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Q. K. Yu J. Lian S. Siriponglert

H. Li Y. P. Chen S. S. Pei

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Qingkai Yu,^{1,a)} Jie Lian,² Sujitra Siriponglert,¹ Hao Li,³ Yong P. Chen,⁴ and Shin-Shem Pei¹

¹Center for Advanced Materials, Department of Electrical and Computer Engineering,
University of Houston, Houston, Texas 77204, USA

²Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute,
Troy, New York 12180, USA

³Department of Mechanical and Aerospace Engineering, University of Missouri,
Columbia, Missouri 65211, USA

⁴Department of Physics and Birck Nanotechnology Center, Purdue University,
West Lafayette, Indiana 47907, USA

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We report an approach to synthesize high quality graphene by surface segregation and substrate transfer. Graphene was segregated from Ni surface under the ambient pressure by dissolving carbon in Ni at high temperatures followed by cooling down with various rates. Different cooling rates led to different segregation behaviors, strongly affecting the thickness and quality of the graphene films. Electron microscopy and Raman spectroscopy indicated that the graphene films synthesized with medium cooling rates have high quality crystalline structure and well-controlled thicknesses. The graphene films were transferred to insulating substrates by wet etching and found to maintain their high quality. © 2008 American Institute of Physics. [DOI: [10.1063/1.2982585](https://doi.org/10.1063/1.2982585)]

Graphene,¹ the two-dimensional (2D) counterpart of three-dimensional graphite, has attracted vast interests in solid-state physics, materials science, and nanoelectronics since it was discovered in 2004 as the first free-standing 2D crystal. Graphene is considered as a promising electronic material in postsilicon electronics. However, large-scale synthesis of high quality graphene represents a bottleneck for the next generation graphene devices. Existing routes for graphene synthesis include mechanical exfoliation of highly ordered pyrolytic graphite (HOPG),^{2,3} eliminating Si from the surface of single crystal SiC,^{4,5} depositing graphene at the surface of single crystal⁶ or polycrystalline metals,⁷ and various wet-chemistry based approaches.^{8–10} However, up to now no methods have delivered high quality graphene with large area required for application as a practical electronic material.

Graphite segregation at surfaces and grain boundaries of metals has been studied for a long time.¹¹ Previous works showed that thin graphite with well-controlled thickness (including monolayer) and low defect density can segregate from metals and metal carbides^{6,12} held at high temperatures in an equilibrium segregation process.^{13,14} However, the number of graphene layers thus segregated at equilibrium and high temperatures cannot be preserved at ambient temperatures due to nonequilibrium segregation of carbon while cooling down. For the application of graphene in electronic devices, it will be of particular interest to explore the graphene synthesis by such nonequilibrium segregation from metal substrates. Unfortunately, the controlled nonequilibrium segregation behavior to produce graphene is not well studied. Here, we demonstrated the synthesis of several layers of graphene on Ni substrate in a large area by the surface segregation with a controlled cooling. Controlling synthesis parameters, especially the cooling rate, is critical to produce thin graphene films (<10 layers). We also demonstrated the transfer of graphene from metal substrates to insulating sub-

strates. The graphene films maintain their high quality after transferring, as confirmed by Raman spectroscopy.

Graphene segregation by cooling is a nonequilibrium process. Nonequilibrium segregation in general involves the transport of vacancy-impurity (vacancy-carbon in our case) complexes to sinks, such as grain boundaries and surfaces during cooling, and strongly depends on the cooling rate.¹⁵ Our strategy is to control the amount of carbon segregated from metals by controlling the cooling rate, as illustrated in Fig. 1. In the first step, Ni foils were placed in a chamber at high temperature with inert gas protection. In the second step (carbon dissolution), hydrocarbon gases were introduced to the chamber as the source of carbon. The hydrocarbon molecules decompose at the Ni surface and carbon atoms diffuse into the metal. The concentration of carbon decreases exponentially from the surface into the bulk. This step was kept with a short time, generally 20 min, in order to keep the carbon concentration low. In the last step (carbon segregation), samples were cooled down. Different cooling rates led to different segregation behaviors. Extremely fast cooling rate results in a quench effect in which the solute atoms lose

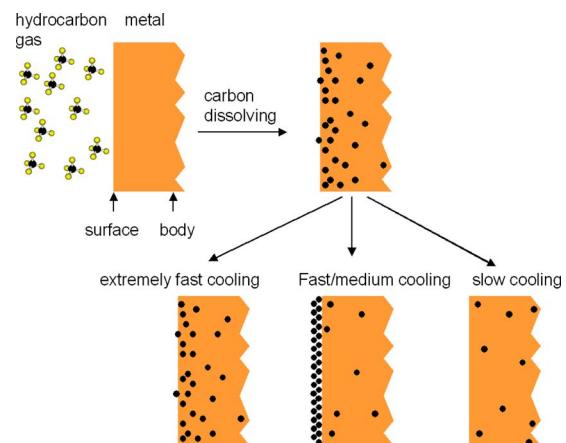


FIG. 1. (Color online) Illustration of carbon segregation at metal surface.

^{a)}Electronic mail: qyu2@uh.edu.

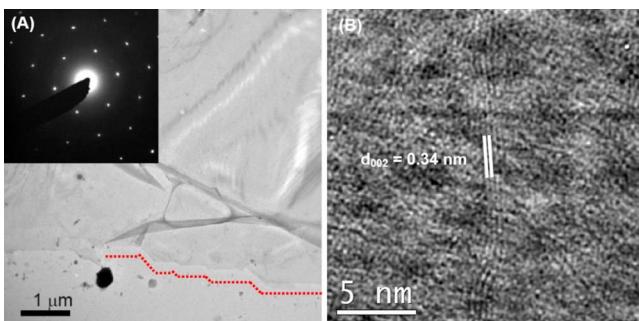


FIG. 2. (Color online) TEM images of graphene. (a) Low magnification image with step shaped edges, highlighted by red dash lines. Inset shows the SAED pattern of the graphene film. (b) HRTEM image of wrinkles in the graphene film, apparently of 3–4 layers.

the mobility before they can diffuse. With a wide range of medium cooling rates, a finite amount of carbon can segregate at the surface. The extremely slow cooling rate allows carbon with enough time to diffuse into the bulk, so there will not be enough carbon segregated at the surface.

In our experiments, polycrystalline Ni foils with thickness of 0.5 mm and purity >99.99% from Alfa Aesar were cut into 5×5 mm² pieces, followed by a mechanical polish. Precursor gases were CH₄:H₂:Ar=0.15:1:2 with a total gas flow rate of 315 SCCM (cubic centimeter per minute at STP) and pressure at 1 atm, with H₂ introduced 1 h before the CH₄ and Ar. Carbon dissolution time is 20 min at 1000 °C. Samples were cooled down by mechanically pushing the sample holder to a lower temperature (in the range of 30–500 °C) zone in Ar atmosphere. Cooling rates were monitored by a thermal couple on the sample holder. Different cooling rates, corresponding to fast (20 °C/s), medium (10 °C/s), and slow (0.1 °C/s), were employed, and the structural characteristics of graphene formed on Ni substrates were studied by transmission electron microscopy (TEM) and Raman spectroscopy (excited by an Argon laser operating at 514 nm).

Samples for TEM were prepared by detaching the graphene films from Ni in HNO₃ solution, followed by rinsing with de-ionized water. The films float on water owing to the hydrophobic nature of graphene. The films, found to be almost transparent, can nonetheless be distinguished from water by their different reflectivity. Copper grids with Formvar films were used to dredge up the graphene films, which were then dried in air naturally. In Fig. 2(a), the red dash lines highlight edges of a graphene film, with step features that can be attributed to graphene cracking along certain crystalline directions. The selected area electron diffraction (SAED) pattern along [001] direction clearly shows the graphite lattice structure, and typically 3–4 layers of graphene were observed at the wrinkles and edges of the films as shown by the high resolution TEM (HRTEM) image [Fig. 2(b)].

Using Raman spectroscopy (with excitation wavelength at 514 nm), we have characterized the quality of the films and the numbers of graphene layers segregated on Ni substrates with different cooling rates (Fig. 3). Generally, four distinct features in the Raman spectrum can be used to characterize graphene and distinguish it from bulk graphite (such as HOPG).^{16,17} (1) The 2D peak at ~ 2700 cm⁻¹ is symmetric for graphene but has a bump at the left side for HOPG. (2) The height of 2D peak is higher than G peak

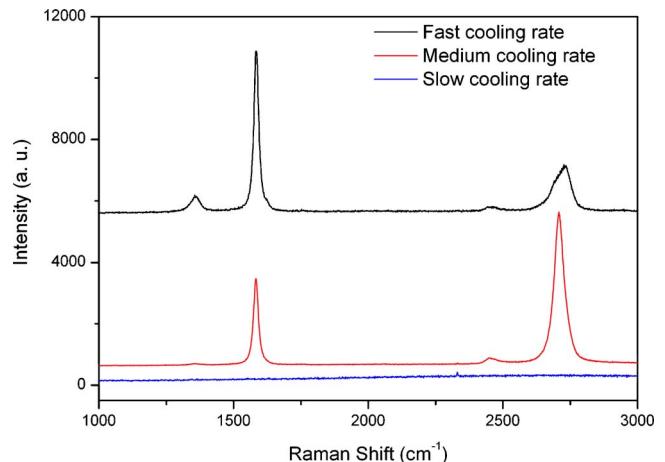


FIG. 3. (Color online) Raman spectra of segregated carbon at Ni surface with different cooling rates.

(~ 1580 cm⁻¹) when the number of graphene layers becomes less than 4. (3) The position of G peak moves to lower wave-number when the number of graphene layers increases (from 1587 cm⁻¹ for monolayer to 1581 cm⁻¹ for HOPG). (4) The profile of D peak (~ 1360 cm⁻¹) reflects the defect density (the absence of D peak corresponds to very low defect density). Analysis of the Raman spectra (Fig. 3) shows that the cooling rate significantly affects the amount and quality of the carbon segregated at Ni surface. With a low cooling rate (0.1 °C/s), no carbon peak is seen in the Raman spectrum (in the wavenumber range 1000–3000 cm⁻¹), indicating few carbon atoms were segregated at the surface, as the carbon atoms near the surface have enough time to diffuse into the bulk of the Ni substrate. With a medium cooling rate (~ 10 °C/s), two prominent peaks appeared at ~ 1583 and ~ 2704 cm⁻¹, corresponding to the G and 2D bands, and the higher peak intensity for the 2D peak relative to G peak suggests that few (four or less) layers of graphene formed. A faster cooling can reduce the rate of carbon migration from near the surface into the bulk and thus enhance the carbon segregation at the surface. With further increase in the cooling rate (up to ~ 20 °C/s), a D band at ~ 1360 cm⁻¹ in the Raman spectrum appeared in addition to the G and 2D bands (Fig. 3), suggesting that although a significant amount of carbon atoms can segregate at the surface in a short time, they may not have enough time to reach a state with a good crystallinity. These results suggest that several layers of high quality graphene can be synthesized on Ni surface with optimized medium cooling rates, while higher cooling rates result in the formation of graphite with more defects.

Transferring graphene from metal substrates to insulators is a critical step for realizing electronic applications. Transferring graphene from metal to insulator substrates and the effect of such transfer on the graphene quality have not been reported previously. Silicone rubber (polymerized siloxanes) was used as the media to transfer 5×5 mm² graphene as-grown on a Ni substrate to a glass plate. After graphene synthesis on metal, a thin layer of silicone was applied on the graphene film, then covered with a glass plate to form a four layer sandwich structure (Ni/graphene/silicone rubber/glass). After a 24 h cure, the silicone rubber was solidified and the metal substrate was etched away with diluted HNO₃ solution. The transferred graphene is transparent to the eye. However, using an optical microscope with polarized light,

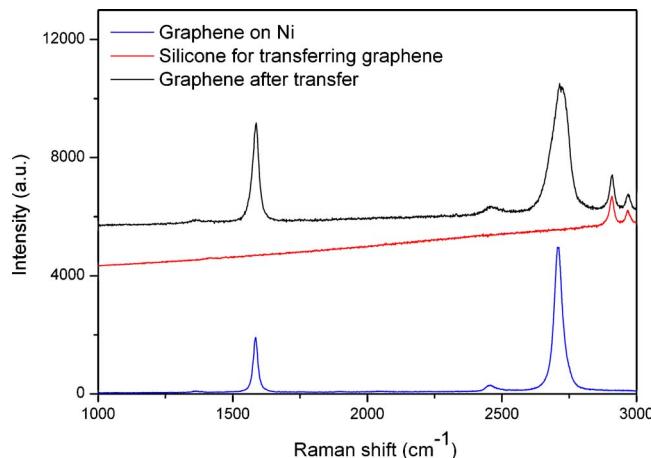


FIG. 4. (Color online) Raman spectra of graphene before and after transferring from Ni to glass.

the graphene and silicone rubber can be easily distinguished. Raman spectra confirmed that the transferred graphene maintained its high quality. In Fig. 4, the blue curve is the Raman spectrum acquired from the graphene segregated on Ni surface with a cooling rate of 10 $^{\circ}\text{C}/\text{s}$, the red curve is the spectrum acquired from the silicone rubber (with two peaks around 2900–3000 cm^{-1}), and the black curve is that from the transferred graphene. Characteristic features in the spectra of the pretransferred graphene are maintained in the spectra of the post-transferred graphene. Silicone peaks can also be seen in the spectra from the transferred graphene on the glass plate, probably because the graphene layer is so thin that the Raman signal from the silicone rubber can be detected.

We also investigated how H_2 in growth atmosphere and the roughness of the metal substrates affect the uniformity of graphene layers synthesized. **With a high dosage of H_2 introduced 1 h before introducing the hydrocarbon gases, as is the case for the data presented in this paper, the uniformity of graphene is significantly enhanced.** This suggests an annealing effect of H_2 . It is believed that H_2 can eliminate certain impurities (such as S and P) that may cause local variations in the carbon dissolvability in the metal substrates.¹⁸ In addition, atomic H can remove defects in carbon (and anneal dangling bonds) at elevated temperatures. We also found that thinner and more uniform graphene can be synthesized on smoother Ni substrates.

In summary, we have synthesized several layers of graphene on Ni substrates by a surface segregation process with controlled cooling and transferred them to glass substrates. TEM and Raman data show that the graphene films can maintain their high quality even after being subject to the usage of HNO_3 and various mechanical operations during the TEM sample preparation and substrate transfer. Cooling rate significantly affects the thickness of graphene synthesized and the amount of defects (with a medium cooling rate found to be optimal), and the quality of graphene films can be controlled by varying other growth conditions (e.g., H_2 in the growth atmosphere and surface roughness of the substrates). These results indicate that the surface segregation from metals in the ambient pressure with controlled cooling rates could offer a high quality and low cost synthesis approach for graphene as a practical electronic material.

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