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Study of 130 Mev Ni Ion Irradiation Induced Surface Modification of DLC Films Grown By Microwave Plasma CVD.

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Abstract: *We report on the 130 MeV Ni ion irradiation induced modification of the surface roughness of DLC films grown by microwave plasma CVD method. The MWCVD system which was used to grow the DLC thin films was designed and developed in-house. The growth of thin films of DLC was studied with different substrate dc bias using Ar/H_2 (2%) and Methane as feedstock. The deposited films were irradiated with 130 MeV Ni ion irradiation to doses of $3e^{11}$, $3e^{12}$ and $1e^{13}$ ions/cm^2. Atomic force microscopy and Raman spectroscopy were used to study the 130 MeV Ni ion irradiation induced modification of surface topography and structure of the DLC films. Raman spectroscopy results of the deposited films show D and G bands at 1380 cm^{-1} and 1558 cm^{-1} characteristic of DLC films and indicate change in sp^3 content with change in –dc bias. The Atomic force microscopy results show that the deposited DLC films have smooth surface and the RMS roughness decreased in the irradiated films relative to the pristine film which can be due to the electronic energy loss of 130 MeV Ni ions being lower than the energy loss threshold for track formation.*
Key words : *MWCVD, DLC, raman, direct dc bias, RMS surface roughness.*

I. Introduction.

Growth of thin films by Chemical Vapor deposition (CVD) involves the deposition of the thin films from a gas state (vapor) on a substrate. The gas molecules used for the deposition of the thin film have to be ionized and dissociated using a plasma before deposition on the substrate. Various types of plasmas, i.e dc , rf , microwave etc have been successfully used to grow thin films on substrates. Microwave discharges have advantages of higher degree of ionization and hence higher rate of reactions between the chemical species in the plasma compared to dc and rf discharges. Thin films of amorphous carbon and ordered carbon nanostructures are widely deposited by microwave plasma CVD (MPCVD) technique with rf induced dc self bias or direct dc bias [1-2]. A microwave plasma CVD system with direct dc bias to substrate holder has been developed at IUAC and used to study the growth of diamond-like carbon thin films. The advantage of using direct dc bias to substrate holder is the control of the energy of the ions impinging on the substrate without significantly effecting the plasma environment [3].

Hard coatings such as TiN, CrN, TiAlN, TiN/TiAlN, DLC and TiN + DLC nanocomposite are of high technological importance due to their use in various tools. The role of the hard coating is to reduce wear and hence increase the lifetime of the tool. One of the factors which contributed to the wear is abrasion which is influenced by the surface roughness of the coating. DLC films have high abrasion resistance and are biocompatible and can be deposited on different surfaces. DLC films are of interest in biological applications such as artificial mechanical heart valve (AMHV) [1, 2] and are potential candidates to reduce UHMWPE wear debris generation[3,4]. The surface roughness of TiC/a-C coatings determined the wear behavior of bearing steel balls and a smooth coating is critical for obtaining a low coefficient of friction [5]. The wear resistance of the UHMWPE against a metal femoral head deposited with DLC by MPCVD showed better performance [6]. The surface of DLC can be modified on the nanometer scale using high energy ion irradiation [7] and self bias [8].
Ion irradiation has been used to produce a wide variety of modifications in different materials due to the energy loss of the ions as they travel through the material. Modifications in DLC thin films by ion irradiation has been previously studied for changes in the properties [9,10]. Recently H. Tani et al[7] have reported that two step Ar-N2 GCIB irradiation has resulted in the reduction of surface roughness in DLC films. In this context it will be interesting to study the influence high energy ion irradiation on surface roughness of DLC films synthesized by microwave plasma CVD.

II. Experimental details.

Description of the system.

A microwave plasma system (Fig 1) consisting of 2.45 GHz microwave excitation has been developed to grow thin films. The system consists of the microwave set-up connected to a plasma chamber with a deposition chamber connected to the other end of the plasma chamber. The microwave set-up consists of the 2.45 GHz microwave radiation source, circulator with a water cooled dummy load, directional coupler, 3 stub tuner, 90 degree bend and TE_{10} to TE_{11} mode converter (National Electronics, USA). The microwave source is powered by a Switching power supply (Richardson Electronics, USA) and is water cooled. The forward and reflected microwave power can be measured using a microwave power meter connected to the directional coupler.

The plasma chamber is designed for TE_{112} excitation. The top flange of the plasma chamber has a quartz window for feeding microwaves into it and also a provision for feeding gases with circular symmetry into the plasma chamber. The gases can be fed at a controlled rate using MKS mass flow controllers (MKS Inc, USA). The deposition chamber and the plasma chamber can be pumped to high vacuum by using a Turbo pump / Dry pump combination and the vacuum in the chamber can be measured using Penning and Pirani gauges. An MKS throttle valve in connected to the deposition chamber to deposit thin films at constant pressure with the pressure measured using an MKS Baratron gauge. The deposition chamber has a substrate holder which is having provision of – dc bias to grow thin films. The substrate holder(MeiVac, USA) can be heated upto a temperature of 900^oC using a PID controller.

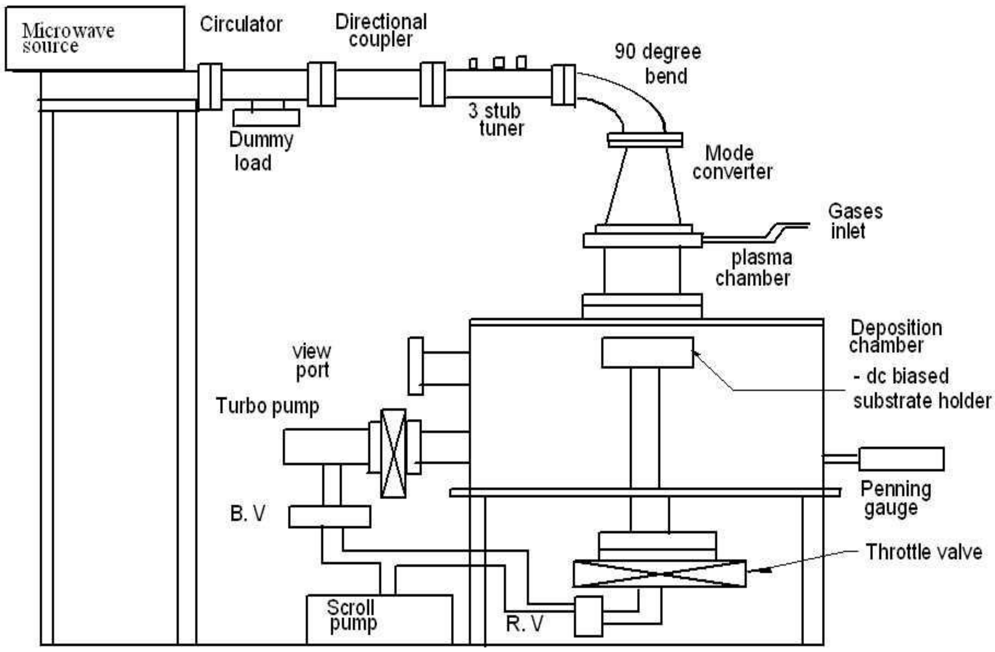

Fig 1. Schematic of Microwave plasma CVD set-up.

For the thin film deposition, the deposition and plasma chambers are pumped to a base pressure of $4x10^{-6}$ torr vacuum using combination of Turbo pump / Dry pump. Then the Ar/H_2 (2 %) gas is introduced into the chamber through MKS mass flow controller and the chamber pressure was maintained at 500 m torr. The microwave plasma was formed by feeding the microwaves through the quartz window and using the 3 stub tuner to form the plasma. A dc bias of - 500 V was applied to the substrate holder on which Si substrates were placed and the substrates were heated for 20 minutes by bombarding it with the ions from the plasma. The – dc bias was then set to the desired voltage and methane gas was introduced into the plasma chamber and the thin films were deposited on the Si substrates for a duration of 30 minutes. The thin films were deposited in different –dc bias to substrate holder without changing the other deposition conditions.

The deposited films were irradiated with 130 MeV Ni ions at $3e^{11}$, $3e^{12}$ and $1e^{13}$ ions/cm^2 doses using the Pelletron Accelerator at IUAC. The deposited and irradiated films were characterized by Raman spectroscopy measurements using In Via Raman microscope (Renishaw) for DLC structure and by Atomic force microscopy measurements using Nanoscope IIIa (Digital/Veeco Instruments) for surface structure.

III. Results and analysis.

Thin films of Diamond-like carbon are formed on Si substrates. The formation of Diamond like carbon in the films is confirmed using raman spectroscopy measurements.

Fig 2 shows the raman spectra of the DLC films deposited with 500 mtorr pressure at -350, -400 and -460 V bias to the substrate holder. The raman spectra of these films (DLC350, DLC400 and DLC460) deposited with different – dc substrate bias shows changes in the intensity, position and FWHM of the G band (table I). The G band position of the DLC350 film has high value of 1582 cm-1 which is usually correlated with films of high content of nanocrystalline graphite [11,12], while the values of the position of the G band peak for the DLC400 and DLC460 films is consistent with highly disordered amorphous DLC [11,12]. The FWHM of the DLC films is mainly sensitive to structural disorder arising from bond angle and bond length distortions. For all the DLC films, the values of FWHM are consistant with the presence of sp^2 clusters with size smaller than 1 nm [13].

Table 1. Calculation of the G band position (wG), intensity (IG) and FWHM (□ G).

S. No	Film	w_G	IG	□ G
1	DLC350	1582	5650	93
2	DLC400	1537	7728	159
3	DLC460	1530	11400	150

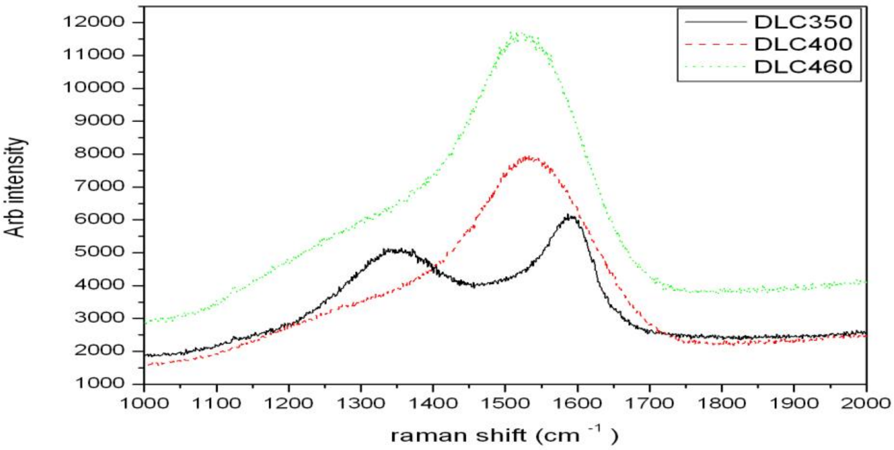

Fig 2. Raman spectra of the DLC films deposited with different –dc bias.

The surface morphology of the DLC films was studied using atomic force microscopy. Fig 3 shows the typical AFM (3 D) and RMS roughness images of the deposited DLC400 film. It can be seen that the film is composed of small particles which are uniform. The measured result of the surface roughness shows that the DLC films has smooth morphology with the RMS (root mean square) roughness being 0.436 nm.

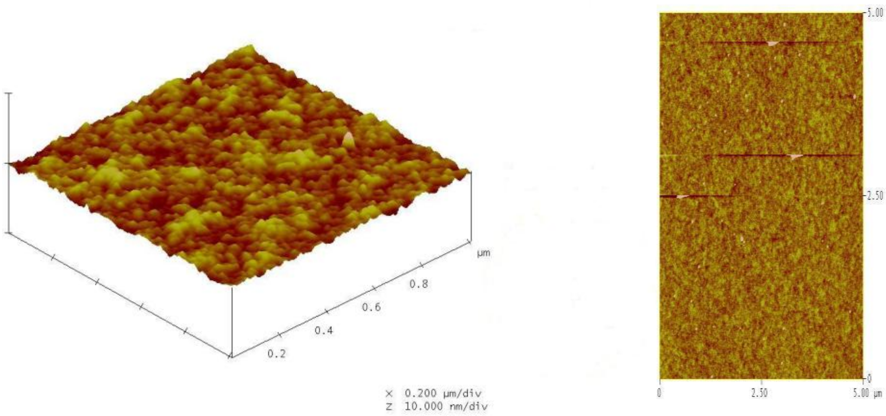

Fig 3a,b. AFM (SD) and RMS roughness images of the DLC400 film.

Fig 4 shows the Raman spectra of the irradiated films. Due to the ion irradiation the G band peak shifted towards higher wavenumber and the intensity of the G band peak increased first and then decreased with further irradiation especially for the $1e^{13}$ ions/cm^2 fluence. These results suggest increase of sp^2 bonding in the films [10] which can be due to the local heating caused by the 130 MeV Ni ions as they pass in the film. The 130 MeV Ni ions predominantly lose their energy in the DLC material by electronic excitation where the energy of the ion is transferred to the lattice atoms through electron-phonon interactions [14]. The thermal energy developed in the lattice leads to the formation of nanodimensional defects in the lattice [14]. The conversion of DLC material from sp^3 to sp^2 in the track of the ions was also observed previously[15].

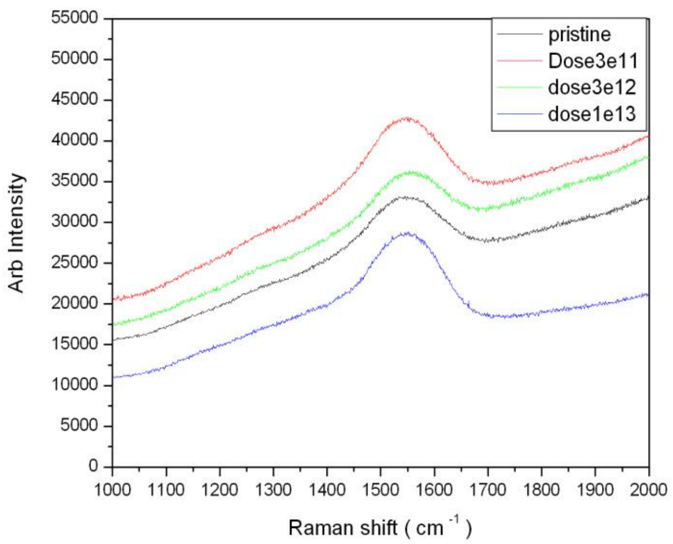

Fig 4. Raman spectra of pristine and irradiated DLC films.

The surface roughness was found to decrease in the 130 MeV Ni ion irradiated films relative to the pristine film from 0.436nm to 0.259 nm , 0.298 and 0.397 nm for the $3e^{11}$, $3e^{12}$ and $1e^{13}$ ions/cm^2 doses, respectively. Fig 5 a,b shows the typical AFM (3 D) and RMS roughness images of DLC film irradiated by 130 MeV Ni ions to a fluence of $1e^{13}$ ions/cm^2.

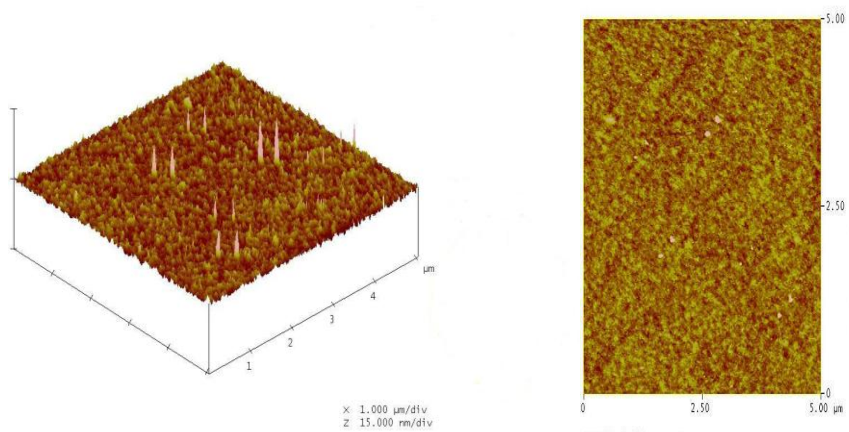

Fig 5 a,b. AFM (3 D) and RMS roughness images of irradiated film ($1e^{13}$ ions/cm^2 dose).

Since no hillock formation at the surface is noticed, it is clear that conducting track did not form in the DLC film as the electronic energy loss (6.7 keV/ nm) of 130 MeV Ni ions calculated using SRIM, is less than the energy loss threshold for track formation (10 +/-2 keV / nm)[15].

IV. Conclusions.

We have developed a microwave plasma CVD system and successfully grown DLC films using $Ar/H_2(2\%)/CH_4$ plasma using direct dc bias to substrate. The raman spectra of the deposited DLC films show the charecteristic D band and G band of DLC material and indicate the sp^3 content changed with change in dc bias to substrate holder. Instead of the formation of hillocks on the surface of the film, the RMS roughness was found to decrease in the 130 MeV Ni ion irradiated films relative to the pristine film when the films are irradiated with ions having electronic energy loss below the energy loss threshold for track formation.

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