One-Step Wet Chemical Treatment for Fluxless Cu-Sn Thermocompression Microbump Bonding

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Abstract
A new one-step wet chemical treatment has been developed for fluxless Cu-Sn microbump bonding. This treatment simultaneously removes native oxide from the Cu surface and deposits a functional layer on the cleaned surface. The treatment passivates the surface against re-oxidation and activates it for thermocompression bonding (TCB) between Cu and Sn without applying a flux agent. This paper discusses oxide layer removal from the Cu surface and the stability of the formed functional layer for up to 45 weeks. Die-to-die (D2D) microbump bonding was also evaluated through conductivity tests after thermal stress. Additionally, the uniformity of the layer formation on a 300-mm wafer-level application was assessed using dipping and spinning methods.

Key words
Heterogeneous interconnections, Copper surface passivation, Thermocompression bonding, Fluxless microbump bonding

I. Introduction
In recent years, with rapid development of electronic devices, advanced packaging technologies have taken on a critical role in achieving higher performance and greater functionality. Three-dimensional (3D) system integration technology with high-density 3D interconnects is being advanced to improve device performance and reduce energy consumption [1], [2]. The thermocompression bonding (TCB) process between solder and Cu microbumps is often considered a promising methodology to obtain these high-density interconnections [3], [4]. To achieve effective joint formation, a conventional TCB process typically involves the application of flux [5], [6]. However, the flux cleaning process after TCB is challenging for structures with narrower bump pitch, narrower gaps, and/or larger die sizes. Flux residues between the dense microbumps can lead to reliability issues, and the cleaning step is becoming increasingly difficult [7].

To address this potential issue, we have proposed an alternative fluxless approach. In the previous work, we reported that a Cu selective wet chemical treatment protects Cu microbumps from oxidation and activates the surface during the TCB process, thereby enabling good solder wetting and reliable electrical connections without using conventional flux agents [8-10]. In this work, we introduce a new chemical that has been further developed. The new chemical not only maintains its original passivation and activation functions but also removes native oxide from the surface of the Cu microbumps. The previous chemical requires an initial acid pre-cleaning step to remove native oxide that formed on the Cu microbumps during the storage time after the previous process, such as seed etching. The new chemical can allow the omission of the pre-cleaning step prior to the treatment, thus simplifying and shortening the overall process.

The chemical can be used in a conventional wet cleaning tool or spin coating tool for a full wafer. When the chemical comes into contact with the wafer having Cu microbumps, the acid components dissolve Cu oxide, exposing the metallic Cu surface. Subsequently, other chemical components start to react with Cu to form an ionic complex that can act as the functional layer. Since the deposition mechanism includes a reaction with Cu, it does not occur on other materials such as SiO_2, SiN or other dielectric materials [8], [10]. This property of selective deposition is preferable for minimizing residues and to ensure the compatibility with the underfill (UF)

materials used in the following process.

The formed layer has two functions: passivation of the Cu microbumps from re-oxidation and activation of the surface to enhance the solderability. As the passivation layer, it can protect the Cu microbumps from oxidation during shelf life and also during the TCB for the neighboring dies in a die-to-wafer process. While as the activation layer, intermetallic compound (IMC) formation between Cu and Sn can be accelerated near the melting point of Sn. According to our proof-of-concept study, the IMC formation can be observed from a lower temperature compared to the untreated surface, assuming this layer has a catalytic effect to lower the reaction temperature between Cu and Sn [8]. This paper discusses the cleaning properties of the chemicals and the stability of the layers. Then, the formation of microbump interconnects and their reliability, as well as the wafer-level treatment conditions have been demonstrated.

II. Experimental

A. Cu surface treatment

An electroplated Cu substrate was cut into appropriate dimensions for each test. For Cu treatment, a newly developed chemical was used. The standard chemical treatment procedure was to dip the sample in the solution for 60 seconds, followed by rinsing with de-ionized (DI) water and air blow drying. The samples for storage test were then stored under vacuum or ambient atmosphere for varying periods up to 45 weeks. For comparison, an acid cleaning sample was prepared by cleaning the substrate with 5% sulfuric acid and DI water rinsing.

Spin coating was also conducted using a fan-shaped spray nozzle to process a Cu wafer with 300 mm diameter. The spin spray coating was performed at a chemical flow rate of 170 ml/min for 60 seconds and at spin speed of 500 rpm, followed by rinsing with DI water for 60 seconds. Subsequently, the wafer was dried at 2000 rpm. Dip coating on the 300 mm Cu wafers was performed using the standard procedure described above. Infrared reflection absorption spectroscopy (IR-RAS) and X-ray photoelectron spectroscopy (XPS) were employed for chemical evaluation of the sample surfaces.

B. Adhesion strength

TCB of the chemically treated Cu substrate and Sn balls (99.9 % Sn, 0.76 mm diameter) was conducted using a heat press equipped with a pulse heater unit at ramp rate of 100 K/s, pressure of 5 N, temperature of 240 °C and bonding time of 6 seconds. Adhesion strength between Cu and Sn was measured using a tensile tester equipped with a house-made jig at a crosshead speed of 0.5 mm/min.

C. Preparation of the die to die (D2D) stacked samples

A 10 x 10 mm^2 test vehicle with a 40 μm pitch Cu microbump array and corresponding 7 x 7 mm^2 die with a 40 μm pitch Cu microbump array having a Sn-Ag solder cap were obtained from Walts Co. Ltd. These were designed to form 20 daisy chains, each consisting of 576 connections after bonding. The prototype chemical and a conventional flux reagent were applied only on the Cu bump side, and TC bonded with the one with the solder cap.

TCB was conducted by a TC bonder. The bonding force applied for this test was 5 N and the top tool temperature of 350 °C with a bonding time of 6 seconds. After bonding, UF was dispensed directly without any cleaning step, and cured at 150 °C for 2 hours. For the samples using flux reagent, DI water cleaning in an ultrasonic bath was applied prior to the UF dispense process.

D. Reliability test

Reliability test of the temperature cycling test (TCT) for 500 cycles between -55 and 125°C with a dwell time of 30 minutes at each temperature, and the high-temperature storage test (HST) at 150 °C for 1000 hours were conducted in accordance with JEDEC JESD22-A104F.01 and JESD22-A103D, respectively. Electrical measurement of daisy chains was performed after the sample was TCB stacked, and after the TCT and HST.

III. Results and discussion

A. Effect of the copper oxide removal

While some cleaning steps are commonly required to remove native oxide from Cu surface, our new chemical achieves oxide removal simultaneously during treatment in a single step, offering a more efficient process. Fig. 1 shows the O 1s XPS depth profiles of various samples to evaluate the native oxide removal. The as-received sample showed oxygen up to 5 seconds of sputtering, while oxygen disappeared after only 1 second of sputtering in chemically treated samples, regardless of acid cleaning. This indicates that the native oxide layer was effectively removed even without acid cleaning. In addition, the chemical treatment was applied on further intentionally oxidized Cu surface (heated at 100℃ for 2 hours) without acid cleaning. The oxygen concentration on the uppermost surface was less than 5%, which was comparable with the result for the as-received Cu surface. Thus, the chemical effectively removed the oxide layer from even more oxidized surfaces without acid cleaning, demonstrating comparable effectiveness to other acid cleaning pretreatments.

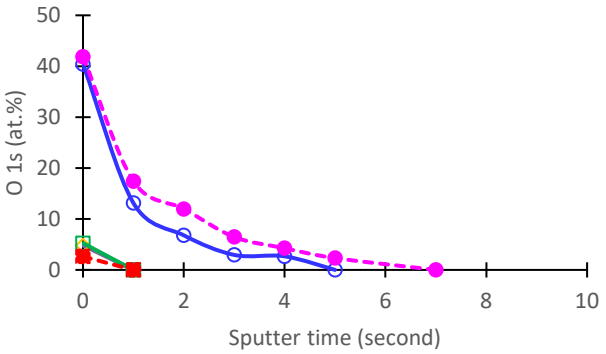

Fig. 1. XPS depth profile of O 1s peaks as a function of sputtering time for: as-received sample (○), chemically treated samples with acid cleaning (◊) and without acid cleaning (□), sample heated at 100°C for 2 hours (●), and chemically treated on the heating sample without acid cleaning (■).

B. Effect of storage conditions and times

The stability of the chemically treated layer has been evaluated under different storage conditions and storage periods. IR absorbance signals pertaining to the activating compound were collected after storage under vacuum and ambient atmosphere for varying periods of time (0 to 45 weeks; 0 week = as prepared), as shown in Fig. 2. Under ambient atmosphere, the normalized absorbance gradually decreased to approximately 80% after 15 weeks, while the intensity maintained to almost 90% after 45 weeks under vacuum. Fig. 2 also presents the shear strength of bonded Sn balls on the treated Cu surface. The shear strength of the samples under vacuum remained high after 45 weeks, whereas under ambient atmosphere, the shear strength remained high for 4 weeks and decreased by 50% after 15 weeks.

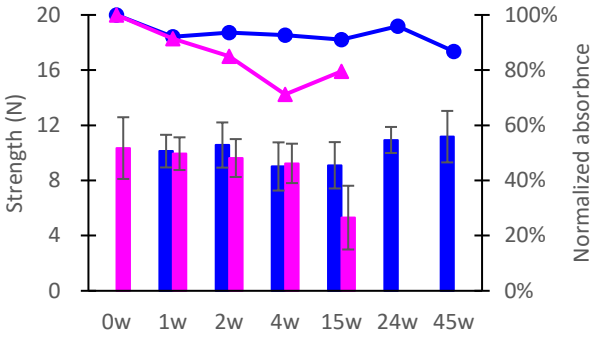

Fig. 2. Shear strength of Sn/Cu joint samples after varying storage periods under vacuum (▮) and ambient atmosphere (▮), along with normalized absorbance under vacuum (●) and ambient atmosphere (▲). Absorbance was normalized to 100% at 0 week.

The quality of the Cu-Sn bonding has been further evaluated by failure mode analysis. As shown in Fig. 3, the amounts of Sn or IMC residues on the Cu surface after the shear test were comparable in both the as-prepared sample and the sample stored under vacuum for 45 weeks, and the failure mainly occurred within the Sn or IMC and/or Sn/IMC interface. In contrast, the sample stored under ambient atmosphere for 15 weeks, the failure surface exhibited a certain amount of Sn remains in the center, while the exposed Cu area had significantly increased around the periphery, indicating a decrease of the IMC formation.

The oxygen concentrations of the stored sample surfaces were analyzed by XPS. As shown in Fig. 4, the oxygen concentrations of the sample surface stored under ambient atmosphere increased to 33 %, while 15 % of oxygen existing on the sample surface stored under vacuum. For the sample stored under ambient atmosphere, the surface oxidation level increased to nearly that of the as-received sample. Significant oxidation on the sample surface is assumed to hinder the good wettability and the IMC formation between Cu and Sn during the TCB process, resulting in weak adhesion.

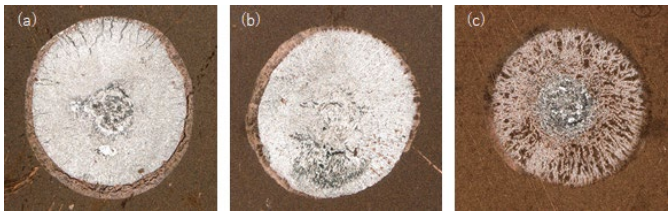

Fig. 3. Optical microscope images of failure surfaces of the Cu side after shear tests: (a) sample as prepared, (b) stored under vacuum for 45 weeks, and (c) stored under ambient atmosphere for 15 weeks.

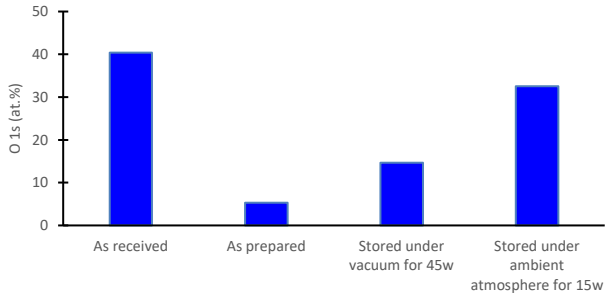

Fig. 4. O 1s surface concentrations of the as-received sample and the chemically treated samples under various conditions.

C. Reliability of D2D microbump connections

The quality of the D2D stacked microbump connections has been examined after subjected to the TCT and HST conditions. Four types of Cu bump samples were used for the TCB stacking process: chemically treated samples that were prepared just before bonding, as well as samples that stored under vacuum for one month, and acid-washed samples with and without flux reagent application.

Fig. 5 shows the electrical measurement data of these TCB stacked samples before subjected to thermal stresses (referred to as after stacking), and after TCT and HST. The acid cleaning sample exhibited an open circuit, indicating a need for chemical agents. The chemically treated samples showed a similar electrical resistivity to the flux sample, even after one month of storage. The chemically treated samples also demonstrated comparable performance to the flux sample after the TCT and HST reliability tests. This indicates that the formed microbump connections are reliable and can withstand thermal stress, and the treated sample can be stored under vacuum at least one month while maintaining effective passivation and activation features to make robust microbump connections. This also suggests that the chemical treatment can replace the role of flux in promoting the IMC formation, especially for finer pitch microbumps, providing practical advantages such as simplifying the process by eliminating cleaning steps and avoiding reliability issues associated with flux residues.

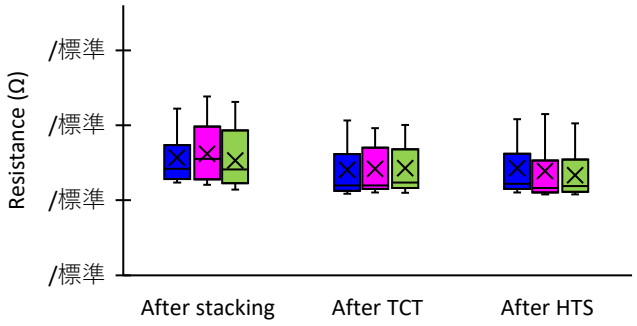

Fig. 5: Electrical data of the stacked samples with the chemical treatment just before bonding (■), stored under vacuum for one month (■), and with the flux agent (■) measured before subjected to thermal stresses and after the TCT and HST.

D. Uniformity of spin-coated and dip-coated layers

The one-step chemical treatment simplifies the treatment process, thereby improving reproducibility, reducing cross-contamination risks, and facilitating scalability. Wafer level treatment has been tested with spin and dip process. The uniformity of the spin-coated and dip-coated Cu wafers with 300 mm diameter has been evaluated using IR-RAS measurement. IR signals were measured at 15 locations along the center line. Fig. 6 shows calculated thicknesses of the spin-coated and dip-coated layers, estimated from IR absorbance using the correlation with the cross-section scanning electron microscopy data obtained separately. The average thickness of the spin-coated and dip-coated layers were 52 ± 4 nm and 42 ± 2 nm, respectively, indicating both layers show good uniformity and process stability. Achieving comparable layer quality with both spin-coating and dip-coating offers flexibility in process selection depending on the substrate type and manufacturing requirements.

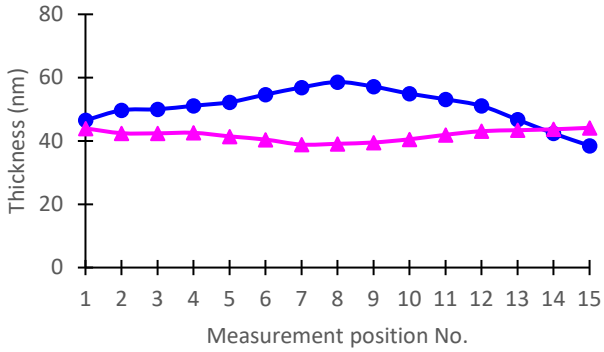

Fig. 6: Thickness of the spin-coated (●) and the dip-coated (▲) layer at various positions along the central line.

IV. Conclusion

A one-step wet chemical treatment has been developed as a pretreatment for the TCB process, which effectively removes native oxide during treatment and simultaneously deposits layers with passivation and activation functions. The chemically treated sample can be stored under ambient atmosphere for 4 weeks without losing its activation property while maintaining the passivation function. Under vacuum, the adhesion strength can be maintained until 45 weeks. Daisy chain electrical tests show that the acid cleaned Cu wafer failed to form reliable connections, resulting in an open circuit, whereas the chemically treated samples showed resistance values comparable to the flux-treated sample after the TCT and HST reliability tests, even after one month storage under vacuum. Both spin-coating and dip-coating methods were able to form a uniform layer on the 300 mm diameter wafer. The one-step wet chemical treatment process simplifies the manufacturing process, and we believe this technology can contribute to higher-density interconnects and enhanced process throughput in advanced packaging technology.

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