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 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°C 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 shown 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 CuO 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 CuO peaks but also increase the peaks of Cu2P and O1s elements which exist on the sample surface.

In Table I, 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°C 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.

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References