CHAPTER 5
EFFECT OF POST DEPOSITION ANNEALING ON THE SURFACE MORPHOLOGY OF THE DLC FILM

5.1 INTRODUCTION

Among various amorphous carbon films, DLC films produced via RF-PECVD have been successfully used in many fields such as low-friction and wear-resistant coatings, protective optical and biomedical coatings, in field emission devices etc, due to their extraordinary properties like chemical inertness, biocompatibility, hardness, optical transparency [5,154-156]. But some of these applications require them to operate at higher temperatures or may causes localized heating on the DLC film due to friction. Therefore, many work indent to study annealing effect of DLC films at various temperature and analyzed various property changes to understand the thermal stability of these films. It is well known that carbon films, in general, exhibit a high level of internal stress in the as-deposited state and that annealing can lead to favorable stress decrease [157-159]. However, the properties of DLC films can become unstable upon thermal annealing. Many studies documented that during thermal annealing of the DLC films in vacuum or in air at temperatures of more than 400 °C shows variations in their properties due to effusion of hydrogen, the conversion of sp³ bonds to sp² bonds, variation in their frictional coefficient, hardness, loss of diamond like properties, etc., [160,161], which limits the performance of these films in the respective areas. Along with the above said issues, upon thermal annealing DLC films shows change in their surface morphology due to coalescence, agglomeration, blistering, bursting,
buckling, delamination, etc., were also reported [162-165]. But there is no much proper investigation dedicated to study the sequential variation in surface morphology of the DLC film during thermal annealing. In the present work, the as deposited DLC films (grown at 100 °C) were subjected to annealing in vacuum to study the surface morphology as the function of annealing temperature.

5.2 EXPERIMENTAL PROCEDURES

The DLC films were deposited using RF-PECVD; the experimental setups and the deposition conditions were discussed in the chapter 3.2. Briefly, DLC films were deposited at 100 °C, and the respective power and flow rate of the precursors are 200 W, 30 sccm (Ar), 10 sccm (CH₄). The deposited DLC films were then subjected to annealing treatment at 400 °C, 500 °C and 600 °C for 15 minutes under vacuum (5 x 10⁻⁶ mbar) and cooled down to room temperature. The samples were then named as S₄₀₀, S₅₀₀ and S₆₀₀ respectively with their annealing temperature as suffix and S_AD is given for the sample as deposited (AD). The surface morphology of the films was characterized by AFM in contact mode and SEM. The bond nature and bond disorder in the films were studied using Raman spectroscopy.

5.3 RESULTS AND DISCUSSION

5.3.1 Morphological Studies

Figure 5.1 shows the surface morphology of the as deposited DLC film S_AD. The film shows uniform and continuous growth over the region of the substrate with nano grains. Figure 5.2 shows the surface morphology of the annealed sample S₄₀₀.
Figure 5.1 AFM image of the as deposited sample $S_{AD}$, (a) 2D and (b) 3D surface morphology.
It is very interesting to see that the surface of the annealed sample shows various surface features at different regions, in some regions buckling nucleates as circular blisters or bubbles (debonding) (Figure 5.2 a,b) just protruded above the surface and in some other regions microcracks and pinholes (Figure 5.2 c,d) were observed. There are various reasons for the nucleation of the blistering on DLC thin films during thermal annealing like coefficient of thermal expansion (CTE) mismatch between the substrate and film, various stress release mechanism, release of bonded/unbonded hydrogen from the film, etc., have been discussed elsewhere. However Ar bubbling at the interface between the substrate and film is also the other major reason for the blistering in DLC film. When DLC film coated in inert atmosphere (especially in argon atmosphere), inert gases present in the chamber during pretreatment and deposition may be entrapped within the substrate as well as in DLC film. These entrapped Ar ions can be released during annealing so as to collect at the interface imperfection and promotes the formation of blistering in the film [163,166].

Further, raise in temperature activates the diffusion of the surface grains in the film and the coalescence phenomenon starts therefore the surface grains combine with the nearby grains to reduce their surface energy. This causes decrease in surface grain density by formation of larger grains which nucleates pinholes and micro cracks. The vertical growth seen near the edges of the microcracks confirms the above discussion (Figure 5.2 b). Thus the continuous film starts to detach as a bigger islands. Surface roughening, film debonding, pinhole formation and film agglomeration are examples of stress relaxation mechanisms [166].
Figure 5.2 AFM image of the sample $S_{400}$, (a) surface showing blistering (c) surface with microcracks and pinholes, (b) and (d) are the respective 3D images.
As the annealing temperature increases (upto 500 °C) these blisters increases in numbers and size (Figure 5.3 a,b) and most of the blisters surrounded by the radial slippage of the film from the substrate, which is due to release of radial stress from the film [166]. During the thermal excursion, the nucleated blisters grow in size laterally and start to buckle out from the substrate until they arrested by reduced gas pressure and/or lower crack opening stress intensity at edges [15].

Finally when the DLC film annealed at 600 °C (Figure 5.3 c,d), the surface morphology of the sample S 600 shows sheet like structures in various range of size (from nm to µm) and some small hillock structures were also seen. As discussed earlier, these sheets were might be resulted from the delamination and coalescence of the surface grains. From the SEM studies (Figure 5.4) it was confirmed that the DLC film shows sheet like structure throughout the substrate.
Figure 5.3 AFM image of the sample S500 (a,b) and S600 (c,d). (a) surface showing blistering with radial slippage (c) surface with sheet like structure, (b) and (d) are the respective 3D images.
Figure 5.4 SEM image of the sample $S_{600}$. 
5.3.2 Raman Studies

Figure 5.5 shows the Raman spectra of the samples $S_{AD}$ and $S_{600}$. The spectrum of all the films shows the formation of a distinct peaks around 1600 cm$^{-1}$ and 1350 cm$^{-1}$, indicates the formation of DLC films [104-107] (refer Ch-2.3.3.2). The shift in G peak position towards higher wavenumber and the variation in the $I_D/I_G$ value indicate a severe degradation of the structural property of the DLC films, i.e. the decreases of the sp$^3$ content and the diamond-like characterization and the increase of graphite-like component [104-107].

Figure 5.5 Raman spectra of the samples, (a) $S_{AD}$, (b) $S_{600}$. 
5.4 CONCLUSIONS

The variations in surface morphology of the RF-PECVD grown DLC film during annealing process have been studied systematically by AFM. Annealing was done at various temperatures above graphitization temperature (400 ºC, 500 ºC, 600 ºC) at vacuum. As the annealing temperature increases the surface of the DLC film exhibit various morphologies like blistering, microcracks, hillocks and finally the continuous film detaches as sheets. All these variation in the morphology of the film is due to delamination and coalescence of the surface grains. The sheets show higher graphitization as detected by Raman spectrum. This confirms that along with the morphological variation bond restructuring also happens on DLC films during post thermal annealing.