

Initial Growth Observation of Networked Nano Graphite on SiO₂ (90nm)/Si dependent on Process Gas Concentration

Yoshihiro Ojio¹, Shuichi Ogawa¹, Motonobu Sato^{1,2}, Mizuhisa Nihei²,
Yuji Takakuwa¹, and Naoki Yokoyama²

¹ Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku Univ.

2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan

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

² Green Nanoelectronics Center (GNC), National Institute of Advanced Industrial Science and Technology (AIST)

16-1 Onogawa, Tsukuba 305-8569, Japan

1. Introduction

Graphene and carbon nanotubes have been approximated to apply for LSI interconnects due to their high electrical mobility and thermal conductivity in spite of microscopic structures. For using LSI production process, graphitic materials are needed to grow as low as $\sim 400^\circ\text{C}$ on whole large sized wafers without remained catalysts. In order to results this problems, we have proposed photoemission-assisted plasma enhanced chemical vapor deposition (PA-PECVD) [1]. In previous study, we can obtain the networked nanographite (NNG) on SiO₂/Si substrates, which have randomly oriented small graphene grains. In addition, a highly oriented multilayer graphene (MLG) is grown at the interface between SiO₂ and NNG [2]. If only MLG can be grown up to ~ 20 nm of thickness with keeping the horizontal orientation, they can be applied for LSI interconnects. In the PECVD, it is well known the concentration of CH₄ affects the crystallographic quality of nanocarbon materials, but its affection to MLG has not been clarified yet. In this study, CH₄ concentration dependence of crystallographic quality and electric resistivity of MLG is investigated.

2. Experimental methods

NNG grew up by PA-PECVD apparatus placed at Tohoku University. The thin film were grown on the SiO₂(90 nm)/Si substrates. The growth temperature was $\sim 650^\circ\text{C}$. The concentration of CH₄ (C_{CH_4}) was changed among 6% and 33%. The CH₄ was diluted by Ar. The growth periods were changed from 1 min to 30 min. The Raman spectroscopy measurements were performed at Tegen CAF of Tohoku University. The electric resistivity was measured by 4 probe method.

3. Results and discussion

Figure 1 shows the CH₄ concentration dependence of discharge characteristics. The current between a substrate and an electrode increases exponentially and then shows rapid increase. The rapid increase of current indicates the discharge manner transition from photoemission-assisted Townsend discharge to glow discharge [3]. The NNG growths were performed at the Townsend discharge ($V_B = 250$ V) shown by open circles in Fig 1. The discharge current at 250 V and transition voltage from Townsend to

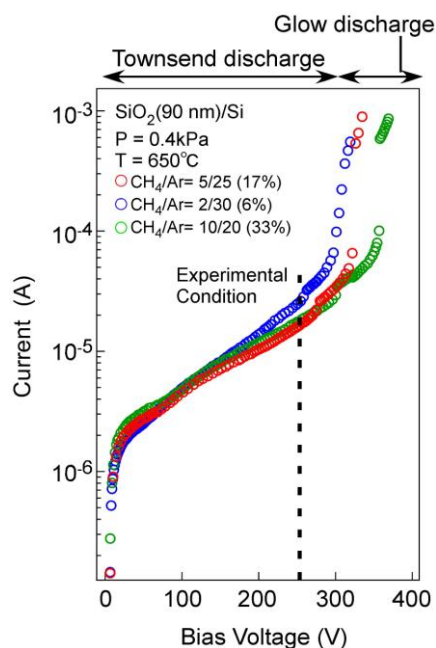


Fig. 1 CH₄ concentration dependence of discharge characteristics of photoemission-assisted plasma.

glow discharge are different depending on the CH₄ concentration. Therefore, the thickness of NNG is also different depending CH₄ concentration as shown in Fig. 2 (a). The discharge current at $C_{\text{CH}_4} = 6\%$ is the highest among the conditions, but growth rate at $C_{\text{CH}_4} = 17\%$ is the largest due to the difference of radicals amount generated in plasmas.

In the Raman spectra of NNG thin films, there are 6 peaks and we especially analyze D band derived from vibration of carbon hexagonal ring and G band derived from vibration of C-C sp² bonding [4]. Figure 2 (b) and (c) show the growth time dependence of G band position and width. The G band position correspond the strain of graphene sheet, indicating lower wave number of G band position is more bent graphene sheets. In the previous study, we have reported that the initial growth of MLG by PA-PECVD can be divided by two regions named “Region 1” and “Region 2”, which the highly oriented MLG is formed in Region 1 and randomly oriented NNG is grown in Region 2, and its regions can be indicated by the cross point of extrapolation line in G band position [5]. The growth time at the transi-

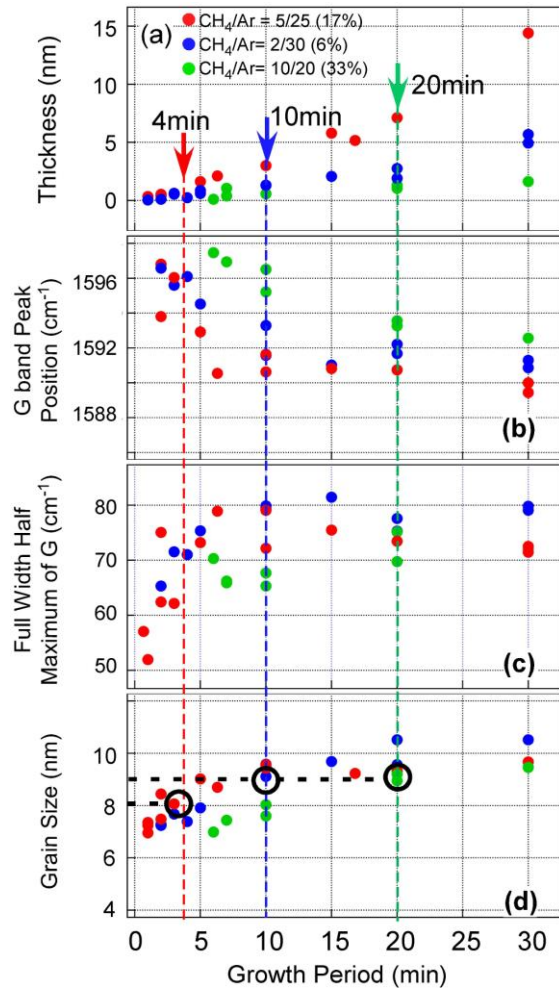


Fig. 2 Growth period dependence of (a) the film thickness decided by Raman intensity ratio derived from NNG and Si substrate I_G/I_{Si} , (b) G band peak position, (c) full width at half maximum (FWHM) of G band, and (d) grain size obtained from G band and D band intensity ratio [6]. The arrows at 4min, 10 min, and 20min. indicate the transition point from Region 1 to Region 2. It is found that the time at transition point strongly depend on the CH_4 concentration.

tion point from Region 1 to Region 2 strongly depends on the C_{CH_4} , but the thickness at the transition point is independent of the CH_4 concentration as shown in Fig. 2 (a). However, the grain size at Region 1 shows the CH_4 concentration dependence. In the case of $C_{CH_4} = 17\%$, the grain size is approximately 8 nm, but it is enlarged up to 9 nm in case of $C_{CH_4} = 33\%$, and 6%, respectively.

The grain size strongly corresponds to the electric resistivity. The resistivity of NNG at the transition from Region 1 to Region 2 is $4.78 \times 10^{-2} \Omega \cdot cm$ at $C_{CH_4} = 17\%$ but $1.63 \times 10^{-2} \Omega \cdot cm$ at $C_{CH_4} = 33\%$ and $1.55 \times 10^{-2} \Omega \cdot cm$ at $C_{CH_4} = 6\%$. It should be noted that the thickness of these samples is same as shown in Fig. 2 (a). This result indicates that the MLG with larger grain size has a smaller electric resistivity.

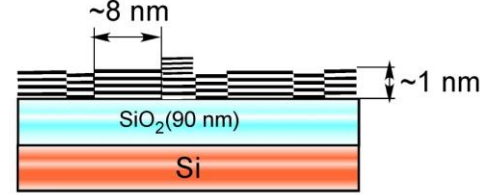
Here, we consider the growth mechanism of MLG depending on the CH_4 concentration. In low CH_4 concentra-

Both Region1

(a) $CH_4/Ar = 5/25(17\%)$

$$\rho_{17} = 4.78 \times 10^{-2} (\Omega \cdot cm)$$

large dispersion



(b) $CH_4/Ar = 2/30(6\%), 10/20(33\%)$

$$\rho_6 = 1.63 \times 10^{-2} (\Omega \cdot cm)$$

$$\rho_{33.3} = 1.55 \times 10^{-2} (\Omega \cdot cm)$$

small dispersion

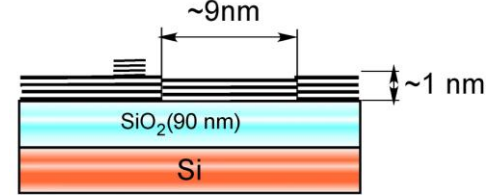


Fig. 3 Growth model at transition point. (a) show $CH_4/Ar = 5/25$ (17%) condition and (b) show the others.

tion (6%), the amount of supplied radicals to the substrate is small, so that adsorbed radicals can migrate and reach the edge of graphene sheet leading to the growth of large domain size of graphene. The growth rate is also small in the case of high CH_4 concentration (33%) because of the small discharge current, the enough migration of adsorbed radicals can be occurred. On the other hand, the growth rate in middle concentration (17%) is faster than that in another conditions, the enough migration for enlargement of graphene domain does not occur.

4. Conclusions

The CH_4 concentration dependence of NNG growth kinetic was investigated. In low growth rate condition either high or low concentration, large size grains was grown due to enough radical's migration. The large grains help the electric resistivity small.

5. Acknowledgements

This study is partly supported by the Japan Society for the Promotion of Science (JSPS) through the "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program).

References

- [1] T. Takami *et al.*: e-J. Surf. Sci. Nanotechnol. **7**(2009)882.
- [2] S. Ogawa *et al.*: Ext. Abstr. SSDM, 2009, p. 559.
- [3] M. Yang *et al.*: Thin Solid Films (2012) in press.
- [4] A. C. Ferrari *et al*, *Phys. Rev. B.* **61**(2000)14095.
- [5] Y. Ojio *et al.*: Ext. Abstr. SSDM, 2011, p. 765.
- [6] L. G. Cançado *et al*, *Appl. Phys. Lett.* **88**(2006)163106.