

Supporting Information for:

# Graphene as a Long-term Metal Oxidation Barrier: Worse Than Nothing

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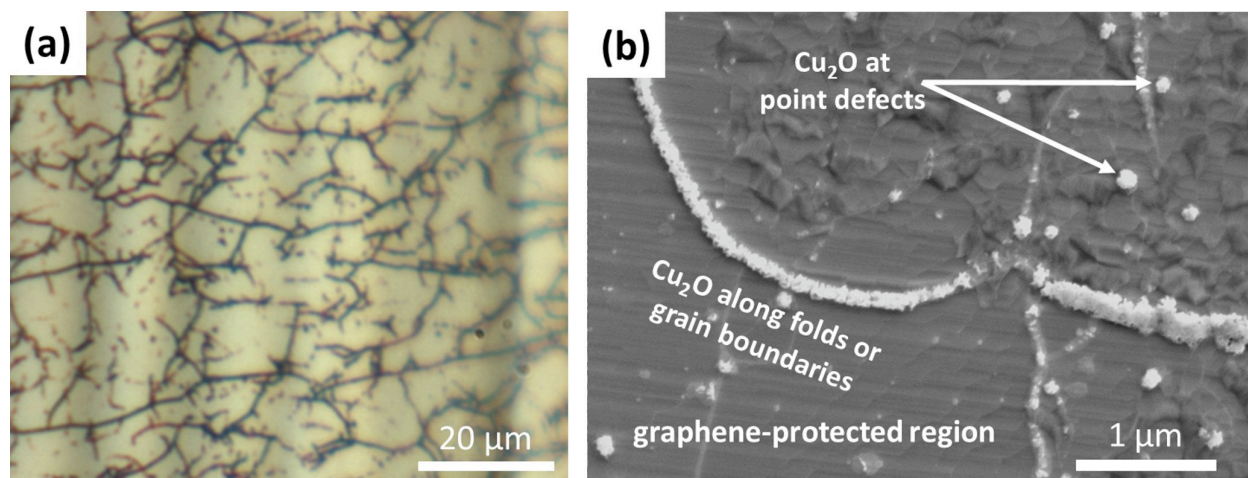
## Supporting Table

**Table S1.** Peak areas and energies for XPS data.

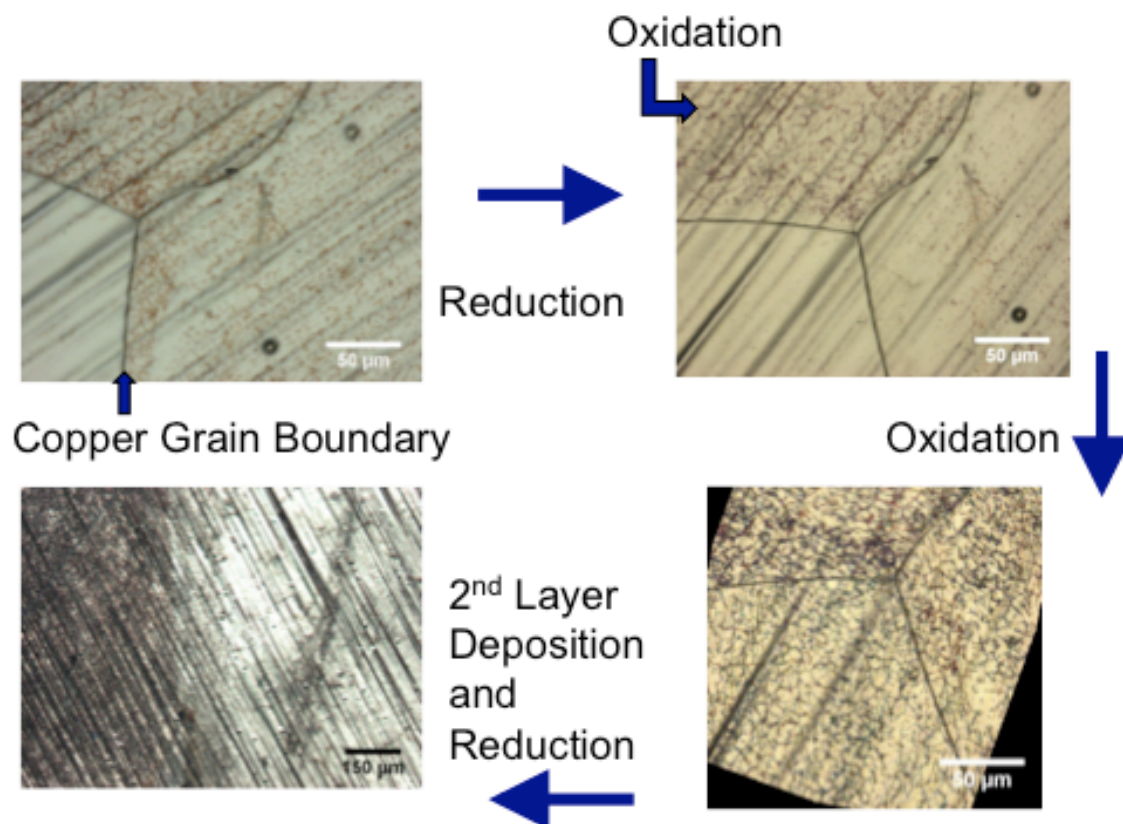
## Supporting Discussion

EDAX provides convincing but not complete information on the surface phase of the corroded, graphene-covered Cu. For bare Cu with a native oxide, we observe a Cu:O stoichiometry of approximately 71:29 at. %. The reason for the high Cu ratio is that the 2kV electron will tend to penetrate many nanometers of copper oxide before being absorbed. For thin native oxides, many electrons will reach the bulk Cu, thus skewing the measured stoichiometry in favor of Cu. For non-oxidized, graphene-covered Cu the observed Cu:O ratio varies from 80:20 at. % to almost 100% Cu. For aged, heavily-oxidized graphene-covered Cu, we typically measure Cu:O ratios of 67:33 at. %. The exactness of the  $\text{Cu}_2\text{O}$  stoichiometry indicates that the oxide layer is at least tens of nanometers thick.

## Supporting Figures

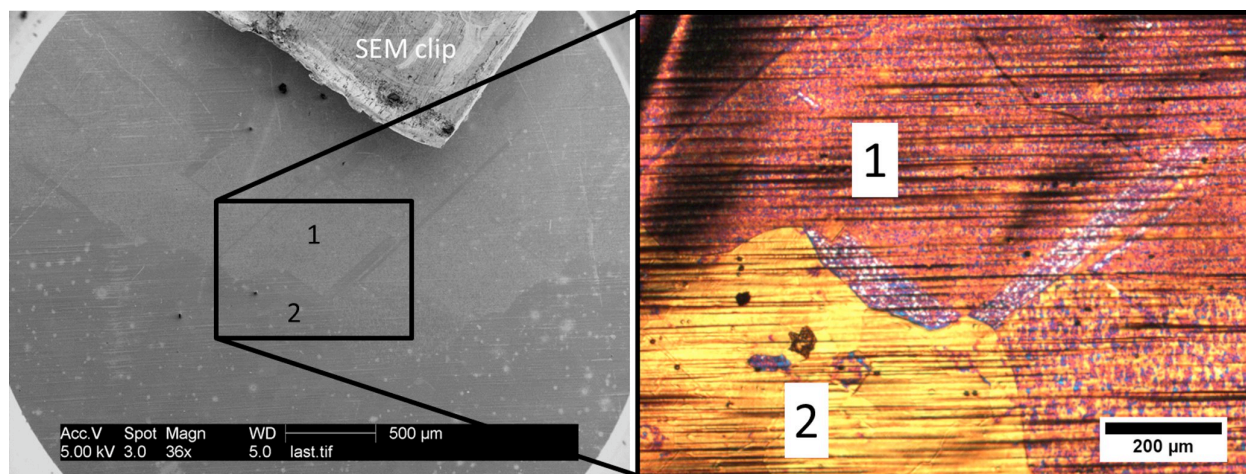


**Figure S1. Short-term oxidation resistance of graphene-covered Cu.** (a) Optical micrograph of CVD graphene grown on Cu foil, shown after oxidizing the foil at 185°C for 20 minutes. Most of the Cu remains protected, due to the impermeability of pristine graphene to  $\text{O}_2$ , and Cu oxidation is only seen at point defects, cracks, or grain boundaries in the graphene. (b) Scanning electron micrograph of the same oxidized graphene-covered Cu, revealing graphene's impressive short-term utility as an oxidation barrier.



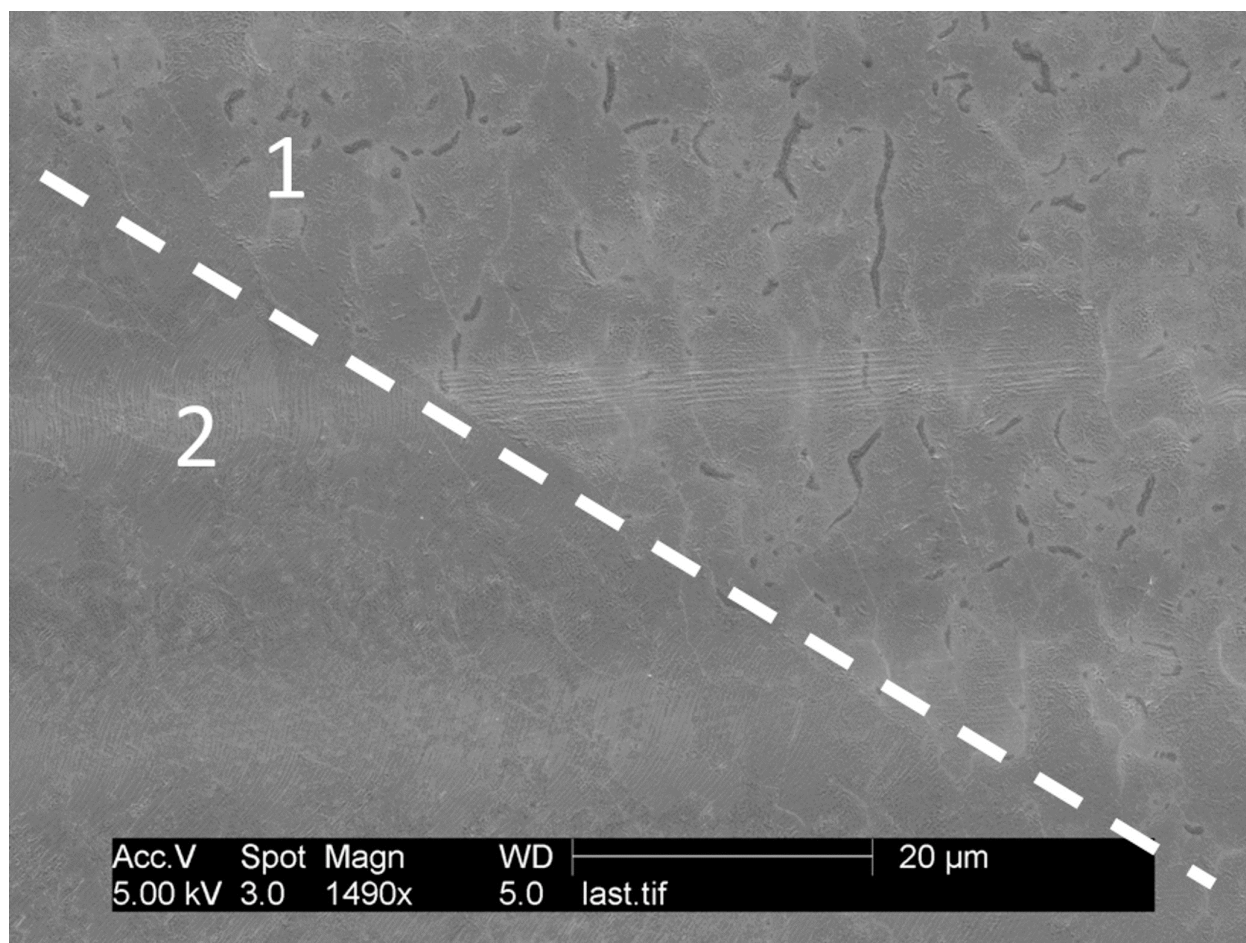
**Figure S2. Short-term oxidation and reduction through graphene mono- and bi-layers.**

These optical micrographs reveal that oxidation (by  $O_2$  gas at 225°C) and reduction (by  $H_2$  gas at 450°C) happen readily through a single as-grown graphene monolayer, but transfer of a second layer of graphene protects the Cu substrate from further oxidation (again by  $O_2$  gas at 225°C). This is explained by a simple geometric argument. It stands to reason that bilayer graphene should be a more robust anti-corrosion barrier than monolayer graphene, as the intersection of line defects in the two graphene layers will typically be point defects. (Trilayer graphene should prove better yet, as three layers of randomly aligned line defects will rarely coincide at even a single point.) Thus, Cu oxidation through bilayer graphene should proceed most quickly at sparse point defects (where line defects on the two layers coincide), and perhaps more slowly along line defects at the surface monolayer at a rate determined by the diffusion of  $O_2$  and  $H_2O$  between the graphene layers.



**Figure S3a. Varying  $\text{Cu}_2\text{O}$  thickness on different Cu grains for “aged” graphene-Cu.** The nature of the graphene-Cu interaction appears to vary depending on the local Cu facet and results in different thicknesses of copper oxide, as seen in the different Cu grains denoted by 1 and 2 in the SEM (left) and optical (right) images. This sample, monolayer graphene on Cu, has been aged in ambient conditions for 18 months since graphene growth. The copper oxide phase is  $\text{Cu}_2\text{O}$  in all regions, as determined by EDAX.



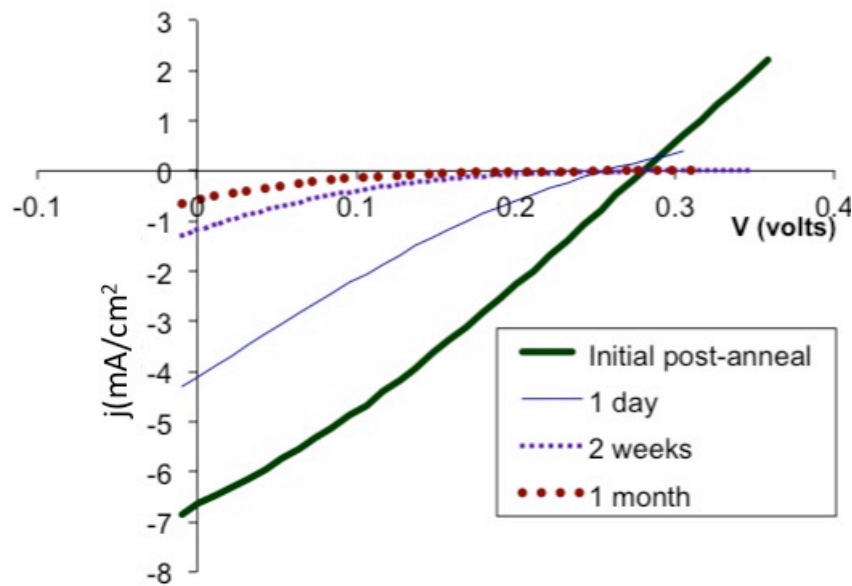


**Figure S3b. Varying microstructure of Cu corrosion for “aged” graphene-Cu.** A closer examination in the SEM of the border between Cu grains 1 and 2 (shown in Fig. S3a) reveals that the local microstructure of the  $\text{Cu}_2\text{O}$  varies significantly depending on the local graphene/Cu interaction. In region 1, the region in Fig. S3a with red/orange/purple coloration, the  $\text{Cu}_2\text{O}$  is rough and non-uniform, with cracks (dark lines) appearing to form on roughly the same size scale as the line defects in graphene. In region 2, the  $\text{Cu}_2\text{O}$  is more uniform. It is possible that the graphene-Cu interaction is more uniformly weak in region 2 than in region 1, permitting uniform diffusion of  $\text{O}_2$  and  $\text{H}_2\text{O}$  between the graphene and Cu. The dashed line separating regions 1 and 2 is not the exact border but an approximate guide to the eye.

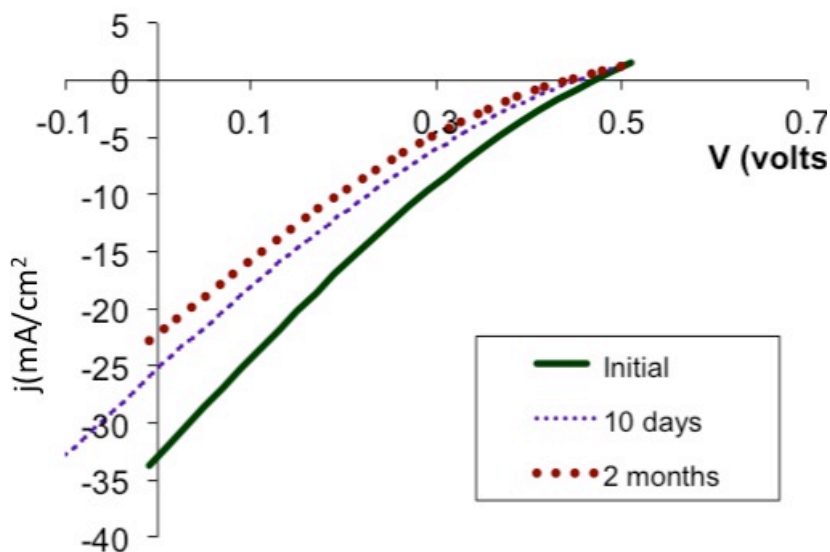
**Discussion of Fig. S4:** Graphene-Si Schottky barrier solar cells are fabricated using previously published methods.<sup>26</sup> If thick ( $> 2$  nm)  $\text{SiO}_2$  were to form at the graphene-Si interface it would hinder performance due to increased series resistance. We ensure no  $\text{SiO}_2$  is present initially by etching the Si surface with buffered hydrofluoric acid before deposition of the first layer of graphene, followed by a reducing  $\text{H}_2$  anneal after graphene deposition. We compare a device with a single layer of graphene to a device with a second graphene layer deposited immediately after the reduction anneal. Fig. S5 shows the vastly different long-term performance of monolayer (Fig. S5a) and double layer (Fig. S5b) graphene-Si solar cells. The monolayer device degrades quickly, whereas the double layer device maintains most of its initial power output for

many weeks. Each additional layer of graphene considerably slows the diffusion of  $O_2/H_2O$  to the substrate, thus slowing the formation of oxide. While the degradation of the double-layer graphene on silicon device appears to slow over time, the long-term performance of the photovoltaic device is unknown. It is important to note that graphene grown as a bilayer, rather than two successively transferred monolayers (i.e. double layers) is unlikely to have this beneficial effect because cracks would often coincide in both layers, whereas in double layer configurations cracks do not align.

### a. One layer Graphene on n-cSi



### b. Two layers Graphene on n-cSi



**Figure S4. Air stability of monolayer and bilayer graphene-Si solar cells.** All cells were tested with simulated AM1.5 illumination. (a) The performance of monolayer graphene on n-cSi decreases rapidly over time, likely due to the formation of resistive SiO<sub>2</sub> between the graphene and Si. Atmospheric doping of graphene, if it were the dominant factor, should tend to p-dope the graphene and decrease its resistance, improving device performance. (b) The performance of double layer graphene on n-cSi is more stable over time, with only modest degradation between 10 days and 2 months. This stability is likely due to the slowed diffusion of O<sub>2</sub>/H<sub>2</sub>O through the additional graphene layer.

	Binding Energy (eV)	Bare	Graphene
<b>Carbon</b>	285	14337	31367
<b>Oxygen</b>	532	54874	61878
<b>Si<sup>4+</sup></b>	103.4	11142	12800
<b>Si<sup>0</sup></b>	99.53	51122	28157

**Table S1. Peak areas and energies for XPS data.**

Size and binding energy for Gaussian fits to data shown in Fig. 5 of the main text. The peak areas show that there is as much oxygen present underneath the graphene as on the bare silicon, and that it is bonded to the silicon, resulting in silicon in the 4+ oxidation state. The relatively smaller Si<sup>0</sup> peak in the graphene-covered sample is likely due to the limited penetration depth of the X-ray beam.