Graphene Subgrain-Defined Oxidation of Copper

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ABSTRACT: The correlation between the crystal structure of chemical vapor deposited (CVD) graphene, the crystal structure of the Cu growth substrate and their mutual effect on the oxidation of the underlying Cu are systematically explored. We report that natural oxygen or water intercalation along the graphene-Cu interface results in an orientation-dependent oxidation rate of the Cu surface, particularly noticeable for bicrystal graphene domains on the same copper grain, suggesting that the relative crystal orientation of subgrains determines the degree of Cu oxidation. Atomistic force field calculations support these observations, showing that graphene domains have preferential alignment with the Cu(111) with smaller average height above the global Cu surface as compared to intermediate orientations, and that this is the origin of the
heterogeneous oxidation rate of Cu. This work demonstrates that the natural oxidation resistance of Cu coated by graphene is highly dependent on the crystal orientation and lattice alignment of Cu and graphene, which is key information for engineering the interface configuration of the graphene-Cu system for specific functionalities in mechanical, anticorrosion, and electrical applications of CVD graphene.

INTRODUCTION

Understanding the microstructure of chemical vapor deposition (CVD) grown graphene and interactions like alignment, adhesion, friction, and coupling between the grown graphene and growth substrate is a prerequisite for both systematically improving graphene quality and delaminating graphene from the growth substrate for various applications\textsuperscript{1-3}. Different visualization techniques have been developed for studying the microstructure of CVD graphene grains and grain boundaries\textsuperscript{4-6} in addition to some traditional characterization methods such as transmission electron microscopy (TEM) and scanning tunneling microscopy (STM)\textsuperscript{7-11}. Much recent attention has focused on decoupling graphene from the growth substrate of Cu via oxygen or water intercalation (Cu oxidation)\textsuperscript{12-16}. It is found that the graphene is intimately involved in the Cu oxidation process and plays a quite conflicting role when different oxidation conditions are applied. Graphene on Cu can prevent oxidation of Cu during fast annealing in air\textsuperscript{17}, while it conversely accelerates oxidation of Cu when exposed to air at room temperature for a long duration\textsuperscript{18, 19}. These conflicting findings have been ascribed to the tendency of graphene to promote galvanic corrosion, favoring the electrochemical oxidation of Cu beneath graphene over long time scales and overcoming the passivating and anti-oxidation properties observed during shorter timescales or fast annealing. Although these successes are enormously encouraging,
some of the processes involved in Cu oxidation beneath graphene, especially during long duration exposure to ambient conditions, are still unclear. For instance, little is known about the factors that determine the oxidation resistance over long timescales in the coupled graphene-Cu system. Indeed, the occurrence of both homogeneous and inhomogeneous oxidation of the Cu surface under graphene is a common phenomenon\textsuperscript{18, 19} that remains to be elucidated. To understand the disparate Cu oxidation results, factors such as the initial nucleation, the resulting morphology, microstructure, and relative alignment of graphene versus the underlying Cu during CVD growth processes should be taken into account. It has been reported that structural defects of graphene, such as grain boundaries, wrinkles, and nucleation sites, can allow diffusion of oxygen and cause preferential Cu oxidation near such sites\textsuperscript{4, 20-22}. However, the effects on Cu oxidation from other aspects involved in the graphene-Cu interaction such as crystallographic orientation and alignment of graphene on Cu remain unexplored. Despite a recent report on the Cu (111) face-dependent antioxidation properties of graphene coatings\textsuperscript{23}, there is still a lack of direct evidence and experiments in the literature for the variation of the oxidation barrier with the relative orientation between the graphene and Cu crystal structures.

In this work, the oxidation of Cu in the presence of graphene under ambient conditions has been followed for up to one year to reveal the dependence of Cu surface oxidation on the crystal orientation of both CVD grown graphene and the Cu surface itself. We make the striking observation that over long time scales oxidation rates for the copper surface depend strongly on the mutual orientation between the copper (111) surface and graphene, as observed in multiple graphene bicrystals on copper (111) grains. The study of graphene bicrystals allows us to ascribe the oxidation differences purely to orientation, eliminating sample-to sample variations. These results demonstrate that the slow oxidation resistance of Cu coated by CVD graphene is highly
dependent on the crystallographic orientation of graphene. Through atomistic force field calculations, we are able to attribute this differing oxidation rate to the crystal lattice misorientation between graphene and Cu which results in a varying mean height of carbon atoms above the copper surface. In other words, the degree of lattice misalignment between graphene and Cu determines the strength of the oxidation barrier of Cu, an observation which is of fundamental importance in understanding the properties of graphene corrosion barriers and for designing graphene-Cu systems for mechanical, anticorrosion, and electrical applications of CVD graphene.

**Figure 1.** a and b) A schematic illustration showing the full process of natural oxidation of Cu under graphene by exposure to the air for a long duration. c) Optical image of an as-grown graphene domain on Cu. d) Optical image of the graphene domain on Cu after thermal annealing at 200 °C for 10 min in air. e) Optical image of the different degree of Cu oxidation under the graphene domain after exposure to air for 12 months.
EXPERIMENTAL SECTION

CVD Growth of Graphene on Cu. Graphene samples were grown on Cu foils by low-pressure CVD. Cu foils (99.8% purity, 25 µm thick, Alfa Aesar) were used as growth substrates within an Aixtron Black Magic cold wall CVD system. After an annealing process in an argon (Ar) atmosphere, growth is initiated by introducing a methane (CH₄) feedstock and hydrogen (H₂) carrier gas in the chamber. The annealing was performed under an Ar flow of 1000 sccm (standard cubic centimeters per minute) at 1000 °C for 30 min. Then 1 sccm CH₄ and 20 sccm H₂ were introduced for the growth of graphene for 1-3 hours. Both annealing and growth were carried out at low pressure (20 mbar). After growth, CH₄ was turned off, and the Cu foil was cooled down by keeping the other CVD parameters unchanged.

Oxidation of Graphene-Cu System. Thermal oxidation in air at 200 °C was applied to the as-grown samples for 10 min resulting in oxidation of the bare Cu surface, highlighting the morphology of graphene domains on Cu. Then, the samples were kept in a covered but otherwise unsealed petri dish in ambient environment in a drawer in a climate controlled laboratory at 20 °C and 50% R.H. for 6-12 months to study its long-term oxidation behavior.

Transfer of Graphene. A sacrificial layer of poly(methyl methacrylate) (PMMA) was spun (1000 rpm, 60 s) on the Cu substrates after graphene growth, and then baked at 100 °C for 30 min. Graphene on the back side of the foils was removed by oxygen plasma (50 W, 2 min). Subsequently, the as-grown graphene domains were transferred onto SiO₂/Si substrates or TEM grids after etching the copper foils in an aqueous solution of 5% hydrochloric acid with hydrogen peroxide. The PMMA polymer support layers were finally dissolved with hot acetone, leaving the graphene layers adhered to the target substrates.
Characterization of Graphene and Cu. Graphene domains were observed after Cu oxidation by a Nikon Eclipse L200N microscope equipped with a programmable Prior Scientific XYZ stage. Scanning electron microscopy (SEM) (Zeiss Supra VP 60, 10 kV) was used to characterize the morphology and location of as-transferred graphene on TEM Cu grids. TEM (Tecnai G2 F20, operated at 200 kV) combined with selected area electron diffraction (SAED) (with a 200 nm diameter SAED aperture) was used to characterize the crystalline orientation of the as-transferred graphene domain. Raman spectroscopy was performed with a Thermo Fisher DXR microscope under ambient conditions using a 455 nm excitation laser source. The nominal spot size is 700 nm. The power of the laser is kept below 1 mW. The interface structure between subgrains and the main grain of graphene was observed by using an atomistic force microscope (AFM) (Dimension Icon-PT from Bruker AXS) under AFM mode of ScanAsyst in air. Electron backscatter diffraction (EBSD) measurements were performed with a FEI Nova NanoSEM600 (EDAX Hikari Camera). The accelerating voltage of the primary electron beam was 15 kV, and the aperture diameter was 120 μm.

RESULTS AND DISCUSSION

Figure 1 shows an example of a misoriented graphene subgrain stitched to its host grain, together comprising an isolated graphene bicrystal domain. Fast thermal annealing at 200 °C in air of graphene on Cu samples results in visible oxidation of the exposed Cu surface which allows individual graphene domains to be identified by optical microscopy (Figure 1 c, d). A clear isolated graphene domain (Figure 1d) was observed because graphene is thermally stable at this temperature in air and protects the underlying Cu from oxidation24. The sample is left in ambient conditions for 12 months, during which time the graphene is expected to galvanically enhance the oxidation of Cu18, 19. In principle, this enhancement of Cu oxidation is only
dependent on the conductivity and electrochemical mobility of graphene, and therefore homogeneous oxidation of Cu should be expected. Strikingly, quite different degrees of oxidation are observed beneath graphene bicrystals on individual copper grains, as shown in Figure 1e and Figure S1, with the differing rotational mismatch between the Cu and graphene in the bicrystal subgrains being the only factor that varies. Indeed, the differing degree of oxidation under the bicrystal is what allows the bicrystal to be optically identified on the surface in the first case. Such bicrystals are likely to be the result of multiple nucleation events at a single or closely associated sites, or nucleation at multiple sites on a single particle (Figure 1a, b, and Figure S2). As shown in Figure 1e, the Cu area covered by the main graphene grain shows relatively lower levels of oxidation of Cu, while the Cu area covered by the graphene subgrain generates a more severe oxidation of Cu, visible from the more saturated color of Cu oxides. From the view of CVD growth of graphene, the microstructure of graphene is primarily determined by its growth history. Growth, in turn, is driven by the crystal structures of both graphene and the substrate.
Figure 2. a) Dark-field optical image of a graphene domain on Cu with different degree of oxidation. b) Raman intensity mapping of the Cu$_2$O peak at ~ 644 cm$^{-1}$. c) Raman spectra of the different area as labeled A, B, and C in part b. d) AFM topography, e) peak force error, and f) adhesion image of the interface between graphene subgrain and main grain as marked by the red arrow in part a.

The color contrast of Cu oxides is clearly seen using dark-field optical microscopy (Figure 2a), displaying differing oxidation of Cu for each graphene grain. This observation of differing oxidation levels is confirmed by the clear correlation between the optical image and the Raman spectroscopic map of the intensity of Cu$_2$O$^{26,27}$ at ~ 644 cm$^{-1}$. As shown in Figure 2b, the Raman intensity mapping of Cu$_2$O shows regions with different colors, which are related to the different extent of Cu oxidation, showing the heterogeneity in the distribution of Cu oxides. Extracted Raman spectra for the areas labeled A, B, and C in Figure 2b, which correspond to the bare Cu,
graphene main grain, and graphene subgrain, respectively, exhibit obvious intensity difference for Cu oxides (Figure 2c). As shown, the area with a stronger intensity of Cu oxides indicates a stronger degree of Cu oxidation (bare Cu (A) > subgrain (C) > main grain (B)). Considering that fast annealing has already been applied prior to the slow oxidation in ambient conditions, one might reasonably expect the bare Cu area to show the most severe oxidation as we indeed observe. The graphene subgrain area shows much more extensive oxidation than the main grain area. We attribute this to a better lattice match between the main graphene grain and the Cu substrate. In addition, we can directly visualize the interface (grain boundary) between the main graphene grain and the subgrain. As shown in Figure 2 d-f, apparent line features can be distinguished from those AFM images which are taken from the area marked by the red arrow in Figure 2a (also see Figure S3a, b). Considering that no such grain boundary features appear under fast-annealing conditions alone (see Figure 1d) this oxide build up and visualization of the grain boundary is based on the robust oxidation of Cu substrate via long-term diffusion of oxygen and formation of Cu oxides as further confirmed from the higher-resolution AFM images (Figure S3c, d). With the continuous supply of oxygen through the grain interface, the width of the oxidized Cu beneath the defective graphene grain boundaries would occupy a larger space than the gap, thereby allowing the visualization of the grain boundaries. Whilst the graphene subgrain and its grain interface are visible on Cu based on the differing degree of oxidation, we note that there is no way of distinguishing optically between these regions after transfer to SiO$_2$/Si (Figure S4).
Figure 3. a) Bright-field optical image of a polygonal graphene domain on Cu after thermal annealing, b) SEM image of the polygonal graphene domain transferred onto a TEM Cu grid. c) Magnified SEM image taken from the upper corner of the graphene domain on Cu grid. d and e) The corresponding SAED patterns on the regions marked by number 1 and 4 in part b).

In order to identify the differing graphene orientations present in such bicrystals, we employ TEM and SAED to determine the crystalline structure of the as-grown graphene domains. A typical irregular polygonal graphene domain (Figure 3a) suspected of being a bicrystal was selected and transferred onto a copper grid for TEM observation. Figure 3b,c are low and high magnification SEM images of the graphene domain on the TEM copper grid. As shown, the red dotted line indicates the profile of the transferred graphene domain (Figure 3b) which corresponds exactly to its optically identified boundary (Figure 3a). Moreover, the high magnification SEM image (Figure 3c) taken from the upper corner of Figure 3b exhibits brighter
contrast of monolayer graphene with a jagged edge, indicating the successful transfer of graphene. Multiple SAED patterns were acquired from 9 different regions selectively distributed across the 2 grains of the bicrystal (see Figure 3b) to determine the crystalline structure of the graphene domain. Supplementary Figure S5 and Figure 3d,e corresponding regions marked with number from 1 to 9 in Figure 3b, generated a single set of hexagonal diffraction pattern characteristic of graphene monolayers. A ~20° rotation angle between the subgrain (marked with 1, 2, 3, 9) and main grain (marked with 4, 5, 6, 7, 8) was observed. This crystallographic misorientation results in a different coupling between the graphene and underlying Cu, and leads to a heterogeneous activation barrier for oxygen intercalation\textsuperscript{20, 28, 29}. In this scenario, Cu oxidation progress along the crystallographic orientation of each graphene grain with different oxidation rate, resulting in observable differences in Cu oxidation under the graphene domain. For single-crystalline graphene domains, homogeneous Cu oxidation is instead observed under the same conditions (Figure S6) due to the homogeneous activation barrier for oxidation.

Electron back scatter diffraction (EBSD) maps of the graphene bicrystal-Cu systems were obtained to confirm the crystal orientations of the underlying Cu grains. As shown in Figure 4a and b, the graphene domain contains a graphene subgrain readily identified by the differing degrees of oxidation of Cu underneath the graphene. Its corresponding EBSD characterization in Figure 4b shows that the area covered by the whole graphene domain has a homogeneous Cu(111) facet, which might be expected to display natively homogenous oxidation dynamics. This means that the graphene bicrystal crystalline orientation and resulting coupling with the same facet of Cu(111) (Figure 4c and d) results in the differing degree of oxidation and is responsible for the heterogeneous activation barrier for oxygen/H\textsubscript{2}O intercalation.
Figure 4. a) Optical image and b) the corresponding EBSD orientation map of graphene bicrystal domain on single Cu facet with different degree of oxidation. c) Schematic diagram of graphene lattice on Cu(111) with commensurate match and d) without commensurate match.

To elucidate the mechanism for the heterogeneous barrier of Cu corrosion and the resulting oxidation behavior, atomistic force field theory calculations were performed to investigate the
Figure 5. a) Top view of the most energetically stable H$_{60}$ GNF deposited on Cu (111) face. b) A zoomed view of the center of H$_{60}$ GNF. The primitive cells of Cu (111) surface and graphene are shown with yellow and white vectors, respectively. Blue and red carbon atoms denote the armchair and zigzag orientations in the GNF, respectively. Inset marks surface Bridge, Hollow and Top sites. c) Total relative energies of the graphene-Cu (111) coupling system. d) Average heights of GNF carbon atoms with respect to the Cu(111) surface. The average height is defined by the average value of all the GNF carbon atoms heights with respect to the Cu(111) surface as shown in the inset of d).

characteristics of a graphene domain with varying orientation over a Cu surface (see the Supporting Information for details). In order to deal with the periodic boundary conditions in atomistic modeling, we use a periodic infinite Cu(111) model and a large graphene nanoflake (GNF) deposited on the surface to mimic graphene. We then rotate the nanoflake stepwise and
translate it in the surface plane systematically to find the lowest energy ground state of this system pertaining to the preferred graphene growth direction (see Figure 5c). In addition, to cover many possible geometries of graphene on top of Cu, a center carbon atom in the GNF is used as a pivot point for the rotations, and for each set of rotations a new pivot is used by shifting the NGF until this pivot atom is in either of these three positions: I) on top of a Cu atom (T); II) over the bridge of a Cu-Cu bond (B); III) over a hollow site of Cu (H). Then, in each case of B, H and T, the GNF is rotated by 180° in 1° steps, around the pivot atom and the system is relaxed each time. Figure 5a, b shows the case of H with 60° rotation (H_{60}). The relative total energies of all of the obtained GNF-Cu(111) systems (Figure 5c) shows that there is strong similarity between the energies for B, H and T arrangements except for specific angles, and here the H position has the lowest energy. It is in this configuration that we also find the smallest average carbon heights above the Cu surface (Figure 5d), which indicates that the crystallography well-aligned GNF on Cu has a stronger coupling. This supports the notion that the minimum energy configuration for graphene on Cu also provides the most efficient barrier towards the O\_2/H\_2O diffusion along the interface. The variation of carbon atoms heights in different arrangements is investigated by measuring the carbon atoms z coordinates standard deviation for each arrangement (Figure 6a). Based on this, the contour of carbon atoms heights of H_{60} GNF on Cu (111) is plotted in the Figure 6b, showing a small fluctuation of graphene height from Cu(111).
Figure 6. a) Standard deviation of carbon atoms heights with respect to the Cu (111) surface. b) The contour plot of carbon atoms heights of H$_{60}$ GNF on Cu (111) face.

Overall, this suggests that graphene grows on Cu(111) surface to form a commensurate coupling system$^{23,30}$. The introduction of a subgrain with a differing orientation from the main grain then deviates from this commensurate configuration (Figure 4d) and the ultra-tight coating protection for Cu will be no longer in existence. In these regions of graphene subgrains/Cu surface, the graphene is not epitaxial with the underlying surface, and the interfacial strain would be released through local loss of adhesion, causing graphene wrinkles$^{23,30}$. This would make Cu oxidation faster by facilitating the diffusion of oxygen/H$_2$O into the interface.

We have shown that all of the variation we observe in the oxidation of Cu under graphene bicrystals can be ascribed to the misorientation of the graphene subgrain in the bicrystal which further misaligns with the lattice of Cu surface. This Cu-graphene misalignment affecting the degree of oxidation can also be observed in graphene single crystals which span multiple Cu domains. Figure S7 shows two Cu grains which display differing oxidation due to having two different orientations relative to the overlying single crystalline orientation of the graphene domain. This also results in different coupling strength of the graphene-Cu system, yielding a
heterogeneous oxidation resistance of Cu, therefore inducing a faster orientation influenced Cu oxidation over long timescales than would otherwise be observed, similarly to the bicrystal case.

CONCLUSION

In conclusion, we have observed and explained the differing degree of oxidation of Cu in the presence of graphene by exposing it to ambient conditions for long durations, and have demonstrated that the crystal structures of both graphene and the Cu substrate play a very important role in the coupling of graphene-Cu system and the resulting degree of oxidation observed. The slow Cu oxidation was found to proceed differently depending on the orientation of the graphene domains as a consequence of different strength of graphene-Cu interactions. Inhomogeneous thickness of Cu oxides, clearly seen using optical microscopy and Raman spectroscopy, directly indicates the crystallographic misorientation and grain boundaries of a graphene subgrain for each graphene domain, with these observations supported by atomistic force field calculations. This discovery provides insight into the mechanism of graphene barrier properties, and has important implications for a wide range of other 2D materials, as well as for important information for designing lattice-matched or mismatched graphene-Cu configurations, which are anticipated to possess unique properties and show potential in mechanical, anticorrosion, and electronic applications of CVD graphene.

ASSOCIATED CONTENT

Supporting Information

Optical, AFM images, additional SAED patterns and the details of atomistic force field calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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