Synthesis of nitrogen-doped graphene by thermal chemical vapor deposition method from a single liquid precursor

JianFeng Bao*, Naoki Kishi and Tetsuo Soga

Department of Frontier Materials, Nagoya Institute of Technology, Nagoya 466-8555, Japan

Abstract

In this work we report the synthesis of nitrogen-doped graphene using an ambient pressure chemical vapour deposition technique on polycrystalline Ni substrates with a single liquid precursor, as the source of both carbon and nitrogen. Nitrogen atom substitution of the so-formed graphene was confirmed by X-ray photoelectron spectroscopy. The signal from sp^2 bonded carbon atoms decreased in the nitrogen-doped graphene at longer deposition times. Spatially resolved Raman mapping results and transmission electron microscopy images show that the nitrogen-doped graphene formed with varying thickness from a single-layer to >10 layers. The effects of growth temperature and deposition time on the level of nitrogen doping, number of layers, and the quality of the nitrogen-doped graphene layer were investigated.

Keywords: Nitrogen-doped graphene, Raman mapping, Chemical vapor deposition.

Telephone number: +81-52-735-5532 Fax number: +81-52-735-5532

E-mail address: baojianfeng0920@yahoo.co.jp

1. Introduction

Graphene, a monolayer of carbon atoms arranged in a two-dimensional honeycomb lattice, has attracted attention because of its unique properties and many potential applications [1-5]. Doping of graphene by foreign atoms [6-9] is of interest because this doping allows modification of the band structure and physicochemical properties of the materials, further extending the potential applications. Among numerous potential dopants, nitrogen is considered to be an interesting element for chemical doping of graphene with a wide variety of potential applications for the materials, including lithium batteries [8], electrochemical biosensor [10] and fuel cells [11, 12].

A number of approaches have been proposed to synthesize nitrogen-doped graphene, such as heat treatment of graphene oxide under an ammonia atmosphere [13], nitrogen plasma treatment of graphene [10], and wet chemical reactions [14]. Recently, chemical vapor deposition (CVD) growth has been demonstrated using hydrocarbon gases in an ammonia atmosphere [11], or using a single precursor compound~~s~~ that contain both carbon and nitrogen [15, 16]. Development of liquid precursors based on nitrogen and carbon containing material may be expected to be a milestone in nitrogen-doped graphene synthesis because of their ease of use. In this paper, we report the synthesis of nitrogen-doped graphene by an ambient pressure CVD technique using monoethanolamine as the sole source of both carbon and nitrogen. The graphene materials obtained were characterized by scanning electron microscopy (SEM), spatially resolved Raman spectroscopy, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). We have investigated the effects of the deposition time and growth temperature on the nitrogen/carbon composition and number of layers of the nitrogen-doped graphene.

2. Experimental

Nitrogen-doped graphene was synthesized on polycrystalline Ni substrates (thickness of 0.1 mm, Nilaco) using CVD from a single liquid precursor. The deposition apparatus consisted of two horizontal furnaces fitted with a quartz tube having a length of 120 cm and an internal diameter of 26 mm. Monoethanolamine was placed at the centre of the first furnace. The Ni substrates were inserted at the centre of the second furnace. The CVD process was carried out under a nitrogen atmosphere at ambient pressure. The second furnace was raised to the desired reaction temperature (1000–1100 °C) under a nitrogen flow of 500 ml/min, and then annealed at the reaction temperature for 10 min. After annealing, the temperature of the first furnace was raised to 120 °C. The reaction was carried out by introducing monoethanolamine into the second furnace for the desired deposition time (from 3 to 12 min). After the reaction, the Ni substrates were pushed mechanically to the cool temperature zone and cooled to around 100 °C at a rate of 200 °C/min. After cooling, the products were characterized by scanning electron microscopy (SEM, JEOL JSM7001FF), transmission electron microscopy (TEM, JEOL JEM-2100F), X-ray photoelectron spectroscopy (XPS, SSX-100 using an Al Kα X-ray source at 1486.6 eV), and spatially resolved Raman spectroscopy. The Raman mappings were measured over 50 μm × 50 μm in 5-μm steps. The excitation wavelength of the laser used in the Raman measurement was 532 nm.

3. Results and discussion

First of all we investigated temperature dependence of the nitrogen-doped graphene from 1000 to 1100 °C. Raman measurements were carried out to determine the number of layers and the graphene materials quality. The intensity ratio of the G peak at around 1580 cm^{-1} to the 2D peak at around 2700 cm^{-1} (I_G/I_{2D}) and full width at half maximum (FWHM) of the 2D peak provide information on the number of graphene layers [17, 18]. Fig. 1 (a-c) shows the Raman mappings for the I_G/I_{2D} of samples synthesized at 1000, 1050, and 1100 °C on polycrystalline Ni substrates with deposition time of 7min. The samples synthesized at 1000 and 1050 °C shows a higher intensity ratio of I_G/I_{2D} (coloured blue and green). Compared with the samples synthesized at 1000 and 1050 °C, there were smaller intensity ratio of I_G/I_{2D} regions (coloured red), in the mapping of the sample synthesized at 1100 °C. Fig. 1 (d-f) shows a Raman spectra taken from point A and B marked in Fig. 1 (a-c). At point A (in Fig. 1 (f)) there are a small of I_G/I_{2D} 0.41 and a narrow 2D peak with an FWHM of 26.9 cm^{-1}; this indicates formation of single layer graphene. The Raman spectrum at point B (in Fig. 1 (f)) has a large I_G/I_{2D} (3.06) and FWHM (73.8 cm^{-1}) indicating thicker-layer graphene were formed. As the growth temperature increased from 1000 to 1100 °C the D-band peak decreased as shown in Fig.1 (d-f). We infer that increasing growth temperature both improves the quality and decreases the number of layers formed on the Ni substrates [19].

We also investigated deposition time dependence of the nitrogen-doped graphene formation from 3 to 12 min. Fig. 2 (a-c) shows SEM images of nitrogen-doped graphene sheets synthesized on polycrystalline Ni substrates at 1100 °C with deposition time of 3, 7, and 12 min, at low magnification, and Fig. 2 (d-f) shows a high magnification SEM images of the regions in Fig. 2 (a-c). Large area homogenous graphene films were formed at shorter deposition times.

To investigate the synthesized materials composition, XPS was performed on the films formed at 1100 °C and various deposition times. The survey scans from the XPS analysis in Fig. 3 (a) shows the C1s peak around 284.5 eV, the N1s peak at 401.3 eV, the O1s peak at 534.5 eV and the Ni main peak Ni 2p 3/2 at 853 eV. The nitrogen doping levels were 0, 1.5, and 2.9 at %, at deposition times of 3, 7, and 12 min, respectively. The nitrogen content clearly increased with deposition time. In the high-resolution scan of the N1s peak as shown in Fig. 3(b), no N1s peaks could be observed for the sample synthesized at a deposition time of 3 min. The N1s peaks were observed for the samples grown at longer deposition times and could be fitted by three components, centred at ~398.3, ~401.3, and ~402.9 eV, corresponding to pyridinic, pyrollic, and graphitic nitrogen atoms doped into the graphene, respectively [8]. Fig. 3 (c) shows high-resolution scans of the C1s peaks. All the C1s peaks could be fitted by five components centred at ~284.8, ~285.4, ~286.5, ~288.6, and ~291.3, corresponding to sp^2C-sp^2C, N-sp^2C, N-sp^3C/C–O (epoxy and alkoxy), carboxyl functionalities, and the π-π^* satellite peak, respectively [7, 8, 20]. Increasing the doping level of nitrogen reduced the proportion of sp^2 bonded carbon. This indicates that the graphene sheets were partially substituted by nitrogen atoms shown in Fig. 3 (c).

Fig. 4 (a-c) shows the Raman mapping results for the FWHM of the 2D-band peak of nitrogen-doped graphene materials synthesized at 1100 °C with deposition times of 3, 7, and 12 min. In Fig. 4 (a) the samples synthesized at a deposition time of 3 min show Raman mapping result for 2D-bands with a narrow FWHM over a large area of the substrate, coloured red. In Fig. 4 (b) (in the same area with Fig. 1 (c)), 2D-bands with a narrow FWHM regions were decreased compared with the samples synthesized at a deposition time of 3 min. Extending the deposition time broadened the FWHM of the 2D-bands (coloured blue) in Fig. 4 (c). This indicates that the number of nitrogen-doped graphene layers increased with the deposition time. Fig. 4 (d-f) shows the Raman spectra obtained at points A and B marked in Fig. 4 (a-c). We also found that as the deposition time increased from 3 to 12 min, the intensity of the D-band peak increased. We consider that extending the deposition time both the nitrogen doping levels and amorphous carbon amounts increased and results to increase the D-band peak intensity.

To confirm the nitrogen-doped graphene numbers of layers TEM characterization were carried out. The sample synthesized on Ni substrates with 7 min at 1100 °C were dispersed in ethanol and transferred to TEM grids. High-resolution TEM examination (Fig. 5 (a-c)) confirmed formation single layer, three layers, and >10 layers of nitrogen-doped graphene and close agreement with our Raman mapping results (Fig. 1 (c) and Fig. 4 (b)).

4. Conclusion

We have presented the synthesis of nitrogen-doped graphene using an ambient pressure CVD technique and monoethanolamine as a precursor that combines carbon and nitrogen on polycrystalline Ni substrates. As the growth temperature increased from 1000 to 1100 °C, the intensity of the D-band peak decreased. This indicated that increasing the growth temperature improved the nitrogen-doped graphene quality. XPS and spatially resolved Raman spectroscopy results indicate that longer deposition times increased the nitrogen doping level and the number of nitrogen-doped graphene layers deposited on the substrates. High-resolution XPS C1s spectra show that the relative proportion of sp^2 bonded carbon atoms decreased as the nitrogen doping level increased. Spatially resolved Raman spectroscopy results and high-resolution TEM images confirmed that nitrogen-doped graphene layers formed with thicknesses between a single layer and >10 layers. We believe that these results will play an important role in the development of facile synthetic routes to nitrogen-doped graphene using liquid precursors.

References

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Figure captions

Fig. 1 (a-c) Raman mappings of I_G/I_{2D} of nitrogen-doped graphene sheets synthesized for 7 min on polycrystalline Ni substrates using monoethanolamine at (a) 1000 °C, (b) 1050 °C, and (c) 1100 °C. Fig. 1 (d-f) Raman spectra obtained at point A and B corresponding to Fig. 1 (a-c).

Fig. 2 (a-c) Low magnification SEM images of nitrogen-doped graphene synthesized using monoethanolamine at 1100 °C on polycrystalline Ni substrates for (a) 3 min, (b) 7 min, and (c) 12 min. Fig. 2 (d-f) High magnification SEM images corresponding to Fig. 2 (a-c).

Fig. 3 (a) XPS survey scans of nitrogen-doped graphene synthesized on polycrystalline

Ni substrates using monoethanolamine at 1100 °C for 3 min, 7 min, and 12 min. Fig. 3 (b) high-resolution XPS of N1s signal of nitrogen-doped graphene corresponding to Fig. 3 (a). Fig. 3 (c) High-resolution C1s signal corresponding to Fig. 3 (a). The black dotted lines denote the experiment data. The black solid lines and the orange solid lines indicate the fitting curves and the sum of the fitting curves, respectively.

Fig. 4 (a-c) Raman mappings of the 2D-band FWHM in samples synthesized using monoethanolamine at 1100 °C on polycrystalline Ni substrates for (a) 3 min, (b) 7 min, and (c)12 min. Fig. 4 (d-f) Raman spectra obtained at point A and B corresponding to Fig. 4 (a-c).

Fig. 5 High-resolution TEM images of nitrogen-doped graphene sheets synthesized at 1100 °C using monoethanolamine for 7 min showing (a) single-, (b) three-, and (c) 10>layers.

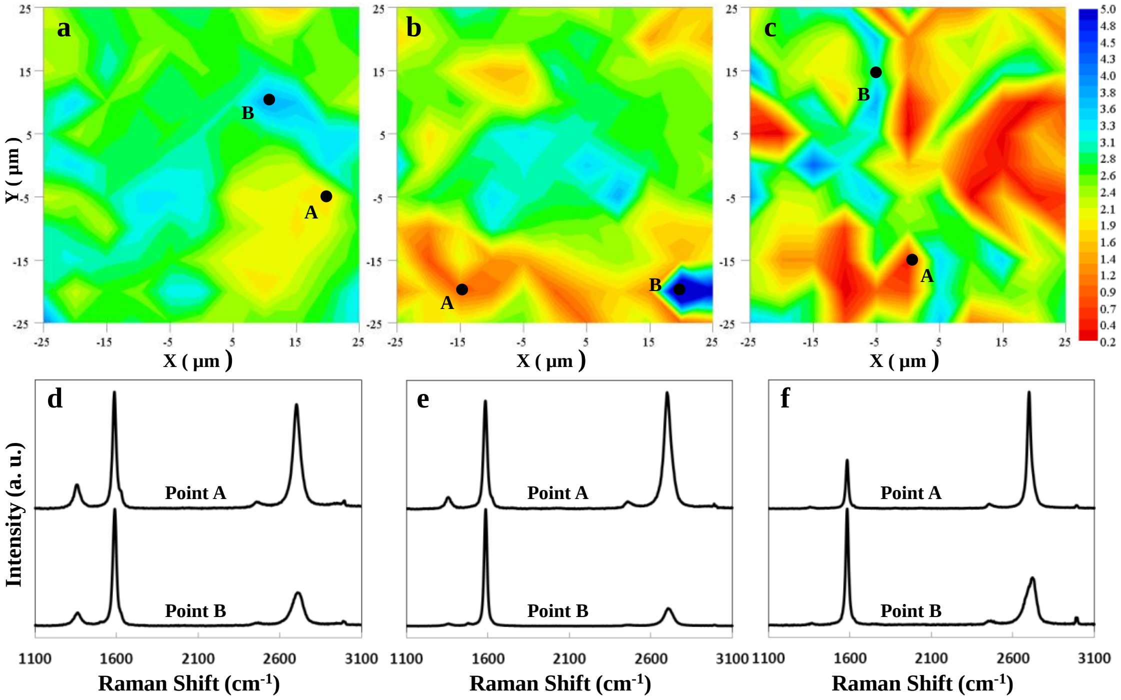

Fig. 1 Bao. J *et al*

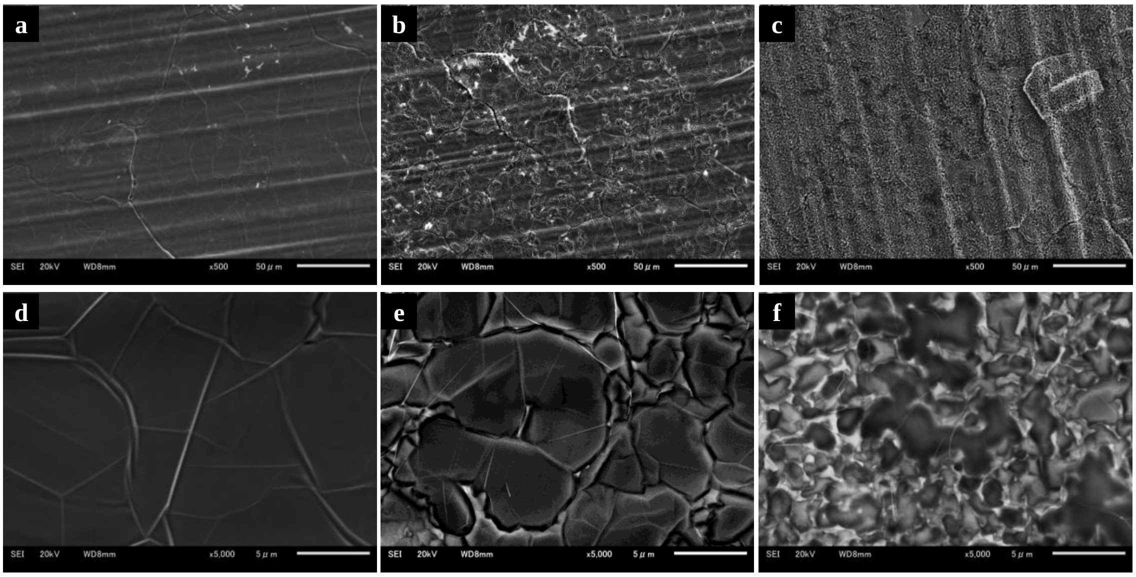

Fig. 2 Bao. J *et al*

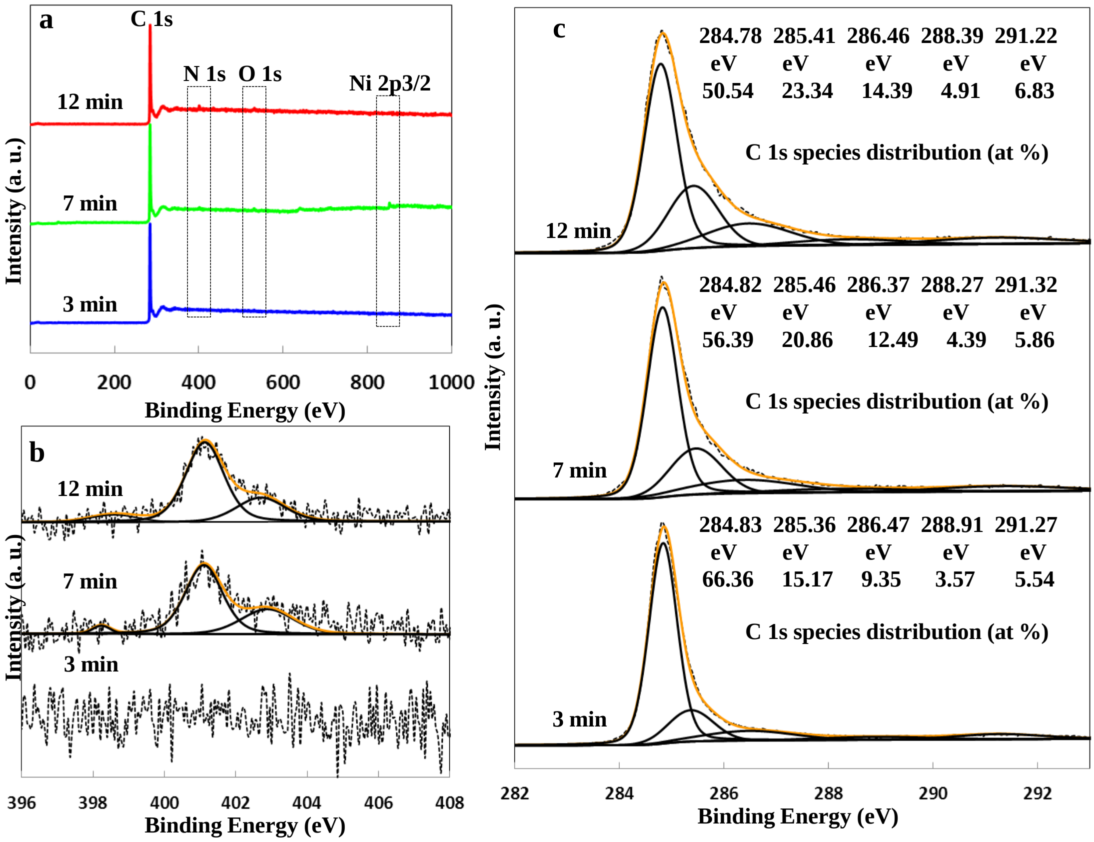

Fig. 3 Bao. J *et al*

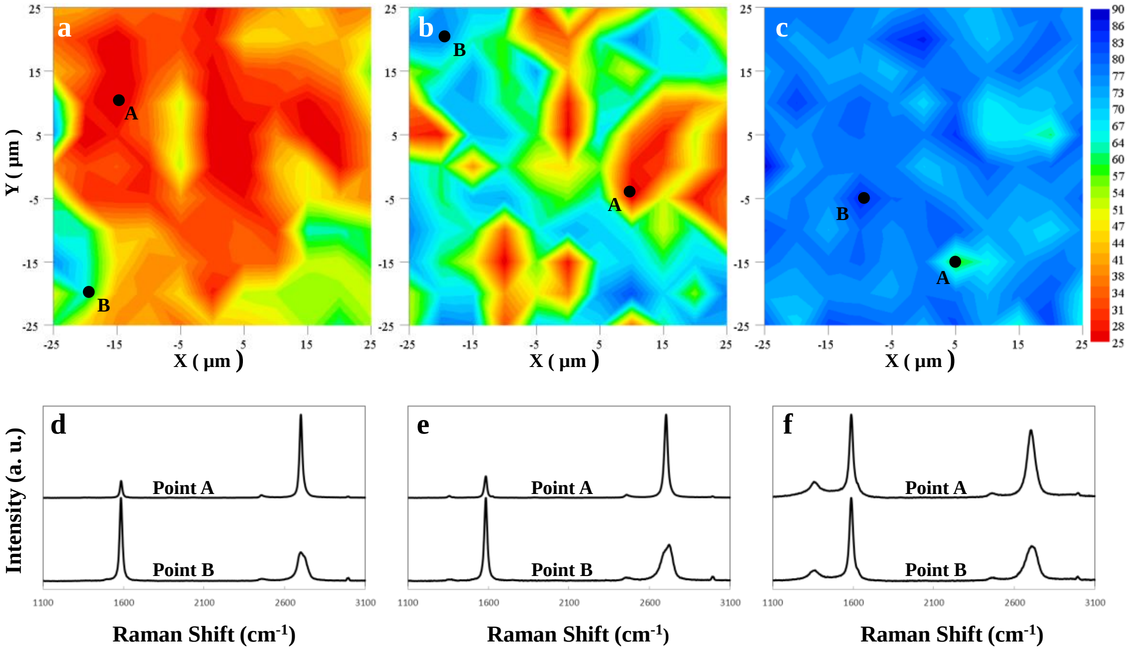

Fig. 4 Bao. J *et al*

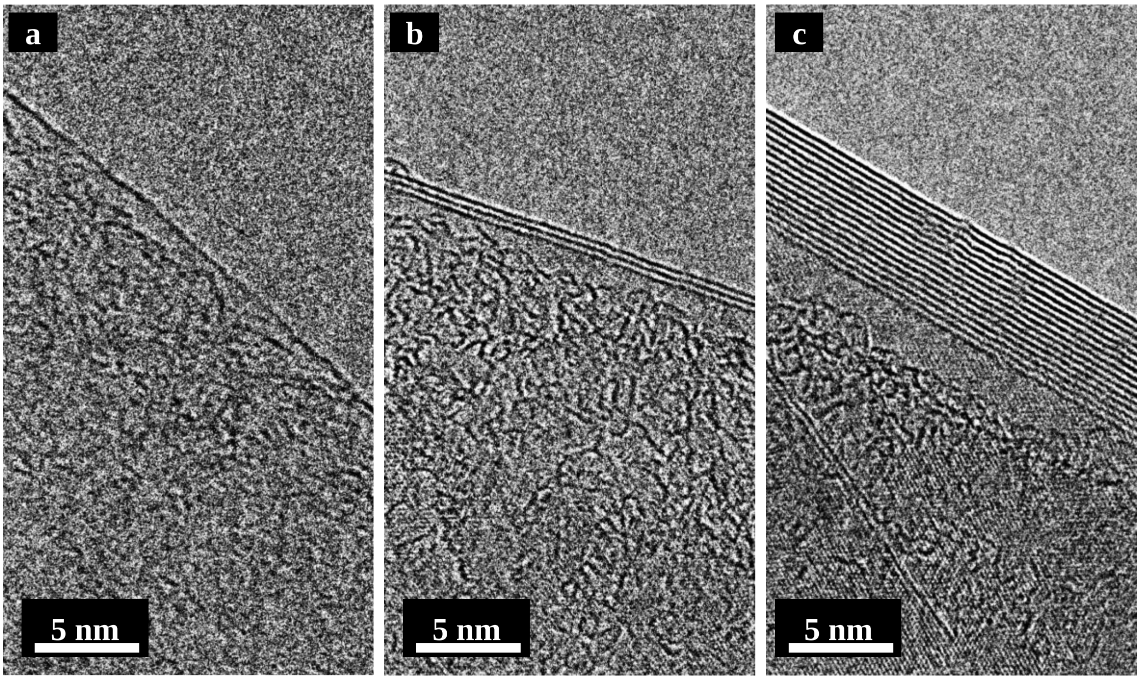

Fig. 5 Bao. J *et al*