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Concentric dopant segregation in CVD-grown N-doped graphene single crystals

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Abstract

Heteroatom doping in graphene leads to bandgap opening and tunable electronic, magnetic and optical properties, which are important for graphene-based electronics applications. In recent years, scalable growth of nitrogen-doped graphene (NG) by chemical vapor deposition (CVD) has been extensively studied because of its potential for practical applications. A phenomenon that occurs exclusively for CVD-grown NG films is the segregation of doping concentration. However, most studies to date are conducted using highly polycrystalline NG films comprising small grain sizes. It is still unknown whether dopant segregation occurs in single crystalline NG domains. Here, we used hexamethylenetetramine ($((\text{CH}_2)_6\text{N}_4)$) as a single-source solid precursor to grow hexagonal-shaped monolayer NG single crystals of ~ 20 μm on Cu substrates. The NG single crystals exhibit discrete concentric hexagonal rings comprising N depleted regions as determined by Raman spectroscopy. Supported by scanning tunneling microscopy experiments, we propose that the segregation of N dopants is caused by a competing N attachment mechanism to either zigzag or Klein edges during growth; where the former should result in higher N concentration and the latter with lower N concentration. This work provides critical insights into the growth mechanism of CVD-grown NG and enables new opportunities to engineer the properties of graphene by fabrication of lateral heterostructures.

Keywords: Chemical vapor deposition, nitrogen-doped graphene, monolayer, single crystal, dopant segregation, Raman spectroscopy

1. Introduction

Graphene is an atomically thin, two-dimensional material comprising sp^2 -hybridized carbon in a honeycomb structure [1]. This phenomenal material has thus been extensively researched since its discovery in 2004[1] due to many of its superior properties such as extremely high intrinsic carrier mobility [1], thermal conductivity [2] and mechanical strength [3], which enable a diverse range of potential applications such as high-frequency field-effect transistors [4], thermal interface material [5], ultrathin protective coatings [6], and space applications [7]. However, since graphene is considered a semi-metal with no bandgap, there are substantial limitations for its practical utilization in many electronic and optical applications. The ability to modulate the electrical properties of graphene is hence important for the integration of graphene-based electronics [8]. To date, one of the most controllable methods to open the bandgap in graphene is by substitutional doping with foreign atoms such as nitrogen (N) or boron (B); thereby enabling either an n-type or p-type semiconductor [9-11].

Doping of graphene can be obtained through: (i) direct synthesis processes such as chemical vapor deposition (CVD) [9], arc-discharge [12, 13], and solvothermal [14], and (ii) post-synthesis processes such as thermal annealing [15], plasma exposure [16, 17], and ion bombardment [18] with N-containing gases. Among these synthesis methods, CVD is considered as a more pragmatic approach to fabricate large-scale doped graphene films with relatively high quality. In particular, most studies have been allocated to N-doped graphene (NG) because of the availability of N- and C-containing precursors such as using a mixture of gaseous sources including methane and ammonia [9, 19, 20], bubbling of liquid sources including acetonitrile [21] and pyridine [22, 23] or by sublimation of solid sources such as melamine [24] and pentachloropyridine [25]. Differing from post-synthesis doping processes where the dopants are randomly distributed, CVD-grown NG films have well-segregated regions comprising higher and lower doping concentration [26]. In addition, sublattice

segregation is also known to occur for N dopants in NG, where the N atoms reside in the same sublattice within regions extending beyond 100 nm [18, 27].

To this end, investigations on the variations in N doping concentration are mainly conducted on highly polycrystalline films with small grain sizes [22, 26, 28]. It is still unknown whether dopant segregation occurs within a NG single crystal. Here, we report the synthesis of hexagonal-shaped monolayer NG single crystals with sizes of $\sim 20\ \mu\text{m}$ on Cu substrates using hexamethylenetetramine (HMTA, $(\text{CH}_2)_6\text{N}_4$) as a single-source solid precursor. We observed discrete segregation of concentric hexagonal rings within a single crystal comprising N depleted regions with widths spanning from ~ 0.5 to $1\ \mu\text{m}$ as determined by Raman spectroscopy. The number of concentric rings that are parallel to the domain edges may vary between individual crystals. We gain further insights into the different dopant sublattice distributions by performing scanning tunneling microscopy (STM).

2. Experimental section

2.1 CVD Growth of NG

NG was grown on Cu foil via thermal CVD. Prior to growth, the Cu foil was dipped into dilute hydrochloric acid and rinsed in deionized (DI) water to remove the coating on Cu surface. The Cu foil was then loaded into a one-inch quartz tube under a constant Ar/H₂ flow of 200:20 sccm. The furnace was ramped up to 1050 °C in 40 min and kept constant for another 1h to anneal the Cu and to remove the surface oxide. After annealing, 3 mg hexamethylenetetramine (HMTA, VWR, product no. 24560, 99%), which was placed in a ceramic holder outside the heating zone, was sublimated at 80 °C to commence film growth. The furnace was kept at 1050 °C for 30 min for film growth. After growth, the lid of the furnace was lifted up for fast cooling.

2.2 Transfer Process

The NG film was transferred onto SiO₂/Si substrate by electrochemical delamination or bubbling transfer [29]. A layer of poly(methyl methacrylate) (PMMA) was first spin coated on top of the NG/Cu sample at 3000 rpm for 30 s. During the electrochemical delamination process, a constant voltage of 5 V was applied using the PMMA/NG/Cu as the cathode, a Pt plate as the anode, and 1 M of NaOH as the electrolyte. The PMMA/NG/Cu was then slowly submerged into the electrolyte for delamination until the PMMA/NG was completely detached from the Cu. The PMMA/NG was rinsed in DI water for several times and was transferred onto a SiO₂/Si substrate. The as-transferred sample was baked at 50 °C for it was dried, and the PMMA was subsequently removed by submerging the sample in acetone for several hours.

2.3 Characterization

Thermogravimetric analysis (TGA, Shimadzu DTG-60H thermal analyzer) was performed to analyze the thermal decomposition profile of HMTA. Scanning electron microscopy (SEM, JSM IT100) was used to determine the morphologies and structures of the NG domains. Raman spectroscopy with laser excitation wavelength of 532 nm (Witec) was performed at room temperature to determine crystalline structure and study the doping profile of the transferred NG domains on SiO₂/Si substrates. Atomic force microscopy (AFM, Cypher scanning probe microscope) was done using tapping mode to measure the thickness of the NG domains. X-ray photoelectron spectroscopy (XPS, PHI Quantera II, using an Al Ka X-ray source) was used to determine the types of bonding and the concentration of N dopant in the NG films. Transmission electron microscopy (TEM, JEOL 2100F) was used to determine the atomic structure of the NG single crystals. The N doping concentration and its atomic configuration within the graphene lattice in as-grown NG single crystals on Cu were determined by Scanning Tunneling Microscopy (STM). The STM measurements were

performed at room temperature in an ultra-high vacuum ScientaOmicron system using tungsten electrochemically etched tips.

3. Results and discussion

Fig. 1a shows the schematic setup of the atmospheric pressure (AP) CVD used to grow monolayer NG single crystals. For this growth, Cu was chosen as a catalytic substrate because of its relatively low C solubility which enables a surface-mediated growth [30, 31], and HMTA was used as a single-source solid precursor for the simultaneous release of C- and N-containing gases. Fig. 1b shows the thermogravimetric analysis (TGA) and its corresponding differential thermal analysis (DTA) spectra of HMTA under an inert environment. A gradual weight loss of 0.8% can be observed at 100 °C, indicating that HMTA starts to sublime even at lower temperature and it fully decomposes with one endothermic peak at 200 °C. Fig. 1c depicts the possible thermal decomposition paths for HMTA. When HMTA sublimates at an elevated temperature, it decomposes into various compounds such as trimethylamine ((CH₃)₃N), dimethylamine ((CH₃)₂NH), methylamine (CH₃NH₂), ethylene imine ((CH₂)₂NH), propionitrile (CH₃CH₂CN), and acetonitrile (CH₃CN) [32, 33]. These heavier compounds (or HMTA itself) can be further (directly) broken down into lighter gases such as methane (CH₄), ammonia (NH₃), hydrogen (H₂), and nitrogen (N₂) [32, 33], which are essentially the sources needed to fabricate NG films [9]. Since the release of the precursor gases can be controlled by using an appropriate sublimation temperature, the use of this single-source solid precursor can thus enable a relatively uniform growth of NG single crystals. We determined that the optimal sublimation temperature is 80 °C which resulted in well-defined hexagonal-shaped NG domains with sizes of up to ~20 μm, whereas higher temperature would yield continuous layer(s) of NG film. We also found that a growth temperature of 1050 °C is needed to synthesize good quality monolayers, whereas lower

growth temperature would result in more disordered and multilayer growth (Fig. S1–S3, Supplementary materials).

Because of the impermeable nature of graphene [34], the underlying Cu has temporal resistance to oxidation [6, 35]. Hence, a quick method to determine the presence of graphene is to oxidize the Cu surface by heating the as-grown sample in air [36]. Fig. 2a shows an optical image of an air-oxidized NG/Cu sample which clearly reveals the hexagonal edges of the NG domains. The regions that are covered by the NG domains retained the same optical contrast as nonoxidized Cu (bright contrast), whereas the regions that are exposed became oxidized (dark contrast). Fig. 2b shows a typical SEM image of NG domains on Cu. Some of the observed domains have a complete hexagonal shape, which is referred to as a single crystal, whereas others comprise merged domains because of closely situated nucleation sites. Fig. 2c shows an optical image of the transferred NG domains on the SiO₂/Si substrate. The hexagonal shape of a NG single crystal is outlined, showing that the morphologies of the NG domains are well preserved after transfer. Fig. 2d shows an AFM image of a NG domain with a thickness of ~0.8 nm corresponding to a single layer. Transmission electron microscopy (TEM) was used to determine the microstructure of the NG crystals. Fig. 2e shows a typical bright-field TEM image of a suspended NG film covering over a grid hole. Folding and tears in some regions of the transferred film can be readily observed because of the rough handling procedures of transfer process. The monolayer nature and crystalline structure of the NG film were further determined by the high-magnification TEM images which were taken at the edge and the interior of the suspended NG film, as shown in Fig. 2f,g, respectively. The corresponding SAED pattern showed one set of hexagonal diffraction spots, which confirms the hexagonal lattice structure of the NG single crystal.

The chemical composition and bonding structures of the transferred NG were investigated using XPS. Fig. 3a,b shows the deconvoluted high-resolution C 1s and N 1s XPS spectra,

respectively. There are four components in the C 1s spectrum; the main peak at 284.7 eV corresponds to the graphitic sp^2 C [9], indicating that most of the C atoms in the NG are arranged in a conjugated honeycomb lattice, whereas the peaks centering at 285.9 eV, 287.1 eV, and 289.1 eV are attributed to the N- sp^2 C, N- sp^3 C bonds, and oxidized C, respectively [9, 37]. For the N 1s spectrum, two components can be distinguished. The peak located at 399.7 eV corresponds to graphitic N which means that N atoms are substitutionally doped into the graphene lattice, while a less intense peak at 402.2 eV corresponds to oxidized N [13, 15, 22, 38, 39]. The extracted N doping concentration based on the integral intensities of C 1s and N 1s peaks is ~0.6%. The relatively low doping concentration is attributed to the high growth temperature that favors the formation of C–C bonds while suppressing N–C bonds [20, 40]. Raman spectroscopy was further carried out to investigate the crystallography and doping characteristics of the as-prepared NG (Fig. 3c). Besides two typical peaks of graphene at $\sim 1588\text{ cm}^{-1}$ (G band) and $\sim 2676\text{ cm}^{-1}$ (2D band), the NG single crystal showed two additional peaks at $\sim 1343\text{ cm}^{-1}$ (D band) and $\sim 1623\text{ cm}^{-1}$ (D' band) [41] which are activated by defects or lattice distortion and are characteristic of NG [40, 42-44].

Fig. 4a,b shows an optical image of NG domains transferred onto a SiO_2/Si substrate and its corresponding Raman spectra collected at various positions within a single-crystal domain. The Raman spectra are consistent which comprise all the characteristic peaks (D, G, D' and 2D peaks), indicating that N dopants are present throughout the entire domain [9, 45, 46]. To investigate the dopant distribution, we performed Raman mapping over the domain within the black boxed region in Fig. 4a. Fig. 4c–e shows the intensity maps of the D, G and 2D bands, respectively. Remarkably, concentric hexagonal rings with widths of ~ 0.5 to $1\text{ }\mu\text{m}$, parallel to the edges of the domain, can be readily observed in the D and 2D intensity maps, whereas the G band intensity remained almost consistent throughout the domain. These rings comprise

Raman spectra with a slight attenuation in the D band and a more intense 2D band (Fig. 4f), indicating that these regions have a relatively lower doping concentration [26].

Raman intensity ratios of I_D/I_G and I_{2D}/I_G have been previously used to monitor the doping level in graphene, it is found that I_D/I_G increases while I_{2D}/I_G decreases for increasing doping [47-49]. Thus, to further verify the inhomogeneous distribution of N dopants within the single crystal, we mapped out the intensity ratios of I_G/I_D and I_{2D}/I_G in Fig. 5a,b respectively. Note that I_G/I_D instead of I_D/I_G is mapped to enhance the contrast. As can be seen in the corresponding plots below each Raman maps extracted across the black lines, the concentric rings (indicated by blue arrows) exhibit a decreased I_D/I_G ratio of $\sim 0.107 \pm 0.022$ and a increased I_{2D}/I_G ratio of $\sim 0.146 \pm 0.047$ compared to regions outside the concentric rings. Hence, we can reasonably conclude that there are well-segregated regions comprising relatively lower concentration of N dopants within the single crystal which extends up to $\sim 1 \mu\text{m}$ [47]. Because of the opposing trends in I_D/I_G and I_{2D}/I_G , the I_{2D}/I_D ratio amplifies the doping variations within the NG single crystals and can be used as a quick method for doping homogeneity characterization [26]. Fig. 6a–d shows four representative I_{2D}/I_D Raman maps collected within one transferred sample under the same CVD growth. It is observed that the number of concentric rings may vary between individual single crystals, and even for adjacent merged grains as shown in Fig. 6c. From our 15 randomly selected samples of single crystals, we observed that these rings can range from 1 to 4, and none of them is without any concentric ring. Furthermore, by increasing (decreasing) the H_2 flow to reduce (increase) the growth rate of the single crystal, the presence of concentric ring(s) is consistently observed (Fig. S4, Supplementary materials).

Atomic resolution STM measurements were performed on the NG/Cu samples to obtain direct visualization of the N dopants and their atomic configurations. Fig. 7a shows an atomically resolved topography of the NG sample. In agreement with previous reports [11, 27,

50-52], graphitic N dopant in graphene appears dark in the STM image, while the three surrounding C atoms are bright, forming a triangle, due to an increased local density of states (DOS). The line profile across the dopant (inset of Fig. 7a) yielded atomic corrugation with an apparent maximum out-of-plane height of ~50 pm. STM measurement of the differential conductance, dI/dV , was performed on the N dopant indicated in Fig. 7a. The dI/dV curve in Fig. 7b shows distinct gap-like features centered at zero bias and a local conductance minimum at ~230 meV. The gap-like feature arises from phonon-mediated inelastic tunneling electrons into graphene, and the -230 meV feature results from inelastic tunneling to the Dirac point of an electron-doped graphene layer. Given that the geometry, the height of the N atoms and the distinct features in the dI/dV curve are all in correspondence to graphitic N doping [26, 27, 52, 53], we use this to further analyze the occupancy of the N dopants within the graphene sublattice.

Recently, there have been several groups that reported heterogeneity and segregation of N dopants in CVD-grown NG films [18, 26, 27]. For example, Zhao et al. evidenced heterogeneity of N doping concentration in polycrystalline NG films where N dopants are depleted along the grain boundaries and edges for over micron length scales [26]. Zabet-Khosousi et al. reported the segregation of N dopants where the N atoms preferentially occupy the same sublattice which extends to over 100 nm [18]. In our STM measurement on NG sample, we observed similar phenomenon where N dopants can occupy two different sublattices of graphene, as can be seen within the mirroring blue and red triangles in Fig. 7c. However, segregation in the distribution of the N dopants can be observed where clusters of N atoms often occupy the same sublattice [18, 27]. Fig. 7d shows an STM image of the NG sample, where N dopants occupying two different sublattices are indicated by the blue and red triangles, respectively. Importantly, Fig. 7d also shows a phenomenon of sublattice

segregation of N dopants, that is, the two clusters of N dopants located at different sublattices are obviously segregated from each other.

From our aforementioned analysis on relatively large hexagonal-shaped single-crystal NG, we denote three important observations that provide further insights into the growth mechanism: (i) the concentric rings comprising depleted N dopants have parallel edges to the single-crystal NG domain with widths spanning up to $\sim 1\ \mu\text{m}$, (ii) the number of concentric rings is not uniform and can vary between adjacent domains, and (iii) there is a segregation of N dopants that occupy two different sublattices of graphene.

Because the hexagonal concentric rings shown in the Raman maps of our NG sample have parallel edges to the single-crystal domain, which are very similar to the isotope-labeled Raman maps of graphene [31], they must form along the growth fronts of the NG domain by edge attachment in a surface-mediated growth process [30, 31, 54]. The variation in concentration of N-containing precursor gas (i.e., NH_3) during growth is unlikely the reason for dopant depletion because the number of concentric rings may vary between similar-sized single-crystal domains where the distances between each successive rings are different. Furthermore, the decomposition of HMTA cannot yield such intermittent trend comprising alternating high and low concentration of N when using a constant sublimation temperature. The depletion of N dopants along grain boundaries [26] also cannot explain our observation because the segregation occurs within a single crystal with no grain boundary. Hence, based on our STM measurements, we propose that the observed heterogeneity is the consequence of sublattice selectivity of N dopants.

For CVD growth of NG, two types of N edge attachments are considered where energy is at minima: zigzag and Klein edges [18]. These edges thus dictate the corresponding sublattices the substitutional N atoms occupied within the graphene lattice. Although N

attachment to either edges are considered to be energetically stable, as evidenced by the N atoms occupying different sublattices, the zigzag edge is slightly more favorable than the Klein edge (< 0.04 eV) [18]. Therefore, we expect that edge attachment of N to the zigzag edges should be more dominant and these regions should comprise slightly higher N concentration as compared to Klein edges. However, because the difference in energy between zigzag and Klein edges is relatively small, the occurrence of N attachment to Klein edges is viable as well. The discrete segregated regions with N dopants in different sublattices that extend to over micrometer length scales imply that the same edge attachment of N (to either zigzag or Klein) replicates itself in successive rows as a consequence of energy minimization [18]; thereby resulting in the formation of concentric segregated hexagons in the Raman maps of hexagonal-shaped NG domains.

The transition of N attachment via zigzag edges to Klein edges is more complex and not fully understood. Zabet-Khosousi et al. suggested that this could arise from either merged NG grains or an abrupt change on the Cu surface such as transient terrace steps [18]. However, both these explanations are not applicable in our hypothesis. The segregation of N dopants is observed in a single crystalline structure and the concentric hexagonal rings that have parallel edges to the NG domain cannot be caused by the underlying Cu structure. The transition from high to low N concentration and vice-versa must have happened during the growth of the single crystal and their occurrences may differ between individual crystals as observed by the non-uniformity in the number of concentric rings.

4. Conclusions

In summary, large hexagonal-shaped monolayer NG single crystals were grown on Cu substrates by CVD using HMTA as a single-source solid precursor. Importantly, Raman characterization evidenced that dopant segregation exists in monolayer NG single crystals.

Concentric hexagonal rings with edges parallel to the NG crystal and widths of ~ 0.5 to $1\ \mu\text{m}$ comprising N depleted regions are readily observed as determined by the attenuation in D band and more intense 2D band. We observed that the number of concentric rings is not dependent on the size of the NG crystal and may vary between adjacent single crystals. STM measurements confirmed that N atoms are introduced into different sublattices of graphene in substitutional sites. The doping inhomogeneity is attributed to sublattice selectivity of the N dopants by attachment via zigzag or Klein edges, where the former resulted in higher doping concentration and the latter are N depleted regions. This work provides important insights into the growth mechanism of CVD-grown NG single crystals and enables new opportunities for tailoring the electronic and optical properties in graphene.

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Supplementary materials

Figs. S1–S4, showing additional optical, SEM, AFM images and Raman maps of various NG single crystals grown under different conditions.

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Figure captions

Fig. 1. (a) Schematic layout of the CVD setup for NG films growth. (b) TGA (black trace) and DTA (blue trace) spectra of HMTA under an inert atmosphere. (c) Possible reaction pathways for the formation of NG by using HMTA as the single-source precursor.

Fig. 2. (a) Optical image of an air-oxidized NG/Cu sample. The bright and dark contrasts correspond to the NG domains and oxidized Cu surface, respectively. (b) SEM image of the as-grown hexagonal-shaped NG single crystals on Cu substrate. The inset shows the corresponding magnified SEM image. (c) Optical image of the transferred NG on SiO₂/Si substrate. (d) AFM image of an edge of a hexagonal-shaped NG single crystal on SiO₂/Si substrate. The inset shows the height profile along the blue line. (e) Typical low-magnification TEM image of a suspended NG film over a TEM grid hole. High-resolution TEM images taken at the (f) edge and (g) interior of the NG film. The inset in (g) shows its corresponding SAED.

Fig. 3. Deconvoluted high-resolution (a) C 1s and (b) N 1s XPS spectra of transferred NG on SiO₂/Si substrate. (c) Raman spectrum of monolayer single-crystal NG on SiO₂/Si substrate.

Fig. 4. (a) Optical image of the transferred NG single crystals on SiO₂/Si substrate. (b) Raman spectra acquired at different positions over a NG single crystal in (a). (c–e) Raman intensity maps of the (c) D, (d) G, and (e) 2D bands over the black boxed region in (a). (f) Comparison of the Raman spectra acquired at the black and red spots as indicated in (e).

Fig. 5. Raman maps of the intensity ratios, (a) I_G/I_D and (b) I_{2D}/I_G , of the NG single crystal. The corresponding plots below are extracted across the black line.

Fig. 6. (a–d) Raman maps of I_{2D}/I_D of various NG single crystals which exhibit different number of concentric hexagonal rings for different individual domains.

Fig. 7. (a) An atomically resolved STM image of an N dopant. The inset shows the height profile across the dopant. (b) dI/dV curve obtained at the N dopant. (c) STM images of individual N dopants occupying different graphene sublattices indicated by blue and red triangle. (d) Large-area STM image showing discrete segregation of the N dopants occupying different sublattices.

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Supporting materials

Concentric dopant segregation in CVD-grown N-doped graphene single crystals

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Fig. S1. (a–e) SEM images of NG/Cu grown at (a) 800 °C, (b) 900 °C, (c) 950 °C, (d) 1000 °C, and (e) 1050 °C. The insets show their corresponding magnified SEM images.

Fig. S2. (a–e) Optical images of transferred NG on SiO₂/Si substrates grown at (a) 800 °C, (b) 900 °C, (c) 950 °C, (d) 1000 °C, and (e) 1050 °C. (f) Corresponding Raman spectra of the NG in (a–e).

Fig. S3. AFM images of NG on SiO₂/Si substrates which were grown at (a) 900 °C, (b) 950 °C, (c) 1000 °C, and (d) 1050 °C.

Fig. S4. Raman maps of I_{2D}/I_D of the NG single crystals grown using (a) 10 sccm, (b) 20 sccm and (c) 40 sccm of H_2 flow rate.