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PAPER

Effects of temperature and ammonia flow rate on the chemical vapour deposition growth of nitrogen-doped graphene†

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We doped graphene *in situ* during synthesis from methane and ammonia on copper in a low-pressure chemical vapour deposition system, and investigated the effect of the synthesis temperature and ammonia concentration on the growth. Raman and X-ray photoelectron spectroscopy was used to investigate the quality and nitrogen content of the graphene and demonstrated that decreasing the synthesis temperature and increasing the ammonia flow rate results in an increase in the concentration of nitrogen dopants up to *ca.* 2.1% overall. However, concurrent SEM studies demonstrate that decreasing both the growth temperature from 1000 to 900 °C and increasing the N/C precursor ratio from 1/50 to 1/10 significantly decreased the growth rate by a factor of six overall. Using scanning tunneling microscopy we show that the nitrogen was incorporated mainly in substitutional configuration, while current imaging tunneling spectroscopy showed that the effect of the nitrogen on the density of states was visible only over a few atom distances.

1. Introduction

Graphene has many exceptional properties and is expected to have several important applications.[1,2] However, as graphene is a zero gap semiconductor with an inert surface, changing its electronic properties or surface chemistry may be beneficial for particular applications, for example, nanoelectronic devices and sensors. Heteroatomic doping is a powerful way to tailor material properties, with initial studies into demonstrating the capability to alter the electronic properties of graphene.[3] In recent years several experimental techniques have been developed to dope the carbon lattice, including *in situ* methods, where doping occurs simultaneously as graphene domains form,[4–6] and post-production modification techniques.[7,8] However, comparing results from different laboratories, that were obtained using diverse equipment, and with various growth parameters is difficult if not impossible. Therefore, it is important to conduct detailed and systematic parameter studies using a constant experimental set-up. The influence of individual parameters on

the growth of graphene can then be identified and harnessed to promote desirable properties. Systematic growth studies are therefore fundamentally important before doped CVD graphene can be industrially exploited.

Although heteroatomic doping seems a straightforward way to tune the properties of graphene films, controlled introduction of dopants is challenging. Since bonding of sp²-hybridized carbon atoms in graphene is very strong, substitutional doping (*i.e.*, replacing carbon atoms in a hexagonal lattice with atoms of another element) hardly occurs, except for chemical bonding between dopants and carbon atoms at imperfection sites, such as point defects or edges. Schiros *et al.* have shown that different C–N bond types, including graphitic, pyridinic, and nitrilic, can exist in a single nitrogen-doped graphene sheet and that these bond types have profoundly different effects on the carrier concentration. Consequently, control over the dopant bond type is a crucial requirement in advancing graphene electronics.[9] The incorporation of nitrogen into the carbon network is energetically unfavourable,[10] and so less doping is likely at high temperatures. For example, increasing the growth temperature from 800 to 900 °C decreased the nitrogen content of carbon nanotubes by half.[11] On the other hand, Kidambe *et al.* have shown that the quality of the graphene is compromised at lower growth temperature,[12] even though lower growth temperature would be beneficial to reduce the substrate evaporation and step formation during graphene growth.[13,14] The temperature also has a significant influence on the graphene

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Phys. Chem. Chem. Phys., 2014, **00**, 1—7 | 1

growth rate, which cannot be ignored. Therefore we investigated the effect of the most important experimental parameters: (i) the synthesis temperature and (ii) the ammonia concentration on the growth of nitrogen-doped graphene. This work shows the relationship between these synthesis parameters and the quality, growth rate, and dopant concentration of nitrogen-doped graphene, allowing the optimum conditions to be identified for the growth of graphene with desirable properties for use in new materials for future applications. The incorporation of nitrogen was investigated using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM) and current imaging tunneling spectroscopy (CITS).

2. Experimental

2.1. Synthesis of nitrogen-doped graphene

Graphene was synthesised by low-pressure chemical vapour deposition using CH_4 as the carbon source and NH_3 as the nitrogen source, in the presence of excess H_2 on 25 μm thick Cu foils (99.999%; Alfa Aesar). The CVD set-up consisted of a quartz tube (20 mm ID) located inside a horizontal cylindrical furnace and connected to a scroll pump. The Cu substrates were washed in acetic acid for 10 minutes and placed inside the quartz tube but kept outside the hot zone of the furnace. The system was evacuated to a base pressure of <0.01 Torr, purged with Ar, backfilled with 500 sccm H_2 at 3.2 Torr and the furnace was heated to 1035 °C. The Cu substrates were rapidly heated by shifting them into the hot zone of the furnace and annealed at 1035 °C for 30 minutes using the same H_2 flow. Once the substrates were annealed, the furnace was cooled to the growth temperature in 20 minutes, and nitrogen-doped graphene was grown using 5 sccm CH_4, 0.1–0.5 sccm NH_3 and 100–500 sccm H_2 flow for 5–30 min at 900–1000 °C. The reference pristine (undoped) sample was grown using 5 sccm CH_4 and 500 sccm H_2 flow for 5 min at 1000 °C. Depending on the total gas flow the pressure changed between 1.3 and 3.3 Torr. After the growth period the precursor flow was switched off and the substrates were quenched by rapidly shifting out of the hot zone to cool in a hydrogen atmosphere.

2.2. Characterisation of the samples

The samples were characterised by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM)/current imaging tunnelling spectroscopy (CITS). A JEOL JSM-6500F was operated at 5 kV for SEM imaging. TEM was conducted on a JEOL 2010 TEM operated at 200 kV. A JY Horiba Labram Raman spectrometer equipped with a 532 nm laser was used to collect Raman data. Care was taken to use low laser power (<1 mW) in order to avoid any laser-induced sample damage during the measurements. We observed some fluctuation of the peak position and intensity ratios on the same sample[3,15] and so present representative spectra with peak positions near the average of multiple measurements. XPS measurements were performed using a

Kratos AXIS Ultra DLD with monochromatic Al Kα excitation. The STM/CITS images were recorded with a Veeco Nanoscope E in air at 500 pA and 100 mV using Pt90/Ir10 tips on as-grown samples without transferring from Cu foil. Although contamination species were present on the graphene, consecutive scans of the same area with a small tip-sample distance removed the physisorbed contamination. Images were recorded once consecutive scans stabilised and showed no observable differences.

3. Results and discussion

We investigated the effect of the experimental parameters on the quality and growth rate of nitrogen-doped graphene. A TEM image of a nitrogen-doped graphene domain and the corresponding electron diffraction pattern characteristic to single-layer graphene are shown on Fig. S1 (ESI†). Bilayer and multi-layer regions were also identified *via* TEM imaging. In order to achieve uniform incorporation of nitrogen in the graphene lattice, the nitrogen precursor was introduced simultaneously with the carbon precursor. Since the incorporation of nitrogen in graphitic carbon network is more likely at lower temperatures[11] and nitrogen atoms are less strongly bound to Cu surfaces than carbon atoms,[16] it is expected that graphene grown at lower temperature should have higher nitrogen content. Therefore we investigated the effect of the synthesis temperature and the ammonia flow rate on the dopant concentration, growth rate, nucleation density and coverage of nitrogen-doped graphene.

We confirmed the nitrogen doping of graphene synthesised with NH_3 using Raman spectroscopy (Fig. 1). Changes in the position of the characteristic Raman bands of graphene – the G peak and 2D peak (also known as G′ peak) – indicate n-type doping due to the influence of substitutional nitrogen dopants.[17]
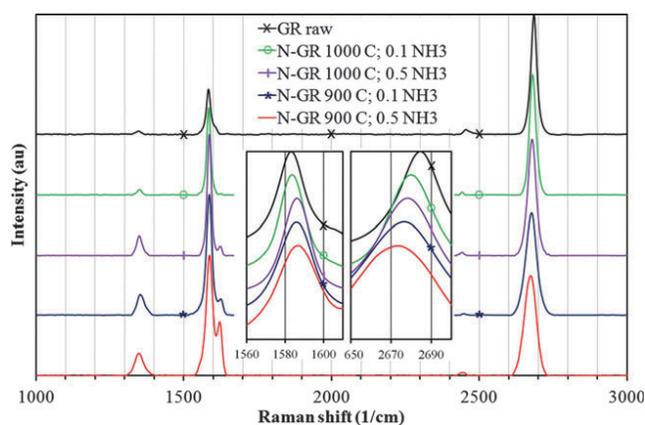
Fig. 1 Representative Raman spectra of nitrogen-doped and raw graphene domains on Cu recorded with 532 nm laser. A decrease in the 2D/G intensity ratio, increase in the D and D′ peak intensity, and shift in the position of the G and 2D peaks (inset) demonstrates the incorporation of nitrogen dopants. Greater doping is observed for lower synthesis temperatures and higher NH_3 flow rates. We observed fluctuation of the peak positions in the range of 2 cm^{-1}, the figure shows representative spectra with peak positions near the average of multiple measurements.

In addition, heteroatom doped samples typically show a strong D peak, and also exhibit an additional peak at 1620 cm^{-1} (known as the D$'$ band) due to the inter-valley and intra-valley double resonance process in graphene.[18,19] We compared the position of the G and 2D peaks for graphene samples synthesised using NH$_3$ with peak positions from a pristine graphene sample that was synthesised under equivalent conditions of 5 sccm CH$_4$ and 500 sccm H$_2$ at 1000 °C for 5 minutes. For the pristine graphene the G peak appeared at 1583 cm^{-1} and the 2D peak at 2685 cm^{-1} (Fig. 1). The G peak position was blue-shifted and the 2D peak position was red-shifted for graphene synthesised with NH$_3$, thereby confirming nitrogen doping (Fig. 1).

Once nitrogen doping was confirmed, Raman spectroscopy was used to investigate the quality and relative dopant concentration of nitrogen-doped graphene synthesised with different NH$_3$ flow rates (0.1 and 0.5 sccm) and at different synthesis temperatures (900 and 1000 °C). Although a quantitative estimate of dopant concentration is possible through the shift of peak positions, this can be misleading.[18] Instead, the relative amount of doping between samples can be inferred by the magnitude of different peak shifts. The intensity of the D and D$'$ peaks also provides some quantitative indication of dopant concentration.

Our experiments demonstrate that increasing the NH$_3$ flow rate from 0.1 sccm to 0.5 sccm resulted in a blue-shift of the G peak, and a red-shift of the 2D peak, suggesting an increase in nitrogen doping (Fig. 1). For instance, when comparing nitrogen-doped graphene produced at 1000 °C using 0.5 sccm NH$_3$ with samples synthesised using 0.1 sccm NH$_3$, the average 2D peak position red-shifted by ∼2 cm^{-1} and the average G peak position blue-shifted by ∼2 cm^{-1}. We therefore conclude that a higher dopant concentration was achieved by increasing the ammonia flow rate.

Further studies demonstrate that decreasing the synthesis temperature from 1000 °C to 900 °C also resulted in a blue-shift of the G peak position, and a red-shift of the 2D peak position (Fig. 1, comparing green line with blue line, and purple line with red line). For instance, comparing nitrogen-doped graphene produced at 1000 °C using 0.1 sccm NH$_3$ with samples synthesised at 900 °C the average 2D peak position red-shifted by ∼4 cm^{-1} and the average G peak position blue-shifted by ∼2 cm^{-1} (Fig. 1). We therefore conclude that a higher dopant concentration was achieved by reducing the synthesis temperature. This is the first observation demonstrating the importance of synthesis temperature on the dopant concentration of nitrogen-doped graphene, and is in agreement with previous studies on the influence on temperature on the nitrogen-doping of carbon nanotubes.[11]

The magnitude of the shift of Raman peak positions was greater for samples synthesised at lower temperatures (e.g. 900 °C rather than 1000 °C) compared to samples synthesised with higher ammonia flow rates (e.g. 0.5 sccm rather than 0.1 sccm). For instance, the two samples synthesised at 900 °C, with 0.1 sccm NH$_3$ and 0.5 NH$_3$, have 2D peaks red-shifted ∼8 cm^{-1} and ∼11 cm^{-1} and G peaks blue-shifted ∼3 cm^{-1} and ∼4 cm^{-1}, respectively, whereas the two samples synthesised at 1000 °C, again with 0.1 NH$_3$ and 0.5 sccm NH$_3$, have 2D peaks

red-shifted only ∼4 cm^{-1} and ∼5 cm^{-1} and G peaks blue-shifted only ∼1 cm^{-1} and ∼3 cm^{-1}, respectively. The synthesis temperature therefore has a greater influence on the peak shift (and hence nitrogen dopant concentration), rather than the NH$_3$ flow rate as one might be expected. In other words, reducing the synthesis temperature by 100 °C results in a greater increase in nitrogen doping than a five times increase in NH$_3$ flow rate. We therefore conclude that the synthesis temperature is an overriding parameter for controlling the concentration of nitrogen-doped graphene. This observation has important implications if manufacturers are to maximise the concentration of nitrogen-doped graphene while reducing production costs.

From the Raman spectra in Fig. 1, an increase of the intensity of the D peak and the D$'$ peak is concurrently observed for increasing nitrogen-doping of the sample. For instance, an increase in D and D$'$ peak intensity is observed between samples synthesised at 1000 °C with 0.1 sccm NH$_3$ and 0.5 sccm NH$_3$, and this trend continues for samples synthesised at 900 °C with 0.1 sccm and 0.5 sccm NH$_3$ (Fig. 1). The increase in the disorder in the graphene lattice with increased nitrogen-doping also results in a decrease in the 2D peak intensity. This is due to the fact that increased disorder in the lattice decreases the probability of two phonon scattering required to generate the 2D peak.[20]

Based on the Raman spectroscopy the nitrogen content of the graphene domains produced at lower temperatures and higher NH$_3$ flow rate are expected to have the highest nitrogen concentration. Therefore, we conducted complementary XPS analysis of nitrogen-doped graphene synthesised at 900 °C with 0.5 sccm NH$_3$, (Fig. 2) to determine the maximum concentration and bonding configuration of N in the samples. XPS measurements were performed both before and after a 300 °C anneal in UHV (Fig. 2a, c, e, and Fig. 2b, d, f, respectively). C 1s peaks detected at ∼284.4 eV and ∼285.0 eV (Fig. 2a and b) correspond to graphite-like sp^2-hybridised carbon and other hydrocarbon species respectively. The sp^2-hybridised carbon peak is typical for graphene surfaces but also for other carbon contaminants as well, two peaks at ∼288.3 eV and ∼286.4 eV are also observed and nominally assigned as acid ester and alcohol groups respectively.[21] These peaks are associated with contaminants on the surface that have been adsorbed whilst the sample was in ambient conditions. These peaks also coincide with the O 1s peak observed in Fig. 2c and d at ∼531.7 eV, which is attributed to oxygen-bound carbon species. This peak is also related to copper hydroxide,[22] as elemental analysis shows that this peak cannot be solely due to carbon contaminants. A copper oxide peak is also observed in the O 1s spectra at ∼530.3 eV.

The comparative spectra in Fig. 2a and b therefore show a reduction in carbon contaminants after the annealing process. The peaks associated with acid ester and alcohol groups are shown to decrease, as do the peaks associated with hydrocarbons. The peak in the O 1s spectra associated with organic species also reduces significantly, as expected.

The XPS spectra in Fig. 2e and f relate to the nitrogen content in the sample. Two distinct peaks are visible even with
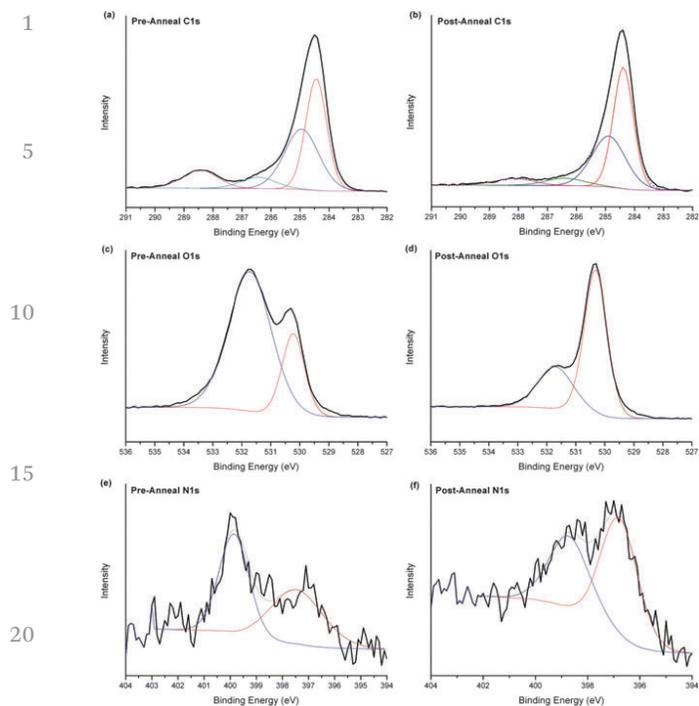
Fig. 2 XPS spectra for nitrogen-doped graphene synthesised with 5 sccm CH_4 and 0.5 sccm NH_3 at 900 °C. XPS obtained on a copper substrate before (a, c, e) and after (b, d, f) the sample was annealed at 300 °C for 30 min in UHV, with the associated C 1s (a and b), O 1s (c and d) and N 1s (e and f) peak-fitted spectra.

Fig. 3 SEM images of graphene domains on Cu. (a) Sample grown at 1000 °C with 0.1 sccm NH_3, 5 sccm CH_4 and 500 sccm H_2 in 5 min, with growth rate of ~1.58 μm min^{-1}; (b) decrease of growth temperature to 900 °C decreased the growth rate of the nitrogen-doped graphene domains significantly to ~0.34 μm min^{-1}; (c) nearly full coverage for sample grown at 1000 °C with 0.5 sccm NH_3 in 10 min, but equivalent to a reduced growth rate of only 1.34 μm min^{-1} due to increased NH_3 flow; (d) incomplete maximum surface coverage at 900 °C with 0.5 NH_3 and 100 H_2 in 30 min.

a low signal due to the proportionally small amount of nitrogen present in the surface. These two peaks relate to carbon-bound nitrogen and copper nitride species in the sample, with peak positions of ~398.7–399.8 eV and ~396.8–397.5 eV respectively. After annealing the amount of nitrogen associated with carbon is still approximately the same, however, the proportion of copper nitride present in the sample increases and appears to be distributed deeper in the sample due the rise in background on the high binding energy side of the peak caused by inelastically scattered electrons. Although separate peaks are not fitted for pyridinic and pyrrolic conformations due to the low signal-to-noise ratio and the large uncertainty in the peak positions from literature,[23] a shift from 399.8 eV to 398.7 eV is observed for the C–N peak after the sample is heated, indicating a reduction in pyrrolic species as the contamination on the surface is reduced, and an increase in the ratio of pyridinic/pyrrolic species present. There is no peak wholly attributed to amide species in the C 1s spectra due to the larger percentage of carbon–oxygen species obviously present.

By comparing the C 1s peaks – that are associated with graphene (and other sp^2-hybridised carbon) – with the N 1s peak – associated with carbon-bound nitrogen after the annealing process – we can suggest that the more heavily nitrogen-doped graphene sample has a nitrogen content of ca. 2.1% overall. However, the true percentage of nitrogen present in the graphene could only be determined if there was no adsorbed contamination still present after the annealing process. For comparison, an undoped graphene sample that was prepared using the same procedure, but without any NH_3 exposure, was found to have a carbon-bound nitrogen content of 0.8% due to adventitious contamination, present because of unavoidable exposure to ambient conditions before XPS analysis.

To investigate the influence of the synthesis parameters on the growth rate of nitrogen-doped graphene experiments were stopped before the copper substrate was fully covered by graphene domains. Domain sizes were then compared via SEM imaging (Fig. 3). Our experiments demonstrate that decreasing the synthesis temperature and increasing the ammonia flow reduces the growth rate of nitrogen-doped graphene. With respect to the influence of temperature, the average graphene domain size was ~7.9 μm at 1000 °C (Fig. 3a), but only ~1.7 μm at 900 °C (Fig. 3b) when using 5 sccm CH_4, 0.1 sccm NH_3 and 500 sccm H_2 for 5 minutes. This equates to a growth rate of 1.58 μm min^{-1} at 1000 °C, which decreased nearly three times to 0.54 μm min^{-1} at 950 °C, and further decreased to 0.34 μm min^{-1} at 900 °C (Fig. 4). These observations follow a similar trend to previous studies into the influence of synthesis temperature on the growth rate of pristine graphene.[24] Increasing the NH_3 flow also decreased the growth rate, and as a consequence it was necessary to increase the duration of experiments and/or decrease the hydrogen flow so that domains were of an appreciable size for SEM imaging. This change in time and hydrogen concentration helped to grow larger graphene domains without influencing their quality, and provides the opportunity for comparing the growth rate between experiments with different NH_3 flow. For example, at 1000 °C using 5 sccm CH_4, 0.5 sccm NH_3 and 500 sccm H_2 for 10 minutes resulted in average domain size of 13.4 μm (Fig. 3c). Comparing this growth with Fig. 3a, a five times increase of ammonia concentration (from 0.1 sccm to 0.5 sccm) decreased the average

4 | Phys. Chem. Chem. Phys., 2014, 00, 1–7

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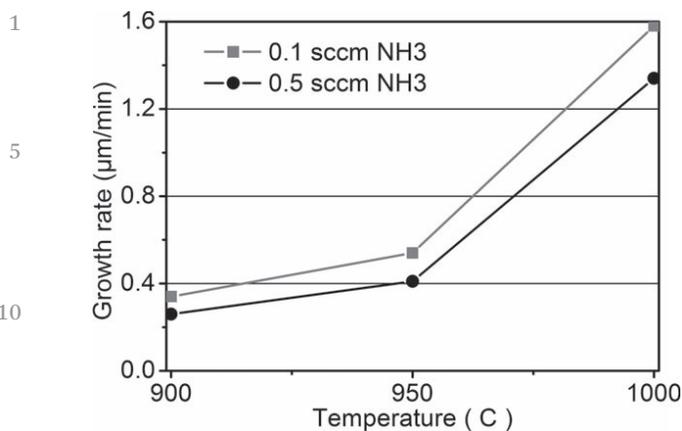
Fig. 4 Influence of the temperature and ammonia concentration on the average graphene growth rate. The temperature caused significant change, while the effect of ammonia concentration appeared less important.

Fig. 5 (a) Lower resolution STM image of nitrogen–doped graphene showing substitutional nitrogen atoms (arrows)[25] and larger defects likely containing multiple nitrogen atoms (oval). (b) Higher resolution STM image revealing typical patterns around individual substitutional nitrogen atoms oriented differently on different sublattices as highlighted by triangles. The inset presents the FFT of the STM image: the outer hexagon corresponds to the atomic lattice, the inner hexagon arises from the intervalley scattering induced by nitrogen dopants. (c) Additional examples of nitrogen atoms (d) a defect resembling the pyridinic configuration.[29]

growth rate by approximately 15% (from 1.58 μm min^{-1} to 1.34 μm min^{-1}). At lower temperatures, 950 and 900 °C, a similar increase in ammonia concentration decreased the average growth rate approximately 25% (Fig. 4). Therefore, production of nitrogen-doped graphene at 900 °C using 5 sccm CH_4 and 0.5 sccm NH_3 required extended synthesis times (*e.g.* 30 minutes) and reduced H_2 flow rates (*e.g.* 100 sccm H_2) (Fig. 3d). Collectively, we conclude that a decrease in synthesis temperature and increase of ammonia concentration caused a significant decrease in the growth rate of nitrogen-doped graphene (*e.g.* 100 °C reduction and five times increase in NH_3 flow rate resulted in approximately six times decrease in μm min^{-1} coverage) (Fig. 4).

The temperature and ammonia concentration also influenced the graphene nucleation density and the maximum achievable surface coverage. Full coverage (or nearly full coverage) was observed when using high temperatures and high ammonia concentrations, *i.e.* 1000 °C; 0.5 sccm NH_3; 500 sccm H_2; 10 min (Fig. 3c), or low temperatures and low ammonia concentrations, *i.e.* 900 °C; 0.1 sccm NH_3. However, only half of the copper substrate was covered at low temperatures and high ammonia concentrations, *i.e.* 900 °C; 0.5 sccm NH_3. Even for experiments with reduced H_2 flow rate (to minimise etching of domains) and extended synthesis time (*e.g.* 30 minutes or longer) the size of the graphene domains did not increase significantly (Fig. 3d), meaning only incomplete maximum surface coverage is achievable under such conditions. We believe this is due to the ammonia damaging the copper surface and inhibiting the growth of domains. Consequently, using the right balance between the experimental parameters, it is possible to tune the surface coverage and growth rate of nitrogen-doped graphene. These findings have important implications for optimising the sample quality while minimising the production time and associated costs of manufacturing nitrogen-doped graphene if this material is to become viable for commercial applications in the future.

A typical lower resolution STM image of the nitrogen-doped graphene synthesised at 900 °C with 0.5 sccm NH_3 is shown in Fig. 5a. STM measurements found that there was physisorbed

contamination present on the surface after exposure to ambient conditions (not shown), as observed with XPS. Comparison of the STM images with computer simulations revealed that the nitrogen was incorporated mainly in substitutional configuration. Several larger defects likely containing more than one nitrogen atom were also observed (circled in Fig. 5a). Similar STM studies of pristine, undoped graphene did not reveal any substitutional nitrogen. Higher resolution STM imaging of nitrogen-doped graphene shows rotated patterns (highlighted with triangles in Fig. 5b) indicating substitutional nitrogen atoms are incorporated on different graphene sublattices. The STM image shows good correspondence with the DFT calculations reported by Lambin *et al.*[25] The substitutional nitrogen incorporation was also confirmed by STEM and EELS investigation of the nitrogen-doped graphene samples.[26] During STEM/EELS measurement only substitutional nitrogen atoms were identified, which indicates that the concentration of other types of nitrogen atoms was low. The fast Fourier transform (FFT) of Fig. 5b (inset) shows two sets of points arranged in hexagons. The outer hexagon corresponds to the atomic lattice, while the inner hexagon shows intervalley scattering induced by nitrogen dopants.[3,27] These strong intervalley peaks caused by electron scattering processes between two non-equivalent Dirac cones[28] indicate a significant influence of the nitrogen atoms on the electronic properties of the graphene. This observation is in agreement with the increase in intervalley scattering detected by the increased I_D/I_G ratio in the Raman spectra. Additionally, defects resembling the pyridinic configuration[29] were also observed (Fig. 5d).

We investigated the effect of nitrogen on the density of states of nitrogen-doped graphene using CITS. Fig. 6a shows an atomic resolution STM image with nitrogen atoms
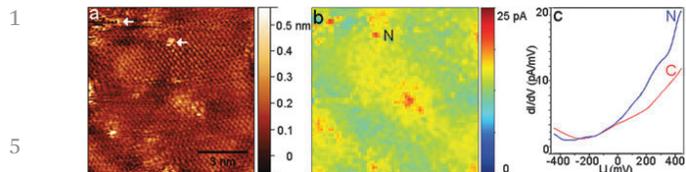
Fig. 6 (a) STM image of nitrogen-doped graphene domain. (b) Corresponding CITS image at 335 mV. A minor translational shift exists between the STM in (a) and CITS image. (c) dI/dV recorded above a nitrogen atom (marked N on image b) and a carbon atom.

incorporated in the graphene lattice. The localized high current regions on the CITS image (Fig. 6b) correspond to substitutional nitrogen atoms (indicated by arrows Fig. 6a, with minor translational shift). The diffuse maxima are due to the defects containing more than one nitrogen atom, as observed in STM. The measurements show that the electronic structure of nitrogen-doped graphene was strongly modified only within a few lattice spacing of the site of the nitrogen. The minimum of the dI/dV curve measured above the substitutional nitrogen atom marked by letter 'N' was near −300 meV (Fig. 6c), similar to other measurements reported in literature.[3] This suggests the nitrogen-doped graphene displays n-type doping, in agreement with our Raman measurements. Local densities of states above the Fermi level around nitrogen atoms increased dI/dV at positive voltages as it could be expected from DFT calculations.[25]

4. Conclusions

We investigated the effect of the experimental parameters on the growth of nitrogen-doped graphene produced by LPCVD and doped *in situ* during growth using NH_3. STM imaging confirmed that nitrogen was incorporated mainly in substitutional configuration, while CITS demonstrated that the nitrogen-doped graphene has n-type doping. We showed that the synthesis parameters influence the dopant concentration and growth rate of nitrogen-doped graphene. Raman spectroscopy demonstrated that reducing the synthesis temperature and increasing the NH_3 flow rates increased the concentration of nitrogen dopants. Our results demonstrate that the synthesis temperature, not NH_3 flow rate, is the overriding parameter, as a 100 °C decrease in temperature increased the concentration of nitrogen dopants more than a five times increase in NH_3 flow rate. XPS analysis showed that the highest overall nitrogen concentration was approximately 2.1%, achievable by using a lower synthesis temperature (900 °C) and higher NH_3 flow rate (0.5 sccm). However, decreasing the temperature and increasing the NH_3 flow rate also significantly decreased the growth rate of nitrogen-doped graphene. Furthermore, under particular conditions that would maximise nitrogen doping – using low synthesis temperatures (*e.g.* 900 °C) and high NH_3 flow rate (*e.g.* 0.5 sccm, or above) – the growth of nitrogen-doped graphene was inhibited so that full coverage of the Cu surface was not possible even with extended synthesis time. Therefore the right balance between the nitrogen content and growth rate must be found, and consequently accurate optimisation is needed to produce high quality nitrogen-doped graphene.

These findings have important implications for optimising the dopant concentration and sample quality, while minimising the production time and associated costs, if nitrogen-doped graphene is to find commercial applications in the future.

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6 | *Phys. Chem. Chem. Phys.*, 2014, **00**, 1–7

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Phys. Chem. Chem. Phys., 2014, **00**, 1–7 | **7**