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Growth and structure control of graphene by plasma CVD
プラズマCVDによるグラフェン合成と構造制御

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A transfer-free method for growing carrier-density controlled graphene directly on a SiO_2 substrate has been realized for the first time by plasma chemical vapor deposition (PCVD). Using this method, high-quality single-layer 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 PCVD are critical to the success of this unique method of graphene growth.

1. General

Graphene is a monolayer carbon sheet including high carrier mobility, flexibility, and high optical transmittance [1,2]. 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. A graphene layer on an insulating layer, especially on an insulating SiO_2 substrate, is an important structural arrangement used in the fabrication of graphene-based electrical devices. Currently, graphene layers on SiO_2 substrates are fabricated by the following process. First, graphene is grown on Ni, Cu, or Co surfaces. These surfaces are necessary for the growth of graphene as they decompose hydrocarbon gases and promote the nucleation of graphene. The graphene layer is then transferred to a SiO_2 substrate using polymer capping and chemical etching techniques. This process can fabricate relatively large-scale graphene sheets on an insulating substrate. However, it is difficult to transfer specific and fine graphene structures, such as graphene nanoribbons or nanoscale patterned graphene, to specific points on a device. This precise placement of graphene is important when fabricating many widely used silicon-based electrical devices. The direct growth of graphene on the insulating substrate is an alternative approach to the above method. It is a challenging method, however, and only a few studies about the direct growth approach have so far been reported. Several critical issues relating to the yield, layer number control, large scale growth, and tunable carrier doping are still to be resolved before the direct growth method will be suitable for industrial processes to generate graphene-based electronics.

Here we report a novel, simple, and scalable method for the direct growth of graphene on an insulating substrate with a tunable carrier doping. It is revealed that by adjusting the growth parameters using plasma CVD (PCVD) [3-6], the graphene layer can be made to grow along the interface of the Ni layer and the SiO_2 substrate instead of on top of the Ni layer.

2. Experimental

A homemade plasma CVD system was used to grow single-layer graphene. Inductively coupled plasmas were generated by supplying a radio frequency (RF; 13.56 MHz) signal to the coils, which were positioned outside a quartz tube. An electrical furnace was heated to a desired temperature prior to moving a substrate from outside the quartz tube into its center. A 9:1 mixture of methane and hydrogen gas was blown over the area after the substrate reached a desired temperature, after which the RF power was switched on to generate the plasma. After the desired growth time, the RF power supply was switched off and the substrate was cooled rapidly by the ambient room temperature.

3. Results and Discussions

Scanning electron microscope (SEM) observations and Raman mapping measurements are carried out for the produced material. It is found that hole-like structures are formed on the entire surface of the Ni film (Fig. 1a). Figure 1b-d show the optical microscope image (Fig. 1b) and the integrated Raman intensity mappings of the Si-peak

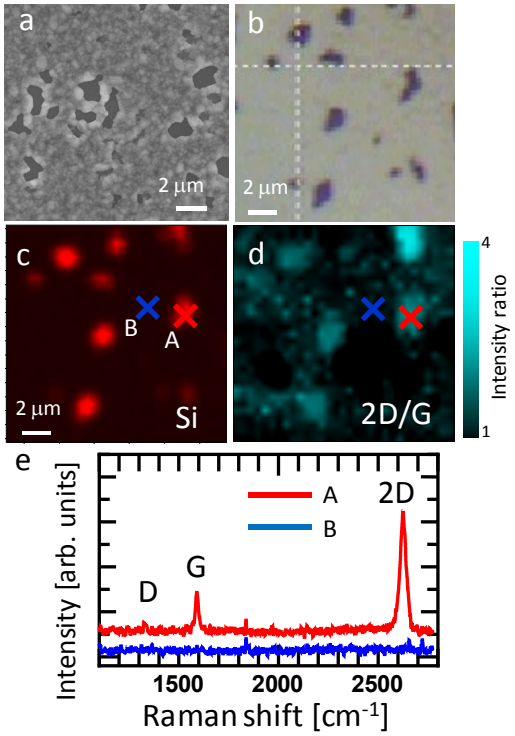

Fig. 1. (a) SEM and (b) optical microscope images of the Ni surface after PCVD. (c,d) The integrated Raman intensity mapping of the Ni surface after PCVD of the (c) Si-peak and (d) peak ratio of 2D to G. (e) The raw Raman scattering spectra taken at the position A and B shown in (c).

(Fig. 1c) and the peak ratio of 2D to G (Fig. 1d). It should be noted that Fig. 1b-d are described at the same scale. Since the strong Si-peak appears only at the hole-like structures, the Ni film should be partially evaporated and the SiO_2 surface appears at the hole-like structures (Fig. 1c). The G-peak and 2D-peak are detected only at the hole-like structures, and the intensity of the 2D-peak is much higher than that of the G-peak at the hole-like structures (Fig. 1d). This is also confirmed with the raw Raman scattering spectra taken at the position A and B, which are described at the hole-like structure and the top of the flat Ni film, respectively (Fig. 1e). The spectrum of A in Fig. 1e shows the low D-peak, sharp G-peak, and high and sharp 2D-peak with higher 2D/G intensity ratio (~3). These features are consistent with those of high -quality single-layer graphene sheet.

After removing the Ni film by the chemical etching, interestingly, it is found that high-quality graphene are also grown at the inter layer between the Ni film and SiO_2 substrate. Figure 2a-c are the optical microscope image (Fig. 2a), the integrated Raman intensity mapping of the 2D/G (Fig. 2b),

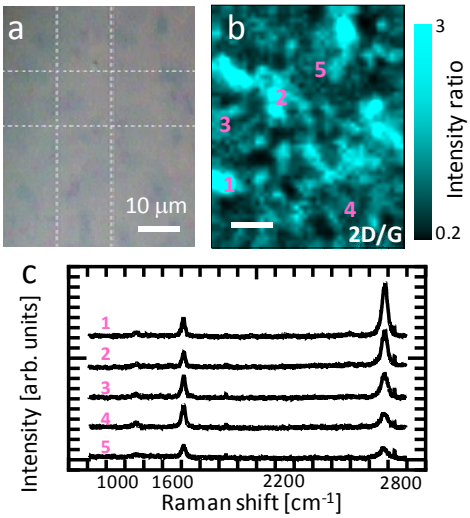

Fig. 2. (a) The optical microscope and (b) integrated Raman intensity mapping for 2D/G of substrate after removing the Ni film. (c) The raw Raman scattering spectra of graphene taken at the position 1-5 shown in (b).

and the raw Raman spectra (Fig. 2c) of the substrate after the Ni etching. Although certain variation of the 2D/G intensity ratio is observed depending on the position, high-quality single- or few-layer graphene are grown on the entire substrate area.

4. Conclusion

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 PCVD is critical elements for the selective growth of graphene at the inter layer between the Ni film and SiO_2 substrate.

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