Copper Oxidation Effect in the EMC/Cu Interfacial Adhesion Improvement for a Novel Copper Interconnection Substrate Application

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Abstract

Copper oxidation structure, cupric oxide (CuO) and cuprous oxide (Cu_2O), under Ar/H_2 plasma reaction mechanism for the EMC/Cu interface adhesion improvement was studied in this work. This work is utilized TGA to figure out Cu oxidized state and sample preparation, and using plasma treatment Cu oxidation layer to evaluate the EMC/Cu interface adhesion strength by shear testing method. Results show a plasma reduction on Cu oxidation layer provide a better interface adhesion, and the layer structure has a significant composition change, Cu/Cu_2O/CuO/EMC → Cu/Cu_2O/CuO/Cu_2O/EMC. These layer structures were identified by high-resolution TEM mapping with EELS spectrum fitting, it was also verified for CuO reduction to form Cu_2O, following the Cu_2O hydration would provide much hydrogen-bonding in the EMC/Cu interface. This kind of chain reaction mechanism including CuO reduction and Cu_2O hydration was described by $2CuO + H_2 \rightarrow Cu_2O + H_2O \rightarrow 2CuOH$ (hydration molecular). The reaction mechanism of the EMC/Cu bonding has been investigated and verified in this experimental study and our conclusion is that hydrogen bonding on the Cu oxidation layer surface can strengthen the EMC/Cu interface adhesion.

Key words

Cupric Oxide, Cuprous Oxide, Epoxy Molding Compound, Transmission Electron Microscope, Electron Energy Loss Spectroscopy.

I. Introduction

Epoxy molding compounds (EMCs)/Copper (Cu) interfacial adhesion characterization was investigated to reduce delamination issues by considering a key factor of this material technology. The key factor, copper trace/interconnection in the EMC/Cu interface is associated with bottom-up substrate development. This low-cost novel substrate can be used instead of the popular BGA (Ball Grid Array) substrate and can be a replacement for other advanced packaging technologies such as WLCSP (Wafer Level Chip Scale Package), fcCSP (Flip Chip-Chip Scale Package), PoP (Package on Package), eWLB (Embedded Wafer Level Ball Grid Array), and SiP (System in Package), etc. In 3D package development, these packages face many materials property challenges since these substrate materials have to possess high heat dissipation efficiency, high reliability to meet high-density packaging requirements and fine-pitch technology applications. Therefore, this kind of copper trace/interconnection constructed in the structure is an attractive solution, the delamination usually happen at EMC/Cu interface due to this structure has a weakness of the EMC/Cu adhesion. This study is researching a Cu oxidation effect in the EMC/Cu interfacial adhesion improvement as a solution for delamination of advanced packaging [1].

Copper oxidations have two species, Cu_2O of semi-oxidized state (cuprous oxide, Cu^{+}) and CuO of full-oxidized state (cupric oxide, Cu^{++}) oxidized state, adhesion strength of two oxidized states and oxidation thickness was studied at different temperatures and times in Chong's research [2]. Cupric oxide of monoclinic structure has been measured to obtain higher the enthalpy (ΔH_f) and lower bonding energy than cuprous oxide of cubic structure [3]. Zhu et al. reported the activation energies (Q_a) of CuO and Cu_2O for different temperature ranges [4]–[7], they have utilized thermos-gravimetric and surface analysis to claim Cu_2O lattice diffusion at higher isothermal temperature (800 ºC~1050 ºC), Cu_2O Grain boundary + lattice diffusion at temperature (300 ºC~550 ºC), results also showed that rich CuO percentage and lower the Q_a were at lower temperature, it seems to explain the Q_a of CuO less than Cu_2O, this conclusion also approach their the physical properties as the enthalpy and bonding energy. Higher temperature has benefited the formation of Cu_2O species due to the Cu_2O species formation need consume more Cu.

In this study, TGA under air flow has been utilized to research Cu foil oxidation rate and Arrhenius relationship with isothermal temperature to determine the thermal condition. This work also utilize the transfer EMC molding on Cu foil as a pudding structure and using shear testing method to determine the EMC/Cu interfacial adhesion performance for different surface experimental conditions. These experimental conditions of Cu oxidation thickness and the EMC/Cu interfacial observation were measured and analyzed by FIB, and we utilize TEM/EELS analysis to identify the Cu oxidation composition and the EMC/Cu interfacial bonding characterization.

II. Experiment

A. Cu Oxidation

A 6x6 mm Cu foil was constructed by C194 with EBO material as pudding mold sample preparation, Cu base contain Fe(2.1~2.6%), Zn(0.05~0.2%), and P (0.015~0.15%). The Cu foil oxidation conditions were utilized Thermos-Gravimetry Analyzer (TA Instruments, the Discovery TGA) to control isothermal, using air flow to proceed isothermal oxidation, the flow was keep 100 mL/min till the temperature ramp down to 25^{o}C. Isothermal curve of Cu oxidation function of time was fitted, Cu oxidation rate of the fitting result has been drawn Arrhenius plot with different oxidation temperatures to evaluate $Cu/Cu_2O/CuO$ layer structure why are kinds of diffusion and estimated its the activation energy [4]-[7].

B. Plasma Treatment

A 500 watt and 2.45 GHz microwave plasma (PVA TePla GIGA 690 model) with electron couple resonance (ECR) mode was utilized as surface reaction experiment for Cu oxidation layer, a strip size (76mm x 256mm including 390 pcs 6x6 mm Cu foil sample) with the ECR slot magazine (78mm x 258mm) was studied as plasma reaction chamber‘s the sample and jig of experimental substrate, this chamber was keep 0.2 mbar vacuum under microwave power on, the ECR mode was suggested proceeding for 600s.

C. Adhesion Testing Method

Transfer mold technology was utilized as a pudding mold sample preparation, its operation conditions were at 175^{o}C, 7MPa for 100s, following post-mold curing condition was performed 175^{o}C for 4 hours. A precision bond-testing instrument (Nordson Dage 4000plus) was used to determine the EMC/Cu interface adhesion force [8], [9], the adhesion force can be measured at room temperature and 260^{o}C by shear testing method as Fig. 2(a) and 2(b), respectively. Experimental testing sample was sampling at strip front and center and back, total around 30 pcs. Three samples were studied as experimental verification, sample 1 was as a manufacturing base line, no process treatment, samples 2 and 3 were as comparison of plasma treatment, sample 2 was experimented at 100^{o}C for 48hrs and without plasma treatment, 150^{o}C for 48hrs with plasma treatment has been performed in sample 3.

D. TEM/EELS Analyses

Focus Ion Beam (FEI Helios G4 Dual-Beam System, FIB) was utilized to observe Cu oxidation layer and prepare the TEM/EELS sample within the EMC pudding mold on Cu interface, the sample was confirmed thin film quality and layer structure stability by Transmission Electron Microscope (FEI Talos F200X G2, TEM) with Energy Dispersive X-ray Spectroscopy (EDS). Electron Energy Loss Spectroscope (Gatan Quantum 965, EELS) was equipped in Cs corrector Field Emission-TEM (Jeol ARM-200F), this technology was utilized to identify CuO and Cu_2O species [10]-[13] and determine the interface chemical composition, and precise to evaluate the material adhesion characterization.

III. Results and Discussion

Cu oxidation and plasma treatment were studied in this work due to the EMC/metal interface delamination improvement was an important action in assembling manufacture. Before EMC molding, the EMC/metal adhesion improvement in metal surface is not only remove oxidation layer in wet bath but also reduction the oxidation layer using dry cleaning treatment. Lee and Kim had reported that the Cu oxidation had better adhesion than surface cleaning Cu in epoxy base compound [1], according to Cu oxidation conditions and its oxidized state as the EMC/Cu improvement aspect was considered. This work had utilized TGA analysis for different isothermal temperatures, weight gain of Cu oxidation, to draw Arrhenius plot as showed in Fig. 1, activation energy of Cu oxidation and its related parameters was obtained in Table 1. High temperature range from 300 to 900^{o}C, this range was pointed out Cu_2O lattice/grain boundary layer’s diffusion [4], low temperature range of below 300^{o}C might suppose CuO layer formation. The highest activity energy (Q_a) of Cu oxidation was shown at 150^{o}C~160^{o}C of Table 1, this lower temperature range should be CuO due to the final Cu oxidized status possess higher the Q_a value, this conclusion was different with some researcher’s result [4]–[7], due to those Q_a didn’t have literature reporting below 300^{o}C.

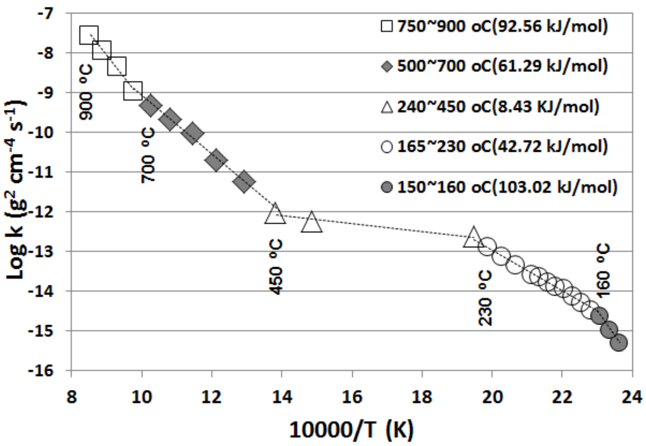


Fig. 1. Arrhenius plot of Cu oxidation isothermal fitted by weight-time curve from 150 to 900ºC.

Table 1. Arrhenius relationship of fitting results, k = a * exp (-b/T), b = Q_a/R.

Temperature range (°C)	log a	b	R^2	Q_a (kJ/mol)
150~160	13.983	1.2391	0.9995	103.02
165~230	-2.6943	0.5138	0.9942	42.72
240~450	-10.667	0.1014	0.9589	8.43
500~700	-1.6893	0.7373	0.9911	61.29
750~900	1.9643	1.1133	0.9925	92.56

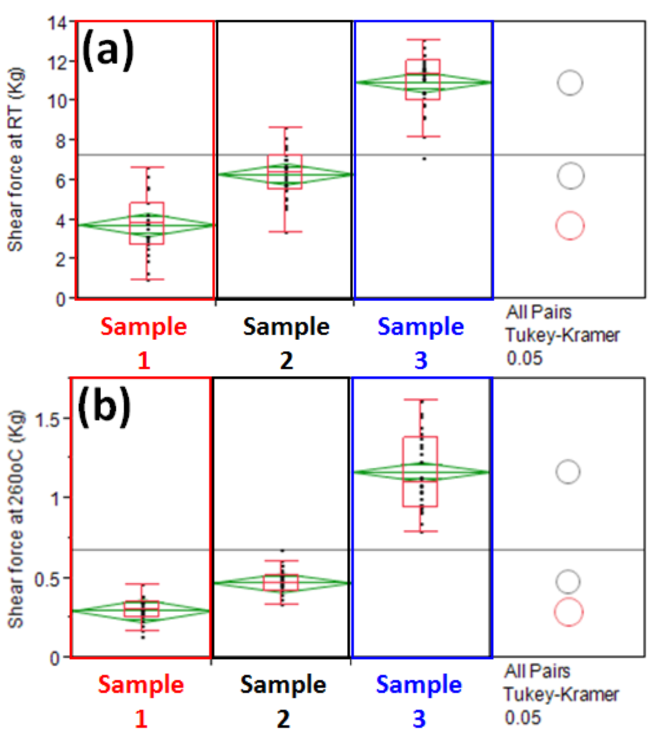


Fig. 2. Adhesion testing result of the EMC/Cu interface for sample 1: no plasma/no oxidation, sample 2: no plasma on Cu oxidation, and sample 3: plasma on Cu oxidation, shear testing at (a)RT and (b)260ºC.

This work was designed to obtain Cu oxidation at isothermal condition from the thermodynamic data determining as an experimental verification of the EMC/Cu interface adhesion testing. In the former research we utilized AES (Auger Electron Spectroscopy) to identify the oxide species for different process treatments and verify adhesion performance for delamination improvement [9], it was clarified that surface structure of Cu oxidation could be described as Cu/Cu_2O/CuO, this structure should be verified to possess better adhesion characterization, this investigative conclusion could compare with Lee and Kim pull-off adhesion testing result: CuO > CuO+Cu_2O > Cu_2O > bare Cu [1]. In this study, the EMC/Cu interface adhesion has a similar result in former study [8], [9]. The adhesion testing result: sample 3 > sample 2 > sample 1, the result was verified that Cu oxidation and plasma treatment conditions would enhance the EMC/Cu interface adhesion as showed in Fig. 2. Shear testing condition has been performed in room temperature and 260ºC to compare the adhesion characterization for simulation of reflow as Figs. 2(a) and 2(b), respectively. Results have shown a same trend whatever shear testing is at room temperature and 260ºC.

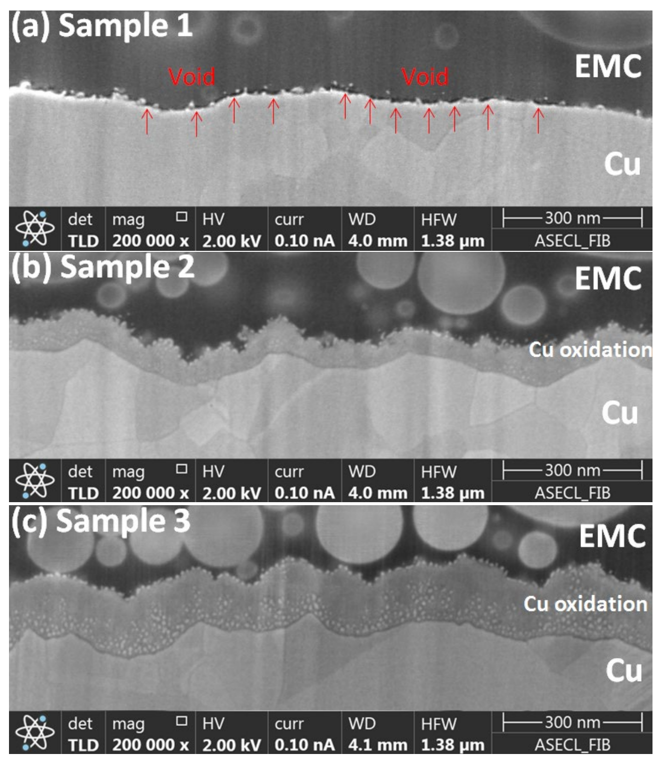
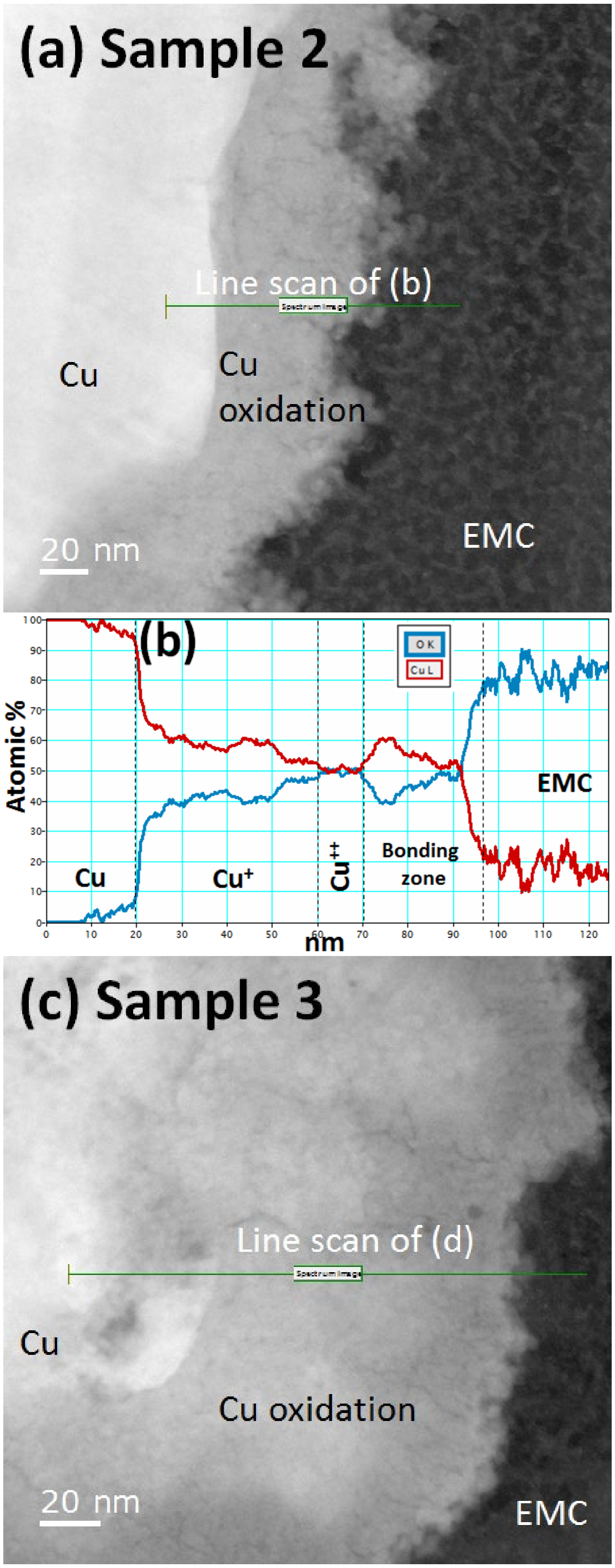


Fig. 3. FIB low kV SEM image observation of the EMC/Cu and EMC/Cu(O)/Cu interface for no plasma/no oxidation (sample 1), no plasma on Cu oxidation (sample 2), and plasma on Cu oxidation (sample 3) as samples of Fig. 2.



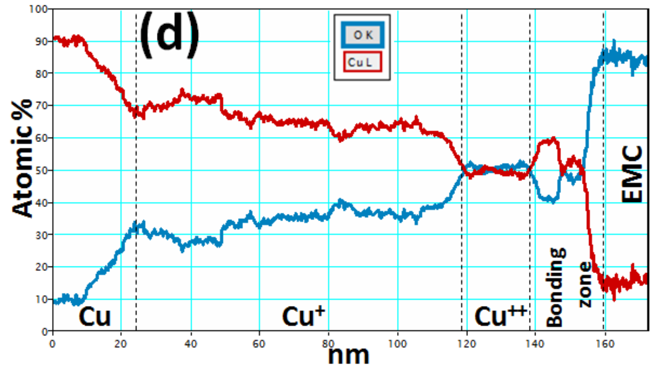


Fig. 4. TEM/EDS analysis of the EMC/Cu(O)/Cu interface without (sample 2) and with (sample 3) plasma treatment on Cu oxidation, (a) and (c) are high-resolution TEM image with dark-field mode, (b) and (d) are EDS line scan from (a) and (c) line mark in TEM image, respectively.

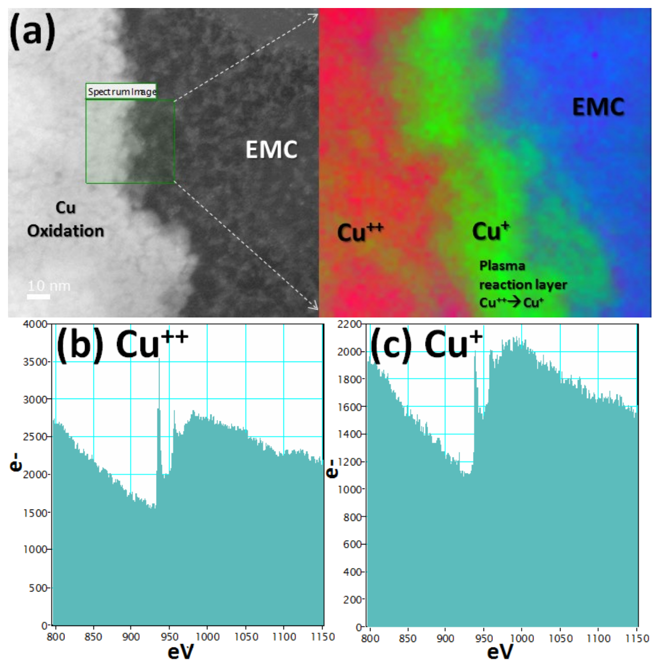


Fig. 5. EELS mapping analysis of the EMC/Cu(O) interface for plasma on Cu oxidation (sample 3), (a) is TEM image with dark-field mode and EELS mapping as inserted area, (b) and (c) are Cu L edge spectrum have been identified to draw the mapping for CuO and Cu_2O species, respectively.

Due to clarify the EMC/Cu interface had obtained different adhesion results, a precision FIB with Ga ion was utilized to mill cross section of the interface, using low kV SEM inspection to observe the morphology was shown in Fig. 3. Sample 1 is no Cu oxidation and no plasma treatment in Fig. 3(a), result shows a void exist in the EMC/Cu interface, it is suspected that a weak adhesion is caused by void trap in the EMC/Cu interface, due to it may have a poor wettability while the EMC molding on the Cu surface. These SEM results also think about why using benefit of lower isothermal temperature due to oxygen over-diffusion cause to more vacancy trap in Cu concern layer for higher temperature, it will influence intra-structure of Cu oxidation layer [6] and the EMC/Cu interface adhesion testing result.

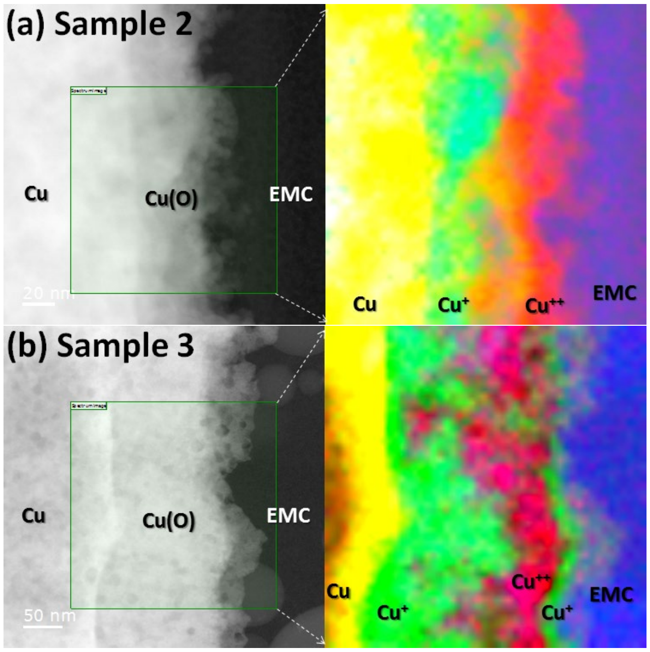


Fig. 6. EELS mapping analysis of the EMC/Cu(O)/Cu interface without (a) and with (b) plasma treatment on Cu oxidation, TEM BF mode is lift image and EELS mapping as inserted area is right image, (a) is sample 2 (without plasma): EMC/CuO/Cu_2O/Cu, (b) is sample 3 (with plasma): EMC/Cu_2O/CuO/Cu_2O/Cu.

Samples 2 and 3 could see that a good adhesion in the EMC/Cu interface and a dense Cu oxidation layer on Cu, around 100nm and 200nm Cu oxidation layer at 100ºC and 150ºC isothermal was obtained. Both samples were prepared as the TEM laminar 100nm thin film below, using easy lift tooling system and GIS (Gas Injection System) Pt metal deposition to bond on Mo grid had been performed by FIB. The TEM/EDS analysis of samples 2 and 3 were shown in Figs. 4(a)–4(d), results had shown a Cu oxidation structure Cu/Cu_2O/CuO for 100ºC and 150ºC of the isothermal temperature. According to EDS line scan composition, Cu and O elements ratio, results have also shown a bonding zone between CuO and EMC, this zone is tricky for Cu/O ratio uncertainly the composition identify to figure out, and it has been interesting to clarify that this important change of the interface composition lead to its promotion obviously of adhesion characterization. This work has utilized EELS analysis to identify Cu oxidized state due to Bertho and Stolojan, Abel, and Watts have also utilized EELS technology to reporting that the oxygen occupancy of the epoxy/metal interface and its adhesion has relationship [12]. Bertho et al. researcher description that d-electron occupancy of 3d and 4d transition metals was studied by Pearson, Ahn, and Fultz [13], this analyzed technology was used in this study as reference. Fig. 5 is following EELS spectrum fitting of CuO and Cu_2O species to obtain an interface composition mapping [10], [11], it is clarified the layer composition change of the bonding zone of Fig. 4(d) from 10~20nm Cu_2O structure identification between CuO and EMC, it is also suspected for surface CuO reduction to Cu_2O under Ar/H_2 plasma treatment. EELS mapping analyses of samples 2 and 3 with/without plasma treatment comparison were shown in Figs. 6(a) and 6(b), respectively. Results have clarified an oxidation layer difference with different conditions in the EMC/Cu interface, sample 2 is a binary Cu oxidation structure constructed by Cu/Cu_2O/CuO/EMC, and sample 3 is a ternary Cu oxidation structure constructed by Cu Cu/Cu_2O/CuO/Cu_2O/EMC. Compared these results can verify to certain reduction mechanism CuO reduction to form Cu_2O while Ar/H_2 plasma treatment is applying, result also show this significant composition change is correlated with the EMC/Cu interface adhesion characterization.

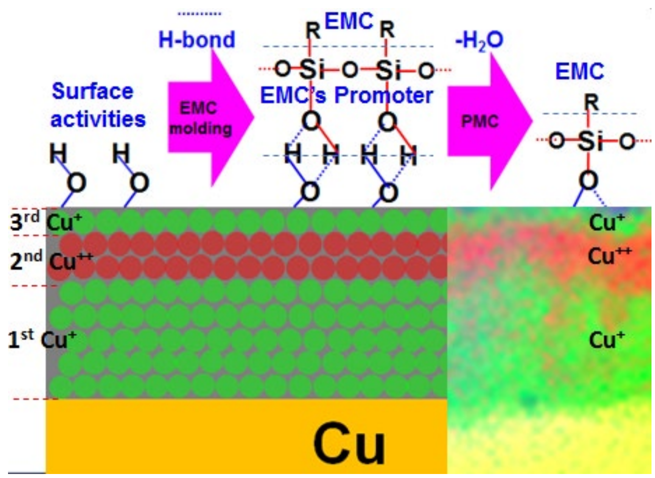


Fig. 7. Schematic diagram of the EMC/Cu adhesion reaction mechanism from EMC molding → post molding cure (PMC), according to sample 3 (with plasma treatment) was analyzed by TEM/EELS mapping result.

Due to samples 2 and 3 have different shear testing results, sample 3 with plasma treatment has higher adhesion force than sample 2. Adhesion testing result was supposed that using Ar/H_2 plasma treatment would strengthen the EMC/Cu adhesion force in former our study [8], [9], it was also concluded that surface CuO structure would be reacted to form hydrogen-bonding (H-bonding) and increase the adhesion force during EMC molding. After Ar/H_2 plasma treatment, the interface reaction could be provided more H-bonding groups to obtain an excellent adhesion property in the EMC/Cu interface. This reaction model was descripted from according adhesion experimental verification and AES identify, these conclusions were described as below reaction mechanism:

$$2CuO + H_2 \rightarrow Cu_2O + H_2O \quad (1)$$

$$Cu_2O + H_2O \rightarrow 2CuOH \text{ (hydration molecular)} \quad (2)$$

This is a significant chemical composition change for Cu oxidation surface under plasma treatment in equations (1) and (2), (1) is CuO reduction, (2) is Cu_2O hydration. The EMC/Cu adhesion chemical mechanism of ternary Cu oxidation structure ($Cu^+/Cu^{++}/Cu^+$) was identified by EELS mapping and identifying. The EMC/Cu bonding chemical mechanism of ternary Cu oxidation structure under Ar/H_2 plasma treatment from EMC molding → PMC was shown in Fig. 7. These results suppose that the hydration molecular, 2CuOH, have much surface activities, during molding process EMC's promoter functional group, -OH, will provide H-bonding on surface activities of third-layer cuprous oxide. After PMC process, a strong chemical bonding formation at the EMC/Cu interface can be verified in this experiment.

IV. Conclusion

The delamination of the EMC/Cu interface of copper interconnection substrate was studied in this work. Emphasis was on the reaction mechanism of CuO reduction under Ar/H_2 plasma treatment which was analyzed and identified as a key adhesion factor. The results are summarized below:

(a)Cu oxidation below 160°C has the highest Q_a. From this we suspect that the formation of final oxidized Cu, CuO, must overcome an energy barrier.

(b)Plasma treatment in Ar/H_2 atmosphere of the Cu oxidation, sample 3, forms significant H-bonding due to surface CuO reduction which strengthens the EMC/Cu interface to have the highest adhesion force.

(c)It was found that no surface treatment, sample 1, resulted in a weaker EMC/Cu adhesion interface than when a surface treatment was applied.

(d)A dense and uniform structure of oxidation layer was observed with FIB and TEM/EELS analyses in binary Cu oxidation structure of $Cu/Cu^+/Cu^{++}$/EMC without plasma treatment and ternary Cu oxidation structure of $Cu/Cu^+/Cu^{++}/Cu^+$/EMC with plasma treatment.

(e)Chemical mechanism of the EMC/Cu interface adhesion has been described in this study from experimental verification and identification.

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