Nucleation control for the fabrication of carbon nanoplatform based on vertical nanographene

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Abstract: Carbon nanowalls (CNWs) can be described as graphite sheet nanostructures with edges that are composed of stacks of planar graphene sheets standing almost vertically on the substrate. The large surface area of CNWs is useful as templates for the fabrication of other types of nanostructured materials, electrodes for energy storage devices and biosensors. Area-selective growth of CNWs for device application was attained by controlling the substrate biasing in combination with the use of Ti nanoparticles.

Keywords: carbon nanowalls, nanographene, plasma enhanced-CVD

1. Introduction

Carbon nanowalls (CNWs) can be described as self-assembled, vertically standing, few-layer graphene nanostructures. The sheets form a self-supported network of 3-dimensional wall structures with thicknesses ranging from a few nanometers to a few tens of nanometers, and with a high aspect ratio (Fig. 1) [1]. The large surface area and thin edges of vertically standing CNWs are useful as platform for electrochemical applications as well as tissue engineering such as scaffold for cell culturing. Recently, electrochemical glutamate biosensor for bioelectronic applications has been demonstrated using platinum (Pt)-functionalized graphene nanoplatelet prepared from graphene oxides [2]. CNW film has many graphene edges on the top and CNW sheet itself is composed of nano-domains of a few tens of nanometers in size. Pt nanoparticles were preferably on the defects such as grain boundaries on the surface of graphite [3]. Therefore, the structure of CNWs can be suitable for the platform of the electrochemical and biosensing applications.

Fig. 1. Schematic illustration of CNWs with TEM image of a piece of CNW.

To date, CNWs have been grown using various plasma-enhanced chemical vapor deposition (PECVD) methods employing microwave plasma, radio frequency inductively coupled plasma (ICP), and dc plasma. In general, a mixture of hydrocarbon and hydrogen or argon gases, typically CH₄ and H₂, is used as a source gas for the synthesis of CNWs. CNWs can be fabricated on a variety of substrates, including Si, SiO₂, Al₂O₃, and metals at substrate temperatures of 500–750°C without the use of catalysts. The distribution of CNWs is relatively uniform over the whole substrate surface. At the same time, it is difficult to realize area-selective growth of CNWs. Meanwhile, we have experienced that the morphology and growth rate occasionally depend on the substrate materials. In the case of planar graphene synthesis, Ni and Cu have been used as catalytic substrates. These materials have a very different solubility of carbon in them. Carbon easily dissolves into Ni owing to the high solubility of carbon in Ni at high temperatures, but hardly dissolves into Cu owing to the very low solubility of carbon in Cu. These findings give us useful hints to control the density of CNWs and realize area-selective or position-controlled growth of CNWs.

In view of the practical use of CNWs for device applications such as biosensors or electrochemical sensors in micro-total analysis system, further investigations should be performed to enable their nucleation control. In this work, we have investigated the early growth stage of CNWs using ICP-CVD employing a CH₄/Ar mixture to control the structures of CNWs for the fabrication of carbon nanoplatform based on vertical nanographene.

2. Experimental

CNWs were fabricated using ICP employing an Ar/CH₄ mixture [4]. Figure 2 shows a schematic of the ICP reactor used for the growth of CNWs. The ICP chamber was 16 cm in diameter and 30 cm in height. A one-turn coil antenna with a diameter of 10 cm was set on a quartz window at the top of the chamber. RF (13.56 MHz) power was applied to the coil antenna and plasma was generated in the chamber. The growth experiments were carried out at an RF power of 500 W, a total gas pressure of 20 mTorr, a substrate temperature of 720 °C. Si or SiO₂-coated Si substrates were set on the middle of the substrate holder at 10 cm below the quartz window.
3. Results and discussion

Growth experiments were carried out using Si substrate for different periods (0.5–120 min). The height of CNW film almost linearly increased with the increase in growth period in the range from 10 to 120 min, while it took approximately 5 min for the nucleation. The growth rate of CNWs under the steady-state condition was constant at approximately 60 nm/min. Meanwhile, the thickness of the nanowall sheet near the base estimated by the SEM observation was almost constant at approximately 10 nm during the steady-state growth.

Figure 4 shows Raman spectra of deposits at the nucleation stage of CNWs on SiO$_2$-coated Si substrates. The broad D band peak at 1340 cm$^{-1}$ and upshifted G band peak at 1600 cm$^{-1}$ in the Raman spectrum of deposits formed for 30 sec indicate that the deposits were amorphous carbon. Typical Raman spectrum for CNWs was obtained for 5 min. Namely, during the nucleation period on Si and SiO$_2$ substrates, the graphene component was scarcely contained in the underlying interface layer shown in Fig. 3(b).

In order to investigate the effect of metal nanoparticles on the growth enhancement, growth experiments were carried out using Si substrates coated with Ti, Co, Ni, Fe, and Pt nanoparticles. Metal nanoparticles were prepared by laser ablation or pulsed arc plasma deposition. Figure 5 shows the relative height of CNW films grown for 30 min on Si substrates coated with metal nanoparticles. As seen in Fig. 5, growth was enhanced by metals, but morphologies after 30 min growth were not changed. Height difference was caused by the difference of nucleation period.
To investigate the effect of the catalytic metals on the nucleation enhancement of nanographene, Ti nanoparticle coated SiO$_2$ was used as a substrate for the growth experiment. Figure 6(a) shows a tilted close-up view of the nucleated region. This image indicates that nanographenes have been nucleated by Ti nanoparticles during this short period. Figure 6(b) shows the TEM image of peeled off carbon nanosheets grown on Ti/SiO$_2$ for 2 min. The nucleation of nanographenes was enhanced at the Ti nanoparticles, while no underlying distinct amorphous carbon layer was formed for the nanosheets grown from the Ti nanoparticles. It was quite a contrast to the TEM image of the interface in the case of growth without Ti nanoparticles shown in Fig. 3(b), where an underlying amorphous carbon layer of 30 nm thickness was formed before the onset of isolated nanosheet growth.

Figure 7 shows Raman spectra of deposits at the nucleation stage of CNWs on Ti-catalyzed SiO$_2$-coated Si substrate. The Raman spectrum of deposits formed for short period of 30 sec is similar to that for the nanographenes or CNWs. The strong and sharp D band peak and D’ band peak in the Raman spectrum are mainly attributed to the edge region of the nanometer-sized graphene, indicating that graphene nucleation occurred directly from the Ti nanoparticles in the case of CNW growth on the Ti-catalyzed SiO$_2$-coated Si substrate. From the analyses using Raman spectroscopy and SEM and TEM observations in the very early growth stage, the nucleation mechanism of nanographene on the Ti-catalyzed surface is very different from the mechanism of catalyst-free growth on the SiO$_2$ and Si substrates.

In the case of CNW growth without catalytic Ti nanoparticles in the present work, the interface layer under the CNWs was an amorphous or diamond-like carbon. Moreover, ion bombardment on the surface will play an important role in nucleation by creating active sites for neutral radical bonding. The existence of the amorphous carbon interface layer will enable us to grow CNWs and similar structures on a variety of substrates without a catalyst. In contrast, in the case of CNW growth on the Ti-catalyzed substrate, planar nanographenes were nucleated directly from Ti nanoparticles without forming an interface layer, as was indicated by TEM observation shown in Fig. 6(b). Furthermore, from the SEM observation shown in Fig. 6(a), the leading edges of nucleated nanographenes are found to curl upward. Carbon solubility in Ti is low at around 700 °C, as is the case with Cu, although Ti is highly reactive with carbon at high temperatures of around 900 °C or more resulting in the formation of TiC. In the present case using a Ti-catalyzed substrate, it is possible that planar nanographene would be nucleated on the surface of the Ti nanoparticle. Once nucleated, the
size of expanding nanographenes would rapidly exceed the size of Ti nanoparticles, and the resultant floating edges of expanding nanographenes would be curled upward.

Figure 8 shows SEM images of deposits for 1 min growth on Ti particle-coated SiO$_2$ with different particle number densities. Here, Ti:800 pulses of pulsed arc plasma corresponded to the cumulative Ti nanoparticle density of approximately $10^{13}$ cm$^{-2}$. The density of nucleated vertical nanographene depended on the density of cumulative Ti nanoparticles, indicating that the density of CNWs can be controlled by changing the density of Ti nanoparticles.

![SEM images of deposits for 1 min growth on Ti particle-coated SiO$_2$ with different particle densities.](image)

**Fig. 8.** SEM images of deposits for 1 min growth on Ti particle-coated SiO$_2$ with different particle densities. 800 pulses of pulsed arc plasma corresponded to the cumulative Ti nanoparticle density of approximately $10^{13}$ cm$^{-2}$.

Ion bombardment on the surface would play an important role in the nucleation by creating active sites for neutral radical bonding. Owing to the low-pressure operation in the case of ICP-CVD, the ion bombardment would be more effective for the nucleation of CNWs, compared with the case using microwave plasma CVD at high-pressure operation above 10 Torr. The effect of ion bombardment at low-pressure operation indicates that, under a typical growth condition, the CNWs are nucleated sooner or later on the Si or SiO$_2$ substrate whether coated with Ti nanoparticles or not, although the period required for the nucleation on the catalyst-free surface would be longer than that on the surface coated with Ti nanoparticles. Raman spectrum (a) in Fig. 9 corresponds to the CNWs grown for 30 min on SiO$_2$ without bias, exhibiting typical Raman spectrum of CNWs. Meanwhile, the fluxes and energies of incident Ar ions would influence the nucleation of vertical nanographenes, as reported using multibeam CVD [5]. By controlling the substrate biasing to decrease the ion energy or ion flux incident on the substrate, it became possible to suppress the nucleation of CNWs (Raman spectrum (b) in Fig. 9). In the case of growth on Ti nanoparticle-coated SiO$_2$ substrates, planar nanographenes were directly nucleated from the Ti nanoparticles without forming base layer, even when the substrate was positively biased to suppress the nucleation of CNWs (Raman spectrum (c) in Fig. 9). These results indicate the possibility of area-selective growth of CNWs for the device application such as biosensors or electrochemical sensors in micro-total analysis system.

![Raman spectra of CNWs grown for 30 min on SiO$_2$ without bias and positively biased SiO$_2$ and Ti/SiO$_2$.](image)

**Fig. 9.** Raman spectra of CNWs grown for 30 min on SiO$_2$ without bias and positively biased SiO$_2$ and Ti/SiO$_2$.

4. Conclusion

The area-selective growth of carbon nanowalls was attained. The idea is as follows: (1) In the case of carbon nanowall growth on Si or SiO$_2$, ion bombardment on the surface would play an important role in the nucleation by creating active sites for neutral radical bonding. By controlling the substrate biasing to decrease the ion flux or ion energy incident on the substrate, it became possible to suppress the nucleation of carbon nanowalls. (2) On the other hand, we have found the nucleation enhancement of nanographene by using several metals. In the case of growth on Ti nanoparticle-coated SiO$_2$ substrates, planar nanographenes were directly nucleated from the Ti nanoparticles, even when the substrate was positively biased to suppress the nucleation of carbon nanowalls. These results indicate the possibility to control the density of CNWs and realize area-selective or position-controlled growth of CNWs for the device applications.

5. References


