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Moisture Barrier Properties of Single-Layer Graphene Deposited on Cu Films for Cu Metallization

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Abstract

The moisture barrier of single-layer graphene (SLG) for Cu metallization is demonstrated under the conditions of high temperature and high humidity (HTHH) test at various time. Optical microscopy is used to observe the color change of a Cu film. X-ray photoelectron spectroscopy (XPS) is performed to investigate the Cu oxidation after HTHH test. The different quality of graphene film is considered to measure the thickness of oxidized Cu by using spectroscopic ellipsometry. SLG film exposes the high efficient film to against the Cu oxidation from moisture.

1. Introduction

Graphene has been expected to be atomically thin coating for Cu interconnects as a Cu diffusion barrier with enhanced conductivity and higher electromigration reliability [1-3]. Graphene was also reported as an impermeable film against gas and moisture [4, 5].

In this paper, the moisture barrier properties of single-layer graphene (SLG) directly deposited on Cu by CVD was investigated to study the potential of CVD-SLG barrier for Cu metallization in long-term storage memories using HTHH test. The SLG deposited on epitaxial Cu which features large grain-sizes as large as 50-100 μm [6] to determine the future target of SLG quality for moisture barrier in Cu metallization.

We found that pure SLG can prevent Cu oxidation during HTHH tests and the enhancement of grain size in the SLG film is important to obstruct the oxidation of Cu.

2. Experimental Methodology

Figure 1(a) and 1(b) show a SLG-coated Cu and bare Cu samples, respectively. The large grain size SLG was deposited on Cu (111) / *c*-plane sapphire as previously reported [6]. To observe and compare the difference of oxidation, HTHH tests were performed under the conditions of 85℃ and 85% humidity at various time, such as 25, 50, and 100 hrs. After HTHH test, the optical microscopy is employed to observe the color change of both films. XPS is then used to identify the Cu2p and O1s elements which exist on the sample surface.

In this paper, two main experiments are carried out. The first experiment is the investigation of moisture barrier of SLG for Cu layer using a uniform SLG/Cu sample.

The second experiment, a non-uniform film of graphene/Cu film is used to evaluate the performance of oxidation barrier by measuring the thickness of oxidized Cu layer by the spectroscopic ellipsometry, correlating with the variation of graphene quality at measurement points as show in figure 2.

3. Results and Discussion

On the first experiment, figure 3 (a-d) shows the optical images of SLG-coated Cu and (e-h) bare Cu samples under the HTHH test at various time, respectively. The color of Cu film in figure 3(a-d) show the same color tone of Cu, but gradually occur the dark lines on Cu surface after keeping under the HTHH test. The surface of bare Cu after HTHH test changes to dark color after keeping in HTHH test, as show in figure 3(e-h). The results indicate that the most areas of Cu film under SLG can be protected from oxidation by moisture. The dark lines of SLG-coated Cu sample may be due to the oxygen leak in the area of SLG grain boundaries.

Figure 4 and 5 show the XPS spectra of SLG-coated Cu and bare Cu sample, respectively, after keeping both samples under the HTHH conditions. The peak intensity is proportional to the amount of elements within the area of X-ray radiation. The results of SLG-coated Cu at each time of HTHH test show the similar Cu2p spectra corresponding to metallic Cu and Cu_2O but slightly change the amplitude only, as in figure 4. On the other hand, the XPS spectra of bare Cu is not only reduce the amplitude of metallic Cu and Cu_2O peaks but also increase the peaks of CuO after a long time of HTHH test, as shown in figure 5. Table I shows the comparison of the O1s/Cu2p atomic concentration ratio between with and without SLG before and after 100 hr HTHH tests. The XPS results clearly show that SLG can prevent the Cu surface from the moisture. The results are corroborated by the first-principles molecular dynamics simulations (FPMD) that oxygen atoms/molecules could not pass through the SLG layer as shown in figure 6.

The second experiment shows the thickness of oxidized Cu layer after 200 hr HTHH test depends on the various characteristic of graphene layer modeled by spectroscopic ellipsometry using the database of SLG and amorphous-carbon (a-C). In Table II, point 1-4 and point 5-10 correspond to the area that covered by pure SLG layer and the area covered by mixed layer of SLG and a-C, respectively. The last two points correspond to the area that covered by pure a-C layer, as in point 11 and 12. The oxidized Cu thickness of SLG-coated Cu area is thinner than those of mixed SLG/ a-C and pure a-C. It means that the pure SLG film has the highest performance for obstruction the oxidation of Cu film.

4. Conclusions

To evaluate the moisture barrier properties of CVD-SLG for Cu film, the HTHH test at 85℃ and 85% humidity is performed. The results show that SLG has the potential of atomic layer barrier to prevent Cu oxidation from moisture. It is suggested that the enhancement of grain size and the elimination of grain boundary diffusion will be critical issues for the moisture barrier application of graphene.

Acknowledgements

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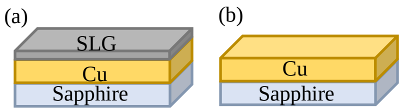

Fig. 1 (a) SLG-coated Cu film and (b) bare Cu samples.

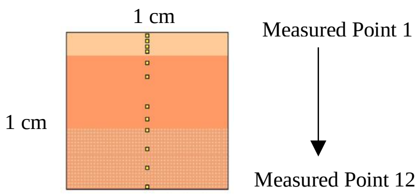

Fig. 2. Ellipsometer measured points for Cu covered by graphene with area variation.

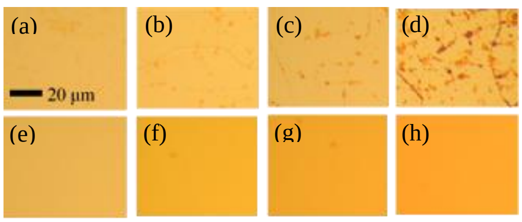

Fig. 3. (a-d) and (e-h) show optical images of SLG-coated Cu and bare Cu sample after HTHH test at 0, 25, 50, and 100 hr, respectively.

Table I. Comparison of O1s/Cu2p atomic concentration ratio.

Sample	O1s/Cu2p	
	Before HTHH	After 100 hr HTHH
SLG-coated	0.15	0.34
Without SLG	0.94	1.56

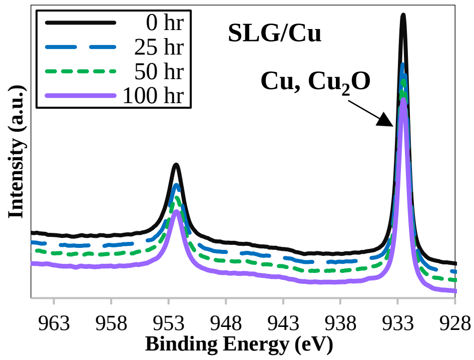

Fig. 4. XPS spectra of Cu2p for SLG-coated Cu sample after HTHH test at 0, 25, 50, and 100 hr.

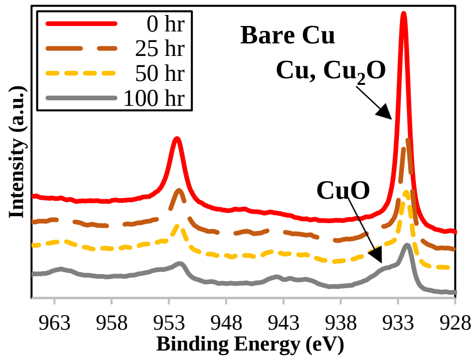

Fig. 5. XPS spectra of Cu2p for bare Cu sample after HTHH test at 0, 25, 50, and 100 hr.

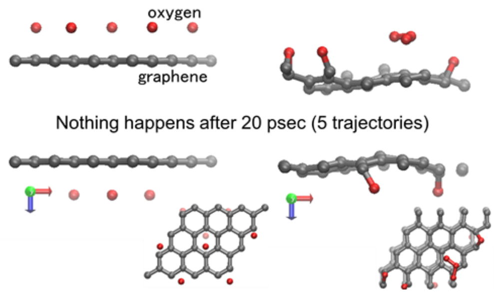

Fig. 6. Geometric structures of oxygen molecules separated from vacuum spacing by two SLG layers at 2000K after 20 psec MD time.

Table II. Thickness of oxidized Cu vs. SLG quality (mixing ratio).

Measured	SLG mixing ratio (%)		Thickness (nm)	
Point	a-C	Graphene	Oxidized Cu	SLG
1	0.0	100.0	0.82	0.21
2	0.4	99.6	1.93	0.48
3	0.0	100.0	2.64	0.63
4	0.0	100.0	4.99	0.85
5	48.0	52.0	16.05	3.17
6	53.8	46.2	13.36	2.42
7	57.6	42.4	12.35	2.26
8	55.9	44.1	12.42	2.29
9	59.6	40.4	11.20	1.57
10	61.5	38.5	10.42	1.18
11	100.0	0.0	10.89	0.79
12	100.0	0.0	10.88	0.98