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Oxidation of Copper in the Presence of Graphene

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ABSTRACT

Graphene is a promising barrier material for Cu interconnects due to its ability to reduce surface electron scattering and thereby lower resistivity in integrated circuits. However, literature reports graphene also shows a propensity to intercalate and dissociate water molecules that could lead to the oxidation of the underlying Cu. This work focuses on understanding the conditions under which the presence of graphene could exacerbate the oxidation of Cu. We discover that exposure of graphene-Cu to a high intensity light source such as a laser, in the presence of ambient moisture, could dramatically increase the rate of Cu oxidation, whereas a more dry environment like an oven would lead to less Cu oxidation, compared to a bare Cu surface.

INTRODUCTION

Copper is a commonly used metal in the advanced semiconductor industry where its oxidation needs to be prevented to ensure low resistivity at nanometer-scale pitch interconnect levels in integrated circuits (IC).[1] Therefore, the development of an ultrathin barrier to protect Cu is important to the manufacture of ICs. Typical barrier materials that are used in the industry include Ta, TaN, SiN and SiCN, but as Cu interconnect dimensions decrease, diffuse surface scattering of electrons becomes dominant and Cu resistivity increases.[2,3] Graphene has been shown to be a promising barrier material to reduce surface scattering and thereby resistivity in Cu.[4,5] Furthermore, numerous studies suggest single crystal continuous graphene can make Cu more resistant to thermal oxidation and wet corrosion.[6,7] However, single-crystal graphene synthesis is limited by high temperature growth conditions and slow kinetics, which prevents its implementation and scalability in ICs. On the other hand, scalable graphene deposited in a manufacturing environment is typically polycrystalline and defective in nature and hence its performance as an oxidation/corrosion barrier largely depends on the grain size and defectivity.[8, 9] The purpose of this study is to understand the oxidation behavior of Cu with polycrystalline graphene in ambient environment during thermal, water exposure, and laser-induced oxidation.

METHODS

We investigated the oxidation of polycrystalline Cu with mono- to bi-layer graphene deposited on Cu using a unique, selective, low temperature (<400°C) process. Cu substrates were 100nm of polycrystalline physical vapor deposited Cu on top of 10 nm of Ta on single crystal Si. Thermal oxidation was performed in an ambient environment oven at 200°C for durations of 10, 20 and 30 min. Water exposure oxidation was done at room temperature by allowing a droplet of water to dry on the surface of graphene-Cu. Finally, laser oxidation was induced by increasing laser power or number of scans during Raman measurements being performed in ambient environment at room temperature. Laser oxidation was performed at 25 mW power. Lower powers were tested too, but it didn't result in any detectable level of oxidation.

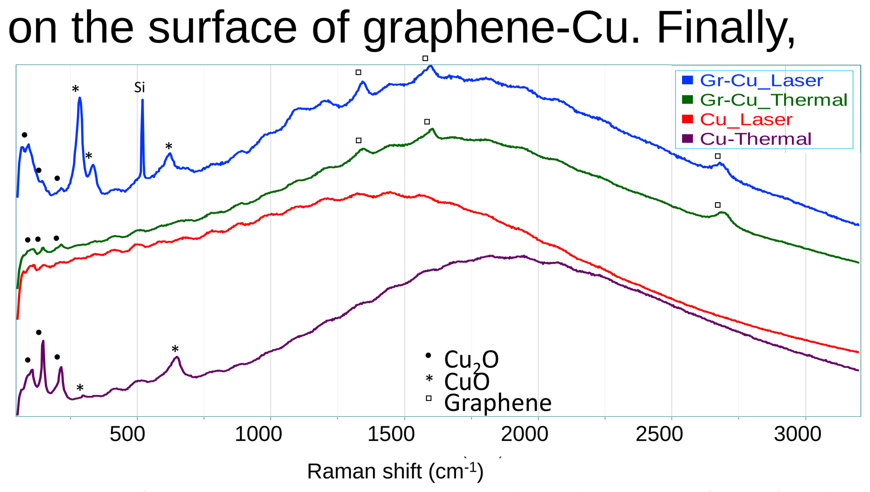

FIGURE 1. a) Representative Raman spectra of graphene on Cu (Gr-Cu) and reduced Cu oxidized by laser and thermal oxidation.

REFERENCES

(1) Chawla, et al. *Applied Physics Letters* **2010**, *97* (13), 132106. DOI: 10.1063/1.3489357
(2) Moon, et al. In *IEEE International Electron Devices Meeting (IEDM) 2003*, pp 35.31.31-35.31.34. DOI: 10.1109/IEDM.2003.1269410
(3) Chawla, J. S.; Gall, D. *Applied Physics Letters* **2009**, *94* (25), 252101. DOI: 10.1063/1.3157271.
(4) Mehta, et al. *Nano Letters* **2015**, *15* (3), 2024-2030. DOI: 10.1021/nl504889t.
(5) Nogami, et al. In *IEEE International Electron Devices Meeting (IEDM)*, 2021, pp 22.2.1-22.2.4, DOI: 10.1109/IEDM19574.2021.9720525.
(6) Chen, et al. *ACS Nano* **2011**, *5* (2), 1321-1327. DOI: 10.1021/nn103028d.
(7) Kirkland, et al. *Corrosion Science* **2012**, *56*, 1-4. DOI: https://doi.org/10.1016/j.corsci.2011.12.003.
(8) Seifert, et al. *2D Materials* **2015**, *2* (2), 024008. DOI: 10.1088/2053-1583/2/2/024008.
(10) Hong, et al. *ACS Applied Nano Materials* **2018**, *1* (6), 2515-2520. DOI: 10.1021/acsanm.8b00646.
(12) Castrejón-Sánchez, et al. *Materials Research Express* **2019**, *6* (7), 075909. DOI: 10.1088/2053-1591/ab1662.
(13) Feng, X.; Maier, S.; Salmeron, M. *Journal of the American Chemical Society* **2012**, *134* (12), 5662-5668. DOI: 10.1021/ja3003809.
(14) Vecera, et al. *Nature Communications* **2017**, *8* (1), 15192. DOI: 10.1038/ncomms15192.

RESULTS & DISCUSSION

TABLE 1. Copper oxide phase and Raman signal of Cu and Gr-Cu under various oxidation conditions.[11]
Key: VS = very strong, S = strong, M = medium, W = weak, VW = very weak Raman signal.

Film	Oxidation method	unknown 69 cm^{-1}	Cu 93 cm^{-1}	Cu_2O 107 cm^{-1}	Cu_2O 148 cm^{-1}	Cu_2O 215 cm^{-1}	CuO 285-299 cm^{-1}	CuO 335 cm^{-1}	CuO 621-649 cm^{-1}
Cu	Thermal	-	M	M	S	S	VW	-	S
Cu	Water	-	S	-	W	M	-	VW	-
Cu	Laser	-	-	-	-	-	-	-	-
Gr-Cu	Thermal	-	-	W	W	W	-	-	-
Gr-Cu	Water	-	S	-	W	W	S	W	W
Gr-Cu	Laser	S	S	-	W	W	VS	S	S

The thermal oxidation of bare Cu led to the growth of a Cu_2O/CuO film up to 30-40 nm thick across the entire surface of Cu (Fig. 1, 2a, 2b, Table 1). Whereas the thermal oxidation of graphene-Cu led to the growth of predominantly Cu_2O, the more thermodynamically accessible phase, present only at the grain boundaries of graphene (Fig. 2c, d, Table 1).[8,9,10,11] Interestingly, room temperature laser-induced oxidation led to zero oxidation of bare Cu (Table 1, Fig. 1) but significant CuO phase formation in the graphene-Cu system (Table 1, Fig. 4). CuO, the more oxidized phase of Cu, is typically not accessed until high temperature (>200°C) or long periods of thermal oxidation,[12] suggesting that there may be a catalytic effect imposed by the presence of graphene on Cu. Similarly, water droplet oxidation of Gr-Cu shows the presence of both Cu_2O and CuO, whereas water oxidation of bare Cu does not form significant CuO. Intercalation and dissociation of water under graphene has been reported in the literature,[13,14,15,16] which could explain the more significant oxidation of underlying Cu to the CuO phase in the presence of graphene and moisture. As the graphene intercalates water and dissociates it to –OH groups and the Cu surface is locally heated by the laser energy, Cu readily oxidizes by the close proximity of –OH to its surface. In addition, top-down SEM shows the presence of highly crystalline CuO nanostructures on the Gr-Cu laser-oxidized sample (Fig. 4), compared to the more amorphous mixed Cu_2O/CuO appearance of thermally oxidized Cu (Fig 1a, b).

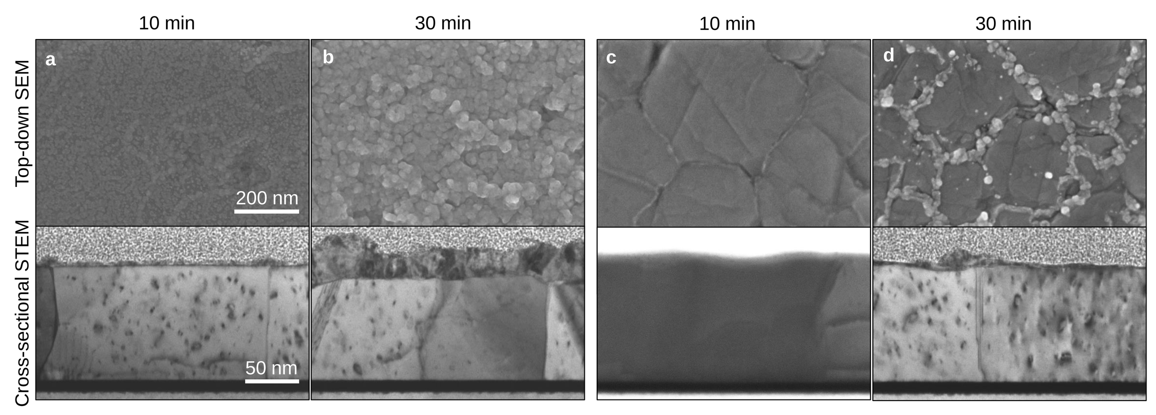

FIGURE 2. Top-down SEM and cross-sectional STEM of various time durations of thermal oxidation on bare Cu and graphene on Cu. a) 10 min and b) 30 min thermal oxidation of bare Cu. c) 10 min and d) 30 min thermal oxidation of graphene-Cu.

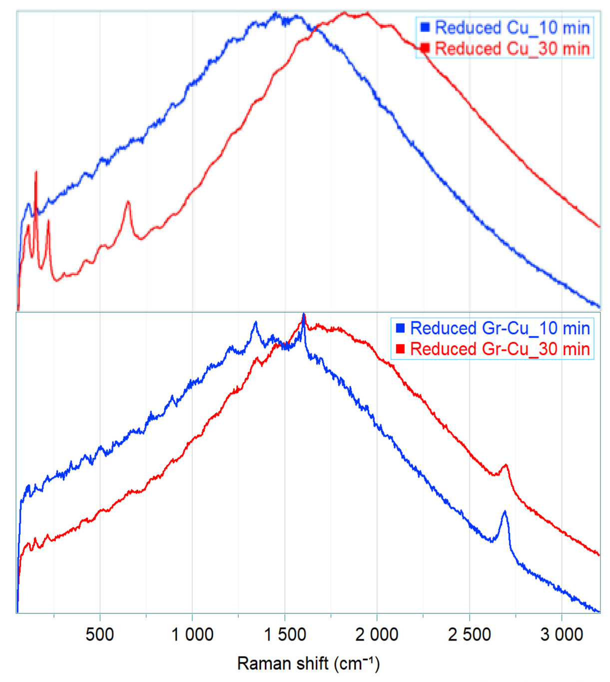

FIGURE 3. Representative Raman spectra of reduced Cu (a) and graphene on Cu (Gr-Cu) (b) substrates after thermal oxidation durations of 10 and 30 min.

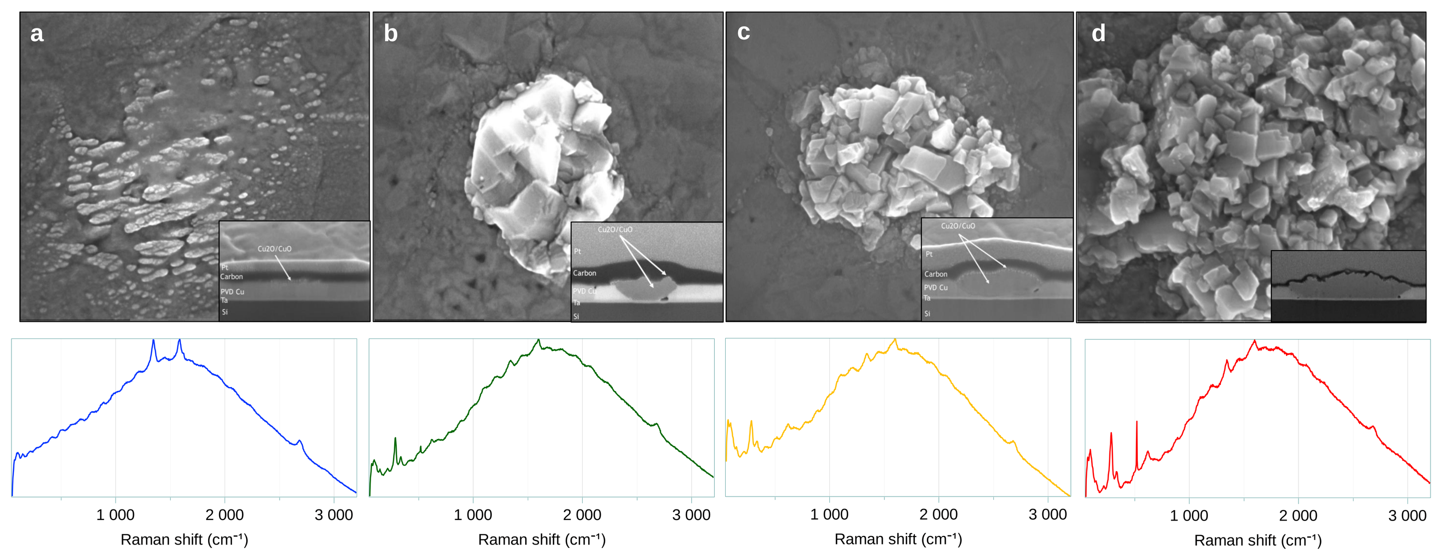

FIGURE 4 Top row (a-d): top-down SEM and cross-sectional STEM for different levels of oxidation using 25 mW, 532 nm laser. Raman was used to monitor the degree of oxidation (bottom row).

SUMMARY

Overall, this work shows that graphene in the presence of water can catalyze the growth of CuO on the surface of Cu and understanding this phenomenon is important for the implementation of graphene as a protective barrier for Cu. Increasing quality of graphene can help reduce this effect as water intercalation likely occurs at defect sites (grain boundaries and sp^3-bound C). In addition, this is the first study of laser oxidation of Gr-Cu at low laser power where we use the energy derived from the laser power to exacerbate the growth of CuO. Hence, limiting the exposure of Cu to moisture and high temperature is of critical importance in preventing CuO_x growth in interconnect fabrication.

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