GROWTH AND CHARACTERIZATION OF NANO STRUCTURED COMPOSITE CARBON FILMS

Ph.D Thesis
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2007-Ph.D-Phy-02

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2013
IN THE NAME OF ALLAH, THE MOST MERCIFUL, THE MOST BENEFICIENT
DECLARATION

I hereby solemnly declare that this is my own piece of work based on original and empirical study. This thesis has never been submitted anywhere for a degree or publication in this form. The work cited in the thesis is properly referenced and acknowledged.

Arslan Usman

2007-Ph.D-Phy-02
ACKNOWLEDGEMENT

The whole praise to ALLAH, the Sovereign power, the creator of universe, WHO gave us knowledge, made us the super creature, blessed us with knowledge and enabled me to accomplish this task.

All respects are for Holy Prophet Muhammad (Sallallaho-Alaihe-Wasallum), WHO is forever a source of knowledge and guidance for whole mankind.

My greatest appreciation is for my supervisor Prof. Dr. M. Shahid Rafique, Chairman Department of Physics U.E.T Lahore, for his guidance, keen interest in the project and continuous encouragement during the completion of this research work. His friendly behavior encouraged me to conduct research in burden less environment. He made research very easy and entrusting for me. I am extremely thankful to him for his kind cooperation and encouragement in this project.

I also express my profound gratitude to Prof. Dr. M. Khaleeq-ur-Rahman, Ex-chairman Department of Physics, UET Lahore, for his personal interest, tremendous cooperation and valuable suggestions. His leadership abilities gave me a passion towards research work; this is all due to his encouragement and guidance that I am able to accomplish my task.

I further extend my greatest appreciation and thanks to Dr. Khurram Siraj for his keen interest and guidance during the project work. He is always available for discussion about the project.

My best regards to my mother, brothers and sisters for their love, affection, encouragement and prayers that are always with me in every front of my life. I also want to pay regards to my father (late), who did a lot for me and was a source of inspiration for me.

Most importantly I would like to thank my best friend and wife, Afshan Ashfaq for her care and unconditional support throughout this project. Her confidence in me always gave me strength and courage to achieve my goal.

I also want to say thanks to Dr. Anwar Latif, Dr. Abdul Waheed Anwer, Dr. Safia Anjum and Dr. Hamid Latif for their sincere support and friendly behavior which helped me a lot to complete this project. I would like to express my deep wishes and thanks to my best friend Muneeb Irshad, Hamid Jamil, Safdar Hussain, Iftikhar Husain Shah, for their co-operation and moral support.

At the end, I am extremely thankful to Higher Education Commission (HEC) for the financial support to carry out this PhD research work.

Arslan Usman
Dedicated to my wife who helps me in every walk of my life.
Abstract

The structural and surface morphology of metal-incorporated diamond like carbon films have been investigated. These films were deposited on Si (111) substrates using Pulsed Laser Deposition (PLD) technique. A KrF Excimer laser (λ= 248 nm) was used for co-ablation from multi component Ni-graphite and Ag-graphite targets. The carbon composite films were prepared without and with external magnetic field applied transverse to the plume. The structural analysis was performed using X-ray Differactometer (XRD) and Raman spectroscopy. Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) analyses were performed to explore the surface morphology, texture and roughness of films. The application of external magnetic field has significantly improved the film quality. Films prepared in the presence of external magnetic field have comparatively larger crystallite size of Ni as well as of Ag. Another important aspect of application of external field is the enhancement in the graphitization and shifting of G-band towards higher wave number. The nucleation and growth process of carbon films are strongly dependent on the size and energies of the ablated species. The ID/IG ratios for the films prepared under external magnetic field indicate that the chain length and the six-fold aromatic rings of carbon clusters have developed substantially in that film matrix and thus graphitization is enhanced. The metal intercalated atoms support to the formation of carbon ring clusters by taking the π-electron which reduces the excited state of molecule.

The surface morphological investigations reveal that surface texture and organized growth of the particles varies with concentration as well as with the applied field. The roughness has also been influenced by the application of magnetic field as well as by the Ni and Ag dopants in the prepared composite films.

The purpose of developing such kind of films is to enhance the conventional properties of the films and to achieve some exceptional results which are not possible in ordinary films. These films have a vast variety of applications in photo-voltaic, bio-medical, tribological and semiconductor industry.
Contents

CHAPTER 1: INTRODUCTION AND LITERATURE SURVEY ........................................... 1

1.1 OVERVIEW ............................................................................................................. 1
1.2 INTRODUCTION TO CARBON ............................................................................... 3
  1.2.1 Carbon Structure ............................................................................................. 3
  1.2.2 Vibrational Modes of Carbon ......................................................................... 4
1.3 THE CARBON FAMILY .......................................................................................... 6
  1.3.1 Graphite & Diamond ...................................................................................... 6
  1.3.2 Graphenes ....................................................................................................... 7
1.4 CARBON THIN FILMS .......................................................................................... 7
  1.4.1 Amorphous carbon thin films .......................................................................... 8
  1.4.2 Diamond like carbon thin films ...................................................................... 9
1.5 COMPOSITE THIN FILMS ................................................................................... 10
  1.5.1 Doping and alloying ....................................................................................... 11
  1.5.2 Metal incorporated carbon thin films ............................................................. 12

CHAPTER 2: EXPERIMENTAL SETUP .................................................................. 14

  2.2 PARAMETERS EFFECTING THE GROWTH OF THIN FILMS ................................. 15
    2.2.2 Effect of external magnetic field ..................................................................... 15
    2.2.3 Laser Fluence .................................................................................................. 15
  2.3 EXPERIMENTATION ............................................................................................. 16
  2.4 EXPERIMENTAL ARRANGEMENT ....................................................................... 18
  2.5 DEPOSITION PARAMETERS AND DEPOSITION SCHEME .................................. 19
  2.6 CHARACTERIZATION TECHNIQUES ................................................................... 21

CHAPTER 3: RESULT AND DISCUSSIONS ............................................................... 23

  3.1 NI-GRAPHITE THIN FILMS ............................................................................... 23
    3.1.1 Films deposited without magnetic field (B=0 T) ........................................... 23
      3.1.1.1 XRD analysis ............................................................................................ 23
      3.1.1.2 Raman Analysis ....................................................................................... 25
      3.1.1.3 SEM analysis ............................................................................................ 28
      3.1.1.4 AFM analysis ............................................................................................ 29
    3.1.2 Films deposited with magnetic field (B = 0.1 T) ............................................. 31
      3.1.2.1 XRD analysis ............................................................................................ 32
      3.1.2.2 Raman analysis ....................................................................................... 34
      3.1.2.3 SEM analysis ............................................................................................ 37
      3.1.2.4 AFM analysis ............................................................................................ 38
  3.2 COMPARISON OF NI-GRAPHITE FILMS GROWN WITH AND WITHOUT MAGNETIC FIELD .... 45
3.3 AG-GRAPHITE THIN FILMS ........................................................................................................ 47
  3.3.1 Films deposited without magnetic field (B= 0 T) .............................................................. 47
    3.3.1.1 XRD analysis .............................................................................................................. 47
    3.3.1.2 Raman analysis ......................................................................................................... 48
    3.3.1.3 SEM analysis ............................................................................................................. 51
    3.3.1.4 AFM analysis ............................................................................................................. 52
  3.3.2 Ag-graphite films deposited with magnetic field (B= 0.1 T) ............................................ 55
    3.3.2.1 XRD analysis .............................................................................................................. 55
    3.3.2.2 Raman analysis ......................................................................................................... 57
    3.3.2.3 SEM analysis ............................................................................................................. 60
    3.3.2.4 AFM analysis ............................................................................................................. 61
3.4 COMPARISON OF AG-GRAPHITE FILMS .............................................................................. 68

CHAPTER 4: CONCLUSION AND FUTURE WORK ........................................................................... 70
REFERENCES .................................................................................................................................... 72
LIST OF PUBLICATIONS .................................................................................................................. 79
List of Figures

Figure 1.1: Atomic orbitals and sp hybrid orbitals of carbon .......................................................... 4
Figure 1.2: The G and D vibrational modes of carbon ................................................................. 5
Figure 1.3: The phase diagram of carbon .................................................................................. 6
Figure 2.1: A schematic of Ni-Graphite multi-target disc ....................................................... 17
Figure 2.2: The schematic of Pulsed Laser Deposition system .................................................. 19
Figure 3.1: (a)-XRD spectra of the deposited films at B=0 (b)- Variation of crystallite size as a function of laser pulses on Ni .......................................................................................................... 24
Figure 3.2: (a)-Raman Spectra of deposited films at B=0 (b)-I_D/I_G ratio of Ni-graphite films with the increasing number of laser pulses on Ni .................................................................................... 26
Figure 3.3: Variation in peak position of G and D band as function of laser pulses on Ni ............. 27
Figure 3.4: SEM micrographs of the deposited Ni-graphite films with varying number of laser pulses on Ni (B=0) ........................................................................................................................... 28
Figure 3.5: AFM micrographs exhibiting 2D (a, d, g, j & m) and 3D (b, e, h, k & n) and line profile (c, f, I, l & o) of Ni-graphite films as a function of increasing Ni-concentration ............... 30
Figure 3.6: Roughness profile of the films deposited with varying Ni concentration .......... 31
Figure 3.7: XRD pattern of Ni-graphite thin films grown with B= 0.1 T ...................................... 32
Figure 3.8: Variation in Crystallite size of (a)-Ni (111) (b)- Carbon (111) with Ni concentration ......................................................................................................................................................... 33
Figure 3.9: Raman Spectra of the deposited Ni-graphite films ...................................................... 35
Figure 3.10: (a)- Peak positions of D and G bands (b)- I_D/I_G ratio as a function Ni-concentration36
Figure 3.11: SEM micrographs of the deposited Ni-graphite films with varying no of pulses on Ni (B=0.1 T) ........................................................................................................................................ 37
Figure 3.12: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-300) .......................................................................................... 39
Figure 3.13: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-500). ................................................................. 40
Figure 3.14: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-700). ........................................................................ 41

Figure 3.15: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-900). ........................................................................ 42

Figure 3.16: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-1100). ................................................................. 43

Figure 3.17: RMS roughness profile along with linear fit for Ni-graphite films deposited with different Ni concentration with B= 0.1 T ........................................................................ 44

Figure 3.18: (a)-XRD spectra for Ag-graphite films (b): Ag crystallite size as a function of number of laser pulses on Ag ........................................................................................................ 47

Figure 3.19: Raman Spectra of the deposited Ag-graphite films ......................................................................................... 49

Figure 3.20: (a)- I_D/I_G ratio (b)- Peak position of G and D bands as a function of number of laser pulses on Ag ................................................................................................................ 49

Figure 3.21: SEM Micrographs of the deposited Ag-graphite films by varying the concentration of Ag. .......................................................................................... 51

Figure 3.22: AFM micrographs exhibiting 2D (a, d, g, j & m) and 3D (b, e, h, k & n) and line profile (c, f, i, l & o) of Ag-graphite films as a function of increasing Ag-concentration. ............. 53

Figure 3.23: Roughness profile with linear fit of Ag-graphite films ......................................................................................... 54

Figure 3.24: XRD spectra for Ag-graphite films deposited with B= 0.1 T................................................................. 55

Figure 3.25: Crystallite size of a)- Ag(111) b)- Carbon as a function of Ag-concentration ...... 56

Figure 3.26: Raman spectra of Ag-graphite films deposited with B= 0.1 T ................................................................. 58

Figure 3.27: (a)- Peak positions for D & G bands (b)- I_D/I_G ratio as a function of Ag-concentration ......................................................................................................................... 59

Figure 3.28: SEM micrographs of the Ag-graphite films prepared under B= 0.1 T. ................. 60

Figure 3.29: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ag under the magnetic field (Ag-B-300) ................................................................. 62

Figure 3.30: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 500 pulses on Ag under the magnetic field (Ag-B-500) ........................................................................ 63

Figure 3.31: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 700 pulses on Ag under the magnetic field (Ag-B-700) ........................................................................ 64
Figure 3.32: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 900 pulses on Ag under the magnetic field (Ag-B-900) ................................................................. 65

Figure 3.33: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 1100 pulses on Ag under the magnetic field (Ag-B-1100) .......................................................... 66

Figure 3.34: Roughness profile and linear fit of the Ag-graphite films under B=0.1 T............... 67
# List of Tables

<table>
<thead>
<tr>
<th>Table No</th>
<th>Table Caption</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Ionization energy of carbon</td>
<td>6</td>
</tr>
<tr>
<td>2.1</td>
<td>KrF Excimer Laser specification</td>
<td>17</td>
</tr>
<tr>
<td>2.2</td>
<td>Silicon Characteristics</td>
<td>18</td>
</tr>
<tr>
<td>3.1</td>
<td>XRD Data for Ni-graphite films deposited with B= 0 T</td>
<td>25</td>
</tr>
<tr>
<td>3.2</td>
<td>Peak positions and I_D/I_G intensity ratio obtained from Raman spectra of Ni-graphite films</td>
<td>28</td>
</tr>
<tr>
<td>3.3</td>
<td>Roughness of the Ni-graphite films deposited at different Ni concentration</td>
<td>31</td>
</tr>
<tr>
<td>3.4</td>
<td>XRD Data for Ni-graphite films deposited with B= 0.1 T</td>
<td>33</td>
</tr>
<tr>
<td>3.5</td>
<td>Peak positions and I_D/I_G intensity ratio obtained from Raman spectra for deposited Ni-graphite films</td>
<td>36</td>
</tr>
<tr>
<td>3.6</td>
<td>Surface Roughness of the films deposited at different Ni concentration at B= 0.1T</td>
<td>44</td>
</tr>
<tr>
<td>3.7</td>
<td>XRD Data for Ag-graphite films deposited with B= 0 T</td>
<td>48</td>
</tr>
<tr>
<td>3.8</td>
<td>Peak position &amp; I_D/I_G ratio of the Ag-graphite films</td>
<td>50</td>
</tr>
<tr>
<td>3.9</td>
<td>Roughness of the Ag-graphite films deposited at different Ag concentration</td>
<td>54</td>
</tr>
<tr>
<td>3.10</td>
<td>XRD data obtained from Ag-graphite composite films deposited with B= 0.1 T</td>
<td>57</td>
</tr>
<tr>
<td>3.11</td>
<td>Data obtained from Raman spectrum for the Ag-graphite films deposited under B= 0.1 T</td>
<td>59</td>
</tr>
<tr>
<td>3.12</td>
<td>Films roughness of Ag-graphite films deposited under B=0.1 T</td>
<td>66</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction and Literature Survey

1.1 Overview

The special feature of carbon’s chemistry with reference to its surprising ability of bonding with carbon as well as with other elements in variety of ways is the basis of organic chemistry. This chemical flexibility also gives rise to vast diverse structures of solid carbon. This chapter describes the wide range of available carbon materials which are of prime importance due to their chemical bonding and structure. The materials under review are; (i) crystalline forms of carbon i.e diamond, graphene, fullerenes in the form of thin films (ii) amorphous carbon i.e. graphite and their thin films (iii) composite-carbon thin films.

Elemental carbon exists in different phases and plays a vital role in human life long before the term “element” was even used. Attempts were made to alter the physical and chemical properties of these allotropes. Scientists tried to develop new architectures of these carbon based materials so that it can be placed in the category of smart materials [1]. Thin films of carbon were prepared and investigated because at micro and nano scale the properties of materials change as compared to that of bulk [2, 3]. Investigation of composite thin films of carbon is the most recent and very promising field of research in the present era [4-6]. Incorporation of metals as well as non-metals within the carbon films to grow composite thin films is considered to be an emerging field of nanotechnology. By doping of these elements, it is possible to achieve such properties which cannot be obtained in individual component films [7-8]. Nano crystalline as well as amorphous composite structures including nano composite and nanometric multilayer films can successfully be prepared by controlling the growth conditions and stichiometry.

One of the promising candidate amongst the carbon composite structures is diamond like carbon (DLC) [9]. The DLC was firstly used by the two scientists Aisenberg and Chabot [10] in 1971 for amorphous carbon thin films which possess properties nearly resembling
Chapter 1

Introduction & Literature Survey

with diamond instead of graphite. Amorphous carbon thin films normally consist of \( \text{sp}^2 \) hybridized bonding structure.

Amorphous carbons (a-C) as well as diamond like carbon (DLC) films at present are of paramount importance which is being widely used on commercial scale. Various research groups [11-13] are working on different aspects of these materials. These DLC films possess dynamic and amazing properties, i.e. thermal conductivity, electrical resistance, hardness, optical transparency starting from ultraviolet region to infrared region [14]. DLC films comprise enormous properties from graphite to incredibly close of diamond. These films also have broad range of application in semi-conductor and coatings industry [15-17], bio-medical industry [18] and in the recording of denser magnetic media [19]. During the last few years or so, DLC films have gradually moved from novel research materials to practical coatings suitable for protective applications in industry.

Presently, attempts were made to re-engineer these films by doping some suitable elements during the growth process that results into enhanced properties of the films. Moreover, in order to improve adhesion of film to the substrates and to eliminate large internal compressive stress [20], metal containing DLC films have been developed. These films can also be used to explore appropriate optical band gap energy [21] and also for the enhancement of dielectric constant [22]. Additionally, the encapsulated metal nano particles contained by the graphene layers have got preference to naked metal nano particles [23]. The inclusion of hetero atoms in the carbon complex have enormously broaden the majority of physical properties of DLC films that results a new architecture of metal DLC (\( \text{Me-DLC} \)) films similar to multilayered structures or nano composites[24]. These \( \text{Me-DLC} \) films have the properties of nano particles as well as film matrix [25-26].

Photovoltaic applications which are based on high-efficiency and low-cost solar cells [27-28] have attracted tremendous attention. Up to now, Silicon has been mainly used as the core material for such kind of devices [29]. Efforts have been made to minimize the cost of photovoltaic. For that purpose, new hybrid type of solar cell materials has been fabricated [30]. Amongst these materials, Carbon based materials/thin films is predicted to be solar cell material because of their semiconducting behavior. These solar cell materials have many advantages as compared with silicon based solar cells. They have high conversion efficiency due to the tunable band gap energy [31]. It is well known fact that mono material approach will act as biomaterials for new improved medical devices. Laser matter
interaction based plasma processing therefore significantly tailors the functional properties [32-33] and has a pivotal role in bio-device fabrication. Suitable implants use metals, such as medical compatible grade stainless steel, nickel, titanium, silver, chromium and polymers. A broad range of medical devices include coated or uncoated nano particles have good flexibility, low surface roughness, high chemical resistance and good bio-compatibility. New modified techniques are used to enhance the lubricity of the device in order to decrease body-implant ordeal, and improve bio-compatibility with the body [34].

1.2 Introduction to carbon

The sixth element contained by the periodic table is Carbon and is an important constituent of the organic chemistry for the development of novel materials. It also has the ability to form stable compounds with more electropositive and more electronegative “elements”. Another important feature that attracts the attention of scientists and engineers is the occurrence of various allotropes of carbon and its ability to be modified by conventional and non-conventional doping to acquire completely distinct properties. Due to its exceptional properties, rapid development has been made within the last few decades [35-36] to recognize its impact in different fields like; carbon’s perspective in chemistry, material science, physics and engineering.

1.2.1 Carbon Structure

Carbon atom has total six electrons from which two are tightly bound to the nucleus and the remaining 4 are valence electrons. Carbon has the electronic configuration $1s^2, 2s^2, 2p^2$ as revealed in figure 1.1. Carbon is tetravalent in the majority of its compounds. Recently [37] studies have been made on molecules with higher coordination number, e.g Al$_2$Me$_6$ [38] and in many carbaynes [39]. Since the last few years [40] research on amorphous carbon films has become significant on large scale. Its commercial use is contributing enormously in the area of scratch free coatings and in many other passive devices [41].
The versatility in properties of the carbon material is based on the different hybridized structure that exists in nature. Carbon has four valance atoms which gives rise to many different bonding configurations. Based on these configurations the Carbon films can exist with a combination of any of these bonds with other carbon atoms or with dopant atoms. This ability of carbon provides firm base to form some dynamic and variable material properties.

The microstructure of carbon based materials is such that it favors the coexistence of sp, sp² and sp³ hybridization, not only within the carbon system but also in impurities and dopants that enter into its microstructure. The sp² hybridization is more stable than sp³ hybridization at room temperature when compared thermodynamically, while sp bonds do not contribute significantly to the microstructure. Atomic simulation shows that if the proportion of sp² bonds is more than 80% in its structure (which is much greater than the percolation threshold), its electrical behavior is still semiconducting rather than metallic ones. This is due to highly localised nature of the sp² hybridization, which does not play a role in the conduction process with its closest neighbor until the planes of the two sp bonds or clusters aligned in a three-dimensional manner.

**1.2.2 Vibrational Modes of Carbon**

In order to understand the behavior and structure of the carbon/graphite, it is more appropriate to have some knowledge about the type of bonding and the typical vibrational modes that exist in that particular material, because physical and chemical properties are based on these vibrations and the density of states. These vibrational modes normally
known as bands are a unique feature of the material and have a fundamental role in the determination of the materials properties.

There exist two vibrational modes in graphite normally called the G and D mode. The G band has a stretching vibration of pairs of sp² sites and only exists when the sp² sites are stacked as olefinic chains or in the form of aromatic rings [42]. Conversely, the D mode has a breathing vibration of six-fold aromatic ring, which are induced by disorder. If the aromatic rings are sp² hybridized then this band exists [43]. The vibration scheme of these bands is clearly explained in figure 1.2.

![Figure 1.2: The G and D vibrational modes of carbon [44]](image)

These vibrational bands vibrate inelastically in the resonant process, in which the scattering of a photon by a phonon is due to polarisability change linked with that phonon. In these configurations the excitations takes place when the band gap is equal to the excitation energy. In an ordered crystal, when the momentum difference of photons and phonons give the selection rule q = 0 [45]. In the case of nano crystalline systems when the grain size is L, the selection rule for the phonons of wave vector can be written as Δq=1/L. In the amorphous system i.e a-Si the selection rule is described as Δq<< 1/(bond length) [46].

When the material contains graphite or diamond regions, it is better that the samples are illuminated with visible light. When the lattice constant is equal to the illuminated light wavelength only then the vibrations of the absorbing regions can be measured. The result of different absorptions is very important when the domain size of the absorbing regions (graphite) is equal to or bigger than the absorption length of graphite (~20 nm). Therefore, the concentration as well as crystallite size of graphite have significant role in the vibration and the structural modification [47].
1.3 The Carbon Family

Carbon is an important main group element of the periodic table due to its outstanding properties. The electronegativity of carbon is 2.55 on the Pauling scale and is very near to the adjacent elements of the periodic table for instance, P(2.1), B(2.0), or S(2.5). Its first ionization energy is 1086.5 kJ mol\(^{-1}\) as mentioned in table 1.2. Its molar weight is 12.011 gmol\(^{-1}\). Its importance can be determined from the fact that in archeology, it is utilized to find out the age of objects (radiocarbon dating). It is also a valuable tool for determination of molecular structure by spectroscopic investigation as it has nuclear spin quantum number \( I = \frac{1}{2} \).

There is a large variety of phases of carbon that exists at different pressures and temperatures. The phase diagram of carbon is revealed in figure 1.3. A few allotropes of carbon i.e Graphite, Diamond, Graphenes and Fullerenes are discussed.

![Phase diagram of carbon](image)

**Table 1.1: Ionization energy of carbon**

<table>
<thead>
<tr>
<th>Ionization energy</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
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<tr>
<td>kJ mol(^{-1})</td>
<td>1086.5</td>
<td>2351.9</td>
<td>4618.8</td>
<td>6221.0</td>
</tr>
</tbody>
</table>

Figure 1.3: The phase diagram of carbon [48].

1.3.1 Graphite & Diamond

**Graphite** was first predicted by Debye et.al in 1917 [49]. There are various kinds of deposits of graphite found in the form of big pieces, flakes and in microcrystalline powder. The microcrystalline powder is mostly (and falsely) called “amorphous” because of its small particle size. It is usually characterized by layered structure that constitutes over a \( xy \)-plane to form regular hexagons. At the corner of each hexagon carbon atoms are present to form a two dimensional lattice, with each C–atom three other atoms are connected through \( \sigma \)-bonds which correspond to \( sp^2 \) hybridization and thus form a long chain of
hexagonal structure. There are two main categories of graphite, the hexagonal graphite or $\alpha$-graphite, and the rhombohedral or $\beta$-graphite. The $\beta$-graphite is very frequent in nature and can be transformed into more stable $\alpha$-graphite thermodynamically by heat treatment.

**Diamond** is the second allotrope of carbon. Diamond has tetrahedral structure which has sp$^3$ hybridized covalent bonds and all have 1.54 Å in length. It has a refractive index of 2.41 at $\lambda= 644$ nm, 2.54 at 300 nm and 2.70 at 230 nm [49]. At room temperature the absorption edge lies at $\lambda= 230$ nm and moves toward higher wavelengths with increasing temperature. In the type I diamond there are two characteristic bands at $\lambda=415$ nm and $\lambda=503$ nm and the absorption edge is usually at higher wavelength $\lambda=330$ nm as compared to perfect diamond.

### 1.3.2 Graphenes

A thin sheet of monolayer carbon atoms positioned in a two-dimensional manner. When one atomic diameter thick sheet of sp$^2$ hybridized carbon atoms are bunched in honeycomb crystal lattice, therefore known as Graphene. The carbon to carbon bond length is about 0.142 nm in graphene [50]. A large number of graphene sheets are stacked to form graphite having an interplanar spacing of 0.335 nm. Thus, when 3 million sheets were stacked together only 1 mm thick graphite is obtained. Graphene is the fundamental building block of a number of carbon allotropes like graphite, fullerenes, and carbon nanotubes.

The Nobel Prize in Physics for the year 2010 was honoured to Andre Geim and Konstantin Novoselov "for innovative research about the two-dimensional material graphene" and confirms its importance [50]. Graphene are the isolated atomic planes of graphite. Natural graphene has zero bandgap and is categorized as semiconductor. The graphene electronic structure is the basis for determining the band gap energy of the graphite. It is well considered fact that the E-k relation has a linear trend at small energies close to the corners of hexagonal Brillion region that gives to zero effective mass for holes and electron [51-52].

### 1.4 Carbon thin films

Carbon as a bulk material has outstanding properties as discussed in detail earlier. Now thin films of carbon and its derivatives are to be discussed. A thin film of a material is a
thin layer of that material on nano metric dimensions which is deposited on a suitable substrate (base). These films are prepared by different deposition techniques i.e physical methods and chemical methods. Inspite of the deposition conditions and processes, thin films of carbon shows some exceptional properties which are not achieved in the bulk material. A large family of compounds and materials in the category of carbon thin film are manufactured and investigated. The two main categories of carbon thin films depending on its microstructure are i)- Amorphous carbon thin films ii)- Diamond like carbon thin films. These films have wide applications in electronics, protective coatings, engineering and bio-medical industry.

1.4.1 Amorphous carbon thin films

Amorphous carbon films are generally classified into: a)- amorphous carbon films known as \textit{a}-C films, b)- hydrogenated amorphous carbon films known as \textit{a}-C:H films. These two types of films have varying amount of sp\textsuperscript{2} and sp\textsuperscript{3} hybridized carbon atoms. The amorphous carbon films are synthesized from carbon containing gases through a Physical Vapor Deposition (PVD) process or by a Chemical Vapour Deposition (CVD) process. These two processes can be plasma based thermally-activated or electric field-assisted processes [53].

Most of the a-C films contain sp\textsuperscript{2} bonded carbon and variable sp\textsuperscript{3} content ranging upto 55.5% [54]. Usually the hardness of the films increases as a function of sp\textsuperscript{3} content. The hydrogen content within the hydrogenated films can also be varied and the hardness of a-C:H films has an inverse relation with hydrogen content. On the other hand, films having high sp\textsuperscript{3} content (80-90%) show high hardness and are typically identified as tetrahedral amorphous carbon films (\textit{ta-c}) [55]. These hard films are classified as diamond-like carbon DLC films. In short, it can be concluded that by increasing sp\textsuperscript{3} content the hardness increases and its 'diamond like' character becomes dominant. On the other hand, the films having more sp\textsuperscript{2} content or more hydrogen content become softer which reflects the dominancy of 'graphite-like' carbon, which indicates that the range of properties that can be achieved in these carbon based films by precisely controlling the processing parameters.

The versatility of applications of amorphous carbon thin films is due to its dynamic properties and its ability to be deposited on different substrate materials. The interfacial layer formed between the substrate and amorphous carbon film is the primary step in film
deposition process. Interface is basically a transition region between the intrinsic substrate material and the carbon film, which can strongly dominate the technological effectiveness of thin film although its dimension is in few tens of nanometer. Usually, the amorphous carbon films possess comparatively high intrinsic stress [56] due to its poor interfacial properties. These stresses can be reduced by providing proper adhesion and limiting the diffusion through the formation of strong chemical bonds. The rapid miniaturization of thin film structures enhances the role of the interface, where electrical as well as mechanical properties are of prime importance. In most of the cases, carbon thin films are grown onto crystalline silicon substrate due to proper interface formation and film structure [57-58]. Optical properties of the amorphous films are also powerful tool to investigate density-of-states (DOS) of electrons. In semiconductors, the Tauc gap is an important parameter and has a close relation to the mobility gap and plays a significant role in deciding the electronic nature of the films [59]. In amorphous carbon based materials, the Tauc gap has a little impact when it is used as a first-order parameter to characterize films [60]. The interaction of photons with matter and the transfer of energy has influence on the optical parameters like absorption, emission and transmission and hence on the bandgap energy. These optical properties are also dependant on sp$^2$ and sp$^3$ content within the amorphous carbon thin films [61].

1.4.2 Diamond like carbon thin films

These films have polycrystalline layers of diamond like structures with thickness ranging from nanometer to micrometers. It can be deposited on a suitable substrate with perfect lattice matching. Mono crystalline diamond like films upon suitable preparation is recognized as films of distinct orientation of the crystal lattice. These films are exhibiting a uniform face centered cubic (FCC). In most of the cases (100) plane is observed, whereas (111) and (110) faces are less frequent. The surface morphology of these diamond films is resolved using growth of these planes. The growth rate is measured by the growth parameter $\alpha$. As long as $\alpha$ is smaller the crystallites shape becomes more cubic [62]. The growth parameter also plays a significant role to control the orientation of the crystallites with respect to substrate plane. Those crystallites which has largest growth rate are aligned perpendicular to the substrate and hence all crystallites exhibit similar orientation. In this way, the shape and texture of crystallites of diamond films are
controlled by the crystal growth rates. The single crystalline diamond films have low proportion of sp² hybridized carbon atoms as contrast to polycrystalline thin films. This indicates large number of grain sizes and has considerable impact on the electron transport properties within these films.

Nano composite thin films consist of minimum two phases, a matrix phase and dopant phase [63]. Dopants may form crystallites or clusters within the matrix. The general characteristics of nano composite coating describe that within a host material another material homogenously incorporated or immersed. The characteristic length of these materials approximately varies with a scale of 1–100 nm.

1.5 Composite thin films

Composite films consist of a main film known as the matrix in which the doping species are to be incorporated. The purpose of developing such kind of architecture is to enhance the conventional properties of the films and to achieve some exceptional results which are not possible in ordinary films. It is widely used in different applications i.e photo-voltaic, bio-medical, tribological and semiconductor industry [64]. These composite films can be prepared with conventional methods of chemical vapor deposition, sputtering, pulsed laser deposition (PLD) and by thermal evaporation. Therefore, no special arrangement is required to fabricate these films.

Nanocomposite carbon films are usually developed to increase the hardness [65]. Hardness is defined as resistance of crystalline materials to plastic deformation which occurs due to dislocation under applied load [66-67]. Therefore, higher the resistance of a material greater will be its hardness. One way to obtain high resistance coatings is to modify the architecture to form stable dislocations [68].

There are many important contemporary technologies that have been employed for converting solar energy into other forms of energy such as electricity and heat, nano composite films are among them. Nano composite films having high absorption and low thermal emission at the device operating temperature will be best suited for such kind of application. So the addition of doping materials in the carbon film matrix will tune its absorption band and thus maximum absorption region can be achieved.
1.5.1 Doping and alloying

Composite Carbon based materials are attracting the attention of scientist and researchers as compared to pure carbon films due to exceptional physical and electronic properties [69]. Hybrid composite materials are fabricated by doping (incorporation) of an external agent in small proportion within the growing carbon films. The external agent may be in gaseous phase, a metal or a non-metal. These doped diamond-like carbon (DLC) films are usually labeled as a-C:X, and “X” represents the doped element [70-72]. Microstructure and properties of the a-C: X films depend significantly upon the doped element nature, its chemical affinity with carbon and the deposition process [73].

Doping in the DLC films has been done with different metals including Ti, Ni, Ag, Cr, Mo which are dispersed throughout the carbon film matrix [74-76]. The structural investigation of these films has been under process but in most cases, metals exist in the form of small nano crystallites. The best known benefits of metals incorporating in DLC coating are to lower the compressive internal stresses and improvement of adhesion. In this way, interesting optimum wear properties can be achieved for a specific metal dopant, and the concentration depends on its nature. The properties of these films are able to be improved by obtaining the so called nano composite films in which a high density nanometer sized crystals are embedded in an amorphous film matrix [77]. On the other hand if the nano composite film consists of significantly bigger grains about some tens of nanometres with large inter spacing of amorphous phase between nano crystallites i.e. 10±50 nm, it allows dislocation formation, but this will not support cracks development.

In many cases the doping or alloying will reduce the surface energy, for example the incorporation of fluorine in the DLC films will alter the surface energy so as to enhance stiction of heads in magnetic hard disks [78]. The reduction in surface energy of these films eventually reduce the polar part of surface energy, which in turn is due to loss of dangling bonds and sp² hybridization [79]. As, Si and F only forms single bond with carbon, therefore it is assumed that this will force carbon to a sp³ bonding state. The fluorine incorporation into DLC films is considered the most effective way to enhance the hydrophobicity [80-81], because it reduces the density of carbon network structure [82]. In tribological coatings industry, DLC films must have sufficient adhesive force to overcome the high internal stresses to adhere properly to the substrate material otherwise the film
would peel off the surface. In many cases, metal doping to form metallic interlayers are suitably considered good for adhesion of DLC films [83-84].

N. Sbaï-Benchikh et.al [85] investigated the properties of Ni-doped amorphous carbon (a-C:Ni) films by femto second pulsed laser deposition of Ni and graphite targets. The optical properties with individual metal and carbon phases are examined with the help of the Maxwell-Garnett theory [86]. This analysis reveals that a change of phase is observed with Ni concentration. The microstructure of the carbon matrix goes through significant change with the restructuring of clusters at small concentration of Ni and the growing carbon have sp² fraction for very high concentration.

The consequences of doped silver nanoparticles in DLC films were reported by F.R. Marciano et.al [87]. The key objectives were to get low friction coefficient, a low engraving rate in an atomic oxygen atmosphere, high extent of hardness, low total stress and adherence to the substrate during deposition process. The spectrometry analysis reveals the drop of the volatile species like (C⁺, CO⁺ and CO₂⁺) for sample with additional silver nanoparticles. This confirms that DLC films have more wear resistance against oxidation when doped with silver nanoparticles. In this work, a method of obtaining uniform nanoparticle density and size is also discussed.

Takanori et.al [88] discussed the activation energy of different metals (Co, Mo, W) incorporated in the diamond-like carbon (DLC) films. The films were prepared onto Si substrates through RF discharged methane plasma and co-sputtering of metal target. The results describe that crystalline metal clusters are randomly dispersed in amorphous carbon film matrix. The activation energy was numerically calculated using $\sigma=\sigma_0 \exp(-E/kT)$, whereas the calculated activation energy has an inverse relation with the metal concentration. This is because of the varying size of the metal clusters. The radius of these metal clusters is also discussed.

### 1.5.2 Metal incorporated carbon thin films

Nano composites thin films in the form of metal encapsulated carbon matrices are the most promising field of nanotechnology from application point of view. The metal incorporated carbon thin films possess a variety of structures like amorphous, crystalline and graphene intercalated compounds [89]. The composite films containing nanocrystalline diamond, immersed in the amorphous carbon film matrix were developed by Zhou et al. [90].
The intercalated compounds have diverse chemical behavior and are formed by embedding atoms or molecules within the graphene sheets known as “sandwiched” structure. Their weak atomic interaction is the main cause of the formation of such kind of compounds. During the intercalation, a rearrangement of charges in the carbon layers takes place which results in either positive or negative polarization depending on the type of dopant (embedded atom). As a result of doping, electrons are transferred from dopant specie to the \( \pi \)-bands (or bond) of graphite and hence increase the carrier charge density in the valence band or conduction bands. Similarly, the electrons leaving the dopant generate holes in the valence band. Whereas the dopant fills the conduction band of the acceptor. As a consequence of this process, usually the graphite intercalated compounds possess high electrical conductivity [91].

Thin composite films of carbon can be fabricated by various methods like; i)- Ion-beam sputtering, ii)- Thermal evaporation method, iii)- Pulsed Laser Deposition (PLD) and iv)- Chemical Vapor Deposition (CVD). PLD technique is considered to be very useful for the development of thin nanocomposite carbon films, as it gives better control over particle size and density [92]. In this technique, a suitable pulsed laser is utilized as a power resource for irradiation of single multi-target. After a complex process of energy transfer from photonic to thermal, ablation takes place and material is ejected out from the surface. That ablated material is used to deposit onto a substrate placed in front of the target. The ablated material from multi-targets, when condensed on the substrate like a layer, forms a thin composite film.

In this project, thin composite films of amorphous carbon are deposited onto the silicon substrate through PLD technique. These composite films are prepared by a self assembled doping technique. In which a few percentage of metallic species is incorporated in the graphitic film matrix. The aim was to achieve those surface and structural properties which are usually not possible in the pure carbon films.
Chapter 2: Experimental Setup

Thin films of diamond like carbon have been deposited on silicon (111) substrate employing Pulsed Laser Deposition Technique. A series of thin films of Graphite-Nickel (Ni) and Graphite-Silver (Ag) have been grown with the multiple ablations of both the target materials under different deposition parameters. These thin films were characterized by X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and Raman Spectrometry (RS). In this chapter, the experimental setup and the characterization techniques employed in this project are discussed in the following sections.

2.1 Pulsed Laser Deposition Technique

The use of pulsed laser deposition technique in thin-film growth process is widely adopted due to simplicity in implementation. It is a class of physical vapor deposition, which is carried out under conditions or in the ambient environment. An energetic pulsed laser is focused through an optical system onto a target material which is to be deposited. The sharp energy density of the laser pulse transfers energy into material and vaporizes the target material by generating a plasma plume. These ablated species ejected from the target move in highly forward direction called forward peaking. This forward peaking of the plume provides the necessary flux required for the film growth. In the multi component target ablation schemes, the ablation conditions are selected such that primarily the plume consists of low-mass species i.e. atomic, diatomic and other low dimensional structures. It can be achieved by selecting a suitable laser which is absorbed by a small volume of the target material.

A suitable substrate i.e. Silicon or glass strip is placed in front of the plume so that the ablated material is deposited in the form of thin film. The choice of a substrate plays a critical role in thin film growth, because it provides the solid base to initiate the nucleation process. For proper adhesion to the substrate it should be lattice matched with the film.
2.2 Parameters effecting the growth of thin films

There are numerous parameters that affect the structural, morphological, optical and electrical properties of the thin films, a few of these are;

1. Substrate temperature
2. External magnetic field
3. Laser Fluence
4. Doping of metals (Ni, Ag)

2.2.1 Effect of substrate temperature

During deposition process, the substrate temperature can significantly affect the growth of DLC films. As the substrate temperature increases, thus kinetic energy of the surface atoms increases; as a result the adsorption of the ad-atoms leads to the formation of bigger molecules. The concentration of the particles on the surface of the substrate increases which reduces the spacing between the particles. This reduction in spacing eventually causes to increase the thickness of the films. The optimized substrate temperature initiates the crystal growth of diamond like carbon films [93]. If the substrate temperature during growth exceeds the optimum value, the desorption rate increases due to the higher energies of the atoms. This decreases the rate of film growth and hence the thickness of the film [94].

2.2.2 Effect of external magnetic field

The external magnetic field also affects the quality of thin film. When external magnetic field is applied to transverse direction of propagation of the plume, the smooth and homogeneous films are formed with less root mean square (r.m.s) roughness and reduce defects. The applied magnetic field increases the thickness of the thin film by confining the plasma. The applied magnetic field also influences the structural, morphological, optical and electrical properties of the thin films [95].

2.2.3 Laser Fluence

Laser fluence also plays a critical role in thin film growth. For low laser fluence lower than a threshold level there will be low energy density and the laser pulse simply heats up the target. When the laser fluence is increased, the number of photons per unit area
transferred to the material will increased significantly and the value of energy density exceeds ablation threshold value necessary for material’s ejection.

2.2.4 Doping of metals (Ni, Ag)

Amorphous carbon thin films or diamond-like carbon (DLC) films are considered as smart material for protective coatings and in many other applications due to its high hardness, high resistant to wear and low friction coefficient. These films are widely used in optoelectronic industry in numerous semiconductor applications.

Doping of a material in these films to prepare nano structured composite thin films is a new method to enhance the efficiency of carbon based materials (thin films). Addition of few atomic % of a metal in the carbon film matrix will change the structural properties significantly without affecting the other physical properties. Pulsed laser ablation method is employed for doping of metals (Ni & Ag) into the carbon film matrix.

2.3 Experimentation

The procedure of thin film deposition consists of the following steps;

- PLD chamber
- Excimer Lasers
  - Targets (Ni-graphite and Silver-graphite)
  - Substrate

2.3.1 PLD chamber

Stainless steel chamber with 6 ports was used for the fabrication of few-layers of graphite. Each port is utilized for a specific purpose. Laser window, vacuum system power supply connections were attached with these ports. The internal diameter of each port is 4 cm with wall thickness of ~0.5 cm. Along with these ports, the circular chamber has well organized arrangement of rotator motorized target holder, DC electric stepper motor, heater and substrate holder. The internal diameter of the chamber is 30 cm with wall thickness ~1.5 cm.

2.3.2 Excimer Lasers

Excimer laser (KrF) was used to ablate the targets. As laser hits the target, ablated target material moves in forward direction normal to the surface and is deposited on the
substrate that is placed at a particular distance from the target surface. The main specification of KrF excimer laser used in the experiment are given in table 2.1;

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>248 nm</td>
</tr>
<tr>
<td>Laser energy</td>
<td>20 mJ</td>
</tr>
<tr>
<td>Pulse repetition rate</td>
<td>20 Hz</td>
</tr>
<tr>
<td>Pulsed duration</td>
<td>20 ns</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>2150 Pa</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>27 °C</td>
</tr>
</tbody>
</table>

### 2.3.3 Target Preparation

A multi-component target of Ni and graphite was fabricated. By embedding a disc of Ni into a graphite disc, external diameter of graphite disc is 80 mm and that of Ni is 20 mm. A schematic of the target is shown in figure 2.1. A single crystal Si (111) substrate with dimension (10mm×10mm×2mm) was used to deposit these films. The Si substrate was cleaned by the standard wet cleaning process before the deposition.

![Figure 2.1: A schematic of Ni-Graphite multi-target disc](image)

### 2.3.4 Substrate

Composite films of graphite were deposited on silicon (111) substrate surface. Silicon was chosen as substrate as it has good uniformity, chemical stability, thermal
conductivity and high melting point 1414°C. Some Si characteristics are given in table 2.2;

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic weight</td>
<td>28 g/mol</td>
</tr>
<tr>
<td>Color</td>
<td>Silver to gray</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Diamond cubic</td>
</tr>
<tr>
<td>Lattice spacing</td>
<td>5.4 Å</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>149 W/mK</td>
</tr>
<tr>
<td>Band gap</td>
<td>1.11 eV</td>
</tr>
</tbody>
</table>

2.4 Experimental arrangement

Pulsed Laser Deposition (PLD) is a versatile method for depositing thin films of about all complex materials. Figure 2.2 shows a schematic of PLD system used in this project, consists of multi-ported stainless steel vacuum chamber. The chamber has a target holder which is attached with the stepper motors for translation and rotation motion of the target so that the whole surface of the target disk is used during the deposition. The purpose of making such an arrangement was to attain a facility that brings the Ni or graphite targets alternatively at the focus point. A substrate assembly was designed so as to keep it in front of the ablated material; it also has the ability of providing the temperature to the substrate during the deposition. The chamber is evacuated using Turbo molecular pump up to ~10^-6 torr. A high intensity, Excimer (KrF) Laser (248 nm) operated at 20 Hz is used as an energy source to ablate and vaporize the Ni-graphite and Ag-graphite target materials to fabricate the thin films [96]. A UV lens of 40 cm is used to focus the laser beam on the surface of the target. A substrate holder equipped heating arrangement is placed in front of the target at a distance of 20 mm. The substrate temperature is kept constant at 300°C during the deposition process.
Figure 2.2: The schematic of Pulsed Laser Deposition system

2.5 Deposition parameters and deposition scheme

In this work four sets of thin films of graphite/Ni and graphite/Ag are deposited using the following deposition scheme;

**Set I & III**: The growth of DLC with/without external magnetic field

<table>
<thead>
<tr>
<th>Samples</th>
<th>No. of laser pulses</th>
<th>Deposition sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Graphite</td>
<td>Ni</td>
</tr>
<tr>
<td>Ni-300</td>
<td>1000</td>
<td>60</td>
</tr>
<tr>
<td>Ni-500</td>
<td>1000</td>
<td>100</td>
</tr>
<tr>
<td>Ni-700</td>
<td>1000</td>
<td>140</td>
</tr>
<tr>
<td>Ni-900</td>
<td>1000</td>
<td>180</td>
</tr>
<tr>
<td>Ni-1100</td>
<td>1000</td>
<td>220</td>
</tr>
</tbody>
</table>
Set II & IV: The growth of DLC with/without external magnetic field

<table>
<thead>
<tr>
<th>Samples</th>
<th>No. of laser pulses</th>
<th>Deposition sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Graphite</td>
<td>Ag</td>
</tr>
<tr>
<td>Ag-300</td>
<td>1000</td>
<td>60</td>
</tr>
<tr>
<td>Ag-500</td>
<td>1000</td>
<td>100</td>
</tr>
<tr>
<td>Ag-700</td>
<td>1000</td>
<td>140</td>
</tr>
<tr>
<td>Ag-900</td>
<td>1000</td>
<td>180</td>
</tr>
<tr>
<td>Ag-1100</td>
<td>1000</td>
<td>220</td>
</tr>
</tbody>
</table>

Two sets of thin films of graphite/Ni and graphite/Ag are deposited under the influence of external magnetic field applied transverse to the propagation of the plume and two sets are prepared without the application of field. The source of applied field is the circular shaped disk of samarium cobalt (permanent magnet).

The change in the concentration of Ni component was attained by varying the number of laser pulses on the metal part of the multi-component target during the deposition. The process to deposit each Ni-graphite films was completed in a five step process. In the first step, 60 numbers of pulses were taken on Ni part of the target and 1000 pulses on the graphite part. This was achieved by utilizing the facility of bringing the Ni or graphite targets alternatively at the focus point. This step was repeated five times to obtain 300 pulses on the Ni part and 5000 pulses on the graphite part of the target.

The purpose of such an arrangement was to get a homogenous film matrix with Ni particles evenly immersed in the entire film matrix. Films with different compositions of Ni are grown by keeping laser pulses constant over the graphite part of target and changing the number of laser pulses on Ni part.

In order to vary the concentration of the Ni content in the graphite matrix, different numbers of laser pulses were taken on the Ni part of the target keeping constant number of pulses (5000) for graphite. In this way five thin films are deposited with varying pulses
scheme for the Ni part of target i.e 300, 500, 700, 900 & 1100. Using the same above mentioned scheme and method, five films of graphite/Ag are deposited.

### 2.6 Characterization techniques

These prepared Ni–graphite films were analyzed by JSPM-5200, JEOL Atomic Force Microscopy (AFM) for surface topography. In order to explore surface morphology of the deposited films, microscopy was performed by a JEOL JSM-7600F and Scanning Electron Microscope (SEM) operated at 15 kV with resolution of 1.0 nm. The structural analysis was performed with the help of high resolution Raman Spectroscopy system MST-4000A made by Dongwoo Optron. A PANalytic XpertPro X-ray diffractometer with Cu kα source of λ= 1.54˚A was used for crystallographic measurements. A short explanation of these techniques is given in the next section.

**X-ray diffraction** is used to analyze the microstructure and crystallography of all type of manufactured and natural materials and thin films. The source of X-rays or electromagnetic radiations is copper. The characteristic wavelength (λ) for the copper Kα radiation is 1.5418Å, which is compatible with the size of an atom.

It depends upon the certain arrangement or geometry of atoms, the constructive interference occurs when the path difference between any two diffracted beams is integral multiple of an integer of wavelength.

This condition can be represented by the Bragg law 1912 [97].

\[ n\lambda = 2d \sin(\theta) \]

Where, λ is the wavelength of diffracted X-rays, θ is the angle between the incident and reflected beam, d is the inter-planar distance.

**Raman spectroscopy** is an important non-destructive research and analytical tool. It is widely used for characterization of all kind of applications like pharmaceuticals, polymers, forensic science, and semiconductors thin films. It is a Spectroscopic technique which is used to study vibrational, rotational and other low frequency modes in a system [100]. It works on in-elastic scattering of a laser light, usually from near ultraviolet, visible and near infrared range.
**Scanning Electron Microscopy** is used for analyzing the morphology and to observe the nano structure on the surface of Diamond like carbon films. In SEM electron beam falling on the surface of the sample interacts with the surface of the sample about several microns deep. In this technique, different types of detectors are used to receive the various electron-sample interaction signals to study the sample surface topography or elemental composition.

**Atomic Force Microscope (AFM)** technique is used to carry out the surface topography and morphology of solids samples [98-99]. AFM is same in design as the Scanning tunneling microscope (STM), but it quantifies the force between the microscope tip and surface of the atoms. Typically, the deflection of the tip is measured using a laser spot which is reflected from the top of the cantilever and detected by an array of photodiodes.
Chapter 3: Result and Discussions

This chapter deals with characterization and analysis of composite thin films of carbon deposited by Pulsed Laser Deposition (PLD) technique. Four sets of films were deposited on Si substrates which are categorized as follows:

(i) Ni-graphite thin films without external magnetic field
(ii) Ni-graphite thin films with external magnetic field applied across the plume
(iii) Ag-graphite thin films without external magnetic field
(iv) Ag-graphite thin films with external magnetic field applied across the plume

In order to accomplish the diagnostic task, X-ray diffraction and Raman spectroscopy were employed. The combination of these methods allows structural characterization in terms of phase, density, layering and vibrational modes of carbon films. Furthermore, the Atomic Force Microscopy (AFM) is used to determine the surface morphology and roughness of the deposited films.

3.1 Ni-graphite thin films

In the first part of the project, thin films of Ni-graphite are deposited on Si-substrate using PLD technique. These films are prepared without external magnetic field and as well as with the application of external magnetic field transverse to the plume direction. Ni-incorporation through a modified PLD technique is employed for doping of nickel content into the carbon film matrix. Detailed descriptions of the results are given in the following sections.

3.1.1 Films deposited without magnetic field (B=0)

3.1.1.1 XRD analysis

X-ray Diffraction technique is used to explore the changes induced in the structure of Ni incorporated Ni-graphite films. Figure 3.1(a) represents the X-ray diffraction patterns of the deposited thin films. The XRD data obtained from the spectra are listed in table 3.1.
The diffraction patterns indicate that the film is mainly amorphous with no carbon peaks. Two Ni planes having orientation (220) and (111) grow gradually with increasing no of laser pulses on Ni (increasing Ni concentration).

The pattern of the deposited film with 300 laser pulses on Ni i.e. Ni-300 clearly indicates that there is no peak for carbon as well as for Ni. However, when the laser pulses on the Ni component of target are increased to 500, 700, 900 and 1100, there is growth of Ni (111) plane at 44.51° in the deposited films. The film deposited at Ni-900 and Ni-1100, two additional peaks were also observed at 51.83° and 76.37° which correspond to the growth of Ni (200) and Ni (220) planes, respectively.

The plane (111) is the principal plane of Ni. The mean crystallite size of Nickel calculated using Sherrer’s formula is found to be reduced with the growth of Ni content due to slight shifting in the planes of Ni as represented in graph in figure 3.1 (a). The reduction in the crystallite size of Ni indicates the fine structured growth.

Figure 3.1: (a)- XRD spectra of the deposited films at B=0 (b)- Variation of crystallite size as a function of laser pulses on Ni
Table 3.1: XRD Data for Ni-graphite films deposited with B= 0 T

<table>
<thead>
<tr>
<th>Sample</th>
<th>h k l</th>
<th>d spacing Å</th>
<th>2θ (degrees)</th>
<th>FWHM in Degree β</th>
<th>Crystallite size D(nm)=kλ/βcosθ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-1100</td>
<td>111</td>
<td>2.03</td>
<td>44.72</td>
<td>0.38</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.76</td>
<td>51.84</td>
<td>0.31</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>1.24</td>
<td>76.33</td>
<td>0.27</td>
<td>39</td>
</tr>
<tr>
<td>Ni-900</td>
<td>111</td>
<td>2.03</td>
<td>44.65</td>
<td>0.33</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.76</td>
<td>51.83</td>
<td>0.27</td>
<td>32</td>
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<tr>
<td></td>
<td>220</td>
<td>1.24</td>
<td>76.41</td>
<td>0.31</td>
<td>34</td>
</tr>
<tr>
<td>Ni-700</td>
<td>111</td>
<td>2.02</td>
<td>44.58</td>
<td>0.26</td>
<td>34</td>
</tr>
<tr>
<td>Ni-500</td>
<td>111</td>
<td>2.02</td>
<td>44.51</td>
<td>0.23</td>
<td>40</td>
</tr>
</tbody>
</table>

3.1.1.2 Raman Analysis

An efficient, nondestructive tool for the analysis of microstructure of carbon based films is Raman spectroscopy. The ordering of the carbon’s network can easily be determined by this technique. It describes two main features, the characteristic G and D bands of carbon. Usually G band describes the degree of graphitization [101,102]. Raman spectra in figure 3.2 represent that for all the films, the characteristic G band ranges from 1529 cm\(^{-1}\) to 1547 cm\(^{-1}\) which originates due to C-C stretching mode of carbon. The range of D band is from 1348 cm\(^{-1}\) to 1356 cm\(^{-1}\) which is due to breathing modes of six-fold rings observed for amorphous carbon films [103].

The G-band at 1529 cm\(^{-1}\) has a wide shoulder at low concentration but there is decreasing trend in FWHM for increased Ni content. However, the intensity is increasing with higher metallic concentration. The decrease in the width of G-band is attributed to enhanced graphitization which is due to reduced inter-layer spacing. The data obtained from the raman measurement is listed in table 3.2.
Figure 3.2: (a)-Raman Spectra of deposited films at B=0 (b)-I_D/I_G ratio of Ni-graphite films with the increasing number of laser pulses on Ni
Figure 3.3: Variation in peak position of G and D band as function of laser pulses on Ni

The ratio of intensities of D and G peaks represented by $I_D/I_G$ is an important parameter for the determination of the phase transition and the degree of graphitization induced in the film matrix. Figure 3.2 (b) describes that the $I_D/I_G$ ratio decreases with increasing Ni content. The decrease in the $I_D/I_G$ ratio can also be attributed to increase in the chain length (decrease in $I_D$) caused by the incorporation of metallic content. This has eventually increased the degree of graphitization in the film. The enhanced peak intensity and reduced width of G-band (table 3.2), indicates the dominance of sp² bonding which is due to ordering of aromatic carbon rings and clustering. This trend in the sp² bonding is attributed to the clustering of the deposited film (graphite phase). This indicates the presence of mixed sp³ and sp² hybridization in the deposited films, but with an increasing proportion of sp² bonding [104]. There is much symmetry in G band than D band with a little shift in G-band towards higher wave number as shown in figure 3.3. This shift is due to decrease in compressive stresses within the film by incorporating the Ni nano particles in the Ni-graphite nano composite film [105].
Table 3.2: Peak positions and $I_D/I_G$ intensity ratio obtained from Raman spectra of Ni-graphite films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>G-band peak (cm$^{-1}$)</th>
<th>D-band peak (cm$^{-1}$)</th>
<th>FWHM G-band (cm$^{-1}$)</th>
<th>FWHM D-band (cm$^{-1}$)</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-500</td>
<td>1529</td>
<td>1354</td>
<td>112.8</td>
<td>108.4</td>
<td>0.79</td>
</tr>
<tr>
<td>Ni-700</td>
<td>1535</td>
<td>1352</td>
<td>114.4</td>
<td>184.5</td>
<td>0.78</td>
</tr>
<tr>
<td>Ni-900</td>
<td>1540</td>
<td>1348</td>
<td>129.0</td>
<td>192.7</td>
<td>0.62</td>
</tr>
<tr>
<td>Ni-1100</td>
<td>1547</td>
<td>1356</td>
<td>132.0</td>
<td>202.2</td>
<td>0.54</td>
</tr>
</tbody>
</table>

3.1.1.3 SEM analysis

Micrographs shown in figure 3.4 describe that the films prepared at low Ni concentration i.e. Ni-300, contains nano and micron sized Ni particulates which are randomly distributed in the film matrix. When the concentration of the metallic component Ni is further increased i.e. (Ni-500, Ni-700), the initialization of planer structure of Ni and subsequently the growth of Ni planes has been observed as evident from XRD.

Figure 3.4: SEM micrographs of the deposited Ni-graphite films with varying number of laser pulses on Ni ($B=0$)
The growth of clusters on the film surface will eventually roughen the surface since the RMS roughness increases with the increase in the Ni concentration as mentioned in table 3.3. For the films with higher concentration i.e Ni-900 and Ni-1100, the clustering are further enhanced. In addition to that, there are chances of encapsulation of Ni atoms within the cages of carbon. The incorporation of Ni will lower the internal compressive stress within the film which leads to the growth of aromatic carbon ring clusters as evident by the Raman spectroscopy.

3.1.1.4 AFM analysis

AFM micrographs in figure 3.5, give detailed information about the surface morphology and the texture development at the film surface by Ni incorporation. The film prepared at low concentration of Ni i.e. (Ni-300) is composed of some aggregates of Ni which are immersed in the carbon film matrix and are randomly distributed. The line profile in figure 3.5 (c) reveals the existence of nano sized structures.

When the concentration of Ni is gradually increased (Ni-500, Ni-700), the aggregation of Ni leads to the cluster formation on the surface (figure 3.5 d & g). Moreover, in the film growth process Ni acts as a catalyst which enhances the graphitization and eventually clustering of aromatic rings in the carbon network.

For the films with higher concentration i.e (Ni-900, Ni-1100), the surface consists of clusters of carbon which are induced by the increasing Ni concentration. The reason for the cluster formation is that the Ni atoms tend to accumulate the carbon species around them under the charge transfer process [106-108]. The heights of these structures increases from 15 nm to 50 nm with the increase in the Ni concentration as listed in Table 3.3.
Figure 3.5: AFM micrographs exhibiting 2D (a, d, g, j & m) and 3D (b, e, h, k & n) and line profile (c, f, i, l & o) of Ni-graphite films as a function of increasing Ni-concentration.
Table 3.3: Roughness of the Ni-graphite films deposited at different Ni concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elevated surface Structure growth (nm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-300</td>
<td>15</td>
<td>7.7</td>
</tr>
<tr>
<td>Ni-500</td>
<td>24</td>
<td>8.1</td>
</tr>
<tr>
<td>Ni-700</td>
<td>34</td>
<td>7.2</td>
</tr>
<tr>
<td>Ni-900</td>
<td>44</td>
<td>8.4</td>
</tr>
<tr>
<td>Ni-1100</td>
<td>50</td>
<td>13.1</td>
</tr>
</tbody>
</table>

Figure 3.6: Roughness profile of the films deposited with varying Ni concentration

The calculated RMS roughness values increase from 7.7 nm to 13.1 nm (table 3.3) which indicates that the surface of deposited films becomes rougher with the increase in the Ni concentration, as shown by graph in figure 3.6. This increase in the roughness is due to the growth of elevated structures which originate on the surface of the thin film as evident by line profile of the surface of the films.

3.1.2 Films deposited with magnetic field ($B = 0.1 \, \text{T}$)

In order to improve the quality of the film in terms of graphitization, crystallinity and roughness, magnetic field is applied transverse to the plume. The other parameters were kept exactly the same as those for the films deposited without field.
3.1.2.1 XRD analysis

The glancing incident 1.54Å X-ray beam on the prepared composite Ni-graphite thin film gives the diffraction pattern as shown in figure 3.7 and the data obtained from the spectra are listed in the table 3.4. Three Ni planes (111), (200) and (220) describes that the nickel planes grow substantially with the increasing metallic concentration. The applications of magnetic field have played a vital role in the growth of the planer structure of graphite. The film matrix composed of single crystalline form of graphite C (111) in which the Ni nano crystallites of different orientations are dispersed.

![Figure 3.7: XRD pattern of Ni-graphite thin films grown with B= 0.1 T](image)
The XRD spectra and the data presented in the relevant table describe that the films prepared under magnetic field are more crystalline as compared to the films prepared without magnetic field. The transverse magnetic field when applied to the plume,
quenches the plume. The carbon atoms have now reduced mean free path and have more probability of interacting each other with greater force required to form necessary bonding. In this process, the sp$^2$ hybridized structure grows in the carbon based network because it requires less energy for bond formation than sp$^3$ hybridized carbon. The films with lowest concentration of Ni have no peak of any nickel plane. When the concentration of the Ni content is increased i.e. (Ni-B-500, Ni-B-700), only one Ni plane (111) is developed which is the principal plane. When the Ni concentration is further increased i.e. (Ni-B-900, Ni-B-1100) two new planes (200), (220) have further developed with more aligned crystallites of Ni at highest concentration. It suggests that at higher concentration the crystallites are composed of more than one grain. The maximum crystallite size of Ni (111) as calculated from data using Scherrer’s formula [109] is found to be 75 nm.

A graphitic plane of orientation C (111) at an angle 26.59° has grown in these films regardless of Ni- concentration. This C (111) plane was not found in the film with B=0. The application of magnetic field to the plume gave rise to the temperature of ejected carbon vapors and a decomposition process of carbon species takes place. The applied magnetic field has changed the vibrational and rotational temperatures of electronically excited carbon atoms and molecules. The large discrepancy between rotational temperatures of C atoms implies the differences in their recombination mechanisms. Carbon atoms and molecules are mostly formed by recombination of two carbon atoms, which have no activation barrier. This leads to the formation of hexagonal as well as disordered carbon atoms [110]. When the temperature of ablated carbon species reduces to a critical point, condensation and nucleation takes place. As a consequence, a principle plane of graphite (111) is developed. The reduced width and increased intensity of the peak C (111) with the increasing Ni concentration indicates that the crystallite size is increasing as evident from figure 3.8. The maximum crystallite size of C (111) is calculated to be 56 nm.

3.1.2.2 Raman analysis

The Raman Spectra of Ni-graphite films grown under B field is presented in figure 3.9, which describes the convolution of important structural parameters for the carbon films. The spectra give information of the ordering and bonding structure of the multi-component films.
The two characteristic Raman bands i.e. D-band at ~1360 cm$^{-1}$ and G-bands at ~1579 cm$^{-1}$ reflect the presence of sp$^2$ hybridized graphitic phase. The presence of the D-band indicates a disorder rate [111] while the shape, width and peak position of the G-band reflect the perfect stacking of the graphene planes. Normally, the term “disorder” means the existence of the elastic scattering regions for phonon. Thus, for a perfect crystal of finite size, i.e. smaller than mean free path of phonons or electrons it will show the D-band. The domain boundaries which are scattering the phonons and electrons can also be considered as disorder or defects.

![Raman Spectra of the deposited Ni-graphite films](image)

**Figure 3.9:** Raman Spectra of the deposited Ni-graphite films

The FWHM of the G-band also indicates that the peak is becoming sharp having reduced width and increased intensity by incorporating the Ni metallic component. That nickel intercalated atoms help to compensate the compressive stress and enhance the aromaticity of the carbon rings [112]. It is observed that the G-band (trigonal bonded) has a little shift towards higher wave number from 1574 cm$^{-1}$ to 1584 cm$^{-1}$ with increase in Ni-
concentration which is due to the enhancement and ordering of the sp\textsuperscript{2} bonded clusters. This shift in wave number is called blue shift which is due to reduction of compressive stresses. The D-band peaks on the other hand show no such deviation from its mean position (table 3.5) but significant change in the FWHM. The increased width of the D-band with increasing metal concentration is attributed to the disorder in the sp\textsuperscript{2} type of bonding and change in the bond angle by linking with the sp\textsuperscript{3} type of hybridized carbon.

Table 3.5: Peak positions and I\textsubscript{D}/I\textsubscript{G} intensity ratio obtained from Raman spectra of deposited Ni-graphite films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>G-band Peak position (cm\textsuperscript{-1})</th>
<th>D-band Peak position (cm\textsuperscript{-1})</th>
<th>FWHM G-band (cm\textsuperscript{-1})</th>
<th>FWHM D-band (cm\textsuperscript{-1})</th>
<th>I\textsubscript{D}/I\textsubscript{G}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-B-300</td>
<td>1574</td>
<td>1357</td>
<td>74.3</td>
<td>86.8</td>
<td>1.25</td>
</tr>
<tr>
<td>Ni-B-500</td>
<td>1576</td>
<td>1359</td>
<td>89.2</td>
<td>132</td>
<td>1.42</td>
</tr>
<tr>
<td>Ni-B-700</td>
<td>1579</td>
<td>1360</td>
<td>78.2</td>
<td>101</td>
<td>1.1</td>
</tr>
<tr>
<td>Ni-B-900</td>
<td>1582</td>
<td>1361</td>
<td>73.1</td>
<td>67.4</td>
<td>0.41</td>
</tr>
<tr>
<td>Ni-B-1100</td>
<td>1584</td>
<td>1364</td>
<td>63.2</td>
<td>122</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Figure 3.10: (a)- Peak positions of D and G bands (b)- I\textsubscript{D}/I\textsubscript{G} ratio as a function Ni-concentration

The ratio of integrated intensities of G and D-bands (I\textsubscript{D}/I\textsubscript{G}) represents not only the degree of graphitization, but also represents the edge ratio, i.e. number of atoms on the edges of basel planes in graphene. Figure 3.10, shows I\textsubscript{D}/I\textsubscript{G} ratio along with linear fit, which reveals the existence of graphitic phase and the well established π-electronic system. Moreover, it also indicates the appearance of five-membered or seven-membered rings within the
planes of hexagonal aromatic rings [113]. The main parameters obtained from the Raman spectra are summarized in the table 3.5.

### 3.1.2.3 SEM analysis

Surface morphologies of the deposited films were examined using Scanning Electron Microscopy (SEM). Ni-graphite composite films were prepared with the same concentration scheme as that for films deposited without field. The only difference is that the films were prepared under applied external field (B= 0.1 T).

![SEM micrographs of the deposited Ni-graphite films with varying no of pulses on Ni (B=0.1 T)]](image_url)
The surface has coverage of the cluster like structures embedded in the carbon film matrix. When the metallic concentration of the Ni is low, the surface of the deposited film matrix is a bit rougher and the density of the graphitic clusters is increased for the sample (Ni-B-500) as compared to the first sample named Ni-B-300. The increasing density of the clustered objects is due to the stress relaxation within the film and the reduced chain length of C-C bonds. The average diameter of the clustered objects is approximately 200 nm to 300 nm as estimated from SEM (line intercept method). The external magnetic field quenches the plasma and therefore the plume density is enhanced due to which ablated particles are more probable to interact with each other. This interaction enhances the probability of accumulation in the form of clusters. The increase in the concentration of metallic specie in the Ni-graphite films reveals that the clustering is enhanced in the Ni-graphite films. This also shows that the density of the particulates and the clusters grows gradually and the agglomeration is also observed for the films deposited with maximum Ni concentration i.e. Ni-B-1100.

3.1.2.4 AFM analysis

Surface morphology and the texture development of the composite films were examined by Atomic Force Microscopy. The micrographs shown in figure 3.12, describes that the surface is composed of small objects of spherical geometry. In this figure two dimensional and three dimensional (3D) surfaces are shown with their surface line profiles. The surface reveals that there are clusters growth on the surface which range from few hundreds of nanometers to micron in the diameters. The line profiles taken from different sections of the surface show the agglomeration of the particulates on the surface. The maximum height of the cluster is found to be 65 nm (encircled). The size ranges between 20-30 nm for the sample Ni-B-300. Similarly the maximum height is of 43 nm having size range between 30-35 nm for film Ni-B-500.
Figure 3.12: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-300).
Figure 3.13: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-500).
Figure 3.14: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-700).
Figure 3.15: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-900).
Typical AFM morphologies of the Ni-graphite films prepared in the presence of magnetic field reveal that surfaces are composed of a large number of particles with size of less than 100 nanometer. When the concentration of Ni content is increased (from 300 to 1100) the particles size decreases to several nanometers. The stresses growth in the layered thin films

Figure 3.16: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ni under the magnetic field (Ni-B-1100).
can change the film quality. The tensile stresses are usually evolved due to dislocation generation or by some plastic deformation such as grain boundary densification due to diffusion. As the Ni concentration is increased under magnetic field the intrinsic stresses are compensated, so it is obvious that the surface of the films are becoming smooth as the root mean square (rms) roughness slightly decreases. It can also be seen that the roughness of the films decreases with increase in the Ni concentration. The surface contains spherical clusters of random sizes. When the metallic concentration is further increased in the presence of magnetic field the heights of the elevated structures is reduced and the random distribution of the clustered objects shifts towards ordering. This ordering leads towards the growth of smooth surfaces. The rms roughness data and the maximum elevated texture growths are listed in table 3.6.

Table 3.6: Surface Roughness of the films deposited at different Ni concentration at B= 0.1T

<table>
<thead>
<tr>
<th>Sample</th>
<th>Height of elevated structure (nm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-B-300</td>
<td>65</td>
<td>8.2</td>
</tr>
<tr>
<td>Ni-B-500</td>
<td>43</td>
<td>8.1</td>
</tr>
<tr>
<td>Ni-B-700</td>
<td>48</td>
<td>7.9</td>
</tr>
<tr>
<td>Ni-B-900</td>
<td>35</td>
<td>7.3</td>
</tr>
<tr>
<td>Ni-B-1100</td>
<td>45</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Figure 3.17: RMS roughness profile along with linear fit for Ni-graphite films deposited with different Ni concentration with B= 0.1 T
A graph in figure 3.17 shows that the surface roughness of the deposited films also reduces with increasing Ni concentration which is also a clear evidence of uniformity and the increased crystallite size as confirmed by XRD results. The Ni incorporation will relive from compressive stresses by reducing the probability of sp$^3$ hybridization. Thus, the atoms in the carbon network can easily be settled down at low bond formation energies.

### 3.2 Comparison of Ni-Graphite films grown with and without magnetic field

Carbon composite films (Ni-graphite) prepared with and without applied field are discussed in the previous sections. The comparison of the results reveals that the application of external magnetic field transverse to the plume propagation has significantly improved the films quality.

The structural analysis performed using XRD, shows that the films prepared in the presence of external magnetic field have comparatively larger crystallite size of Ni. Another important aspect of application of external field is that an additional plane of carbon (111) having crystallite size of 56 nm has been developed which means that graphitization is enhanced in these films. The graphitization process means improvement in the stacking of the graphite planes. It is thermally activated process, which is initiated when external field quenches the plume, the density of the plume species increases and the mean free path is reduced. Thus the kinetic energies of the plume species are increased. The increased energies of the species lead to the growth of highly planner structure instead of turbostratic (irregular) structures. The stacking of hexagonal carbon layers having reduced interlayer spacing are found in well crystallized natural graphite and large crystallite sizes along and c-axis.

The structure and modes of vibration within the prepared composite films were analyzed by Raman spectroscopy. The stacking of nano graphene layers in an amorphous film matrix and the quantum confined sp$^3$/sp$^2$ nano-layers were determined by this method. It is seen that the G-band has been shifted towards higher wave number for the films prepared in the presence of magnetic field. The nucleation and growth process of carbon films are strongly dependent on the size of the ablated species. In the resulting films the structure is formed due to the condensation of large aromatic clusters which did not undergo other fragmentation or activation. The decreased values of $I_D/I_G$ for the films prepared under
external magnetic field indicate that the chain length and the six-fold aromatic rings of carbon clusters have developed substantially in that film matrix.

It appears from the surface morphologies of the composite films that it is possible to attain a suitable density of Ni nano particles with the present methodology. The surface of the Ni-graphite films consists of small aggregates of carbon clusters which are linked with the increasing nickel concentration. When the Ni concentration is increased, there is a growth of nano and micron sized particulates which are completely immersed in the composite film matrix. However, these particles are partially immersed and randomly distributed on the surface. It is observed that the films prepared in the presence of applied magnetic field have comparatively larger aromatic ring clusters of graphite. Mainly the process is kinetic and more stable sp² hybridized bonds are formed along the plume direction, giving rise to aromaticity of the graphite planes.

Surface roughness and texture development on the surface of the prepared film changes drastically with the increasing Ni concentration. The smoothing probability enhances due to the diffusion of energetic carbon ions. In the case of energetic species, compressive stresses are induced in the films due to diffusion of grain boundaries. When the concentration of metallic species is increased these stresses are relaxed and thus more clustered objects are developed. The morphology of the films indicates that there are small cone like structures on the surface and their density and uniformity increases by Ni incorporation when films are prepared in the presence of magnetic field.
3.3 Ag-graphite thin films

In the second part of the project, composite thin films of Ag-graphite are grown onto the Si substrate using PLD technique. Ag contents were added in the film during the growth process. The results obtained from various diagnostics are discussed in the following section.

3.3.1 Films deposited without magnetic field (B=0)

3.3.1.1 XRD analysis

X-ray diffraction technique is used to investigate the structure of the Ag-graphite film matrix. The addition of the metallic silver particulates within the amorphous carbon films can alter the microstructure of the film matrix. Figure 3.18 represents the diffraction spectra of the deposited films at varying Ag concentration. The diffraction peaks at 38.2° and 44.46° represents the silver (111) and (200) planes, respectively.

![XRD spectra for Ag-graphite films](image1)

![Ag crystallite size as a function of number of laser pulses on Ag](image2)

Figure 3.18: (a)-XRD spectra for Ag-graphite films (b): Ag crystallite size as a function of number of laser pulses on Ag
The patterns indicate that at concentration above Ag-500, a single (111) peak at 38.2° is observed which corresponds to the existence of Ag cubic phase in the pure carbon films. With the increase in Ag concentration there is a slight increase in the peak intensity. When the concentration of silver is further increased i.e (Ag-1100), another plane (200) of Ag develops in the amorphous film matrix. It is observed that the growth of Ag planes is due to the increased density of the silver nano particles which facilitate the formation of nano crystallites, dispersed in the carbon films matrix.

Table 3.7: XRD Data for Ag-graphite films deposited with B= 0 T

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Element</th>
<th>h k l</th>
<th>d spacing Å</th>
<th>2θ (degrees)</th>
<th>FWHM in Degree β</th>
<th>Crystallite size D(nm)=kλ/βcosθ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-1100</td>
<td>Silver</td>
<td>111</td>
<td>2.35</td>
<td>38.26</td>
<td>0.31</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>200</td>
<td>2.04</td>
<td>44.51</td>
<td>0.43</td>
<td>20</td>
</tr>
<tr>
<td>Ag-900</td>
<td>Silver</td>
<td>111</td>
<td>2.35</td>
<td>38.23</td>
<td>0.39</td>
<td>22</td>
</tr>
<tr>
<td>Ag-700</td>
<td>Silver</td>
<td>111</td>
<td>2.35</td>
<td>38.23</td>
<td>0.47</td>
<td>19</td>
</tr>
<tr>
<td>Ag-500</td>
<td>Silver</td>
<td>111</td>
<td>2.35</td>
<td>38.20</td>
<td>0.51</td>
<td>17</td>
</tr>
</tbody>
</table>

The tabulated data exhibit a decrease in FWHM as a function of increasing Ag concentration. As the concentration is increased the density of newly developed Ag crystallites increases and thus the reflected intensity of Ag (111) peak increases. The appearance of Ag (200) peak is attributed to the increased metallic density upto a certain level which in turn develops a second ordered plane of Ag.

3.3.1.2 Raman analysis

Raman spectroscopy is very efficient and non destructive tool for the characterization of carbon films as it can provide information about periodicity of the carbonaceous network. The Raman spectra as described in figure 3.19 exhibit two main features of the carbon films, the standard G band and the D band at slightly lower wave number which becomes prominent at higher metallic concentration. The G-band is an important parameter for determination of degree of graphitization. The D and G band peak positions were determined by taking Gaussian profile of each spectrum.
Figure 3.19: Raman Spectra of the deposited Ag-graphite films

Figure 3.20: (a)- $I_D/I_G$ ratio  (b)- Peak position of G and D bands as a function of number of laser pulses on Ag

Raman spectra in figure 3.19, show that the characteristic G-band center ranges from 1535 cm$^{-1}$ to 1544 cm$^{-1}$ which originates from all vibration modes of sp$^2$ bonded C atoms in the aromatic rings. The D-peak center ranges from 1343 cm$^{-1}$ to 1354 cm$^{-1}$ which originates
from breathing modes of six-fold rings and not for chains as observed in amorphous carbon films [114].

It is observed that at lower concentration i.e Ag-300, Ag-500 there is a merged peak from 1300 cm\(^{-1}\) to 1600 cm\(^{-1}\). According to Robertson [115], sp\(^2\) sites have a variable gap, which depends on the configuration of each sp\(^2\) clusters and the sp\(^3\) bond act as a tunnel barrier between each sp\(^2\) cluster. This distribution of sp\(^2\) gaps creates inhomogeneous disorder [116]. This disorder is the reason for the merger of the peaks at lower concentration. The Plasmon band reshapes its structure and a red-shifting is observed which indicates the aggregation of nano particles. The decrease in the FWHM of G-band with the increasing metal concentration is attributed to enhanced graphitization and reduced inter-layer spacing. The key parameters obtained from the spectra are summarized in Table 3.8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>G-band peak position (cm(^{-1}))</th>
<th>D-band peak position (cm(^{-1}))</th>
<th>FWHM G-Band</th>
<th>I(_D/I_G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-700</td>
<td>1539</td>
<td>1354</td>
<td>89.7</td>
<td>1.21</td>
</tr>
<tr>
<td>Ag-900</td>
<td>1535</td>
<td>1343</td>
<td>129.0</td>
<td>0.89</td>
</tr>
<tr>
<td>Ag-1100</td>
<td>1544</td>
<td>1349</td>
<td>101.7</td>
<td>0.67</td>
</tr>
</tbody>
</table>

The relative intensities of D and G peaks were used to determine I\(_D/I_G\) ratio. It is an important parameter for the determination of the phase and the structural changes induced in the film matrix. Figure 3.20 (a) describes the variation in the I\(_D/I_G\) ratio as a function of Ag content. It indicates the existence of mixed sp\(^3\) and sp\(^2\) bonding in the deposited films but with an increasing trend of sp\(^2\) bonding. This increasing trend in the sp\(^2\) sites is attributed to the enhanced clustering of the deposited material and an increase in the chain length which is caused by the insertion of the metallic content. This leads to the increase in the degree of graphitization of the film. The induced ordering caused a shift in the G-band peak position with the increase in Ag concentration as shown in figure 3.20 (b). The G band is generally associated with the relative motion of sp\(^2\) hybridized carbon. It usually occurs from sp\(^2\) type C=C vibrations of olefinic carbon chains. The metal insertion in these
composite structures enhances the aromaticity and chain length of carbon which favors the sp² bonding in the film matrix. The D peak shift is associated to the activated disorder breathing motion of six-fold aromatic rings and usually forbidden in perfect graphite structure [117].

### 3.3.1.3 SEM analysis

SEM images shown in figure 3.21, reveals that the surface morphology of the prepared films alters gradually by the incorporation of Ag in the graphite films matrix. The surface is covered with clustered-like structures. All the Ag-graphite films are composed of small and compact particles of spherical geometry. It appears that with the increase in the Ag concentration, the size of the cluster has increased. At low concentration of Ag i.e. Ag-300, nano and micron sized particulates are observed and are randomly distributed in the film matrix.

![SEM Micrographs](image)

Figure 3.21: SEM Micrographs of the deposited Ag-graphite films by varying the concentration of Ag.

When the concentration of the metallic component Ag is increased from Ag-500 to Ag-700 the silver atoms have the tendency of accumulation at atomic level to form nano structures. The films with higher concentration i.e Ag-900 & Ag-1100 the clustering is further enhanced. In addition to that there are chances of encapsulation of Ag atoms within the
cages of carbon. The incorporation of Ag lowers the internal compressive stress within the film which leads to the growth of aromatic carbon ring clusters as evident by the Raman spectroscopy (discussed in section 3.3.1.2). Moreover, the growth of clusters on the film has eventually roughened the surface since the RMS roughness increases with the increase in the Ag concentration as mentioned in table 3.9.

3.3.1.4 AFM analysis

The surface morphology and the elevated texture development at the film surface by the incorporated Ag nano particles is examined using AFM. Figure 3.22 represents the micrographs of the film prepared at different concentrations. At low concentration of Ag i.e. (Ag-300) the surface is composed of some clusters of Ag which are partially immersed in the film matrix. The random distribution of these Ag particulates is due to inhomogeneous density of the plume. The line profiles in figure 3.22 indicate the presence of nano structures.

The increasing concentration of Ag i.e. Ag-500 and Ag-700 leads to the growth of aggregates of silver on to the surface. The surface consists of some bigger structures which are, in some cases the agglomerates of comparatively small structures. These surface features have developed further and the number density of particles forming them has also increased. Moreover, the vertical growth of these structures on the surface is observed by line profile, which ranges from 12 nm to 54 nm in heights.
Figure 3.22: AFM micrographs exhibiting 2D (a, d, g, j & m) and 3D (b, e, h, k & n) and line profile (c, f, i, l & o) of Ag-graphite films as a function of increasing Ag-concentration.

The composite carbon films prepared with higher Ag concentration i.e (Ag-900 and Ag-1100) the surface consists of clustered object in addition to some spherical objects of
carbon. The fact can be summarized that clustering of Ag atoms when exceeds to a certain size, it accumulates the carbon species around them which is initiated by the charge transfer process. When the metallic content is gradually increased the film’s surface becomes rougher as the root-mean-square roughness has been increased from 2.41 nm to 10.1 nm, as shown by the graph in figure 3.23. The RMS roughness for the composite films are listed in table 3.9.

Table 3.9: Roughness of the Ag-graphite films deposited at different Ag concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elevated surface Structure growth (nm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-300</td>
<td>12</td>
<td>2.4</td>
</tr>
<tr>
<td>Ag-500</td>
<td>15</td>
<td>3.5</td>
</tr>
<tr>
<td>Ag-700</td>
<td>28</td>
<td>6.2</td>
</tr>
<tr>
<td>Ag-900</td>
<td>40</td>
<td>8.3</td>
</tr>
<tr>
<td>Ag-1100</td>
<td>54</td>
<td>10.1</td>
</tr>
</tbody>
</table>

Figure 3.23: Roughness profile with linear fit of Ag-graphite films
3.3.2 Ag-graphite films deposited with magnetic field (B= 0.1 T)

3.3.2.1 XRD analysis

X-ray diffraction measurement technique is used to analyze the structure of the composite Ag-graphite films. These diffraction patterns are presented in figure 3.24, and the data obtained from the XRD spectra are listed in table 3.10.

It can be seen that when the metallic concentration of Ag species are increased, one additional plane (200) with the standard (111) plane of Silver has been developed within the film matrix. The spectra reveal the growth of Ag (111) plane for all concentration of Ag. The intensity has increased as compared to the peaks observed for the films grown without field. For higher concentration of Ag i.e. 900 and above, the additional plane (200) has appeared. This is because the magnetic field increased the density of the atoms within the ablated plume and hence imparts more kinetic energy for the formation of particular plane [118].

![XRD spectra for Ag-graphite films deposited with B= 0.1 T](image_url)

Figure 3.24: XRD spectra for Ag-graphite films deposited with B= 0.1 T
Figure 3.25: Crystallite size of a)- Ag(111)  b)- Carbon as a function of Ag-concentration

The XRD spectra also reflect a carbon (111) plane, which appears for all the concentrations. By careful observation of the spectra and the tabular data, it is concluded that the films prepared under applied external magnetic field and increasing metallic concentration are more crystalline as compared to the films grown without field. This C (111) peak was not observed in case of the films deposited without field. Under the magnetic field the ablated graphitic atoms when move in helical path in forward peaked direction, the interaction probability is increased and due to their increased energies they form aromatic type of structures rather than the turbostratic ones. In this manner, sp² type of carbon bonds are formed which needed less energy than sp³ hybridized carbon atoms [105].

The increased intensity and reduced FWHM of the graphite plane (111) with increasing Ag concentration indicates that stacking is enhanced and the crystallite size is increasing, as presented in table 3.10. The crystallite size of graphite ranges from 28 nm to 47 nm. At the lowest incorporated Ag content e.g Ag-B-300, there is no evidence of the growth of Ag planes. Because of very low doping ratio the density is not sufficient to occupy the lattice sites of the crystal.
Table 3.10: XRD data obtained from Ag-graphite composite films deposited with B = 0.1 T

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Element</th>
<th>h k l</th>
<th>d spacing (Å)</th>
<th>2θ (degrees)</th>
<th>FWHM in Degree β</th>
<th>Crystallite size D(nm)=kλ/βcosθ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-B-1100</td>
<td>Silver</td>
<td>111</td>
<td>2.35</td>
<td>38.23</td>
<td>0.25</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>200</td>
<td>2.04</td>
<td>44.52</td>
<td>0.38</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Carbon</td>
<td>111</td>
<td>3.34</td>
<td>26.61</td>
<td>0.18</td>
<td>47</td>
</tr>
<tr>
<td>Ag-B-900</td>
<td>Silver</td>
<td>111</td>
<td>2.35</td>
<td>38.30</td>
<td>0.31</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>220</td>
<td>2.04</td>
<td>44.58</td>
<td>0.38</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Carbon</td>
<td>111</td>
<td>3.34</td>
<td>26.57</td>
<td>0.22</td>
<td>38</td>
</tr>
<tr>
<td>Ag-B-700</td>
<td>Silver</td>
<td>111</td>
<td>2.35</td>
<td>38.32</td>
<td>0.32</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Carbon</td>
<td>111</td>
<td>3.34</td>
<td>26.56</td>
<td>0.25</td>
<td>34</td>
</tr>
<tr>
<td>Ag-B-500</td>
<td>Silver</td>
<td>111</td>
<td>2.35</td>
<td>38.28</td>
<td>0.30</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Carbon</td>
<td>111</td>
<td>3.34</td>
<td>26.51</td>
<td>0.28</td>
<td>30</td>
</tr>
<tr>
<td>Ag-B-300</td>
<td>Carbon</td>
<td>111</td>
<td>3.35</td>
<td>26.53</td>
<td>0.30</td>
<td>28</td>
</tr>
</tbody>
</table>

When the concentration of the Ag component is further increased i.e. (Ag-B-500, Ag-B-700), only one standard (111) plane of Ag has been developed. When the Ag concentration is further increased i.e. (Ag-B-900, Ag-B-1100) one new plane (200) has been developed. When the laser ablates metal–carbon composite target in the presence of magnetic field the vaporized region mainly consists of saturated Ag vapor with high temperature, which is a dominant energy carrier. When the temperature of silver vapor reduces to a certain critical point of condensation and nucleation, silver nano particles of orientation (200) are formed. The silver crystallite size ranges from 27 nm to 35 nm.

3.3.2.2 Raman analysis

Raman scattering is used to determine the bonding and structure of the Ag-graphite films which have prepared in the presence of external magnetic field. Figure 3.26 presents the Raman spectra of films deposited by varying composition of silver. The spectra consist of five curves, each represents the scattering information from each sample. It can be seen that the spectra consist of two main peaks, one for the standard G-band and second for D-band of carbon. These two bands are usually found in carbon films and give important information about the ordering and stacking of the graphite planes. It is
observed that there is a shift in G-band from 1566 cm\(^{-1}\) to 1583 cm\(^{-1}\) with the increase in Ag concentration. This shift is due to the increasing density of the trigonal bonded carbon atoms because at longer chain lengths high frequency photons will excite these atoms. This would also increase the aromaticity of the sp\(^2\) hybridized clusters. It is a well-established fact that the metallic incorporation reduces the compressive stress within the film [119].

![Raman spectra of Ag-graphite films deposited with B= 0.1 T](image)

**Figure 3.26**: Raman spectra of Ag-graphite films deposited with B= 0.1 T

The observation of the spectra reveals that the FWHM is decreasing and the relative intensity of the G-band is increasing, which is clear evidence of the ordering of aromatic rings of carbon. The external magnetic field also favors the stress relaxation by providing the required kinetic energy to the ablated atoms. The silver intercalated atoms support to the formation of carbon ring clusters around them. It is also observed that the shifting of G-band to higher wave number is attributed to the increasing sp\(^2\) content in the film matrix. This shift is due to the transformation of sp\(^2\) clusters from rings to chains and at some times into dimers. The parameters obtained from Raman spectrum are listed in table 3.11.
Table 3.11: Data obtained from Raman spectrum for the Ag-graphite films deposited under B= 0.1 T.

<table>
<thead>
<tr>
<th>Samples</th>
<th>G-band Peak (cm⁻¹)</th>
<th>D-band Peak (cm⁻¹)</th>
<th>FWHM G-band (cm⁻¹)</th>
<th>FWHM D-band (cm⁻¹)</th>
<th>I_D/I_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-B-300</td>
<td>1566</td>
<td>1338</td>
<td>67.1</td>
<td>55.0</td>
<td>0.60</td>
</tr>
<tr>
<td>Ag-B-500</td>
<td>1570</td>
<td>1358</td>
<td>51.7</td>
<td>45.6</td>
<td>0.55</td>
</tr>
<tr>
<td>Ag-B-700</td>
<td>1578</td>
<td>1364</td>
<td>79.2</td>
<td>36.3</td>
<td>0.41</td>
</tr>
<tr>
<td>Ag-B-900</td>
<td>1581</td>
<td>1359</td>
<td>51.3</td>
<td>61.4</td>
<td>0.53</td>
</tr>
<tr>
<td>Ag-B-1100</td>
<td>1583</td>
<td>1360</td>
<td>78.2</td>
<td>31.3</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Figure 3.27: (a)- Peak positions for D & G bands (b)- I_D/I_G ratio as a function of Ag-concentration

Peak position, peak intensity and the I_D/I_G ratio is used to classify the nature of hybridization that exists in the composite carbon film. The presence of the sp² or sp³ content helps us to evaluate the degree of graphitization and also the edge ratio (atoms in the basal planes).

The integrated I_D/I_G ratio and its linear fit are shown in figure 3.27 (a). The decreasing trend of the I_D/I_G with the increase in Ag concentration indicates that the graphitization is enhanced within the films matrix. The changing peak positions of D and G band can easily be visualized in figure 3.27 (b). The existence of graphitic planes is an evidence of the establishment of π-electronic system within the carbonaceous network. It is concluded that
the existence of silver nano particles would effectively support the formation of graphitic clusters in the film matrix.

3.3.2.3 SEM analysis

The surface topography of the films prepared using multi-component target in the presence of magnetic field is shown is figure 3.28. It is seen that the film which is prepared with the lowest Ag concentration (Ag-B-300) has less uniformity in size distribution of clustered objects. Moreover, some voids are present in the film which is reduced for higher metallic concentration.

Figure 3.28: SEM micrographs of the Ag-graphite films prepared under B= 0.1 T.
The film labeled as Ag-B-500 is prepared at a higher concentration of Ag. It is observed that the film is a bit uniform with some clustering observed on the surface. This clustering is due to the partially immersed nano particles of Ag which are trapped within the graphitic planes. When the metallic concentration is further increased, the topography of the film changes in a gradual manner. Figure 3.28 reveals that the surface consists of clustered objects and their density is increasing with increasing Ag-concentration. When the metallic content is increased the stresses are relaxed and the probability of formation of sp$^2$ type of clusters is enhanced. Therefore bigger clustered objects are formed on the surface of these films. When the number of laser pulses is increased onto the silver target, subsequently the incorporated silver content is increased. Therefore, the growth of Ag crystals takes place. The amorphous carbon films have intrinsic compressive stress which form micro voids in the film. When the growing crystal size of the silver becomes comparable to these voids, it will relieve the stresses. The stress relaxation improves the quality of the film and bigger sized clustered objects are found on the surface.

### 3.3.2.3 AFM analysis

The surface topography and the growth of surface features are well defined using the AFM micrographs. In figure 3.29, two dimensional and three dimensional view along with line profile of Ag-graphite composite film is presented. The film prepared under magnetic field for the concentration Ag-B-300, the surface morphology reveals that there is random distribution of particulates. The size of these particulates varies from sub-micron to micron in width and in nanometers in height. It is seen that the particulates are of triangular (cone type) shape which are most probably due to the growth of new planes along step edges (defects). The surface line profile gives information about the height of the individual particle. The maximum height is observed to be 120 nm. The RMS roughness for the film prepared with lowest Ag content under magnetic field is found to be 21.4 nm.
Figure 3.29: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 300 pulses on Ag under the magnetic field (Ag-B-300)
Figure 3.30: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 500 pulses on Ag under the magnetic field (Ag-B-500)
Figure 3.31: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 700 pulses on Ag under the magnetic field (Ag-B-700)
Figure 3.32: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 900 pulses on Ag under the magnetic field (Ag-B-900)
Figure 3.33: AFM micrographs 2D, 3D and line profiles for the films prepared by taking 1100 pulses on Ag under the magnetic field (Ag-B-1100)

Table 3.12: Films roughness of Ag-graphite films deposited under B=0.1 T

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elevated surface Structure growth (nm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-B-300</td>
<td>120</td>
<td>21.4</td>
</tr>
<tr>
<td>Ag-B-500</td>
<td>123</td>
<td>25.6</td>
</tr>
<tr>
<td>Ag-B-700</td>
<td>122</td>
<td>28.7</td>
</tr>
<tr>
<td>Ag-B-900</td>
<td>133</td>
<td>26.3</td>
</tr>
<tr>
<td>Ag-B-1100</td>
<td>125</td>
<td>33.5</td>
</tr>
</tbody>
</table>
Figure 3.34: Roughness profile and linear fit of the Ag-graphite films under B=0.1 T

The micrographs presented describe the morphology of the Ag-graphite films. It is seen that the films are bit uniform and has random distribution of the clustered like triangular objects. The growth flux, surface energy and the substrate temperature are the important parameters that affect the grain structure and surface reconstruction of the thin films. The growth flux represents the mass flow rate onto the film surface. When the external magnetic field quenches the plasma plume, the degree of saturation of the incoming vapor is increased. This generates variation in the free energy of the atoms reaching the substrate. There are also some distribution of surface defect like; steps, dislocation line and grain boundary traces which provide sites for nucleation. The surface energy of the system is reduced by relaxation of the surface lattice sites, which favors the formation of new bonding sites within the film structure.

A homogenous coverage of clusters is observed for all the films with a slight increase in size. Some areas of this coverage reveal bigger clustered-like structures with sizes from 20 nm to 120 nm in height. Openings “holes” are also observed in the grown thin layers, as indicated by flat regions in the line profiles. The surface morphology exhibits very similar features to the films prepared with varying Ag content except for the film labeled Ag-B-1100, which has bigger clusters in respect of diameters.
The islands found on the surface of the films are due to the mismatch of the lattice constant of the substrate and the film material. The incoming Ag metallic nano particles reduce the stress and the bonding probability of the carbon network is enhanced. Consequently, the surface free energy [120] of the substrate is reduced and flat conical shape islands are formed. The line profile gives the maximum height of the clustered object found on the surface, which is given in the table 3.12. It is seen that the number density of the clustered object is larger for the film prepared with maximum number of Ag concentration. This is due to the fact that when comparatively energetic species are embedded in the film matrix, the probability of stress relaxation is increased. Thus, the graphitic clustering is enhanced. The growth of elevated structures on the surface is attributed to this enhanced clustering. The heights of these clustered objects are increasing gradually by gradual increase in Ag concentration consequently the surface roughness is increased, as shown by the graph in figure 3.34.

### 3.4 Comparison of Ag-graphite films

The comparison of Ag-graphite films deposited with and without the application of external magnetic field reveals that the Ag-graphite films prepared by the application of external magnetic field have an ordered structure as compared to the films prepared without field. The application of external magnetic field has significant impacts on the structural as well as on the topography of the prepared films. In addition to the growth of Ag planes, it is also observed that it has increasing density of the trigonal bonded carbon atoms within the film i.e C (111) plane. This leads to shift in the peaks because at longer chain lengths high frequency photons are able to excite these molecules. The silver intercalated atoms support to the formation of carbon ring clusters by taking the π-electron which reduces the excited state of molecule. Similarly, when comparing trend of the I_D/I_G, it indicates that the graphitization is enhanced within the films matrix and establishment of π-electronic system. The I_D/I_G ratio indicates that degree of graphitization is significantly enhanced in the case of films deposited with field. The density of the elevated structures at the surface of the films has been increased substantially by the application of magnetic field. Actually, there are some distribution of surface defect like; steps, dislocation line and grain boundary traces which provide sites for
nucleation, thus surface free energy of the atoms is reduced and flat conical shape islands are formed on the surface of the films.

The smoothness reduces due to the diffusion of energetic carbon ions and bigger metallic particles. Due to energetic species, compressive stresses are induced in the films. When the concentration of metallic specie is increased, these stresses are relaxed and thus more clustered objects are developed. The morphology of the films indicates that there are small cone like structures which have been developed on the surface of the films and their density and uniformity increases by Ag incorporation.
Chapter 4: Conclusion and Future work

Composite amorphous carbon films grown by pulsed laser ablation were investigated at varying Ni and Ag contents with and without the application of external magnetic field. The increasing metal concentration enhances the sp² bonding and eventually enhances the degree of graphitization. In a controlled manner, when Ni and Ag are added during the film growth process, the microstructures of the host film matrix undergo subsequent changes with the ordering of aromatic clusters and growth of carbon sp² hybridization for higher concentrations. The atomic mass of the doping element and the length of covalent bond cause the increase in sp² hybridized structures. The surface morphologies of the composite films have changed drastically by increasing metallic concentrations. The density of clusters on the surface has increased by the incorporation of increasing metallic concentration. There is also a change in smoothness due to metallic species. The Ni incorporated films are smoother than those of Ag incorporated graphite films.

The application of magnetic field also supports the graphitization and causes the growth of larger clusters at the same metallic concentrations. The nucleation of nano-clusters and the aromaticity of the carbon species depend on the energies of the ablated species. The process is primarily kinetic, therefore as long as more sp² bonds are formed along the plume direction more aromatic non-interacting carbon planes will be formed. Ni induced more graphitization under magnetic field as compared to Ag. Magnetic field enhanced the topographic features and induced more clustering in the films as compared to films prepared without field. The smoothness has also been influenced by magnetic field in the prepared composite films. In the case of Ni, the smoothness of the film has increased as compared to Ag. This increased surface smoothness is due to smaller clustered growth in the Ni incorporated thin films.

The application of magnetic field enables us to control the degree of graphitization at a constant desired concentration of Ag or Ni species. Thus, a particular smoothness can be attained at a particular metallic concentration by adjusting magnetic field. In conclusion, the observed changes in the structure of carbon’s network extend the physical properties of
the graphite films for specific applications like, cutting and abrasive wear tools, bio-resistant coatings, solid lubricant coatings, tunable optical windows and photovoltaics.

In future, this work is extendable in a way that the increasing concentration can be controlled to obtain a suitable optical band gap for materials, so that the material can be used in photovoltaic as optical windows. The electrical properties could also be a potential area of interest which could be controlled by doping as well as by the application of magnetic field.
References


   doi:10.1103/PhysRev.71.622


List of Publications


