Development of nanostructured carbon thin films

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Development of Nanostructured Carbon Thin Films

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Summary

In this thesis, experimental investigation of the growth mechanism of unique nanostructured carbon films and their properties as well as different fabrication techniques of these films is reported. Using experimental results, the presented mechanisms have been evaluated and developed. This work has enabled a larger range of deposition parameters to create user-specific nanostructured carbon films. The parameters examined include heat, depositing ion energy, plasma density and post treatments such as laser and thermal annealing. Electrical, thermal and field emission properties of nanostructured carbon films have also been studied.

First, the effects of deposition temperature and ion energy on the microstructure of the carbon films have been investigated. To do this, the microstructure of carbon films deposited at temperature range of 25 to 600⁰C and substrate bias range of 25 to 600 V have been studied by plan view and cross section transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS) and Raman spectroscopy. It is found that at low deposition temperatures (150⁰C) the microstructure of the film depends on the substrate bias. at low substrate biases (lower than 400V) the films are amorphous in the microstructure. Increasing the bias to 600V results in formation of preferred oriented nanocrystals in the microstructure. This is attributed to the formation of high temperature thermal spikes due to impinging of high energy ions to the growing film. Increasing the substrate temperature to 400 and 600⁰C leads to formation of preferred oriented nanocrystals even at floating substrate bias. The nature of the nanocrystals however

depends on the applying bias. Low substrate biases (lower than 600V) results in the formation of graphitic like nanocrystals while at 600V tubular nanostructures are formed. This is due to higher formation enthalpy of tubular carbon structures compare to graphene sheets.

In order to study the effect of plasma parameters, carbon films were prepared under two different plasma densities (2.5 and 12.5 mA/cm²) and different substrate biases (25 to 500 V). It is found that by applying high ion density plasma, nanocrystals are formed at room temperature even at low substrate biases (300 V). Meanwhile, decreasing the ion density increases the threshold ion energy for graphitization. More importantly it is experimentally shown that the nature of the nanocrystals strongly depends on the depositing ion energies. High ion energy (higher than 500 eV) results in formation of tubular nanostructures while lower ion energies (300 to 500 eV) results in formation of graphitic nanostructures. Stability of different nanostructures have been discussed in terms of the thermal spike temperature. The experimental results of the formation of different nanostructures have been proven by molecular dynamics simulations.

Separately, the properties of textured nanostructure carbon films were also studied. The first property investigated was the electrical conductivity of the films. It is found that formation of preferred oriented nanocrystals results in significant increase in the conductivity. The conduction in the amorphous films is limited through Poole-Frenkel mechanism. Electron will hop between the conductive sp² sites. Therefore, the conductivity of the amorphous films is controlled by the amount, size and distribution of sp² bonded nanocrystals embedded in the

amorphous sp^3 matrix. Formation of preferred oriented nanocrystals results in the formation of continuous sp^2 bonded channels which enhances the conductivity by three orders of magnitude.

In order to induce the nanostructures locally a local post deposition treatment is needed. Hence, the application of the laser annealing has been studied. To do this, a wide range of initial a-C structures (from ta-C to high sp^2 content a-C films) have been irradiated by a KrF Excimer laser with pulse width of 23 ns. The structural changes have been studied by Raman spectroscopy, TEM and EELS. It has been shown that the behavior of carbon films upon laser irradiation strongly depends on the initial bonding structure of the films. Using high sp^2 content a-C film as the initial structure, results in the formation of graphitic nanocrystals at moderate laser energies (higher than 360 mJ/cm^2). However, ta-C films are stable even at higher laser energies.

Field emission and thermal conductivity of textured carbon films have also been investigated. It is found that formation of conductive sp^2 channels throughout the thickness of the films which is achieved by the formation of texture in the microstructure, affects the emission threshold field significantly. This is mainly due to simultaneous activation of two field enhancement mechanism namely the presence of highly conductive phase (sp^2 bonded filaments) embedded in an insulative (amorphous sp^3) matrix and the formation of high aspect ratio graphitic filaments. As such, the threshold emission field on an a-C film decreased from 12 to $3.5 \text{ V/}\mu\text{m}$ by a single nsec laser irradiation at 462.5 mJ/cm^2 .

Summary

It is also shown that thermal conductivity of carbon films depend on the microstructure of the films. Pulsed photothermal reflectance (PPR) has been used to study the thermal conductivity of carbon films deposited at different temperatures (amorphous and nanocrystalline carbon films). It is found that formation of highly conductive graphitic nanostructures perpendicular to the substrate, increases the thermal conductivity. Compare to thermal conductivity of a-C films (~ 1 W/m.K) textured carbon films show an order of magnitude (upto 17 W/m.K) increase in thermal conductivity.

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Chapter 1: Literature Review, Motivations and Objectives

Sixth element of the periodic table, Carbon, is remarkable for its extraordinary ability to form different materials with wide range of properties. In the first glance and considering the electronic structure of $1s^2, 2s^2, 2p^2$ it seems that carbon should have a bivalence structure. However, this is only observed in a few structures namely the carbenes [1]. The energy difference between 2s and 2p levels of atomic carbon [2] is much lower than that released due to formation of chemical bonds. Therefore, the trivalence and tetravalence are usually observed in carbon compounds. The preferred trivalence and tetravalence structures can be achieved by hybridization of 2s and 2p orbitals and formation of 3 sp^2 or 4 sp^3 hybridized orbitals respectively (Figure 1-1). The sp hybridization can also be achieved through hybridizing of the 2s orbital with one 2p orbital. Therefore, depending on the degree of hybridization, a carbon atom may bond with one to four other atoms and hence show different structural properties. sp bonded carbon forms linear chains while sp^2 and sp^3 bonded atoms form planar and three dimensional tetrahedral networks respectively. One major difference between sp^3 with the other two hybridizations is that in sp and sp^2 bonded atoms, there are p orbitals which do not participate in hybridization. These orbitals can form additional π bonds which affects the properties dramatically.

Owing to different hybridization, carbon is able to form different allotropes with different properties. Graphite and diamond are the most well-known natural allotropes of carbon. Recently, the discovery and outstanding properties of carbon

nanostructures such as fullerenes [3], Carbon nanotubes [4-5], graphene [6-7], carbon onions [8-9] and carbon nanofibers [10] attract the researchers and industries to introduce a new era of carbon based devices. In the next section, different crystalline and amorphous forms of carbon will be introduced. Moreover, microstructural dependency of properties of carbonaceous materials is illustrated.

Figure 1-1: Carbon Hybridizations

1.1 Crystalline Carbon

1.1.1 Graphite

The microstructure of graphite was first investigated by Debye in 1917[11]. As shown in Figure 1-2, graphite is formed from planar sp^2 bonded carbon sheets known as graphene. Each carbon atom in the graphene plane has strong σ bonds with three other carbon atoms in the neighbor corners of a hexagon. The graphene sheets are connected in the z direction through weak van der waals π interactions of the non-hybridized electrons. The in plane bond spacing is 141.5 pm while the spacing between the graphene sheets is 335.4 pm. The delocalized π -cloud behaves as a two dimensional electron gas on the entire graphene sheet. Anisotropic

properties of graphite, such as high directional electrical conductivity is a result of the above mentioned delocalized π -cloud.

Figure 1-2: Crystal structure of graphite

It should also be noted that besides the hexagonal graphite (also known as α -graphite) which is thermodynamically the most stable form of carbon, rhombohedral graphite (known as β -graphite) is naturally available [12-13]. The stacking sequence of the graphitic planes in β -graphite is ABCABC while that of α -graphite is ABAB [14]. The β -graphite can be converted to α -graphite by heating above 1025⁰C [15-16] while the inverse reaction can be achieved by applying high pressures [17].

The layered structure of graphite, results in anisotropic physical (such as electrical and thermal conductivities) and mechanical properties. For instance, the modulus of elasticity is found to be 1060 and 36.5 GPa in the directions perpendicular and parallel to the c axis respectively [18]. Moreover, the electrical conductivity of graphite is due to the π electrons which specifically belong to certain sheets. Hence,

graphite has a very good conductivity ($\rho = 2.5\text{-}5 \times 10^{-6} \Omega\cdot\text{m}$) in the basal planes direction while possess a much lower conductivity ($\rho = 3 \times 10^{-3} \Omega\cdot\text{m}$) in the direction perpendicular to the basal planes [19].

1.1.2 Diamond

Having a formation enthalpy of 1.9 KJ mol^{-1} higher than graphite in standard conditions [20], diamond forms a metastable phase under normal conditions. Cubic diamond can be converted to hexagonal graphite upon heating to temperatures higher than 2700K under the pressure of 15 GPa [21]. Outstanding isotropic properties of diamond make it a considerable candidate for wide range of applications. Thermal conductivity of diamond ($\sim 700 \text{ W cm}^{-1} \text{ K}^{-1}$) is the highest conductivity among the materials known so far [22]. For the sake of comparison, it is worth mentioning that this conductivity is five times higher than that of copper which is being used commercially as heat conducting channels. Undoped, defectless diamond is an insulator with a wide band gap of 5.5 eV [23].

As shown in Figure 1-1, in crystalline diamond each carbon atom is placed at a center of a tetrahedron and has four immediate neighbors at the corners of the tetrahedron. Therefore, all carbon atoms are essentially sp^3 hybridized with bond length of 154.45 pm. It should also be noted that hexagonal structure of diamond (known as Lonsdaleite) also exists [24] but since cubic diamond is the dominant natural form of diamond, Lonsdaleite will not be discussed here. The crystal lattice of cubic diamond can be understood as two face-centered cubic lattices shifted against each other along the space diagonal of the unit cell. This structure is

commonly known as diamond cubic and many other elements and compounds (such as ZnS) possess diamond cubic structure.

Figure 1-3: unit cell of cubic diamond

1.2 Carbon Nanostructures

Besides graphite and diamond several carbon nanostructures with outstanding properties have been observed and fabricated. The first discovery goes back to 1985 when Kroto [25] found the C_{60} molecule. Thereafter, many theoretical and experimental efforts focused on synthesis and properties of these carbon cages. The second breakthrough on carbon nanostructures was made by Iijima in 1991 [5] by observing the tubular nanostructure of carbon named as multi-wall carbon nanotube (MWCNTs). Two years later, Iijima and Ichihashi [26] and at the same time Bethune et al. [27] discovered the single walled carbon nanotubes (SWCNTs). However, maybe the biggest breakthrough in physical sciences in the past few decades was done by Novoselov and Geim in 2004 [6] by fabrication of single atomic layer graphite known as graphene. Huge amount of works have thereafter

been focused on synthesis methods as well as properties of graphene and graphene based nanostructures. Shiny horizons of graphene based structures especially in the microelectronics, dedicates the 2010 physics noble prize to Geim and Novoselov.

Among different carbon nanostructures, carbon nanotubes and graphene will be discussed in the following sections.

1.2.1 Carbon Nanotubes

MWNT were first discovered in the soot of the arc discharge process used for the synthesize of fullerene [5]. SWNTs were discovered two years later through application of a metal catalyst in arc discharge process [26]. Chemical vapor deposition of catalytic grown nanotubes was first introduced by Yacaman in 1993 [28]. An outstanding breakthrough was done by Smalley et al. in 1996 through applying laser ablation to produce bundles of aligned SWNTs with small diameter distribution [29].

Along with efforts in the fabrication methods of CNTs, interesting works have also been done on studying mechanical and physical properties of this new class of nano carbon. Stiff in-plane C-C bonds leads to extraordinary high young's modulus and tensile strength [30-31]. As such, carbon nanotubes (CNTs) are among the most suitable filler candidates to fabricate light composites with superior mechanical properties [32]. Due to their large aspect ratio which results in very high field enhancement, carbon nanotubes are ideal structure for electron field

emission devices [33]. Electron field emission at electric fields of less than 1 V/ μm has been demonstrated. Multiwall nanotubes have been used to electro-catalyze an oxygen reduction reaction, which is important for fuel cells [34]. Outstanding ability of SWNTs in reversible adsorption of hydrogen makes them a choice of ideal for hydrogen storage applications [35].

Despite interesting properties, there are still many practical challenges in the production of high quality CNTs compatible with many industries. In the following section the fabrication methods and the formation mechanism of CNTs will be introduced.

1.2.1.1 Fabrication of Carbon nanotubes

Different methods have been investigated to fabricate SWNT and MWNTs [36]; However from structural point of view, all the methods proposed so far are suffering from a common point: the available techniques always yield a mixture of CNTs with significantly wide range of length and diameter which results in non-uniform properties. Therefore, understanding the growth mechanism and purification methods have also become an interesting and hot field of study. Most of the methods used so far, are common in the point that they are using a vapor phase precursor to fabricate the CNTs. In this section, the most common fabrication methods of CNTs will be introduced.

1.2.1.1.1 Arc Discharge Method

Arc discharge was the first method used to fabricate CNTs [5]. The basics of the method are similar to that used by Kratschmer et al. [37] for the fabrication of

fullerenes. Basically, to grow CNTs rather than fullerenes, the process should be prolonged to prevent the closure of the fullerenes cage. To achieve this, two important parameters need to be selected carefully. These two factors are the pressure of the inert gas (usually Helium) and second, the distance between the electrodes. To obtain SWNT, the carbon source (the anode) will be mixed by a transition metal catalyst. Metals such as iron [38], cobalt [27], platinum and mixture of transition and noble metals [39-40] have been successfully used to fabricate SWNT. After the arc process, a soot-like deposit will be formed on the cathode which contains a hard gray shell and a black core. The black core contains graphite, graphitic nanoparticles, amorphous carbon (a-C), MWNTs and SWNTs. However, SWNT consist a very small fraction of the above mentioned deposit.

SWNTs formed by the arc discharge method have a diameter of 1.2 to 1.5 nm. Diameter of the tubes can be controlled by the temperature of the reaction[41]. Increasing the reaction temperature increases the tube diameter. The length of the tubes on the other hand depends on the catalyst.

The MWNTs formed by arc discharge methods are usually 2-30 nm in diameter and about 1 μm in length. Due to large Van der Waals interaction between individual MWNT, they usually form bundles.

1.2.1.1.1.1 Arc Discharge Growth Mechanism of MWNTs:

One of the areas with attracts experimental and theoretical attentions soon after the discovery of the CNTs was the growth mechanisms. Based on the experimental and theoretical results, different growth mechanisms have been proposed. Here, we will

briefly introduce the vapor phase, liquid phase and solid phase mechanisms which are more widely accepted in the community.

The earliest theories for the formation of nanotubes was based on direct condensation of nanotubes from the gas or plasma phase. It was also believed that the electric field which is produced by the arc plays a critical role on one dimensionality of the nanotubes [42].

The other theory which was first proposed by De Heer et al. [43] is based on a liquid phase growth. Considering the beads decorating the nanotubes, they proposed that nanotubes are formed from the liquid globules ejected from the anode due to its local heating made by the cathode electron bombardment. High vapor pressure of liquid carbon results in the formation of a supercooled region at the surface of the globule. De Heer believes that the nanotubes are nucleated and grown in this supercooled region.

The other theory which was first proposed by Harris et al. [44] is based on the solid phase growth. They found that heating of fullerene soot to 3000⁰C (which is below its melting temperature) transforms them to carbon nanohorns and tubular-like structures. Based on this observation, they suggest that the nanotube formation is a solid phase transformation with fullerene soot as an intermediate phase. Since nanotubes are formed at a temperature below the melting temperature of the fullerene soot, the presence of a solid phase transformation is acceptable. However, their suggestion that fullerene soot is always an intermediate phase can be a point of question. This becomes more significant by considering the later works of other

groups who successfully demonstrate the production of the nanotubes from other carbon based materials. For instance, Chadderton and Chen [45] reported the fabrication of nanotubes by heating of the mechanically milled graphite powder at 1400⁰C. Regardless of whether a fullerene based structure can be an intermediate phase or not, the point that nanotubes can be synthesized by a pure solid phase transformation is a noticeable fact.

1.2.1.1.2 Laser Ablation

Laser ablation is another physical method which has been used to fabricate both SWNTs and MWNTs. The process and the mechanisms involved are very similar to that of arc discharge method. The only noticeable difference is that in this method the arc is replaced by a high energy laser to evaporate the graphitic target. The method was first introduced by Smalley et al [29]. Similar to arc discharge method catalyst is essential for the growth of SWNTs. The most common catalyst being used is nickel, cobalt or a mixture of these two transition metals [46]. However, other transition metals such as platinum and copper has also been used in this process [47]. The formation of SWNTs strongly depends on the temperature. The reactor temperature will usually be set to about 1200-1600⁰C and at temperatures lower than 850⁰C the yield of the process drops dramatically [48].

1.2.1.1.3 Chemical Vapor Deposition (CVD)

Similar CVD approach which was used from 1960s to fabricate carbon filaments and fibers (eg. see [49-50]) was used for the first time by Yacaman et al. [28] to fabricate CNTs. In general, this method is based on decomposition of a hydrocarbon with assistance of a catalyst. The catalyst which is deposited by PVD

or a chemical driven technique, will be subjected to a carrier gas containing the hydrocarbon. A mixture of substrate heating ($550-750^{\circ}\text{C}$) and another external source of energy (such as plasma) will then be used to decompose the hydrocarbon into atomic carbon and a gaseous by-product. The atomic carbon which is absorbed on the surface or the bulk of the metallic catalyst will then be desorbed in the form of nanotubes during the cooling process. It is believed that depending on the adhesion of the catalyst nanoparticles to the substrate two types of growth namely the top and base growth will be achieved. In the case of high adhesion between the catalyst and the substrate, base growth will be dominant while the top growth will be activated if the adhesion is poor [49, 51].

Perhaps the biggest breakthrough in the field of CNT fabrication was achieved when Li et al. used CVD to fabricate aligned carbon nanotube films [52]. This breakthrough, opens a field of study for potential application of CNTs for different microelectronics applications [53].

1.2.2 Graphene

For many years, graphite was described as stacking of sp^2 bonded carbon sheets but these sheets themselves doesn't attract the attention of experimentalists till the work of Novoselov and Geim in 2004 [6] which can be considered as a valuable revolution in nanoscience and nanotechnology. Duo to outstanding electrical properties of graphene [54], physicists were the first community that intensively grab this new class of nanocarbon and introduced many potential applications for 2-D graphene. Thereafter, materials scientists and technologists look into different

means for incorporation of graphene into real practical devices and structures. Eventually, the need of mass production of graphene and controlled growth of graphene nanostructures on substrates opens a hot field for chemists.

To my knowledge, the first effort to thin the graphite down to atomic layer was done in 1960 when Fernandez-Moran was trying to thin a single crystal graphite down to atomic layer to fabricate an electron transparent membrane for transmission electron studies [55]. He was successful in thinning the graphite down to 5 nm by simple cleavage process. In 1962, Boehm for the first time observed the monolayer and bilayer graphite oxide using transmission electron microscope (TEM). Although fabrication of single atomic layer structures of layered materials remains as a point of interest, most of the experimental works turns towards other materials such as tungsten sulfide [56].

After discovery and outstanding properties of other carbon nanostructures (such as fullerenes and CNTs) in 1990s, efforts have again focused on different methods to fabricate a single atomic layer carbon. Ebbesen [57] was probably the first one who used AFM manipulation to mechanically thin down HOPG and successfully fabricate a monolayer graphene. However, this single layer was not transferrable to any other substrate. In 1994, Lu et al. fabricated 10 nm thick graphite by rubbing microfabricated graphite pillars onto another substrate. The same group has then proposed that the same technique can be used to fabricate single layer structure as well [58]; However, despite the efforts that tried to modify the process (e.g. see [59]), this technique has not been able to produce a single atomic carbon layer so far. In 2004, Geim et al. have successfully fabricated a single layer graphene

through continuous cleaving of graphite by a simple adhesive tape. Soon after that and in just a few months, huge amount of successful efforts focused on digging the properties of this new class of carbon nanostructure as well as other possible fabrication methods. In the following section two methods which are currently being used to fabricate single- and few-layer graphene will be discussed.

1.2.2.1 Fabrication Methods

1.2.2.1.1 Mechanical Exfoliation

This method which was the first method used by Geim et al. is still one of the most common and reliable methods to fabricate (sub)square millimeter size single layer graphene. Weak van der Waals interaction (with energy of 2 eV/nm^2 [60]) results in very easy exfoliation of bulk graphite by simple methods such as using normal adhesive tapes. Therefore, by successive exfoliation of single crystal graphite, single and multi layer graphene can be transferred to any substrate.

One major drawback of this technique is the residue of the tape which limits the carrier mobility of the nanostructures [61-62]. To overcome this problem, post annealing by joule heating [63] or oven heating under hydrogen/argon environment have been proposed [64].

Since the graphene is formed from a high quality single crystal graphite, mechanical exfoliation is still the best known method to fabricate graphene nanostructures with good electrical properties and structural quality. However, it is a big challenge to hire this method for large area fabrication of graphene. Moreover,

fabrication of graphene nanostructures on desired position is another practical point of challenge.

1.2.2.1.2 Epitaxial and Catalytic Growth

Decomposition of a metal carbide and CVD growth of epitaxial graphene through decomposition of a hydrocarbon are other methods which are widely investigated to fabricate graphene with different structures and hence properties. Silicon carbide (SiC) was the first material studied for this technique. At about 1300⁰C, SiC decomposes to silicon and carbon and the resultant carbon can be recrystallized to a graphene sheet during the graphitization at higher temperatures. Berger et al. demonstrated [65-66] wafer size production of thin few layer graphene through accurate controlling of SiC sublimation process. An important breakthrough was achieved by Emtsev et al. [67] through sublimation of Si terminated (0001) SiC under 1 bar argon atmosphere and 1650⁰C. Using these conditions, large area monolayer graphene with electrical properties comparable to that of mechanical exfoliated graphene was achieved. Besides SiC other carbides such as TiC [68] and TaC [69] have also been used for this process.

Similar to nanotubes growth, CVD decomposition of hydrocarbons to graphene on metal catalyst substrate has been extensively studied. The first successful attempt was through application of (111) platinum as the catalyst [70] which leads to formation of nanometer-sized graphene layers at 800K.

1.3 Amorphous Carbon

Besides crystalline forms of carbon, amorphous carbon (a-C) also attracts attentions due to its wide range of properties as well as easy fabrication methods [71].

a-C is formed from a mixture of disordered sp^2 and sp^3 bonded atoms. At one extreme, tetrahedral amorphous carbon (ta-C) consists of very high sp^3 content (upto $\sim 85\%$) [72]. ta-C has physical (such as transparency[73], high electrical band gap [74] and chemical inertness [75]) and mechanical (such as hardness [76]) properties comparable to that of diamond. Different methods such as ion beam deposition [77], mass selected ion beam deposition [78], sputtering [79-80], laser ablation [81] PECVD [82] and filtered cathodic vacuum arc (FCVA) [83] have been used to fabricate amorphous carbon films. The ability to control the ion energy during the deposition and hence the film properties makes FCVA a very common and useful method to fabricate different types of a-C films. Since FCVA has been used in this work as well, this technique is introduced in detail in the next chapter (Section 2.1).

Despite interesting properties of ta-C films, stabilization of metastable sp^3 hybridization is still a big while interesting point of debate in the community. In the following section the two mechanisms proposed by McKenzie [84] and Lifshitz [85] will be introduced.

1.3.1 Stress induced stabilization of sp^3 hybridization in a-C films

Figure 1-4 shows the Berman-Simon equilibrium phase diagram of carbon [86].

As it is shown, diamond is stable at high temperatures and pressures.

Figure 1-4: Equilibrium phase diagram of Carbon

McKenzie [87] proposed that the intrinsic biaxial compressive stress of the carbon films plays the same role as the pressure in diamond/graphite phase diagram and results in the stability of sp^3 hybridization in carbon films. as shown in Figure 1-5, he found that there is a direct relation between the intrinsic stress and the stability of sp^3 hybridization.

Figure 1-5: Plasmon density and film stress as a function of deposition beam energy [87]

According to McKenzie's theory, depending on deposition ion energy, four phenomena may occur. At very low ion energies (less than 25 eV) the impinging ion does not have enough energy to affect the underlying layers. At higher energies, (25-80 eV) the ions compress the underlying atoms and increase the film stress. In the energy range of 80-100 eV the incident atoms penetrate more deeply and induce knock-on collisions which displace the underlying atoms even deeper in the film. This results in local increase in film density and therefore sp^3 becomes the dominant stable hybridization. At higher energies however, the same process takes place but the excess amount of energy of the ions results in formation of high temperature thermal spikes which leads to local relaxation of the structure and stabilizes the sp^2 hybridization.

Although this theory satisfies some of the experimental data's, some other works put a noticeable question mark on this theory. For instance by studying the stress

and structural evolution of carbon films upon post thermal annealing, Ferrari et al[88] found that the sp^3 content of the film does not change significantly upon annealing at 1100°C while the stress is almost fully recovered at 600°C (Figure 1-6). This finding is in direct contradiction with McKenzie's theory who correlated the stability of sp^3 hybridization with the compressive stress of the film.

Figure 1-6: (A) change in sp^3 content and (B) stress reduction of a-C films by post thermal annealing [88]

The other theory which is more widely accepted in the community is the subplantation model. In the next section we will briefly introduce this model which was first introduced by Lifshitz et al.

1.3.2 Subplantation model for sp^3 stabilization

Lifshitz et al. [85], believe that subplantation of impinging ions is the crucial factor for stabilization of sp^3 hybridization. Based on this model, the impinging ion penetrates the target substrate provided that sufficient amount of energy is supplied. The penetration profile depends on the mass and the energy of the impinging ions

as well as the substrate properties. Next step is the stoppage of the impinging ions due to three main energy loss mechanisms. These mechanisms are atomic displacement, phonon excitation and electron excitation. Depending on the substrate which acts as a mold, the impinging ion will occupy a distinct site. However, due to further collisions or concentration gradient induced diffusion, the ion may change its site during the deposition of other ions. Since the deposition is accompanied by subplantation, during the early stages of the growth, the surface is just composed of the substrate atoms. However, the surface is gradually evolved by mixing of substrate and impinging ions and eventually a uniform phase consisting of depositing ions is formed.

Using depth profile Auger spectroscopy, Lifshitz et al. proves the presence of subplantation in PVD growth of carbon films. Supported by Moller modeling work [89], they have then claimed that sp^2 and sp^3 sites would be displaced into interstitial sites and then return back to sp^2 or sp^3 sites. sp^3 percentage will increase if there is a preferential displacement of sp^2 sites. Lifshitz used the displacement threshold of 25 and 80 eV for sp^2 and sp^3 bonded carbon proposed by Kelly [90] and Clark [91] respectively. However, more recent direct measurements of displacement thresholds show similar values for displacement of sp^2 and sp^3 bonded atoms (~ 35 eV) [92-94]. Robertson has then proposed that subplantation results in local increase in density which in turn results in stabilization of sp^3 bonding [95-96].

Based on this model, a low energy carbon ion cannot penetrate the substrate or the growing film and will stick to the surface at its lowest possible energy

configuration which is in sp^2 sites; however, if the ion energy is higher than the required penetration energy, the ion penetrates into the subsurface and increases the density locally. Density increase, stabilizes the sp^3 hybridization. If the ion energy is further increased, the ion penetrates deeper into the surface. However, the excess energy is transferred to the neighboring atoms as thermal energy and results in relaxation of sp^3 sites to lower energy sp^2 hybridization through formation of high temperature thermal spikes.

In summary, according to subplantation theory low energy ions lead to formation of high sp^2 content a-C films. Increase in ion energy (~ 100 eV), results in stabilization of sp^3 hybridization through local increase in density. Further increase in ion energy on the other hand, relaxes the sp^3 sites and hence increases the sp^2 content of the a-C film.

Although subplantation theory is widely accepted by the community, some experimental observations are yet to be explained by this mechanism. For instance, it is experimentally observed that the dependence of sp^3 hybridization on ion energy is different for ion beam deposited and cathodic arc deposited carbon films [87, 97-98].

1.4 Formation of nanocrystals with preferred orientation in graphitization of a-C films

The internal energy of any thin film (U) is the summation of the interfacial energy of the substrate and film (σ_{sf}), bulk energy of the film (ΔG_v) and surface energy of the film (σ_f):

$$U = \sigma_{sf} + \Delta G_v + \sigma_f$$

Although the deposition is a non-equilibrium process, but considering the film stress as the constant pressure (P) and the substrate or local thermal spike temperature as the temperature (T) of the system, equilibrium thermodynamics can be used to predict the structure to which the system tends to transform. F. Nye shows that for a system under a specific stress field, the Gibbs free energy of the system is defined as [99]:

$$G = U - \sum_{ij} \epsilon_{ij} \sigma_{ij} - TS$$

For systems having more than one structural phase, different stress fields may result in stabilization of different phases. McKenzie and Bilek proposed that assuming the Gibbs free energy of one of the phases at the standard temperature and acquired stress condition to be zero (as the reference state), the Gibbs free energy of the n^{th} phase can be given by [100]:

$$G = G_0 - \sigma \sum_{ij} \epsilon_{ij}^{(n)} \hat{\sigma}_{ij} - \frac{1}{2} \sigma^2 \left(\sum_{ijkl} S_{ijkl} \hat{\sigma}_{ij} \hat{\sigma}_{kl} \right)$$

where G_0 is the Gibbs free energy of the phase at standard conditions, $\epsilon_{ij}^{(n)}$ is the transformation strain tensor when the reference phase is transformed to the n^{th} phase, σ is the magnitude of the stress, $\hat{\sigma}_{ij}$ is the tensor describing the stress field and S_{ijkl} are the elastic compliances. Using matrix notation for the last term, Eq. 1.3 can be written as:

$$G = G_0 - \sigma \sum_{ij} \epsilon_{ij}^{(n)} \hat{\sigma}_{ij} - \frac{1}{2} \sigma^2 [\hat{\sigma} S \hat{\sigma}^T]$$

where S and $\hat{\sigma}$ are the compliance matrix and the stress vector respectively.

In summary, in the presence of a stress field, the most stable microstructure (lowest Gibbs free energy) is determined by simultaneous consideration of formation energy of each phase (second term in Eq. 1.4) as well as the orientation which results in the lowest possible free energy (third term in Eq. 1.4). Clearly, in transformations where there is no phase competition, such as graphitization of amorphous carbon, the second term of Eq. 1.4 vanishes and the Gibbs free energy only depends on the orientation of the crystal with respect to the stress field. In a-C, the stress field is a biaxial compressive stress in the growth plane (x-y plane). Biaxial stress field ($\hat{\sigma}_b$) can be expressed as a combination of a hydrostatic pressure ($\hat{\sigma}_h$) and a uniaxial tensile stress ($\hat{\sigma}_z$) rotated to the crystallographic axis of graphite:

$$\hat{\sigma}_b = \hat{\sigma}_h - \hat{\sigma}_z$$

Therefore, the Gibbs free energy can be expressed as:

$$G = G_0 - \frac{1}{2} \sigma^2 [\hat{\sigma}_h S \hat{\sigma}_h^T + \hat{\sigma}_z S \hat{\sigma}_z^T - \hat{\sigma}_h S \hat{\sigma}_z^T - \hat{\sigma}_z S \hat{\sigma}_h^T]$$

Nye shows that in the case of a hexagonal structure, Eq. 1.6 reduces to:

$$G = G_0 - \frac{1}{2} \sigma^2 [2(s_{11} + s_{12} - s_{33} - s_{13})\sigma_3 + (1 - \sigma_3)^2 s_{11} + \sigma_3^2 s_{33} + \sigma_3(1 - \sigma_3)(2s_{13} + s_{44})]$$

where σ_3 is the third component of the rotated stress. It should be noted that in Eq. 1.7 G only depends on the angle between the crystallographic c axis of graphite and the rotation angle of the stress field (φ). The values of elastic compliances for a perfect single crystal graphite are tabulated in Table 1-1.

Table 1-1: Values for the elastic compliance tensor of a perfect single crystal graphite [90]

Compliance	Graphite Value (GPa)⁻¹
S₁₁	0.98×10⁻³
S₁₂	-0.16×10⁻³
S₁₃	-0.33×10⁻³
S₃₃	27.5×10⁻³
S₄₄	240×10⁻³

Anisotropic nature of graphite arises from large values of S_{33} and S_{44} . S_{33} is responsible for the Young's modulus while S_{44} is responsible for the shear modulus anisotropy. McKenzie and Bilek [101] solved Eq. 1.7 as a function of φ and found that for a *perfect* single crystal graphite the G minimizes when the angle between the stress plane and the c axis is equal to 41°. However, S_{44} strongly depends on

structural defects such as curvature of sp^2 bonded layers. An order of magnitude reduction in S_{44} can easily be achieved through changing the curvature of sp^2 basal planes [102]. Considering different values for S_{44} McKenzie has solved Eq. 1.7 as a function of ϕ and found that there are four distinct answers for the first derivative of G as a function of ϕ (shown in Figure 1-7 inset). Figure 1-7 shows the second derivative of G as a function of S_{44} for three distinct roots of the first derivative. As shown in Figure 1-7 in the fourth region, the only possible answer which results in positive second derivative and hence minimization of G is $\cos^2\theta = \frac{2S_{12}-2S_{33}+S_{44}}{4S_{13}+2S_{44}-2S_{33}-2S_{11}}$. At high values of S_{44} , ϕ approaches to 45° . However, as it decreases ϕ moves toward zero and when $S_{44} = 2S_{33} - 2S_{12}$ c axis lies on the stress plane. This is in agreement with McKenzie results where he found that in-plane c axis texture can be achieved by ion irradiation of glassy carbon [103].

In regions 2 and 3, the answer which gives the minimum Gibbs free energy is the in-plane c axis texture. In region 1 ($S_{44} \leq 2S_{12} + 2S_{11} - 4S_{13}$), the orientation which c axis is perpendicular to stress axis becomes the local minimum while the in-plane c axis orientation is still the global minimum.

Figure 1-7: Variation of the second derivative of G as a function of S_{44} for roots of first derivative of G (shown in the inlet) [100]

Experimental and molecular dynamics simulations results of McCulloch et al. [104] on high energy ion irradiation of glassy carbon, confirms the stress induced formation of preferred orientation proposed by McKenzie. More recently McCulloch et al. reported on formation of preferred orientation in low density (high sp^2) layers of high density/low density carbon multilayers upon annealing at 600°C [105]. It is believed that the presence of high stress due to high sp^3 layers results in formation of such a structure provided that the required activation energy is supplied.

1.5 Motivations and Objectives

Outstanding improvements of the microelectronics industry in the past few decades have been largely achieved through decreasing the size and increasing the density

of devices on a chip. However, the International Technology Roadmap for Semiconductors (ITRS) projects the end of CMOS shrinkage by around 2024 [106]. Extraordinary properties of carbon nanotubes and graphene such as ballistic transport [107], large current carrying capacities (in the order of 10^9 A/cm²) [108], high thermal conductivity [109] and the ability to be metallic or semiconducting makes these two new class of carbon nanostructures as the first choice of candidate for the post-silicon world. Based on the properties, different applications of these nanostructures for wide range of electronic devices such as interconnects [53], field emission [110] and memory devices [111] has been demonstrated.

Despite many interesting properties of CNTs and graphene they are still suffering from a few basic practical problems. For instance, as it was also discussed in 1.2.1.1, fabrication of high quality CNTs needs high temperature processes which limits its applications for many industries. Besides, although individual CNTs have high current carrying capacity, but in order to achieve a high current capacity, very high density nanotubes need to be grown. Moreover, for every individual application, nanostructures need to be grown on the specific site with specific properties. For instance, to use CNTs as interconnect in via holes, dense metallic nanotubes are needed while semiconducting nanotubes are needed for FETs. However, selective growth of nanotubes and graphene on the exact point of interest is still a big point of challenge.

The points mentioned above and many other practical problems attracted many attentions worldwide and huge effort has been focused to overcome the barriers. However, despite CNTs and graphene, nanostructured carbon thin films attract less

attention. Although the formation mechanism has been studied in detail, the dynamics of the transformation and the properties of these nanostructured thin films have not been investigated in detail. More importantly, the nature of the nanocrystals has not been studied in detail yet. McKenzie pointed out that the presence of biaxial compressive stress results in formation of carbon nanostructures with preferred orientation but the real nature of these nanostructures is still unclear. For instance, are they formed from tubular nanostructures (like CNTs) or preferred oriented graphene nanostructures or any other nanostructure? Besides, the properties of these nanostructured carbon thin films have not been investigated. It should be reminded that anisotropic nature of hexagonal graphite results in very different physical and mechanical properties in the basal planes and the direction perpendicular to the basal planes. Hence, controlling the texture of the carbon films during the deposition or by any post treatment process can lead to a thin film with directional mechanical and physical properties. Therefore, the main objectives of this work will be on the following three main points:

1. Studying the dynamics of the amorphous carbon to nanocrystalline carbon transformation. By careful consideration of the transformation dynamics we will try to develop different in-situ and post treatment processes for the fabrication of textured carbon thin films.
2. The nature of the nanocrystals achieved by different process will be studied in detail.

3. The effect of preferred oriented nanocrystals on thermal and field emission properties of nanostructured carbon thin films will be studied.

1.6 Major Contributions of the Thesis

- The effect of deposition parameters on formation and nature of nanocrystals in FCVA grown carbon films is studied in detail. It is found that by controlling the deposition parameters different nanocrystals (tubular nanostructures and graphene based nanostructures) can be achieved.
- By understanding the effect of ion energy and density during the deposition, nanostructured carbon films are fabricated at room temperature only through controlling the plasma density and deposition ion energies. This finding is of considerable practical importance should these structures be used for different applications.
- Microstructural changes of carbon films upon laser irradiation have also been studied. Despite the above mentioned methods, laser irradiation can be used to control the microstructure of the films locally.
- Thermal properties of nanostructures and amorphous carbon films have been studied. It is shown that formation of nanocrystals with preferred orientation results in considerable increase in thermal conductivity of carbon films. This is thought to be due to formation of highly conductive graphene sheet in the direction perpendicular to the substrate.

- Electron field emission properties of nanostructured and amorphous carbon films have been studied. It is shown that formation of preferred oriented sp^2 bonded nanocrystals results in considerable increase in local field enhancement and hence decreases the emission threshold field.
- Thickness dependency of field emission in amorphous, nanostructured and carbon films with preferred oriented nanocrystals have been studied. It is shown that in amorphous and nanostructured carbon thin films the emission doesn't depend on the film thickness. However, in carbon films with preferred oriented nanocrystals, the emission strongly depends on the film thickness.

1.7 Organization of the Thesis

Different carbon allotropes and nanostructures, amorphous and nanostructured carbon films are reviewed in chapter one. In the second chapter, the deposition and characterization techniques which have been used in this work are explained. In chapter three the microstructure of in-situ annealed carbon films is studied. The nature of the nanocrystals and the Si/C interface of high temperature deposited carbon films is also studied in this chapter. The structural evolution of the post thermal annealed films is also studied in chapter 3. In chapter four, the effect of deposition plasma density and ion energy on the formation and the nature of nanocrystals have been studied. In the fifth chapter the thermal and electrical conductivity of nanocrystalline carbon films is studied. In the sixth chapter, the effect of laser irradiation on the microstructural changes of carbon films has been

studied while in the seventh chapter, field emission from laser irradiated carbon films is studied. Besides, thickness dependency of field emission of different types of carbon films has been studied in this chapter. Finally chapter eight gives the conclusions and recommendations for future research.

Chapter 2: Experimental Methods

2.1 Filtered Cathodic Vacuum Arc

From one point of view, all plasma deposition techniques can be categorized into two distinct classes namely the chemical vapor deposition (CVD), and physical vapor deposition (PVD) methods. The only difference between the PVD and CVD methods is the first step which is the production of deposition species. In the PVD methods, these species are formed by physical processes such as evaporation and sputtering while in the CVD methods these species are formed through chemical means.

Arc discharge, is a low voltage, high current plasma discharge which takes place between two conductive electrodes. Thomas Edison for the first time used arc process to produce plasma from solid targets for thin film deposition [112]. The cathode spot size is 1-10 μm which carries a high current density in the range of $10^6 - 10^8 \text{ A/cm}^2$. Despite interesting characteristics of this method such as high deposition rate and versatility to deposit different kinds of materials, the presence of macroparticles is the most important practical problem which limits the application of this method for production of high quality films for microelectronic industries [113]. In order to overcome this practical barrier, different kinds of electromagnetic filters were used to eliminate the macroparticles [114]. As it is shown in Figure 2-1, charged ions can pass through the electromagnetic field while the macroparticles are filtered by the filter walls [71].

Figure 2-1. Schematic of filtered cathodic vacuum arc technique [115]

An outstanding advantage of filtered cathodic vacuum arc (FCVA) compared to other PVD methods is that the acquired arc produces highly ionized plasma and hence by applying and controlling the substrate bias, the impinging energy of the constituent ions can be controlled. Despite interesting properties of FCVA, the plasma instabilities and low deposition efficiency are the limiting drawbacks. Movement of the arc discharge towards the edge of the cathode is the main reason for the “Direct Current” (DC) FCVA plasma instabilities (especially for metallic targets) [116-117]. Pulsed FCVA which acquires high frequency ignition rates has been developed to overcome this barrier. However, the pulsed FCVA itself suffers from very low deposition rates and complexity of the arc system.

2.2 Transmission Electron Microscopy (TEM)

The investigation of the morphology, structure, and local chemistry of metals, ceramics, and minerals is an important aspect of materials science. Transmission

Electron Microscope is an analytical tool that allows detailed micro-structural examination through high-resolution and high-magnification imaging. It also enables the investigation of crystal structures, orientations and chemical composition of phases, precipitates and contaminants through the diffraction patterns, X-ray, and electron energy loss analysis.

Using TEM, Magnifications of up to 1,000,000x and detail resolution of below 1 nm can be achieved routinely. Quantitative and qualitative elemental analysis can be provided from features smaller than 1 nm. Using TEM it is also possible to study structural defects, including stacking faults, interstitials, precipitates and vacancies.

The idea of TEM was first proposed by Knoll & Ruska in 1932 [118]. In 1939, the first commercial electron microscope (Metropolitan Vickers EM1) was produced; However, for materials scientist the most important breakthrough takes place when Heidenreich thinned the metal foils down to electron transparency[119].

Figure 2-2 shows the schematics of a TEM. TEM images are formed in two stages. At the first stage, the objective lens focuses the scattered electrons which have passed the specimen and form a primary image. In this process, the objective lens produces the diffraction pattern at its back focal plane. The diffraction pattern is the Fourier transform of the scattered electron wave. The primary image on the other hand, is the Fourier transform of the diffraction pattern. In the second stage, the primary image is magnified by subsequent lenses to form a high magnification image.

Figure 2-2: Schematics of different parts of TEM [120]

Diffraction pattern is usually produced using a parallel electron beam. These patterns are called “Selected Area Electron Diffraction (SAED)” patterns. In this

case, the area under study will be chosen by a “selected area” aperture in the image plane of the objective lens. The size of the aperture (a few microns) is sometimes bigger than the area which needs to be studied. In this case, “Convergent Beam Electron Diffraction” (CBED) technique can be used to acquire the pattern from the small area of interest. The focused electron beam is generated by converging the beam by suitable adjustments of the condenser-lens aperture. Figure 2-3 shows the SAED and CBED pattern of a single crystal silicon.

Figure 2-3: (a) SAED and (b) CBED patterns of single crystal silicon on [111] zone axis [120]

Being created from the diffraction of electrons from individual crystals, SAED can be used for unknown phase identification and determination of the crystal structure and orientation. The center spot corresponds to the transmitted electron beam while the other spots are diffracted portions of the initial electron beam. As it is also the case in other diffraction techniques (such as X-ray or neutron diffraction), the location of the spots are governed by the Bragg's law. In the SAED technique, an

aperture is placed in the first image plane below the objective lens. This is to select an area on interest in the TEM image.

In a single crystal, the electrons diffracted from one plane intersect on one single spot of the Ewald sphere. This leads to a diffraction pattern made of individual spots (as shown in Figure 2-3-a). On the other hand, in a polycrystalline material, since the grains are oriented in different directions, the same planes of different grains will diffract the beam in different directions. However, since the interplanar spacing of the planes is the same in all grains, the distance between the diffraction spot and the central beam (transmitted beam) will be identical. Therefore in the case of ideal polycrystalline material, each plane is represented by a full ring around the central transmitted beam (Figure 2-4-a). Depending on the grain size of the polycrystalline material the rings are made up of discrete spots. Finer grain sizes produce a more continuous ring pattern but the widths of the rings become broader. If the polycrystalline specimen is textured, then there is usually one special plane with the same orientation in all of the grains. Therefore as it is also shown in Figure 2-4-b, the rings change to separate arcs.

Figure 2-4: diffraction pattern of (a) polycrystalline and (b) textured materials [120]

Figure 2-5 shows the geometry of an electron diffraction experiment. For small angle scattering, the Bragg law can be approximated as:

$$\lambda = 2d\theta \quad 2.1$$

Considering Figure 2-5, it can be deduced that:

$$\frac{R}{L} = 2\theta = \frac{\lambda}{d} \Rightarrow R = \frac{\lambda L}{d} \quad 2.2$$

Therefore, the distance between the diffraction spot and the central transmitted beam varies inversely with interplanar spacing. The constant λL is called the “camera constant”

Figure 2-5: Schematics of the electron diffraction experiment [120]

So far, the formation and interpretation of diffraction patterns have been explained. However, as any kind of ray passes through an object in a plane, it would produce an image of certain contrast in any other plane. The image contrast in TEM is due to the scattering of the incident beam by the specimen. As the beam passes the specimen, both the amplitude and the phase of the electron wave may change. Any of the above mentioned changes can give rise to the image contrast.

In general, although both the amplitude and phase contrast play part in formation of the image, one of them will have a dominant effect. It should be noted that in any case although different electrons with different interactions are present in the transmitted beam, the final image is only made by the electrons which pass through the objective aperture. Therefore, the size and position of the objective aperture are the most crucial parameters in determining the nature of the contrast which will be seen in the image. Therefore, image contrast can be achieved by selecting or

excluding certain electrons from the imaging system through inserting the objective aperture into the back focal plane of the objective lens. The aperture itself can be moved through external drivers so that any special diffracted or transmitted beam can be selected. Based on this, two different amplitude contrast imaging methods can be selected. Based on this, two different amplitude contrast imaging methods can be introduced. As it is shown in Figure 2-6-a, the objective aperture can be used in a way that only the direct transmitted electrons are being selected. This type of imaging is called the “*Bright Field Imaging*”. On the other hand, objective aperture can be used to select the electrons which have been diffracted from a certain plane (Figure 2-6 b-c). This type of imaging is called the “*Dark Field Imaging*”. Dark field imaging, can be acquired in two different ways. In the first technique, the aperture can be moved to select the diffracted electrons of interest (Figure 2-6-b). In another technique however, the electron beam can be tilted to let the diffracted electrons pass through the objective aperture. These two technique are called Off-axis and On-axis dark field imaging, respectively.

Figure 2-6: Schematics of (a) bright field , (b) Off-axis dark field and (c) On-axis dark field imaging techniques [120]

Besides amplitude contrast, phase contrast will also give valuable information about the microstructure of the specimen. Phase contrast is due to the change in the phase of the electrons which pass through the thin specimen. Phase contrast imaging is very sensitive to different factors such as small change in the thickness, orientation and the scattering factor of the specimen as well as variation in the focus and the astigmatism of the objective lens. Compare to amplitude contrast imaging where only a single beam is selected, in phase contrast imaging, more than one beam will be selected. Selection of more than one beam forms a structure image or “*High Resolution Image*”. The intersect of lattice fringes gives rise to a pattern of dark and bright spots corresponding to atomic columns.

In order to acquire a good HRTEM image, the specimen should be thin enough to eliminate the effect of multiple scattering. Moreover, the microscope lenses should be aligned as good as possible to get the sharpest possible beam. The stigmatism of the objective lens should be minimized. Finally and the most important factor which should be taken into account is to tilt the specimen (or the beam) so that the beam direction coincides with a specific crystallographic axis. The last point is probably the most important point which should be considered in any HRTEM study since the final image needs to be interpreted and modeled considering the relative direction of the beam and the crystallographic directions of the specimen. Figure 2-7 shows the HRTEM image of the silicon single crystal in [110] zone axis.

Figure 2-7: HRTEM image of silicon single crystal in [110] zone axis [121]

2.3 Electron Energy Loss Spectroscopy

Besides the elastic scattering of the electrons which is used for diffraction studies, a variety of inelastic phenomena also happen when the electron beam is passing the adequately thin specimen. Acquiring and analyzing the energy loss spectra of the inelastically scattered electrons, give rise to outstanding the structural information which are summarized here. As shown in Figure 2-8, three main noticeable areas exist in the energy loss spectra:

Figure 2-8: Typical (a): Zero-loss, Low-loss and (b) High-loss EEL spectra of amorphous carbon films

2.3.1 The Zero-Loss peak

As can be understood by the name, zero-loss peak resembles the electrons which pass the specimen without a noticeable energy loss. It should be noted that since the resolution of the spectrometers is limited (at best in the range of ~ 0.2 eV), the term zero-loss seems to be a misnomer. This is further noticeable while considering that phonon excitations usually happen at such small energy-losses which can't be distinguished from the real zero-loss electrons. Nevertheless, the main constituent of the zero-loss peak (which itself is the most dominant peak in the loss spectrum) are the electrons that pass the specimen without any inelastic scattering. Moreover, since the diffraction scattering angle (~ 20 mrad) is larger than the electron energy loss spectroscopy (EELS) collection angle, the zero-loss spectrum mainly contains the electrons which pass the specimen without any interaction. These electrons are the same electrons which constitute the 000 spot in the diffraction pattern

2.3.2 The Low-Loss Spectrum

By convention, energy loss of lower than 50 eV constitutes the low-loss EEL spectra. In this region of EEL spectra, we are focusing on two important phenomenon which are plasmons and inter- or intra- band excitations.

2.3.2.1 Plasmons

Plasmons are longitudinal oscillations of weakly bonded electrons. Having a lifetime of about 10^{-15} s plasmons are localized in the size of about 10 nm. Plasmon peak is the second dominant peak in the EEL spectra. The energy (E_p) that an electron losses to activate a plasmon of frequency ω_p is given by:

$$E_p = \frac{h}{2\pi} \omega_p = \frac{h}{2\pi} \left(\frac{ne^2}{\epsilon_0 m} \right)^{1/2} \quad 2.3$$

where h is the Planck's constant, e and m are the electron charge and effective mass respectively. ϵ_0 is the free space permittivity and n is the free electron density. For different materials, typical values of E_p are in the range of 5-25 eV.

Since the typical value of plasmon mean free path (λ_p) is about 100 nm, a single plasmon peak will be observed for well prepared thin specimen while for thicker specimens, multiple peaks (known as plural scattering phenomena) is expected.

The plasmon excitation explained above, occurs due to interaction of electrons in the bulk of the specimen. Hence, they are usually named as “bulk plasmon excitation”. The interaction may also happen due to interaction of incident electrons with the electrons of the surface of the specimen which can be assumed

as transverse charge waves. Surface plasmons have about half energy of bulk plasmons.

2.3.2.2 Inter- and Intra-Band Transitions

The incident electron may supply enough energy to a core electron and cause it to change its orbital state for instance to an orbital of higher quantum number. These “single electron interactions” result in energy losses of up to about 25 eV which lie in the low loss region of EEL spectra.

2.3.3 The High-Loss Spectrum

Conventionally, Energy losses of higher than 50 eV are called high-loss. This region of EEL spectra contains information about inelastic interactions with inner shells.

When an electron of sufficient energy hits the specimen, it can penetrate to and knock out the core level electrons. The energy loss of the incident electron which is equal to the ionization energy gives outstanding information on the electronic structure of the atom. The ionization process is usually a high energy process. Even in case of light elements like Li, the K ionization edge exceeds 50 eV. Increasing the atomic number enhances the ionization energy due to stronger bonding of core electrons to the nucleus. Therefore, ionization edges of all materials, lie in the high-loss region of EEL spectra. It is worth mentioning that K ionization edge, represents the excitation of an electron from a 1s state and therefore gives rise to a single edge. However, the situation is different for higher

energy edges (i.e. L, M, etc.). For instance, in the L shell, the electrons are either in 2s or 2p orbitals. Excitation of the electron in the 2s orbital leads to L₁ edge while the excitation of electrons in 2p orbitals results in L₂ and L₃ edges. L₂ and L₃ may not be resolvable for atoms with low ionization energies. Therefore a single edge will be observed for this type of excitations (also called as “dual” excitation). The edge in this case will be denoted as L_{2,3} edge.

Ionizations edges have lower intensity in the EEL spectra compare to that of plasmons and zero loss excitations. Large mean free path of ionization excitations prevents plural scattering; however, a combination of ionization excitation and plasmon excitation is very common which makes troubles in interpretation of the high-loss EEL spectra.

2.4 Raman Scattering

When a laser beam of E₀ amplitude and ν₀ frequency shines a material, the polarization of the material’s dipoles depends on the polarisability tensor $\vec{\alpha}$:

$$\vec{P} = \vec{\alpha} \times \vec{E}_0 \cos(2\pi\nu_{las}t) \quad 2.4$$

Using Taylor approximation, individual terms of polarisability tensor can be described as a function of the normal vibration coordinates Q:

$$\alpha_{ij} = \alpha_{ij}^0 + \left(\frac{\partial \alpha_{ij}}{\partial Q} \right)_{Q=Q_0} \times Q \quad 2.5$$

polarization can then be written as:

$$\begin{aligned}
 P_i &= \sum_j \alpha_{ij} \times E_j \\
 &= \sum_j \left[\alpha_{ij}^0 E_{0j} \cos(2\pi\vartheta_0 t) + \frac{E_{0j} Q_0}{2} \left(\frac{\partial \alpha_{ij}}{\partial Q} \right)_{Q=Q_0} \right. \\
 &\quad \times [\cos(2\pi(\vartheta_0 - \vartheta_{vib})t) + \cos(2\pi(\vartheta_0 + \vartheta_{vib})t)] \\
 &\quad \left. + \dots \right]
 \end{aligned} \tag{2.6}$$

As shown in equation 2.6, both quasi-elastic ($\nu \sim \nu_{\text{las}}$) and inelastic ($\nu = \nu_{\text{las}} \pm \nu_{\text{vib}}$) light scattering will be present in the scattered beam. The elastic scattering is known as Rayleigh scattering while the inelastic scattering is known as Raman scattering [122]. It should be noted that Raman scattering occurs only if the vibrations change the polarisability ($\partial \alpha_{ij} / \partial Q \neq 0$). Vibration modes are usually referred by their wavenumbers $\bar{\nu} = \nu_{\text{vib}} / C$ where C is the speed of the light.

The Raman spectrum of polycrystalline graphite shows two distinct vibration modes known as "D" and "G" modes [123-125]. As Shown in Figure 2-9, G mode vibration which occurs at around 1500-1630 cm^{-1} is related to zone center phonons of E_{2G} symmetry which is bond-stretching motion of pairs of sp^2 bonded carbon atoms and hence doesn't require the sixfold rings. The D mode on the other hand, is related to A_{1G} symmetry of phonons near the K zone boundary. The presence and intensity of D mode (known as disorder or breathing mode) strongly depend on the

presence of the sixfold aromatic rings and hence, this mode is not present in perfect single crystal graphite.

Figure 2-9: (a) G and (D) mode of vibration of sp^2 bonded carbon

Visible photons preferentially excite the π states compare to that of σ . Therefore, Visible Raman spectroscopy is 50-230 times more sensitive to sp^2 compare to sp^3 bonded atoms [126-127]. However, there is an interest to probe the $sp^2 \setminus sp^3$ percentage of carbon films and the presence and size of sp^2 bonded clusters by visible Raman spectroscopy. Tuinstra and Koenig (TK) [123] found that the ratio of intensity of D peak compare to that of G peak is inversely related to the size of sp^2 clusters (L_a):

$$\frac{I_D}{I_G} = \frac{C_{(\lambda)}}{L_a} \quad 2.7$$

where the constant “C” for 515.4 nm laser is about 44Å [128-129].

As shown in Figure 2-10, the shape of the Raman spectrum strongly depends on four main factors. Clustering of the sp^2 phase, bond disorder, presence of sp^2 rings or chains and the sp^3 / sp^2 ratio are the factors governing the Raman spectrum of the carbon films. Ferrari et al. [130] studied the change in Raman spectra of a wide

range of carbon films (from ta-C to crystalline graphite) and presented a three stage model for the amorphization of crystalline carbon films:

Figure 2-10: Typical Raman spectrum of carbon films

Stage 1: From Graphite to Nanocrystalline Graphite:

As shown in Figure 2-11, in this stage the following changes will be observed in the Raman spectra:

- (a): The position of the G peak moves from 1581 to $\sim 1600 \text{ cm}^{-1}$
- (b): The appearance of the D peak. The intensity of the D peak changes according to the TK equation mentioned before.

The main structural change in this region is the transformation of single crystal graphite to nanocrystalline structure. No sp^3 site is formed during the whole transformation. The shift in the position of G peak is mainly related to the formation and merging of second-order D' peak located at about 1620 cm^{-1} .

Stage 2: From Nanocrystalline Graphite to a-C:

In this region, the order slakes progressively. The end point of this stage will be a 100% sp^2 bonded amorphous carbon. The main changes of the Raman spectra in this stage are as follows:

(a): The position of the G peak changes from 1600 to $\sim 1510 \text{ cm}^{-1}$.

(b): The I_D/I_G ratio decreases.

(c): The TK equation is no longer valid.

Since the number of ordered ring decreases, the I_D will also decrease; however, since the intensity of the G peak is only affected by the bond stretching of sp^2 bonded pairs, the intensity of the G peak doesn't change. Thus, amorphization leads to decrease in I_D/I_G ratio. As mentioned before, KT equation is no longer valid in this stage and Ferrari et al. proposed a new equation for this stage [130]:

$$\frac{I_D}{I_G} = C'(\lambda)L_a^2 \quad 2.8$$

where $C'(514 \text{ nm}) \sim 0.0055$.

Figure 2-11: Evolution of Raman spectra in amorphization of carbon films

Stage 3: From a-C ta-C:

The sp^2 content increases from ~10 to ~85% in this stage. The microstructure of sp^2 bonded atoms will also change from rings to that of chains. The final structure will be sp^2 dimers embedded in sp^3 matrix [131-132]. The main changes of the Raman spectrum in this stage are as follows:

(a): I_D/I_G is small or zero.

(b): The position of the G peak increases from ~1510 to ~1570 cm^{-1} .

Different fitting procedures have been used so far to fit the Raman spectrum and hence finding the position of the G peak and I_D / I_G ratio. The simplest fit is based on two Lorentzian or two Gaussian curves. However, the most widely accepted and used fitting is a Breit-Wigner-Fano (BWF) curve for G peak, and a Lorentzian for the D peak [133-134]. The BWF curve is given by:

$$I(\omega) = \frac{I_0 [1 + \frac{2(\omega - \omega_0)}{Q\Gamma}]^2}{1 + [\frac{2(\omega - \omega_0)}{\Gamma}]^2} \quad 2.9$$

where I_0 is the peak intensity, ω_0 is the peak position, Γ is the full width at half maximum (FWHM) and Q^{-1} is the BWF coupling coefficient.

Chapter 3: Microstructure of In-Situ and Post Annealed Carbon Films

3.1 Introduction

In chapter 1, it was thermodynamically shown that the biaxial compressive stress of the carbon films results in formation of preferred orientation upon graphitization of a-C films. However, as it was noted, the kinetics of this phase transformation has not been studied in detail yet. Moreover, the nature of the nanocrystals formed under different conditions is also unclear. In this chapter, we will study the effect of deposition temperature and negative substrate bias on the microstructure of the films. Supplying the activation energy through direct heating and/or controlling the energy of depositing impinging ions are thought to be two important parameters affecting the microstructure of the film. Besides, the effect of post thermal annealing has been examined.

3.2 High-Temperature Deposition of Carbon Films

3.2.1 Experimental

FCVA was used to deposit carbon films at different temperatures and substrate bias as illustrated in Figure 3-1.

Figure 3-1: Bias-Temperature deposition scheme

The microstructure of the films was analyzed by cross section and plan view TEM, EELS and Raman spectroscopy. The compressive stress of the films was estimated by measuring the curvature of the substrate before and after the deposition through the Stoney's equation [135]:

$$\sigma = \frac{E_s}{(1 - \nu_s)} \frac{t_s^2}{t_l} \left[\frac{1}{R_2} - \frac{1}{R_1} \right] \quad 3.1$$

where E_s and ν_s are the Young's modulus and Poisson's ratio of the substrate, t_s and t_l are the substrate and film thicknesses and R_2 and R_1 are the substrate curvature after and before the deposition respectively.

3.2.2 Results and Discussion

3.2.2.1 Stress Analysis

Figure 3-2 shows the variation of biaxial compressive stress of the films as a function of deposition temperature and bias. At constant deposition temperature,

the film stress decreases by increasing the substrate bias; however, it is noticeable that even the lowest stress is about 2 GPa.

Figure 3-2: Intrinsic compressive biaxial stress of carbon films deposited at different temperatures and substrate bias

3.2.2.2 Raman Spectroscopy

Figure 3-3: Raman spectra, G peak position and I_D/I_G ratio of carbon films deposited at (A,B) 150°C, (C&D) 400°C and (E&F) 600°C and different substrate biases.

Figure 3-3 (A, C and E) shows the Raman spectra of the carbon films deposited at different substrate biases and temperatures. The curves were then deconvoluted by a G band at 1550-1590 cm^{-1} (BWF) and a D band at about 1350 cm^{-1} (Lorentzian). The results of the deconvolution are shown in Figure 3-3 (B, D and F).

The Raman spectra of the carbon films deposited at 150⁰C and 25, 100 and 300V substrate biases can be fitted by a single G band. This suggests that these films are purely amorphous and no sp^2 cluster is formed. However, by increasing the substrate bias the position of the G peak shifts to lower wavenumbers which indicates that the sp^3 content of the films is decreasing. The film deposited at 600V on the other hand, shows a large I_D/I_G . The position of the G peak is also shifted to 1564 cm^{-1} . Considering the three stage model presented by Ferrari, the carbon film deposited under these conditions is shifted to the stage 2 where nanocrystalline graphite is being formed in the a-C matrix. These results will be further confirmed by the TEM analysis.

Irrespective of the substrate bias, the films deposited at 400⁰C show a large I_D/I_G . Increasing the substrate bias increases the I_D/I_G which shows that the in-plane sp^2 cluster size increases by increasing the substrate bias. The position of the G peak on the other hand doesn't show a significant change which shows that the sp^3 content of the films doesn't change significantly by changing the substrate bias at 400⁰C. Position of the G peak and the large I_D/I_G suggest that the films deposited at 400⁰C are a mixture of a-C and nanocrystalline carbon.

Carbon films deposited at 600°C, show a considerable I_D/I_G . Besides, the position of the G peak increases from 1582 cm^{-1} for 25V deposited film to 1588 cm^{-1} for 600V deposited film. This shows that by increasing the substrate bias the microstructure of the films moves towards a more crystalline state. Moreover, increase in I_D/I_G shows that by increasing the substrate bias the average in-plane size of the sp^2 clusters increases.

3.2.2.3 Transmission Electron Microscopy and Electron Energy Loss

Spectroscopy

Figure 3-4 shows the cross section TEM images of carbon films deposited at 150°C and 25, 100 and 300 V substrate bias. As it is shown in the high magnification HRTEM images, the films are fully amorphous in structure and no considerable sp^2 clusters can be observed in the microstructure. This can be further proved by considering the diffraction patterns of the films which are shown as the insets in respective images. The diffraction pattern of the films shows a continuous diffused ring around the central beam (blocked by the mechanical beam blocker) which confirms that no special ordering is present. This is in agreement with the Raman results which do not show any significant D band for these three films.

As shown in Figure 3-5, increasing the substrate bias to 600V changes the microstructure of the film significantly. As it can be observed in Figure 3-5D which shows the respective diffraction pattern of the film, beside the continuous diffused ring, two arcs which can be indexed as the diffraction of (002) graphitic planes are also present. Figure 3-5B shows the HRTEM image at the silicon/carbon interface. As it can be observed, prior to formation of the textured film, a thin (~10

nm) amorphous layer is formed at the interface. The formation and nature of this amorphous layer will be studied in detail in the next chapter. Both the TEM image and the diffraction pattern show a preferred orientation in the graphitic nanocrystals formed in such a way that the (002) planes are oriented perpendicular to the substrate. This can be explained considering the high internal stress (~ 2.5 GPa) and the stress induced mechanism for the formation of preferred orientation discussed in chapter 1.

Figure 3-4: Low and high magnification HRTEM image of the carbon films deposited at 150°C and (A&B) 25 V, (C&D) 100 V and (E&F) 300 V

Figure 3-5: TEM images of carbon films deposited at 150⁰C and 600 V substrate bias. (A) Low magnification, (B) High magnification HRTEM at the film/substrate interface, (C) high magnification HRTEM of the bulk of the film and (D) diffraction pattern of the carbon film

Figure 3-6 shows the plan view HRTEM images and the respective diffraction pattern of the carbon film deposited at 150⁰C and 600V substrate bias. As it is shown in the HRTEM images, the graphitic basal planes in the plan view are oriented in different directions. However no obvious tubular structure can be observed in the microstructure. The (002) diffraction ring (the innermost ring) in the diffraction pattern consists of two wide arcs. This confirms that there is no special preferred orientation in the plan view microstructure of the films; However,

since the (002) diffraction is not a complete ring, the orientation of the crystals is not uniformly distributed.

Figure 3-6: (A, B & C) plan view HRTEM images of the carbon film deposited at 150°C and 600 V substrate bias and (D) respective diffraction pattern of the film

Considering both the plan view and cross section TEM analysis of the carbon film deposited at 150°C and 600 V substrate bias, we can deduce that the structure is a

mixture of amorphous and nanocrystalline carbon. Moreover, the graphitic nanocrystals show a preferred orientation in such a way that (002) basal planes are perpendicular to the substrate. However, considering the plan view TEM images, although the crystals are not distributed uniformly in all orientations, but there is no special preferred orientation in the plan view of the films.

Figure 3-7 shows the cross section TEM analysis of the carbon film deposited at 400⁰C and floating bias. As it can be seen, by increasing the deposition temperature to 400⁰C preferred oriented nanocrystals are formed even at floating substrate bias. As shown in Figure 3-7(B) which shows the high magnification HRTEM image at the Si/C interface, compare to the carbon film deposited at 150⁰C and 600V the interface is sharper and no distinct intermixing layer can be observed. As shown in Figure 3-7(D) which is the dark field image, the nanocrystals are uniformly distributed throughout the bulk of the film except the first few nanometers at the Si/C interface which is purely amorphous. The diffraction pattern again consists of two (002) sharp arcs which further confirms the presence of preferred orientation in the microstructure of nanocrystalline graphite.

Figure 3-8 shows the plan view HRTEM images of the film deposited at 400⁰C and 25 V. As it can be observed, the same structure which was also observed for the 150⁰C and 600V bias is also observed here.

The same analysis is done for the samples deposited at 400⁰C, 100 and 300 substrate biases and the cross section and plan view TEM results are summarized in Figure 3-9. Similar to 25 V deposited film, preferred oriented nanocrystals are

observed in the cross section images. The plan view image of 100V deposited film shows a preferred orientation in the plan view as well. However, the 300V deposited film shows a different microstructure in the plan view. As can be observed from both the TEM image and the diffraction pattern no distinct preferred orientation is observed and graphitic nanocrystals have random orientations.

Figure 3-7: (A) Low magnification, (B) High magnification at the Si/C Interface (C) High magnification at the bulk of the film (D) Dark field and (E) diffraction pattern of the carbon film deposited at 400°C and 25 V substrate bias

Figure 3-8: (A,B&C) Plan view high magnification HRTEM image of the carbon film deposited at 400°C and 25V and (D) respective diffraction pattern.

Figure 3-9: Dark field and cross section HRTEM image of the carbon film deposited at (A&B) 400°C and 100V and (C&D) 400°C and 300V. Plan view HRTEM image of carbon films deposited at (E) 400°C and 100V and (F) 400°C and 300 V

The plan view and cross section TEM images of carbon film deposited at 400°C and 600V bias are shown in Figure 3-10. The cross section image shows a similar microstructure to that at lower substrate biases. However, the plan view TEM image indicates a different microstructure. The diffraction pattern (Figure 3-10B inset) clearly shows that there is no distinct preferred orientation in the microstructure. Moreover as confirmed by the TEM images, compared to lower substrate biases where graphene-like structures were formed, at 600V tubular nanostructures are observed in the plan view microstructure.

Figure 3-10: (A) cross section and (B) plan view HRTEM image of carbon film deposited at 400°C and 600V bias

The same analysis has been done on the samples deposited at 600°C and different biases. Similar to 400°C deposited films, cross section TEM images (not shown here due to similarity) show preferred oriented nanocrystals regardless of the substrate bias. Figure 3-11 shows the plan view HRTEM images of carbon films

deposited at 600°C and different biases. As it can be observed, the films deposited at 25 and 100V bias are formed from planar graphitic nanostructures while increasing the bias to 300 and 600V results in formation of tubular nanostructures.

Figure 3-11: Plan view HRTEM image of carbon films deposited at 600°C and (A)25, (B)100, (C)300 and (D)600V substrate biases. The insets show the respective diffraction pattern

EELS was used to study the local structure at the Si/C interface. Figure 3-12 shows the EELS analysis of the carbon film deposited at 600°C and 600V. Interestingly, silicon $L_{2,3}$ edge can be detected at positions about 10 nm into the carbon film. This shows that due to high temperature and high energy of impinging ions, silicon diffuses into the carbon film. As it is shown in Figure 3-12(B), the silicon $L_{2,3}$ edge changes its shape from that of pure Si (with a peak around 100.5 eV) in the substrate and at the interface to that of SiC in the carbon film. It is worth mentioning that SiC would have peaks at 108 and 115 eV. Amorphous silicon would have the same overall edge shape as crystalline silicon, but with a less well-defined peak at 100.5 eV. At positions beyond 9.9 nm of the interface no obvious silicon $L_{2,3}$ edge was observed.

As it can be observed from Figure 3-12(c), the carbon K-edge signal can be observed upto 3 nm into the silicon substrate. No distinct signal was observed at depths higher than 3 nm into the silicon. Moreover, No obvious $\pi \rightarrow \pi^*$ transition at 285 eV could be observed in the signal at this region which shows that all the carbon atoms at this region are in carbide form. From 1 nm distance onward, a π^* peak around 285 eV appears, indicating the presence of trigonally (sp^2)-bonded carbon atoms. Moreover, considering the shape of $\sigma \rightarrow \sigma^*$ band, it can be concluded that the carbon present at positions upto 1 nm inside the carbon is amorphous in structure while the presence of a peak at 293 eV in the EEL spectrum at distances higher than 1 nm reveals the presence of crystalline graphitic carbon in the structure [136].

Figure 3-12: EELS analysis of carbon film deposited at 600°C and 600V substrate bias. (A): Annular dark field STEM image of the silicon/carbon interface. The red line is assumed as the interface (B) Silicon $L_{2,3}$ -edge and (C) Carbon K-edge EEL spectrum at different positions with respect to the interface shown in Figure A

3.3 Post-Annealing of Carbon films

Figure 3-13 shows the HRTEM image of the carbon film deposited at 300V substrate bias and room temperature. As shown in the image and the inset which shows the respective FFT of the image, the film is purely amorphous and no crystallinity can be observed in the microstructure.

Figure 3-13: HRTEM image of the carbon film deposited at 300V substrate bias and room temperature. The inset shows the respective FFT of the image

The specimen shown in Figure 3-13 has then been heated up in-situ to 200°C and the TEM images are shown in Figure 3-14. As it can be seen from the FFT (Figure 3-14(A) inset), nanocrystals with preferred orientation are formed even at temperatures as low as 200°. Clusters are uniformly distributed throughout the whole film. The average interplanar spacing of basal planes in the sp^2 bonded nanocrystals is found to be 3.567 nm (Figure 3-14(B))

Figure 3-14: (A) HRTEM of the carbon film deposited at 300V substrate bias and annealed at 200°C. The inset shows the respective FFT of the image. (B) Magnified image and the FFT of the square shown as [1] in figure A.

The temperature has then been ramped up to 300°C and the HRTEM images are shown in Figure 3-15. Compare to 200°C annealed image, the preferred orientation is more enhanced in the 300°C heated specimen (by comparing the FFTs). Comparing the TEM images, it can also be deduced that increasing the temperature to 300°C enhances the crystallinity while the preferred orientation of the nanocrystals is also enhanced.

Figure 3-15: (A) HRTEM of the carbon film deposited at 300V substrate bias and annealed at 300°C. The inset shows the respective FFT of the image. (B) Magnified image and the FFT of the square shown as [1] and [2] in figure A.

Figure 3-16 and Figure 3-17 show the microstructure of the films heated at 400 and 500°C respectively. Considering the FFTs, compare to the sample heated at 300°C, the 400°C annealed specimen shows higher degree of preferred orientation. The 500°C heated sample, on the other hand, shows a very different microstructure. Compare to lower temperatures, 500°C heated sample doesn't show considerable preferred orientation and nanocrystals are distributed at random directions.

Figure 3-16: (A) HRTEM of the carbon film deposited at 300V substrate bias and annealed at 400°C. The inset shows the respective FFT of the image. (B) Magnified image and the FFT of the square shown as [1] and in figure A.

Figure 3-17: : (A) HRTEM of the carbon film deposited at 300V substrate bias and annealed at 500°C. The inset shows the respective FFT of the image. (B) Magnified image and the FFT of the square shown as [1] in figure A.

Compared to heating at lower temperatures, increasing the temperature to 600⁰C results in a considerable decrease in lateral distribution of (002) arc in the FFT of the HRTEM image. This means that heating at 600⁰C (Figure 3-18) results in more uniform interplanar spacing of (002) basal planes in different nanocrystals.

Figure 3-18: (A) HRTEM of the carbon film deposited at 300V substrate bias and annealed at 600°C. The inset shows the respective FFT of the image. (B) Magnified image and the FFT of the square shown as [1] and [2] in figure A.

Compared to the lower temperature heated films, the sample heated at 600°C shows a distinct feature. Besides graphitic nanocrystals, tubular like nanostructures can also be observed in the microstructure. One of these tubular nanostructures is shown as point 1 in Figure 3-19 (B). This can be further understood from the FFT of the point 1 which doesn't show any preferred orientation. Considering the FFT of the whole image shown as the inset, it can be deduced that although a preferred orientation is still present in the structure of the nanocrystals, the crystals are oriented in more random orientations. Besides, the interplanar spacing of the nanocrystals is more uniform in the whole structure of the film.

Figure 3-19: (A) HRTEM of the carbon film deposited at 300V substrate bias and annealed at 700°C. The inset shows the respective FFT of the image. (B) Magnified image and the FFT of the square shown as [1], [2] and [3] in figure A.

3.4 Discussion and Conclusions

In summary, the microstructure of the carbon films deposited at high temperatures and post annealed carbon films has been studied by Raman, TEM and EELS. Crystalline graphite is the most stable phase of carbon at STP conditions. Therefore, any post or in-situ treatment which supplies energy to any non-equilibrium or

metastable phase of carbon (such as diamond) results in transformation of metastable carbon to graphite. Considering an amorphous phase consisting a mixture of different hybridizations, graphitization includes both transformation of different hybridization to sp^2 bonding as well as crystallization. Therefore, as it was also obviously shown by the Raman spectroscopy results, increasing the deposition temperature or post annealing results in formation of films with higher sp^2 content.

crystallization of the amorphous clusters however depends on the temperature or post annealing conditions. It was shown that under different conditions, different nanostructures are formed. Stability of carbon nanostructures has been studied theoretically and experimentally by different groups. From a general point of view, the stability of planar graphene based and rolled carbon nanostructures (such as nanotubes) can be discussed by considering two main factors. due to high bond bending energy, tubular nanostructures have higher energy compare to the planar structures. On the other hand, the planar structures have higher energy due to the dangling bonds at the edges [137]. Sawada and Hamada, for different types of nanotubes, there is an optimum diameter at which the tubular structure is energetically more favorable compare to that of the planar structure. As an example, Figure 3-20 shows the variation of the binding and bending energies for a (n,2) nanotube of different diameters. Decrease in the tube diameter increases the bond bending energy. Therefore, at small tube diameters, the formation energy of a tubular structure becomes positive and hence, planar structures become energetically favorable.

In another similar but experimental study, Levchenko et al. [138] studied the formation enthalpies of bundles of (10, 10) single wall CNTs (with diameter of about 1.35 nm) by high temperature oxidation calorimetry. As it is schematically shown in Figure 3-21, the tubular nanostructures are only a few KJ/mol less stable compare to their graphite counterpart.

Figure 3-20: The bond-bending (E_{bend}) and the bond-binding (E_{bind}) energies and the sum of them ΔE , as a function of $1/n$ for a (n,2) tubules [137].

Figure 3-21: Formation enthalpy of different carbon based structures with respect to graphite

In this chapter, the stability of different carbon nanostructures in the a-C matrix is studied. As it is also shown in Figure 3-22 the cross section HRTEM image of the carbon films shows two different microstructures. At low temperatures (150⁰C) and low substrate biases (upto 300V) the film is purely amorphous in structure. Crystallization starts at higher substrate bias (600V) and higher temperatures. Besides, due to the high intrinsic biaxial compressive stress of the films, the crystallization is always accompanied by the formation of preferred orientation (as discussed in chapter 1).

Figure 3-22: Typical cross section HRTEM image of (A) the carbon films deposited at 150°C and 25, 100 and 300V substrate bias and (B) the carbon films deposited at 150°C & 600V bias, 400°C & 25, 100, 300, 600V bias, 600°C & 25, 100, 300, 600V bias

The nature of the nanostructures however, strongly depends on the deposition conditions. Figure 3-23 shows a summary of the microstructures achieved by controlling the deposition conditions. Considering the microstructure of the carbon films deposited at 400 and 600°C a common feature is observed. At lower substrate biases (300V and below) planar graphitic structures are formed while at high bias (600V) tubular nanostructures are stabilized. This implies that besides the substrate temperature, the deposition bias is another factor which controls the nature of the nanostructures. One possible mechanism for the formation of different nanostructures at high bias is the formation of thermal spikes of different temperature at different substrate biases.

The concept of thermal spike was introduced in section 1.3. The energy of a high energy ion impinging the surface is lost through different stoppage mechanisms. One of the mechanisms is through transferring the energy as thermal energy to the atoms surrounding the impinging ion (in the range of tens of angstrom). This

results in ultrafast heating of the region to very high temperatures (in the order of few thousands of Kelvin) [139]. Obviously the size, shape and the temperature of the thermal spike depends on the impinging ion energy. Increasing the ion energy increases the spike temperature and size. Higher substrate bias results in higher impinging energy of the ions. This in turn results in increase in the temperature of thermal spikes formed due to collision. This increase in the spike temperature leads to stabilization of tubular structure compared to lower temperature spikes where the planar nanostructures are formed.

Figure 3-23: Plan view HRTEM image of the carbon films deposited at (A): 150⁰C & 600V, (B): 400⁰C & 25V, (C): 400⁰C & 100V, (D): 400⁰C & 300V, (E) 400⁰C & 600V, (F): 600⁰C & 25V, (G): 600⁰C & 100V, (H): 600⁰C & 300 V and (I): 600⁰C and 600V

Figure 3-24 summarizes the radial distribution of (002) arc in the plan-view diffraction pattern of carbon films deposited at different temperatures and biases. At low substrate bias, the arcs is not uniform which shows the presence of preferred orientation in the microstructures which in other words shows the formation of planar nanostructures. Increasing the bias to 600V on the other hand results in the formation of tubular nanostructures which coincides with the formation of a full ring in the diffraction pattern.

Figure 3-24: Radial distribution of (002) arc as a function of deposition temperature and bias

We have also studied the effect of post thermal annealing (using a hot stage TEM) on the structural changes of the films. It was shown that graphitic nanocrystals will form at temperatures as low as 200°C. The summary of the results can be found in Similar to high temperature deposition, a-C will transform to graphene based nanostructures in carbon films annealed at lower temperatures (upto 600°C) while at higher temperatures tubular nanostructures could be achieved.

3-25: Microstructure of the carbon film post annealed at (A): 200°C, (B) 300°C, (C): 400°C, (D): 500°C and (E): 700°C

Chapter 4: Room Temperature Fabrication of Nanostructured Carbon Films

4.1 Introduction

In the previous chapter, it was shown that by controlling the deposition temperature and ion energy, the microstructure of the carbon films can be controlled. It was also shown that the nature of the nanocrystals strongly depends on the deposition ion energy. More interestingly, it was found that at low deposition temperatures, the microstructure of the film depends on the magnitude of substrate bias. Low substrate biases (lower than 300V) results in formation of an amorphous film while higher energy deposition (600V) leads to the formation of graphitic nanostructures in the microstructure. These results suggests that besides the substrate temperature, the deposition ion energy plays an important role in the formation of nanocrystals in the microstructure of the films. In this chapter we have investigated the effect of two plasma parameters (namely the ion energy and ion density) on the microstructure of the films.

4.2 Experimental

During the deposition, the ion beam moves as a converge beam inside the magnetic duct and will diverge as it exits it. Hence by controlling the distance between the substrate holder and the magnetic duct exit (shown as “ d ” in Figure 4-1) the density of the impinging ions can be controlled. In order to quantify the ion density a

Faraday cup was used. By choosing proper distance between the sample and the magnetic filter, two ion density plasma profiles which are five times different from each other are achieved and used in this work (Figure 4-2). The average current of the faraday cup was measured to be 12.5 (high density plasma) and 2.5 mA/cm² (low plasma density). DC bias was applied to the substrate to control the ion energy during the deposition. The current of the magnetic filter was kept at 10 A. The initial carbon ion energy was measured to be 20 eV.

Figure 4-1: Schematics of FCVA deposition technique

Figure 4-2: Current Density Vs. time for two different cases where the sample is put far from the magnetic filter (black squares) and when the sample is near to the magnetic filter (red dots)

4.3 Results and Discussion

4.3.1 TEM analysis of carbon films deposited at different substrate bias and plasma density

Figure 4-3 shows the plan view TEM images of the carbon films deposited at 300 and 400V substrate bias and low ion density plasma. As it can be observed from the HRTEM image and the respective diffraction patterns these films are purely amorphous in structure and no crystallinity can be observed.

On the other hand, carbon films deposited at high impinging ion densities show different microstructures at 300 and 400V bias. Figure 4-4 shows the microstructure of the carbon film deposited at high ion density and 300V substrate bias. As it is shown in the bright field image (figure A), two distinct phases are present in the microstructure. This is confirmed by the diffraction pattern (inset), showing two distinct arcs indexed as diffraction of (002) hexagonal graphite planes. Dark field image which was acquired by putting a small objective aperture on the (002) diffraction arc, confirms that the brighter phase in the bright field image contains a texture in the microstructure as it is also shown in HRTEM image (figure D). Figure C which is a high magnification HRTEM image of the Silicon/carbon interface shows that the darker phase in figure A is amorphous in structure.

Figure 4-3: Plan-view TEM image of carbon films deposited at low plasma density and (A) 300V and (B) 400V substrate bias. The insets show the respective diffraction patterns

Figure 4-4: Microstructure of the film deposited at 300V substrate bias and high ion density plasma (A) Bright field, (B) Dark field, (C) HRTEM image of the silicon/carbon interface (shown as 1 in figure A) and (D) bulk of the carbon film (shown as 2 in figure A)

Figure 4-5 and Figure 4-6 show the microstructures of the films deposited using high ion density plasma and 400 and 500V substrate biases, respectively. Bright

field and dark field images, show that the structure is again composed of an initial thin amorphous layer followed by a nanocrystalline film. It should be noted that the thickness of the initial amorphous layer decreases by increasing the energy of the impinging ions.

Based on the above, it can be deduced that plasma density is a critical parameter in determining the formation of nanocrystals with preferred orientation in as deposited PVD grown carbon films. Using low density plasma, results in a fully amorphous film even though substrate biases as high as 400V has been used. Increasing the plasma density leads to formation of nanocrystals even at low substrate bias (300V). However, even at low plasma densities, nanocrystals can be formed at high substrate bias which further confirms the effect of the spike temperature on the formation of nanocrystals with preferred orientation in the as deposited carbon film. Figure 4-7 shows the TEM image of the film deposited with low plasma density and 500V substrate bias. Similar to the other films, prior to the nanocrystalline layer there is an amorphous layer formed at the silicon/carbon interface. However, comparing to high plasma density deposited film it should be noted that increasing the plasma density decreases the thickness of the initial amorphous layer significantly.

As it was shown, changing the plasma density and impinging ion energy has a considerable effect on the microstructure of the film. Moreover, it is found that irrespective of the substrate bias, an amorphous layer will be formed at the immediate interface with the substrate. In the next section the composition of this amorphous layer will be studied using high loss EELS. Moreover, as shown by

dark field TEM images besides the preferred oriented nanocrystals, another phase is detectable. In the next section the nature of this second phase will also be studied.

Figure 4-5: (A) Bright field and the respective diffraction pattern (inset), (B) Dark field, (C) HRTEM image of the silicon/carbon interface and (D) bulk of the carbon film deposited at high ion density plasma and 400V substrate bias

Figure 4-6: (A) Bright field and the respective diffraction pattern (inset), (B) Dark field, HRTEM image of (C) the silicon/carbon interface and (D) bulk of the carbon film deposited at high ion density plasma and 500V substrate bias

Figure 4-7: (A) Low-magnification and the respective diffraction pattern (inset) and (B) HRTEM image of the carbon film deposited at low ion density plasma and 500V substrate bias

4.3.2 Silicon/Carbon interface and non-uniformities in carbon films deposited using high density carbon plasma

As it was shown in the previous section, an amorphous layer is always formed at the silicon/carbon interface. As this discrete interfacial layer may have considerable effect on the overall properties of the film, a careful study is warranted. In addition, as it was shown in the dark field images, the nanocrystalline layer is not uniform throughout the film. The structure of these non-uniformities should also be studied.

EELS was used to study the local structure at the interface and selected positions of the films. Figure 4-8 shows the EELS analysis of the carbon film deposited at high plasma density and 400V substrate bias. As it is shown in Figure 4-8(B), the

silicon $L_{2,3}$ edge changes its shape from that of pure Si (with a peak around 100.5 eV) at positions 1,2 and 3 to that of SiC at positions 6 and 7. It is worth mentioning that SiC would have peaks at 108 and 115 eV; amorphous silicon would have the same overall edge shape as silicon, but with a less well-defined peak at 100.5 eV. For example, in position 3 at the very edge of the silicon substrate, some amorphous silicon is present. Beyond position 7, no significant silicon signal was present.

The presence of SiC in the 4-5 nm on top of the Si substrate can be further proved by considering the carbon K edge at the same locations. No obvious K-edge can be acquired at positions 1 and 2. The carbon K-edge at positions 3 to 5 shows broad peaks around 289 and 303 eV shown earlier by Zheleva *et al.* [140] to arise from tetragonally bonded carbon in SiC.

From position 6, a π^* peak around 285 eV appears, indicating the presence of trigonally (sp^2)-bonded carbon atoms. Moreover, considering the shape of $\sigma \rightarrow \sigma^*$ band, it can be concluded that the carbon present at positions 6 to 11 are amorphous in structure while the presence of a peak at 293 eV in the EEL spectrum at positions 11 and 12 reveals the presence of crystalline, graphitic carbon in the structure [136].

From the above, it can be concluded that the interface is formed from three distinct layers. A 4 nm Si + a-SiC layer is formed at the very first layer. The second layer is composed of a-SiC + a-C layer (area between points 6 and 7) which is about 2 nm thick. The third layer is a pure amorphous carbon layer (area between points 7 to

11) which is about 17 nm thick. The following layer consists of crystalline carbon as deduced from the shape of the $\sigma \rightarrow \sigma^*$ transition. This is in accordance with the dark field TEM image shown in Figure 4-5. Figure 4-8(D) and (E) show the carbon K-edge of the thick layer. This layer contains crystalline graphitic phases as shown in Figure 5(B). As it can be observed from the dark field image, this structure contains a bright phase which is confirmed by the HRTEM image to be consist of crystalline graphitic phase with their basal planes in a parallel direction to the beam; however, the nanocrystals are not uniform throughout the microstructure and other obvious dark areas are also present in the dark field image. To study the nature of these darker areas high-loss EELS was done on the crystalline areas as well as the area with unknown microstructure.

To do the above, CBED was acquired under the STEM mode and a point where the CBED shows (002) diffraction and another point where (002) is not present are chosen for EELS acquiring. Figures 8 (D) and (E) show the carbon K-edge on these two areas. Two important observations arise from these two spectra. Unlike the high-loss EEL spectra of a-C where the $\sigma \rightarrow \sigma^*$ can be fitted by a Gaussian curve, the shape of these two curves reveals the presence of crystalline graphite in the microstructure. Moreover, the $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ peak ratios show a higher value (0.74348) at the location with preferred orientation compare to the point without the preferred orientation (0.51451). As will be shown in the continue, this confirms that as it is also shown in the HRTEM image (Figure 4-5) the graphitic crystals in these areas are more parallel to the electron beam (perpendicular to the substrate) compared to the other areas where basal planes are in the random orientations. To

confirm this, we have examined the high loss K-edge EEL spectra of a single multiwall nanotube and a CNT bundle and the results are shown in Figure 4-9.

Figure 4-8: EELS analysis of carbon film deposited at 400V substrate bias and high plasma density. (A): Annular dark field STEM image of the silicon/carbon interface, (B) Silicon $L_{2,3}$ -edge EEL spectrum at positions 1 to 7 shown in figure A, (C) Carbon K-edge EEL spectra at positions 1 to 12 shown in figure A, (D) carbon K-edge EEL spectra of spots with preferred orientation, (E) carbon K-edge EEL spectra of spots without preferred orientation and (F) carbon atomic ratio with compare to point 12 deduced from the total area under the carbon K-edge spectra at different positions

Figure 4-9 (A) shows the dark field STEM image of a single MWNT while the K-edge EEL spectra at the edge and the center of the nanotube (shown respectively as 1 and 2 in Figure 4-9 (A)) are shown in Figure 4-9 (B) and (C). The experiment was conducted using exactly the same conditions as the data was acquired on the carbon films. Both the edge and the center of the MWNT is formed from parallel graphitic planes. However, in this configuration, the basal planes are parallel to the electron beam at the edge while they are perpendicular to the beam at the center of the nanotube. This in turn results in higher cross section of $\pi \rightarrow \pi^*$ excitation at the edge compare to the same cross section at the center of the nanotube. Therefore the $\pi \rightarrow \pi^* / \sigma \rightarrow \sigma^*$ shows considerably higher value at the edge of the nanotube (0.932) compare to the same value at the center of the nanotube (0.556). Figure 4-9(D) on the other hand shows the dark field STEM image of a MWNT bundle. $\pi \rightarrow \pi^* / \sigma \rightarrow \sigma^*$ ratio on the large area CNT bundle which is a mixture of basal planes with different orientation to the electron beam (Figure 4-9 E) is 0.631 which is between the values at the edge and the center of the nanotube.

Figure 4-9: (A): Dark field STEM image of a single MWNT, K-edge EEL spectra of (B): the edge (shown by circle 1) and (C): center (shown by circle 2) of the single MWNT shown in figure (A). (D): STEM dark field image of a MWNT bundle. (E): K-edge EEL spectra of the MWNT bundle and (F): variation on the relative areas under the $\pi^*/\pi^* + \sigma^*$ and the respective peak to peak ratios

It should also be noted that besides the orientation of the basal planes, the sp^3 content of the carbon structure also affects the $\pi \rightarrow \pi^*/\sigma \rightarrow \sigma^*$. This is because in sp^3 configuration there is no π bond to be excited. However, since MWNTs can be considered as a pure sp^2 bonded structure the change in $\pi \rightarrow \pi^*/\sigma \rightarrow \sigma^*$ ratio can be used to monitor the change in orientation of basal planes.

Relying to the points mentioned above it can be deduced that higher $\pi \rightarrow \pi^*/\sigma \rightarrow \sigma^*$ ratio in the bright areas of the dark field image compare to that of the dark areas is a sign of higher degree of orientation in the direction parallel to the beam and hence perpendicular to the substrate. Here, it should also be noted that since the orientation of the nanocrystals strongly effects the shape of the high loss EEL

spectra, the method proposed by Muller et al. [136] cannot be used to measure the respective sp^3 content of the nanocrystalline film as it is widely used by previous researchers (e.g. see Lau et al. [141]). Muller et al. proposed that the ratio of the $\pi \rightarrow \pi^* / \sigma \rightarrow \sigma^*$ ratio of amorphous carbon film can be compared to the same ratio of a purely amorphous sp^2 bonded structure (such as glassy carbon) to find out the sp^2 content of the a-C film. Since there is no orientation dependence in a-C films, this method seems to be the most accurate and direct method to measure the sp^2 content of the film. However, as it is shown here, the orientation dependence of the high-loss EEL spectra limits the application of this method for such estimation.

The same study has been accomplished on the carbon film deposited at 500V and under high plasma density and the results are shown in Figure 4-10. The interface here consists of a very thin layer of about 0.8 nm (around positions 1 and 2 in figure 9(A)) of amorphous silicon, mixed increasingly with SiC, while after 4-5 nm (position 7 and higher), the SiC signal decreases and the π^* peak around 285 eV appears, marking the presence of sp^2 -bonded carbon in the deposited film.

Figure 4-10: EELS analysis of carbon film deposited at 500V substrate bias and high plasma density. (A): Annular dark field STEM image of the silicon/carbon interface, (B) Silicon $L_{2,3}$ -edge EEL spectrum at positions 1 to 8 shown in figure A, (C) Carbon K-edge EEL spectra at positions 3 to 8 shown in figure A, (D) carbon K-edge EEL spectra of spots with preferred orientation, (E) carbon K-edge EEL spectra of spots without preferred orientation and (F) carbon atomic ratio with compare to point 8 deduced from the total area under the carbon K-edge spectra at different positions

$\pi \rightarrow \pi^* / \sigma \rightarrow \sigma^*$ ratio in the preferred oriented areas of the carbon films deposited at these conditions is 0.72 (Figure 9(D)). The same ratio in the spot without preferred

orientation is 0.49 (Figure 9(E)). Comparing these ratios with the same ratios for the sample deposited at 400V it can be deduced that increasing the substrate bias from 400 to 500V doesn't change the orientation of crystalline phase significantly. The EELS analysis of 300V deposited sample on the other hand shows a different interface. As shown in Figure 4-11 unlike the films deposited at 400 and 500V substrate biases, the one at 300V shows a sharp silicon/carbon interface. As it can be observed from Figure 4-11(B) which shows the C K-edge of the interface, no obvious carbon can be found at points 1 and 2 while the K-edge at points 3 and 4 shows both the $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions. Figure 4-11(C) on the other hand, shows the Si $L_{2,3}$ edge. Points 1 and 2 show a sharp peak at about 105 eV with slight change to 108 at point 3. No obvious Si $L_{2,3}$ edge can be observed at point 4 which shows that no Si is present beyond point 3.

Figure 4-11: EELS analysis of carbon film deposited at 300V substrate bias and high plasma density. (A): Annular dark field STEM image of the silicon/carbon interface, (B) Carbon K-edge EEL spectrum at

positions 1 to 4 shown in figure A, (C) Silicon $L_{2,3}$ -edge EEL spectra at positions 1 to 4 shown in figure A

It should be noted that H. S. Zhang et al. [142] have also found that the activation energy for the formation of SiC at the interface is ~ 320 eV which is in agreement with our results. The presence of SiC and an amorphous layer in the interface is an important factor which needs to be studied in more detail.

As it can be observed, the composition of the interface strongly depends on the impinging ion energy. Although higher ion energies results in formation of a more uniform crystalline film, but it also leads to the formation of a carbide layer at the interface.

4.3.3 Nature of the nanocrystals formed through controlling the impinging ion energies

The nature of the nanocrystals formed has been examined by plan view TEM. Figure 4-12 shows the HRTEM image of the high plasma density deposited films using 300 and 400V substrate bias. Diffraction patterns shown in the inset reveal discontinuous (002) diffraction arcs. This suggests that as it can also be observed in the HRTEM images, there is a preferred orientation direction in the growth plane as well. Considering the preferred orientation in both the cross section and the plan view images, it can be deduced that the graphitization in this stage can be assumed as formation of graphitic basal planes perpendicular to the growth direction. It is noticeable that the (002) diffraction ring is more uniform in the film deposited at 400V compared to the 300V deposited one. Hence, increasing the ion energy

decreases the probability of preferred orientation in the growth plane and the basal planes can be oriented in different orientations in the direction perpendicular to the growth direction (considering the cross section image) and hence other structures such as tubular nanostructures can also be formed. This can be obviously observed in the microstructure of the film deposited at 500V substrate bias which is shown in Figure 4-13. Spherical nanostructures can be observed in the microstructure. As it is shown, no distinct preferred orientation can be observed in the diffraction pattern as well. Considering the cross sectional TEM images which confirms the presence of preferred orientation perpendicular to the substrate, it can be deduced that tubular carbon nanostructures are formed by applying higher ion energy while the plasma density is kept constant.

Figure 4-12: Plan view HRTEM image of the films deposited at (A) 300 and (B) 400V substrate bias and high density plasma. The insets show the respective diffraction patterns

Figure 4-13: (A), (B) and (C) plan view HRTEM images of the carbon film deposited at high plasma density and 500V substrate bias and (D) the respective diffraction pattern

4.3.4 Theoretical studies on the formation on nanostructures

In order to study the effect of thermal spike temperature on the formation of carbon nanostructures, we carried out computer simulations of the a-C wires of different densities (2.2-3.5 g/cc) with the initial diameter of 4 Å and more at 1500-3500 K.

The temperature induced formation of nanostructures in a-C was studied by density functional Frauenheim's tight-binding molecular dynamics (MD) [143-144] using the package for Linear-combination of Atomic orbitals (PLATO) code[145]. Three samples of amorphous carbon with densities of 2.2, 3 and 3.5 g/cc (containing 20, 50 and 80% of sp^3 bonded atoms respectively) were prepared by quenching of gaseous carbon phase. Thin wires with circle cross-section of the width of 4-12 Å and the lengths of 15-18 Å were cut off the amorphous carbon networks. Periodic boundary conditions were applied in the direction along the tube. The Γ -point Brillouin zone sampling was used for the electronic calculations. The MD step was 1 femtosecond. The wires were then heated up to temperatures of 1500, 2000, 2500, 3000 and 3500 K respectively during 50-100 ps. The structures obtained were visualized with visual molecular dynamics (VMD) package [146].

In the process of heating, the a-C wires transform into sp^2 carbon structures. As shown in Table 4-1 the result of the transformation depends on the initial diameter of a-C wire, temperature and the density of initial amorphous carbon.

Table 4-1: Structural transformations of amorphous carbon nanowires of different densities under annealing at different temperatures

Density	Diameter (Å)	Temperature		
		2000 K	2500 K	3500 K
2.2 g/cc	7.4	graphite	graphite	graphite
	9.49	graphite	graphite	graphite
	11.55	graphite	graphite	CNT
3.0 g/cc	7.93	sp ² amorphous	CNT	CNT
	8.37	sp ² amorphous	sp ² amorphous	graphite
	10.93	sp ² amorphous	graphite	CNT
3.5 g/cc	5.32	sp ² amorphous	graphite	CNT
	8.6	sp ² amorphous	CNT	CNT
	12.63	sp ² amorphous	CNT	CNT

Table 4-1 shows that the probability of formation of CNT increases with increasing temperature. The temperature of 2000 K was found to be ineffective for formation of CNTs. At this temperature the low density wires with small diameter transforms into graphite, while the wires of larger diameter remain to be amorphous.

If the temperature is above 2000 K, the results fall in two groups. In some cases the a-C wires transform into damaged graphene sheet (Figure 4-14) and in other cases a-C wires transform into damaged CNT (Figure 4-15).

The probability to form CNT is low for low density wires. Most of them transform into graphite at the temperatures of 2500-3500 K. For a density of 2.2 g/cc there was only one case, when our a-C wire transforms into CNT (wire of 11.55 Å in

diameter heated up to 3500 K). On the other hand most of high density a-C wires with big diameters (8 Å and more) transforms into damaged CNT.

The mechanism of the transformation looks as follow. In the process of heating, the fraction of sp^3 hybridized carbon atoms in a-C nanowires of high density (3-3.5 g/cc) decrease essentially. Atoms rearrange to form a number of curved damaged graphitic stripes and planes which can intersect. Then the newly formed graphitic planes join together to form a single curved graphitic sheet. If the density and the temperature are low these graphitic sheets straighten out into a graphitic plane. If the density and the temperatures are high, this graphitic sheet curved into CNT.

Both the graphitic and the CNT structures formed by this way are highly defective. They contain pentagons and heptagons. However all the carbon atoms in these structures are sp^2 hybridized. Figure 4-14 and Figure 4-15 show that all sp^3 hybridized atoms (red atoms) disappear during the transformation, and only sp^2 and sp -bonded atoms (blue and white balls respectively) remain.

The results of the simulation reveal that the temperature and the density are two crucial factors, which define the transformation of amorphous carbon wires. Initial diameter of wire is also an important parameter.

Figure 4-14: Transformation of a-C tube with density of 3 g/cc and with diameter of 10.93 Å, heated at the temperature of 2500 K. (left-top view, right-side view). Red balls represent sp^3 hybridized carbon atoms, blue balls represent sp^2 hybridized carbon atoms, and white balls represent sp hybridized carbon atoms.

Figure 4-15: Transformation of a-C tube with density of 3 g/cc and with diameter of 7.93 Å, heated at the temperature of 3500 K. (left-top view, right-side view). Red balls represent sp^3 hybridized carbon atoms, blue balls represent sp^2 hybridized carbon atoms, and white balls represent sp hybridized carbon atoms

The results of the simulation are in agreement with the experiment above, where the carbon film deposited using high bias (which locally creates a high temperature thermal spike) leads to formation of a-C into tubular nanostructures. Meanwhile, lower substrate bias which leads to lower spike temperatures results in formation of graphite like structures.

4.4 Summary and Conclusions

The effect of deposition ion energy (substrate bias) and deposition temperature on the microstructure of carbon films was studied in chapter 3. It was shown that both the deposition temperature and ion energy play a significant role on the formation as well as the nature of the nanostructures. Since it was shown that the plasma parameters are critical factors in controlling the microstructure of the films, in this chapter the effect of deposition plasma density was studied. Changing the deposition ion energy (through controlling the deposition substrate bias) controls the thermal spike temperature while changing the plasma density controls the spike density.

The summary of the effect of plasma energy and density can be found in Figure 4-16.

As it was expected, it was found that as well as the deposition ion energy, plasma density has also a significant effect on the microstructure of the films. Increasing the plasma density results in formation and stabilization of nanostructures at lower ion energies and room temperatures. This can be attributed to the higher density of the spikes formed during the growth. Besides, as it was found and discussed in chapter 3, at constant plasma density the nature of the

nanostructures formed is a function of the ion energy. At higher ion energies tubular nanostructures are formed while at lower biases planar structures are more favorable. This can be attributed to the higher stability of the tubular nanostructures at higher temperatures. The experimental results was confirmed by MD simulation which confirms the higher probability of formation of tubular nanostructures at higher temperatures.

Figure 4-16: Plan view HRTEM image of the carbon deposited at high plasma density and (A): 300, (B): 400 and (C) 500 V substrate bias.

The effect of the ion energy on the silicon/carbon interface was also studied. It was found that prior to formation of the nanocrystalline film, an amorphous layer is formed at the interface. The thickness of the amorphous layer decreases with increasing the substrate bias. The structure of the interface however, depends on the ion energy.

Chapter 5: Thermal and Electrical Conductivity of Textured Carbon Thin Films

5.1 Introduction

Graphite has among the highest (19.1 W/cm.K) thermal conductivity [147] in the direction parallel to the basal planes while possess four orders of magnitude lower conductivity in the perpendicular direction [148]. High thermal conductivity of crystalline forms of carbon such as graphite, diamond and carbon nanotubes is attributed to be due to the stiffness of the carbon bonds in these structures which results in high group velocity and Debye temperature (θ_D) and therefore reduction in the phonon-phonon scattering; Thus, high θ_D of diamond [149] (≈ 1880 K) and graphite in the basal planes [90] (≈ 2280 K) compare to that of metals, results in much higher thermal conductivity of these structures at room temperatures. Experimental and theoretical efforts have been focused to measure the thermal conductivity of carbeneous structures from that of amorphous carbon (a-C) to graphite and diamond by using different techniques [147, 150-152].

Formation of preferred orientation in the direction perpendicular to the substrate during graphitization of amorphous carbon films may result in an increase in the thermal conductivity of the carbon films. In this chapter we will study the effect of preferred orientation on the thermal conductivity of carbon films.

Moreover, formation of conductive channels (sp^2 bonded nanocrystals with preferred orientation) throughout the film thickness may results in enhancement of

electrical conduction of carbon films. In this chapter the electrical conductivity of amorphous and nanocrystalline carbon films will be studied.

5.2 Experimental

5.2.1 Thermal Conductivity Measurement

Pulsed photothermal reflectance (PPR) [153-155] technique was used to investigate the thermal conductivity of the films while TEM and EELS were used to study the microstructure of the films. The PPR technique is schematically shown in Figure 5-1. In this technique, the sample is first irradiated by a Nd:YAG laser pulse with full width at half maximum of 8 ns, spot size of 3 mm and pulse energy of 5 mJ as the heat pump. To enhance the heat absorption, a gold layer is deposited on the carbon film. The sample's surface temperature rises sharply and then relaxes with time. This phenomenon, gives rise to a temperature excursion profile that depends on the thermal properties of the underlying film and also the thermal resistance between the layers. As shown in Figure 5-2, the surface temperature change of the gold layer induces a change in the refractive index of the surface[156]. A continuous He–Ne laser (1 mW) beam is focused at the center of the pump spot to monitor the changes in the light reflection from the sample surface. Since the temperature and the reflectivity of gold are inversely related, the temperature excursion profile can be obtained by inverting the obtained signal.

The heat conduction problem can be considered as a one dimensional problem. The laser diffusion length can be estimated by $(2\sqrt{\alpha_{Au} \times \tau_{Exp}})$ where t_{exp} is the

duration to detect the surface temperature excursion, and $\alpha_{\text{Au}} = 127.3 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ is the thermal diffusivity of gold. Since the radius of the pump laser spot size is much bigger than the effective thermal diffusion length ($\sim 30 \text{ } \mu\text{m}$), the measurement can be completed before there is any significant lateral heat conduction and the heat conduction problem can be simplified to a one dimensional problem. Moreover, since the skin depth of the pump beam on the gold layer is smaller than the thickness of the gold layer, there will be no volume heating of the film and the heating is just due to heat transfer from the top gold layer to the carbon film.

Figure 5-1: Photothermal reflection experiment setup

Figure 5-2: Change in reflectivity of gold as a function of temperature

The temperature profile is fitted by a three-layer heat conduction model to obtain the thermal conductivity of the films. The heat diffusivity length in silicon ($2\sqrt{\alpha_{Si}\tau_{Exp}}$, where $\alpha_{Si}=89.21\times10^{-6} \text{ m}^2\text{s}^{-1}$ is the thermal diffusivity of silicon) can be estimated as $17.9 \text{ }\mu\text{m}$; Since the silicon thickness is much higher than $18 \text{ }\mu\text{m}$, the substrate can be modeled as an infinite medium. The surface temperature profile $T(s)$ can be described by [157]:

$$T(s) = \frac{Q(s)}{e_1\sqrt{s}} \left[\frac{(\cosh \eta_2\sqrt{s} + e_{32} \sinh \eta_2\sqrt{s}) \cosh \eta_1\sqrt{s} + (e_{31} \cosh \eta_2\sqrt{s} + e_{21} \sinh \eta_2\sqrt{s}) \sinh \eta_1\sqrt{s}}{(e_{31} \cosh \eta_2\sqrt{s} + e_{21} \sinh \eta_2\sqrt{s}) \cosh \eta_1\sqrt{s} + (\cosh \eta_2\sqrt{s} + e_{32} \sinh \eta_2\sqrt{s}) \sinh \eta_1\sqrt{s}} \right]$$

where $e_i = \sqrt{\rho_i C_i K_i}$, $e_{ij} = e_i/e_j$, $\eta_i = d_i/\sqrt{\alpha_i}$ and $i=1,2,3$. Subscripts 1, 2 and 3 stand for the gold, carbon and silicon respectively. ρ , C , K , e , α , and d are the bulk density, specific heat, thermal conductivity, thermal effusivity, thermal diffusivity,

and thickness of each layer respectively. $Q(s)$ is the Laplace transform of the Nd:YAG laser pulse, which can be described by:

$$Q(s) = \left[1 + \operatorname{erf} \left(\frac{b}{c} - \frac{cs}{2} \right) \right] \exp \left[-bs + \frac{1}{4} c^2 s^2 \right] \quad 5.2$$

where $b=2.0 \times 10^{-8}$ s and $c=4.36 \times 10^{-9}$ s are the fitted values to Nd:YAG pulse. In order to fit the temperature excursion profile, equation 5.1 is inversely Laplace transformed into the time domain using Stehfest numerical method [158]. The bulk density and specific heat of the gold layer are assumed to be 1.93×10^4 kg/m³ and 129 J/kg.K respectively. The fitting parameters are the thermal conductivity of the Au and the carbon films. The fitted K_{Au} should be about 218 W/mK.

5.2.2 Electrical conductivity measurements

Electrical conductivity measurements were performed using sandwich structures. 100 nm thick titanium was sputtered on a highly doped Si wafer as the back electrode. A square titanium top electrode of 1.27×10^{-3} mm² in area and 100 nm thickness was deposited on the carbon films using a shadow mask. Electrical measurement was carried out using a Keithley 236 sourcemeter at room temperature.

5.3 Results and Discussions

5.3.1 Thermal conductivity of amorphous and nanocrystalline carbon films

As it was discussed in chapters 2 and 3, either high temperature or high plasma deposition can be used to form carbon thin films with different microstructures. However, as it was shown in section 4.3.2, application of a high substrate bias at high plasma density results in formation of an interfacial layer at the Silicon\Carbon interface. The change in the interface composition may result in significant change in Kapitza boundary resistance which affects the PPR spectra significantly. Therefore, in order to maintain the interface the same for different microstructures, and solely study the thermal conductivity of the bulk of the film, we have used different deposition temperatures while the substrate bias was kept at 200V.

Figure 5-3 shows the HRTEM image of the carbon films deposited at 200 V substrate bias and different temperatures. The film deposited at 200⁰ C is purely amorphous and no crystallinity can be observed in the microstructure. On the other hand, preferred oriented nanocrystals are formed at 300 and 400⁰C deposited films.

Figure 5-3: HRTEM image of carbon films deposited at 200V substrate bias and (A): 200, (B): 300 and (C): 400°C. The insets show the respective diffraction patterns

Thermal conductivity of a-C films has been investigated by different groups and it was found that increase in density and hence the sp^3 content of the film increases the conductivity of the amorphous films; Therefore depending on the density of the film a conductivity of between 0.2 to 3.5 W/m.K can be achieved for pure a-C films [159]. Moreover, it was found that the presence of even very small nanocrystalline phase in the structure dramatically affects the heat conduction in both sp^3 and sp^2 rich structures. For instance, S. Ahmed et al. [160] found that the thermal conductivity of ultra nanocrystalline diamond (UNCD) with density and sp^3 content of slightly higher than pure sp^3 rich a-C film is enhanced to 26 W/m.K. It was also found that the presence of small sp^2 nanoclusters in sp^2 rich carbon films increases the conductivity significantly.[90]

Figure 5-4 shows the PPR spectra of the films and the thermal conductivities are tabulated in Table 5-1. The PPR spectra are fitted by equation 5.2 and the thermal conductivities are deduced. The room temperature deposited film possesses a very

low conductivity of 0.95 W/m.K. Figure 5-5 shows the Raman spectra of the carbon films deposited at 200V substrate bias and room temperature and 200°C. The Raman spectra of the room temperature deposited film can be fitted using a single BWF curve centered at 1542 cm^{-1} . The fact that no “D” peak is needed to fit the spectra shows that there is no clustering of sp^2 bonded atoms in the microstructure. The low conductivity is predictable considering pure amorphous structure of the film as well as low sp^3 content of the film.

Figure 5-4: PPR Spectra of carbon films deposited at 200V substrate bias and (A) room temperature, (B) 200°C, (C) 300°C and (D) 400°C.

Increasing the deposition temperature to 200⁰C leads to formation of conductive sp² clusters in the structure (as confirmed by the Raman spectra which is shown in Figure 5-5) which increases the conductivity to 3.2 W/m.K which is in accordance with Kelly's [90] predictions.

Table 5-1: Thermal Conductivity of carbon films deposited at 200V substrate bias and different temperatures

Deposition Temperature (°C)	Thermal Conductivity (W/m.K)
25	0.95
200	3.2
300	5.32
400	16.72

Figure 5-5: Raman spectra of carbon films deposited at 200V substrate bias and (A): room temperature and (B) 200⁰C. The gray curves are the original extracted data's. The red line show the fitted curve

Further increase in deposition temperature increases the thermal conductivity significantly. The 300 and 400⁰ C deposited films possess thermal conductivities of 5.32 and 16.72 W/m.K respectively. Increase in conductivity can be interpreted through formation of preferred orientation in the microstructure of the film. Klemens et al. [147] Show that thermal conductivity of bulk graphite in the basal plane is in the range of 1900 W/m.K which is about 100 times higher than the conductivity of the graphite in the direction perpendicular to the basal planes; therefore, it is believed that formation of a texture in (002) basal planes in the a-C matrix, results in significant change in the thermal properties of these films.

The increase in the conductivity of 400⁰ C deposited film compared to that of 300⁰C deposited can be understood by considering the high-loss EEL spectra of these two films. Figure 5-6 shows the high-loss and low-loss EEL spectra of the films. The $\pi \rightarrow \pi^*/\sigma \rightarrow \sigma^*$ ratio for the film deposited at 300⁰C is 0.58 while the same ratio for 400⁰C deposited film is 0.66. Increase in $\pi \rightarrow \pi^*/\sigma \rightarrow \sigma^*$ ratio shows that (002) planes are more ordered in the direction parallel to the electron beam (perpendicular to the substrate). Therefore, preferred orientation is enhanced in 400⁰C deposited film compare to that deposited at 300⁰C and therefore the thermal conductivity is enhanced.

Figure 5-6: (A): Low-loss and (B): High-loss EEL spectra of carbon films deposited at 200V substrate bias and different temperatures

5.3.2 Electrical conductivity of amorphous and nanocrystalline carbon films

As it was shown in chapter 4, nanocrystalline carbon film with different microstructures and interfaces can be developed by controlling the depositing ion energy and density at room temperature. In this section, the effect of formation of nanocrystals with preferred orientation on the electrical properties of the carbon films is studied.

Figure 5-7 shows the I-E characteristics of the carbon films deposited at different substrate biases and 12.5 mA/cm² plasma density. Figure 5-7 (d) shows the log of current density vs. square root of the electric field. As it is shown, the log of current density shows a linear relationship with the square root of the E. This suggests that the conduction mechanism can be described either by Schottky effect at the contact or bulk limited Poole-Frenkel transport mechanism.

Figure 5-7: I-E characteristics of carbon films deposited at (a): 100 & 200, (b) 300 and (c) 400 & 500 volts substrate bias. (d) Log of current density vs. square root of electric field for carbon films deposited at different substrate biases. (e) Log of electric fields vs. current density

To understand the transport mechanism, careful consideration of the bulk microstructure and the interface is needed. As shown in Figure 5-8 (and was shown and discussed in more detail in chapter 4), there is always an amorphous layer prior to formation of nanocrystalline layer. The thickness of the interfacial amorphous layer decreases with increasing the substrate bias. The carbon films deposited at 100 and 200 substrate bias are purely amorphous in structure while at higher deposition bias, preferred oriented nanocrystals are formed in the bulk of the film.

Figure 5-8: dark field TEM image of carbon films deposited at 12.5 mA/cm² plasma density and (A): 300, (B): 400 and (C): 500V substrate bias

As shown by Miyajima et al. [161] electrical transport in amorphous carbon films is bulk limited through Poole-Frenkel mechanism. Conduction in these films is through hopping of the carriers in conductive sp^2 bonded sites which are surrounded by sp^3 bonded matrix. Poole-Frenkel happens when the trapping sites of the band gap are positively charged when they are empty and neutral when they are occupied by the carrier [162]. The electron can only hop from one site to another when it has enough energy to overcome the Coulombic force of the

positively charged site behind. Obviously the conduction in this case strongly depends on the size and density of the conductive sites (in this case percentage and cluster size of sp^2 bonded atoms).

The carbon films deposited at 100 and 200V are amorphous in structure. However, Since the carbon film deposited at 200V has higher percentage of sp^2 bonded atoms, it is slightly more conductive than that deposited at 100V (Figure 5-7 e).

The bulk of the films deposited at 300, 400 and 500V substrate bias is formed from graphene sheets perpendicular to the substrate. Moreover, there is an interfacial a-C layer at the interface. Compared to the amorphous films deposited at 100 and 200V substrate bias, the presence of preferred oriented nanocrystals results in a noticeable increase in the conductivity of the films. The carbon films deposited at 400 and 500V bias show almost three orders of magnitude increase in the conductivity.

It should also be noted that compared to the 300V deposited film, the carbon films deposited at 400 and 500 V show slightly lower conductivity. This might be attributed to the difference in the structure of the film/substrate. The 300V deposited film shows a thicker a-C layer at the interface however due to lower depositing ion energy, the thickness of the intermixing layer is lower compare to that of the films deposited at 400 and 500V bias.

5.4 Summary and Conclusions

In this chapter, we have studied the effect of the microstructure of the films on the electrical and thermal conductivity of the carbon films. To study the effect of crystallization of the films on the electrical conductivity, the carbon films were deposited using high plasma density and different substrate biases. It was found that at low substrate biases (upto 200V) where the film is amorphous in the microstructure, the electrical conductivity of the film is three orders of magnitude lower than the nanocrystalline films which were deposited at high substrate biases. The conduction in the amorphous films is through hopping of the electrons between the conductive sp^2 clusters which are distributed among the insulative sp^3 matrix. Obviously, the size, amount and distribution of sp^2 clusters are the crucial factors governing the electrical conductivity of the amorphous films. formation of sp^2 bonded graphitic crystals with a preferred orientation in the perpendicular direction to the film surface, increases the conductivity significantly. Comparing to the amorphous films, the textured carbon films can be considered as a film with continuous sp^2 bonded medium. This in turn, increases the conductivity since the activation energy for hopping of electrons will be reduced if not eliminated. The experimental results show that formation of preferred oriented nanocrystals enhances the conductivity at least by three orders of magnitude.

Using PPR technique, the thermal conductivity of amorphous and nanocrystalline and films has also been studied in this chapter. Carbon films deposited at different substrate temperatures were used for this study. Amorphous carbon films have low

thermal conductivity in the range of 1 W/m.K which is in agreement with the previous results. Formation of conductive sp^2 clusters results in slight increase in the conductivity which can be assumed due to formation of graphitic clusters with very high conductivity. This has been also observed before in nanocrystalline diamond film where formation of nanometer sized diamond clusters with very high thermal conductivity results in noticeable increase in the conductivity. It should be noted that graphite possess a thermal conductivity of 19100 W/m.K which is five order of magnitudes higher than the amorphous films. The conduction in both of the crystalline diamond and graphite is through phonon conduction. Formation of preferred orientation in the microstructure of the carbon films, results in the formation of crystalline channels of sp^2 bonded graphite in the bulk of the film. This in turn increases the thermal conductivity of the films noticeably. As it was shown by increasing the ordering in the microstructure of the film, the thermal conductivity increases by one order of magnitude.

Chapter 6: Structure changes of carbon films by laser irradiation

6.1 Introduction

In chapter three it was shown that in situ and post annealing can be used to control the bonding structure and microstructure of the carbon films. These two techniques are suffering from high temperature nature of the process. On the fourth chapter it was shown that this problem can be tackled through controlling the plasma properties and different microstructures could be achieved through controlling the plasma density and depositing ion energies at room temperature. However, all the three techniques mentioned above can only be applied at large scales and local processing of the films is not possible. In this chapter, we will investigate the effect of laser irradiation on the structural changes of carbon films. Besides giving the ability to induce local phase transformation, the ability to control the annealing energy gives us the ability to study the energetics of the phase transformation as well.

To my knowledge, laser annealing of electronic materials goes back to 1979 where Liu et al. studied the laser irradiation of silicon [163]. Laser annealing and processing (such as nitriding) of different materials have then been widely investigated by different groups [164-166]. Despite very complex nature of the laser-material interaction which includes intricate physical phenomenon such as absorption, heating, melting, evaporation, recoil pressure [167], laser supported absorption waves [168] and Marangoni convection [169], laser irradiation of

materials can be considered as a powerful technique for local and fast treatment of materials. Through accurate control of the annealing energy, rapid amorphization and crystallization of different structures can be achieved and studied [170].

Laser irradiation of a-C films has been recently studied by Miyaji et al.[171]. Raman studies show that laser irradiation can be a very useful technique to control the bonding structure of the carbon films. Miyajima et al. have then shown that the electrical conductivity of the carbon films can be easily controlled through post laser irradiation of the films [172]; However, detailed microstructural changes of laser irradiated carbon films has not been investigated in yet. No solid data on crystallization of a-C films through laser irradiation has been reported so far. Moreover, the effect of initial bonding structure of the film has not been studied. These two issues will be studied in this chapter.

6.2 Experimental

Carbon films were prepared by FCVA using different substrate biases. 248 nm KrF Excimer-laser with pulse width of 23 nsec was used to irradiate the samples in ambient conditions. The laser spot was a square of 3 mm in length. The spatial energy distribution of the laser pulse was studied in a separate study [173] and it was shown that the laser has a uniform near-flat-top energy profile (Figure 6-1) . The samples were irradiated by one and multiple pulses.

The structure of the as deposited and laser irradiated films were studied by Raman spectroscopy, TEM and EELS.

Figure 6-1: Spatial distribution of the laser used for laser irradiation of carbon films [173]

6.3 Results and discussions

6.3.1 Raman spectroscopy

Figure 6-2 shows the Raman analysis of the single pulse laser irradiated carbon films deposited at 70V substrate bias and room temperature. As it is shown, the Raman spectra of the as deposited carbon film can be fitted by a single BWF curve located at 1542 cm^{-1} which shows the presence of about 50% sp^3 bonding in the structure. Irradiation of the films with energies of upto 206 mJ/cm^2 doesn't change the bonding structure significantly as shown by the Raman spectrum. Higher energy laser irradiation (302 mJ/cm^2) on the other hand shifts the position of the G peak to 1534 cm^{-1} . It is noticeable that the Raman spectra can still be fitted by a single BWF band and no D band is required to fit the spectra. This shows that although the sp^3 content of the film is decreased to about 42% the film is still purely amorphous in structure and no clusters are formed in the microstructure.

Increasing the laser energy to 362 mJ/cm^2 increases the G peak position to 1553 cm^{-1} . Besides, the Raman spectra cannot be fitted by a single BWF band and a D peak is also required to fit the spectrum. The I_D/I_G ratio of 0.34 shows the sp^2 cluster size of about $8 \text{ \AA}$. Increase in laser energy increases both the position of the G peak and the I_D/I_G which shows an increase in both the sp^2 content of the film as well as the average size of the sp^2 clusters.

Figure 6-2: Raman Analysis of laser irradiated carbon films deposited at 70V substrate bias and room temperature

Figure 6-3 shows the Raman spectroscopy analysis of laser irradiated carbon films deposited at 100V and room temperature. The as deposited film can be fitted by a single BWF peak located at 1553 cm^{-1} . This shows that the film consists of about 60% sp^3 bonding and no distinct sp^2 clusters are formed in the microstructure. Low energy laser irradiation (upto 283 mJ/cm^2) increases the position of the G peak to 1556 cm^{-1} while the curve can still be fitted by a single BWF peak and no D band is required to fit the spectrum. This shows that the sp^3 content of the film has slightly

increased by laser irradiation. Besides, the sp^3 bonding is stable at energies lower than 368 mJ/cm^2 . As it can be observed, at laser energies lower than 368 mJ/cm^2 the sp^3 content of the film doesn't change significantly and no distinct clustering occurs.

Figure 6-3: Raman Analysis of laser irradiated carbon films deposited at 100V substrate bias and room temperature

Figure 6-4 shows the Raman spectra of the as deposited and laser irradiated carbon films deposited at 300V substrate bias. The as deposited film can be fitted by a single G band centered at 1536 cm^{-1} which shows the presence of about 44% sp^3 bonded atoms. Besides, no sp^2 clustering is present in the microstructure. Irradiation of the film with laser energies of upto 160 mJ/cm^2 slightly shifts the G band center to lower wavenumbers which shows an slight decrease in the sp^3 content of the film. Further increase in the laser energy on the other hand, results in dramatic decrease in the sp^3 content of the film while sp^2 clusters will also be

formed in the microstructure. Increasing the laser energy in this region increases the I_D/I_G which shows an increase in the in-plane sp^2 cluster size. Detailed structural changes of 300V deposited films is presented in the next section.

Figure 6-4: Raman Analysis of laser irradiated carbon films deposited at 300V substrate bias and room temperature

Figure 6-5 shows the Raman analysis of laser irradiated carbon films deposited at 700V substrate bias. The as deposited film cannot be fitted by a single BWF peak and a Lorentzian peak as D band is also needed to fit the spectrum. The I_D/I_G of 0.29 shows the sp^2 clusters of about 7 Å in diameter.

Figure 6-5: Raman Analysis of laser irradiated carbon films deposited at 700V substrate bias and room temperature

Laser irradiation decreases the sp^3 content of the film while the sp^2 cluster size is increased.

Comparing the results presented above, we note that laser irradiation in general results in decrease in sp^3 hybridization and formation of sp^2 clusters in the microstructure of the film. However, it should also be noted that the behavior of the film strongly depends on the initial bonding structure of the film. sp^3 bonding is more stable in carbon films consisting of higher initial sp^3 bonding. On the other hand, the carbon film deposited at 700V bias shows a noticeable change at both sp^3 bonding and size of the sp^2 clusters even at low laser energies.

6.3.2 TEM and EELS characterization of laser irradiated carbon films

Cross section TEM and EELS were used to study the microstructure and bonding structure of the as-deposited and laser irradiated carbon films deposited at 300V substrate bias, respectively. As shown in Figure 6-6 (A) the as deposited film is

purely amorphous and no crystallinity can be observed in the microstructure. The low loss EEL spectrum shows the bulk plasmon peak at 28.1 eV. The mass density can be derived from the valance electron density “ n_e ” by assuming that the film is hydrogen and nitrogen free and also each carbon atom contributes four valance electrons [130]:

$$\rho = \frac{3\epsilon_0 M_C m^* E_p^2}{12\hbar^2 N_A e^2} \quad 2.1$$

The mass density will then be estimated to be 2.49 g/cm³. It should be noted that no π Plasmon peak (4.5 to 5.5 eV) can be observed in the low-loss spectrum which confirms that there is no ordering of π bonds in the microstructure [174]. The high-loss spectrum on the other hand, shows a sharp π - π^* transition at 285 and a broad σ - σ^* transition at 285-315 eV intervals. The sp^2 content of the film can then be determined by comparing the high loss spectra of the film with that of glassy carbon acquired at the same condition [175]:

$$sp^2 = \frac{\left[\frac{area(\pi^*)}{area(\pi^* + \sigma^*)} \right]_{sample}}{\left[\frac{area(\pi^*)}{area(\pi^* + \sigma^*)} \right]_{100\% sp^2 reference}} \quad 3.1$$

Figure 6-6: (A): HRTEM image, (B) Low-loss and (C) High-loss EEL spectra of carbon film deposited at 300V substrate bias and room temperature

Figure 6-7 shows the low-loss and high-loss EEL spectra of the glassy carbon acquired at the same conditions as the EELS spectra of the carbon films has been acquired. Comparing the relative areas under the $\pi-\pi^*$ and $\sigma-\sigma^*$ it can be deduced that the film consists of 56% sp^3 hybridization which is slightly higher than that predicted by the Raman results.

Figure 6-7: (A) Low-loss and (B) high-loss EEL spectra of glassy carbon

Figure 6-8 (A) shows the HRTEM image and the diffraction pattern (inset) of the carbon film irradiated at 362.5 mJ/cm^2 . As it can be seen, very small sp^2 clusters in the range of 1 nm (shown by the ellipses) can be observed in the image which is in agreement with the Raman spectrum. On the other hand, the diffraction pattern shows a unique feature. Beside the presence of diffused ring which is due to the presence of the amorphous matrix phase, two dim arcs (shown by the arrows) can also be observed. The arcs are indexed to be due to the diffraction of (002) graphitic basal planes as it is also observed in the HRTEM image. However the most important point is that the (002) ring is not continuous and just two distinct arcs are observed indicating the presence of a preferred orientation in the sp^2 clusters. Figure 6-8 (B) shows the low-loss EEL spectrum of the carbon film irradiated at 362.5 mJ/cm^2 . Besides the bulk Plasmon peak located at 25.1 eV, a shoulder at 5 eV can also be observed which is related to π Plasmon excitation [24].

The presence of this shoulder shows the nucleation of short range order in the sp^2 bonded atoms which is in agreement with the TEM and Raman results.

Figure 6-8: (A): HRTEM image, (B) Low-loss and (C) High-loss EEL spectra of carbon film deposited at 300V substrate bias and room temperature and irradiated at 362 mJ/cm²

Figure 6-9 (A&B) show the HRTEM image of the carbon film irradiated by 462.5 mJ/cm² excimer laser. As it is shown in the diffraction pattern, the arcs related to (002) diffraction are enhanced as compared to the 362.5 mJ/cm² irradiated which shows that the crystallinity has increased in this film. More importantly the radial

distribution of the arcs is smaller compared to the 362.5 mJ/cm^2 irradiated diffraction pattern, which shows that the degree of preferred orientation is enhanced by higher energy irradiation. As it is shown in the higher magnification image, the preferred orientation in this case is distributed uniformly throughout the whole thickness of the film.

Figure 6-9: (A&B) HRTEM images, (C) Low-loss and (D) High-loss EELS of carbon films deposited at 300 V and irradiated by 462.5 mJ/cm^2 laser

Figure 6-9 (C&D) shows the low-loss and high-loss EEL spectra of the film irradiated at 462.5 mJ/cm². As it is shown, the π Plasmon peak at 5 eV is obviously enhanced which is an evidence of ordering of π bonds in the microstructure of the film. Moreover, the high-loss doesn't show Gaussian profile and a peak at about 290 eV can be observed which confirms the presence of nanocrystalline carbon in the microstructure.

As it was shown in this chapter, single pulsed laser irradiation is a fast, easy and local method to control the bonding and microstructure of carbon films. Formation of nanostructures has significant effects on field emission properties of carbon films. In the next chapter the effect of laser induced nanocrystals on the field emission properties of carbon films will be studied.

6.4 Summary and Conclusions

In this chapter, structural changes of the carbon films upon irradiation of a single pulse of 248 nm excimer laser have been studied. Carbon films with different initial bonding hybridizations were irradiated with different energies and the structural changes were monitored by Raman spectroscopy, TEM and EELS. In general, similar to thermal annealing laser irradiation also results in transformation of sp^3 hybridization to more stable sp^2 bonding. However, the initial bonding

structure has a significant effect on the degree of stability of the sp^3 hybridization. The sp^3 hybridization is more stable in carbon films with higher initial sp^3 bonding. This is in agreement with thermal annealing experiments which show that ta-C films are stable at temperatures as high as 1100°C while high sp^2 bonded films goes sp^3 to sp^2 transformation at temperatures as low as 300°C . Besides our TEM and EELS studies show that high energy laser irradiation (higher than 486 mJ/cm^2) results in formation of preferred orientation in the microstructure of the films.

Chapter 7: Field Emission of Laser irradiated carbon films

7.1 Introduction

In the previous chapter it was shown that laser irradiation is a powerful technique to control the bonding structure as well as the microstructure of the carbon thin films. In this chapter we will study different factors governing the field emission from amorphous and laser treated carbon films.

Electron field emission (FE) from a-C films [176] is widely investigated in the past few years due to its outstanding emission properties such as low macroscopic emission field [177-178]. Much effort has been concentrated to reduce the threshold field (F_{th}) at which the electron emission occurs [179]. In addition, the mechanisms responsible for the easy emission of a-C films as well as all other carboneous materials are also of great interest [180-182].

As it was shown, electronic properties of a-C films strongly depend on the sp^2 content of the film as well as the presence, size and distribution of sp^2 bonded clusters within the sp^3 matrix. For instance, the electrical conductivity of a-C films is governed through the hopping of electrons between the conductive sp^2 clusters and hence depends on the microstructure and orientation of the sp^2 bonded atoms [183]. These unique sp^2 clusters will also provide a local field enhancement mechanism which results in electron emission at very low macroscopic fields.

It is believed that the sp^2 bonded atoms are the emission sites in a-C films [184] as it is also the case in CVD grown nanocrystalline diamond films where the emission is found to be from sp^2 bonded atoms at the grain boundaries [185]. Although the sp^3 content of the film governs the band structure of undoped a-C films, it was found that the change in sp^3 content and hence the band gap, does not affect the work function of the film which remains in the range of 4-5 eV [186]. It was also found that in the case of pure a-C films, the emission properties are independent of the film thickness [187]. Therefore, despite other systems, the bulk properties of the carbon film are not the crucial factors that govern the easy emission in a-C films as it is also not the case in all other carbon structures such as diamond, graphite and CNTs [188].

Robertson et al. [181] found that for different types (undoped, hydrogenated and nitrogenated) of a-C films, there is an optimum sp^2 cluster size in which the film shows the lowest threshold field. Therefore, it was deduced that the microstructure of the sp^2 bonded atoms plays an important role in the emission mechanism.

Carey et al. [183] proposed a mechanism for large field enhancement in carbon film which is responsible for emission at low macroscopic fields. The presence of a conductive sphere embedded in an insulating matrix leads to small field enhancement. However, the presence of two or more such spheres can further increase the enhancement; For instance, the field enhancement of two conductive spheres in the bispherical coordination system was studied and it was found that the presence of two gold spheres which are placed five nanometers apart from each other results in enhancements of 56 which can be increased to 400 for a 1 nm

separation [189]. Carey et al. showed that in the case of a-C films, the presence of conductive sp^2 clusters within the sp^3 matrix plays a very important role in the local field enhancement near the sp^2 sites which leads to FE at low macroscopic fields. This phenomenon is schematically shown in Figure 7-1.

Figure 7-1: : Schematic representation of FE from carbon film. The film is formed from sp^2 nanoclusters (yellow spheres) embedded in insulating sp^3 bonded matrix.

Based on this model, different methods such as thermal annealing [180], nitrogen doping [178] and incorporation of metallic nanoparticles in the microstructure of the film [190] have been used to improve FE properties of carbon films.

Besides the above mentioned methods, as it was also shown in the previous chapter laser irradiation can be widely used to modify the structure and hence electrical properties of the carbon films. Miyajima et al.[191] found that UV laser irradiation increases the conductivity of carbon films through formation of sp^2 bonded nanocrystals. Besides a-C, laser irradiation has been widely used to control the microstructure and field emission properties of CNTs as well. Li et al. [192] found

that laser irradiation of CNTs results in decrease in threshold field and significant increase in the emission current density. It is believed that photon bombardment induced degeneration of graphite structure is the key mechanism in emission enhancement in the laser treated CNTs.

Laser irradiation has also been used to modify the microstructure and hence the emission properties of amorphous silicon (a-Si) film [193]. It was shown that besides the morphological changes, laser irradiation leads to formation of columnar nanocrystals which are thought to be the enhancement factor for easy emission of a-Si films.

Here, we will study the field emission properties of single pulse laser irradiated a-C films. The change in field emission properties will be discussed with respect to change in the bonding and microstructure of the films which was studied in detail in the previous chapter.

7.2 Experimental

a-C films deposited at 300V substrate bias were used in this study. The films were deposited on antimony doped (100) silicon wafers with resistivity of 0.01 Ω .cm. To eliminate possible effect of film thickness on FE properties, all the samples which were used in this study were deposited in one deposition and then were cut into smaller square pieces of 3mm in length. The thickness of the films was measured to be 150 nm using a surface profiler.

248 nm KrF Excimer-laser with pulse width of 23 nsec was used to irradiate the samples in ambient conditions. The laser spot was a square of 3 mm in length.

Details of the laser treatment can be found in chapter 6.

FE was tested in a parallel plate configuration with an indium tin oxide (ITO) coated glass as the cathode, with anode-cathode spacing of 100 μm in a pressure lower than 5×10^{-6} Torr. In order to check the repeatability of the data, two samples were annealed at each laser energy. FE tests have been done on two different positions of every individual sample. More than ten measurements have been done on each test spot.

7.3 Results and discussion

7.3.1 Field emission from single pulse laser irradiated carbon films

The laser induced structural changes of carbon films deposited at 300V substrate bias was studied in detail in the previous chapter. As a reminder, the Raman spectra of the as deposited and laser irradiated films are also shown in Figure 7-2. The as deposited spectrum can be fitted by a single BWF curve located at 1537 nm^{-1} . The fact that the spectrum can be fitted by only a single G peak reveals that the film is purely amorphous in structure with no short range order in the microstructure [194].

Figure 7-2: Raman spectra of the as deposited and laser irradiated carbon films. (B): G peak position and ID/IG ratio and

Figure 7-3 shows the FE spectra of the as deposited and laser irradiated carbon films. The field at which the respective current density is $20 \mu\text{A/cm}^2$ is taken to be the F_{th} in this study. As it is also shown in Figure 7-3(B), the F_{th} for the as deposited film is $12 \text{ V}/\mu\text{m}$. Figure 7-3(B) shows the variation of F_{th} as a function of laser energy. Three distinct regions can be observed in this figure. At the first region where the film is irradiated by low laser energy, (up to 117 mJ/cm^2) the F_{th} decreases from 11 to $6 \text{ V}/\mu\text{m}$. In the second region, ($117 - 362.5 \text{ mJ/cm}^2$) F_{th} increases from 6 to 9.4 mJ/cm^2 . Irradiating the film by a single pulse of 472.5 and

510 mJ/cm² however, leads to a very sharp decrease in the F_{th} . The F_{th} in this region is decreased to 4.4 V/μm.

Figure 7-3: FE from as deposited and laser irradiated carbon film and (B) the variation of F_{th} as a function of laser energy

The Raman spectra (Figure 7-2) show that, the decrease in F_{th} in the first region is due to the formation and growth of sp^2 clusters in the amorphous sp^3 matrix. The curve cannot be fitted by a single G peak and a second D peak is needed to fit the original spectrum. The I_D / I_G increase indicates that the sp^2 cluster size is increasing. The sp^2 cluster size in this region can be determined by [194]:

$$I_D/I_G = C'_\lambda L_a^2$$

Where C'_{514} is 0.0055 and L_a is the sp^2 cluster size. Our curve fitting shows that the sp^2 cluster size in this region increases to about 4 Å. As the laser energy increases, the cluster size will also increase.

In the second region, the cluster size increases from about 4 to 14 Å. As it was shown by the HRTEM study of the carbon films irradiated by a single pulse of

362.5 mJ/cm², very small sp² clusters in the range of 1 nm (shown by the ellipses) can be observed in the image (Figure 6-8) which is in agreement with the Raman spectrum.

The larger cluster size increases the ability to carry emission current but on the other hand decreases the field enhancement. Hence, the critical diameter of the cluster for easy FE is a tradeoff between these two parameters. Therefore, in the second region although the film conductivity increases, the F_{th} will also increase which is due to the lower structural field enhancement. This observation is in agreements with previous work of Ilie et al. [181]

The samples irradiated using 462.5 and 510 mJ/cm² on the other hand show a significant decrease in F_{th} . As it is shown in Figure 7-2, the in-plane sp² cluster size increases to about 15 Å but the F_{th} has sharply decreased from 9 to 5.1 V/μm which suggest that there should be another mechanism activated by high energy laser irradiation.

Figure 7-4: Fowler-Nordheim plots for FE from laser irradiated carbon films

Figure 7-4 shows the Fowler-Nordheim plot of the emitted current using simplified F-N equation [195]:

$$J = aV^2 \exp\left(-\frac{b \times \phi^{3/2}}{\beta E}\right)$$

Where ϕ is the barrier height, E is the field, β is the dimensionless field enhancement factor and b is a constant ($b=6.8 \times 10^9 \text{ eV}^{-3/2} \text{ Vm}^{-1}$). All F-N plots show a linear relation which confirms that the emission obeys the F-N equation.

Moreover, the slope of the F-N curve (which is proportional to $\phi^{3/2}/\beta$) decreased from 91.2 for the sample irradiated at 44.5 mJ/cm^2 to 70.9 for the samples irradiated at 160 mJ/cm^2 which as discussed above shows an increase in field enhancement factor (β) due to the formation of sub-nano sp^2 clusters in the first region (assuming that sp^2 bonded phase is the emission site and hence the work function is the same for all the samples). The slope has increased to 99.7 for the

sample irradiated at 362.5 mJ/cm^2 which shows a decrease in the β due to further increase in the cluster size. However, the slope of the F-N plot for the sample irradiated at 462.5 mJ/cm^2 has decreased to 39.7 which shows a significant increase in the field enhancement factor.

The microstructure of the film irradiated by 462.5 mJ/cm^2 laser energy has been studied in detail in the previous chapter (Figure 6-9). As it is shown in the diffraction pattern, the arcs related to (002) reflections are enhanced compared to the 362.5 mJ/cm^2 irradiated which shows that the crystallinity has increased in this film. More importantly the radial distribution of the arcs is smaller compare to the 362.5 mJ/cm^2 irradiated diffraction pattern, which shows that the degree of preferred orientation is enhanced by higher energy irradiation. As it is shown in the higher magnification image, the preferred orientation in this case is distributed uniformly throughout the whole thickness of the film. The formation and propagation of preferred orientation in the film leads to formation of sp^2 bonded filaments throughout the film.

Formation of preferred orientation in the microstructure of the film, leads to formation of conductive sp^2 channels in the entire cross section of the film. In this case, two different field enhancement mechanisms will be activated. As it is schematically shown in Figure 7-5, preferred orientation in this case leads to formation of emitting sp^2 filaments perpendicular to the substrate and hence in the emitting direction. Therefore, beside the presence of a conductive phase embedded in an insulating matrix which enhances the field, the formation of sp^2 filaments with large aspect ratio activates a new field enhancement mechanism. Field

enhancement due to a filament of length h and diameter r can be approximated as h/r . [196] Assuming h to be the thickness of the film and r the average diameter of the channels which can be estimated from the Raman spectrum, another field enhancement factor with an enhancement factor of 100 is activated which results in sharp decrease in the threshold field as it is shown in Figure 7-3. Field emission enhancement in this case, depends on the average diameter of the channels and also the length of the channels which can be assumed as the thickness of the film. Further increase in laser energy leads to further promotion of preferred orientation and hence the average diameter of the channels and hence reduces the field enhancement from its optimum amounts as it is also the case in the sample irradiated at 510 mJ / cm^2 which then leads to a slight increase in threshold field.

Figure 7-5: Schematic presentation of conductive sp^2 channels in insulating sp^3 matrix formed due to high energy laser irradiation

7.3.2 Thickness dependency of field emission in amorphous, nanocrystalline and textured carbon films

As it was mentioned before, Carey et al. [182] suggest that the emission occurs from the surface sp^2 clusters. Based on this theory, emission should be independent of the film thickness. However, Thickness dependence of emission has been studied by different groups and distinct noticeable results have been achieved. Forrest et al. [197] studied the effect of different parameters including film thickness on field emission of pure, nitrogenated and hydrogenated carbon thin films. As it is shown in Figure 7-6 they found an optimum thickness for the lowest F_{th} in the hydrogenated and nitrogenated carbon films.

Figure 7-6: Variation of threshold emission field as a function of film thickness for nitrogenated and hydrogenated carbon films[197]

Obviously, the classical F-N mechanism cannot be used to describe the thickness dependency of the emission in these films. No obvious thickness dependent field enhancement mechanism can be discussed. Moreover, there is no theoretical

relation between the film thickness and the work function of the films. In a separate study Robertson [198] discussed the possible effect of non-uniform surface hydrogen termination on emission properties of carbon films. This mechanism is also unable to describe the thickness dependency of emission from these films since there is no logic dependence of surface termination and film thickness.

The only mechanism which can be used to describe the thickness dependency of field emission is space-charge induced interlayer band bending for semiconductors [199]. Carrier depletion across the film thickness results in field enhancement at the Si/C interface; therefore, the electrons will be emitted from the conduction band of the silicon substrate to highly curved conduction band of the film. As it is shown in Figure 7-7, at very thin samples, although the emitted electrons possess very high energies but they still cannot overcome the emission barrier (the work function of the film). At very thick samples on the other hand, the electrons will lose energy while they are passing the film and hence they cannot overcome the emission barrier. Therefore there is an optimum film thickness at which the emission occurs at lowest possible field.

Figure 7-7: Schematic representation of space-charge induced bandbending mechanism for emission of carbon films [200]

It is noticeable that Forrest et al. did not report on thickness dependency of pure carbon films. In another study, Zhao et al. [201] studied the thickness dependency of the field emission of pure a-C films. As shown in Figure 7-8, they found that for pure a-C films deposited at 200V substrate bias, the F_{th} doesn't strongly depend on the film thickness. By challenging the space-charge interlayer induced band bending model proposed by Forrest, they suggest that the F-N tunneling theory is the most suitable model to describe the emission from a-C films.

Figure 7-8: Effect of thickness on field threshold electric field of amorphous carbon films [202]

The model proposed by Carey et al. on the effect of (sub)nano sp^2 clusters can be used to explain the high field enhancement in amorphous films. According to this mechanism, the emission is supposed to be thickness independent.

It is worth mentioning that in the work of Zhao et al. [201] they have only examined a carbon films deposited at 200V. Although they haven't present any information regarding the structure on the film, application of such a bias should result in a purely amorphous film (without any considerable sp^2 clustering) with moderate amount of sp^3 bonds.

Here, we will first study the thickness dependency of emission on a wide range of a-c films (with different bonding structures and microstructures). More importantly, we will study the thickness dependency of field emission in high energy laser treated carbon films. As we have shown before, in high energy irradiated films continuous sp^2 channels will be formed throughout the thickness of the films which

act as a high aspect ratio conductive element and hence decreases the threshold field.

Figure 7-9: Thickness dependency of field emission and Raman spectra of carbon films deposited at (A&B): 100V, (C&D): 1000V and (E&F): 2000V

Figure 7-9 shows the Raman spectra and thickness dependency of field emission from three different a-C films. The first film is a ta-C film deposited at 100V substrate bias. As it can be deduced from the Raman spectra (Figure 7-9(B)) which can be fitted by a single BWF peak located at 1560 cm^{-1} , the sp^3 content of the film can be estimated to be about 75%. Moreover there is no sp^2 clusters formed in the microstructure. As it is shown, (Figure 7-9(A)) there is no distinct relation between the film thickness and emission threshold field. Increasing the substrate bias to 1000V, increases the sp^2 content of the film to 60% (Figure 7-9(D)). However, since the Raman spectra can still be fitted by a single BWF curve located at 1531 cm^{-1} , no clustering of sp^2 bonded atoms is formed in the microstructure. As it is shown in Figure 7-9(C) the emission from this film is still independent of the thickness. However, it is noticeable that increase in sp^2 content of the film decreases the F_{th} dramatically. Increasing the deposition bias to 2000V on the other hand results in formation of sp^2 clusters in the size of about one nanometer in diameter. The Raman spectra can be fitted by a G band centered at 1542 cm^{-1} and a D band with $I_{\text{D}}/I_{\text{G}}$ of 0.35. As it can be observed, similar to previous purely amorphous films, there is still no correlation between the film thickness and F_{th} .

Figure 7-10 on the other hand shows the evolution of F_{th} of 460 mJ/cm^2 single pulsed laser irradiated carbon film as a function of film thickness. Despite the amorphous films there is a direct relation between the film thickness and the F_{th} . Carbon film of 25 nm thick shows high F_{th} of about $12\text{ V}/\mu\text{m}$. Increasing the film thickness to 150 nm decreases the F_{th} to about $4\text{ V}/\mu\text{m}$. Further increase in film thickness (250 nm) doesn't alter the emission threshold significantly.

Figure 7-10: (A): Thickness dependency of field emission of carbon film deposited by a single pulse of 460 mJ/cm² and (B): respective Raman spectra of the film

As shown before, high energy laser irradiation results in formation of conductive channels throughout the thickness of the film which decreases the threshold field through formation of large aspect ratio filaments. Increasing the film thickness increases the aspect ratio of the filaments and as it is shown in Figure 7-10(A) the F_{th} decreases. The film shows its lowest threshold field at about 150 nm. However further increase in film thickness doesn't affect the F_{th} . As it was shown by the TEM analysis in chapter 6, even at 150 nm thick film, the filaments are not uniform in the film thickness. Therefore, further increase in the film thickness doesn't affect the average diameter of the filaments and hence has no significant effect on the threshold field.

7.4 Summary and Conclusions

Field emission from amorphous and nanocrystalline carbon films has been studied in this chapter. It is shown that formation of preferred oriented nanocrystals results in significant decrease in the threshold emission field. This is discussed through activation of two simultaneous field enhancement mechanisms. These two mechanisms are namely the formation of high aspect ratio conductive filaments as well as the presence of a conductive phase embedded in an insulative matrix. Thickness dependency of field emission in amorphous, nanocrystalline and carbon films with preferred orientation has also been studied in this chapter. It is shown that in amorphous and nanocrystalline carbon films the emission is independent of the film thickness while in preferred oriented nanocrystalline films the emission strongly depends on the film thickness. This observation suggests that the formation of nanocrystals with preferred orientation leads to further field enhancement on the emitting sp^2 sites and in turn further reduces the threshold field.

Chapter 8: Summary, Conclusions and Recommendations for future Research

8.1 Summary and Conclusions

Fabrication of nanostructured carbon thin films as well as the effect of crystallization on the field emission and the electrical and thermal conductivity of the carbon films have been studied. It was shown that by controlling the deposition parameters namely the deposition temperature and bias the microstructure of the carbon films can be controlled. At low substrate temperature (150°C) and low substrate biases (lower than 400V) the films will be amorphous in the microstructure. Increase in the substrate bias increases the sp^2 content of the film. Increasing the substrate bias to 600°V results in the formation of preferred oriented graphitic nanoclusters. The formation of graphitic nanocrystals by increasing the substrate bias is attributed to the formation of high temperatures thermal spikes due to impinging of the high energy ions to the growing film. At temperatures higher than 400°C and regardless of the deposition substrate bias preferred oriented nanocrystals will be formed in the microstructure of the film. Plan view TEM shows that at constant temperature, the microstructure of the nanocrystals strongly depends on the substrate bias during the deposition. Increasing the substrate bias results in stabilization of tubular nanostructures rather than graphene based nanostructures. This is attributed to higher formation energy of tubular nanostructures compare to graphene based sheet nanostructures. This finding

clearly shows the effect of impinging ion energy on the microstructure of the film which was studied in the fourth chapter.

The effect of deposition ion energy and the plasma density on the microstructure of the carbon films were studied in chapter four. It was shown that nanocrystalline carbon films can be achieved at room temperature and only through controlling the deposition plasma density. It is discussed that the presence of high temperature thermal spikes due to high energy impinging ions results in formation of nanocrystalline films at room temperatures and substrate biases as low as 300V. Similar to high temperature deposition, the structure of the nanocrystals depends on the thermal spike temperature which itself can be controlled through controlling the deposition ion energy and hence the substrate bias. It has also been shown the Si/C interface strongly depends on the impinging ion energies. At low substrate biases (lower than 400 V) there will be a sharp interface at the Si/C interface; However increasing the substrate bias results in the formation of an interfacial SiC layer at the interface. The thickness and the exact composition of the interfacial layer depend on the deposition substrate bias. The penetration depth and the formation of interfacial layers are attributed to the energy level of the impinging ions. Higher ion energy results in higher penetration depth and also formation of carbide at the interface while low energy deposition results in formation of a sharp interface

In the fifth chapter we have studied the effect of the microstructure of the films on the electrical and thermal conductivity of the carbon films. Carbon films deposited at high plasma density but low substrate biases are amorphous in the microstructure. Conduction in these films is limited through Poole-Frenkel mechanism. Electrical

conduction in these films is achieved through hopping of the electrons between conductive sp^2 nanoclusters. On the other hand, at higher substrate biases, the formation of preferred oriented nanocrystals changes the conductivity dramatically. Formation of continuous conductive sp^2 bonded filaments results in increase in the electrical conductivity of the films by three orders of magnitude.

Thermal conductivity of amorphous and nanocrystalline films has also been studied in chapter five. It is shown that the formation of sp^2 bonded nanocrystals increases the conductivity compare to that of amorphous films. Besides, the formation of preferred orientation in the microstructure of the film results in formation of highly conductive graphene sheets in the direction perpendicular to the substrate. This in turn, increases the conductivity significantly. Further increase in the ordering of basal planes increases the conductivity considerably. Noticeable Increase in the thermal conductivity of the films by the formation of preferred oriented nanocrystals can be attributed to enhancement of phonon transfer due to formation of graphitic based nanocrystals in the direction perpendicular to the substrate.

In the sixth chapter, structural changes of carbon films upon irradiation of a single pulse of 248 nm Excimer laser have been studied. As shown by Raman spectroscopy, TEM and EELS, low energy laser irradiation results in transformation of sp^3 to sp^2 bonded atoms and formation of sp^2 (sub) nanocrystals embedded in the amorphous matrix. Further increase in laser energy on the other hand results in formation of nanocrystals with preferred orientation throughout the thickness of the film. Besides, it was also found that the stability of the carbon films upon laser irradiation is a function of the initial structure of the carbon films.

Carbon films with higher initial sp^3 hybridization and density are more stable against laser irradiation.

Field emission from amorphous and nanocrystalline carbon films has been studied in chapter seven. It is shown that the formation of preferred oriented nanocrystals results in significant decrease in the threshold emission field. This is discussed through activation of two simultaneous field enhancement mechanisms. These two mechanisms are namely the formation of high aspect ratio conductive filaments as well as the presence of a conductive phase embedded in an insulative matrix. Thickness dependency of field emission in amorphous, nanocrystalline and carbon films with preferred orientation has also been studied in this chapter. It is shown that in the amorphous and nanocrystalline carbon films the emission is independent of the film thickness while in the preferred oriented nanocrystalline films the emission strongly depends on the film thickness. This further proves that the formation of preferred oriented nanocrystals results in activation of a second field enhancement mechanism due to formation of high aspect ratio graphitic filaments.

8.2 Recommendations for Future Works

In chapter three we have studied the effect of deposition temperature and bias on the microstructure of carbon films. It was found that by controlling the deposition conditions different nanostructures could be achieved and stabilized. The formation of these nanostructures may have considerable effects on electrical properties of carbon films which need to be studied in detail.

As it was shown in the fourth chapter, different nanocrystals can be stabilized through controlling the deposition parameters at room temperature. However, it was shown that the composition and the structure of the interface strongly depend on the deposition ion energy. Besides, in chapter five it was shown that electrical properties of these nanostructured films strongly depends on the interface. Post treatments such as thermal annealing can be used to engineer the interface and hence the properties of carbon films. This issue needs to be studied in more detail.

Through plane thermal conductivity of different carbon films has been studied in the fifth chapter. However, beside through plane thermal conductivity other thermal properties of carbon films such in in-plane thermal conductivity, thermal diffusivity and specific heat of these films need to be studied in more detail. To do this, other techniques (such as 3ω and thermal transient grating (TTG)) need to be used to extract the above mentioned thermal properties.

The main focus of this thesis was on fabrication and properties of pure nanocrystalline carbon thin films. However, doping and incorporation of other elements such as metallic elements and the effect of these doping is another interesting point of study. Composite targets have been used before to fabricate composite thin films. However, different sputtering yield of the elements results in non-uniformity of the films. To overcome this problem we suggest the application of double source to fabricate composite films. As shown in Figure 8-, by controlling the plasma parameters, different types of metal/carbon composites and multilayers can be fabricated and studied

Figure 8-: HRTEM image of Ni/C composite thin film fabricated by Y-bend double source FCVA

Besides thermal and laser annealing used in this study, other methods can also be used to control the microstructure of carbon films. For instance, our group has recently demonstrated high electric field induced phase transformation in carbon films [203]. However, microstructural changes of carbon films upon electric field breakdown needs to be studied in more detail. This finding is of particular interest for applications such as phase shift memories.

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