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Citation: Applied Physics Letters **100**, 253107 (2012); doi: 10.1063/1.4729823 View online: http://dx.doi.org/10.1063/1.4729823 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/100/25?ver=pdfcov Published by the AIP Publishing

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(Received 3 February 2012; accepted 4 June 2012; published online 20 June 2012)

Microwave plasmas were employed to synthesize single- or double-layer graphene sheets on copper foils using a solid carbon source, polymethylmetacrylate. The utilization of reactive plasmas enables the graphene growth at reduced temperatures as compared to conventional thermal chemical vapor deposition processes. The effects of substrate temperature on graphene quality were studied based on Raman analysis, and a reduction of defects at elevated temperature was observed. Moreover, a facile approach to incorporate nitrogen into graphene by plasma treatment in a nitrogen/hydrogen gas mixture was demonstrated, and most of the nitrogen atoms were verified to be pyridinelike in carbon network. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4729823]

The exotic physical properties of graphene, such as ultrahigh carrier mobility, tunable band gap, and quantum confinement effect,^{1–3} have led to its great application potentials in the devices such as field effect transistors (FETs),⁴ transparent electrodes,⁵ supercapacitors,⁶ and rechargeable lithium ion batteries.⁷ Since graphene was first demonstrated by Geim and Novoselov,⁸ various synthesis methods have been developed, e.g., mechanical exfoliation of highly oriented pyrolytic graphite,⁸ thermal exfoliation of purified natural graphite,⁹ and chemical vapor deposition (CVD).^{10–12} Among these approaches, CVD has been successfully employed to grow uniformly single- or few-layer graphene films of large-scale on copper and Ni foils.^{10,13,14} Epitaxial growth of graphene on single crystal SiC and Ru substrates,^{15,16} and graphene growth by carburization of stainless steel from carbon-containing gas sources such as CH₄ by CVD have also been demonstrated.¹⁷

In contrast to gaseous carbon sources, solid carbon sources, e.g., C_{60} ,¹⁸ amorphous carbon,¹⁹ and polymethylmetacry-late (PMMA),^{11,20} have also be utilized for the graphene growth by CVD. For the PMMA source, PMMA-precoated Cu foil was subjected to the hot zone around 1000 °C of a tube furnace fed with hydrogen and argon for 10-20 min, and then the Cu foil with graphene was fast-cooled to room temperature by removing it from the hot zone.¹¹ It was, however, reported by Byun et al. that no Raman signals of graphene could be observed after repetition of the experiment for many times, which was considered to be due to the rapid evaporation of PMMA before it was decomposed and dissolved into Cu.¹² In the same work, it was further reported that graphene could be grown by employing a Ni/PMMA/SiO₂/Si sandwich structure, where the Ni top layer functioned as a catalyst for graphene growth and as well as a capping layer to protect PMMA from evaporation.¹² In this work, we report the synthesis of graphene by microwave plasma CVD (MWCVD) using PMMA precoated on Cu foils as a solid carbon source. The influence of substrate temperature on the quality of graphene layers was studied systematically based on Raman analysis. In addition, nitrogen-doping has been shown to be a promising approach to tune the electronic properties of graphene, which may lead to its potential applications in electrochemical biosensors, high-performance supercapacitors, and nanoelectronic devices.^{21–23} A facile approach for nitrogen doping of graphene by plasma treatment in N₂/H₂ gas mixture was also demonstrated in this work, and the x-ray photoelectron spectroscopic (XPS) results revealed that nitrogen induced in the graphene lattice was dominantly in the pyridinelike format.

25 μ m-thick Cu foils (Alfa Aesar) of 1×1 cm² in size were used as substrates for the synthesis of graphene. After the foils were sequentially cleaned in acetone, isopropyl alcohol, and deionized (DI) water by sonication, $120 \,\mu L$ PMMA (Sigma Aldrich) solution (4% in toluene) was deposited on Cu foils by spin coating at 4000 rpm for 1 min. The PMMA/Cu films were put in a vacuum oven at 70 °C for 2 h to distill the solvent. The thickness of resulting PMMA films was about 100 nm. The PMMA/Cu films were then subjected to the 1.5 kW ASTeX MWCVD system. When the substrate was heated to desired temperature (400-700 °C measured by a thermal couple just below the substrate holder), hydrogen plasma was switched on at a microwave power of 1300 W. The hydrogen flow rate was 100 SCCM (standard cubic centimeter per minute at standard temperature and pressure), and the total pressure was maintained at 23 Torr during the plasma treatment. It should be noted the generation of plasma further increased the foil temperature by about 150 °C as measured by an infrared pyrometer. The duration of plasma treatment was kept at 20 min for all samples. After the plasma was switched off, samples were cooled down slowly at a controlled rate of 25 °C/min. To transfer the asgrown graphene sheets, a PMMA layer was spin coated on the graphene/Cu. The samples were baked at 100°C for 1 min, and then merged in $FeCl_3$ solution (0.05 g/ml) at 40 °C overnight to remove the Cu substrates. The graphene/ PMMA layers were transferred to SiO₂/Si substrates, and the PMMA layer was finally dissolved by acetone. For the nitrogen doping of graphene layers, the as-synthesized graphene/ Cu samples were treated in N2/H2 plasmas. The flow rate of H₂ and N₂ were 200 SCCM and 10 SCCM, respectively. The

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FIG. 1. (a) AFM image of a graphene sheet transferred onto SiO_2/Si wafer, (b) Raman spectrum of a graphene sheet atop SiO_2/Si substrate, (c) 2D (2662 cm⁻¹), (d) G (1585 cm⁻¹), and (e) D band (1330 cm⁻¹) Raman mapping images of a graphene sheet, respectively.

microwave power was 400 W, and the pressure was 12 Torr. The duration of treatment was 2 min with the substrate only heated by plasmas.

Fig. 1(a) shows atomic force microscopy (AFM) image of a graphene layer transfered onto SiO₂/Si wafer (substrate temperature set at 700 °C during plasma treatment). The graphene sheet was revealed to be smooth and uniform over the observed area. The observation was performed at the edge region of the graphene layer, and the thickness of graphene was measured to about 1.3 nm, suggesting the as-grown graphene was of single- or double-layers.⁸ Visible Raman spectroscopy (633 nm) was carried out to characterize the graphene films. The laser spot size is about $1 \,\mu$ m in diameter. A typical spectrum collected on the graphene film atop SiO₂/ Si substrate is shown in Fig. 1(b) with the following bands denoted. (i) G band at 1585 cm^{-1} assigned to the sp² inplane phonon vibrations. The integrated area of G peak (A_G) was illustrated to be proportional to the number of C-C sp² bonds.²⁴ (ii) 2D band at 2662 cm^{-1} characteristic to the formation of graphene.²⁴ The intensity ratio A_{2D}/A_{G} was demonstrated to be sensitive to the number of graphene layers and defect density.¹² The Raman spectrum in Fig. 1(b) with $A_{2D}/A_G > 1$ and the full width at half maximum (FWHM) of 2D band $(W_{2D} \sim 31 \text{ cm}^{-1})$ further verifies that the graphene film is of single- or double-layers, being consistent with AFM observations. (iii) D and D' bands centered at 1360 and 1620 cm⁻¹, respectively, are associated with defects in the graphene films.^{25,26} The observation of relatively strong D and D' peaks indicates that the graphene sheets synthesized by the plasma-assisted process are defective.

Raman mapping was also performed in this work to investigate the uniformity of the as-synthesized graphene sheet. Figs. 1(c)-1(e) depict the 2D, G, and D band Raman mapping obtained on the graphene sheet as-grown on Cu foil, respectively, indicating that the graphene sheet is reasonably uniform almost over the entire growth area. The variation of D band intensity, nevertheless, suggests that the defects may not be evenly distributed, which is believed to be due to the polycrystalline nature of the Cu foil substrate. The carbon atoms could have different diffusion rates in grain bulk and boundaries. Scanning electron microscopy (SEM) observations revealed that the as-grown graphene layer was partly delaminated from Cu foil substrate (image not shown here). The boundaries between the graphene grains could be distinguished, and the average grain size of the as-grown polycrystalline graphene was estimated to be $\sim 20 \,\mu\text{m}$.

The formation mechanism of graphene on metal catalyst substrates by thermal CVD has been widely studied.⁹ The carbon species (either from gaseous or solid sources) dissolved into the metal bulk at an elevated substrate temperature, and then diffuse back to the metal surface and construct graphene lattice due to surface aggregation and structure relaxation at gradually reduced substrate temperature. In comparison with the conventional thermal CVD processes using polymeric solid source, hydrogen plasma, instead of heat, was utilized to decompose the PMMA covered atop the Cu substrate into carbon species. The decomposition could occur in plasmas at a temperature lower than that of conventional thermal CVD, thus no capping layer was required in this case. During the plasma treatment, the Cu substrates were subjected to a substrate temperature ranging from 500 to 850 °C for 20 min that drove the decomposition of PMMA, the recrystallization of copper foil, and dissolution of carbon species into it. As a reference, initial preheating and annealing of Cu substrates were generally required in a thermal CVD process for the recrystallization of Cu foil and the formation of Cu grains on which graphene domains were nucleated and grown.¹⁰ As the plasma was turned off, the carbon species dissolved in Cu diffused back to foil surface and reconstructed to graphene structure at gradually decreased temperatures. The graphene was suggested to grow actually after the plasma was switched off.

To support the discussion, the role of cooling process in growing graphene was investigated. Two PMMA-coated Cu



FIG. 2. Raman spectra of the graphene sheets grown with the cooling processes at a controlled rate of $25 \,^{\circ}$ C/min (black) and cooling naturally (red). Two samples were subjected to the same plasma treatment process.

foils were treated with plasma under identical conditions, and the substrate temperature was set at 700 °C during plasma treatment. However, after the plasma was turned off, one sample was cooled down at a controlled rate of 25 °C/ min, and another one was cooled down naturally (at a rate approximately 50-100 °C/min). Fig. 2 depicts Raman spectra of two samples. The sample grown with the cooling rate 25°C/min presented much stronger and sharper 2D and G peaks, implying a better crystallinity of the graphene layer grown with controlled cooling at a lower rate. The observations revealed that the cooling process played a predominant role in the growth of graphene, and a lower cooled rate is preferred for the precipitated carbon to reconstruct to hexagonal structure. Moreover, switching off the plasma caused a steep drop of substrate temperature by 100-150 °C (e.g., from 850 to 700 $^{\circ}$ C for the sample in Fig. 1(b)), which led to insufficient structure relaxation and hence the formation of defects as indicated by the appearance of D and D' peaks.

In this work, the microwave power was varied in a range from 800 to 1300 W, and only little influence of microwave power on the quality of graphene sheets was revealed based on Raman analysis. However, the substrate temperature was found to play a predominant role in the growth of graphene sheets. Fig. 3 shows the Raman spectra of graphene sheets



FIG. 3. Raman spectra of graphene films on Cu foils synthesized at substrate temperatures of 400, 500, 600, and 700 $^{\circ}$ C. The microwave power was maintained at 1300 W for all samples.

TABLE I. The FWHMs (W) of D, D', G, and 2D bands and A_G/A_{2D} values of samples grown at different temperatures.

	400°C	500°C	600°C	700 °C
WD	41.0	41.0	22.1	18.9
$W_{\mathbf{D}'}$	19.4	21.4	13.5	18.2
$W_{\rm G}$	43.0	39.0	23.4	18.7
W_{2D}	72.3	70.4	40.1	33.7
A_{2D}/A_G	1.0	1.6	3.6	6.0

on Cu foils synthesized at substrate temperatures of 400, 500, 600, and 700 °C (the temperature without switching on the plasmas). The sample grown at 400 °C showed obvious D, D', G peaks, and a faint and broad 2D peak, indicating poor quality of the graphene sheet. However, it is noted that utilizing plasmas enables growing graphene at a temperature much lower than that of conventional CVD (400 °C vs. over 1000 °C). As the substrate temperature increased from 400 to 700 °C, the intensities of both 2D and G peaks increased, and their peak width reduced significantly. Meanwhile, the intensity of D' peak decreased. The FWHMs of D, G, and 2D peaks, and A_{2D}/A_G values of the samples are summarized in Table I. It is shown clearly that the peak width decreased and A_{2D}/A_G ratio increased with the elevation of substrate temperature. Since the peak broadening and the intensity ratio A_{2D}/A_G have been demonstrated to be reversely proportional to defect intensity, the above Raman observations suggest that a higher temperature is favorable to the growth of graphene sheets with reduced defect density.²⁶⁻²⁸

The as-grown graphene sheets were further treated in in a 5% N₂/H₂ plasma to incorporate nitrogen into graphene lattice. The graphene sheets were exposed to plasmas for 2 min, and prolonged treatment was found to lead to etching of the graphene. Fig. 4(a) shows the Raman spectra of graphene sheets before and after treatment. The intensities of both G and 2D peaks were found to decrease dramatically. However, the relative intensity of D peak with respect to 2D peak increased, indicating the increase of defect density in the graphene sheet after plasma treatment. XPS (VG ESCALAB 220i-XL equipped with a monochromatic Al $K\alpha$ (1486.6 eV) x-ray source) was carried out to study the state of nitrogen in the graphene sheet. The survey spectrum in the insect of Fig. 4(b) shows clearly carbon, oxygen, and copper (substrate) signals and a week nitrogen peak at about 398.2 eV. The oxygen signal was believed to be due to the surface adsorption of oxygen, and the percentage of nitrogen in graphene was estimated to be about 5%. High-resolution XPS spectra of C 1s and N 1s of nitrogen-doped graphene were depicted in Figs. 4(b) and 4(c), respectively. The C1s peak at 284.4 eV is assigned to graphite-like sp² C, and the small peaks at 285.0 eV and 288.2 eV could be attributed to the N-sp² C and N-sp³ C bonds, respectively.²⁹ The deconvolution of N 1s signal reveals three components centered at 398.2 eV, 400.4 eV, and 403.8 eV, as shown in Fig. 4(c), which have been demonstrated to correspond to pyridine-like N, pyrrolelike N, and nitrites (NO_x), respectively.^{29,30} The strongest peak at 398.2 eV implies that most nitrogen atoms incorporated are in pyridinelike structure (N atom has two carbon



FIG. 4. (a) Raman spectra of a graphene sheet on copper foil before and after plasma treatment in N_2/H_2 gas mixture. (b) C1s and (c) N1s high-resolution XPS spectra of nitrogen-doped graphene. The inset in (b) is the XPS survey spectrum.

neighbors in a hexagonal ring). The pyridinelike N was shown to present mostly at the edge of graphene sheets or in case if a carbon vacancy is created next to the nitrogen atom in the carbon network.³⁰ The schematic of pyridine-like and pyrrolelike N structures has been depicted in the previous report.²⁹ In our work, the incorporation of pyridinelike N is believed to be due to the polycrystalline nature of the graphene sheets and the exposure of graphene to reactive hydrogen/nitrogen plasmas which might easily lead to the formation of carbon vacancies.

In summary, we have demonstrated a microwave plasma-assisted CVD method to synthesize single- or double-layer graphene sheets on copper foils using a solid carbon source of PMMA. The utilization of plasmas enables decomposition of PMMA and growth of graphene at reduced substrate temperature as compared to the conventional thermal CVD methods. It was revealed that the cooling process played a predominant role in the growth of graphene, and a lower cooled rate is preferred for the precipitated carbon to reconstruct to hexagonal structure. Raman spectroscopy and Raman mapping were carried to evaluate the quality and uniformity of the graphene sheets. The growth temperature was demonstrated to play a key role in determining the quality of graphene sheets, and elevated temperatures were shown to benefit the growth of graphene with reduced defects. In addition, the plasma treatment of graphene sheets in a nitrogen/ hydrogen gas mixture resulted in doping of graphene sheets with nitrogen. The XPS analysis revealed that most of the nitrogen atoms are in the pyridinelike structure in carbon network.

This work was supported by National Natural Science Foundation of China (NCFC Grant No. 61176007) and CityU Applied Research Grant (No. ARG9667045). One of the authors (C. D. Wang) is grateful to Professor. L. W. Liu, Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Science, for helpful suggestions.

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