

## 論文の内容の要旨

論文題目 Radiation Microscopy of Chemical Vapor Deposition Growth of Graphene

(放射顕微鏡を用いたグラフェン化学気相成長の研究)

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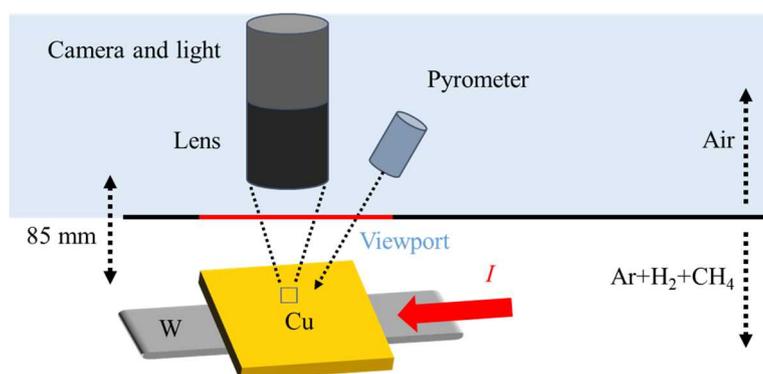
### **1. Introduction**

The rapid progress of the 2D layered materials such as graphene has attracted much attentions because of its remarkable properties, as reported by A. K. Geim and I. V. Grigorieva [*Nature* **499**, 419–425 (2013)]. Chemical Vapor Deposition (CVD) is considered the most promising method to produce high quality and large area graphene and other 2D materials. In CVD the precursor molecules decomposed from the source gases gathered on the substrate to build up the desired materials under high temperature and ambient pressure conditions. Therefore, the situation during the reaction could not be observed in real time, which low energy electron microscopy or other electron microscopic techniques had achieved for the growth in a vacuum conditions.

Optical microscopy can work under such high temperature and ambient pressure conditions. In the case of observing the reflection light from a sample, the sufficient contrast could not be obtained between graphene and Cu, a common catalytic substrate to produce graphene. On the other hand, there is a large difference in emissivity between graphene (0.8) and Cu (0.03) under the condition in which blackbody radiation occurs. Here, I propose a radiation microscopy (RM) for *in-situ* and real time observation on the CVD growth of graphene. Due to the large difference in emissivity the graphene looks much brighter than Cu in RM. The growing island of graphene could be observed in real time by a microscope and a camera, enabling the precise discussion of the CVD growth mechanism of graphene.

### **2. Experimental**

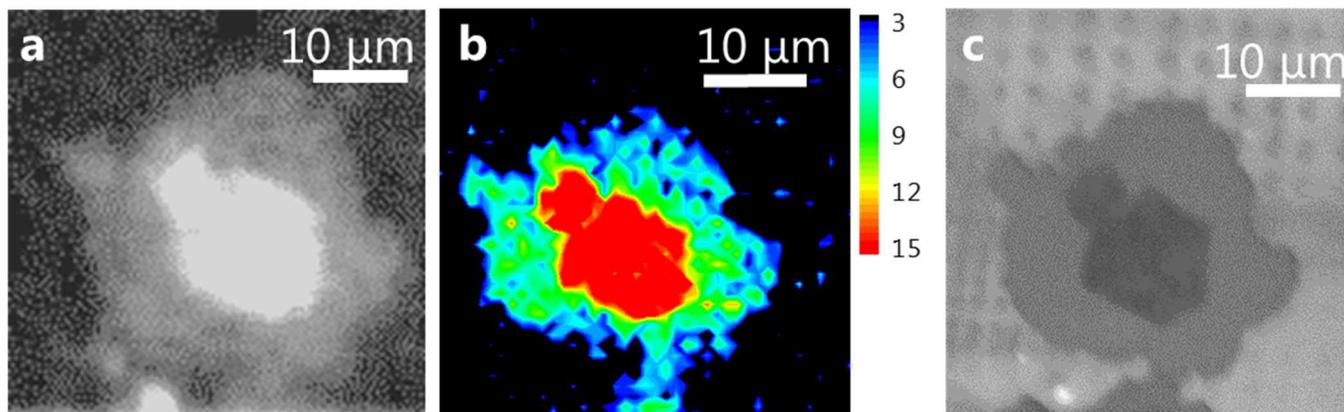
A Cu foil used as a substrate for graphene growth was welded onto a W ribbon and loaded into a vacuum chamber. The schematic image of the system was shown in Fig. 1. The direct current in a W ribbon heated the sample to approximately 1000 °C. The surface of the Cu foil was flattened and cleaned by annealing at 920 °C for 10 min with Ar (1000 sccm) and H<sub>2</sub> (100 sccm) atmosphere at 2700 Pa. Then the substrate temperature  $T_s$  was adjusted to the desired temperature and CH<sub>4</sub> (5 sccm) was introduced into the chamber to grow graphene. In my experimental conditions the grown graphene was observed to shrink responding to the shut-off of CH<sub>4</sub> flow. By conducting the sequential growth and shrinkage, I obtained the temperature dependence of the growth and shrinkage of graphene. The whole experiments were recorded by the camera and lens system, described in Fig. 1. After cooling down to room temperature, SEM observation and Raman spectroscopy were carried out *ex situ*.



**Figure 1 Schematic illustration of equipment to observe growth of graphene.** The sample surface was observed by the microscope and the pyrometer through the viewport from the outside of the chamber.

### **3. Result and discussion**

#### *3.1. Confirmation of observation of graphene by radiation microscope*

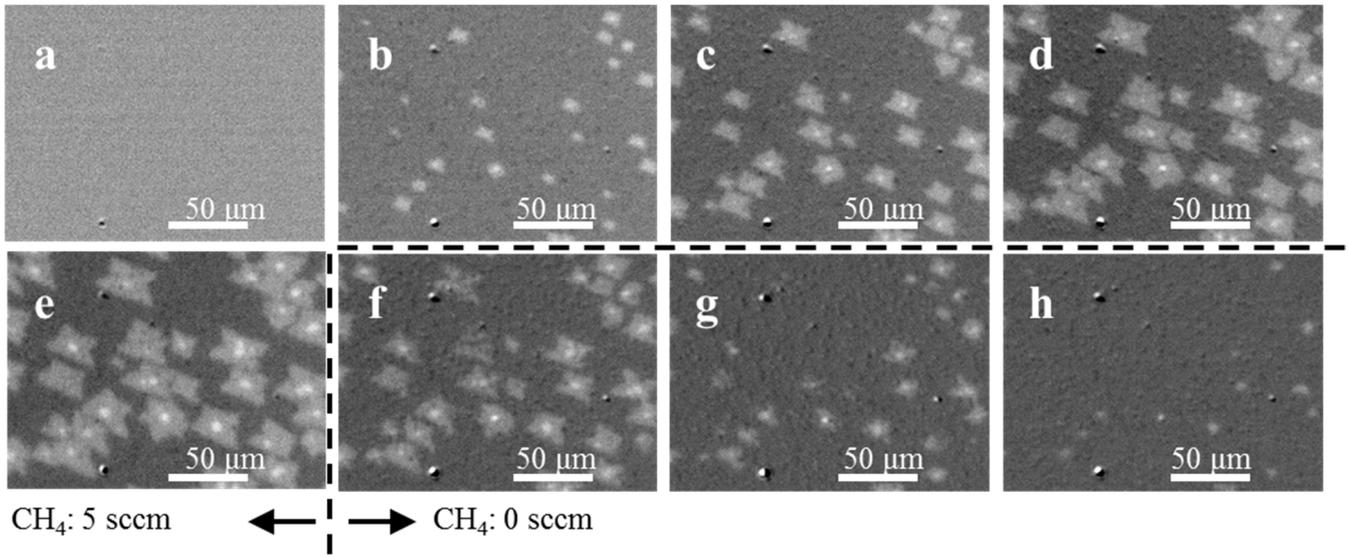


**Figure 2 Images of radiation microscopy, Raman G band intensity map, and SEM.** **a**, Radiation microscopic image of graphene on Cu substrate. **b**, Raman G band intensity map indicating amount of  $sp^2$  C rings in graphene. **c**, Scanning electron microscopic image of the same grain.

Figure 2a shows the RM image taken just before the supply of CH<sub>4</sub> stopped. The brightness in Fig. 2a due to the radiation intensity of the sample suggested that the amount of C atoms on the surrounding area, periphery of the grain, and the center part of the grain increased as this order. Raman G band intensity in Fig. 2b, corresponding to the amount of hexagonal  $sp^2$  C rings, is larger on the center part of the grain than that on the periphery. Therefore I concluded that the center part of the grain, the periphery of the grain, and the surrounding area corresponded to a bilayer graphene, monolayer graphene, and Cu substrate, respectively. The SEM image shown in Figure 2c also described that the shape and the layer number of the graphene grain can be recognized in the RM image similar to the commonly used method.

#### *3.2. Real time observation of growth and shrinkage of graphene*

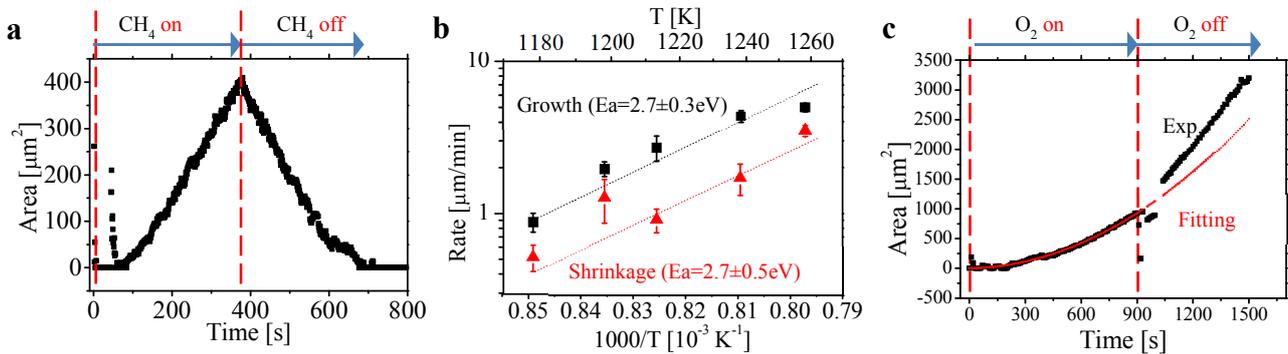
Figure 3 shows the RM images obtained in real-time during the growth (0 to 380 sec) and the shrinkage (380 to 700 sec) at the  $T_s$  of 985 °C. The graphene islands grew keeping their shapes as shown in Figs. 3b-3e, while the islands started to shrink after the methane supply was stopped as shown in Figures 3f-3h.



**Figure 3 Radiation microscopy images of graphene growth and shrinkage.** a-e, The growth at 0, 100, 200, 300, and 380 sec with the CH<sub>4</sub> flow rate of 5 sccm. f-h, The shrinkage at 500, 600, and 700 sec with the CH<sub>4</sub> flow rate of 0 sccm.

### 3.3. Growth and shrinkage mechanism of graphene

To discuss the mechanism of the lateral growth and shrinkage of graphene, the area of a typical graphene island at  $T_s$  of 985 °C is plotted as a function of time in Fig. 4a. In CVD, CH<sub>4</sub> is decomposed to the C precursor which attaches to the graphene lattice to grow graphene. If the density of the C precursor is constant during the growth, the square root of the area of graphene  $A$  is linear to the elapsed time. When the coverage of graphene on Cu substrate increased, on the other hand, the precursor production was suppressed resulting in the decrease in the C precursor density. In this case, the growth rate  $R_g$  according to  $dA^{1/2}/dt$  is no longer constant. I evaluated  $R_g$  for five graphene islands at various  $T_s$  as long as



**Figure 4 Analysis on growth and shrinkage of graphene.** a, Time evolution of representative grain area at 985 °C. b, Arrhenius plots of growth (square) and shrinkage (triangle) of graphene. The vertical and horizontal axis correspond to log scale of the rates and the reciprocal scale of the temperature. c, Time evolution of grain area with and without O<sub>2</sub> supply.

$A^{1/2}$  seemed to be linear to the time. The  $R_g$  increased from 0.9  $\mu\text{m}/\text{min}$  to 5.0  $\mu\text{m}/\text{min}$  as  $T_s$  increased from 905 °C to

985 °C. The temperature dependence of  $R_g$  is plotted versus  $T^{-1}$  as the squares in Fig. 4b. From the Arrhenius plots, the activation energy  $E_a$  for  $R_g$  is determined to be 2.7 eV which suggest the rate limiting step of the growth of graphene is the attachment of the C precursor at the periphery as reported by K. Celebi *et al.*[*Nano Lett.* **13**, 967–974 (2013).].

The shrinkage rate  $R_s$  was evaluated in a similar way, which increased from 0.5 to 3.5  $\mu\text{m}/\text{min}$  as  $T_s$  increased from 905 °C to 985 °C. The activation energy for  $R_s$  is also determined to be 2.7 eV in Fig. 4b (triangles). During the both of the growth and shrinkage process the carbon atoms were considered to detach from the graphene lattice to provide C precursor. After the switching off of the  $\text{CH}_4$  supply, the decrease of the precursor density on the substrate shifted the equilibrium of the surface carbon density to enhance the detachment of the carbon atoms from the periphery.

To confirm the effect of the precursor density on the CVD growth of graphene, I also investigated the graphene growth with and without the supply of  $\text{O}_2$ . The surface  $\text{O}_2$  was decomposed to O atoms and reacted with C precursor to produce volatile CO and/or  $\text{CO}_2$  molecules, which is expected to decrease the C precursor density. The time evolution of graphene area shown in Fig. 4c indicated the growth rate of graphene increased as the  $\text{O}_2$  supply was shut-off. Therefore I concluded that the balance of the production and consumption of C precursor played an important role in the CVD growth of graphene.

#### **4. Summary**

In this work, I proved that RM could directly observe the growing graphene islands and shrinkage even under high temperature and pressure conditions. The analysis of the temperature dependence of the growth rate indicated that the attachment of C precursor to the graphene lattice is the rate limiting step. The present method of RM is not limited to the growth of graphene on Cu but expected to be applicable to other crystal growth at high temperatures in various atmosphere toward the future electronic devices.