Preparation of a-C:H Thin Films by Pulsed Laser Ablation of a PMMA and a Polyethylene Targets

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a-C-H films with rich sp³ bonding fraction could be deposited by pulsed laser deposition using a PMMA and a polyethylene targets. This was possible because the species ejected from these hydrogenated carbon targets by laser ablation were dissociated into atomic species and atomic hydrogen thus generated had an sp² etching effect. At pressures higher than 10 mTorr, sp³ bonding fraction increased due to the additional sp² etching effect of the atomic hydrogen dissociated from the ambient hydrogen. All of the films deposited using the PMMA and the polyethylene targets showed the peaks due to vibrations of carbon-hydrogen combines in the infrared absorption spectra, and thus it is considered that the ejected species from the target are not completely dissociated into atomic species by laser ablation and the deposition species contain clusters composed of hydrogenated carbon in addition to the carbon and hydrogen atoms, resulting in the generation of hydrogenated carbon thin films.

Key words: PLD, a-C:H, Ablation, sp², sp³

1. INTRODUCTION

The preparation of sp³-rich amorphous carbon films by Pulsed Laser Deposition (PLD) has received much attention in recent years. because this method produces films that have unusual properties such as good adherence on a variety of substrates, very high hardness, good environmental resistance [1], low friction coefficient [2]. In addition, for the preparation of diamond films, the low temperature epitaxial growth on a sapphire substrate was reported in these days [3]. In a previous study, we investigated the effects of the main deposition parameters such as substrate temperature and laser wavelength on the film growth [4,5,6]. However, these parameters have their limits. For example, the sp³ bonding fraction of the deposited film cannot be enhanced by varying only these parameters. Therefore, additional parameters are required in order to improve the film properties further. In chemical vapor deposition of a-C:H films, it is known that the presence of atomic hydrogen affects the etching sp^2 bonding fractions in the films [7,8]. By combining a chemical effect such as this and the energetic deposition of the PLD method, additional improvement of various properties might be expected. Laser ablation can be adapted for any kind of materials, and the species ejected from the target are dissociated into atomic species when an ultraviolet laser is used as the ablation source. Therefore, by using a target such as PMMA, which contains hydrogen atoms, atomic hydrogen can be generated during the ablation process. This hydrogen should have the effect of etching sp^2 bonds in the deposited films. If, in addition, hydrogen gas is present in the chamber, the amount of atomic hydrogen

should increase further, enhancing the sp^2 bond etching effect. Thus these chemical effects may be useful in improving the film properties of films prepared using PLD. However, these effects in PLD have not yet been investigated in detail[9]. In this paper, we report the results of a study in which we investigated the effect of using a PMMA and a polyethylene targets and of ambient hydrogen gas.

2. EXPERIMENT

Carbon films with thickness of 100 nm were deposited on glass and silicon substrates at temperature of 20°C by PLD using a PMMA and a polyethylene targets. The substrates were set parallel with the target at a distance of 25 mm from the target. The laser source was an ArF excimer laser with energy of 100 mJ. The beam was focused with a spherical lens onto a rotating target, and the beam struck the target at 45°. The irradiation area on the target was approximately 2 mm^2 and the laser fluence was 5 J/cm². The irradiance was 1.5×10^8 W/cm². The repetition rate of the laser pulse was 10 Hz. The base pressure in the chamber was less than 10^{-6} Torr, and the ambient pressure during the film preparation was changed between 10^{-6} Torr and 1 Torr by adjusting the amount of hydrogen flowing into the chamber. For these conditions, the typical deposition rate was 0.5 nm/sec at the base pressure for both PMMA and polyethylene targets. This is 25 % higher than that of graphite target[3]. The absorption spectra of the deposited films were measured using a spectrophotometer (SHIMADZU UV-160A) and a FTIR (JASCO FT/IR-620). The Raman spectra of the deposited films were measured using JASCO NRS-2000.

3. RESULTS AND DISSCUSSION

Fig.1 show the typical optical absorption spectra of films deposited using a graphite, a PMMA and a polyethylene targets. The films deposited using the PMMA and the polyethylene targets show lower absorption than that of the films deposited using the graphite target. This indicates that the films deposited using the PMMA target contain a higher sp^3 bonding fraction due to atomic hydrogen generated from the PMMA target etching sp^2 bonding.

Using the tauc plotting method, the optical band gap was estimated from the absorption spectrum. The estimated optical band gap as a function of the hydrogen is shown in Fig.2. The optical band gap is 0.6-0.7 eV for the film prepared using the graphite target and 1.3 eV for those prepared using the PMMA and polyethylene targets, at low pressure, less than 10 mTorr, and increases significantly as the hydrogen pressure



Fig. 1 Typical absorption spectra of films deposited using a graphite, a PMMA and a polystyrene targets.



Fig. 2 Dependence of the optical band gap of films deposited using a graphite(\bigcirc), a PMMA(\blacktriangle) and polyethylene(\Box) targets on the hydrogen pressure.

increases. At low pressure, the films deposited using the PMMA and polyethylene targets have twice as large optical band gap as those deposited using the graphite target. The optical band gap is proportional to the amount of sp³ bonding fraction in the film[10]. And so, this indicates that the films deposited using the PMMA target contain a higher sp³ bonds fraction. The species ejected from the PMMA target are dissociated into atomic species, and the atomic hydrogen thus generated has the effect of etching sp^2 bonding in the film. As the hydrogen pressure rises, the optical band gap increases. This can be attributed to the additional sp² etching effect due to atomic hydrogen generated from the ambient hydrogen gas, and can be explained as follows. The distance between the target and the substrate in this study was 2.5 cm, which corresponds to the mean free path of the ambient gas at 10 mTorr. Thus, the species ejected from the target begin to collide with molecules of the ambient gas at a pressure of 10 mTorr, and at higher pressures, the number of collisions increases as the pressure rises. These collisions cause the dissociation of ambient hydrogen molecules into hydrogen atoms, which are extremely reactive with carbon atoms and the effect of etching sp² bonds. Therefore, at pressures of more than 10 mTorr, the sp² etching effect of the dissociated hydrogen atoms becomes important, and hence, the optical band gap increases as the hydrogen pressure increases[11].

Figure 3 shows Raman spectra measured for the deposited films. All of the films deposited using the graphite target show a broad peak with a center of 1550 cm⁻¹[5], and the spectra resemble those reported for typical sp³-rich carbon films prepared by other methods[12]. On the other hand, the films deposited using the PMMA and polyethylene targets show two peaks due to G and D bands. For the films deposited using the



Fig. 3 Raman spectra of films deposited using (a) a PMMA and (b) a polyethylene targets for different hydrogen pressures



Fig. 4 Infrared absorption spectra of films deposited using (a) a PMMA, (b) a polystyrene, (c) graphite targets for different hydrogen pressures.

graphite target, the appearance of these peaks coincide with the generation of the graphite crystallites in the films [5]. It is expected that the graphite crystallites cannot grow at the substrate temperature of 20°C as well as the cases of using the graphite target. Thus, the appearance of these peaks might be due to the incorporation of hydrogen atoms in the film.

Figure 4 shows infrared absorption spectra measured for the deposited films. All of the films deposited using the PMMA and polyethylene targets show the peak due to sp²-C-H (3000cm⁻¹), sp^{3} -C-H (2925 cm⁻¹) and sp^{3} -CH₂ (2860 cm⁻¹) vibrations [13]. The films deposited even at the base pressure shows the peaks due to vibrations of carbon-hydrogen combines, and thus it is considered that the deposition species contain clusters composed of hydrogen and carbon. Therefore, the species ejected from the PMMA target consist of clusters and atomic species such as hydrogen and carbon atoms. The former is deposited on the substrate and consequently the generated films contain hydrogen. The hydrogen atoms of the latter etch the sp² bonding fraction and thus the sp³-rich films can be generated. As the hydrogen pressure was increased, the intensity of the sp³-C-H (2925 cm⁻¹) peak increases critically at more than 100 mTorr. The films deposited using the graphite target shows the peak due to sp³-C-H (2925 cm⁻¹) at the hydrogen pressure of 1 Torr, as shown in Figure 4(c). Thus, at more than 100 mTorr, it is considered that ambient hydrogen incorporates into the deposited films and generates the sp³-C-H bonding. The films deposited using the PMMA target also shows high intensity peak of sp³-C-H bonding at more than 100 mTorr, and therefore this is

attribute to the incorporation of ambient hydrogen into the films as well as using the graphite target. For using the polyethylene target, the nearly same results as the films deposited using the PMMA target were obtained. It is thought that the species ejected from the polyethylene target also contain clusters composed of hydrogen and carbon. The estimation of hydrogen contents in the deposited films is difficult and is under investigation.

4. CONCLUSION

a-C:H films with rich sp³ bonding fraction could be deposited by PLD using hydrogenated carbon targets. This was possible because the species ejected from these targets by laser ablation were dissociated into atomic species and atomic hydrogen thus generated had an sp^2 etching effect. At pressures higher than 10 mTorr, sp³ bonding fraction increased due to the additional sp² etching effect of the atomic hydrogen dissociated from the ambient hydrogen. All of the films deposited using the PMMA and the polyethylene targets showed the peaks due to vibrations of carbon-hydrogen combines in the infrared absorption spectra, and thus it is considered that the deposition species contain clusters composed of hydrogenated carbon in addition to the carbon and hydrogen atoms. The deposition of hydrogenated carbon clusters generates the hydrogen-carbon combines such as sp²-C-H, sp³-C-H and sp³-C-H. On the other hand, at more than 100 mTorr hydrogen, ambient hydrogen incorporates into the films and generate mainly sp³-C-H combine. There was not apparent difference in the film properties between using the PMMA and polyethylene targets. It is possible to fabricate sp^3 -rich a-C:H films using the hydrogenated carbon target, but the deposited films contained hydrogen due to the deposition of hydrogenated carbon clusters.

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REFERENCES

- [1] J. Robertson, Diamond. Relat. Mater., 1, 397 (1992).
- [2] K. Miyoshi, R. L. C. Wu and A. Garscadden, Surf. Coat. Technol., 54/55, 428 (1992).
- [3] M. Yoshimoto, K. Yoshida, H. Maruta, Y. Hishitani, H. Koinuma, S. Nishio, M. Kakihana and T. Tachibana, *Nature*, **399**, 340 (1999).
- [4] T. Yoshitake, T. Nishiyama, H. Aoki, K. Suizu, K. Takahashi, and K. Nagayama, Appl. Sur. Sci., 141, 129 (1999).
- [5] T. Yoshitake, T. Nishiyama, H. Aoki, K. Suizu, K. Takahashi, and K. Nagayama, Diamond Relat. Mater., 8, 463 (1999).
- [6] T. Yoshitake, T. Nishiyama, H. Aoki, K. Suizu, K. Takahashi, and K. Nagayama, *Trans. MRS-J*, 24, 599 (1999).
- [7] B. V. Spitzyn, L. L. Bouilov and B. V.
 Derjaguin, J. Cryst. Growth, 52, 219(1981).
- [8] A. P. Dementiev and M. N. Petukhou, *Diamond Relat. Mater.*, 6, 486 (1997).
- [9] Z. F. Li, Z. Y. Yang and R. F. Xiao, Appl. Phys., A63, 243 (1996).
- [10] J. Robertson, Diamond Relat. Mater., 5, 457 (1997).
- [11] T. Yoshitake, T. Nishiyama and K.

Nagayama, *Diamond Relat. Mater.*, in press [12] T. Sato, S. Furuno, S. Iguchi, and M.

Hanabusa, Appl. Phys., A45, 355 (1988).
[13] B. Dischler, in P. Koidl and P. Oelhafen (eds.), Proc. Symp. On Amorphous Hydrogenated Carbon Films, Strasbourg, June 2-5, 1987, Symposia Proceedings, Vol. 17, Les Editions de Physuque, Les Ulis, 1987, p. 187.

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