Deposition of fine carbon particles using pulsed ArF laser ablation assisted by inductively coupled plasma

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Abstract

Carbon thin films containing many fine carbon particles were deposited by a pulsed ArF laser ablation technique assisted by inductively coupled plasma (ICP). The sizes of the particles were found to be ~ 100 nm. The particles seemed to be coagulated from several finer particles of size ~ 10 nm. When ICP was applied to a plume, the shape of the coagulated particles became spherical. The deposited surface was assumed to be diamond-like carbon based on the binding energy of carbon (1s) in the particle obtained by XPS spectra.

Keywords: Laser ablation; Inductively coupled plasma (ICP); Particle growth; Ambient gas; Diamond like carbon (DLC)

1. Introduction

A pulsed laser deposition (PLD) technique has been used for fine particle production as well as thin film deposition because it can be applied in a wide range of ambient gas pressures. Nanometer-size silicon particles have been made for the fabrication of luminescent devices by PLD in Ar or He gas at ~ 100 Pa. [1-3] The grown size of the particles was controlled by varying the ambient gas pressure. [1]

Since, in principle, PLD can produce energetic atoms and ions, this technique enables us to deposit thin films at relatively low substrate temperatures. Amorphous carbon films produced at room temperature have actually showed very good physical properties, e.g. high hardness, high electrical resistivity, high thermal conductivity, and high optical transparency. [4, 5] Amorphous carbon composed of sp^2 and sp^3 bonds is called diamond-like carbon (DLC). [4] DLC is also well known as an electron emitter, where electrons are emitted from the 'emission site' located among minute DLC particles. [6]

In this study, we have proposed using a PLD technique assisted by ICP to control fine carbon particle growth. The structure and properties of the particles and the deposited carbon films are examined by SEM and XPS. The effect of ICP on particle growth is discussed.

2. Experimental setup and procedure

Fig. 1 shows a schematic diagram of the present PLD experimental apparatus. The PLD chamber, in which a rotating substrate and six target holders were included, is 350 mm in diameter and 600 mm in height. The chamber was evacuated by a turbo molecular pump up to

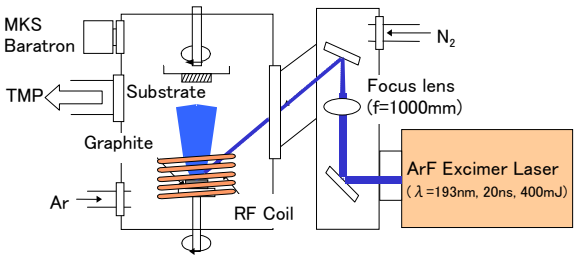

Fig. 1. Experimental setup

2.7×10^{-6} Pa.

We used an ArF excimer laser (LAMBDA PHYSIK COMPex 205; wavelength: 193 nm; pulse duration: 20 ns; repetition rate: 30 Hz; and fluence: 5 J/cm^2). The laser light path was enclosed with nitrogen gas. A gold-coated RF plasma coil (113 mm in diameter, 25 mm in height, and five turns) was introduced between the substrate and the target holder.

We used sintered graphite (20 mm in diameter, 5 mm in thickness, purity 99.999%) as a target and Si (111) as a substrate. The target surface was first polished with abrasive paper and cotton and then cleaned by acetone and ethanol in an ultrasonic cleaner. An oxidized layer on the substrate surface was eliminated by immersion in a solution of hydrofluoric acid. The deposition was continued for 30 min at room temperature in Ar gas at pressures $\leq$ 53 Pa and RF powers $\leq$ 60 W. The distance d_{st} between the substrate and target was 35 mm in vacuum and 20 mm in a 53-Pa Ar gas. The deposition rate of the carbon film was approximately 2 nm/min.

The surface morphology and physical properties were examined with a scanning electron microscope (SEM) and an X-ray photoelectron spectroscope (XPS).

3. Results and discussion

3.1. Surface morphology

Fig. 2a,b show SEM micrographs of the surface of carbon films obtained in the vacuum environment. Many fine particles with sizes of ~ 100 nm could be seen on the surface. Their shape was irregular and deformed as shown in Fig. 2b. Particles in a plume generated from the target by laser ablation could be categorized as follows [7]: (1) exfoliation from the bumpy target surface due to laser irradiation; (2) solidification of molten droplets generated from the super-heated subsurface layer on the target; and (3) nucleation of ablated atoms due to cooling down by collision with ambient gas atoms during their flight. [8] It has been reported that when ArF laser light (193 nm) was used, ablated carbon ions formed clusters (C_n^+) with n = 1 ~ 3. [10-12] With an ArF laser, it may be possible to cut the sp^2 bond (7.4 eV) [9] by two-photon absorption (2 x 6.4 eV). In a vacuum, the clusters in an ablation plume may go directly to the substrate without colliding with other clusters. Consequently, hardly any nucleation of fine particles is generated. From these considerations, the particles deposited in a vacuum may be almost completely provided by exfoliation.

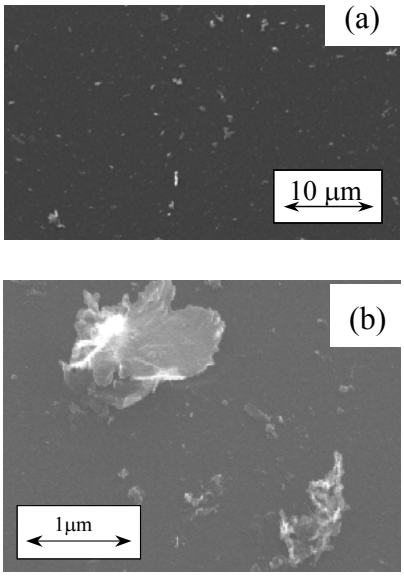

Fig. 2. (a) and (b). Carbon thin film including fine particles deposited in vacuum.

Fig. 3 shows SEM micrographs of the surface of the carbon films deposited in a 53-Pa Ar gas. In a gas environment, the plume volume is smaller than in a vacuum because the ablated atoms quickly lose their energy. In rare gases with pressures larger than several hundred Pa, a plume cannot expand over long distance. [1] As a result of this effect, we could not achieve any deposition on the substrate for d_{st} = 35 mm. Therefore, we shortened the target-substrate distance to d_{st} = 20 mm in Fig. 3. In the case of a 53-Pa Ar ICP, the concentration of the particle seen on the film surface (~ 5.0 x 10^{12} m^{-2}) was slightly larger than that without plasma (~ 4.5 x 10^{12} m^{-2}) as shown in Fig. 3. Furthermore, the particle size became larger. This point will be discussed later.

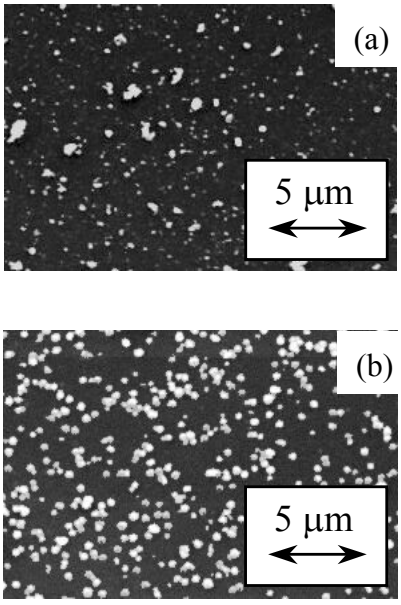

Fig. 3. Carbon particles deposited in 53 Pa Ar for d_{st} = 20 mm: (a) without plasma; and (b) with a 60-W plasma.

Fig. 4 shows the normalized size distribution of the particles provided on the film surface. Without the plasma, more than 70% of the particles were smaller than 0.3 μm, as shown in Fig. 4a. On the contrary, in the plasma more than 70% of the particles were larger than 0.3 μm, as shown in Fig. 4b. In comparison to the size of fine silicon particles grown in a laser ablation plume in a 266-Pa He gas studied by Makimura et al., [1] the present carbon's particle size was a few times larger.

Enlarged pictures of Fig. 3 are shown in Fig. 5. This figure suggests that the particles on the surface were coagulated by several finer particles (~ 10 nm). When the plume was assisted by ICP, the particle shape became spherical, as shown in Fig. 5b. This spherical shape was obtained in ICP, even in a 4-Pa Ar gas.

These results may indicate that the plasma influences the particle growing kinetics in the ablation plume.

Shiratani et al. developed a method to measure the increased volume of nanometer-sized silicon particles in silane RF plasmas. [13] Their results showed that when silicon particles grew to approximately 10 nm, the particles started to coagulate with each other. This coagulation was explained by a model that took account of the attractive force between oppositely charged particles. [14]

It was assumed that initially clustered C_n, C_n^+ (n = 1-3) were ablated and started to nucleate by radical reaction. [10, 15] The nucleated particles continued to grow and become negatively charged. [14] Then the C_n^+ is attracted to the particles. The presence of C_n^+ in the carbon plume is confirmed by the current waveform measurements [15] and the study of mass spectrometry. [10] In an Ar gas environment, the emission spectra from the plume show the presence of excited Ar and Ar^+. [16] Therefore, it may also be considered that the excited Ar and Ar^+ contribute to the growth of the particles. Furthermore, ICP may effectively assist the negative particle charge.

3.2. XPS spectra

Fig. 6 shows C (1s) XPS spectra of the surface, where both carbon particles and the film exist in a vacuum, in Ar gas (~ 53 Pa), and in Ar ICP (~ 53 Pa). Before the analysis by XPS, the carbon films were etched by Ar ions to remove the natural oxidized layer on the surface. The binding energy of C (1s) was determined by deconvolution of the spectra using a Gaussian curve fitting method. The C (1s) energy of sp^2 bonds and that of sp^3 are 284.5 eV and 285.5 eV, respectively. [11] The C (1s) energy peaks in the spectra were in the range from 284.5 to 285.5 eV and tended to shift to higher values as the gas pressure increased. This result suggests that the present carbon particles and films were composed of an amorphous structure between sp^2 and sp^3 bonds, i.e. diamond-like carbon. The particles in the plume could be considered to lose their energies by colliding with ambient gas atoms.

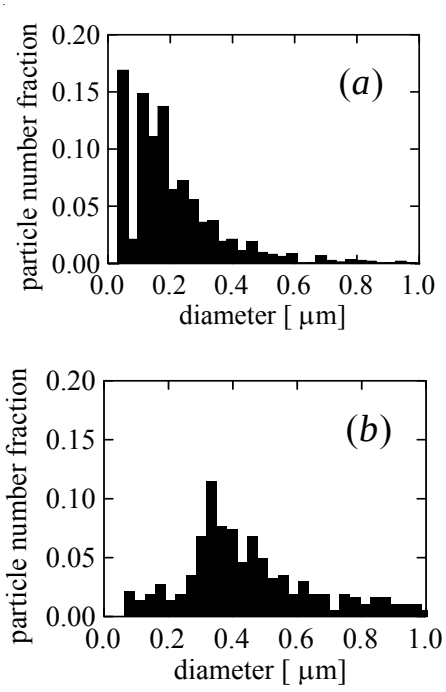

Fig. 4. Distribution of particle size on carbon film in 53 Pa Ar: (a) without plasma; and (b) with a 60-W plasma.

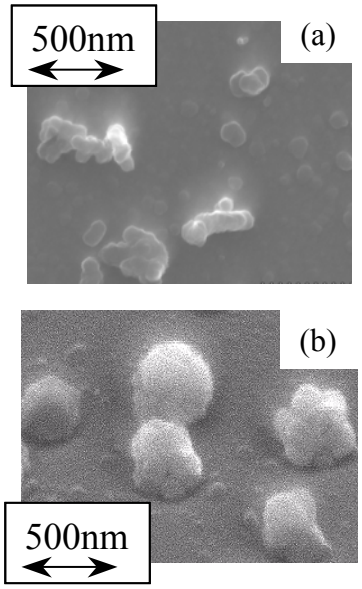

Fig. 5. Enlarged photographs of Fig. 3a,b taken at an angle of 45° from the substrate.

4. Conclusions

Diamond-like carbon particles were deposited on a silicon substrate by a hybrid method of PLD and ICP. Particles with a size of the order of 100 nm were obtained by coagulation of particles with a ~ 10-nm size. The shapes and sizes of the particles deposited by the hybrid method were different from those deposited without plasma. XPS spectra revealed that the deposited particles and films under every experimental condition were composed of sp^2 and sp^3 bonding structures.

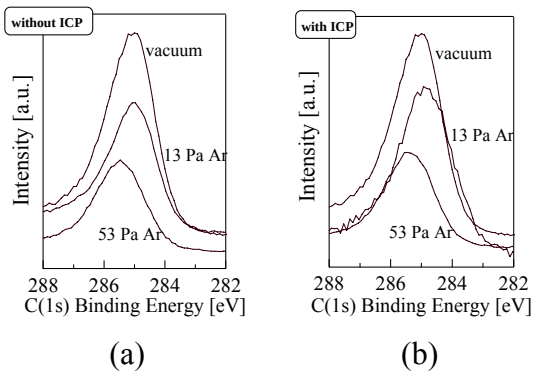

Fig. 6. C (1s) X-ray photoelectron spectra of carbon particles and films deposited: (a) without plasma; and (b) with a 60-W plasma.

5. Acknowledgments

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References

1 T. Makimura, Y. Kunii, K. Murakami, Jpn. J. Appl Phys. 35 (1996) 4780.

2 I.A. Movtchan, W. Marine, R.W. Dreyfus, H.C. Le, M. Sentis, M. Autric, Appl. Surf. Sci. 96-98 (1996) 251.

3 Y. Yamada, T. Orii, I. Umezu, S. Takeyama, T. Yoshida, Jpn. J. Appl. Phys. 35 (1996) 1361.

4 F. Qian, R.K. Singh, S.K. Dutta, P.P. Pronko, Appl. Phys. Lett. 67 (1995) 3120.

5 S. Aoqui, K. Ebihara, Y. Yamagata, Carbon 36 (1998) 591.

6 C. Wang, A. Garcia, D.C. Ingram, M. Lake, M.E. Kordesch, Electronics Lett. 27 (1991) 1459.

7 D.B. Chrisey, G.K. Hubler, Pulsed Laser Deposition of Thin Films, Wiley-Interscience, 1994, pp. 13-19.

8 T. Makimura, Y. Kunii, N. Ono, K. Murakami, Appl. Surf. Sci. 127-129 (1998) 388.

9 R.C. Weast, Handbook of Chemistry and Physics, CRC Press, Boca Raton, 1974, p. D56.

10 J.J. Gaumet, A. Wakikusa, Y. Shimizu, Y. Tamori, J. Chem. Soc. Farady Trans. 89 (1993) 1667.

11 K. Yamamoto, Y. Koga, S. Fujiwara, F. Kokai, R.B. Heimann, Appl. Phys. A 66 (1998) 115.

12 P.T. Murray, D.T. Peeler, J. Electron. Mater. 23 (1994) 855.

13 M. Shiratani, T. Fukuzawa, Y. Watanabe, Jpn. J. Appl. Phys. 38 (1999) 4542.

14 Y. Watanabe, M. Shiratani, H. Kawasaki, S. Singh, T. Fukuzawa, Y. Ueda, H. Ohkura, J. Vac. Sci. & Technol. A14 (1996) 540.

15 Y. Suda, T. Nishimura, M. Mizuno, T. Ono, Y. Sakai, IEE. Jpn., Nat. Conf. No. 1-107 (2000) 133.

16 Y. Suda, M. Mizuno, T. Nishimura, M.A. Bratescu, Y. Sakai, M. Akazawa, Proc. 1999 Annual Conf. Fundamentals & Materials Soc. IEE Jpn., No. 90, (1999) 324.