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Effect of thermal treatment on the mechanical properties of Cu specimen fabricated using electrodeposition bath for through-silicon-via filling

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ABSTRACT

The Cu specimens were fabricated by the UV-LIGA process using the electrodeposition bath for through-silicon-via (TSV) filling. Mechanical properties of the Cu specimens annealed at different temperatures were investigated by a uniaxial tensile test. The results indicated that the yield strength and breaking strength of as-deposited Cu specimens were higher than that of the bulk Cu, while the elastic modulus was lower than that of the bulk Cu. The elastic modulus, yield strength and breaking strength of Cu specimens decreased with the increase of the annealing temperature. When the annealing temperature was 400 °C, the elastic modulus decreased from 95 to 69 GPa, the yield strength decreased from 314 to 202 MPa, and the breaking strength decreased from 367 to 290 MPa, respectively. In contrast, the ultimate strain increased with increasing the annealing temperature. The surface morphology, fractography and crystal structure of the Cu specimens were characterized by SEM, TEM and XRD methods. The results indicated that the particle size increased with the increase of the annealing temperature, which contributed to the decrease of the yield strength and breaking strength according to the Hall–Petch law. The XRD results indicated that as-deposited Cu specimens had a preferred orientation in (220) plane, but (311) plane became the preferred orientation with increasing the temperature. This probably contributed to the decrease of the elastic modulus with increasing the temperature.

1. Introduction

Through-silicon-via (TSV) technology has attracted considerable interests for integrated circuit (IC) in pursuit of reducing wire length and increasing I/O density. The incorporation of TSVs with copper plating process poses a significant challenge to thermo mechanical reliability of the three-dimensional (3D) interconnects. The mechanical properties of the electroplated Cu–TSV are considered to be critically essential to the 3-D IC integration device designing [1,2]. At present, the mechanical properties of Cu used for simulation and design of TSV had to be taken directly from the bulk Cu or Cu thin film due to the lack of the data of Cu TSV [3,4]. It is not accurate because the size of Cu–TSV is in the micrometer level and the mechanical properties of the materials at micro scales are size dependence [5–8]. Although the mechanical properities of electroplated Cu-Damascene films and bright Cu films have been reported in the literatures [9], the mechanical properities of TSV Cu films is necessary to study since they have different deposition process and electrodeposition bath. At the same time, the metal-metal bonding used for TSV is an extremely common technique. Usually, the devices were pressured for 30 min at 350–400 °C firstly. Then, the devices were annealed under nitrogen atmosphere at 350–400 °C. During the bonding and assembly processes, if the subjected force is too large, Cu–TSV will plastically deform even fracture. This will result in the failure of the whole IC. So the mechanical properties of Cu–TSV at a high temperature play a decisive role in the reliability of IC. It has been reported that the mechanical property of Cu–TSV was studied by nano-indentation method [1]. The hardness of Cu–TSV was measured and the elastic modulus was calculated according to the relationship between the elastic modulus and the hardness. But it is an indirect method, and the values of the yield and breaking strength cannot be obtained, which is the direct data to evaluate the reliability of Cu–TSV. The uniaxial tensile test is considered to be the most straight forward and reliable method [10]. Previously, our work has been focused on designing Ni micro-tensile specimen and measuring mechanical properties of Ni thin film [11,12].

The mechanical performance and microstructure of electroplated Cu was directly influenced by the preparation process. In different plating conditions (plating solution and additives types), the mechanical performances of electroplated Cu were different

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[13]. The appropriative additives and plating solution were used in the through-silicon-via filling, so the study of mechanical properties of Cu–TSV was beneficial to simulation and design of TSV.

In this paper, the Cu specimens were fabricated by the UV-LIGA method using the electrodeposition bath for TSV filling, which was based on the sacrificial layer process. The mechanical properties of the Cu specimens annealed at different temperatures were investigated by a uniaxial tensile test. The direction of stress was in perpendicular direction to the growth of the electroplated material. The morphology and crystal structure were characterized by SEM, TEM and XRD methods. The influence of the annealing temperature on the elastic modulus, yield strength, breaking strength and the ultimate strain of Cu specimens was studied and the probable mechanism was discussed.

2. Experimental procedures

2.1. Fabrication of the specimens for tensile test

Table 1 listed the compositions of two kind electrodeposition bath and the electroplating processes used in this study. TSV bath was a commercial electrodeposition chemistry used for TSV filling. It contained accelerators (they increased the copper deposition rate), suppressors (they decreased the copper deposition rate), and levelers (they adsorbed at the end of via filling process and avoided the formation of bumps). During the electrodeposition process, the magnetic stirring was used to ensure that the speed of the convection was higher than that of the diffusion in the electrolyte around the cathode surface. Sulfate bath was commonly used for electroplating Cu film, which was used to electroplate the supporting frame of the Cu specimen to alleviate the intern stress caused by the electroplating process.

Fig. 1(a) showed the sample geometry and size details of Cu specimen. The size of the Cu specimen was optimized by comparing the stress and displacement distributions of the Cu specimens using finite-element method (FEM) according to our previously reported literature [11]. This would allow for measuring at a lower relative error. The size of the specimen was 600 μm in width, 5 mm in length and 20 μm in thickness. Compared with the Cu–TSV in situ with the depth of 20–60 μm, the thickness of specimen had comparability with the depth of Cu–TSV in situ.

The specimens were fabricated on the glass substrate by the UV-LIGA process. The flow chart of the fabrication process for the Cu specimens was in Fig. 2. The preparation of the samples was based on the sacrificial layer process and described as follows. A layer of the positive photoresist with a thickness of 5 μm was spin coated on a cleaned glass substrate as a sacrificial layer. The Cu seed layer with a thickness of 0.1 μm was sputtered on the sacrificing layer. A layer of the positive photoresist with a thickness of 20 μm was spin coated on the seed layer (Fig. 2a), which was soft baked at 95 °C for 30 min. Then it was patterned by UV-lithography and developed (Fig. 2b). The specimens were electroplated with a thickness of about 20 μm on the seed layer at a current density of 10 mA/cm^2 in the TSV bath (Fig. 2c). Then a layer of positive photoresist with a thickness of 40 μm was spin coated on the Cu specimen (Fig. 2d). The patterned photoresist was obtained after photolithography and development (Fig. 2e). The supporting frame with a thick of about 40 μm was electroplated in sulfate bath to align the specimen along the tensile direction, which ensured that it was convenient to clamp the sample during the tensile test (Fig. 2f). After that, the photoresist covered on the specimen and frame was removed by acetone (Fig. 2g). Finally, the test specimen was released from the glass substrate by removing the sacrificing layer in acetone at room temperature (Fig. 2h).

Table 1
Compositions of two kinds electrodeposition bath and electroplating process.

Species	TSV bath	Sulfate bath
$(CH_3SO_3)_2Cu$ (g L^{-1})	110	0
CH_3SO_3H (g L^{-1})	15	0
$CuSO_4 \cdot 5H_2O$ (g L^{-1})	0	75
H_2SO_4 (g L^{-1})	0	180
Cl^- (ppm)	50	50
A (accelerators, ppm)	3	0
S (suppressors, ppm)	10	0
L (levelers, ppm)	7	0
Temperature (°C)	25	25
Current density (A dm^{-2})	1.0	1.0

2.2. Tensile test procedure

The uniaxial tensile test of the specimen was carried out by a DMA Q800 of the TA Instruments Company, USA. The displacement resolution was 1 nm. The samples were preloaded with 1 mN of force. Then the load was applied at a speed of 1 N/min, and the stress as a function of strain was recorded. Before the tensile test, the Cu specimens were heated in vacuum with an increasing rate of 10 °C/min at 100, 200, 300 and 400 °C for 2 h, respectively. The heated specimens were automatically cooled to the room temperature. Fig. 3 showed the Cu specimen mounted on the tool before (a) and after tensile test (b).

2.3. Microstructure characterization of the specimens

The Cu film was electroplated on the seed layer with a thickness of 20 μm for X-ray diffraction (XRD) measurement. The characteristic peaks of the Cu films heated at different temperatures were acquired by a Ultrima IV diffractometer with Cu Kα radiation (Rigaka, Japan). The fractural morphology of the specimen was observed by a FE-SEM measurement (ultra 55, Zeiss, Germany). The bright-field images and the diffraction patterns of the specimenas deposited and heated at 400 °C were characterized by a TEM (JEM-2010, JEOL, Japan) measurement, respectively. An efficient method was developed to fabricate TEM sample by using the UV-LIGA process to avoid the external force from commonly used method for preparing TEM sample. The fabrication process of the TEM samples was similar with that of the Cu specimens for tensile test. Firstly, a layer of the positive photoresist with a thickness of 5 μm was spin coated on a cleaned glass substrate as sacrificial layer. A Cu seed layer with a thickness of 0.1 μm was sputtered on the sacrificing layer. Then, a layer of the positive photoresist with a thickness of 10 μm was spin coated on the seed layer. After photolithography and development, the patterned photoresist was obtained. The specimens with a thickness of about 10 μm for TEM test were electroplated on the seed layer at the current density of 10 mA/cm^2 in the TSV bath. Finally, the TEM sample with a diameter of 3 mm was released from the glass substrate by removing the positive photoresist in acetone at room temperature. The prepared sample before releasing was shown in Fig. 4.

3. Results and discussion

3.1. Tensile test

The typical stress-strain curves for the specimens annealed at 400 °C were shown in Fig. 5. For each kind of sample, 5–8 specimens were fabricated for the micro tensile test. It was found that the elastic stage of five stress-strain curves almost coincided with each other completely, which indicated that the test method was repetitive and reliable.