

Effects of Plasma on the Growth of Graphene Nanoribbon by Plasma CVD

プラズマCVD中グラフェンナノリボン合成におけるプラズマ効果

Hiroo Suzuki, Toshiaki Kato, and Toshiro Kaneko

鈴木 弘朗, 加藤 俊顕, 金子 俊郎

Department of Electronic Engineering, Tohoku University,

Aoba 6-6-05, Aramaki, Aoba-ku, Sendai 980-8579, Japan.

東北大学 大学院工学研究科 〒980-8579 仙台市青葉区荒巻青葉6-6-05

The growth mechanism of graphene nanoribbon during plasma chemical vapor deposition (CVD) has been systematically investigated by comparing evaporation rate of Ni between plasma and thermal CVD. The evaporation rate of Ni can be highly suppressed in plasma CVD compared with that of thermal CVD. Because of the low Ni evaporation rate, the Ni nanobar structures can be maintained even under the high temperature condition, which should be the key factor to realize the growth of graphene nanoribbon from Ni nanobar by plasma CVD.

1. Introduction

Graphene nanoribbons combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. Although graphene nanoribbons can be made in a variety of ways, the reliable site and alignment control of graphene nanoribbons with high on/off current ratios remains a challenge.

We have developed a new, simple, scalable method based on the advanced plasma chemical vapor deposition (CVD) method for directly fabricating narrow (~ 23 nm) graphene nanoribbon devices with a clear transport gap (58.5 meV) and a high on/off ratio ($>10^4$) [1]. Since the establishment of our novel graphene nanoribbon fabrication method, direct conversion of a Ni nanobar to a graphene nanoribbon is now possible. The growth mechanism of graphene nanoribbon, however, is not well understood, which is important for the fabrication of highly-integrated graphene nanoribbon devices in large scale.

2. Method

Plasma chemical vapor deposition (CVD) is known as a fruitful method for the structural-controlled growth and damage-free functionalization of nano carbon materials such as carbon nanotubes [2-4] and graphene [5-7].

In this study, a homemade plasma CVD system was used (Fig. 1). Before the plasma CVD, an electric furnace was heated to the desired temperatures (typically 800–900 °C)

under flowing hydrogen (50 Pa). A substrate was immediately transferred to the center area, and rapid heating was performed. Methane and hydrogen gases at a 9:1 ratio (270 Pa) were flowed just after the desired substrate temperature was reached, and radiofrequency (13.56 MHz) power was then supplied to the coils outside of the quartz tube. Following the plasma CVD, the substrate was moved from the center to the outside of the electrical furnace to rapidly decrease the temperature of the substrate.

The Ni nanobars were prepared by the combination of vacuum evaporation method and conventional lift-off process with electron-beam lithography on the SiO₂/Si substrate.

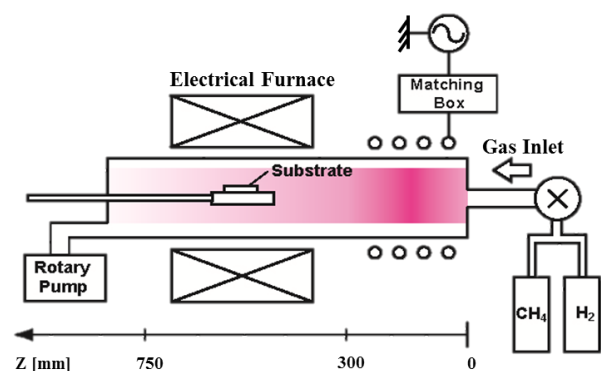


Fig.1. Schematic of experimental apparatus.

3. Results and discussion

In this method, graphene nanoribbon growth occurred with the evaporation of Ni. Thus, estimation of evaporation rate of Ni in plasma CVD processes is very important to

understand the growth kinetics of graphene nanoribbon.

Systematic investigations were carried out for the Ni evaporation using thin Ni film instead of Ni nanobar for the simplification. We attempted to elucidate the effects of plasma on the Ni evaporation through the comparison between plasma CVD and thermal CVD. Figures 2(a) and 2(b) show typical scanning electron microscope (SEM) images of Ni film after thermal and plasma CVD, respectively. The clear difference for the evaporation rate of Ni was observed between plasma and thermal CVD. The film structure of Ni was maintained after plasma CVD (Fig. 2(b)), whereas the Ni film was converted to the particle-like shape due to the high rate evaporation of Ni for thermal CVD (Fig. 2(a)). This indicates that the evaporation rate of Ni is very low in plasma CVD compared with that of thermal CVD (Fig. 2(c)).

It is known that the evaporation rate of Ni in nickel carbide is sensitive to the concentration of carbon. Pure Ni tends to show higher evaporation rate than that of nickel carbide with high carbon concentration. Based on this knowledge, the experimental results can be explained by the difference of carbon concentration in Ni between plasma CVD and thermal CVD. In plasma CVD, large amount of hydrocarbons can be efficiently supplied to the Ni compared with that in thermal CVD due to high rate dissociation of carbon source gas in plasma. For this reason, evaporation rate of Ni can be strongly suppressed only by plasma CVD.

This low Ni evaporation rate under relatively high temperature condition should be the key factor to realize the graphene nanoribbon from Ni nanobar. Since Ni nanobar structure has high surface to volume ratio, the structure of Ni nanobar is easily broken even under the lower temperature conditions than melting point of bulk Ni film. While, the following two conditions should be satisfied for the growth of graphene. (1) The relatively high temperature ($> 800\text{ }^{\circ}\text{C}$) condition is required to nucleate graphene. (2) The Ni catalyst is inevitable to grow graphene. For the growth of graphene nanoribbons from Ni nanobar, both conditions of (1) and (2) should be satisfied, i.e. the Ni nanobar structure has to be maintained even under the high temperature ($> 800\text{ }^{\circ}\text{C}$) condition. This can be only realized by the

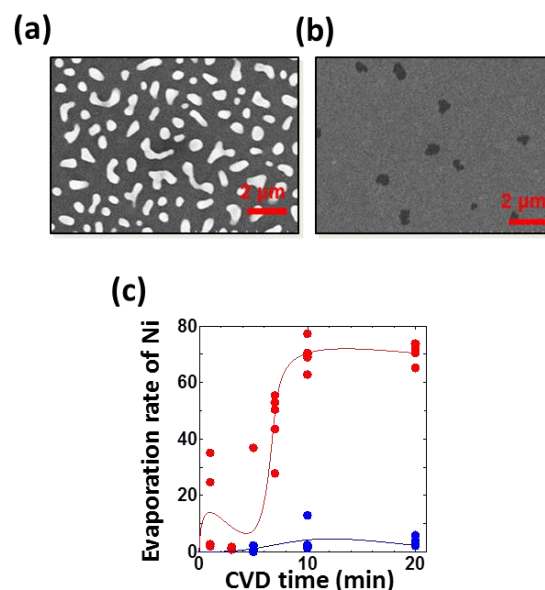


Fig. 2. Typical SEM image of Ni film after (a) thermal CVD and (b) plasma CVD. (c) The CVD time dependence of Ni evaporation rate at 800°C under the thermal CVD (red) and plasma CVD (blue).

plasma CVD, where Ni evaporation rate can be highly suppressed even under the high temperature conditions.

4. Conclusions

The growth kinetics of graphene nanoribbon under the plasma CVD has been systematically investigated. Through the comparison of plasma CVD and thermal CVD, it is revealed that the Ni evaporation rate can be highly suppressed under the plasma CVD, resulting in the stable Ni nanobar structure even under the high temperature condition. This stable Ni nanobar structure is necessary to grow graphene nanoribbon from Ni nanobar, which can be only realized by plasma CVD.

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