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Structural Properties of Amorphous Carbon Thin Films Deposited by LF (100 kHz), RF (13.56 MHz), and Pulsed RF (13.56 MHz) Plasma CVD

Dong-Sun Kim†

Department of chemical engineering, College of Eng., Kongju National University,
182 Shinkwandong, Chungnam 314-701, Korea
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Abstract−Amorphous carbon thin films were deposited by LF (100 kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma CVD with DC self-bias voltage of −300 V and 50 mTorr on Si wafers at 15 °C using a mixture of methane and hydrogen for comparing structural properties of the deposited films in an asymmetric plasma reactor. The surface morphologies of the deposited films were observed by Atomic force microscopy (AFM). The average roughness (Ra) analyzed by AFM data was 4.03, 1,84, 1.52 Å at LF (100 kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma, respectively. From these results, the films deposited by pulsed RF plasma have more smooth and dense surface compared with those deposited by LF (100 kHz), and RF (13.56 MHz) plasma. The ratios of I_D/I_G obtained from Raman data were 2.69, 0.76 and 0.44 at LF (100 kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma, respectively. It is concluded that the film deposited by pulsed RF plasma has more diamond-like properties compared with that deposited by LF (100 kHz), and RF (13.56 MHz) plasma.

Key words: Amorphous Carbon Film, PECVD, LF, RF, Pulsed RF

INTRODUCTION

Amorphous carbon thin films have attracted considerable attention because of their extreme properties in hardness, thermal conductivity, optical transparency, and chemical resistance. Potential applications include scratch-resistant coating, optical coating, and coating on plastics [Ravi, 1993; Angus et al., 1988; Deshpandey et al., 1989]. Amorphous carbon thin films were mainly deposited by plasma enhanced chemical vapor deposition with different frequency of ~100 kHz [Zuniga et al., 2003], 13.56 MHz [Jung et al., 1996], and 2.86 GHz [Inaba et al., 2002]. Recently, pulsed RF (13.56 MHz) plasma has been introduced for tailoring properties of thin films [Fedosenko et al., 2002].

Pulsed RF plasma introduces a modulation into the input electrical energy for plasma discharge and the deposition of good quality films is expected due to alternation of plasma chemistry. During the pulse on phase, ions excited by electrical energy are accelerated towards the substrate, leading to erosion of the soft components of the film and to higher compressive stress caused by ion bombardment. During the pulse-off phase, radicals can be deposited and the stress caused on the depositing films by ion bombardment is released [Lau et al., 2000]. Major important parameters in the pulsed RF plasma are pulse cycle duty and frequency (defined as the ratio of pulse on-time to total cycle time). However, the films deposited by different plasma frequency in the literature [Zuniga et al., 2003; Jung et al., 1996; Inaba et al., 2002; Fedosenko et al., 2002] are difficult to compare their properties because of depositing those films at different types of reactors manufactured by researchers.

In this paper, we investigate the effect of plasma frequency at LF (100 kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma with DC self-bias voltage of −300 V and 50 mTorr for comparing structural properties of the deposited films in an asymmetric plasma reactor.

EXPERIMENT

The deposition of amorphous carbon thin films was carried out

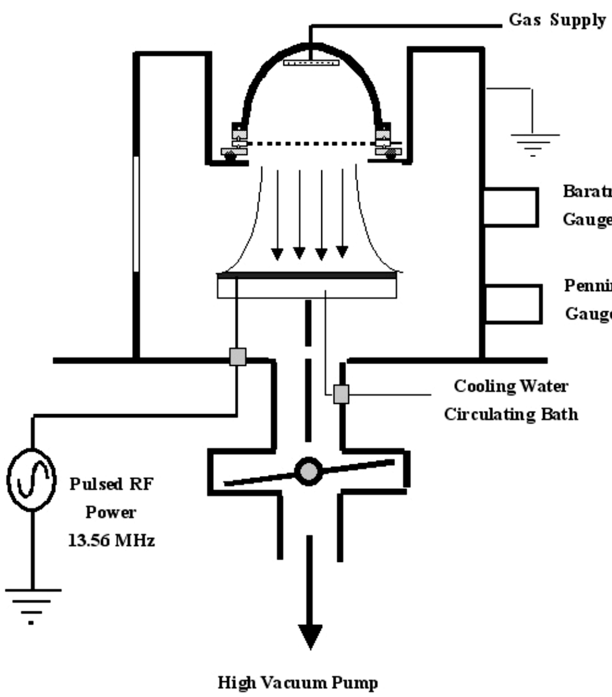

Fig. 1. Schematic diagram of plasma-enhanced chemical vapor deposition apparatus.

†To whom correspondence should be addressed.
E-mail: dskim@kongju.ac.kr

in a capacitively coupled asymmetric plasma reactor driven by LF (100 kHz), 13.56 MHz RF power, and 13.56 MHz RF power with the modulation of cycle duty and frequency for generating pulsed RF plasma. A schematic drawing of the reactor is shown in Fig. 1. The internal dimensions of the reactor were 30 cm diameter cylinder and 50 cm height. The distance between the powered electrode and the top showerhead was 5 cm. The reactor was operated in a reactive ion etcher; the area of the powered electrode is much smaller (10 cm diameter) than that of the grounded electrode. Due to asymmetry, a high DC self bias voltage was developed at the powered electrode [Kasper et al., 1992]. For all runs, the DC self-bias voltage was set at −300 V. The substrates used were a piece of 5 inch (100)-oriented silicon wafer and KBr disk. The gas flow rates were set at 20 sccm of hydrogen and 20 sccm of methane by a mass flow controller (MKS, U.S.A.), and the chamber pressure was maintained at 50 mTorr using a Baratron Gauge with a throttle valve controller (MKS, U.S.A.). The temperature of the substrate holder (the powered electrode) was controlled at 15 °C by a recirculating water bath. The gases were distributed uniformly by a showerhead type distributor. Pulsed RF plasma was set at 5 kHz cycle frequency (defined as the ratio of pulse on-time to total cycle time) and 50% cycle duty.

The film thickness was measured by using an optical method (KLA-200, Korea). The surface morphologies and the average roughness (Ra) of the deposited films were observed by Atomic force microscopy (Park Scientific Instrument, USA). Raman spectra were obtained in a backscattering geometry and recorded at low powers of 100 mW to avoid thermal decomposition of the samples. For the excitation, an argon laser (514.18 nm) focused on the sample surface using a cylindrical lens was used (Jobin-Yvon-Spex, Spectrum-1, USA).

RESULTS AND DISCUSSION

The deposition rates depending on plasma frequency at LF (100 kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma with DC self-bias voltage of −300 V and 50 mTorr are shown in Table 1. The deposition rate at LF (100 kHz) plasma is highest (5.26 Å/sec), while it is lowest (2.39 Å/sec) at pulsed RF (13.56 MHz) plasma. This is due to the duration of the plasma-on and plasma-off phase. Fig. 2 shows the surface morphologies and the average roughness (Ra) of films deposited by LF (100 kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma with DC self-bias voltage of −300 V observed by Atomic force microscopy (AFM). Note that the average roughness (Ra) of film deposited by pulsed RF (13.56 MHz) plasma is lowest. It can be deduced that pulsed RF plasma forms more smooth and dense films. This can be explained as follows: during the pulse-on phase, the carbon and carriers gas ions excited by electrical energy are accelerated towards the substrate, leading to etching of the weakly-bonded components of the film and to higher compressive stress caused by ion bombardment, while during the pulse-off phase, carbon radicals can be deposited and the stress caused on the depositing films by ion bombardment is released [Lau et al., 2000].

Table 1. Deposition rates of the amorphous carbon films deposited on Si wafer by different plasma at −300 V and 50 mTorr

Applied plasma frequency	Deposition rate (Å/sec)
LF (100 kHz)	5.26
RF (13.56 MHz)	3.75
Pulsed RF (13.56 MHz) plasma	2.39

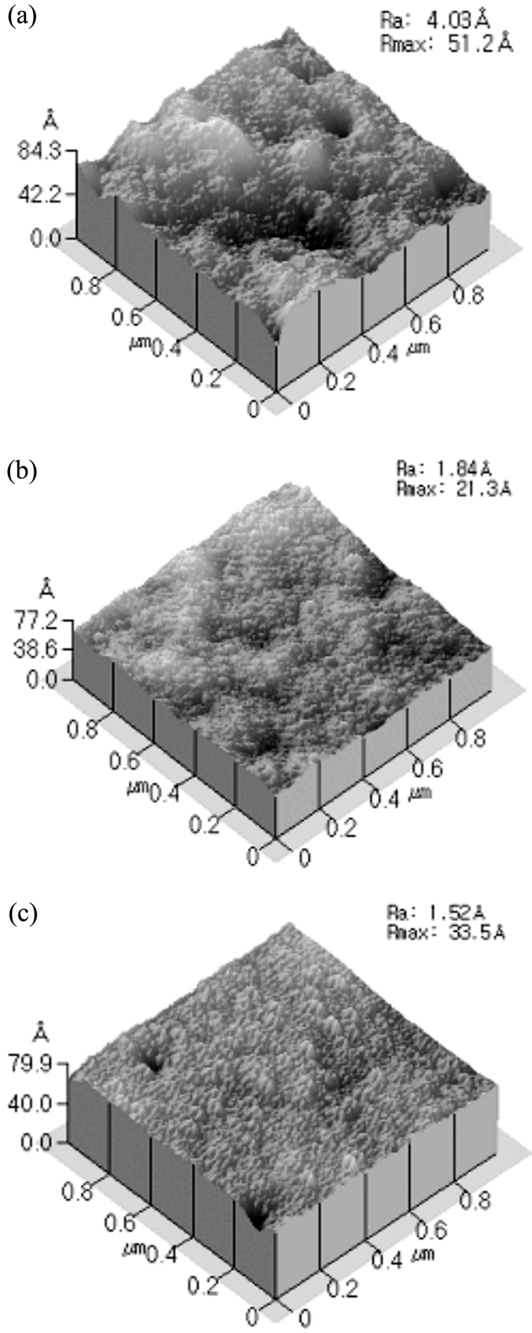

Fig. 2. AFM images and average roughness (Ra) of Amorphous carbon films deposited on Si wafer by (a) LF (100 kHz) plasma, (b) RF (13.56 MHz) plasma, and (c) pulsed RF (13.56 MHz) plasma at −300 V and 50 mTorr.

Infrared spectroscopy (IR) can easily discern C-H_n sp^2 and sp^3 bonds qualitatively, and the FTIR spectra acquired from the a-C : H films deposited by LF (100 kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma with DC self-bias voltage of −300 V and 50 mTorr are shown in Fig. 3. Similar to reports in the literature [Jung

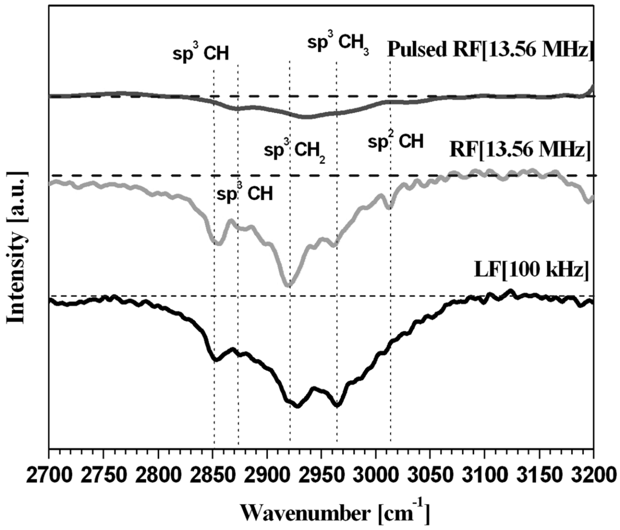

Fig. 3. FT-IR spectra of amorphous carbon films deposited by different plasma at −300 V and 50 mTorr.

et al., 1996; Inaba et al., 2002], fine structures are observed for the C-H absorption at 2,850 cm^{-1} for sp^3 CH (symmetrical), 2,870 cm^{-1} for sp^3 CH (symmetrical), 2,920 cm^{-1} for sp^3 CH_2 (asymmetrical) or sp^3 CH, 2,970 cm^{-1} for sp^3 CH_3 (asymmetrical), and 3,025 cm^{-1} for sp^2 CH (aromatic) or sp^2 CH_2 (olefin) stretching vibration modes. It should be noted that the intensities of these peaks and the wave number at the maximum transmittance depend strongly on the plasma frequency. The well-resolved spectrum of film deposited by LF plasma is indicative of a polymer-like film formation [Inaba et al., 2002]. A transformation from a polymer-like to a hard film is visible in the substantial decrease of the total peak area at pulsed RF plasma [Jung et al., 1996]. Decrease of the total peak area can be related to a decrease of the hydrogen incorporation. Sharp decrease of those peaks by pulsed RF plasma indicates a more efficient hydrogen removal. This can be explained as follows. Good quality film by pulsed RF plasma is deposited due to alternation of plasma chemistry. Quantitative analysis of the sp^3/sp^2 ratio was not carried out, in view of various difficulties associated with accurately deconvoluting the FTIR spectra.

The first order Raman spectra in the range of 1,100 cm^{-1} and 1,700 cm^{-1} of the films deposited by LF (100 kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma with DC self-bias voltage of −300 V and 50 mTorr including their deconvoluted spectra using Gaussian curve fitting are shown in Fig. 4. Those are typical Raman spectra obtained in a-C : H films. It is known that a-C : H films exhibit two major Raman activities in this region: G band (G means "graphitic") near 1,580 cm^{-1} and D band (D means "disorder") near 1,360 cm^{-1} [Dillion et al., 1984; Tuinstra et al., 1970; Nemanich et al., 1988]. One of the most important factors governing the quality of a-C : H films in Raman spectra is the integrated peak ratio of D band to G band (I_D/I_G). It has been reported that I_D/I_G is proportional to the size of the graphite crystallites and/or to the degree of graphitization [Dillion et al., 1984; Tuinstra et al., 1970] and the ratio of sp^2/sp^3 bonds [Sheeja et al., 2000; Jun et al., 2000]. Generally, the lower the ratio, the closer the properties of a-C : H films approach to diamond [Merel et al., 1998]. The ratios of I_D/I_G are 2.69, 0.76 and 0.44 at LF (100

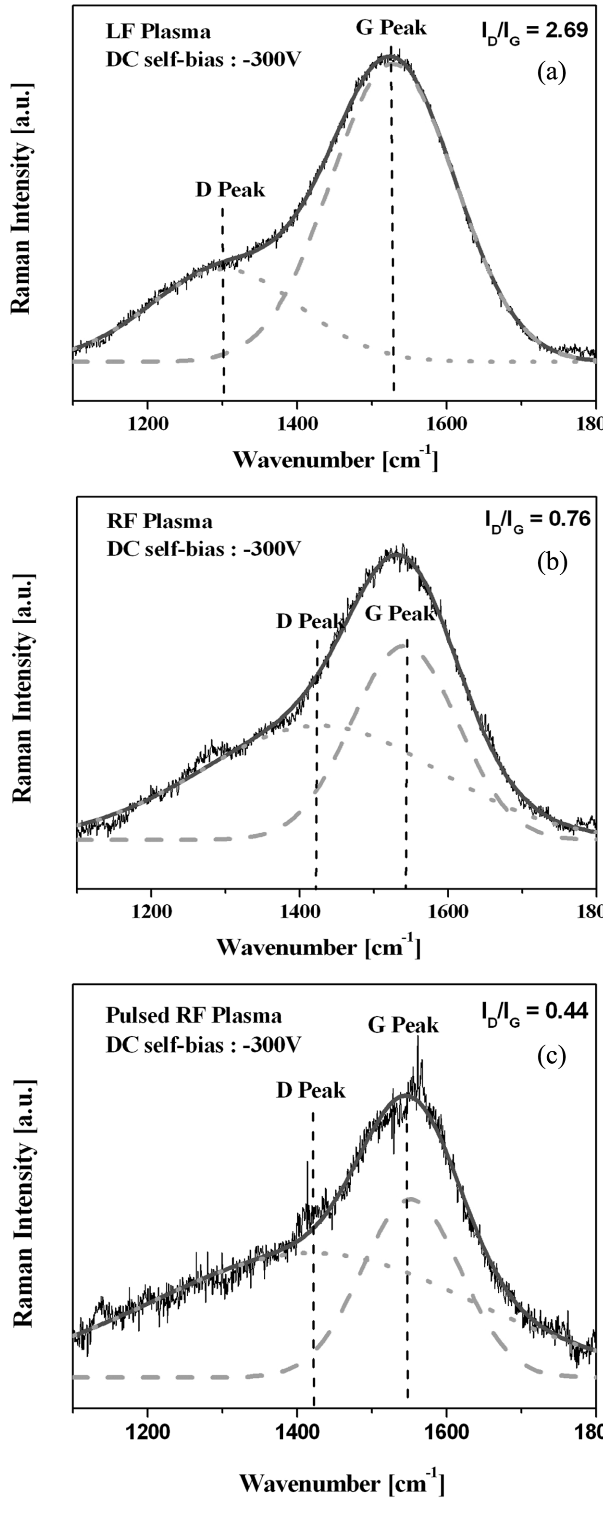

Fig. 4. Gaussian curve fitting of Raman spectra for amorphous carbon films deposited on Si wafer by (a) LF (100 kHz) plasma, (b) RF (13.56 MHz) plasma, and (c) pulsed RF (13.56 MHz) plasma at −300 V and 50 mTorr.

kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma with DC self-bias voltage of −300 V, and 50 mTorr, respectively. Therefore, the film deposited by pulsed RF (13.56 MHz) plasma is highest sp^3 content corresponding to the lowest ratio of I_D/I_G. This can be considered as due to the effects of using pulsed RF plasma mentioned above. According to the literature [Ferrari et al., 2000], an I_D/I_G ratio of approximately 0.7 correlates to ~45% of the sp^3 fraction content in the films.

CONCLUSIONS

Amorphous carbon thin films are deposited on Si wafers at 15 °C using a mixture of methane and hydrogen by LF (100 kHz), RF (13.56 MHz), and pulsed RF (13.56 MHz) plasma at DC self-bias voltage of −300 V and 50 mTorr for comparing structural properties of the deposited films in an asymmetric plasma reactor. It is concluded that the deposited films by pulsed RF plasma have lower deposition rate, but are more smooth and dense and have more diamond-like properties compared with those deposited by LF (100 kHz), and RF (13.56 MHz) plasma. To evaluate more conformed diamond-like properties, the measurement of mechanical properties such as hardness is necessary.

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REFERENCES

Angus, J. C. and Hayman, C. C., *Science*, **241**, 913 (1988).

Deshpandey, C. V. and Bunshah, R. F., "Diamond and Diamondlike Films; Deposition Processes and Properties," *J. Vac. Sci. Technol.*, **A7**, 2294 (1989).

Dillion, R. O., Woollam, J. A. and Katkanant, V., "Use of Raman Scattering to Investigate Disorder and Crystalline Formation in As-deposited and Annealed Carbon Films," *Phys. Rev.*, **B29**, 3482 (1984).

Fedosenko, G, Schwabedissen, A., Engemann, J., Braca, E., Valentini, L. and Kenny, J. M., "Pulsed PECVD Deposition of Diamond-like Carbon Films," *Diamond and Related Materials*, **11**, 1047 (2002).

Ferrari, A. and Robertson, J., "Interpretation of Raman Spectra of Disordered and Amorphous Carbon," *Phys. Rev.*, **B61**(20), 14095 (2000).

Inaba, H., Fujimaki, S., Furusawa, K. and Todoroki, S., "ECR-Plasma Parameters and Properties of Thin DLC Films," *Vacuum*, **66**, 487 (2002).

Jun, Q., Jianbin, L., Shizhu, W., Jing, W. and Wenzhi, L., "Mechanical and Tribological Properties of Non-Hydrogenated DLC Films Synthesized by IBAD," *Surface and Coating Tech.*, **128-129**, 324 (2000).

Lee, J. H., Kim, D. S., Lee, Y. H. and Farouk, B., "Effects of RF Power on Plasma Phase Reaction and Film Structure in Deposition of a-C:H by Styrene/Argon Discharge," *J. of Electrochem. Soc.*, **143**, 1451 (1996).

Kasper, W., Bohm, H. and Hirschauer, B., "The Influence of Electrode Areas on Radio Frequency Glow Discharge," *J. Appl. Phys.*, **71**, 4168 (1992).

Lau, K. K. and Gleason, K. K., "Pulsed Plasma Enhanced and Hot Filament Chemical Vapor Deposition of Fluorocarbon Films," *J. of Fluorine Chemistry*, **104**, 119 (2000).

Mérel, P., Tabbal, M., Chaker, M., Moisa, S. and Margot, J., "Direct Evaluation of the Sp^3 Content in Diamond-like-Carbon Films by XPS," *Appl. Surf. Sci.*, **136**, 105 (1998).

Nemanich, R. J., Glass, J. T., Lucovsky, G. and Shroder, R. E., "Raman Scattering Characterization of Carbon Bonding in Diamond and Diamondlike Thin Films," *J. Vac. Sci. Technol.*, **A6**, 1783 (1988).

Ravi, K. V., "Low Pressure Diamond Synthesis for Electronic Applications," *Mater. Sci. & Eng.*, **B19**, 203 (1993).

Sheeja, D., Tay, B. K., Lau, S. P., Shi, X. and Ding, X., "Structural and Tribological Characterization of Multilayer ta-C Films Prepared by Filtered Cathodic Vacuum Arc with Substrate Pulse Biasing," *Surface and Coating Tech.*, **132**, 228 (2000).

Tuinstra, F. and Koenig, J. L., *J. Chem. Phys.*, **53**, 1126 (1970).

Zuniga, C.,Torres, A. and Kosarev, A., "Carbon Films Deposited by Low Frequency Plasma as Inter-metal Dielectric," *J. Non-Cryst. Solids*, **329**, 174 (2003).