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INFLUENCE OF DEPOSITION PARAMETERS ON THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF AMORPHOUS CARBON AND AMORPHOUS CARBON NITRIDE FILMS GROWN BY PULSED LASER DEPOSITION USING CAMPHORIC CARBON TARGET

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The role of laser fluence (LF) and target to substrate distance (TSD) on the surface morphology, deposition rate, composition, structural, optical and electrical properties of amorphous carbon (a-C) and amorphous carbon nitride (a-CN_x) films deposited by Xe-Cl excimer pulsed laser deposition is reported. At fixed TSD, the surface roughness, particle density and deposition rate increase, whereas the particle size decreases with higher LF. When the LF is fixed, TSD decreases resulting in an increase in the irregular small particle size, particle density, surfaces roughness and deposition rate. We found that the amorphous structure of a-C and a-CN_x films is strongly dependent on the LF and TSD. The a-CN_x films with high deposition rate have relatively high nitrogen content and high electrical resistivity.

Keywords: laser fluence; target to substrate distance; deposition parameter; amorphous carbon; amorphous carbon nitride; pulsed laser deposition

INTRODUCTION

Pulsed laser deposition (PLD) technique used for film preparation has become popular for its simplicity, versatility and capability to generate highly energetic carbon (C) species with large tetrahedral (sp^3) fractions which enhances the synthesis of high quality films with good mechanical and optical properties [1]. It is known that, deposition parameters effect the formation of crystalline phase and amorphous structure of amorphous C nitride (a-CN_x) due to incorporation of nitrogen (N) and change in ratio of sp^3-C to trihedral (sp^2)-C in the films. We have introduced N^2 at 0.8 Torr into the chamber to deposit the N incorporated carbonaceous films on quartz and silicon substrates by excimer laser beams using camphoric C ($C_{10}H_{16}O$) (CC) target on quartz and silicon (100) substrates. We will discuss the different bonding structure that occur in a-CN_x films when they are deposited at different laser fluence (LF) with fixed target to substrate distance (TSD) and at different TSD with fixed LF, and compared with amorphous C (a-C) film which was also deposited in the same range of the corresponding parameters.

EXPERIMENTAL

We report the roles of LF range from 2.8 to 5.2 J/cm^2 at 45 mm fixed TSD and TSD range from 25 to 45 mm at 3.4 J/cm^2 fixed LF, on the deposition of a-CN_x films, deposited at 0.8 Torr N gas ambient, and under similar condition, a-C was also deposited but without N gas ambient. To investigate the roles of LF for a-C films, the CC target was ablated by excimer PLD (NISSIN 10X, XeCl, $\lambda = 308$ nm, $\tau = 20$ nsec, repetition rate = 5 Hz), which is focused on the target normal by a ultraviolet grade plano-convex lens, at an incident angle of 45 degree, at room temperature. The LF was maintained in range from 2.8 to 5.2 J/cm^2 by adjusting the laser energy and the lens to target distance for adjusting the laser spot size. The substrate was mounted on a metal substrate stage holder parallel to the CC target at a distance of 45 mm. In order to ensure a uniform ablation rate, the CC target was rotated at each 50 shots. The deposition chamber was evacuated to a base pressure approximately at 2×10^{-5} Torr using a turbomolecular pump. For a-CN_x films, N gas ambient was allowed until the chamber pressure is attained 0.8 Torr. To investigate the roles of TSD, the CC target was ablated using the above procedure and TSD was set in range from 25 to 45 mm at 3.4 J/cm^2 fixed LF. The variations in the film thickness, surface morphology, compositional, structural, optical and electrical properties of the films have been investigated using standard measurement technique [2].

RESULTS AND DISCUSSIONS

SEM and AFM showed that, the surface morphology of a-CN_x films was smoother compared with the a-C films deposited in the same range of the corresponding parameters. At fixed TSD, the surface roughness and particle density of a-C and a-CN_x films increased, whereas the particle size decreased with higher LF, and this agree with the works of Blank *et al.* [3]. When the LF is fixed, TSD decreased resulting in an increase in the irregular small particle size, particle density and surface roughness. As the TSD increases, the proportion of the smaller particles decreases, and a few larger particles appeared, indicating a merge during flight and the adhesion to the substrate of ejected matter, including the particles and atomic species, is poorer [4].

The maximum average rate of deposited film was calculated as the quotient of the measured maximum thickness and the number of pulses applied. Figure 1 shows the deposition rate plotted as a function of LF in range 2.8 to 5.2 J/cm^2 and TSD in range 25 to 45 mm, while fixed TSD at 45 mm and LF at 3.4 J/cm^2, respectively. As shown in Figure 1(a) and 1(b), the deposition rate of a-CN_x is lower than a-C films deposited in the same range of the corresponding parameters. This may be due to the reason that the increased collisions between the ejected species and the ambient gas as the ambient gas pressure increases [5]. It has been reported [6,7] that despite the slight variation of chemical composition, in accordance with the expectations the films deposited at fixed TSD exhibited a fairly linear deposition rate as a function of LF. It is believed that an almost linear dependence of the deposition rate on the LF is the proof that almost all the

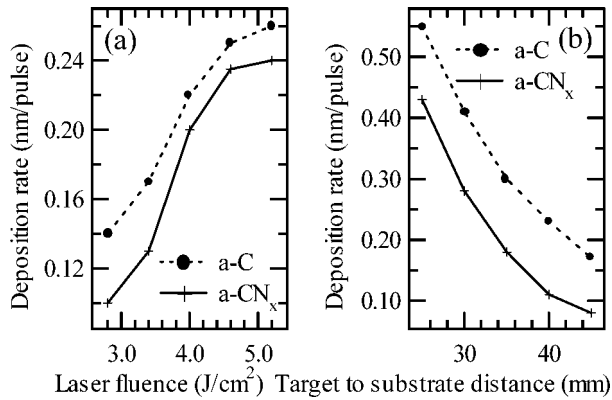

FIGURE 1 Dependence of deposition rate of a-C and a-CN_x films on: (a) laser fluence, and (b) target to substrate distance.

energy absorbed by the target contributed to the deposition [7]. Our experimental results show that at fixed TSD, for both a-C and a-CN_x films the deposition rate, particle density and surface roughness increase, while the particle size decreases with increasing LF. However as shown in Figure 1(a), our result shows that the increase rate of deposition rate reduces at higher LF, indicating saturation. The saturation of the particle and film deposition, in general, is largely due to the saturation in the deposition process [8]. For example, plasma shielding of the target is one of the mechanisms that reduce the ablation rate, and is more often encountered in the PLD using longer wavelength [9]. It should also be noted that, the saturation of the particle density at higher LF may be somewhat exaggerated, since the sticking of the particles to the substrates appears to be poorer at elevated LF [10]. It is clear from Figure 1(b) that at fixed LF, the deposition rate of both a-C and a-CN_x films decreases with increasing TSD. This is can satisfactorily be accounted for by the increased number of collision during deposition [11]. With the decrease of TSD, the deposition rate increased because of increase of actual density of the primary deposition product of the carbon atoms, whereas with the increase of TSD the deposition rate decreased because the reaction products contribute to the film growth [6] and for a-CN_x films also may be due to surface etching by activated N species [12]. We found the deposition rate, particle size, surface roughness and the particle density of a-C and a-CN_x films to be strongly dependent on the deposition parameters, such as the LF and TSD.

Figure 2 illustrates the Auger Electron Spectroscopy (AES) spectra of typical a-C and a-CN_x films, showing that the films were mainly composed of C and N. The existence of a small oxygen (O) signal was a result of air exposure during sample transport. The spectra were compared, revealing that the peak increases with the increase of LF and decrease of TSD. The intensity of N peak in the low energy region corresponds to the LF and TSD, indicating that N was effectively doped into the a-C films during deposition and also implying that N content in the films increases with the increase of LF at fixed TSD and decrease of TSD at fixed LF as the peak intensity shows the increasing tendency.

Figure 3 shows the Fourier Transform Infrared Spectroscopy (FTIR), spectra measured in the wave number range 1200–3500 cm^{-1}. The peak at around 1000–1700 cm^{-1} can be assigned to C–N and C=N bonds and the broad band extending in range 2800–3000 cm^{-1} corresponds to different C–H configurations [13]. It is clear from the spectra that as LF increases, while keeping TSD constant at 45 mm, and as TSD decreases, while keeping LF constant at 3.4 J/cm^2, the intensity of the 1000–1700 and 2800–3000 cm^{-1} peaks become more and more prominent suggests the formation of crystalline structure in the films [14]. The event may be taking place during the deposition process, as well as adsorption from the atmosphere ambient

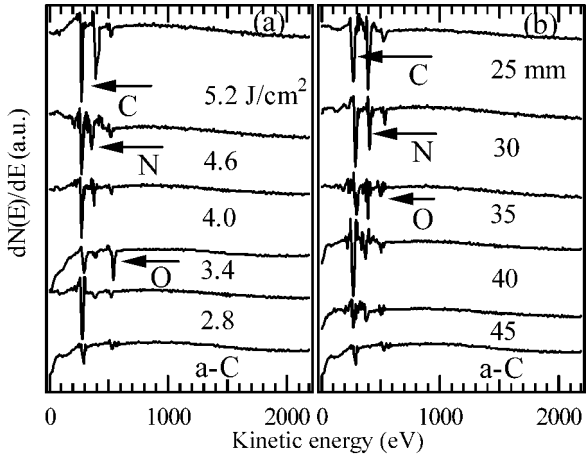

FIGURE 2 The Auger electron spectra of typical a-C and a-CN_x films with various: (a) laser fluence, and (b) target to substrate distance.

may contribute to the hydrogen content. Since the bonding energy of the C-H configurations is relatively low, collisions between carbon containing radicals and hydrogenated products present in the CC target may further increase the probability of H incorporation with the increase of LF and decrease of TSD. The N content in the films gradually increases with the

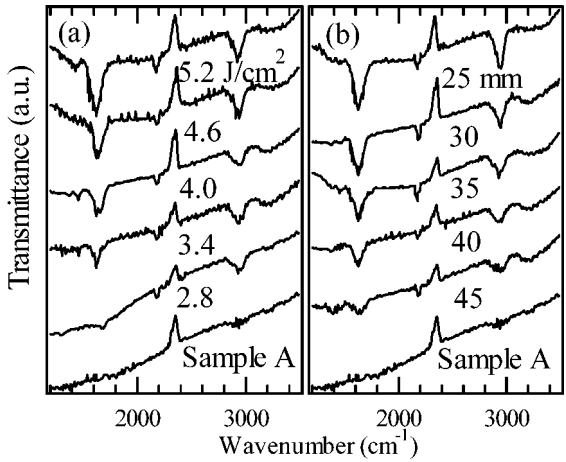

FIGURE 3 The FTIR spectra of typical a-C and a-CN_x films with various: (a) laser fluence, and (b) target to substrate distance.

increase of LF and decrease of TSD, as indicated by the increase in the intensity of the C and N bonding peak areas. The broad band between 1000–1700 cm^{-1} does not appear in a-C films. The absorption peak at around 2350 cm^{-1}, which is observed in a-CN_x and a-C, can be attributed to the CO_2 stretching mode arising from O contamination at the film surface [13]. FTIR shows the N incorporation and crystalline structure of the films increases with the increase of LF at constant TSD and decrease of TSD at constant LF. This is evident the composition of the films can be tuned by the LF and TSD.

Figure 4(a) shows at fixed TSD, the optical gap (E_g) and electrical resistivity (ρ) of a-C film at 2.8 J/cm^2 of LF which is 0.88 eV and 4.6×10^5 [Ω-cm], respectively and increase with higher LF up to 1.0 eV and 8.1×10^5 [Ω-cm] at 5.2 J/cm^2, respectively. The E_g of a-CN_x film decreases to 0.86 eV and ρ is increases to 8.51×10^6 [Ω-cm] at 2.8 J/cm^2. As LF increases, the E_g increases up to 0.93 eV at 3.4 J/cm^2 and thereafter shows the rate of increase reduces at higher LF, indicating saturation. While ρ is increase up to 9.01×10^6 [Ω-cm], at 5.2 J/cm^2. Figure 4(b) shows at fixed LF, the E_g and ρ of a-C film at 45 mm of TSD is 0.95 eV and 5.1×10^5 [Ω-cm], respectively. The E_g decreases and ρ increases with lower TSD up to 0.6 eV and 9.0×10^5 [Ω-cm] at 25 mm, respectively. The E_g of a-CN_x film decreases to 0.93 eV and ρ is increases to 8.61×10^6 [Ω-cm] at 45 mm. As TSD decreases, the E_g decreases to 0.48 eV, while ρ increases up to 9.76×10^6 [Ω-cm] at 25 mm. The increase in ρ with N incorporation may be due to the lattice vibrations

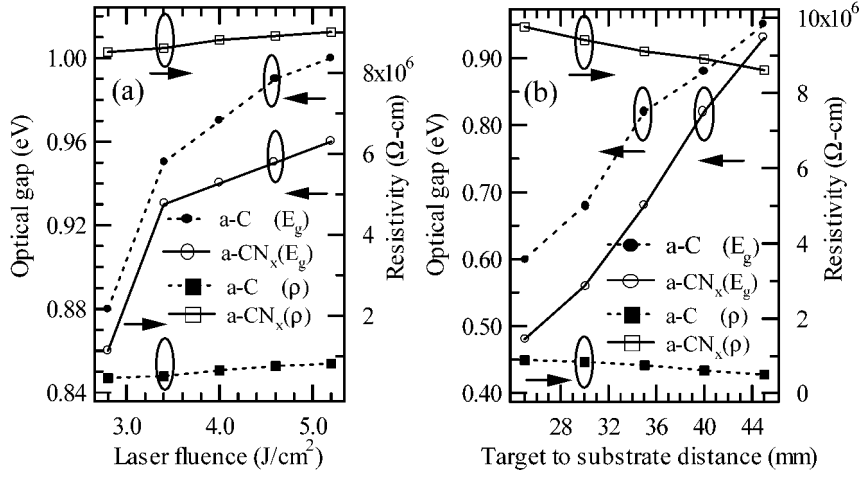

FIGURE 4 Dependence of optical gap and resistivity of a-C and a-CN_x films on: (a) laser fluence, and (b) target to substrate distance.

leading to the scattering of the charge carriers by the N atoms and more amorphous nature of the C films. Variation of the optical and electrical properties of a-CN_x films can be related to interstitial doping of N in C films through compensation of the dangling bonds and modifications of C-N bonding configurations by rearranging N atoms upon increase of LF and decrease of TSD. The increasing rate in Eg decreases at higher LF and the decrease in Eg at lower TSD with N incorporation is also probably due to the graphitization of the a-CN_x films. Perhaps the doping of N accompanied by the increase of LF and the decrease of TSD caused the increase in crystallinity and substitutional doping of N thereby decreases Eg.

CONCLUSIONS

Tuning the LF within the 2.8 to 5.2 J/cm^2 domain and TSD within 25 to 45 mm domain result in significant changes in the surface morphology, deposition rate, chemical composition and electrical properties of a-C and a-CN_x films deposited by PLD using CC target. At fixed TSD, the surface roughness, particle density, deposition rate, E_g and ρ increase, whereas the particle size decreases with higher LF. When the LF is fixed, decreasing TSD results in an increase in the irregular small particle size, particle density, surfaces roughness, deposition rate and ρ, whereas E_g decreases. We found that the amorphous structure of a-C and a-CN_x films is strongly dependent on the LF and TSD. The a-CN_x films with high deposition rate have relatively high N content and high ρ.

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