

Nanographene Synthesis on Cu Film Using Pentacene, H₂ Gas, and Heated W Mesh at Low Temperature

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Abstract

We have investigated the in-plane structural distribution of the nanocarbon film prepared from Pentacene and H₂ gas by hot mesh deposition (HMD). In HMD, pentacene having a 6-membered ring structure was used as a precursor material. The nanocarbon was synthesized at low temperature using polymerization reaction with 6,13-dihydropentacene molecules generated on a heated W mesh. Raman peaks due to nanographene were observed under the optimized condition on the Cu film/quartz substrate. The nanographene synthesis depends on the deposition rate and the ratio of atomic hydrogen to 6,13-dihydropentacene.

1. Introduction

Graphene nanoribbon (GNR), which is a type of nanographene, is a ribbon-like elongated graphene with a width of nanometer order. The property depends on the edge structure (armchair and zigzag edges) and its width [1]. Various methods of GNR synthesis such as zipping of carbon nanotube [2] and bottom-up process of low molecular weight organic material [3] have been actively studied.

We have investigated the synthesis method of nanographene using pentacene (C₂₂H₁₄) and H₂ gas as hot mesh deposition (HMD). So far, the pentacene decomposition reaction (hydrogenation reaction from C₂₂H₁₄ to C₂₂H₁₆) occurs on a heated W mesh above 1300 °C. The 6,13-dihydropentacene (C₂₂H₁₆) is mainly generated from pentacene [4]. A pentacene dimer can be produced on a quartz substrate by installing a double W meshes [5], and a pentacene oligomer (dimer to pentamer) can be formed on a quartz substrate by partially supporting Ni on the W mesh [6]. However, the obtained pentacene multimer has a problem of low yield (6 %). A Cu substrate instead of a quartz substrate enhanced polymerization reaction [7]. It has been reported that graphene can be produced on a Cu substrate (800 °C) using a pentacene [8]. However, in the HMD method, even if the starting material is pentacene, it changes to 6,13-dihydropentacene on the W mesh, so the growth mechanism of graphene is expected to be different. To control the molecular structure and to improve the yield of nanographene, it is necessary to clarify the reaction of pentacene (6,13-dihydropentacene) and the role of hydrogen on the metal catalyst surface.

In this study, we performed the nanographene synthesis on a Cu film deposited on a quartz substrate by electron beam evaporation. The polymerization reaction of pentacene (6,13-

dihydropentacene) on the Cu film and the effect of the ratio of atomic hydrogen to 6,13-dihydropentacene on the film property was studied by in-plane structure distribution of the nanocarbon film.

2. Experimental procedure

A quartz substrate (20 mm × 20 mm × 0.5 mm thickness) was cleaned using alkaline solution (Semicoclean 23). Then, a Cu film was deposited by electron beam evaporation at room temperature. The film thickness and deposition rate were 50 nm and 0.20 nm/s, respectively. Acetone cleaning was performed before nanographene film deposition. The Cu film/quartz substrate and pentacene (30 mg) was set in the HMD apparatus as shown in Fig. 1. After evacuation, H₂ gas was introduced at 400 sccm into the HMD apparatus. The gas pressure was set at 30 Pa by adjusting the valve between the chamber and the exhaust pump. The W mesh was heated up to 1700 °C by electric heating (10.6 V, 19.0 A) and kept for about 700 s. This treatment was performed to remove the natural oxide layer on the Cu film surface. We call this surface modification using atomic hydrogen as atomic hydrogen annealing (AHA). After AHA, the pentacene was sublimated to form the nanocarbon film by the source heater under two deposition conditions (condition 1 and 2). In condition 1, the source heater temperature was maintained at 340 °C for 600 s. In condition 2, the source heater temperature was maintained at 315 °C for 600 s, then the source heater was heated up to 340 °C gradually as shown in Fig. 1 (b). The sublimation rate under the condition 1 was higher than the condition 2. In this study, as shown in Fig. 1, to investigate the relationship between film properties and film thickness, the quartz tube was tilted to the upper of the Cu film/quartz substrate. The sample temperature was 350 °C. The characteristics of the nanocarbon film were evaluated by Raman spectroscopy (Ar⁺ laser, wavelength of 514.5 nm, laser power of 2 mW).

3. Results and discussion

Optical images of the nanocarbon films are shown in Fig. 2. A purple film was confirmed in the upper half (position a) of the Cu film. It is considered that the main component molecule was pentacene. On the other hand, the purple film was not confirmed in the sample prepared under the condition 2. Under the condition 1, the temperature of source heater to sublime pentacene was higher than the condition 2. Therefore, pentacene sublimated rapidly, and a lot of pentacene molecules

arrived W mesh surface. In this case, the pentacene was not decomposed by the heated W mesh.

Raman spectra of the nanocarbon films are shown in Fig. 3. The Raman measurements were carried out at two positions of the upper and lower parts of sample. No Raman peak due to graphene was observed at positions of a, b, and c. On the other hand, the peak at 1346 cm^{-1} corresponds the D band of defect in graphene and the peak at 1605 cm^{-1} corresponds the G band of graphene and/or D' band of defect in graphene were obtained. It was shown that the nanographene can be synthesized at a low deposition rate.

Next, the nanocarbon film formation mechanism is considered by in-plane structure distribution of nanocarbon film based on the ratio of 6,13-dihydropentacene and atomic hydrogen on the Cu surface as shown in Fig. 4. Under the condition 1, the W mesh is covered by pentacene molecules. Therefore, the pentacene was not decomposed by the heated W mesh. A part of the pentacene molecules decomposed and small amount of the 6,13-dihydropentacene was deposited. On the other hand, the pentacene was decomposed by the heated W mesh because the number of arriving pentacene molecules was small under the condition 2. In addition, the ratio of atomic hydrogen and 6,13-dihydropentacene in the lower part of the Ni film/quartz substrate was higher than the upper part. This suggests that the atomic hydrogen acts important role to polymerize the 6,13-dihydropentacene at low temperature.

4. Conclusions

- 1) As the sublimation rate of pentacene was high, the pentacene could not sufficiently react on the heated W mesh. Therefore, the 6,13-dihydropentacene for the polymerization did not generate because of low sample temperature.
- 2) When the sublimation rate of pentacene was low, Raman spectrum originated from nanographene was obtained in the region with high atomic hydrogen density on the Cu film at low temperature of $350\text{ }^{\circ}\text{C}$.

Acknowledgments

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References

- [1] X. L. Li, X. R. Wang, L. Zhang, S. Lee, and H. J. Dai, *Science* **319** (2008) 1229.
- [2] L. Jiao, L. Zhang, X. Wang, G. Diankov, and H. Dai, *Nature* **458** (2009) 877.
- [3] Z. Li, P. Wu, C. Wang, X. Fan, W. Zhang, X. Zhai, C. Zeng, Z. Li, J. Yang, and J. Hou, *ACS Nano* **5** (2011) 3385.
- [4] A. Heya and N. Matsuo, *Jpn. J. Appl. Phys.* **51** (2012) 110204.
- [5] A. Heya and N. Matsuo, *Jpn. J. Appl. Phys.* **57** (2018) 04FL03.
- [6] A. Heya and N. Matsuo, *Thin Solid Films* **685** (2019) 186.
- [7] A. Heya and N. Matsuo, *Thin Solid Films* **675** (2019) 143.
- [8] X. Wan, K. Chen, D. Liu, J. Chen, Q. Miao, and J. Xu, *Chem. Mater.* **24** (2012) 3906.

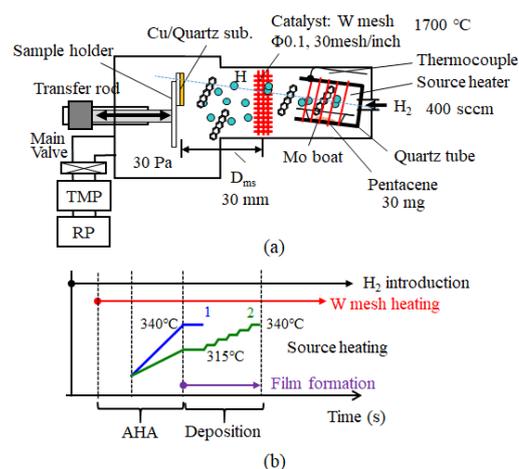


Fig. 1. (a) Schematic diagram of the HMD apparatus. (b) Deposition sequence of nanographene film formation during HMD.

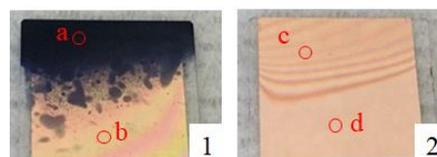


Fig. 2. (a) Optical images of the nanocarbon films deposited on the Cu film by HMD under the conditions 1 and 2. The measurement points (a - d) for Raman measurement are also shown.

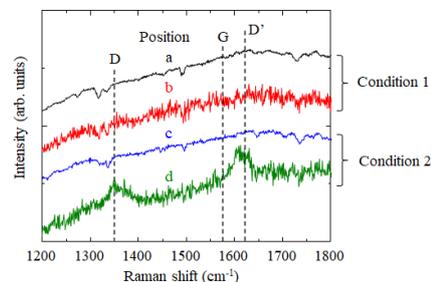


Fig. 3. Raman spectra of the nanocarbon films deposited on the Cu film by HMD under the conditions 1 and 2.

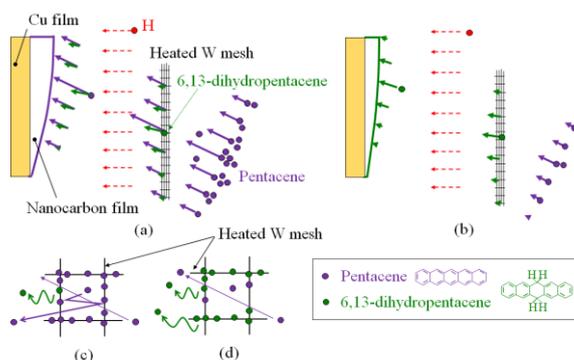


Fig. 4. Formation mechanism of nanocarbon film and surface state of the W mesh under the condition 1 (a, c) and 2 (b, d).