Suppression of Cu Oxidation by Single-Layer Graphene under High Temperature and High Humidity Test

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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 research, the moisture barrier properties of single-layer graphene (SLG), which was directly grown on epitaxial Cu by CVD, was investigated to study the potential of CVD-SLG barrier for Cu metallization in long-term storage memories by high temperature and high humidity (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.

Method: Figure 1(a) and 1(b) show a SLG-coated Cu and bare Cu samples, respectively. The large grain size SLG was grown 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.

Results and Discussion: The color of Cu film in figure 2(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 shown in figure 2(e-h). Most of Cu film areas under SLG can be protected the oxidation from moisture. The dark lines on SLG-coated Cu sample may be due to the oxygen leak in the area of SLG grain boundaries.

Figure 3(a) and (b) 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 analysis area. 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 3(a). 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 3(b).

The results clearly imply that 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.

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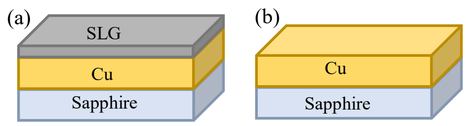

Fig.1 (a) SLG-coated Cu film and (b) bare Cu samples

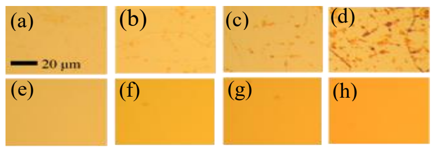

Fig.2 (a-d) and (e-h) show optical images of SLG coated Cu and bare Cu sample after HTHH test

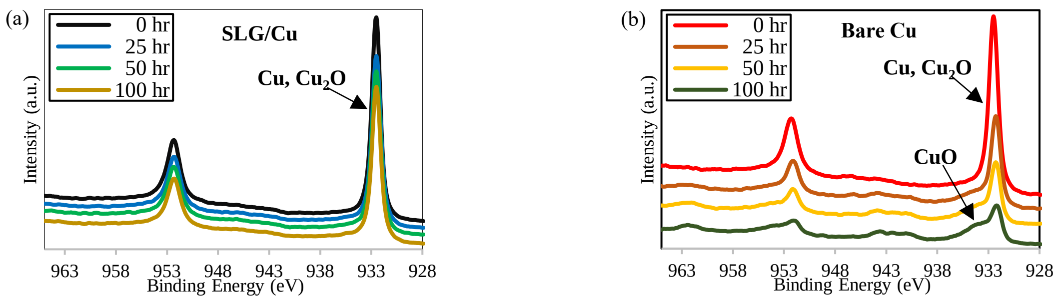

Fig.3 XPS spectra of Cu2p for (a) SLG-coated Cu sample and (b) bare Cu sample after HTHH test 0, 25, 50, and 100 hr.

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