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Structural-Controlled Synthesis and Device Application of Graphene by Non-Equilibrium Mild Plasma Processing
非平衡マイルドプラズマプロセスによるグラフェンの構造制御合成とデバイス応用

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High quality graphene sheets have been directly grown on a SiO_2 substrate by rapid-heating plasma chemical vapor deposition (RH-PCVD), which is based on the non-equilibrium mild plasma processing. The monolayer graphene sheets can be selectively grown between a Ni film and the SiO_2 substrate. Systematic investigations reveal that the relatively thin Ni layer and RH-PCVD are critical to the success of this unique method of graphene growth. We have also developed a new, simple, and scalable method for the controlled growth of narrow (~ 23 nm) graphene nanoribbon using the direct conversion of an Ni nanobar into a graphene nanoribbon by RH-PCVD. For the first time, site- and alignment-controlled growth of graphene nanoribbons with a clear transport gap and a high on/off ratio (> 10^4) has been realized.

1. Introduction

Graphene is a monolayer carbon sheet including high carrier mobility, flexibility, and high optical transmittance. These properties are advantageous if graphene is to be used as a component in electrical devices such as field effect transistors, solar cells, and various gas and chemical sensors. Chemical vapor deposition (CVD) is one of the most promising methods of growing graphene, which can produce large, relatively high-quality graphene sheets. However, the graphene growth by CVD is limited only to the metal catalyst surfaces such as Ni, Cu, or Co, which is one of the most serious problems for the practical application of graphene as electrical devices. Thus, the development of the method for the direct growth of graphene on the insulating substrate, especially on a SiO_2 substrate, is highly required.

Since graphene sheet itself is a zero-gap semiconductor, the band gap opening is another important issue for the industrial application of graphene as electronic devices. Recently, it is revealed that graphene nanoribbons, strips of graphene, show a clear band gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. Many production-stage challenges for fundamental studies and practical applications remain, including high-yield production, structure (width, length, and edge) control, and large-scale site and alignment control. No reliable large-scale methods that can control the site and alignment of graphene nanoribbons with a high on/off ratio have been developed.

Based on these backgrounds, we attempted to develop a novel non-equilibrium mild plasma processing, which can realize direct growth of graphene on an insulating substrate and controllable growth of graphene nanoribbons.

2. Results and discussion

2.1 Direct growth of graphene on the SiO_2 substrate

The graphene growth was realized using a

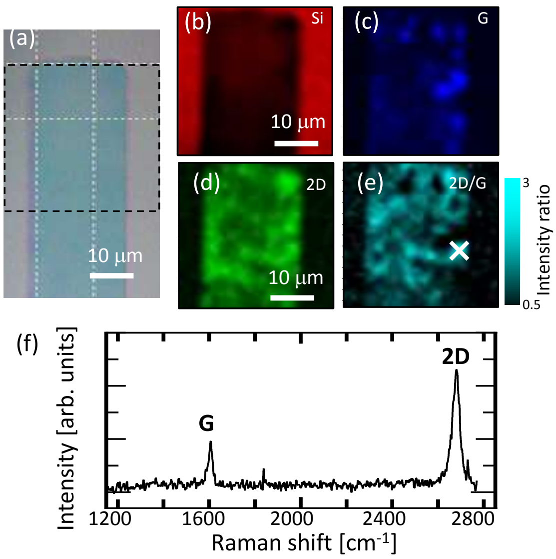

Fig. 1. (a) Optical microscope and (b-e) integrated Raman intensity mapping for (b) Si-peak, (c) G-peak, (d) 2D-peak, (e) 2D/G of patterned graphene. (f) Typical raw Raman scattering spectra of patterned graphene taken at the position (x) in (e).

homemade plasma CVD system [1-4] with a mixture of methane and hydrogen gas. The substrate was heated rapidly up to 900 ºC within 1 min, then plasma CVD was carried out (rapid-heating plamsa CVD (RH-PCVD)). During the cooling process, the graphene layer could be preferentially grown along the interface between the Ni film and SiO_2 substrate. Finally, the deposited Ni film was removed using a conventional chemical etching technique.

After removing the Ni film using a chemical etching process, interestingly, it was found that a high-quality graphene layer was grown along the interface between the Ni film and the SiO_2 substrate (Fig. 1) [5]. Scanning electron microscope (SEM) and Raman mapping measurements show that graphene sheet can be position selectively grown on the SiO_2 substrate by pre-depositing Ni pattern with photolithography technique (Fig. 1(a)-(e)). At the initial growth stage, clear hexagonal domains of graphene were observed. The average hexagonal domain size is about 10~20 μm. This hexagonal domain growth indicates the quality of graphene grown with our established method should be relatively high, which is consistent with the low D-peak Raman scattering spectrum shown in Fig. 1(f).

2.2 Controllable graphene nanoribbon growth

Figure 2(a) shows the basic strategy for the controllable growth of graphene nanoribbon. Ni nanobar structures connected to two Ni electrodes (source and drain) were formed on a SiO_2 (300 nm) /Si substrate using a conventional electron beam lithography technique. Following the RH-PCVD, the Ni nanobar structures were converted into graphene nanoribbon, and the width shrank by up to ~23 nm after RH-PCVD (Fig. 2(b)).

The electrical properties of the as-grown graphene nanoribbon devices were measured under the field effect transistor (FET) configurations. A clear transport gap was obtained from a narrower (less than 30 nm) graphene nanoribbon device. The source-drain current (I_{ds}) vs. gate bias voltage (V_{gs}) curve showed ambipolar transport characteristics at room temperature (300 K) with an on/off ratio of ~16. Notably, when the temperature decreased to 13 K, the on/off ratio increased to 1.5×10^4 and clear transport gap can be observed (Fig. 2(c)). This result is the first indication of a high on/off ratio for the bottom-up-grown graphene nanoribbons [6].

3. Conclusions

We have realized the easy and scalable method for the growth of high-quality graphene directly on a SiO_2 substrate. Based on the systematic investigations, it is revealed that the relatively thin Ni layer with RH-PCVD is critical elements for the selective growth of graphene at the interlayer between the Ni film and SiO_2 substrate. We have also developed a new, simple, and scalable method for integrating graphene nanoribbon devices based on a bottom-up approach. Site- and alignment-controlled growth of graphene nanoribbons with a clear transport gap and a high on/off ratio has been achieved for the first time.

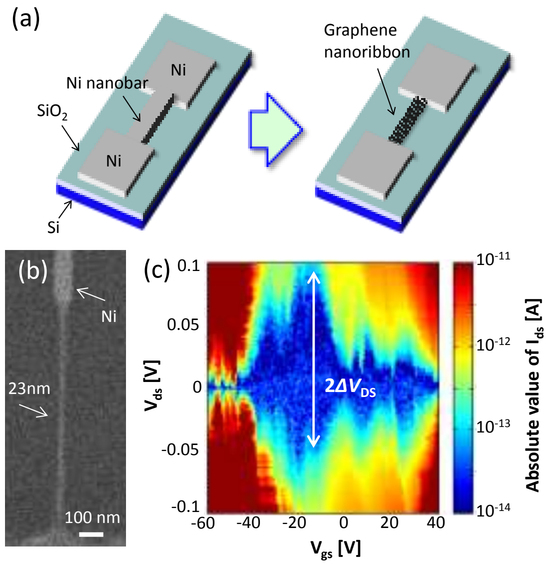

Fig. 2. (a) Schematic illustration of the graphene nanoribbon growth method. (b) Typical SEM images of graphene nanoribbon grown by the RH-PCVD. (c) Contour plot of absolute I_{ds} as functions of V_{ds} and V_{gs}.

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