

Plasma Discharge Condition Dependence of the Crystallographic Quality of Networked Nanographite Grown by the Photoemission-Assisted Plasma-Enhanced CVD

Shuichi Ogawa^{1,2}, Toshiteru Kaga¹, Yudai Ohtomo¹, Motonobu Sato^{2,3}, Mizuhisa Nihei^{2,3} and Yuji Takakuwa^{1,2}

¹ Tohoku Univ., Institute of Multidisciplinary Research for Advanced Materials, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

Phone: +81-22-217-5367 Fax: +81-22-217-5405 E-mail: ogasyu@tagen.tohoku.ac.jp

² CREST-JST, Sanbancho bldg., 5 Sanban-cho, Chiyoda-ku, Tokyo 102-0075, Japan

³ Fujitsu Ltd., 10-1 Morinosato-Wakamiya, Atsugi, Kanagawa 243-0197, Japan

1. Introduction

Graphite-materials such as CNT and graphene have been attracted much attention as the most promising materials for interconnects of LSI. In order to form graphene on the insulators, we have developed the photoemission-assisted plasma-enhanced chemical vapor deposition (CVD) process[1, 2]. The crystallographic quality of the graphite films grown by plasma-enhanced CVD depends on the amounts and energies of radicals and ions in the plasma[3]. These parameters are controlled by a gas pressure and bias voltage. In the case of DC discharge plasma, when the bias voltage decreases under the sustaining voltage, discharge plasma disappears. Photoemission-assisted plasma can keep discharge plasma under the sustaining voltage of glow discharge because a enough photoelectron is emitted from substrate by the UV irradiation to sustain the plasma. Therefore, the influence of bias voltage in DC plasma CVD for crystallographic quality of deposited film can be clarified using photoemission-assisted plasma. In this study, we investigated the networked nanographite crystallinity dependence on the photoemission-assisted plasma discharge condition from the measurement of Raman spectroscopy and emission spectroscopy.

2. Experimental

Networked nanographite was grown on a SiO₂(350 nm)/Si substrate(11×6 mm²) using a photoemission-assisted plasma enhanced CVD apparatus placed at Tohoku University. The block diagram of photoemission-assisted plasma CVD is shown in Fig. 1(a). No wet and dry cleaning of SiO₂/Si substrate was performed before CVD growth. The substrate was contained to a Si heater using a Mo holder with the Mo mask. The substrates were heated by resistive heating of the Si heater. The Ar/CH₄ mixture gas is introduced into process chamber to generate the photoelectron-assisted plasma. In the photoemission-assisted discharge condition, the sample was irradiated by a UV light ($\lambda = 172$ nm) from the Xe excimer lamp. In the glow discharge condition, the UV was not irradiated. The plasma voltage V_p was changed from 200 to 300 V. In the microscopic Raman spectroscopy measurement, the excitation laser and its power is Ar ion laser ($\lambda = 488$ nm) and 0.3 W, respectively. The magnification of object lens is 50 times.

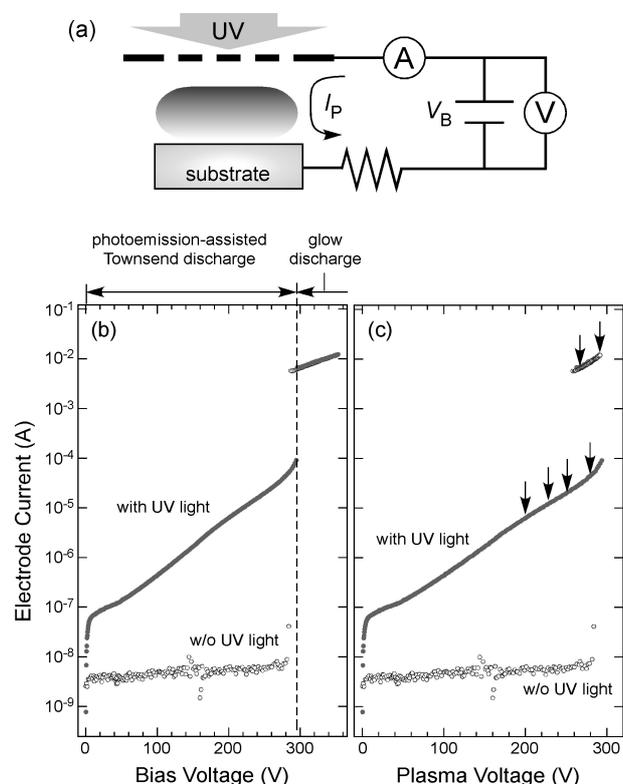


Fig. 1. (a) The block diagram of photoemission-assisted plasma CVD apparatus. (b) The bias voltage dependence of the electrode current with and without the UV irradiation. (c) The plasma voltage dependence of electrode current. The arrows indicate the experimental conditions.

3. Results and Discussion

Figure 1 (b) shows the bias voltage (V_B) dependence of the electrode current (I_p). When the UV light is not irradiated, the I_p is almost constant with increasing V_B , and then I_p increases rapidly up to $\sim 10^{-2}$ A at 290 V. The steep increase is due to the breakdown by the glow discharge plasma. On the other hand, the I_p shows the exponential increase with the UV irradiation to the sample. The exponential increase of I_p is due to α regime between the Ar, CH₄ molecules and photoelectrons. The plasma voltage (V_p) dependence of I_p is shown in Fig. 1(c). The V_p is cal-

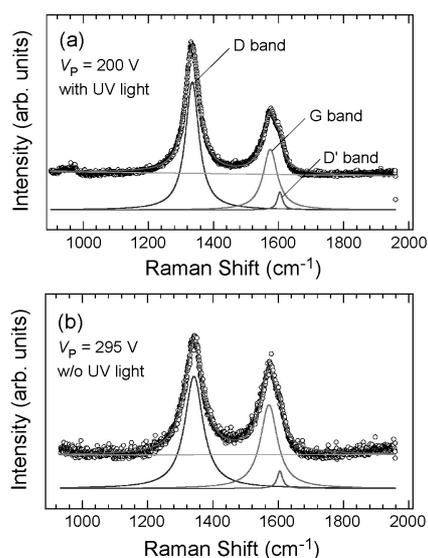


Fig. 2. Raman spectra of networked nanographite grown at (a) photoemission-assisted plasma ($V_p = 200$ V with UV irradiation), and (b) glow discharge plasma ($V_p = 295$ V without UV irradiation.)

culated by the subtracting the voltage applied to resistance from V_B . The growth experiments were performed at the condition indicated by arrows.

Figure 2 shows the Raman spectra of networked nanographite grown by photoemission-assisted plasma (with UV) and glow discharge plasma CVD (without UV). There are three peaks in spectra, named D band derived from the radial breath vibration of the carbon hexagonal structure, G band derived from the stretching vibration of C=C sp^2 chemical bond, and D' band, respectively. The width of G band corresponds to the degree of disorder[4], namely lower G band width indicates the higher oriented graphite. Alternately, it has been reported that the lower D band width corresponds to the lower the number of defect of hexagonal structure such as five- or seven-membered rings[5]. Hence the width of D and G bands are useful for evaluation of the crystallographic quality of graphite.

The V_p dependences of the G and D band width are summarized in Fig. 3. The width of both G and D bands grown by photoemission-assisted plasma is lower than that grown by glow discharge plasma. Furthermore, the width decreases with decreasing the VP. This result indicates that the photoemission-assisted plasma CVD can make the higher oriented graphite than glow discharge plasma and the crystallographic quality of nanographite is higher with decreasing the V_p .

Here, we should consider the reason why the low V_p improves the crystallographic quality of networked nanographite. There are two considerable reasons: one is the low growth rate, and other is the decrease of the energy and amount of collided ions to substrate. It is well known at the CVD growth of Si crystal that the high speed deposition make the defects in the deposited Si films. In the pho-

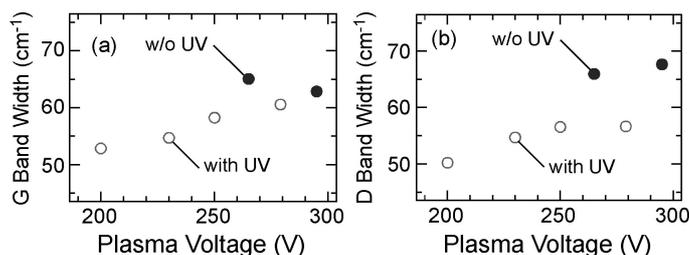


Fig. 3. The plasma voltage dependence of (a) G band width and (b) D band width of networked nanographite. The open and closed circles correspond the growth with UV irradiation and without UV irradiation, respectively.

toemission-assisted plasma, the I_p decreases exponentially with the decrease of the V_p as shown in Fig. 1(c). Therefore, growth rate also become small with lowering the V_B because it can be assumed that the dissociation rate of CH_4 is proportional to the electron density in plasma ($\propto I_p$). The second reason is the reduction of ion corrosion. In the photoemission-assisted plasma CVD, the substrate is placed at the cathode, so that the ions such as Ar^+ and CH_4^+ collide to the grown film. These ions are accelerated by the sheath voltage, which corresponds to the V_p . In the case of low V_B growth, the kinetic energy of ions that collide to the substrates is also small, so that the ions do not break up the graphite structure. In addition, the number of ions also decreases with decreasing the V_B . From this result, it seems that the deduction of ion corrosion to the substrate is key point to grow the high quality graphite materials.

Additionally, it is noteworthy that the G band width of networked nanographite grown by the photoemission-assisted plasma CVD at $V_p = 200$ V (52 cm^{-1}) is lower than that of carbon nanowall (CNW) grown by the microwave plasma CVD (~ 60 cm^{-1})[6]. Generally, it is said that the time of ion collision to substrate in microwave plasma CVD is smaller than that in DC discharge plasma. This result suggests that the moderate ion bombardment to the sample improves the crystallographic quality of graphite materials. Actually, it has been reported that the Ar^+ beam irradiation is required for the nucleation of CNW[3].

4. Conclusions

The V_B dependence of crystallographic quality of networked nanographite is investigated using the photoemission-assisted plasma CVD. The width of G and D bands lowers with decreasing V_B . The considerable reasons are (1) the decrease of growth rate, and (2) the decrease of ion collision to the substrate.

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