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Nitrogen-doped graphene by microwave plasma chemical vapor deposition

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ABSTRACT

Rapid synthesis of nitrogen-doped, few-layer graphene films on Cu foil is achieved by microwave plasma chemical vapor deposition. The films are doped during synthesis by introduction of nitrogen gas in the reactor. Raman spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy and scanning tunneling microscopy reveal crystal structure and chemical characteristics. Nitrogen concentrations up to 2 at.% are observed, and the limit is linked to the rigidity of graphene films on copper surfaces that impedes further nitrogen substitutions of carbon atoms. The entire growth process requires only a few minutes without supplemental substrate heating and offers a promising path toward large-scale synthesis of nitrogen-doped graphene films.

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1. Introduction

Since its discovery in 2004 [1], graphene has attracted the attention of engineers and scientists across many research disciplines and application areas. Rapid development has been made not only in understanding the physics, chemistry and other fundamental properties of graphene, but also in development of graphene-based devices such as transistors [2], solar cells [3], gas sensors [4] and supercapacitors [5]. Doping graphene to change the carrier density is an important method to control electronic properties, and this work reports a facile means of nitrogen doping.

Nitrogen doping of graphene by various methods has been demonstrated previously. These include use of nitrogen-containing precursors in chemical vapor deposition (CVD) [6,7], post treatment of graphene using ammonia [8,9] or nitrogen [10,11] plasma, arc discharge processing [12,13], and other chemical treatment methods [14–16]. The resulting N-doped graphene films can be very useful as electrochemical biosensors [10], can show high electrochemical activity towards oxygen reduction [11,17] and exhibit improved Li-ion intercalation properties as compared to pristine graphene [7].

However, in order to make doped graphene more scalable, a synthesis method capable of rapid, large-area processing is very much needed. Chemical methods and production of graphene by arc discharge, though producing large quantities of both doped [15,16,18] and undoped graphene [19,20], are limited by the size of the graphene flakes. Chemical methods also lead to functionalization of the graphene flakes. Of the different synthesis techniques, chemical vapor deposition [6,7] has shown the greatest promise for large scale synthesis of doped large-area graphene films. However, the technique requires high temperatures and usually requires several hours for the process to be completed.

Microwave plasma CVD (MPCVD) is another promising technique that has been widely used for low-temperature and fast growth of different carbon based nanostructures [21–23] including flat graphene films [24–26] and graphene flakes [27–29]. Recently, the authors reported a method for rapid synthesis of few-layer graphene films over Cu foil by MPCVD [26]. The coupling between methane/hydrogen plasma and a metal foil in the MPCVD process enabled a very rapid and localized heating of the metal foil to produce graphene growth within a few minutes without any supplemental heating. Because of this localized heating on a thermally light substrate (i.e., an elevated foil), the cooling process was also shown to be extremely fast. In this work we show that the same technique can be used for rapid synthesis of nitrogen-doped graphene by introducing nitrogen during the growth process.

2. Experimental methods

Synthesis was carried out using a microwave plasma chemical vapor deposition set up (SEKI AX5200S). The technique has been described in detail in a previous report [26]. Growth was carried out over a 25 μm thick copper foil (99.8% purity) in a H_2 plasma with CH_4 as the carbon source and N_2 gas as the source for nitrogen. With the help of a ceramic pedestal, the growth substrate was elevated from the Mo puck. The elevation of the foil allows for a strong coupling between the Cu foil and the plasma. During the entire growth process the growth chamber was maintained at a pressure of 10 Torr with H_2 flowing at 50 sccm.

First, the sample was heated in hydrogen plasma at 400 W for 3 min, followed by introduction of CH_4 at a flow rate of 10 sccm for
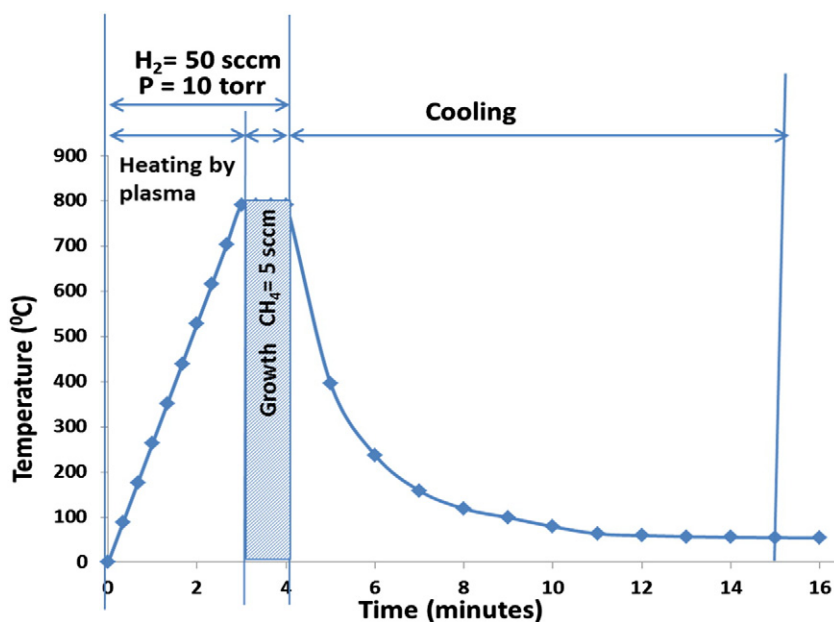
Fig. 1. A schematic of the temperature variation in the growth process as a function of time.

1 min. This process results in formation of a few-layer graphene film over the Cu foil. To obtain N_2 doped films, N_2 at a flow rate of 50 sccm was then introduced either during the 1 min of CH_4 flow or for an additional 1 min at 150 W while CH_4 flow was continued. The plasma power was reduced in order to avoid foil overheating upon introduction of N_2. Thus, depending on when N_2 is introduced, a nitrogen-doped few-layer graphene film can be obtained in a growth lasting 4 or 5 min. The cooling process was initiated by termination of the plasma, followed by a hydrogen purge and vent procedure (taking advantage of the high thermal conductivity of hydrogen gas). In all cases, the foil sample cooled to less than 450 °C (the lower readability limit of the integrated pyrometer) in several seconds. Synthesized films can be transferred onto arbitrary substrates by etching the copper substrate after a layer of PMMA has been coated on top of graphene [26,30].

Graphene films were characterized using scanning electron microscopy (SEM) and Raman spectroscopy. A 532 nm laser with 100× of magnification was used for Raman study. Film thickness was confirmed using transmission electron microscopy (TEM). An FEI Environmental Titan 80-300 TEM operating at 300 kV in plan view was used. The presence of nitrogen in the film was confirmed using X-ray photoelectron spectroscopy (XPS). A Kratos Ultra DLD spectrometer using monochromatic Al Kα radiation was used. Spectra were collected from a 700×400 μm^2 spot size at normal incidence from the sample surface. Pass energies of 160 eV and 20 eV were used for the survey and high-resolution spectra respectively. XPS data were analyzed with commercially available CasaXPS software.

Scanning tunneling microscope (STM) scans on graphene film surface were taken using a UHV STM (RHK-300) at 90 K.

3. Results and discussion

Fig. 1 shows a schematic of the temperature variation in the growth process as a function of time. The heating of the foil is accomplished within 3 min. This is primarily due to the coupling between the plasma and the metal foil. The entire growth including cooling of the sample is complete in approximately 20 min (including full venting of the chamber for sample extraction). Fig. 2(a) and (b) show the SEM image of the Cu foil before and after growth. Recrystallization and grain growth are apparent, indicating that even the short heating time of a few minutes is sufficient for the complete recrystallization of mechanically deformed grains in Cu foils. Foil surface temperature was difficult to measure in the experimental set up. However, using a calibrated pyrometer the peak temperature of the copper surface was estimated to be 700 ± 25 °C, which was sufficient to induce copper recrystallization. However, graphene coating of the copper alters the surface emissivity, making a reliable estimate of temperature difficult. The thermocouple attached to the substrate table recorded a temperature of approximately 65 °C thus indicating localized heating of the elevated foil [26].
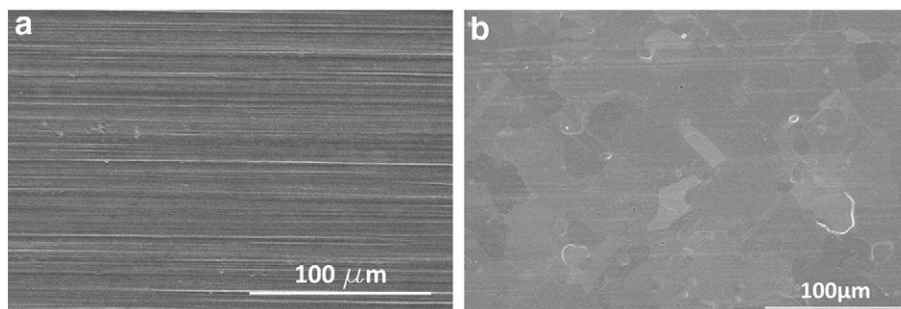

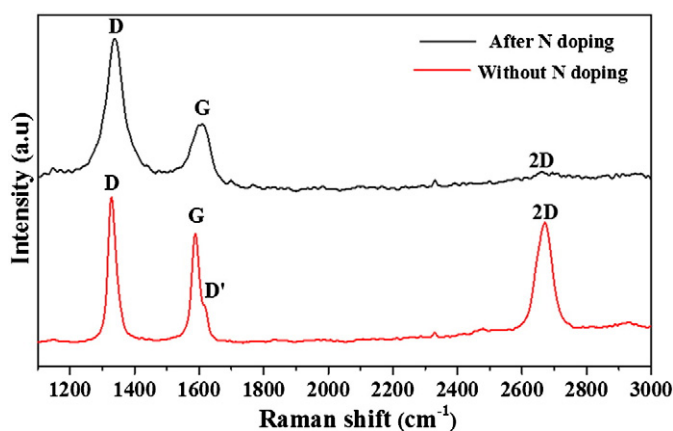**Fig. 2.** SEM image of Cu foil (a) before and (b) after graphene growth.

Fig. 3. Raman spectra of the graphene film with and without any nitrogen doping.

Fig. 3 shows the Raman spectrum of the film with and without any nitrogen doping. Raman spectroscopy has been widely used to characterize graphene films [31,32]. The spectrum in Fig. 3 display a D band near 1335 cm^{-1}, a G band near 1580 cm^{-1} and a 2D band near 2670 cm^{-1}. The films show a moderate amount of defects even without nitrogen doping. This is expected as the growth occurs in the presence of hydrogen plasma which would contain energetic ions and radicals. The D peak intensity increases further with nitrogen doping. The doped nitrogen disrupts the hexagonal symmetry of the graphene film, resulting in a stronger D peak. The symmetric nature of the 2D peak indicates turbostratic graphene layers with weak inter-layer coupling. Such weak coupling between the layers has been previously reported for graphene films grown using atmospheric pressure thermal CVD [32]. The 2D peak in bulk graphite has a distinct asymmetry with a shoulder at its left [31], and such shoulder was absent for synthesized films (Fig. 3). The relative variation of different peak intensities of graphene films with and without nitrogen doping was compared, using area ratios of G, D, and 2D peaks. The ID/IG ratio increases from 1.34 to 2.3 due to nitrogen incorporation. The I2D/IG ratio also decreases from 1.0 to 0.28. These comparisons indicate an increase in defect density as a result of nitrogen doping.
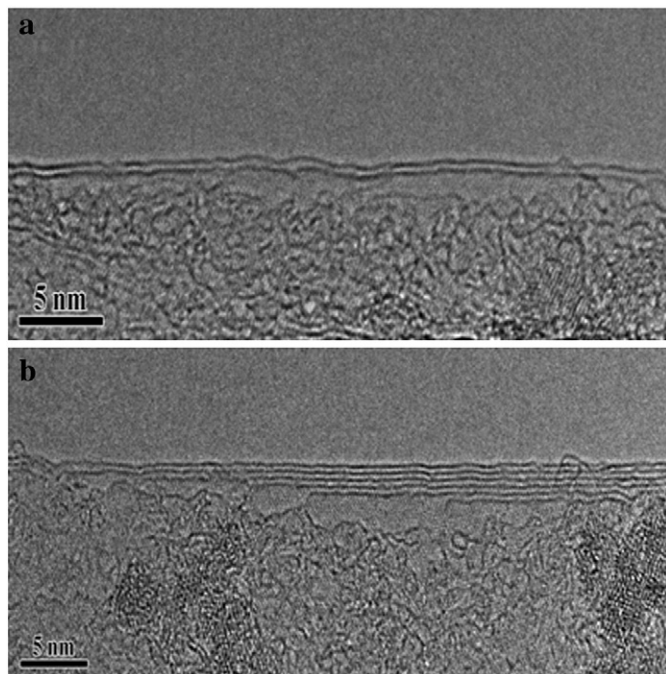

Fig. 4. A high-resolution TEM image of the graphene film grown without any CH$_4$ flow.
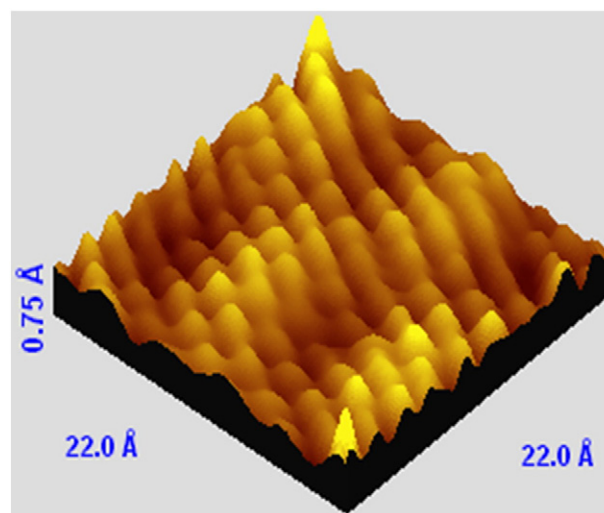

Fig. 5. A high-resolution image of graphene surface measured by a UHV STM at 90 K.

Film thicknesses were evaluated using a high resolution transmission electron microscope. Graphene films grown with a CH$_4$ flow for 1 min after plasma heating were previously found to be 4 to 6 layers in thickness [26]. It was observed that growth could be obtained even without a CH$_4$ flow. TEM study of such films showed that films of about 2 monolayers of graphene could be deposited from H$_2$ plasma without flowing CH$_4$ in the chamber. This finding is attributed to residual carbon deposited on the walls of the growth chamber and on the graphite susceptor that supports the pedestal structure. However, the associated film thickness was not uniform. Fig. 4 contains a high-resolution TEM image of the film grown without any CH$_4$ flow. While two monolayers can be seen in Fig. 4(a), (b) shows a portion of the film with varying thickness between two and seven monolayers.

The N-doped graphene films for STM [33,34] characterization were grown on CMP-polished Cu (111) substrate from MTI. Fig. 5 shows the high-resolution image of graphene surface measured by UHV STM (RHK-300) at 90 K. The 22×22 Å^2 image was obtained at a tunneling current of 0.5 nA and sample bias of 500 mV. The image shows a lattice of carbon atoms with atomic corrugation amplitude of 0.5 Å. The lateral height variations on this image may either be caused by substrate residual roughness or by nitrogen dopants incorporated into subsurface graphene layers.

The presence of nitrogen in the films was analyzed using XPS. Nitrogen content was found to be 2 at.%. Fig. 6 shows the XPS spectra obtained from a nitrogen-doped graphene film. Fig. 6(a) contains a survey spectrum obtained from the film. In addition to the photoemission peaks of carbon and copper, oxygen content is apparent. The oxygen peak was absent in the XPS survey spectrum for the undoped graphene, which was very similar to the spectra provided in a previous report [26]. From the Raman analysis discussed above, the doping of graphene with nitrogen introduces defects that act as favorable sites for oxygen functionalization by the ambient moisture and air [31].

Fig. 6(b) shows a high-resolution spectrum of the C 1s region. The C 1s peak appears near 284.6 eV which is characteristic of graphite [30]. The shoulder at the higher energy of 287 eV is attributed to oxygen-containing functional groups attached to the graphene film. A shake up peak near 291 eV can also be seen. Graphitic films have been reported to show a shake up peak around 290 eV [35]. Prior work on nitrogen-doped graphene has shown that nitrogen can be incorporated either as a pyridine-like nitrogen or as pyrrole-like nitrogen [13,36,37]. Pyridine-like N has two carbon neighbors and is characterized by a N 1s peak near 398.5 eV [36–38], whereas pyrrole-like N has a pentagonal ring structure and has a N 1s peak near 400.5 eV [36–38]. Substitutional doping of nitrogen into the graphene lattice where a N atom simply replaces a C atom has also been reported [37], with the corresponding
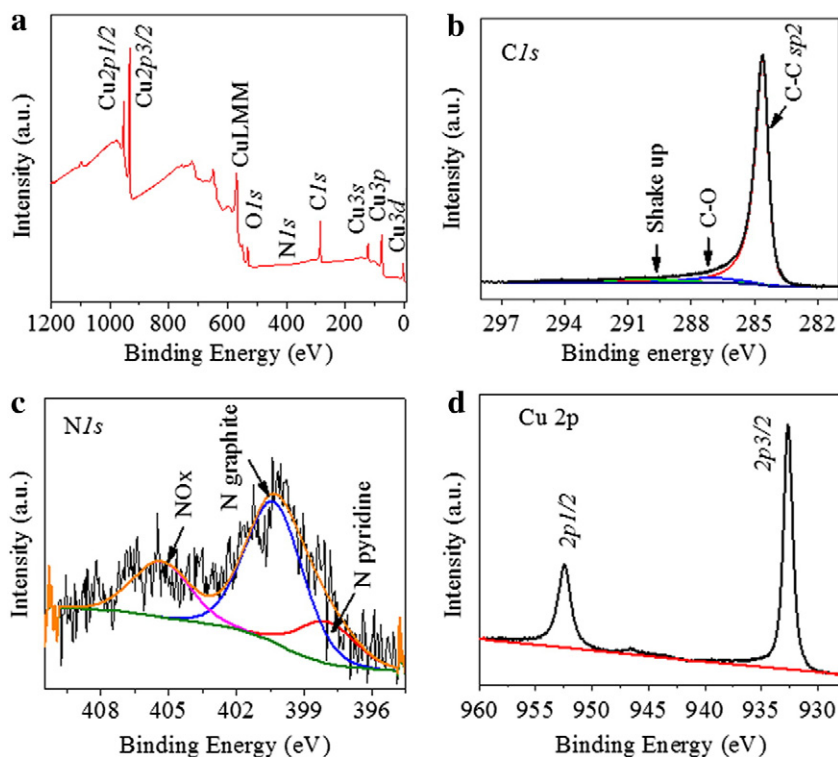
Fig. 6. XPS spectra of the doped graphene film: (a) survey spectrum and high resolution spectrum of (b) C *1s* region (c) N *1s* region and (d) Cu *2p* region.

N *1s* peak near 401 eV [38]. In the present study, the N *1s* high-resolution spectrum has multiple contributing peaks that are apparent in Fig. 6(c). The N *1s* region can be resolved into three distinct peaks. Using the peak assignment references above, these were attributed to pyridine-like nitrogen (near 398 eV) and graphite-like nitrogen (near 400 eV). Oxygenated nitrogen, NOx, was also apparent near 405 eV. Interestingly, the locations of these peaks are very close to those observed in earlier work on nitrogen-doped fullerene-like carbon films that contained incomplete shells with a curved turbostratic morphology [39–41]. In these works the turbostratic hexagonal plane curvature was explained by nitrogen doping leading to the insertion of five-member rings. If such curvature is allowed, the maximum nitrogen concentrations in graphitic planes was found to be as high as 15–20 at.% [41,42]. Thus, it is quite possible that the relatively low 2 at.% incorporation of nitrogen in few monolayer graphene films observed in the present study is limited by the rigidity of the films on the copper substrates, not allowing for film curvature needed to accommodate larger nitrogen concentrations.

As evidence for the integrity of nitrogen-doped graphene films and the lack of any through-film defects, the underlying copper substrate exhibited no oxidation, even as the sample was exposed to laboratory air for several days before the XPS analysis was completed. Fig. 6(d) shows the high resolution spectrum of the Cu *2p* region. Peaks at 933 eV and 952 eV correspond to Cu *2p3/2* and Cu *2p1/2* respectively in the copper non-oxidized metallic state. This indicates that 2 at.% nitrogen-doped graphene has a complete pin-hole-free coverage and provides good oxidation resistance to the copper metallic surface.

4. Conclusion

MPCVD growth of nitrogen doped graphene films is possible in a very short growth process. Nitrogen can be doped in the graphene films up to a concentration of 2 at.%. The reported method suggests opportunities for large-scale and rapid synthesis of nitrogen-doped graphene films. We believe that the same technique can be extended for p-type doping using a suitable gaseous precursor (such as diborane) [18]. It may be possible to increase the nitrogen content further by increasing the duration of N_2 flow. The maximum nitrogen concentration in the present work may be limited by the rigidity of the films on the metallic substrates, hindering the formation of five-member rings in graphene layers needed to accommodate more nitrogen substitution for carbon.

Acknowledgements

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