Abstract
Since the experimental discovery of graphene, research has progressed at an astonishing speed. This 2D honeycomb has already exhibited revolutionary electronic properties and claimed the record for strength. However, getting graphene out of the lab requires improved characterization, especially of imperfections. Hence, this paper explores one of the most important defects in a copper–graphene nanocomposite fabricated by chemical vapor deposition (CVD), which is the method most capable of producing large sheets of high-quality graphene. Through electron microscopies, optical microscopy, and Raman spectroscopy, this work details (1) the room-temperature oxidation of the copper substrate coated with graphene and (2) the heterogeneities of the graphene due to deposition and oxidation. The results indicate that this oxidation can be confined by grain boundaries, forms in the copper substrate as Cu₂O, and minimally affects the graphene quality. This investigation also suggests that CVD can produce a variable number of high-quality, graphene layers.

1. Introduction

Ever since the ‘Scotch-tape method’ produced the first experimental samples of graphene in 2004 [1], research into this ‘wonder material’ has shattered experimental records and redefined materials theory (e.g. review articles [2–9]). After all, the traditional proposition claimed that 2D materials do not exist at finite temperature [3]. Now, modern endeavors seek to discover and apply the record properties of this extraordinary ceramic.

Most graphene research has focused on the unique electronic properties of this gapless semiconductor: ambipolarity, minimum conductivity, chiral quantum Hall effects, quantum electrodynamics from massless Dirac fermions, and extremely high electron mobility (∼10⁶ cm² V⁻¹ s⁻¹) [3, 4, 10]. These features have inspired next-generation transistors, optoelectronics, and batteries. However, graphene’s unique chemical, thermal, and mechanical properties suggest new applications as well. The high ratio of surface area to volume enables sensors capable of single-molecule detection [11]. The homogenous, functionalizable, and impermeable structure may revolutionize drug delivery [12]. The high thermal conductivity (5000 W m⁻¹ K⁻¹) [13] and unique absorption/emissivity are just starting to encourage novel applications, like thermal camouflage [14, 15]. Records in strength (130 GPa) [16], nonlinear elasticity [6, 16], and quality factor (4000) [17] drive interest in nanoelectromechanical systems, tissue engineering, ballistics, and structural composites [18, 19].

Many of these applications demand large areas of single-layer graphene (SLG) with high quality. Unfortunately, mechanical exfoliation by the Scotch-tape method only produces areas on the order of 1 mm [1]. Hence, many investigations have sought to discover and optimize synthesis methods. Of the numerous propositions (e.g. thermal decomposition, molecular beam deposition, unzipping of carbon nanotubes, sodium–ethanol pyrolysis, reduction of graphene oxide, wet chemical synthesis, and ignition of plasma), chemical vapor deposition (CVD) onto a metal substrate seems the most promising [5, 6]. In particular CVD of SLG onto rolled Cu (i.e. Cu–G) produces impressive mobility (16 000 cm² V⁻¹ s⁻¹) and an area on the order of 1 m² [6, 20].

The superiority of graphene can be largely attributed to the limited number and types of defects, which typically drive the failure of covalent solids [9]. Both experiment and simulation suggested that cracks, which are
also called ‘tears,’ nucleate and grow during processing, exfoliation, and even TEM imaging [21, 22]. Experiments also indicated vacancies [23], Stone–Wales defects [23], dislocations [24, 25], and grain boundaries [21, 26–29]. Of these, grain boundaries are arguably the most influential, especially for large graphene sheets. For example, the breaking force and breaking stress from polycrystalline graphene were only 6% (i.e. 100 versus 1800 nN) and 30% (i.e. 35 versus 130 GPa) of the corresponding values of monocrystalline graphene, respectively [16, 26, 29]. Perhaps most importantly, consider that thickness (i.e. number of carbon layers) differentiates the extraordinary graphene from the ordinary graphite. Hence, an excessive or nonuniform number of carbon layers should be considered a crucial defect. Unfortunately, the ‘war on fake graphene’ recently revealed that many commercial suppliers are producing ‘graphene’ with far too many layers [30].

Importantly, consider that these graphene defects can depend on the type, orientation, and defects of the substrate used in CVD. For example, a Cu substrate reportedly promotes SLG rather than the few-layer graphene (FLG) of a Ni substrate [6, 20]. As with the graphene itself, a substrate’s grain orientation plays a key role in graphene defects as well. For a polycrystalline Cu substrate, the (111) grains produced the highest-quality graphene, especially better than the (001) grains [31]. Similarly, single-crystal Cu substrates in the (111) orientation more strongly bonded to graphene than substrates in (001) and (011) orientations [32]. Other than type and orientation, perhaps the most important feature of the substrate is its susceptibility to oxidation. Predictably, oxidation of the substrate can affect area of the graphene through passivation and other processing kinetics [33]. Oxidation of the metal substrate can occur after processing as well. Initially, graphene well protects the substrate from corrosion, even at elevated temperature [31, 34, 35]. However, defects in the graphene can slowly allow oxygen molecules to diffuse into the interface of the graphene and metal substrate. Even at ambient conditions, this diffused oxygen can eventually oxidize a Cu substrate, especially on high-index surfaces [31, 36–40]. The effect of this oxidation on the quality of the graphene is currently unknown.

Overall, both oxidation and uniformity/number of carbon layers crucially limit the record properties of graphene. Hence, the current investigation examined these defects in Cu–G fabricated by CVD, which is the method most capable of producing large areas of high-quality SLG. Through scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), optical microscopy (OM), and Raman spectroscopy (RS), this work revealed that room-temperature oxidation occurs in the polycrystalline Cu, takes the form of Cu2O, can be confined by grain boundaries, and may negligibly affect the graphene quality. The results also indicated that the number of carbon layers can vary across a Cu–G sample produced by CVD.

2. Chemical vapor deposition

A single Cu–G sheet was produced by CVD of methane (CH4) and hydrogen (H2) onto high-purity (99.9%), untreated Cu at 1000 °C, under 16 Pa, and for 45 min. As demonstrated later in this manuscript, this deposition produced a variable number of carbon layers on both the top surface (TS) and bottom surface (BS) of the Cu. Additionally, an oxidation layer formed between the Cu and C layers in some regions of this sheet. Hence, nonoxidized samples and oxidized samples were obtained from the same sheet. Overall, this imperfect Cu–G sheet well served the current goal of assessing oxidation and thickness defects.

3. Scanning electron microscopy

Both TS and BS were first examined with a Tescan Mira3 SEM equipped with an EDAX Octane Pro EDS system and a Hiraki Plus electron backscattered diffraction (EBSD) camera. While performing SEM, EBSD was used to generate inverse pole figure (IPF) maps and to find grains with surfaces normal to (001), (011), and (111) planes.

The quality of the indexing for the IPF maps was assessed with the confidence index (CI) of the EDAX EBSD software (OIM Analysis 8).

Figure 1(a) shows an IPF map of a Cu–G sample with an average Cu-grain size of ~200 μm and texturing that favors the red (001) over the green (011) or blue (111) orientations. This preference for (001) is characteristic of rolled metals. Also, note that this map does not reflect orientation of the graphene, which had small thickness ( <10 nm) and low atomic number so was therefore not likely detected by EBSD. Also, note that the high CI for the entire region in the IPF map in figure 1(a) suggests few defects, such as oxidation, in the Cu substrate.

In contrast to figure 1(a), figure 1(b) provides an IPF map with confetti regions, which corresponded to low CI. Interestingly, see that these regions are largely confined by grain boundaries. To investigate the possibility of a difference of elemental composition in the areas with high CI and with low CI, figure 1(c) provides representative EDS of these two types of regions. See that a grain with a low CI had significantly higher O signal than a grain with high CI. As mentioned earlier, EBSD did not detect the thin C layer, so low CI likely correlates with oxidation of the Cu substrate. This notion was confirmed with both the TEM and RS.
4. Transmission electron microscopy

To evaluate the notion that oxidation occurred in the Cu substrate rather than in the C layer, the Cu–G samples were next examined with an FEI Tecnai F20 TEM equipped with a Gatan UltraScan 1000P digital camera, Fischione Instruments Model 3000 scanning TEM (STEM) detector, and EDAX r-TEM EDS system. TEM was performed in cross-section (XTEM) with both high-resolution XTEM (HR-XTEM) and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) imaging. XTEM specimens were prepared with an FEI Helios Nanolab 600 and conventional methods [41]. For equal comparisons, the XTEM beam direction was aligned with the (011) direction of the Cu grains through prior SEM characterization.

To establish a baseline, figure 2 provides XTEM of oxidation-free regions of all three major cubic orientations on both the TS and BS of the Cu–G sample. All orientations show a mostly defect-free Cu substrate followed by a C layer and finally a protective Pt coating, which was deposited in situ during XTEM specimen preparation. This manuscript often refers to the carbonaceous layer as the ‘C layer’ to avoid assuming a graphene structure. Generally, the interface between the Cu and C layers was more tortuous on the BS than on the TS, but the C was well bonded regardless of roughness. For example, compare figures 2(a) and (b) with figures 2(d) and (e). Further, of the three Cu orientations, (001) appeared to have the roughest interfaces (e.g. compare figures 2(a)–(c)). This finding is consistent with the aforementioned studies that found that (001) produced the weakest Cu–G bonding in both polycrystalline [31] and monocrystalline [32] samples.

Figure 1. (a) IPF map with high CI shows an average Cu-grain size of 200 μm and a Cu texturing that favors the red (001) over the green (110) or blue (111). (b) IPF map shows that a low CI, which appears as a confetti pattern, can be confined by grain boundaries. (c) A representative grain with low CI contains higher O content than a representative grain with high CI.
Figure 2 also shows that surface roughness may relate to the thickness and uniformity of the C layer (e.g. compare figures 2(a)–(c) with figures 2(d)–(f)). For our TEM samples, this thickness generally varied from 1–6 nm. This range only partially overlaps the 0.4–1.7 nm reported in studies on the atomic force microscopy of SLG [42]. Hence, the current TEM suggested (and the current RS later confirmed) that the Cu–G samples contain both SLG and FLG. This finding is interesting in light of the fact that CVD onto a Cu substrate is generally assumed to produce SLG [5, 6].

Finally, from figure 2, we can see how the presence of the organometallic (i.e. C-containing) Pt coating complicated determination of the exact thickness of the C layer. Thus, some samples were coated first by Cr, which has a much higher atomic number than C, and then by Pt for protection from the FIB. For example, figure 3(a) clearly shows the upper boundary of the C layer on the BS. Figure 3(a) also exemplifies the high roughness and heterogeneous thickness of the C layer, parallel lines representative of the graphene/graphite structure (see black arrows), and most importantly, oxidation of the Cu substrate. This oxidation is labeled as Cu$_2$O because of the RS presented later in this manuscript.

The rest of figure 3 further details the Cu oxidation through HR-XTEM of Cu coated with FLG. As shown by figures 3(b)–(d), the oxidized region had unique lattice fringes and low contrast with the pure Cu region. At the
interface between the oxidized region and the Cu, the lattice seemed deformed but still continuous. These contrast and continuity features suggest that the oxidation occurred in the Cu substrate and not in the C layer. This inference is confirmed through EDS of the region depicted by the dashed square in the HAADAF-STEM of figure 3(e). See that the oxidation region included the highest concentration of orange O but still some yellow Cu. Also, see that the oxidized region varied in thickness (e.g. compare figure 3(b) with figure 3(c)) and typically resulted in a linear interface with the Cu regardless of the roughness of the Cu surface (see figure 3(d)). Therefore, the oxidation revealed by the IPF’s (figure 1) is definitively in the Cu substrate rather than in the C layer.

Figure 3. (a) Representative XTEM shows that an oxidized region (i.e. labeled ‘Cu₂O’) can form in the Cu substrate near the C layer, which sometimes reflects graphene/graphite-like structures (see black arrow). This oxidation region can (b), (c) vary in thickness and (d) remain well-bonded with the graphene despite a rough surface. (e) EDS of the region shown by HAADAF-STEM confirms the oxidized region predominantly contains Cu (yellow) and O (orange). The C content (red) is consistent across the Cu and oxidized layers and increases in the organometallic Pt layer.
5. Optical microscopy and Raman spectroscopy

To characterize a larger volume of material than assessed with the TEM, the Cu–G was finally examined with an Olympus BX51 optical microscope and a Renishaw InVia Raman Spectrometer with a 532 nm laser. For pure graphene, the most prominent features of the Raman spectrum are the D-peak ($1350 \text{ cm}^{-1}$), G-peak ($1580 \text{ cm}^{-1}$) and 2D-peak ($2675 \text{ cm}^{-1}$) [43–46]. The locations and relative intensities of these peaks can be used to nondestructively reveal a variety of features, such as the number/orientation of layers, amount of strain, and types/abundances of defects. In particular, this investigation used RS to reveal the number of layers (i.e. from the ratio of the 2D and G peaks) [43], the quality of the graphene (i.e. from the ratio of D and G peaks) [43], and the crystal structure of the oxidized material (i.e. from comparison to previously reported spectra).

Recall that the EBSD demonstrated that oxidation of the Cu substrate could be confined by grain boundaries. This finding is echoed by the OM shown in figure 5(a). See the color contrast among the Cu grains. RS in the lighter grains produced the characteristic peaks of Cu$_2$O at low wavenumbers [36, 47–49] (see figure 5(b)). Therefore, a light color in OM would correspond to a confetti pattern in EBSD. Also, the RS again confirmed that oxidation occurred in the Cu substrate rather than in the C layer.

Figure 4. (a) Optical microscopy reveals that oxidation of Cu–G was confined to lightly colored grains. (b) Low-wavenumber RS confirms that these light regions contained Cu$_2$O. (c), (d) High-wavenumber RS reveals that the number of layers (i.e. ratio of 2D/G) and the graphene quality (i.e. ratio of D/G) varied across the sample.
This RS also confirmed that the C layer contained the graphene structure. The characteristic D, G, and 2D peaks appeared at high wavenumbers [43] (e.g. figures 4(c), (d)). Interestingly, the relative heights of these three peaks varied across the surface. For example, the 2D/G ratio of 1.2 in figure 5(c) suggests FLG while the ratio of 2.7 in figure 5(d) suggests SLG. Hence, the RS is consistent with the TEM in figures 2 and 3 in suggesting a variable number of graphene layers in the current Cu–G sample. Likewise, the D/G ratio, which relates to the defects, varied from 0.25 in figure 5(c) to 0.13 in figure 5(d). However, even a D/G ratio of 0.25 suggests a low number of defects in the graphene [50]. Therefore, the oxidation of the Cu substrate likely minimally induced defects in the graphene. Finally, note that obtaining these graphene peaks in the RS proved especially difficult because of the thinness of the graphene and the nonlinear baseline from fluorescence. The RS was likely far easier in the oxidized regions than in the non-oxidized regions because the CuO separated the graphene from the Cu substrate.

6. Conclusions

Through electron/optical microscopies and Raman spectroscopy, this work characterized the structure of a copper–graphene nanocomposite produced by chemical vapor deposition. The results showed that the presence of the graphene correlated with the oxidation of the copper substrate into Cu2O at room temperature. They also revealed that grain boundaries obstructed the growth of this substrate oxidation. This information may facilitate the design of oxidation-resistant, metal-graphene nanocomposites. Finally, this work demonstrated that the current deposition and the room-temperature oxidation beneficially produced few point defects in the graphene. Unfortunately, the deposition also produced a variable number of carbon layers across the sample. This finding highlights the need for better layer control in future processing endeavors.

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