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Reducing the graphene grain density in three steps

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Abstract

The production of large-scale, single crystalline graphene is a requirement for enhancing its electronic, mechanical, and chemical properties. Chemical vapor deposition (CVD) has shown the potential to grow high quality graphene but the simultaneous nucleation of many grains limits their achievable domain size. We report here that ultralow nucleation densities can be achieved through multi-step optimization of the catalyst morphology. First, annealing in a hydrogen-free environment is required to retain a surface copper oxide which decreases the nucleation density. Second, CuO was found to be the relevant copper species for this process and air oxidation of the copper foil at 200 °C maximizes its concentration. Both pre-treatment steps were found to affect the morphology of the catalyst and a direct correlation between nucleation density and surface roughness was found which indicates that the primary role of the oxidation step is the decrease in catalyst roughness. To further enhance this determining parameter, confined CVD was carried out after sample oxidation and hydrogen-free annealing. Each of these three steps reduces the grain density by approximately one order of magnitude resulting in ultralow nucleation densities of 1.23 grains/mm^2 and high quality, single-crystalline graphene grains of several millimeter sizes were grown using this method.

S Online supplementary data available from stacks.iop.org/NANO/27/105602/mmedia

Keywords: graphene, grain density, single crystalline, CVD

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene, a two-dimensional carbon allotrope [1, 2], has demonstrated significant potential in a multitude of research areas [3–5]. Many of these applications require the production of graphene at large scale and high quality. Chemical vapor deposition (CVD) is a promising approach to prepare high quality graphene on catalytic substrates [6–9]. One drawback of CVD growth is the poly-crystallinity of the graphene film with domain sizes ranging from nanometers to micrometers [10, 11]. The boundaries between grains will deteriorate its carrier transport [12], mechanical strength [10], thermal properties [13], and chemical inertness [14].

Consequently, the increase of graphene's domain size is a focus of significant attention [15–22]. Many promising approaches aim at decreasing the density of simultaneously growing graphene grains through minimization of the nucleation density. Reported approaches include thermal annealing [23, 24], electropolishing [25], and oxidation of copper foil prior to [19, 23] or during the CVD process [17]. The diversity of pretreatment methods indicates the lacking consensus on the mechanism responsible for decreasing the nucleation density. Eras *et al* suggested that the oxidation process removes organic impurities and surface contaminations thus affecting the growth kinetics [23]. Gan *et al* reported that the main effect of the oxidation is a change of

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the catalyst morphology [16]. Finally, Hao *et al* proposed that the oxide layer changes the nucleation kinetics of the growth process [17].

We demonstrate that ultralow graphene nucleation densities can be achieved through a rational arrangement of several pretreatment steps that aim at controlling the catalyst morphology. First, the presence of copper oxide was found to result in a tenfold lowered nucleation density and hydrogen-free annealing conditions are required to retain it. Temperature-dependent air oxidation experiments furthermore reveal that CuO is the relevant copper oxide species for this nucleation control and optimization of its concentration yields an additional tenfold decrease in nucleation density. We identify the decrease in roughness upon oxidation as the underlying mechanism of this decrease. A direct proportionality between catalyst roughness and nucleation density was found irrespective of the details of the treatment processes. The catalyst roughness could be furthermore decreased by confined CVD which reduced the grain density by another order of magnitude. The demonstrated series of optimization steps helps to achieve a nucleation density of 1.23 grains/mm^2 which enables growth of millimeter-sized graphene domains. The domains exhibit single-crystallinity and high quality and demonstrate the potential of our method for the synthesis of graphene for future applications.

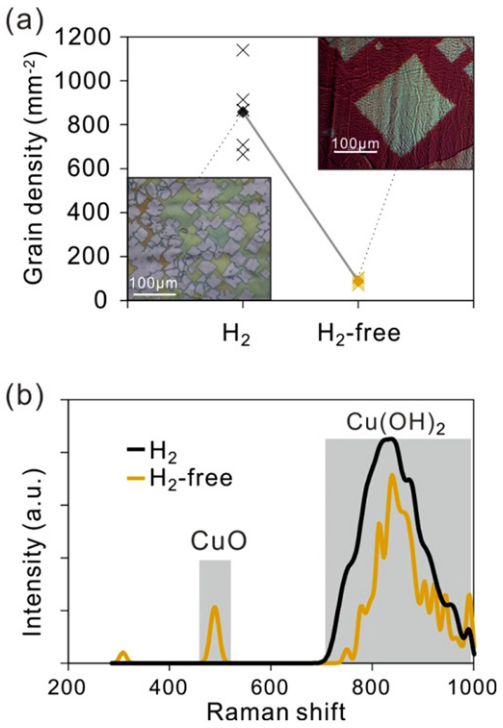

Figure 1. (a) Nucleation density of graphene grown after annealing under hydrogen-containing and hydrogen-free conditions, (b) Raman spectra of copper substrates after both annealing steps.

2. Experiment

Graphene was grown on copper foil (99.8%, Alfa-Aesar, no. 13382) following previous reports [26, 27]. Briefly, copper foil was first cleaned by electropolishing in a H_3PO_4 (85%) electrolyte at a potential of 2 V for 30 min. Oxidation of the copper foil on a hot plate was carried out for 30 min prior to CVD growth. CVD growth consisted of three process steps, heating, annealing, and growth. During the heating step, the reactor temperature was slowly raised to 1040 °C within 50 min under a flow of 320 sccm argon and a pressure of 1 Torr. Annealing was carried out at 1040 °C for 40 min under a flow of 320 sccm argon and 20 (or 0) sccm H_2 under a pressure of 1 Torr. The growth was conducted under a flow of 0.8 sccm CH_4 and 500 sccm H_2 for 80 min and at a pressure of 1 Torr. To visualize graphene on copper after synthesis samples were oxidized in air on a hot plate at 230 °C [25].

Image processing was used to analyze the grain density and grain size at 5 different positions within each sample and error bars represent the sample-to-sample variation. Atomic force microscopy was carried out on an AFM (E-7, Force Precision Instrument Co.) and roughness values represent the average of two 10 × 10 μm images. To quantify differences in morphology within each image, their line-to-line variations are represented as error bars.

For TEM measurements, graphene was transferred to TEM grids (TED PELLA 01881-F graphite lacey carbon) using PMMA as a mechanical support following established process parameters [28]. Raman spectroscopy was performed on a home-made micro-Raman system using 532 nm excitation wavelengths. Seven data points were taken for each sample and each spectrum was fitted with Lorentzian peaks to obtain peak position and intensity information.

3. Results and discussion

A first step to identify the mechanism of oxidative copper pretreatment for graphene nucleation control is to establish at what growth stage the copper oxide has to be present. Previous explanations that cleaning of impurities is the main role of the oxidation step [23], for example, would only require the oxide to be present initially and then be consumed during the annealing stage. We therefore introduce two different annealing methods that differ by the process stage during which hydrogen is introduced. Common graphene growth procedures inject hydrogen during the annealing step [22]. We also carried out annealing without hydrogen to preserve the produced oxide layer. Figure 1(a) compares the average grain density of graphene grown under both annealing conditions. We observe that hydrogen-free annealing can decrease the nucleation density by more than one order of magnitude. This decrease in nucleation density results in larger achievable graphene domain sizes (insets of figure 1(a)) by limiting the interaction between neighboring graphene grains.

Raman characterization of the copper substrate after the different annealing procedures was carried out to investigate the origin of the decreased nucleation density (figure 1(b)). Two different Raman bands can be distinguished at 500 cm^{-1}, and 800 cm^{-1}. These features had previously been

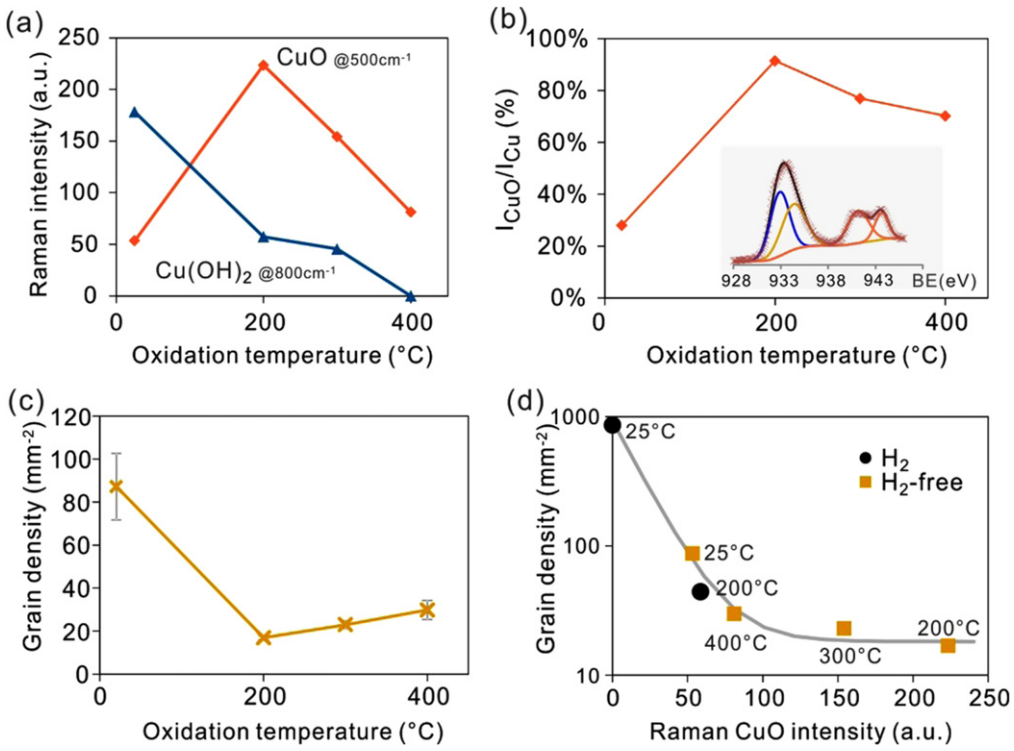

Figure 2. (a) Intensity of copper oxide Raman peaks after oxidation at different temperatures, (b) relative XPS peak intensity of CuO after oxidation at different temperatures, (inset) representative XPS spectrum of Cu $2p_{3/2}$ peak, (c) graphene grain density versus oxidation temperature, (d) grain density versus CuO peak intensity for different oxidation temperatures and annealing conditions (the gray line represents a least square fit as described in the main text).

assigned to CuO and $Cu(OH)_2$, respectively [29]. Comparison of the spectra for both annealing conditions confirms that the hydrogen atmosphere reduces the CuO but does not seem to affect the $Cu(OH)_2$, suggesting that the hydroxide is formed upon exposure to air. Hydrogen-free annealing, on the other hand, was found to retain CuO. We therefore conclude that the copper oxide has to be present after the annealing stage to reduce the grain density and hydrogen-free annealing conditions are required to retain it. To identify the role of copper oxide on the graphene nucleation, the concentration of copper oxides was varied by changing the oxidation temperature between 25 °C and 400 °C. Raman characterization shows that after annealing at 1000 °C the CuO concentration exhibits a maximum for samples that had been oxidized at 200 °C while the concentration of copper hydroxide decreases continuously with oxidation temperature (figure 2(a)). X-ray photoelectron spectroscopy was carried out to confirm this result. The Cu $2p_{3/2}$ peak and its shakeup were deconvoluted into contributions from pristine copper and CuO [30] (inset of figure 2(b)). The relative intensity of the CuO peak shows a similar trend to the results obtained by Raman spectroscopy which corroborates our finding.

The observed difference in the concentration and character of copper oxides can be used to identify correlations between pretreatment and nucleation. Figure 2(c) compares the nucleation density of graphene grown on copper foil that was air oxidized at different temperatures and subjected to hydrogen-free annealing. We observe that copper oxides grown at 200 °C show a lower nucleation density than Cu oxides grown at higher temperatures. The strong correlation of the nucleation density with the concentration of the CuO phase indicates that this oxide phase affects graphene nucleation. A clear trend between the concentration of CuO after annealing and grain density is demonstrated in figure 2(d) and the grain density n can be completely predicted by the concentration of CuO through a simple exponential relation

$$n(c_{\mathrm{CuO}}) = n_0 \exp(-\gamma c_{\mathrm{CuO}}) + \eta,$$

where n_0 is the grain density at vanishing CuO concentrations ($n_0 \sim 850\ \mathrm{mm}^{-2}$), γ is a proportionality constant ($\gamma \sim 0.05$), and η is the lowest achievable graphene grain density at full CuO coverage ($\eta \sim 17\ \mathrm{mm}^{-2}$). The good fit of this model to the experimental data suggests that other details of the annealing process, such as oxidation temperature and hydrogen pressure only affect the nucleation density indirectly by modifying the CuO concentration.

To understand the reason for this correlation between CuO concentration and nucleation density, we carried out AFM characterization of the substrates after pre-treatment (figure 3(a)). We find that the oxidation of copper reduces the substrate roughness (figure 3(b)). This may be due to an enhanced evaporation of CuO compared to Cu [31] that leads to an improved surface recrystallization. Alternatively, the oxide might provide a protection against hydrogen-induced etching of the Copper surface which increases its roughness [16, 31]. The observed lower graphene nucleation density on those flatter substrates indicates that defects and protrusions

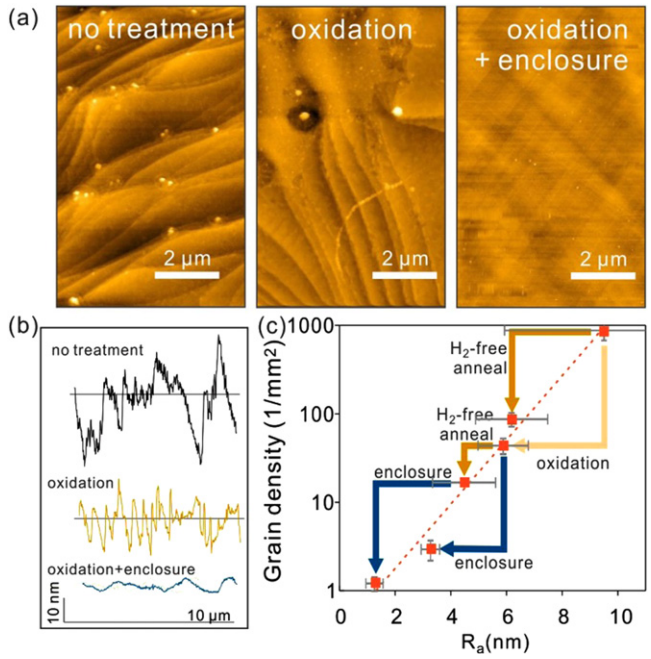

Figure 3. (a) AFM after different treatment steps, (b) representative cross-sections of the AFM images, (c) AFM-derived roughness R_a versus grain density for different combinations of treatments.

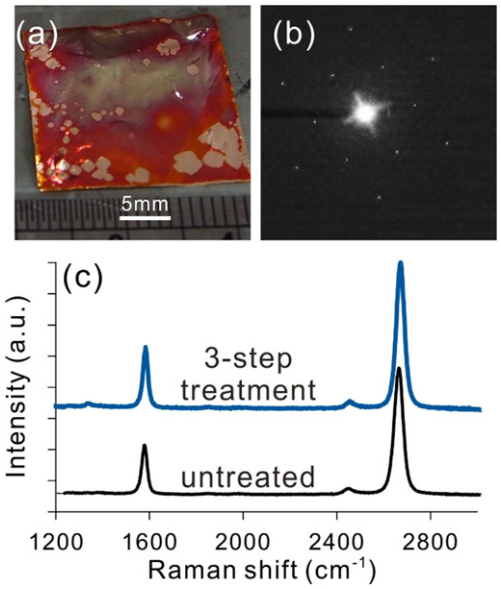

Figure 4. (a) Photograph of 1.5 × 1.5 cm copper sample after air oxidation exhibiting ultralow graphene grain density, (b) selected area electron diffraction (SAED) image of transferred single grain, (c) Raman I_D/I_G ratio for graphene grown on untreated and treated copper.

will act as nucleation centers and their reduction can control the graphene nucleation, in agreement with previous reports [32–34]. Consequently, the main effect of pre-treatment steps aiming at reducing the nucleation density is to decrease the substrate roughness.

Based on this theory, we expect that other approaches to reduce the copper roughness would also decrease the nucleation density. To test our hypothesis, we carry out confined CVD which has been reported to affect the copper evaporation process and result in a smoother copper surface [35]. A confinement effect was achieved by sandwiching a 2 × 7 cm piece of copper foil between two fused silica slides (23 × 75 × 2 mm, Xide Technology Ltd) and we indeed observe a decrease in the roughness after annealing (figure 3(b)). As predicted, the lowered roughness decreases the graphene nucleation density and a tenfold reduction between unconfined and confined CVD on oxidized Cu foil was found.

We quantified the roughness of the substrates by the arithmetic average of their absolute values R_a and demonstrate a direct proportionality between this roughness parameter and the nucleation density (figure 3(c)). The effectiveness of each pretreatment step in reducing the graphene grain density (supplementary figure S1, available at stacks.iop.org/NANO/27/105602/mmedia) was found to be primarily determined by its ability to reduce the substrate roughness. This observation is in contrast to previous reports that suggested the impact of CuO sites on the growth kinetics [17]. Instead, we find no correlation between the graphene growth rate and the grain density (supplementary figure S2). This observation is in agreement with recent reports about the similarity in the graphene growth kinetics on Cu and CuO [36].

The observed exponential dependence of grain density on substrate roughness furthermore suggests the sensitivity of graphene growth on the substrate morphology. The grain density was minimized by combining all three treatment steps —oxidation, hydrogen free annealing, and confined CVD growth. The resulting grain density of 1.23 mm^{-2} is an average over many centimeter-sized samples and is repeatable and stable. Further reduction in grain density could be achieved in the future by optimizing the growth process [23].

Using this method, we produced millimeter-scale graphene grains (figure 4(a)). The difference in grain size was found to be caused by a transport-limited growth process which is not affecting the grain density [37]. Selected area electron diffraction (SAED) shows that each of the millimeter-sized graphene grains is single crystalline (figure 4(b)). Furthermore, Raman characterization suggests that the produced graphene is of a quality that is comparable to unenclosed and non-oxidized growth as indicated by the absence of the defect-related D-band (figure 4(c)).

4. Conclusion

In conclusion, we provide a route to achieve ultralow graphene nucleation densities by combining three steps that aim at controlling the catalyst morphology. First, the formation of copper oxide is a requirement for low nucleation density and hydrogen-free annealing conditions are needed. The oxidation at 200 °C results in the highest concentration of CuO phase and the lowest achievable grain density indicating that the

selectivity of the nucleation process to a certain copper oxide species. A direct proportionality between substrate roughness and nucleation density was found which implies that the main role of the oxidation step is the reduction of substrate roughness. Based on this finding confined CVD growth was used to further reduce the substrate roughness and an additional tenfold decrease in the nucleation density was observed.

The graphene nucleation density after combining all three treatment steps is three orders of magnitude lower than for traditional graphene growth and reaches 1.23 grains/mm^2. This method can be applied to produce high quality macroscopic single crystals of graphene at large scale to facilitate the use of CVD graphene in high performance applications.

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