

Atmospheric Plasma Treatment on Copper for Organic Cleaning in Copper Electroplating Process: Towards Microelectronic Packaging Industry

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Electroplated *Cu* is a cost efficient metallization method in microelectronic packaging applications. Typically in 3-D chip staking technology, utilizing through silicon via (TSV), electroplated *Cu* metallization is inevitable for the throughput as well as reducing the cost of ownership (COO). To achieve a comparable film quality to sputtering or CVD, a pre-cleaning process as well as plating process is crucial. In this research, atmospheric plasma is employed to reduce the usage of chemicals, such as trichloroethylene (*TCE*) and sodium hydroxide (*NaHO*), by substituting the chemical assisted organic cleaning process with plasma surface treatment for *Cu* electroplating. By employing atmospheric plasma treatment, marginally acceptable electroplating and cleaning results are achieved without the use of hazardous chemicals. The experimental results show that the substitution of the chemical process with plasma treatment is plausible from an environmentally friendly aspect. In addition, plasma treatment on immersion *Sn/Cu* was also performed to find out the solderability of plasma treated *Sn/Cu* for practical industrial applications.

Keywords: Atmospheric plasma, Surface treatment of *Cu*

1. INTRODUCTION

Surface treatments using non-isothermal low-temperature plasma is of interest in various applications in the field of bio engineering, printed circuit boards (PCB), and electromagnetic interference (EMI) shielding material[1-3]. In microelectronic packaging industry, *Cu* has been widely utilized as a good interconnect material. Sputtered or chemical vapor deposited (CVD) copper can provide a well-controlled process for the metallization as in semiconductor manufacturing. Recently, numerous efforts to vertically stack chips, including flash memory and system integrated circuits (ICs), have been suggested utilizing a silicon via (TSV) technique. It requires a high aspect ratio silicon TSV, but also the filling of vias with electroplated copper for the metallization. The needs for electroplated copper continuously grow for dual-damascene process as well as high aspect ratio via filling in 3-D chip stacking technology than in a conventional vacuum process.

Cu electroplating process requires multiple steps of pre-cleaning, including organic cleaning and acid cleaning steps, before the actual plating process. For instance, trichloroethylene (*TCE*) and sodium hydroxide (*NaOH*) are frequently used as an organic cleaning solution for copper, but the usage of *TCE* is regulated due to the harm to the environment. The usage of hazardous chemicals is inevitable to achieve a certain quality factor level of electroplated *Cu* film for industrial applications, but the efforts to minimize their usage should be continued. This research was motivated from a hypothesis that plasma surface treatment can be extended to the surface cleaning of organic particles on copper. Environmentally safe gas phase plasma will decompose organic particles into a volatile byproduct and the usage of chemicals can be reduced.

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To confirm the hypothesis, the study employed atmospheric plasma generated by 13.56 MHz RF power for the organic cleaning on *Cu* foil. The atmospheric plasma system is capable to handle samples in line, operated at a low power, and uses *Ar* as a reaction gas delivery carrier. This study examined how to substitute the conventional wet cleaning for helping the environment, but also maintaining manufacturability in terms of material cost and efficiency. To compare the conventional versus the suggested approaches, the study intentionally tried to maintain a real manufacturing environment as much as possible, even though it was at the university research environment. *Cu* foil was sampled from a PCB manufacturing line, and they were prepared for either chemical or plasma cleaning. The rest of this paper consists of three parts. Section 2 describes the experimental apparatus for this experiment, the results and discussion are provided in Section 3, and the conclusion is presented in Section 4.

2. ORGANIC CLEANING FOR *CU* ELECTROPLATING

Plasma treatment was performed with different conditions by modifying the amount of oxygen gas while the RF power was set to 100 watts. Argon is used for reaction gas delivery and atmospheric plasma generation. *MyPL*TM (manufactured by APP, Korea) employed in this experiment can handle the board size of 300 mm in the maximum in-line and is suitable for a high volume microelectronic packaging manufacturing environment. The system consists of three parts, RF power system, gas delivery system, and plasma generation system. RF power system uses 13.56 MHz RF power source with auto impedance matching module. Gas delivery system has four mass flow controllers (MFCs) with digital control system. One is designated to Argon for gas delivery, and others are for oxygen, nitrogen, helium, or mixture gases, depending

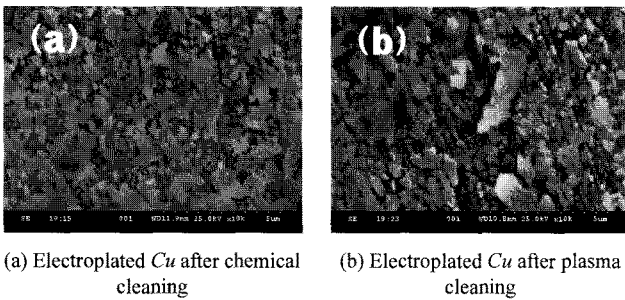


Fig. 1. SEM image of the electroplated *Cu*.

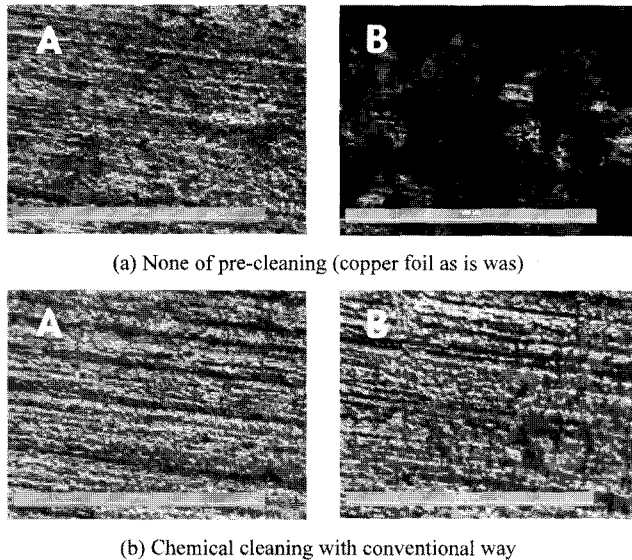


Fig. 2. Microscopic image of the sample as it was and chemical cleaned for reference.

on the gas choices. Electrode for plasma generation module is a cylindrical type, and it is discharged perpendicular to the surface when the gap between electrode and sample is below 15 mm.

The starting point of the experiment was to compare the *Cu* plated samples through a SEM image acquired from sample with conventional chemical cleaning and another with plasma cleaning. Two *Cu* foil samples were water cleaned, organically cleaned with chemicals and plasma, acid cleaned with H_2SO_4 , and the electroplating of cleaned *Cu* samples with $CuSO_4 \cdot 4H_2O$ were performed simultaneously. Figure 1 shows the SEM image after electroplating, however it was not clear that which cleaning method is superior to another. It appears that the Fig. 1(b), which is a plasma cleaned sample, shows slightly larger copper grains that were formed locally, but Fig. 1(a) shows a more uniform surface. Observing the cleaning effect through the SEM image might lead to a myopic view of the surface, so a wider view of observation was chosen in the following experiment.

Since the effect of organic cleaning after electroplating was not clearly observed, it was determined that the comparison should be before the plating in a broad scope on the sample. *Cu* foil samples were divided into three groups: one is without any cleaning for a reference, another is with conventional cleaning, and the other is with plasma

cleaning in various oxygen flow rates. Chemical cleaning was done by immersion of samples for three minutes in chemicals, such as *TCE*, *NaOH*, and H_2SO_4 . For the plasma cleaning, 10, 20, and 30 sccm of oxygen was supplied while 10 lpm of argon carrier gas was delivered. The microscopic images of this experiment are provided in Fig. 2. In Fig. 2(a), the copper foil samples without any pre-cleaning are presented. Figure A shows the most cleaned area (or residual remained area) and Fig. B shows the most polluted area (or not cleaned area), respectively. Some areas of the sample were clean enough and organic cleaning may not be required; however, in some areas very dark spots were contaminated with organic material that should be cleaned before copper electroplating. Figure 2(b) shows the sample pre-cleaned with *TCE* and *NaOH* by immersing samples for three minutes in the designated chemical baths. These samples appear clean without any dark contaminated spots.

Atmospheric plasma surface treatment was able to moderately clean the copper foil surface as presented in Fig. 3. Unfortunately, none of the results were the same as the chemical cleaning as shown in Fig. 2(b). This was an interesting result considering the initial hypothesis since it seems that plasma cleaning is not suitable for organic copper cleaning. Even when 30 sccm of oxygen was used, a dark contaminated area was obvious. When 20 sccm of oxygen was used, the feasibility of the plasma cleaning appeared. However, the cleaning results were not identical with the chemical cleaning. Figure 3(a) shows a cleaned surface observed in A and a chunk of dark pollutant still remained in B, so 10 sccm of reacting gas flow is not sufficient for a given time and power. 30 sccm of oxygen still did not clean the surface well in Fig. 3(c) and more

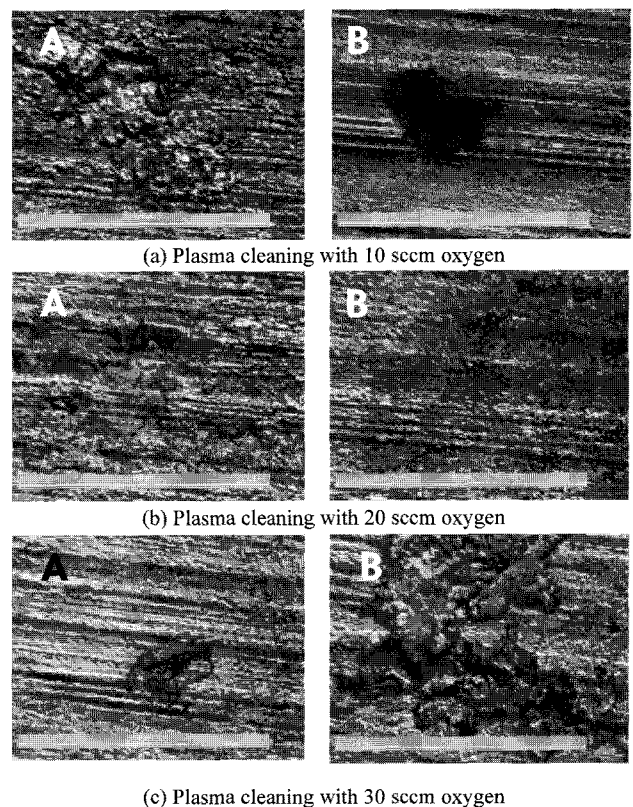


Fig. 3. Plasma cleaning with oxygen (RF Power 100 watts).

pollutant become noticeable the images of Fig. 3(b). In case of 30 sccm of oxygen, ionized oxygen may decompose the organic components on the sample, but the energetic oxygen plasma can also react with copper ions on the surface to form copper oxide. From the experimental result of plasma treatment, about 20 sccm of oxygen gave a comparable cleaning effect with a chemically cleaned surface, and the hypothesis to substitute chemical cleaning with plasma cleaning is somewhat feasible. This infers that oxygen plasma is good for organic removal on metal surfaces, but it may require a prolonged time of acid cleaning for micro-etching on *Cu* surface.

3. PLASMA TREATMENT ON *Sn/Cu*

In order to keep copper from oxidation in component packaging or PCB manufacturing, immersion tin coating on copper metallization is the usual process in the final manufacturing process and it can be safely stored for the next assembly process. In the second phase of plasma surface treatment on interconnecting metal, we have performed *He/Ar* plasma treatment on immersion *Sn/Cu* surface to protect *Sn* from oxidation by replacing dangling bonds with ionic bonds on the tin surface. The underlying

reasoning for the plasma treatment is that the replacement of dangling bonds may decrease surface oxidation by reducing the probability of oxygen to bond with the unbounded tin atoms, and the oxidation protected bonding can assist the solder bonding process in the next assembly step.

In order to compare the effect of plasma treatment, the samples prepared were divided into two groups: one without plasma treatment and another with plasma treatment. Atmospheric plasma treatment on *Sn/Cu* film was performed with 5 % *He/Ar* mixture gas at 300 watts RF power. Surface analysis with XPS is desired to uncover the effect of plasma surface treatment, but we have performed solderability testing of the tin surface by measuring wetting force for the purpose of industrial application[4]. To simulate actual surface mount technology (SMT) assembly process, both types of samples (plasma treated and untreated) were passed multiple times through a reflow oven. The temperature profile of the reflow oven is adopted from a PCB manufacturing site and presented in the following: 1) Pre-heating with 3 °C/sec to 150 °C; 2) Soaking at 150 °C for 90 seconds; 3) Ramping up with 3 °C /sec to 250 °C (more than 30 seconds higher than 220 °C); 4) Cooling down with 5 °C /sec.

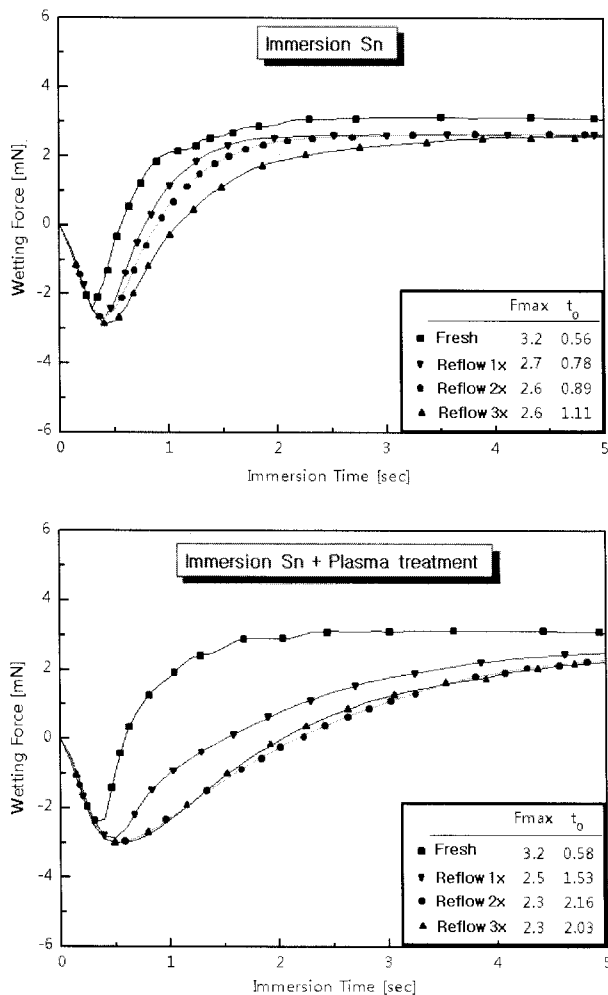


Fig. 4. Wettability test on immersion *Sn*.

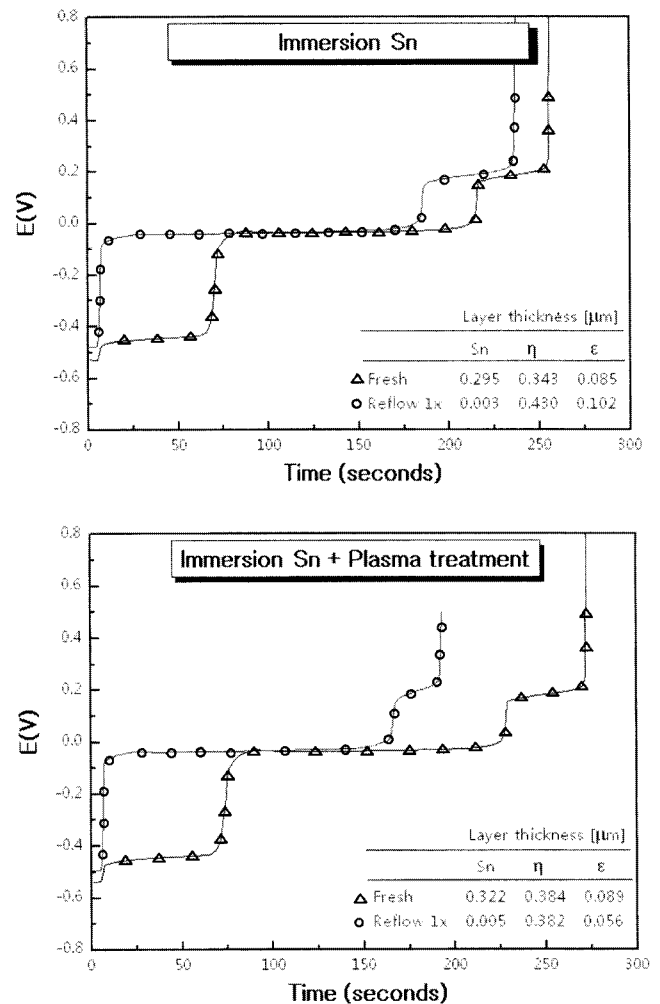


Fig. 5. Sequential electrochemical reduction analysis (SERA) for the analysis of inter-metallic compound (IMC) formation.

Solderability testing with wetting balance measurement was then performed and the results are presented in Fig. 4. Immersion *Sn* coated *Cu* without plasma treated sample shows that no significant variations in wetting force along the multiple times of reflow. This is straightforward in the SMT reflow process. In SMT assembly, the size of electronic component varies in a wide range, so when a variety of sized components are reflowed simultaneously the small components are over heated locally but larger components are not jointed at all. For this reason, larger components are reflowed in a higher temperature first, and smaller components are reflowed in a slightly lower temperature next. Multiple reflow testing in this experiment was reasonable for simulating the actual assembly process for practical usage. The wetting force before reflow, as presented in Fig. 4(b), is identical to the untreated sample. In the hypothesis, the dangling bond on the surface becomes ionic bonded with plasma ion, and it may reduce the probability of oxidation of the surface. It is marginable that plasma treatment is good for avoiding oxidation of tin while maintaining same level of solderability. However, an interesting wetting force measurement was observed at multiple times of reflow, and it turned out that the wetting force decreases as reflow time increases and the time that reaches to maximum wetting force increases. It is also shown in Fig. 4(b). This was a surprising and very dissatisfactory result for developing a new process, since the solderability performance is worse than the untreated sample.

To understand the mechanism of poor solderability with multiple times of reflow, we also performed sequential electrochemical reduction analysis (SERA) for intermetallic compound (IMC) formation between *Sn* and *Cu*. As observed in Fig. 4, both samples without reflow shows similar IMC structure, so the wetting forces were recorded in a similar fashion. After the reflow process, the IMC structure of the two samples showed differences as shown in Fig. 5. IMC of *Sn/Cu* system consists of Cu_6Sn_5 (the eta phase, η) and Cu_3Sn (the epsilon phase, ϵ), and the latter is more thermally stable than the former, so thicker epsilon phase Cu_3Sn is normally seen after the soldering process. Cu_6Sn_5 decreased after reflow once. However, in the plasma treated sample, the thickness of the intermediate phase of η layer has decreased relative to the sample without plasma treated. In addition, the thermally stable epsilon phase also decreased in the plasma treated sample. The reason behind this has not been clearly identified, but it is thought that the *Sn* surface has been modified to have less *Sn-Cu* bonding, so the thickness of the IMC showed a

different pattern. This is a similar phenomenon to the case of *Cu* surface treatment, but we did not expect the poor solderability of the plasma treated sample after the multiple reflow process.

4. SUMMARY

As the demands on *Cu* for high performance interconnecting material, electroplated *Cu* and immersion *Sn* became more frequently used in the field of microelectronic packaging. Atmospheric plasma treatment on interconnecting metal has been investigated for the practical application to organic cleaning for the *Cu* electroplating process and *Sn/Cu* film for copper finishing material. 13.56 MHz RF plasma generated in the atmospheric pressure with the proper amount of oxygen gas could moderately clean organic particles on *Cu* foil samples and provided a closed feasibility of reducing hazardous chemical usage in the conventional cleaning process. In addition, atmospheric plasma treatment of tin finish on copper was also investigated. Oxidation reduction of the tin finish may be beneficial; however, poor solderability was noted as a concern of plasma surface treatment on *Sn* finish. Even though no significant performance improvement for metallization materials has been achieved through the atmospheric plasma treatment, a comparable performance to the conventional process was achieved from the experiment. More intensive research on this topic should be continued for improved benefits to the environment as well as a performance point of view.

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