CHAPTER 3

STUDY OF MORPHOLOGICAL VARIATION DURING THE GROWTH OF DLC FILMS

3.1 INTRODUCTION

The growth mechanism and surface evolution of RF-PECVD grown DLC films are important from both scientific and practical aspects. The present chapter divided into two sections to discuss the morphological variation during the growth of DLC films on silicon (100) substrate.

The first section of this chapter is dedicated to study the importance of the plasma pretreatment on the substrate surface before the deposition of the DLC film and how it influences the morphology of the film on silicon substrate.

The second section of this chapter deals with the morphological evolution and structural changes at various stages during the growth process of the DLC film on the silicon substrate.
3.2 INFLUENCE OF PLASMA PRETREATMENT IN THE GROWTH OF DLC FILM

Despite several advantages, few factors limit the performance of DLC films on silicon substrates like failure of uniform coating over a long range, variation in the surface roughness, poor adhesion due to high compressive stress, etc. There are few methods followed to improve the adhesion and uniform coating of the DLC film on the substrate. For example, fabrication of metal-containing DLC (Me-C:H) [109], whisker composite [110], DLC–Si coating [111] and deposition of interlayer like Si, Ti, Cr, or W [112,113]. But, most of these techniques are complicated and quite expensive at the industrial perspective. Since the initial roughness of the substrate surface greatly influences the growth of the DLC film and its final properties [114], the effect of various surface pretreatments via physical and chemical methods for both diamond and DLC films on CVD have been discussed elsewhere [115-119] to describe the growth and the uniform coating over the range of the substrate. In the present work, the influence of Ar ion plasma pretreatment on the surface morphology of the DLC film during the growth have been studied and compared with the film grown on the silicon substrate without pretreatment.

3.2.1 Experimental Procedures

The DLC films were deposited by RF-PECVD. For the deposition, analytical grade CH₄ and Ar were used as precursor gases. No catalyst was used for the experiments. The complete experimentation was carried out on industrial grade polished silicon (100) substrates. Two silicon substrates were taken and thoroughly cleaned by ultrasonicating in acetone for 30 min. One of the cleaned substrates was placed in the RF-PECVD chamber. The vacuum inside the chamber was maintained at 10⁻⁶ mbar. Ar gas was introduced into
the chamber at 20 sccm. The plasma was created in the chamber using RF power (13.56 MHz) at 300 W. The substrate was exposed by the plasma treatment for a typical amount of time (15 minutes). Figure 3.1 shows the AFM image of the pretreated substrate surface.

![Figure 3.1 Plasma pretreated silicon substrate.](image)

The second substrate was used without any pretreatment. The two substrates were then placed in the RF-PECVD chamber for the deposition of the DLC films. The chamber was evacuated to the base pressure of \(10^{-6}\) mbar. Ar was introduced into the chamber at the flow rate of 30 sccm; while the RF power and the substrate temperature was maintained at 200 W and 100 °C respectively. CH\(_4\) was introduced along with Ar at the flow rate of 10 sccm. The overall pressure of the chamber was maintained at \(2\times10^{-3}\) mbar. The reaction conditions were typically maintained for 45 minutes. The surface
morphology of the DLC film deposited on plasma pretreated ($S_{PT}$) and non-pretreated ($S_{NPT}$) substrate were studied by contact mode AFM. The microstructure of the DLC films was analyzed using Raman Spectroscopy.

3.2.2 Results and Discussion

3.2.2.1 Morphological Studies

The DLC film grown on $S_{NPT}$ was shown in Figure 3.2. The image shows the DLC film with spinodal morphology, which is an indication of carbon agglomeration. No uniform distribution can be noticed in the image. The size of the surface features were found to be around 200 nm as indicated by the AFM line profile. From the RMS roughness histogram of the DLC film surface on $S_{NPT}$, it can be clearly seen that there were vast irregularities in the height distribution over the range of substrate and lot of uncoated regions were seen from the surface morphology, which confirms the non-uniform coating of the DLC film on the surface of the substrate.

The irregular coating of DLC film on $S_{NPT}$ has been attributed to the poor bonding between the surface silicon atoms and the carbon ions. When the carbon ion reaches the substrate it cannot penetrate into the substrate due to its low energy and therefore diffuse along the surface, during this transit the affinity between the surface silicon atoms and carbon atoms is less because of the low entropy of the system due to comparatively lower substrate temperature and the absence of dangling bonds. Thus the film nucleates only in certain regions and therefore the nucleation density of the DLC film on the substrate surface will be reduced. Further adatoms from the vapour phase will attached to the exiting nucleation than being attached to the silicon atoms. Since the bonding energy of C–C (610 ± 2.0 kJ/mol) is higher than that of C–Si (451.5 ± 2.0 kJ/mol), the C–C bonding is preferred to be formed than C–Si
and thus C-C bond is more stable than C–Si bond. This in turn affects the uniform distribution of carbon species on the silicon surface and further leads to the formation of irregular spinodal morphology on the DLC film. It is known that, the formation of nano structured thin film is determined by diffusion of chemical species on the surface [121].

Therefore the probability of the bonding between silicon-carbon atoms should be more when compared to the bonding between carbon-carbon atoms for the formation of uniform thin film coatings.

The DLC film grown on S_{PT} is shown in Figure 3.3. The surface morphology of the film on the pretreated substrate clearly shows a uniform distribution of the surface grains over the region, which confirms that the film has grown uniformly throughout the substrate. The surface grain size as inferred from the line profile ranges from 60 nm to 80 nm. From the RMS roughness histogram it can be seen that, the film has significantly lesser variation in the height distribution. This regularity in height variation of the surface grains in the DLC film on S_{PT} is more when compared with the DLC film on S_{NPT}. This may be due to ordered distribution of the carbon species on the S_{PT}.

The uniform distribution of the surface grains in DLC thin film can be attributed to plasma pretreatment. It is important to note that the plasma pretreatment (Figure 3.1) not only sputter cleans the substrate surface, but also enhances the nucleation of the film by forming craters and sharp edges due to the ion bombardment which in turn act as active sites for nucleation as they offer more dangling bonds. These active sites also enhance the diffusion of ions on the substrate surface which in turn increases adhesion of the film with
Figure 3.2 AFM study of DLC film coated on non pretreated substrate. (a) 2D surface morphology (b) 3D surface morphology (c) AFM line profile (d) RMS roughness histogram.
Figure 3.3 Images of DLC film on pretreated silicon substrate. (a) 2D surface morphology (b) 3D surface morphology (c) AFM line profile (d) RMS roughness histogram.
the substrate. The plasma pretreatment of the substrate surface is an effective way to enhance the nucleation and quality of the carbon film [122].

The presence of the large number of these nucleation sites tends to help in the formation of a strong silicon carbide layer. Further, the uniform distribution of the nucleation sites ensures that the carbon-silicon bond formation is preferred than the carbon-carbon agglomeration as in the case of $S_{\text{NPT}}$.

Mainly three stages involved in the early growth of thin films: they are the arrival cum accommodation of ions on the surface (condensation) from the vapour phase, their migration along the surface (diffusion) and their aggregation into two-dimensional adatom islands (nucleation) [123].

The ions have to dissipate their kinetic energy perpendicular to the surface into the substrate lattice vibrations during the collision in order to stick on the surface. Once the ion has been adsorbed, the excess energy makes ions to diffuse along the surface from one adsorption-site to another. The excess energy comes from the ion kinetic energy parallel to the surface and the thermally activated diffusion of the substrate (deposition temperature). As a result, the ions impinged on the substrate tend to move along the surface, during this transit the ions get attached with the active nucleation sites. Thus the rate of nucleation increases and the carbon-carbon agglomeration is prevented. This in turn results in the formation of uniform nucleation and coating of the DLC film on the silicon substrate over a long range with uniform morphology. The detailed morphological evolution of the surface of DLC film on silicon substrate was discussed in the forthcoming section (Ch-3.3).
3.2.2.2 Raman Studies

The grown DLC thin films were analyzed by Raman spectroscopy. Figure 3.4 shows the Raman spectra of the DLC film grown on both S\textsubscript{PT} and S\textsubscript{NPT}. Spectrum of sample S\textsubscript{PT} (Figure 3.4(b)) shows two peaks around 1550 cm\textsuperscript{-1} (G-band) and 1350 cm\textsuperscript{-1} (D-band), which are the characteristics of DLC thin films [104-107] (refer Ch-2.3.3.2). No distinct peaks were identified on the spectrum of the sample S\textsubscript{NPT} (Figure 3.4 (a)) and this could be due to the fact that the DLC film on S\textsubscript{NPT} was too minimal to be identified using Raman spectroscopy and/or due to more uncoated region. This confirms that the DLC film was uniformly coated on S\textsubscript{PT} and poorly coated on S\textsubscript{NPT}.

![Figure 3.4 Raman spectra of DLC film (a) S\textsubscript{NPT} (b) S\textsubscript{PT}](image-url)
3.3 SYSTEMATIC STUDY OF VARIOUS STAGES DURING THE GROWTH PROCESS OF DLC FILM:
A MORPHOLOGICAL EVOLUTION

In carbon thin film technology, AFM has been used to study the topographical and tribological properties from past few decades. In that, very few researchers have attempted to study the growth process of the CVD diamond films stage by stage using AFM [124-126]. Especially, the growth of DLC films has not been completely (from nucleation to continuous film) characterized by AFM and the related morphological changes not documented explicitly. In the present work, the morphological variation during growth stages of the DLC film has been formulated, starting from nucleation to continuous film completely by AFM. The results are compared with the various available literature and discussed based on the same.

3.3.1 Experimental Procedures

The DLC films were synthesized using RF-PECVD; analytical grade CH₄ and Ar were used as precursor gases and no catalyst or intermediate layers were used. The complete experiment was carried out on industrial grade polished silicon substrates. A set of silicon (100) wafers of dimensions 1×1 cm were taken and thoroughly cleaned by ultrasonicking for 30 minutes in acetone and then with deionized water. These cleaned substrates were then placed in the RF-PECVD chamber. Initially the pressure of the chamber was pumped down to 10⁻⁶ mbar and then Ar gas was introduced into the chamber at 30 sccm. The plasma was created in the chamber using RF power (13.56 MHz) at 200 W and the approximate self bias voltage due to plasma sheath potential was measured to be -17 V. The substrates were exposed to the plasma pretreatment for 15 minutes to enhance the nucleation of the film and the substrates were maintained at room temperature throughout the
experiment. After the plasma pretreatment, CH$_4$ was introduced into the chamber at 10 sccm. The final reaction pressure was $3.8 \times 10^{-2}$ mbar and the complete reaction time was 150 minutes. To study the early stage growth of the film, the reaction was interrupted at 5, 20, 50, 70, 90, 120 and 150 minutes. The samples were named as S$_5$, S$_{20}$, S$_{50}$, S$_{70}$, S$_{90}$, S$_{120}$, S$_{150}$ respectively with their time of reaction in minutes as suffix. The surface morphology of the films was characterized by AFM in contact mode and SEM images were taken to check the long range uniformity of the film. The bond nature and bond disorder of the carbon network in the films were studied using Raman spectroscopy.

3.3.2 Results and Discussion

3.3.2.1 Morphological Studies

DLC film shows three distinct stages during its growth process (i) nucleation (ii) growth of 3D islands (iii) formation of continuous film, as identified by AFM.

i. Nucleation

The plasma pretreated substrate surface before the deposition of the DLC film was shown in Figure 3.1. It can be clearly seen that some of the surface region of the substrate has been sputtered due to energetic Ar ion bombardment during the plasma pretreatment. This leaves the substrate surface with a large number of craters which can act as an active site for the carbon species to nucleate on the silicon surface as they offer more dangling bonds.
Figure 3.5 AFM images of sample Ss. (a) nucleation of the DLC film on the substrate (b) single nucleated site showing nucleation around the surface crater (c) line profile of the single nucleated site.
The Figure 3.5(a) shows the nucleated sites in sample $S_5$. It can be seen that each of these nucleated carbon sites exhibits almost uniform morphology. The Figure 3.5(b) shows a high resolution image of an individual nucleated site. The energetic vapor particulates (atoms or molecules or ions) impinging on the substrate may desorb or adsorb or may remain on the surface for a length of time $T_i$ depending on the energy of the incident ion, temperature of the substrate, diffusion barrier of the surface, surface pretreatment etc. In the present work, various experimental parameters favor the nucleation of the amorphous carbon film, such as the energy of the impinging ions which falls in the region of medium $E_i$ as they are trapped towards the substrate only by the self bias voltage due to plasma sheath potential originated from Ar plasma by RF power [9,127] and at this present reaction pressure the calculated $E_i$ value is approximately 6 eV (about one-third of the bias voltage) [128].

The medium $E_i$ value of the impinging carbon ion increases the surface adatom mobility and leads to island formation rather than penetrating into the surface [129]. Therefore the incident particulates from the vapour phase reach the substrate and diffuse across the surface, resulting in a net mass transport along the surface. The low substrate temperature greatly reduces the desorption rate, therefore the impinging ions stay on the substrate surface for a longer time. The surface pretreatment reduces the spacing between the defects (energetic sites) on the surface. In heterogeneous nucleation, when the diffusion distance of the ions is large compared to the defect spacing the adatoms tend to encounter these defects and get attached to them [130]. Thus the nucleation of the film starts easily at these active sites. In Figure 3.5(b) the brighter region is the nucleated part and the central dark region is the crater on the surface confirmed by the line profile (LP) as shown in Figure 3.5(c).
The LP is a graphical representation of the surface morphology taken from AFM data, which measures the deflection of the cantilever in “Z” direction. From the Figure 3.5(a)-(c) it is clearly seen that the initial nucleation starts mostly around the edges of the craters rather than any other region on the surface.

ii. 3D Island Growth

In the initial stage, nucleation of the film starts at active sites where carbon ions bond with surface atoms and at a later time almost all the surface active sites are covered by the carbon ions. The additional adatoms arriving at the surface bond easily with the nucleated carbon region rather than being bonded with the surface silicon atoms. Thus the nucleated region grow three dimensionally above the surface giving rise to well defined island formation in the sample S20 as shown in Figure 3.6, which follow the Volmer and Weber growth model [131].

During the island formation the nucleated regions grow in size due to the adatoms from the vapour phase and simultaneously decay due to etching by the energetic species in the plasma. Depending on the concentration of the adatoms, the initial clusters may grow or decay. There exists a critical size above which the probability of the growth will be greater than the decay, the cluster which exceeds the critical size becomes stable and continues to grow [132].
Figure 3.6 AFM image of sample S$_{20}$ with well defined 3D islands, boxed region shows early stage coalescence.
Figure 3.7(a)-(c) shows the LP of the samples S₀, S₅ and S₂₀ respectively. The LP of the pretreated substrate surface of the sample S₀ indicates that the surface has lots of craters. The LP of the nucleated sample S₅ shows surface features grown above the surface and also craters on the surface. The LP of the sample S₂₀ shows the surface features are well above the surface with uniform height and also the surface craters have almost filled, indicating the surface nucleation has almost saturated.

The surface morphologies of the samples S₅₀ and S₇₀ are shown in Figure 3.8(a), (b) respectively. In sample S₅₀ the size of the surface features varies only slightly but the height variations are large as arrowed at P and S, attributed to the primary (initially grown islands at particular nucleated regions of the surface which received more adatoms) and secondary (delayed growth of islands on the remaining nucleated region of the surface due to shadowing effect of primary regions) growth in the film respectively.

In sample S₇₀ the surface cluster density increases along with the size of the clusters, which may be due to the growth of the clusters in the secondary regions. But still the two groups of clusters can be distinguished. In the later stage, island growth is governed by two processes; bonding of adatoms from the vapour phase and redistribution with the neighboring islands by a process such as ripening (growth of larger clusters at the expense of smaller clusters), and early stage coalescence (combining of two clusters into a larger one upon impact) [132].
Figure 3.7 AFM line profile (a) sample S_0 (b) sample S_5 (c) sample S_{20}.
Figure 3.8 AFM images (a) sample $S_{50}$, arrow P and S attributed to islands grown from primary and secondary nucleated region (b) sample $S_{70}$ with higher surface island density than the former sample $S_{50}$. 
iii. Growth of Continuous DLC Film

After these clusters have grown in size they start to form a continuous film. Many publications have explained the formation of film from clusters by different methods such as Ostwald ripening, sintering and cluster migration etc. All these mass-transport mechanisms have been proposed to account for the coalescence phenomenon [132]. Figure 3.9 shows the surface morphology of the sample S₉₀ and the figure inset shows the magnified image of the same. From the figure it is clearly seen that the later stage coalescence starts and all the islands combine with their neighbor islands to form a continuous network. This is a critical stage identified, where the micro features start converting into a continuous film.

Figure 3.10(a) and (b) shows the AFM image of the samples S₁₂₀ and S₁₅₀ respectively. The image of the samples S₁₂₀ and S₁₅₀ shows the top surface of the continuous film with traces of micro-features which confirms the continuous growth of the film due to coalescence phenomenon of the micro-features. The arrow marks of the Figure 3.10(a) show discontinuities (gaps left) in the growing film and these gaps were not found in the sample S₁₅₀ (Figure 3.10(b)). Otherwise there is not much difference in the AFM images between the samples S₁₂₀ and S₁₅₀ and they shows good agreement with SEM images.
Figure 3.9 AFM image of sample $S_{90}$, later stage coalescence forming continuous network among neighboring surface islands.
Inset - highly magnified image.
Figure 3.10 AFM images of the continuous DLC film (a) sample $S_{120}$, arrow marks shows the gaps left in between the continuously coated region (b) sample $S_{150}$.

Figure 3.11 SEM images of the continuous DLC film (a) sample $S_{120}$ with lot of uncoated region (b) sample $S_{150}$ showing uniform growth of the DLC film over long range.
Long range uniform coating of the film has been identified by SEM (FEI Quanta 200). Figure 3.11 (a) and (b) shows the SEM image of the samples S\textsubscript{120} and S\textsubscript{150} respectively. The SEM image of S\textsubscript{120} shows continuous film with lots of uncoated regions. After a reasonable time of growth (say another 30 minutes) these regions were coated and the substrate shows perfect thin film covering for very long range only with small voids in it as shown in Figure 3.11(b). This can be attributed to the formation of film from the micro-features at the deposition time of 120 minutes and further increase in time has only led to an increase in its continuity and thickness.

3.3.2.2 Raman Studies

Figure 3.12 shows the Raman spectra of the DLC film at various stages during the growth process. Spectrum of samples shows two peaks around 1550 cm\(^{-1}\) (G-band) and 1350 cm\(^{-1}\) (D-band), which are the characteristics of DLC thin films [104-107] (refer Ch-2.3.3.2). The G peak positions 1576 cm\(^{-1}\), 1570 cm\(^{-1}\), 1554 cm\(^{-1}\) and the respective I\textsubscript{D}/I\textsubscript{G} values 3.12, 2.42, 2.13 were measured from double Gaussian fits for Raman spectra of the samples S\textsubscript{50}, S\textsubscript{90} and S\textsubscript{150} respectively. During the growth process of DLC film, the G peak position tends to move towards the lower wavenumber and the respective I\textsubscript{D}/I\textsubscript{G} values decreases. This confirms that the bond disorder in the graphitic cluster increases due to the increase in sp\(^3\) bond formation, which means an increase in the properties of DLC [10,133]. If the incident carbon ion does not have sufficient energy to penetrate into the surface it will just stick to the surface and remain in its lowest energy state which is sp\(^2\) hybridized [61,127] thus the nucleation of the film starts with more sp\(^2\) bonded carbon compared with sp\(^3\) bonded carbon. The importance of atomic hydrogen during the growth of the DLC film has been explained in many papers. Briefly, in structural modification, atomic hydrogen saturates the C=C bonds by converting them to sp\(^3\) CH\(_x\) groups rather than by increasing the fraction of
C-C bonds [10] and prevents the graphitization process [134]. In growth: the atomic hydrogen present in the plasma removes H from the surface C-H bond and also eliminates the weakly bonded carbon from the network leaving dangling bonds in the growing carbon network, through which further adatoms bond in the network which grows in size [5]. From the results it is clear that the initial nucleation of the DLC film from the medium Ei ions starts with more sp$^2$ clustering rather than sp$^3$ CH$_x$, when the surface features grow in size the growth conditions favor the amount of sp$^3$ CH$_x$ to increase and finally the film shows an amorphous nature.

Figure 3.12 Raman spectrum at various stages during the growth process of DLC film (a) sample S$_{50}$ (b) sample S$_{90}$ (c) sample S$_{150}$.  

![Raman spectrum](image)
3.4 CONCLUSIONS

In the present work, the DLC film has been grown by RF-PECVD in CH₄/Ar plasma. DLC films have been uniformly coated throughout the substrate without any complex procedures and/or any intermediate metallic layers. The DLC film deposited on the substrate without any pretreatment shows a spinodal morphology while the DLC film deposited on the substrate which has been plasma pretreated shows a uniform deposition over the range of substrate. It is quite clear from the results that the plasma pretreatment influences the growth of the DLC film.

The growth of the DLC film on silicon by medium $E_i$ ions follows Volmer-Weber growth model. During the growth process DLC film shows different stages from nucleation to continuous film. The DLC film nucleates in the surface defects as islands and at almost every stage it was confirmed that the growth of the islands occurs not only by adatoms but also by the coalescence among the neighboring islands. The SEM image confirms that the film has grown uniformly throughout the surface and the film has formed at the time of 120 minutes during the deposition. From the Raman spectrum, it was confirmed that the DLC film nucleates as more sp² hybridized state and during the growth process the fraction of sp³ CH₃ increases leading to the amorphous nature of the film.