

論文の内容の要旨

In-situ Radiation-mode Optical Microscopy and XPS Study of Chemical Vapor Deposition Growth of Graphene

(その場観測熱放射光学顕微法および X 線光電子分光法による
グラフェン化学気相成長の研究)

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1. Introduction

Graphene is a monolayer of graphite that has attracted widespread attention because of its outstanding properties. Scalable and rapid production of graphene is required for its industrial applications. Chemical vapor deposition (CVD) is considered the most promising method to synthesize large-area single-crystalline graphene. In a typical CVD process of graphene, CH₄ with Ar and H₂ is supplied onto a Cu foil substrate at a temperature of about 1000 °C, where CH₄ molecules are decomposed to form graphene nuclei. When the density of graphene nucleation is high, the resulting graphene becomes polycrystalline graphene, which exhibits inferior properties to those of single-crystalline graphene. To rapidly produce large-area single-crystalline graphene, suppressing graphene nucleation and accelerating growth must be simultaneously realized. For this purpose, the effects of various parameters such as gas flow rate, total pressure, and substrate temperature on CVD growth of graphene must be elucidated.

Herein, I systematically investigated the effects of two factors: (1) hot filament and (2) hydrogen. In hot-filament-assisted CVD (HF-CVD), the source gas is decomposed by a high-temperature filament before it reaches the substrate [1]. Therefore, the hot filament is a potential candidate for growth acceleration. However, its effects on nucleation and growth are unclear. H₂ is generally supplied with CH₄ onto a Cu foil substrate. Varying effects of hydrogen on the nucleation, growth, and etching of graphene have been reported [2]–[5], but some of the effects seemed inconsistent with others and the major effect remains unclear. To elucidate the effect, in-situ observation of the CVD growth of graphene would be required.

In this study, I used radiation-mode optical microscopy (Rad-OM) [6], which can visualize graphene growth in real time by utilizing the difference in emissivity of graphene and Cu. Further, I combined the Rad-OM with in-situ synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS) to characterize the surface species and evaluate the effect of hydrogen.

2. Experimental

Cu foil wrapped around W or Ta foil was used as a substrate. It was cleaned by ultrasonic cleaning in ultrapure water and acetone, then loaded into a CVD chamber. The Cu foil was heated by passing an electric current through the W or Ta foil. The temperature of the Cu foil was monitored by a pyrometer from outside the chamber. After the Cu foil was pretreated by annealing in Ar and Ar ion bombardment, its temperature was increased, then a mixture of Ar, H₂, and CH₄ was supplied to initiate CVD growth. The growth was observed by Rad-OM.

3. Effect of hot filament

3.1. Experimental

Fig. 1 depicts a schematic of the experimental setup to examine the effect of the hot filament. A filament made of W was placed in the gas flow path before the Cu substrate. The W filament was heated by an electric current, and its temperature was monitored by a pyrometer. After pretreatment, the mixture of 750 sccm Ar and 200 sccm H₂ gases was supplied with a total pressure of 1.0×10^4 Pa. Then, the substrate temperature was maintained at 950 °C and 1 sccm CH₄ was supplied to initiate graphene growth. The temperature of W filament was systematically changed, and growths were observed by Rad-OM to evaluate the effect of hot filament.

3.2. Results and discussion

To examine the effects of the hot filament on graphene nucleation and growth, the filament current (temperature) was gradually increased during graphene growth under a CH₄ flow rate of 1 sccm. Figs. 2 (a), (b), and (c) show the Rad-OM images of the growth, the time evolution of the number of nuclei in (a), and the filament current, respectively. Before heating the W filament, two graphene grains grew at an average rate of 2.4 $\mu\text{m min}^{-1}$. After the W filament was heated, the lateral growth continued without formation of additional grains, until the current was increased to 7.6 A (1270 °C). However, when the current was increased to 7.8 A (1340 °C), three grains were newly observed. When the current was set at 7.9 A, all grains grew at an average rate of 4.2 $\mu\text{m min}^{-1}$, but no more additional nucleation occurred. After the current was increased to 8.1 A, the number of grains drastically increased by 15 and the grains grew further. These results indicated that the hot filament induced nucleation and accelerating growth, which were enhanced by raising the filament temperature. Notably, acceleration without additional nucleation occurred at a filament temperature of 1270 °C. These results could be explained by the difference in the type and quantity of the chemical species generated by the hot filament and catalytic Cu substrate.

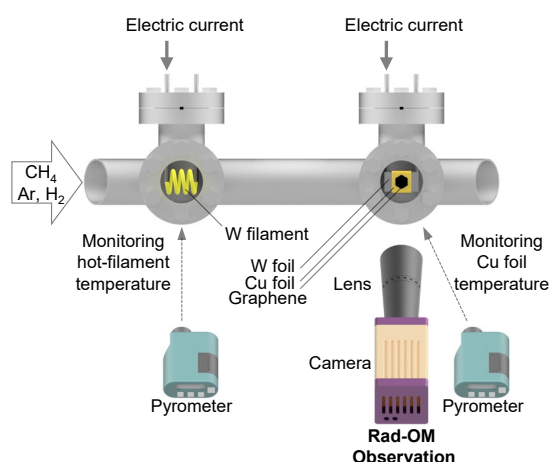


Fig. 1. Schematic of the experimental setup to examine the effect of hot filament. [7] Copyright (2019) The Japan Society of Applied Physics.

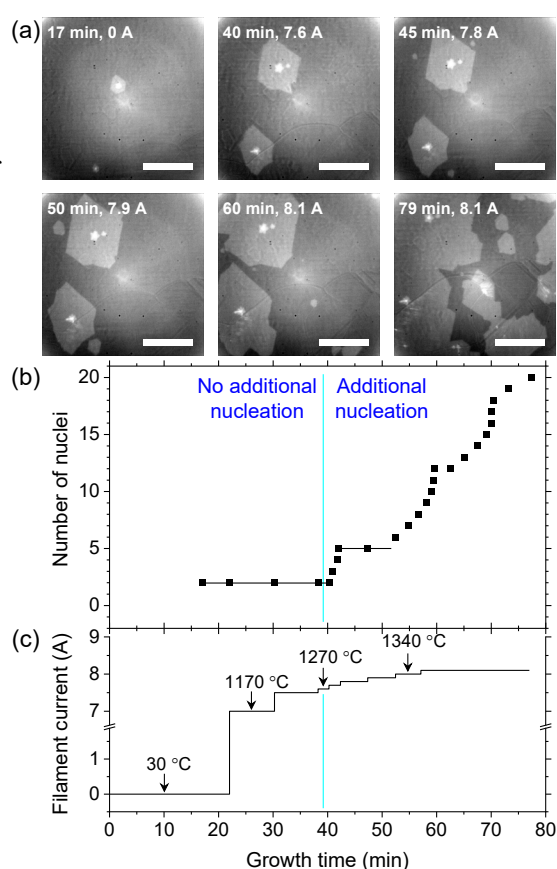


Fig. 2. (a) Rad-OM images of the graphene growth. The growth time and filament current are displayed in the image. White and black area correspond to graphene and Cu, respectively. Scale bars: 200 μm . (b) Number of nuclei counted in (a), and (c) value of filament current as functions of growth time. A corresponding filament temperature is shown in the graph. [7] (Partially modified) Copyright (2019) The Japan Society of Applied Physics.

4. Effect of hydrogen

4.1. Experimental

The Cu foil substrate was pretreated as described in Chapter 2. Then, graphene growth and annealing with and without H₂ were observed by Rad-OM to examine the effect of hydrogen. Further, I combined Rad-OM with SR-XPS at KEK-PF BL-13B. By this setup, graphene growth and annealing were observed by Rad-OM. After the processes, the substrate was transferred to the XPS chamber to evaluate the carbon species by XPS without exposing the substrate to air.

4.2. Results and discussion

To investigate the effect of hydrogen on graphene nucleation, the H₂ flow rate was changed during growth. First, growth with H₂ was switched to that without H₂. Fig. 3(a) shows the Rad-OM snapshots of the growth. During the growth with H₂, hexagonal domains appeared. After the H₂ supply was stopped at 11 min, many small or non-hexagonal domains appeared. These results indicate that hydrogen suppressed the growth of the small or non-hexagonal domains. Next, growth without H₂ was switched to that with H₂. As shown in Fig. 3(b), during the growth without H₂, large-area graphene domains did not appear, but white spots appeared instead. After H₂ was introduced at 12 min, hexagonal graphene domains immediately appeared and grew. The number of domains after H₂ introduction exceeded that during the growth with H₂ shown in Fig. 3(a). These results imply that a large number of optically undetectable graphene domains (< 1 μ m) already nucleated during the growth without H₂, prior to the H₂ introduction.

Based on the above discussion, the etching effect of H₂ on graphene and carbon species undetectable by Rad-OM were investigated using the combination of Rad-OM and SR-XPS. After the Cu foil substrate was cleaned, SR-XPS was used to confirm that the amount of carbon on the substrate was undetectable (Fig. 4(c)). Subsequently, growth with H₂ was observed for 2 min; the nucleation and growth of the domains were observed by Rad-OM (Fig. 4(a)). After the growth was stopped at 2 min, the substrate was measured by SR-XPS and an increase in carbon species was observed (Fig. 4(c)). Then, the substrate was annealed with H₂ for 15 min and the domains became undetectable by Rad-OM (Fig. 4(b)). After the annealing was stopped, SR-XPS results indicated that the peaks of carbon remained, but the intensity decreased (Fig. 4(c)). These results indicate that hydrogen etched the carbon species, and carbon species undetectable by Rad-OM still existed. Next, growth without H₂ on a clean Cu substrate was conducted. During the growth, nucleation and growth of the domains were observed by Rad-OM (Fig. 4(d)). After the growth was stopped at 2 min, SR-XPS measurement revealed an increase in the carbon species (Fig. 4(f)). Then, the substrate was

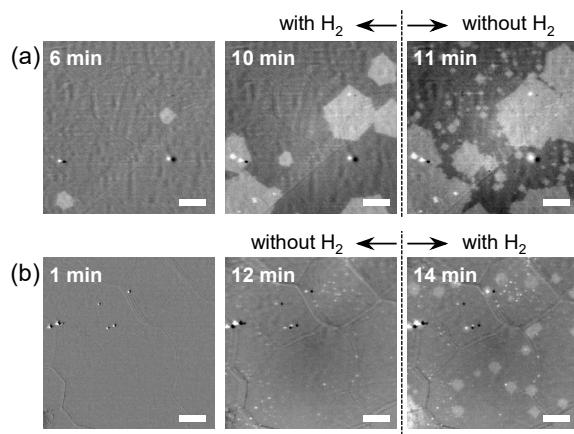


Fig. 3. (a) Rad-OM images of growth with H₂, followed by growth without H₂ at 6, 10, and 11 min. H₂ supply was stopped at 11 min. (b) Rad-OM images of growth without H₂, followed by growth with H₂ at 1, 12, and 14 min. The H₂ supply was initiated at 12 min. Scale bars: 50 μ m.

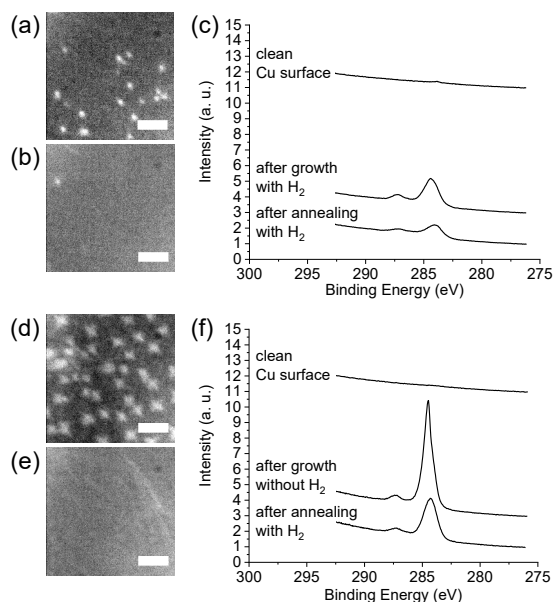


Fig. 4. Rad-OM images of (a) growth with H₂ and (b) subsequent annealing with H₂, (d) growth without H₂ and (e) subsequent annealing with H₂, respectively. Scale bars: 30 μ m. (c), (f) In-situ XPS C1s spectra (h ν =330 eV) after cleaning and each process shown in (a), (b), (d), and (e).

annealed with H₂ for 15 min, and the domains became undetectable by Rad-OM (Fig. 4(e)). After the annealing was stopped, the SR-XPS measurement also indicated that the peaks of the carbon species remained, but the intensity decreased. (Fig. 4(f)). Both Rad-OM observation and SR-XPS measurement revealed that the amount of carbon species after the growth without H₂ was larger than that after the growth with H₂. These results also confirmed that hydrogen etched graphene during CVD.

5. Conclusions

In this study, I reached two conclusions. First, I demonstrated that raising the temperature of the hot filament induced additional nucleation and enhanced the growth rate, but accelerating the growth without additional nucleation occurred at optimized filament temperatures. Thus, the hot filament would be useful for rapidly synthesizing large-area single-crystalline graphene. Second, I concluded that the crucial effect of hydrogen on the CVD growth of graphene is the etching of graphene and the effect suppresses the nucleation density of graphene. Thus, introducing H₂ is favorable for the growth of large-area graphene domains. These conclusions based on in-situ Rad-OM and SR-XPS analyses will be beneficial in establishing guidelines to optimize the CVD growth of graphene and will pave the way for the production of large-area single-crystalline graphene.

References

- [1] E. Lee *et al.*, *2D Mater.*, **6**, 011001 (2018).
- [2] I. Vlassiouk *et al.*, *ACS Nano*, **5**, 6069 (2011).
- [3] S. Shar *et al.*, *Carbon*, **125**, 318 (2017).
- [4] Y. Zhang *et al.*, *ACS Nano*, **6**, 126 (2012).
- [5] S. Choubak *et al.*, *J. Phys. Chem. Lett.*, **4**, 1100 (2013).
- [6] T. Terasawa and K. Saiki, *Nat. Commun.*, **6**, 6834 (2015).

Publication related to the dissertation

- [7] Takanobu Taira, Takuya Shinohara, Seiji Obata, and Koichiro Saiki, “Real-time observation on hot-filament-assisted CVD growth of graphene”, *Japanese Journal of Applied Physics*, **58**, SIIB24-1–SIIB24-5 (2019).