Synthesis of Large-Area Graphene Layers on Poly-Nickel Substrate by Chemical Vapor Deposition: Wrinkle Formation

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Among the various polymorphs of carbon in inorganic form, such as diamond, graphite, fullerene, and carbon nanotubes, a new polymorph, a 2D single graphene layer, has recently attracted considerable interest.[1–3] The single graphene layer is a semi-metal or zero-gap semiconductor, and has excellent electronic properties, for instance, high mobility (15000 cm² V⁻¹ s⁻¹) and room-temperature quantum Hall effect.[1–6] Narrow single graphene ribbons show peculiar metallic and semiconducting behaviors depending on the edge type and width, similar to the graphene ribbons show peculiar metallic and semiconducting behaviors depending on the edge type and width, similar to the graphene ribbons show peculiar metallic and semiconducting behaviors depending on the edge type and width, similar to the graphene ribbons show peculiar metallic and semiconducting behaviors depending on the edge type and width, similar to the

These superb characteristics of graphene open a new possibility of application in many electronic devices, such as flexible thin-film transistors, touch panels, and solar cells.

In order to use graphene for such applications, large-area sample preparation is a prerequisite. Three methods have been tried so far: i) micromechanical cleavage,[1] ii) thermal decomposition of a SiC substrate,[8,9] and iii) carburation and annealing of a metal substrate.[10] In the micromechanical cleavage method, graphene flakes have been transferred by peeling with tape from highly oriented pyrolytic graphite (HOPG). A few graphene layers are easily obtained, but they are limited to small graphene flakes. Ultrathin graphene layers are formed by vacuum graphitization through silicon depletion from a SiC surface.[8] This process, however, causes the produced graphene to be fragile and contain many defects, because of the large lattice mismatch between the SiC substrate and graphene. Large-area synthesis is still limited by the expensive SiC substrate. Moreover, the graphitization takes place at the high temperature of 1400 °C and very-low vacuum pressure of 10⁻¹⁰ Torr (1 Torr = 133.32 Pa).[11] In the carburation method, CO gas is blown onto a Ni(111) single-crystal substrate at 1200 °C under 10⁻⁶ Torr for 100 h, followed by rapid quenching of the sample in water. The sample is then annealed at 900 °C in high vacuum (10⁻¹⁰ Torr).[12] Nevertheless, it has not proved possible to control the ultrathin graphene layers. Other transition metal substrates, such as ruthenium[13] and platinum,[14] have also been used to synthesize graphite.[15]

Chemical vapor deposition (CVD) has been successfully used to synthesize carbon nanotube films.[16] This method consists simply in pyrolyzing the supplied hydrocarbon gases in the chamber at a reasonable temperature. In our strategy for graphene synthesis, the Ni substrate is placed in the chamber at a pressure of 10⁻³ Torr and temperature below 1000 °C for a relatively short time to synthesize ultrathin graphene layers. At the first stage of synthesis, a limited quantity of carbon atoms is incorporated into the Ni substrate at relatively low temperature, similar to the carburation process. The second stage involves a rapid quenching of the substrate, so that the incorporated carbon atoms are out-diffused onto the surface of the Ni substrate to form graphene layers.

The purpose of this Communication is to report the synthesis of highly crystalline large-area graphene on a Ni substrate using optimized CVD conditions. Few-layer graphenes films (1 cm x 1 cm) with high crystallinity were obtained on a poly-Ni substrate by optimizing the growth temperature, the gas mixing ratio C₆H₆/H₂, growth time, and quenching rate. We observed that wrinkles in the graphene layer, which are different from the observed intrinsic ripples,[17] were dominantly present, independent of location of the grain boundary. The formation of wrinkles was systematically investigated. We propose that the wrinkles first form at the step terrace and then bunch, the difference between the thermal expansion coefficients of the Ni substrate and graphene layers causing them to grow further during thermal quenching.

In the production of highly crystalline few-layer graphenes by CVD using a poly-Ni substrate, several critical parameters exist.

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Our first task was to investigate the dependence of the graphene quality on the growth temperature.

Figure 1a presents Raman spectra for various growth temperatures. At a relatively low growth temperature of 700 °C, a large G-band was found, evidencing the formation of a hexagonal lattice in graphene. However, a large D-band appeared near 1335 cm⁻¹, suggesting an abundance of defects in the graphene layers. The intensity of the G'-band, which is a double resonance of the D-band, was larger than that of the G-band. It has been reported that the graphite-like G'-band in general has a smaller intensity than the G-band, but its intensity exceeds the G-band intensity when the graphene is less than five-layers thick. This implies that the synthesized graphene is composed of very thin layers. With increasing growth temperature, the D-band gradually disappeared. No appreciable D-band was observed at 1000 °C. The intensity of the G'-band decreased at 800 °C and 900 °C, but increased rapidly at 1000 °C compared to that of the G-band. The graphene layer was the thinnest at 1000 °C for the temperatures used. If the synthesis process involved solely a CVD deposition, the thickness would simply increase with temperature. This strongly suggests that the growth of the graphene layers involves not only a simple CVD deposition, but also incorporation of carbon atoms into the Ni layer and out-diffusion of such carbon atoms during thermal quenching at a later stage, analogous to the carburization process. The maximum number of carbon atoms incorporated into the Ni layer at different temperatures depends on the carbon solubility, which is governed by the Ni-C phase diagram. The eutectic temperature is 1321 °C, and therefore our growth temperature was far below this point. For instance, the maximum carbon content at 1000 °C is nearly 0.2 wt%.

Figure 1b shows Raman spectra from samples obtained by varying the gas mixing ratio (C₂H₂/H₂) at the optimized growth temperature of 1000 °C. The inset shows the G- and G'-bands for comparison. The spectrum from HOPG was used for comparison. No D-band was observed, independent of the gas mixing ratio (inset). Another criterion to measure the thickness is the peak position of the G'-band. Interestingly, the peak position of the G'-band was down-shifted with decreasing C₂H₂ gas (Fig. 1d), whereas the intensity ratio \( I_{G'}/I_G \) (written as \( I_{G'}/I_G \)) increased rapidly at a gas mixing ratio (C₂H₂/H₂) of 2/45. It is well known that the Raman-shift peak position of the G'-band increases with the number of graphene layers and saturates to that of HOPG. Information on layer dependence was extracted accordingly, as shown in Figure 1d. In particular, at a growth time of 5 min, the peak position of the G'-band was 2706.5 cm⁻¹. This value is equivalent to three graphene layers, which is again consistent with the intensity change of the G'-band. Defect-free and highly crystalline three-layer graphene was obtained using the maximum amount of hydrogen gas. It is understood that the amount of hydrocarbon gas determines the number of layers. Still, introduction of hydrogen gas during growth was a critical condition for graphene growth. No graphene was formed without hydrogen gas with 2 sccm (standard cubic centimeters per minute) C₂H₂. With further reduction of C₂H₂ gas to 1 sccm, again no graphene was formed. Too much hydrogen gas prevents graphene formation by a dominant etching effect by the hydrogen gas, which was also observed in carbon-nanotube synthesis. We also note that the initial reduction process with hydrogen gas was particularly necessary to recover a pure Ni surface. Defects were also generated without initial hydrogen reduction.

Figure 1c presents Raman spectra from samples obtained after various growth times. With increasing growth time, the peak position of the G'-band up-shifted rapidly, while the intensity of the G'-band decreased (inset of Fig. 1d), similar to what was observed in Figure 1b. This indicates that our synthesized graphene layers, particularly at a growth time of 5 min at 1000 °C with a gas mixing ratio (C₂H₂/H₂) of 2/45, were highly crystalline and ultrathin with a negligible amount of defects, similar to HOPG. The spectrum from HOPG was used for comparison. The inset shows similar changes as a function of growth time.
abundant (100) direction after graphene synthesis, as confirmed by X-ray diffraction. This is in good agreement with previous work on graphite synthesis on Ni thin films.[21]

To see the uniformity of the synthesized graphene layers over a large area, we chose a simple optical microscope. Cracks on the poly-Ni substrate were visible, marked as a branched dashed line in Figure 2a, and were caused during the a priori reduction process. At a growth time of 5 min, some dark-gray color was observed. This was identified as the formation of a few graphene layers. Nevertheless, some white spots were still left, which were identified as the formation of a few graphene layers or no graphene layer. These white spots disappeared gradually, and the gray area expanded with increasing growth time, that is, the graphene layers formed became thicker. In this case, the grain boundaries of the poly-Ni substrate were clearly observed, as shown by dotted lines in Figure 2b–d. The circles mark the position of wrinkles. These wrinkles did not appear necessarily on the grain boundary. Some of the grains were still a pale-gray color even after a growth time of 15 min.

The inhomogeneity of the graphene layers observed here suggests that the epitaxial growth rate of graphene layers is dependent on the actual Ni orientation underneath. It is well known that when a Ni substrate is exposed to hydrocarbon gases at high temperature, hydrocarbon gases are dissociated and the released carbon atoms are incorporated into Ni bulk by catalytic enhancement.[19] Upon cooling, the solubility of carbon is lower and therefore the excess carbon atoms should be out-diffused onto the surface of the Ni substrate to form graphene layers. In our experiment, we were able to monitor the formation of graphene layers upon cooling through the window of our CVD chamber. The formation of different thicknesses of graphene layers may originate from the different crystal orientation of the poly-Ni grains, which produces different diffusion rates of carbon atoms to the surface. Once the graphene flakes are formed, they grow in size and meet other adjacent flakes. During joining of such flakes, intense stress is incorporated in the graphene layers. As a consequence of stress minimization, wrinkles could be formed randomly anywhere, independent of the location of the grain boundary. It has been reported that graphene is nucleated at the step edges and can grow downhill.[13] Wrinkles are probably generated when a growing flake starts to overlap another one generated from the next step edge.

The formation of wrinkles is more clearly visualized in the field-emission scanning electron microscopy (FESEM) images in

![Figure 2. Optical microscopy images of the synthesized graphene layers on poly-Ni substrate (1 cm × 1 cm): a) poly-Ni after reduction without graphene synthesis, and after b) 5, c) 10, and d) 15 min of growth. Scale bars: 20 μm.](image)

![Figure 3. FESEM images of synthesized graphene layers on poly-Ni substrate grown for a) 5 min, showing wrinkles crossing over the grain boundary, b) 5 min, with wrinkles on the inner grains, c) 10 min, and d) 15 min. White arrows indicate wrinkles. The dashed lines in c) indicate cracks in the substrate. Scale bars: 1 μm. FLG stands for few-layer graphene.](image)
Figure 3. The inset shows different surface morphologies from different grains. This implies again the different growth rates of graphene layers at an initial stage. The step terrace-like lines (marked by arrows) in Figure 3a are wrinkles. They cross over the grain boundary (white valley). The grain boundary cannot play a role as nucleation site for graphene synthesis. This could be attributed to the slow out-diffusion rate of carbon atoms through the grain boundary. One intriguing point is that the wrinkle density decreased with increasing growth time, as shown in Figure 3b–d.

Figure 4a shows a top-view image of a thick wrinkle (top-right inset: low magnification). The high-magnification transmission electron microscopy (TEM) image was highly symmetric with respect to the center and homogeneous along the wrinkle direction. The bottom-right inset in Figure 4a shows a schematic diagram of this wrinkle. The electron-diffraction pattern in Figure 4b shows two symmetric line spots (circled). This suggests a 1D nature of the wrinkle. The hexagonal spots originate from AB stacking of graphene layers. A slight distortion of the spots indicates a slight misorientation of graphene layers near the wrinkle.

The height distribution of the wrinkles was measured by dynamic force microscopy (DFM) mode in a scanning probe microscope (SPM). In addition to large wrinkles protruding prominently, small wrinkles, indicated by circles in Figure 5, also existed. The height of the small wrinkles increased with growth time, as shown in Figure 5d. With increasing growth time, the thickness of the graphene layers increased and the wrinkle density decreased, as mentioned above. There is a possibility that wrinkles coalesce with each other during cooling, owing to the presence of intense thermal stress between the Ni substrate and the grown graphene layers. This bunching of wrinkles releases thermal stress in the matrix of the graphene layers, and therefore increases the height of the wrinkles.

Step formation is common on Ni single-crystal surfaces. In the case of poly-Ni, in particular near the grain boundaries, more steps will be formed. Graphene nucleation probably takes place at step edges. [13] If we follow this model (Fig. 6a), the flakes will grow downhill, and when adjacent flakes (of different crystalline orientation) start to overlap around a step edge, they will not match perfectly, and a local weakness in the 2D network will be introduced, in the form of a defect line. Because the substrate cools with different thermal expansion than the graphene layers, the graphene layers will tend to absorb the strain energy by mechanical deformation at the defect lines where the 2D network is weaker, thus inducing the formation of wrinkles (Fig. 6b). Some of the defect lines migrate quickly through the wrinkle region and minimize the local stress by coalescence of wrinkles and defect lines. With longer growth times, more carbon atoms are incorporated into the Ni substrate. On cooling, more carbon atoms segregate onto the Ni surface, giving thicker graphene layers on the surface. Simultaneously, there is a higher probability of having more wrinkles in the graphene layers, but these wrinkles rearrange by bunching, lowering their density. As a consequence, the height of the wrinkles increases due to wrinkles overlapping.

In conclusion, we have grown large-area graphene on poly-Ni substrates by using optimized CVD conditions. The D-band and the peak position and intensity of the G’-band in Raman spectroscopy was used to monitor the quality and thickness of the synthesized graphene layers. To synthesize highly crystalline few-layer graphene on a poly-Ni substrate, the mixing ratio of hydrocarbon gas to hydrogen gas, temperature, and growth time were optimized. High temperature, short growth time, and an optimal gas mixing ratio \( \text{C}_2\text{H}_2/\text{H}_2 = 2/45 \) were required to synthesize highly crystalline few-layer graphene. wrinkles were also observed under other growth conditions; they were formed independently of the location of the grain boundary. Based on the experimental observations, we propose that the wrinkles were formed by two processes: i) nucleation of defect lines on step edges between Ni terraces and ii) thermal-stress-induced formation of wrinkles around step edges and defect lines. We believe that our approach for the synthesis of large-area few-layer graphene with high crystallinity may be potentially useful for the development of many electronic devices, such as flexible thin-film transistors, touch panels, or solar-cell applications.
Poly-Ni substrates were chosen in our work because of their availability in large sizes and low cost. Poly-Ni substrates in sizes of 10 cm$^2$ (Ni foil, 0.5 mm thick, 99.98% metals basis) were purchased from Sigma-Aldrich. The substrate was polished by chemical-mechanical polishing (CMP). After polishing, the substrate roughness was around 1–3 nm. This substrate was placed in the rapid thermal chemical deposition (RTCVD) chamber. The temperature increased to 1000 $^\circ$C from room temperature in 5 min. An initial reduction of the Ni substrate was carried out in a hydrogen gas flow of 45 sccm for 30 min at 1000 $^\circ$C. The gas mixing ratio of $C_2H_2/H_2$ was optimized and the obtained synthesis condition of graphene layers was 2/45. The growth time was varied from 5 to 15 min. After completion of growth, the gas supply was terminated, and the chamber was cooled down to 500 $^\circ$C with a cooling rate of 160 $^\circ$C min$^{-1}$.

Measurements: An optical microscope (Leica DML) was used to look at the morphology of the synthesized surfaces. FESEM (JEOL 6700F) was used to observe the morphology of the dispersed nanotubes. Raman spectroscopy (Renishaw RM1000-Invia) with laser excitation wavelengths of 514 nm (2.41 eV) and 633 nm (1.96 eV) equipped with a notch filter with 50 cm$^{-1}$ cutoff frequency was used to investigate the G-band as a function of thickness. SPM (Seiko SPA 400) with a DFM mode was used to study the morphology of the formed wrinkles. For the sample preparation for TEM, the synthesized Ni substrate was sonicated in dichloroethane for 30 min. Graphene layers were then detached from the Ni substrate. The suspended graphene was transferred onto a carbon grid and dried in a vacuum oven for 30 min at 80 $^\circ$C.

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**Figure 5.** Surface morphologies as revealed by a DFM mode for various growth times: a) 5, b) 10, and c) 15 min. Circles mark the wrinkles. The insets show the 3D morphology. d) Height of wrinkle as a function of growth time.

**Figure 6.** Schematic diagrams of wrinkle formation: a) generation of wrinkles from nucleation of defect lines on step edges between Ni terraces and b) thermal-stress-induced formation of wrinkles around step edges and defect lines.
[22] The measurements of the wrinkle height were rather difficult owing to the rough nature of poly-Ni substrate. Therefore, the wrinkle height was measured by averaging the height at several places in the same grain (or layers). The error in measuring the height on both sides of wrinkles was 1–2 nm.