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Growth of Suspended Graphene Nanoribbons and its Optoelectronic Application

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Abstract

The suspended graphene nanoribbon (GNR) arrays have been fabricated in large scale by plasma chemical vapor deposition (CVD) with Ni nanobar catalysts. The growth mechanism of GNRs has also been systematically investigated through the comparison with experimental and theoretical calculations. By following this growth model, the growth condition of GNRs can be adjusted, resulting in the high rate synthesis (~ 98%) of suspended GNRs in wafer-scale. For the optoelectronic application of GNRs, photo irradiation is carried out to the field effect transistor device of GNRs array. It is clearly observed that photoresponse of current contains persistent photoconductivity (PPC). This denotes that the suspended GNR device incluedes a high potential for the application of high-performance non-volatile optical memory.

1. Introduction

Graphene nanoribbons (GNRs) 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 optoelectronic devices. Although GNRs can be made in a variety of ways, the reliable site and alignment control of GNRs ratios remains a challenge. Up to now, we developed a novel method based on the advanced plasma CVD method [1] with nanoscale Ni catalyst (Ni nanobar) for directly fabricating suspended GNRs devices [2]. However, the growth yield of suspended GNRs is low because the growth mechanism of this is not clarified due to its very unusual method. Therefore, resolving these problems is crucial for the high yield synthesis and its optoelectronic device applications.

2. Results

2-1. Growth mechanism and high yield growth of suspended GNR

At first, we propose simple growth model as shown in Fig. 1. According to this model, it needs to be satisfied following two conditions to realize GNR growth. (I) The Ni nanobar should maintain its fine structure even under a high-temperature condition (~900 ℃), at least until just before the cooling process. (II) The Ni nanobar should be spatially dissipated, followed by the GNR growth during the cooling process. By focusing these two required conditions, we attempted to elucidate the growth mechanism of GNR under our plasma CVD. In our method, it was confirmed that suspended GNR can be grown not by thermal CVD but by only plasma CVD, indicating there must be critical difference for the stability of Ni nanobar between these two methods. Through the comparison about the stability of Ni between plasma and thermal CVD, the following difference was uncovered. (i) The Ni nanobar can maintain its fine structure only under plasma CVD. (ii) The Ni film contains significant amount of carbon after plasma CVD compared with that of thermal CVD, which was measured by X-ray photoelectron spectroscopy (XPS). (iii) The Ni nano structures after plasma CVD have small contact angle, whereas that of thermal CVD show higher contact angle against to the SiO_2 surface. (iv) The contact angle difference of Ni nanostructure was also confirmed by molecular dynamics (MD) simulation. By a combination of these experimental results and MD simulation, we clarify that high carbon concentration rate increases the wettability of Ni resulting in stabilization of Ni nanostructure. This can be one of the critical reasons why Ni nanobar can maintain its fine structure only during plasma CVD.

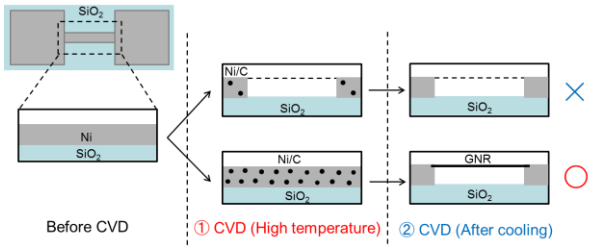

Fig. 1: Model of the required condition for growth of GNR from Ni nanobar.

The possibility of required condition (II) is also investigated through the comparison of experimental data and phase diagram calculation (Fig. 2a). The initial stage of Ni-C before cooling can be plotted as liquid phase in Fig.2a. By decreasing the temperature, graphitic crystallization should occur when it cross to the border line (red curve in Fig. 2(a)). At

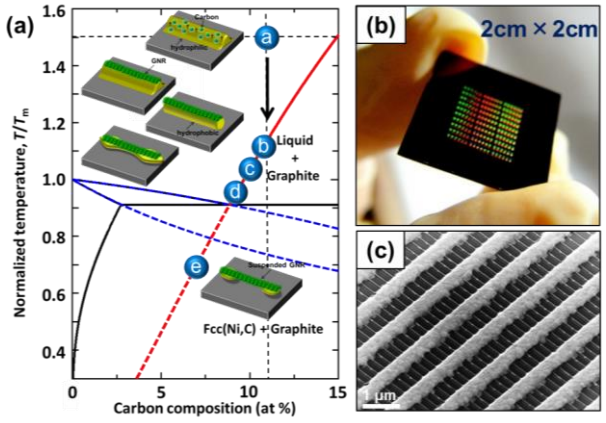

Fig. 2: (a) Calculated phase diagram of Ni-C system and appropriate structure of Ni nanobar during the cooling process. (b) Optical microscope image, and (c) scanning electron microscope image of suspended GNRs array in wafer scale.

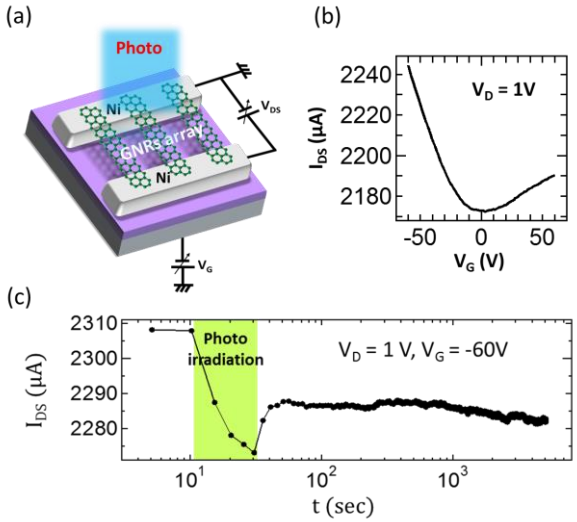

Fig. 3: (a) Schematic illustration of GNRs array FET. (b) Typical V_G-I_{DS} curve of GNRs array-FET under V_D = 1 V. (c) Persistent photo conductivity of GNRs array.

this stage, the GNRs could be nucleated on the surface of the liquid Ni nanobar. In this case, a large number of carbon atoms were used to form GNRs, and the carbon concentration in the liquid Ni nanobar rapidly decreased, which could cause the change in the liquid state of Ni nanobar from hydrophilic-like to hydrophobic-like structures.

Then, the Ni nanobar liquid under the GNRs became unstable and tended to form particle-like structures due to the Plateau-Rayleigh instability which is known as a typical instability happened in the one dimensional structure of liquid. After the breaking of Ni nanobar liquid, it received a capillary force resulting in the dissipation of Ni nanobar. This should be the possible explanation for the required condition (II) relating with the formation of suspended GNRs.

By following this growth model, the yield of suspended GNR growth can be drastically improved (~ 98%) by tuning plasma irradiation time during the plasma CVD process. Based on these results, wafer scale synthesis of 1,000,000 suspended GNRs has been realized (Fig. 2b). The edge structure of GNRs was also analyzed by polarized Raman measurements, revealing near zigzag edge is dominantly formed with high uniformity in our suspended GNR arrays.

2-2. Optoelectronic application of GNRs array

We carried out photo irradiation to GNRs array-filed effect transistor (FET) (Fig. 3a). The typical ambipolar curve of gate voltage (V_G) dependence of source-drain current (I_{DS}) is shown in Fig. 3b which is similar behavior with typical graphene device. The change of I_{DS} between with and without photo irradiation is measured. It is found that the super long persistent photo conductivity (PPC) (Fig. 3c) can be appeared in the suspended GNR device. The modified current can maintain even after stopping the photo irradiation above 1 hour. This phenomenon can be understood to be due to a hot carrier trapping in specific trapping sites, and this is a typical operation principal of non-volatile optical memory.

3. Conclusions

In summary, we investigate the growth mechanism of suspended of GNR by the combination with systematic experimental and theoretical calculations. We found that the suspended GNR growth can be understood by the Ni nanobar stabilization under plasma CVD due to its high concentration rate of carbon in Ni nanobar, and phase separation of Ni-C system with destabilization of Ni nanobar structure during cooling stage. Based on this growth model, we realized high yield growth of suspended GNRs in wafer-scale. Furthermore, non-volatile optical memory functions of GNRs array are demonstrated by the photoresponce measurements. These results are useful for the next generation high-performance optoelectronic device application.

References

[1] H. Suzuki, T. Kato and T. Kaneko, Plasma and Fusion Res. 9, (2014) 1206079.

[2] T. Kato and R. Hatakeyama, Nature Nanotechnology 7, (2012) 651.

[3] H. Suzuki, T. Kaneko, Y. Shibuta, M. Ohno, Y. Maekawa and T. Kato, Nature Communications 7, (2016) 11797.