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Carbon Thin Films Prepared by Pulsed Laser Deposition

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Amorphous carbon films (a-C), which do not have an optical band gap, and diamond like carbon(DLC) films, which do have an optical band gap, were grown by pulsed laser deposition (PLD) using different laser wavelengths (λ = 193 nm, 532 nm, 1064 nm) and substrate temperatures (from room temperature to 500°C). It was found that the various properties of the deposited thin films such as optical absorption coefficient, optical band gap and microstructure, were strongly dependent on both the laser wavelength and the substrate temperature. The morphology of the film surface was observed using an atomic force microscope (AFM). Mechanisms for film growth could be explained well qualitatively, using the subplantation model.

Key words: PLD, DLC, amorphous carbon, subplantation model, Raman spectrum

1. INTRODUCTION

The preparation of carbon thin films by Pulsed Laser Deposition(PLD) has received much attention in recent years, because this method produces films which do not contain hydrogen[1] and have unusual properties such as good adherence on a variety of substrates, very high hardness, chemical inertness, low friction coefficient and electrical resistivity. It is known that the film properties strongly depend on the deposition conditions,[2] but there have been few studies of the correlation between the deposition parameters and the growth mechanism. Therefore, it is necessary to clarify the effects of deposition parameters, such as laser wavelength, fluence, substrate temperature, target material and ambient gas, on the film growth in order to obtain carbon thin films with the desired properties. In particular, two major factors which determine the film growth are the substrate temperature and the properties of the deposited energetic species, which depend on laser wavelength and fluence.[2,3] These two factors control the adatom mobility on the film surface and thereby determine the physical characteristics of the deposited films, such as the optical indices and microstructure.

In this paper, we report the result of a study in which we investigated the effects of the substrate temperature and the laser wavelength on the film structures and optical properties.

2. EXPERIMENT

Carbon thin films with thickness of 100 nm were deposited on glass and silicon substrates at temperatures in the range of 20 ~ 500°C by PLD using a graphite target. The properties of obtained films did not depend on the kind of substrate. The substrates were set parallel with the target at a distance of 30 mm from the target. The laser sources used were an ArF excimer laser beam (Lambda Physik LPX350ST, 193 nm, 24 ns) and a Q-switched Nd:YAG laser (LOTIS LS-2125, 1064 nm or 532 nm, 13 ns). The irradiation area on the target was approximately 2 mm^2 and the laser fluence was 5 J/cm^2. The irradiance of 193nm laser is 1.5×10^8 W/cm^2, and those of 532nm and 1064 nm lasers are 2.7×10^8 W/cm^2. The repetition rate of the laser pulse is 10 Hz. For these conditions, the typical deposition rate was 0.5 nm/sec. The base pressure in the chamber was less than 10^{-6} Torr. The surface morphologies and the microstructure of the deposited films were observed by an atomic force microscope (AFM:Nanoscope) and the transition electron microscope (TEM:JEM-200CX), respectively. The absorption spectra of the deposited films were measured with a spectrophotometer (SHIMADZU UV-160A). The Raman spectra were measured using JASCO NRS-2000.

3. RESULTS AND DISSCUSSION

The optical band gaps E_{opt} were estimated from the absorption spectra. The estimated E_{opt} as a function of the substrate temperature for the different laser wavelengths is shown in Fig. 2. The films deposited with the 1064 nm laser have small E_{opt} at a substrate temperature of 20°C. At higher temperature, they have no E_{opt}, which can be attributed to the generation of a-C with graphitic and metallic properties. For films deposited with the 532 nm laser, E_{opt} is approximately 0.7 eV at 30°C and decreases gradually as the substrate temperature increases, and has a value of zero at 350°C. The absorption coefficient increases as the substrate temperature increases. These results also indicate that the films become more graphitic as the substrate temperature increases. For the films deposited with the 193 nm laser, all the films have an optical band gap of 0.5 – 0.6 eV, and this hardly depends on the substrate temperature. This indicates that the sp^3 bonding fraction is not dependent on the substrate temperature.

Raman spectra of the deposited films as a function of the substrate temperature for the

different laser wavelength are shown in Fig. 2. The films deposited with the 1064 nm laser showed a broad peak, which resemble those of the typical DLC films reported in other publication.[2] As the substrate temperature increases, it splits into the D peak and the G peak. For films deposited with the 532 nm laser, the broad peak splits into two peaks at more than 230°C as well as those deposited using the 1064 nm laser. The change of Raman spectra of films deposited using 1064 nm and 532 nm coincide with the generation of a-C. For films deposited with 193 nm laser, the broad peak splits into two peaks at more than 370°C, but the films showing two peaks have an optical band gap. The transition of Raman spectrum patterns from the broad peak, which is observed in typical DLC films,[2] to two peaks does not always coincide with that from DLC to a-C. As G peak is attributed to the generation of graphite crystallite, the transition of Raman spectrum pattern might indicate the generation of the graphite crystallites. The films showing the broad peak of typical DLC have always an optical band gap. In other words, there is sp^3 bonding in the films.

The microstructure of deposited films was investigated using transition electron diffraction. All DLC films showed halo pattern due to amorphous structure, which is not dependent on the laser wavelength. The a-C films deposited at substrate temperature of more than 450°C using the 1064 nm laser and the 532 nm laser showed weak rings due to the generation of small graphite crystallites, as shown Fig.3(a). These rings can be assigned to be (002), (101), (112) from inside ring to outside one. On the other hand, as shown in Fig.3(b), the DLC films deposited at more than 450°C using the 193 nm laser showed the inclined diffraction rings due to preferred orientation. The rings attributed to (002) and (004) of graphite are obviously inclined. The other rings are too weak for the inclination to be recognized and assigned surely. These might be from (101) and (110) of graphite. This result indicates that the atoms deposited on the substrate using 193 nm laser have energy high enough for the growth of oriented crystallites. In other words, the deposition with the 193 nm laser is most energetic amongst these laser wavelengths. Thus, in order to grow diamond, which is the phase generated in high temperature and high pressure, the 193 nm wavelength and the substrate temperature of more than 400°C are appropriate. Actually, it has been reported that diamond crystals grow in carbon films deposited at 193 nm and around 450°C.[4,5] In our study, however, we could not observe any diamond crystals in carbon films deposited at this condition. This may be attributed to the difference of the other preparation conditions, such as the laser fluence, ambient gas, and pretreatment of the substrate. Thus it is thought that the diamond growth is difficult using the conventional PLD

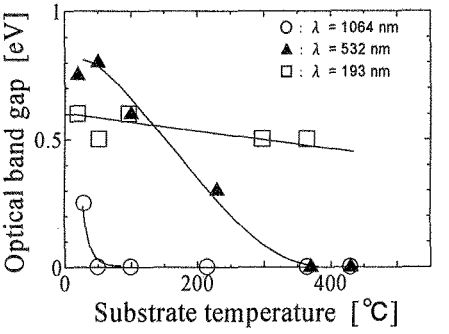

Fig. 1 Dependence of the optical band gap of carbon thin films deposited using the 1064nm, 532 nm and 193 nm lasers on the substrate temperature.

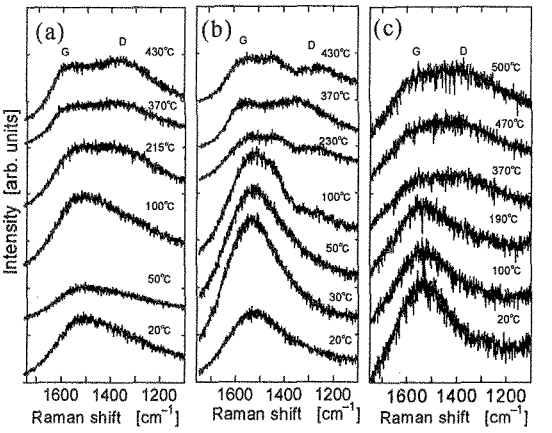

Fig.2 Raman spectra of deposited films as a function of the substrate temperature for the laser wavelengths of (a) 1064 nm, (b) 532nm and (c) 193 nm.

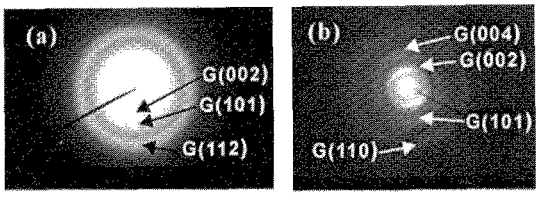

Fig. 3 Electron diffraction patterns of films deposited at the substrate temperature of 450°C using (a) the 1064 nm laser and (b) the 193 nm laser.

method, as in our apparatus. In order to grow diamond films, in addition to deposition using the high energetic atoms and ions, it is necessary to assist the diamond growth by a chemical effect such as the etching of graphitic components using atomic hydrogen and oxygen, as well as chemical vapor deposition. The graphite crystallites generate at the high substrate temperature, which is not dependent on the laser wavelength. The appearance of the G peak and the D peak in Raman spectra might be attributed to the generation of graphite crystallites.

In order to be able to discuss the film growth mechanism using the subplantation model,[6] we observed the surface morphology of the deposited films with AFM. Fig.4 shows the typical AFM images of the DLC films and the a-C films

deposited using the 532 nm laser. As shown in Fig.4(a), the DLC film deposited at 20°C has an extremely smooth surface with a roughness of less than 0.5 nm, which is comparable with DLC films prepared by ion beam deposition with some filtering.[7] On the other hand, the a-C films, which are produced when the temperature is more than 350°C, have a roughness of 50 nm as shown in Fig.4(b).

The effects of substrate temperature on growth of carbon films are explained according to the subplantation model as follows. At a low substrate temperature, C interstitials are immobile for most substrates, so that C species that have penetrated to subsurface sites are trapped, induce stress on incorporation and so sp^3 rich films evolve as shown in Fig.5(b). When the substrate temperature is sufficiently high to allow the C species to migrate to the surface, these stresses are relieved and sp^2 films form via surface processes. The structure change from a-C to DLC with the substrate temperature which was observed in this study can be explained well using the subplantation model. The transition substrate temperature, above which migration of the subplanted carbon species to the film surface occurs, is expected to be approximately 350°C.

The films deposited using the 193 nm laser showed extremely small surface roughness, which is similar to typical sp^3 rich DLC films deposited by ion beam deposition, and is not dependent on the substrate temperature. Because of the independence of the surface roughness and the optical band gap on the substrate temperature, it can be concluded that the subplanted species penetrated too deeply for them to migrate back to the film surface as shown in Fig.5(c). Therefore, for deposition with the 193 nm laser, it is thought that species arriving at the substrate must be either atoms or small clusters of atoms, and their energies must be extremely high, so that their penetration depth is large, resulting in the high transition temperature. It can be considered that the DLC films deposited with the 193 nm laser are generated by subsurface growth accompanied with deep penetration of the deposited species.

The a-C films deposited using the 1064 nm laser showed the surface roughness of 0.5 nm, which is obviously smaller than that of the a-C films deposited using the 532 nm laser at high substrate temperature. In addition, the surface morphologies, including the roughness, hardly depend on the substrate temperature, in contrast to the carbon films deposited using the 532 nm laser, which strongly depend on the substrate temperature. These results indicate that the growth mechanism of the a-C film is different for these two cases. According to the subplantation model, the surface roughness is related to the migration of the penetrated species to the film. Hence, it is expected that for deposition with the 1064 nm laser, the arrival species do not penetrate into the

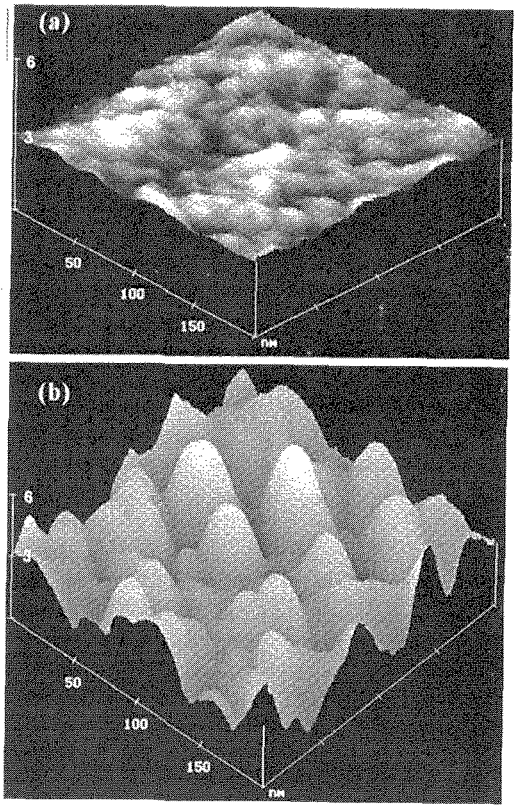

Fig. 4 AFM photographs of films deposited at the substrate temperature of (a) 20°C and (b) 450°C using the 532 nm laser.

film, and thus migration does not take place as shown in Fig.5(a). As a result, the surface morphology does not depend on the substrate temperature. On the other hand, for deposition using a wavelength of less than 532 nm, the arrival species penetrate into the film, thus the migration of the penetrated species to the film surface does takes place. As a result, the surface roughness increases as the substrate temperature is increased.

It was reported that the ejection species are predominantly $C_{5\text{-}15}^+$, $C_{5\text{-}7}^+$ and $C_{1\text{-}3}^+$ for the laser wavelength of 1064nm, 532 nm and 193 nm, respectively.[8,9] Thus the cluster size increases with the laser wavelength. In addition to this, it is thought that the velocity of ejection species decreases with the cluster size increases.[10] Therefore, the long wavelength laser causes little penetration depth due to the deposition of large cluster and low kinetic energy. On the other hand, the short wavelength laser causes deep penetration due to small cluster and high kinetic energy. The deposited species at 1064 nm are large cluster and have low velocity, therefore it is expected that the carbon species arriving at the substrate cannot penetrate to the subsurface enough to generate the sp^3 bonding. Consequently a-C films are produced by surface growth. This explains the result that the surface roughness does not depend on the substrate temperature. The transition substrate temperatures, above which a-C films are generated and below which DLC films are generated,

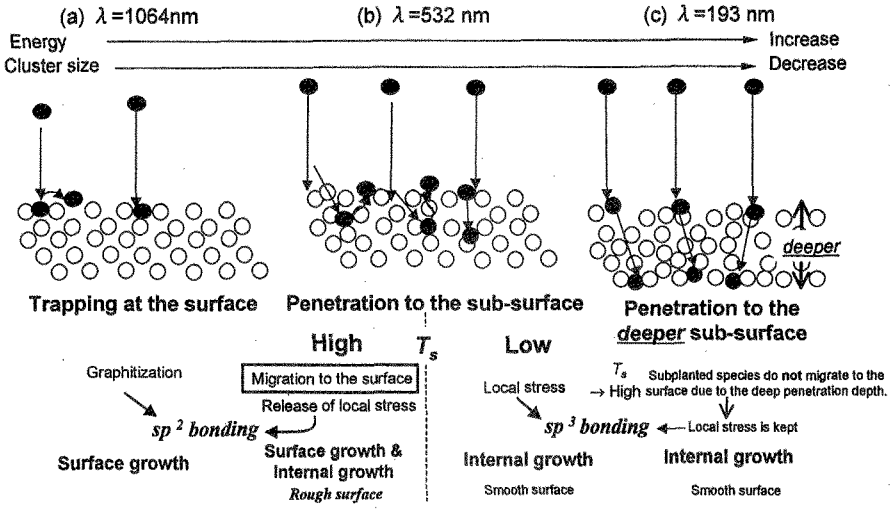

Fig. 5 Illustration of the growth of carbon thin films by pulsed laser deposition using the subplantation model.

increase with decreasing laser wavelength, and they are 20°C, 360°C and more than 400°C for 1064 nm, 532 nm and 193 nm cases, respectively. It has been reported that the transition substrate temperature increases with increasing energy of the deposited species for ion beam deposition.[11] This can be well explained by the subplantation model in that a high diffusion rate to the surface is necessary to compensate for the deeper penetration of the arrival species as their energies increase. As well as this, the increase of the transition temperature with decreasing laser wavelength in our PLD is explained well by the subplantation model, in that the laser with a shorter wavelength causes deeper penetration of the deposited carbon atoms to the film due to the increase of the energy of species arriving at the film surface. This results in transition temperature increasing as the laser wavelength decrease.

4. CONCLUSION

DLC films and a-C films were grown by PLD. It was found that the various properties of deposited thin films such as optical absorption coefficient, optical band gap and microstructure were strongly dependent on both of the laser wavelength and the substrate temperature. The film growth at the laser wavelength of 1064 nm, 532 nm, and 193 nm could be explained qualitatively using the subplantation model to be surface growth, subsurface growth accompanied with the migration of the penetrated species to the film surface, and subsurface growth respectively.

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