-8-5 structure [81].
is an indication of c-axis migration at 723 K, a-axis migration which would involve lesser structural barriers could happen at earlier temperatures. Larger vacancy clusters could also be produced athermally by knock out near a vacancy which does not get enough time to relax. Such defect formation was experimentally demonstrated by in-situ HRTEM measurements where vacancy loops were imaged during the dynamic condition of electron irradiation [122]. These loops were thought to originate from the in plane divacancy that collapses to a vacancy line and which later leads to dislocation dipoles as predicted by Niwase et.al [66]. Another possible vacancy structure which is stable against migration and recombination and which can be formed thermally or otherwise is the inter-planar cross linking di-vacancy. When other vacancy structures in the end of range are removed in the relaxation process prior to 523 K, these stable entities come to the fore as prominent trapping sites. Vacancy loops of appreciable size are shown to exist till very large temperatures like 1773 K. Also the migration energy for in-plane divacancy has been consistently modelled to be large of the order of 7 eV and hence once it forms in the temperature range of present annealing there is only possibility for its growth and no chance of any movement. However beyond 723 K there is marked movement of the structure towards surface. Thus the most possible structure giving a separate peak from 523 – 673 K is inter-planar divacancy. This is the first time any evidence is given for such structure and a temperature range where it could exist is shown. It has greater probability to form at the end of implantation range when the primary knock on has only enough energy to create at most one more secondary. Along the c-axis, it is only when the primary knock on is displaced at acute angles forcing it travel through the inter layers that the vacancies in corresponding layers be widely separated. Otherwise the vacancies can be at least in second nearest neighbour position in adjacent layers causing it to interact and form interlayer bonds via the John-Teller
distorted atom near a vacancy. Its presence is also related to vacancy density i.e. probability of having two nearby vacancies at adjacent layers reduce with reduced density thereby not making them homogeneously distributed to efficiently trap positrons.

The interlayer divacancy structure becomes unstable beyond 723 K and this result in release of vacancies at adjacent planes. The released vacancies are seen to move towards the surface. This is surprising given the high barrier for c-axis migration for vacancies. It could be noted in the channelling data there is no movement or drop of disorder at the implanted range even at 1373 K annealing and hence the drop here in the peak S-parameter near to \( R_p \) at 723 K has to be due to divacancy disassociation. The observed migration towards surface warrants a theoretical relook at vacancy diffusion along c-axis. The observed threshold in the “intensity ratio” and “FWHM” recovery near 523-723 K could be attributed to this transition from the first to the second recovery phase. In the first phase maximum possible near surface defect recovery has been achieved till 523 K and in the second phase at 723 K there is vacancy migration towards surface thereby maintaining the D-peak intensity at around the same value. The surface bound vacancy recovery process is slow due to the complexity of c-axis migration. After complete removal of vacancies by annealing up to 1273 K, the S-parameter in the damaged region is lower than the bulk S-value. It was assumed that single I migrate beyond 423 K above. This may also lead to the formation of highly stable di-interstitials or their clusters which form very strong interlayer bonds. The densification due to such \( sp^3 \) natured clusters could explain the occurrence of lower than bulk S-value in the damaged region as well as in near surface region. It has to be remembered that when basal plane vacancies are removed positrons annihilate mainly from interlayer regions. Similar argument was given before for the observed positron lifetime drop in neutron irradiated samples [69].
In the case of low dose sample however the vacancy annealing mechanism is much simpler because of the presence of mostly isolated Frenkel defects. Through Raman spectroscopy and AFM it is clear that there is not much disorder along the c-axis and hence interlayer cross linking defects (I and V) will be less dense. Thus I would be mostly bridge type and vacancies would have John Teller distortion however little cross linking. This is evidenced by sharp drop seen in Raman intensity ratio as well as S-parameter recovery both from the front and back surface that could be attributed to the I-V recombination from 373 K. Compared to 373 K, there is larger S-parameter recovery at 423 K and no change at 473K. Taking clue from the recovery in high dose sample from 423 K, it can be argued that recovery from 373-423 K is due to migrating isolated bridge interstitials where as from 423 K – 473 K the cross linking interstitials also become mobile and contribute to recombination. However, the little S-parameter change at 473 K shows that for further large scale annealing the recombination barrier has to be overcome. This is found true by the pronounced drop at 523 K. The S-W correlation plot had shown a change of defect pattern at 373 K from as irradiated state which is followed up only by decrease in its intensity with annealing signalling the existence of different vacancy states in as-irradiated state. From 623-773 K there is a movement of defects towards surface (again showing a c-axis migration) and this coincides with the increase seen in the Raman intensity ratio. Thus the threshold region seen for intensity ratio recovery at 523-723 K is again associated with fast recovery followed by the complex process of c-axis migration of defects towards surface and hence is slow.

Here no mention has been given when the basal plane migration of vacancies start. No such indications of basal plane migration were obtained from the positron beam measurements; however an intelligent guess can be made based on the following arguments. Since basal plane migration is energetically and structurally more simple than
c-axis migration, the basal plane migration has to be before 623 K i.e. before \textit{c-axis} migration. If vacancy migration starts before the recombination barrier is achieved then pronounced vacancy and interstitial clustering would be there which would not result in the observed S-parameter drop seen at 523 K for higher dose sample. Hence the migration should be after 473 K. This agrees well with the theoretical value of around 1.7 eV [89].

### 3.5 Summary

The defect annealing mechanism has been investigated at different depth scales in HOPG samples irradiated to two different doses. AFM, Raman and Slow positron spectroscopy has thrown light on the microstructural changes due to irradiation and their thermal recovery. The major findings of this study are

- For higher dose implantation a highly ridged structure is obtained which is due to the breaking, bending and curling of the graphitic sheets. Recovery of sub-surface defects at surface sink has some effect on topography with enhanced stress relief via wrinkling. Low dose shows near flat surface after sub-surface defect recovery although small amount of curling remains.

- The integrated intensity ratio obtained from Raman spectrum shows a fast recovery process followed by a threshold region and a slow recovery up to 1273 K for both high and low dose sample. Recovery via I-V recombination is responsible for the fast near surface recovery. Threshold region is due to the transition from fast I-V recombination process to a slow defect migration process where there is migration of vacancies to surface.

- For low dose sample open volume defect recovery as seen by positron Doppler broadening spectroscopy, starts from 373 K itself and is due to I-V recombination
as pointed out before. Isolated point defects which do not contribute to inter layer bonding like the bridge interstitials and monovacancies play a major role here. After the recombination barrier is overcome an enhanced S-parameter recovery is seen. c-axis migration starts from 623-773 K, which is much less than the migration barrier reported.

For high dose sample surface recovery starts at 423 K which gets enhanced beyond the I-V recombination barrier at 473 K. Cross linking single interstitials and vacancy clusters which could absorb interstitials play a major role here. Such structures was assumed to account for observed large FWHM of G-band and its fast recovery in Toto with near surface S-parameter drop. Interlayer divacancy is shown to trap vacancies near the projected range from 523-673 K, beyond which they break and show a migration towards surface from 723 K, the existence of which is shown for the first time. The migration also correlates well with threshold region seen in both FWHM and intensity ratio recovery seen in Raman spectrum. Complete recovery is obtained after 973 K.

An indication of when the basal plane migration starts was obtained indirectly to be between 473 and 623 K.

When compared to channelling data by Venkatesan et.al. [36], it becomes clear that interstitials are locked up in stable structure near the implanted range and are responsible for the low S - value obtained at 1273 K. As interstitials are mobile from 423 K, cross linking di-interstitials could be responsible for S-parameter values lower than that in the bulk.
3.6 Conclusion & Future outlook

A comprehensive vacancy annealing mechanism in irradiated HOPG was brought out by using slow positron beam, Raman and AFM measurements. It was shown that the defect annealing mechanism is dependent on the dose of implantation and the density as well as type of defects produced at different implantation. New theoretical studies have to be invoked on c-axis migration of vacancies as surface migrations at lower temperatures were reported here. Experimental evidence for vacancy trapping defect types was also provided for the first time along with their thermal stability.

It is possible to identify pin-pointedly the various defect process reported here by the identification of defect structures involved by carrying out beam based positron lifetime experiments. Isothermal annealing studies can be carried out to find the activation energies of various processes reported here. It is also important to track surface restructuring using STM which provides much higher resolution than AFM with each annealing step. The studies could be complemented by ab-initio calculation to find positron parameters – lifetime as well as momentum distribution – for various exotic defect structures like the interplanar divacancy, intimate I-V pair and cross linking interstitial clusters which can be compared with the obtained experimental values.

References:


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The previous two chapters discussed about defect creation via ion implantation and their thermal evolution using slow positron beam Doppler broadening spectroscopy. Even though this technique could give a qualitative idea on the vacancy annealing mechanism including possible impurity complex formation, the exact nature of defects remained sketchy. This is because of the inability of defining a proper defect related functional form for the Doppler broadening of the 511 keV $\gamma$ curve. These are two example cases were positron lifetime as a function of temperature would have given a more rigorous proof for some of the defect structures proposed. There are many other possible applications like in thin film technology where it is important to identify open volume defects in a depth resolved manner. In these applications a positron beam based lifetime system would be a good tool to supplement the findings of a beam based Doppler broadening results.

In the following chapters, an attempt at the design and development of a pulsed positron beam is described starting from the development of a slow positron beam for Doppler measurements. A methodology based on radio frequency pulsing, which has been successfully used for getting a beam based lifetime system worldwide has been utilized here.