Effect of chamber pressure and atmosphere on the microstructure and nanomechanical properties of amorphous carbon films prepared by pulsed laser deposition

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We have investigated the effect of chamber pressure and atmosphere on the microstructure and nanomechanical properties of amorphous carbon thin films prepared by pulsed laser deposition. The amorphous carbon films were deposited in various atmospheres such as nitrogen and argon at different chamber pressures. We used Raman spectroscopy to study the bonding characteristics of the deposited amorphous carbon films. Atomic force microscopy and optical microscopy were utilized to observe the surface conditions and the microstructures of the deposited films. Nanoindentation measurements were carried out on various samples prepared under different conditions to study the effect of chamber pressure and atmosphere on the elastic modulus and nanohardness of the films. It was found that reduced vacuum leads to formation of amorphous carbon films with reduced elastic modulus and nanohardness. Amorphous carbon films prepared under higher chamber pressures exhibit an increased density of particulates and significantly roughened surface. The results were understood in combination with the optical emission and electrostatic measurements of the laser plasma plume. It was found that the presence of atmosphere decreases the leading edge ionic energies of the species in the laser plasma plume and increases the thermalization of the laser plasma due to an increased possibility of collision. © *2001 American Vacuum Society.* [DOI: 10.1116/1.1322641]

I. INTRODUCTION

Due to its wealth of atomic structure and properties, amorphous carbon has been drawing research interest for the past two decades. The wide spectrum of the atomic structure and properties of amorphous carbon stems from the capability of carbon to form different hybridizations. Depending on the short-range environment, physical and mechanical properties of amorphous carbon can vary between the two crystalline extrema of carbon, i.e., graphite and diamond. When amorphous carbon mainly consists of tetrahedrally bonded carbon atoms, it is called diamondlike carbon (DLC), or tetrahedral amorphous carbon (t-aC). Highly tetrahedral carbon material can possess properties comparative to those of crystalline diamond. For example, the elastic modulus and hardness of crystalline diamond are about 1000 and 100 GPa, respectively.[1] The elastic modulus and hardness of mostly tetrahedral DLC can be as high as 700 and 70 GPa, respectively.[2] Furthermore, the mechanical and physical properties of DLC can be tailored with ease by changing the sp^3/sp^2 ratio. Combined with all the unique properties, DLC thin coatings have found wide applications such as tribological thin coatings that require chemical stability, good wear resistance and low coefficient of friction; infrared antireflective coatings; field emission sources for advanced flat panel displays; sensors; and so on.[3,4]

About one decade ago, it was considered that the presence of hydrogen would be necessary to stabilize the sp^3 bonding states and to saturate the dangling bonds in DLC materials, analogous to amorphous silicon. However, the successful production of hydrogen free, highly tetrahedral DLC films by pulsed laser ablation of a graphite target, and by other techniques, has established the fact that hydrogen is not necessary for the fabrication of DLC films.[5–8] What is more, investigations in the past few years have demonstrated that the presence of hydrogen in DLC films is detrimental to many of their properties, including hardness, thermal stability, etc.[9,10] It has now become common practice to produce hydrogen-free DLC using various thin film deposition techniques, such as pulsed laser deposition (PLD), mass selected ion beam deposition (MSIBD)[11] and filtered cathodic vacuum arc (FCVA)[12] deposition. A number of investigations have corroborated that ultraviolet (UV) pulsed laser ablation of a high purity polycrystalline graphite target is able to produce high quality DLC films with a Tauc gap of ~1.0–2.0 eV and an sp^3/sp^2 ratio of ~80%.[13] The interesting aspect of pulsed laser ablation is that it is a nonequilibrium process and the species produced in the laser plasma possess very high kinetic energy. For instance, the kinetic energy of atomic species produced by electron beam evaporation is around kT (0.025 eV at room temperature) (k is the Boltzmann constant and T is the absolute temperature) whereas those produced by pulsed laser ablation may be as high as 100–1000 kT

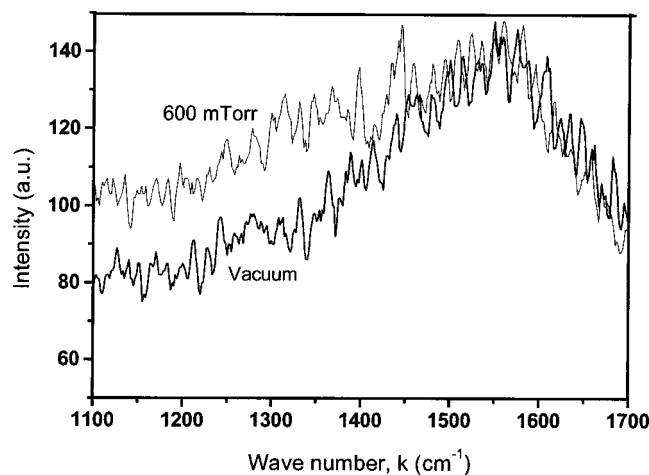[a)]Electronic mail: quiming@ncat.edu; qwei@eos.ncsu.edu

FIG. 1. Visible Raman spectra of amorphous carbon prepared via PLD *in vacuo* and amorphous carbon prepared under 600 mTorr of nitrogen.

FIG. 2. AFM micrograph of a DLC film prepared in high vacuum (5×10^{-7} Torr). The scale for the X and Y directions is 200 nm/div, and that for the Z direction is only 10 nm/div. The surface is atomically smooth.

($\sim$2.5–25 eV).[14] An additional advantage of PLD is that the vacuum chamber is isolated from the laser source, which makes it much easier to manipulate the target, the substrate, and a number of other deposition parameters. For example, up to four targets can be loaded into the target carousel, which gives one much more freedom to monitor the composition of the films to be deposited. Therefore, PLD has proved itself to be the most successful technique by which to fabricate hydrogen-free DLC films compared with other deposition techniques such as ion beam deposition, cathodic arc, plasma enhanced chemical vapor deposition, and so on.

The effects of substrate temperature, laser wavelengths, laser power, etc. on the resultant DLC films by PLD have been studied to some extent.[15,16] However, not much is known about the effect of chamber pressure and atmosphere on the preparation and properties of amorphous carbon films by PLD. For completeness of the understanding of the whole process of producing superhard amorphous carbon via pulsed laser deposition, and for the best use of the advantages of PLD, it is imperative to study the effect of chamber pressure and atmosphere on the structure and properties of amorphous carbon films prepared by PLD. In this article, we present results on the effect of chamber pressure and atmosphere on the microstructure and nanomechanical properties of amorphous carbon thin films prepared by pulsed laser deposition. The amorphous carbon films were deposited in various atmospheres such as nitrogen and argon at different pressures. A secondary motive for using N_2 atmosphere is to check the feasibility of obtaining the presumably superhard CN_x films by PLD. We used Raman spectroscopy and optical microscopy to study the bonding characteristics and microstructures of the films. Atomic force microscopy (AFM) was employed to study the surface condition of the amorphous carbon films. Nanoindentation measurements were carried out on various samples prepared under different conditions to study the effect of chamber pressure and atmosphere on the Young's modulus and nanohardness of the films. The results are discussed in combination with optical emission study and electrostatic measurements of an ablation plasma plume of a
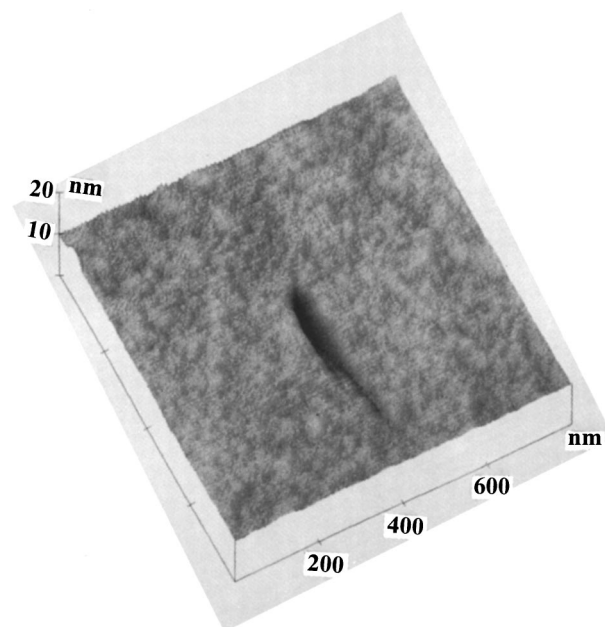
graphite target in various atmospheres and vacuum conditions.

II. EXPERIMENTAL DETAILS

We used (001) silicon wafers as the substrates for amorphous carbon deposition. The substrates were cleaned in acetone and methanol ultrasonic baths and dipped in HCl:HF to remove the native silicon oxide; they were then transferred into the vacuum chamber. The amorphous carbon thin films were deposited using a KrF excimer laser ($\lambda=248$ nm, duration $\tau=25$ ns) at a repetition rate of 10 Hz, with an energy density close to 3.0 J/cm^2, which gives an average power density of $\sim 10^8$ W/cm^2. All the depositions were performed at room temperature in a stainless steel chamber that can be evacuated to a high vacuum of about 5×10^{-7} Torr, and the chamber pressure can be monitored by introducing a certain amount of gas. We prepared pure DLC films under a vacuum of 5×10^{-7} Torr. In order to study the effect of chamber pressure and atmosphere on the microstructure and nanomechanical properties of the amorphous carbon films, we also prepared films under various pressures of argon and nitrogen. The chamber pressures with nitrogen are 63, 100, 200, 300, 500, and 600 mTorr, while those with argon are 100, 200, 300, and 500 mTorr, respectively. We used visible Raman spectroscopy, atomic force microscopy, and optical microscopy to study the bonding characteristics and microstructure (especially the surface morphology) of the thin films, and we used Nanoindenter^{XP} manufactured by MTS to study the nanomechanical properties of the films.

In order to understand the effect of background gas on the laser plasma plume, both optical emission studies and electrostatic measurements were conducted for the diagnostics of
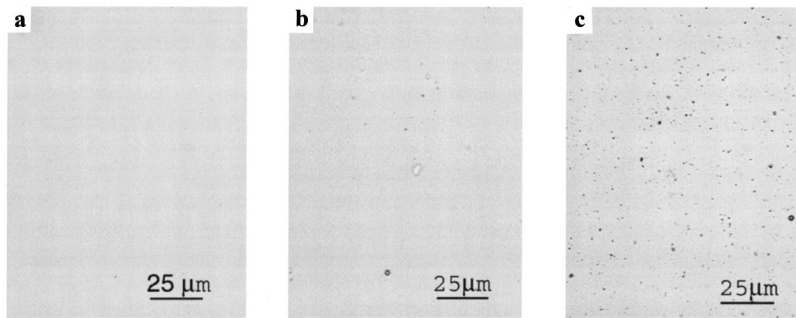
FIG. 3. Optical micrographs of diamondlike carbon film prepared by pulsed laser deposition in a vacuum of 5×10^{-7} Torr (a), amorphous carbon film prepared by pulsed laser deposition in an atmosphere of 500 mTorr argon (b), and amorphous carbon film prepared by pulsed laser deposition in an atmosphere of 63 mTorr nitrogen (c).

the plasma plume. The diagnostics involved an optical multichannel analyzer (OMA) and a triple Langmuir probe. Details of the diagnostics are described elsewhere.[17,18]

III. RESULTS AND DISCUSSION

Optical profilometry of the samples showed that the thickness of the amorphous carbon films prepared in nitrogen atmosphere increases with chamber pressure, from 300 nm under 67 mTorr N_2 to 1200 nm under 500 mTorr N_2. It also shows that those prepared in argon atmosphere have a relatively constant film thickness of about 400 nm.

The Raman spectra of two amorphous carbon films are given in Fig. 1. Figure 1 consists of two visible Raman spectra, one from a DLC film prepared with 200 mJ laser energy in vacuum (5×10^{-7} Torr), and one from an amorphous carbon film prepared in nitrogen atmosphere under 600 mTorr. Visible Raman spectra of amorphous carbon usually consist of two bands. The first one is a hump centered in the range of 1510–1557 cm^{-1}, which is associated with an optically allowed E_{2g} zone center mode of crystalline graphite (1580 cm^{-1}), and is thus designated as the G band. The other band is a shoulder at around 1350 cm^{-1}, which is associated with the disorder-allowed zone edge mode of graphite and is thus designated as the D band (A_{1g} mode). It is observed that increased background pressure increases the D component of the Raman spectrum of amorphous carbon. It is known that the D component in the Raman spectrum of amorphous carbon indicates the existence of micro- or nanocrystallites of graphite in the specimen, which means, consequently, poor quality in terms of diamondlike carbon properties. Pure, high quality DLC films (with a high fraction of sp^3 bonded carbon atoms) exhibit a relatively vanishing D component in the visible Raman spectrum.[19]

Figure 2 is an AFM micrograph of a DLC film prepared in high vacuum, in the absence of any intentionally introduced background gas. It should be noted that the scale in the X and Y directions is 200 nm per division, while that in the Z direction is only 10 nm per division. The indent in the center of the micrograph was for hardness measurement. It is observed from Fig. 2 that the surface of the DLC film prepared in high vacuum is atomically smooth. The atomically smooth surface of PLD processed DLC films is an advantageous attribute of PLD, particularly of short wavelength excimer lasers. Usually the very smooth nature of the deposited films is explained based on surface energy considerations.

The total surface energy is equal to the product of the surface tension and the surface area, and the drive to minimum total energy corresponds to a drive to a minimum area. The driving force is proportional to the surface tension which is dependent on the energy of the species on the surface. In the case of highly energetic and nonequilibrium incident species, such as produced by laser ablation, the surface tension is unusually large and thus provides a strong drive to a minimum surface area.

Figure 3 shows optical micrographs of high vacuum DLC and amorphous carbon films prepared in various atmospheres under different pressures. The micrograph of diamondlike carbon film shows that the surface is almost free from particulates [Fig. 3(a)], consistent with AFM observations (Fig. 2). The amorphous carbon thin films prepared under 500 mTorr of argon exhibit particulates of various sizes, as shown in Fig. 3(b). The worst surface condition was obtained for amorphous carbon films prepared in various pressures of nitrogen atmosphere, where a large density of small particulates can be observed. An example is given in Fig. 3(c).

It is also observed that the surface condition and density of particulates are a function of the chamber pressure, especially in the case of nitrogen background gas. Figure 4 shows an optical micrograph of two amorphous carbon films prepared by pulsed laser deposition under different chamber pressures of nitrogen atmosphere. It is observed that, with increased background nitrogen pressure, both the particulate density and, consequently, the surface roughness are increased. However, this tendency is not very significant in the
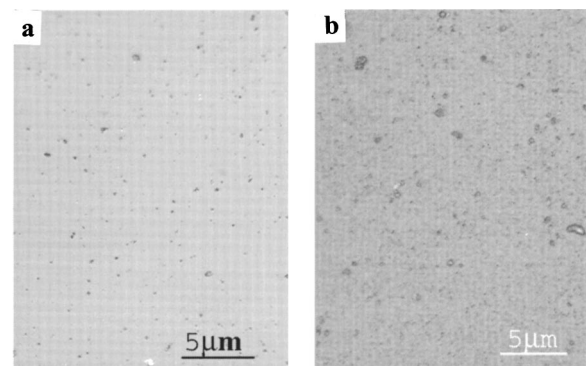

FIG. 4. Optical micrographs of amorphous carbon prepared in a nitrogen atmosphere of 200 (a) and 500 mTorr (b). The latter has a greater density of particulates and, therefore, more surface roughness.
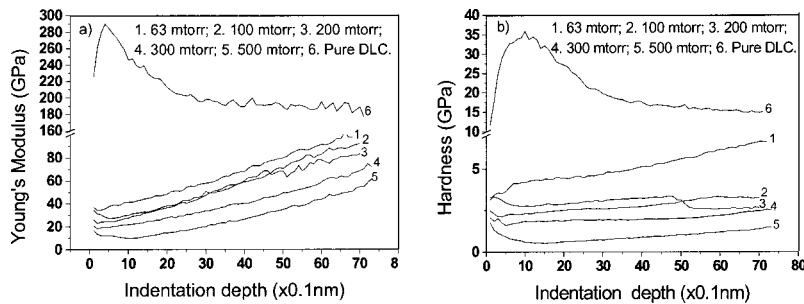
FIG. 5. Elastic modulus (a) and nanohardness (b) as a function of indentation depth of amorphous carbon films prepared in vacuum and in different pressures of nitrogen atmosphere.

case of amorphous carbon films prepared in argon atmosphere where, although a poor surface condition is also observed, the effect of changing pressure is not as considerable. It has previously been recognized that high quality DLC films prepared by UV pulsed laser possess an atomically smooth surface due to the nonequilibrium characteristics of the PLD process, which produces highly energetic species in the laser plasma. A resultant rough surface may indicate less-energetic incoming species when other conditions remain unchanged. Since particulates are absent from the DLC films prepared in vacuum, those particulates observed in the amorphous carbon films might be formed in the plasma plume in the presence of atmospheres. It should also be noted that the geometric shape of the particulates observed in the amorphous carbon films produced in Ar or N_2 background gas does not suggest that they are due to the splashing mechanism.[20] The splashing mechanism produces liquid droplets from the target, which are subsequently solidified onto the substrate, giving well defined spherical particulates.

In order to understand the effect of atmosphere and chamber pressure on the properties of the amorphous films, nanoindentation measurements were performed on the samples. The nanoindentation technique we have used measures the load as a function of displacement. The design of the nanoindenter allows us to acquire a depth-sensing measurement of the mechanical properties of thin films. The following equations were then used to calculate the hardness and Young's modulus of the specimen from the load-displacement curves,

$$H = \frac{P_{max}}{A},$$ (1)

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i},$$ (2)

where P_{max} is the peak indentation load and A is the projected area of the hardness impression; E_r is the reduced modulus, ν and E the Poisson ratio and Young's modulus of the specimen; ν_i and E_i are the Poisson ratio and the Young's modulus of the diamond indenter. The built-in area function, A, was calibrated using the method proposed by Oliver and Pharr.[21]

Figure 5 gives the elastic modulus and nanohardness of the DLC films prepared in vacuum and those prepared in various pressures of nitrogen atmosphere. The curve corresponding to vacuum DLC is typical of nanoindentation measurements for a hard film on a soft substrate, where the hardness and elastic modulus values increase as the indentation depth, and reach a peak value, then decrease as the indenter goes deeper.[22–24] This behavior is associated with the relatively soft substrate underneath which leads to a sink-in effect even though the indenter is not yet through the film. Those curves corresponding to the amorphous carbon films prepared in nitrogen background are typical of nanoindentation measurements for a soft film on a hard substrate, where the values of the elastic modulus and hardness increase toward those of the substrate, and microscopic observations as well as finite element analysis revealed a build-up phenomenon around the hardness impressions.[25,26] It is therefore observed from Fig. 5 that the presence of nitrogen in the chamber remarkably reduces the mechanical properties of the amorphous carbon films, and that the hardness and elastic modulus decrease with increased background gas pressure.

Figure 6 shows the elastic modulus and nanohardness of amorphous carbon films prepared in vacuum and in various pressures of argon. Again we can see that the presence of atmosphere in the deposition chamber reduces the nanomechanical properties of the resultant amorphous carbon films. From Fig. 6, it is also observed that the elastic modulus and
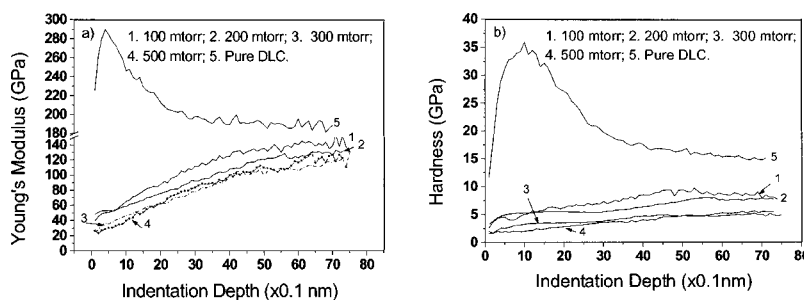

FIG. 6. Elastic modulus (a) and nanohardness (b) as a function of indentation depth of amorphous carbon films prepared in vacuum and in different pressures of argon atmosphere.

nanohardness of the amorphous films prepared in the presence of argon decrease with the background gas pressure.

While the DLC films prepared in high vacuum and the amorphous carbon films prepared under various background gas pressures exhibit strikingly different properties, the only difference in the preparation parameters is the presence of background gas and gas pressures. Therefore, to understand the observed effect of atmosphere and chamber pressure on the microstructure, bonding states, and nanomechanical properties of amorphous carbon, we will have to invoke the diagnostics of the plasma plume associated with PLD in different atmospheres and under different background gas pressures. It was observed in this work that, apart from the laser parameters such as laser wavelength,[27,28] energy density,[29] and substrate parameters (thermal conductivity and temperature, for example), another important parameter that has a strong influence on the preparation of amorphous carbon is the chamber pressure and atmosphere. This aspect of the phenomena can be understood by means of laser plasma diagnostics using electrostatic measurement of plasma plume[18] and optical emission study of the laser plasma.[17] For example, OMA has revealed that with increasing background nitrogen pressure up to 500 mTorr, the emission intensities of the C_2 Swan band and the carbon–nitrogen (CN) violet band increase. It is known that only atomic and ionized carbon species contribute to the formation of highly tetrahedral amorphous carbon, which is the justification for the application of the MSIB (Ref. 11) and FCVA (Ref. 12) deposition techniques for DLC preparation. Studies using an ArF excimer laser (193 nm) even revealed that only vanishing peaks of molecular carbon bands could be observed in the emission spectra of the laser plasma.[29] The high vacuum, UV laser ablated plasma emission spectra are dominated by monoatomic neutral (C_I) and ionic (C_{II}) emission lines. During UV laser ablation of a graphite target, carbon ions can be generated from the following three possible mechanisms:[29] (1) the multiabsorption of photons to the graphite surface to reach the ionization threshold of carbon which is 11.264 eV $[C(s)+Nh\nu\Rightarrow C^+(g)+e^-]$, (2) the multiphoton ionization of gaseous carbon atoms to release ions $[C(g)+Nh\nu\Rightarrow C^+(g)+e^-]$ or the multiphoton absorption of atomic carbon to excited state and autoionization to ion, and (3) the collision of neutral atoms with energized electrons via inverse bremsstrahlung $[C(g)+e^-\Rightarrow C^+(g)+2e^-]$. The third mechanism is considered to be less important than the first two for the UV excimer laser due to the small absorption coefficient of electrons in the short-wavelength regime. It is easy to understand that the presence of background gas may reduce the probability of the second and third mechanisms of ionization and results in more molecular carbon species, which is detrimental to the preparation of high quality DLC films.

It has been found both experimentally[30] and theoretically[31] that the expansion of the plasma plume of ablated matter can be significantly affected by the collision between the laser-ablated and the background gas particle. Monte Carlo simulations[32] of the influence of a background
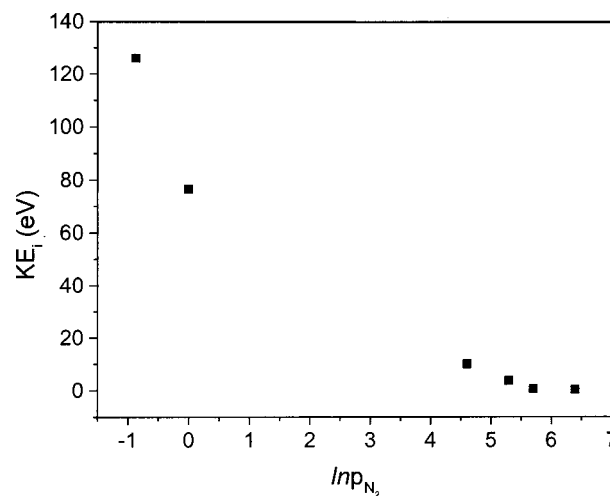

FIG. 7. Leading edge ionic energies of the plasma plume as a function of background nitrogen pressure. The leading edge ionic energy decreased almost exponentially with the background nitrogen pressure, from ~126.0 eV at 1.6×10^{-7} Torr to 0.24 eV at 600 mTorr.

gas on the expansion dynamics of a laser-induced carbon plasma plume indicated that the dynamics of the expansion of the plume under high residual pressure appears to be different from that in low-pressure cases. The former is accompanied by stronger thermalization of the plume and is evidence of the oscillatory behavior of the plasma plume expansion. Electrostatic measurements of the plasma plume further indicated that the leading edge ion kinetic energy of the plasma plume decreased almost exponentially with the background nitrogen pressure, from ~126.0 eV at 1.6 $\times10^{-7}$ Torr to 0.24 eV at 600 mTorr. This observation is shown in Fig. 7. Investigations of the relation between sp^3 fraction and ion kinetic energy of PLD processed diamond-like carbon showed that the optimal ion kinetic energy for highly tetrahedral amorphous carbon lies in the range of ~60 eV and up, with around 100 eV giving the maximum sp^3 bonded carbon.[33] The decrease of ionic energy with background pressure also helps one to understand the deterioration of surface condition of the amorphous carbon films in the presence of background atmosphere. The formation of particulates in the case of nitrogen atmosphere can be understood on the basis that carbon and nitrogen form clusters en route to the substrate surface. Whereas in the case of argon atmosphere, no such clusters could be formed, yielding a much lesser density of particulates.

Recently, several groups reported preparation of amorphous CN_x films by ablating a graphite target in N_2 atmosphere.[34–36] These authors used Raman, x-ray photoelectron spectroscopy, infrared spectroscopy, etc. to study bonding structures of the films. However, mechanical properties have not been provided. Considering that the hypothetical crystalline counterpart of CN_x, namely, β-C_3N_4, is predicted to be even harder than crystalline diamond, we propose that nanomechanical testing be performed for such CN_x films to verify whether they are superhard, or at least hard, films. Our nanomechanical measurements on the amor-

phous carbon films prepared in N_2 atmosphere do not suggest any close relation between these films and the hypothetical crystalline β-C_3N_4 phase.

IV. SUMMARY AND CONCLUDING REMARKS

The effect of chamber background gas pressure and atmosphere on the microstructure and nanomechanical properties of amorphous carbon thin films prepared by pulsed laser deposition was investigated. The amorphous carbon films were deposited in various background gases such as nitrogen and argon at different pressures. We used Raman spectroscopy, atomic force microscopy, and optical microscopy to study the bonding characteristics and microstructures, particularly the surface conditions of the amorphous carbon films. Amorphous carbon films prepared under high vacuum exhibit an atomically smooth surface. It was found that reduced vacuum leads to softer amorphous carbon films, with increased surface roughness and particulate density. The density of particulates and the roughness of the surface of the amorphous carbon films prepared in nitrogen background gas are a function of the gas pressure. Nanoindentation measurements were carried out on various samples prepared under different conditions to study the effect of chamber pressure and atmosphere on the Young's modulus and nanohardness of the films. The presence of background gases drastically reduces the elastic modulus and hardness of the amorphous carbon films. The results can be understood in terms of laser plasma diagnostics by means of emission and electrostatic measurements, which showed increased molecular carbon emission and almost exponentially decreased leading edge ion kinetic energy with background gas pressure.

ACKNOWLEDGMENT

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