Characterization of Cu/Cu Bonding Interface Prepared by Surface Activated Bonding at Room Temperature

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***Abstract*-We studied Cu/Cu direct bonding by surface activated bonding at room temperature for the application in 3D integration. The Cu film surfaces were activated by irradiating with an Ar fast atom beam in a high vacuum. For the successful bonding, it is necessary to sufficiently remove the native oxide layer and contaminants on the sample surface. The microstructure of the Cu/Cu direct bonding interface was investigated by transmission electron microscopy, and no intermediate layers or voids were visible at the bonding interface. The absence of oxide at the bonding interface was confirmed by energy dispersive X-ray spectroscopy and electron energy loss spectroscopy. Tensile testing revealed that the bonding strength of the Cu-Cu interface was higher than 8 MPa. The current-voltage characteristic of the bonding was linear.**

Keywords- Surface Activated Bonding; Room Temperature Bonding; Cu Film; Bonding Interface; Transmission Scanning Microscope (TEM); Energy Dispersion Spectroscopy (EDS); Electron Energy Loss Spectroscopy (EELS)

I. INTRODUCTION

It has been said recently that if micromachining on silicon devices continues according to Moore's law, we will soon approach the fundamental limit. To counter this, three-dimensional integration technology has been actively studied as a promising solution for increasing functionality, high-speed processing, and large memory capacity. This technology is based on stacking large-scale integration (LSI) or heterogeneous devices and connecting between the devices with fine through-silicon vias (TSVs). Since the conventional bonding process requires high-temperature annealing to achieve strong bonding [1, 2], there exist various problems such as thermal damage, low throughput, and low alignment accuracy. The surface activating method for direct bonding (surface activated bonding; SAB), which is a bonding method carried out at room or low temperatures, is expected to solve these problems [3, 4]. In the SAB method, surface layers, such as the native oxide and contaminant layers, are removed by Ar fast atom beam etching in an ultrahigh vacuum, and atoms on the surface are activated to create strong inter-atomic bonds [5]. It is necessary to perfectly remove the oxide layer in order to achieve strong bonding [6], as residual oxygen affects the electrical characteristic between vias. The bonding interface of bonded Al/Al or Cu/Cu has been previously investigated by transmission electron microscopy (TEM) [7-9]. Further, the cleanliness and oxidation state of the Cu surface was investigated by Auger electron spectroscopy (AES) [8] and X-ray photoelectron spectroscopy (XPS) [10], respectively, before and after surface activation. However, the ultimate state analysis to study, e.g., the residual oxygen and the oxidation state of the metals at the bonding interface prepared by SAB has never been carried out so far, even though these parameters are extremely important.

Our goal is to apply Cu/Cu bonding by SAB to 3D integration technology. It is very important to evaluate the residual oxygen and the oxidation state at the bonding interface for improving the bonding characteristics and the reliability between vias. Therefore, in this study, we have newly investigated the elemental composition of the bonding interface of Cu/Cu films bonded by the SAB method by energy dispersive X-ray spectroscopy (EDS) and the oxidation state of Cu in the bonding interface by electron energy loss spectroscopy (EELS) combined with TEM. We evaluated the bonding strength of Cu/Cu by tensile testing, and the electrical characteristics through the bonding interface by measuring current-voltage curve.

II. EXPERIMENTAL PROCEDURE

A. Sample Preparation

A single 8 inch Si wafer with 48 mesa structures was prepared for this bonding experiment. The mesa structures were fabricated on the surface of the wafer by anisotropic wet etching at 16 mm intervals. The size of each mesa structure was 7×7 mm^2 and the height was about 20 μm. The mesa structures were thermally oxidized after fabrication. The thickness of the oxide layer was about 300 nm. 50 nm Ti and 300 nm Cu films were then sequentially deposited on the wafer surface by sputtering. An 8 inch thermal oxide Si blanket wafer was also prepared with the same metal films. To achieve strong bonding by the SAB method at room temperature, it is necessary to reduce the surface roughness; therefore, the as-deposited Cu surface was treated by a chemical mechanical polishing technique (CMP). The surface roughness was measured by atomic force

microscopy (AFM) over an area of 1×1 μm^2. The AFM images of Cu surface before and after CMP treatment are shown in Fig. 1. The arithmetic average roughness (Ra) value of the as-deposited Cu surface and the Cu surface after CMP are 1.183 and 0.770 nm, respectively. The native oxide layer of surface must be sufficiently removed to achieve strong bonding by the SAB method at room temperature; therefore, it is very important to measure the thickness of the native oxide layer. The depth profile of the Cu film was investigated by using XPS combined with Ar ion sputtering. Fig. 2 shows the XPS depth profile. At a depth of about 10 nm, the O concentration is less than a few %, and the Cu concentration is greater than 98%. To activate the surface sufficiently, it is necessary to etch deeper than 10 nm into the Cu surface.

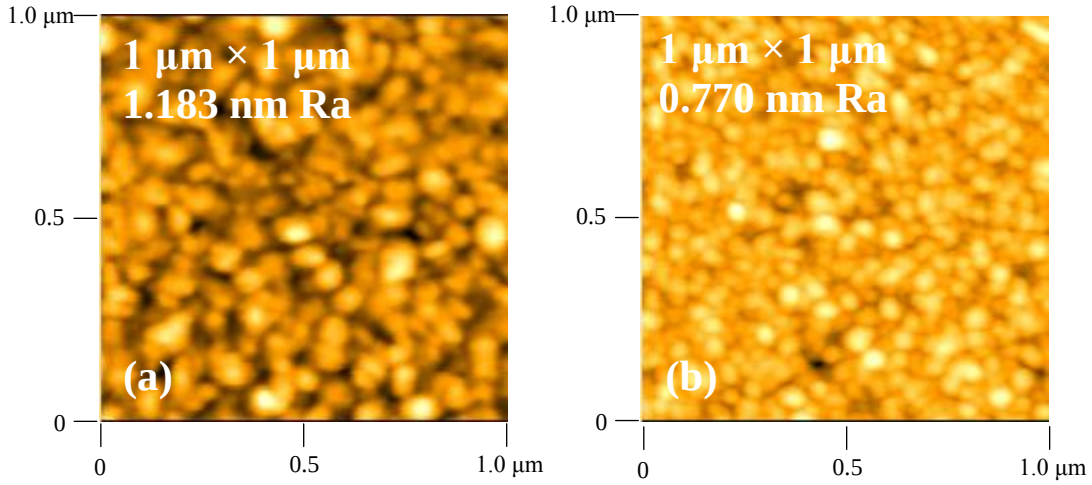

Fig. 1 AFM images for the Cu surface (a) before and (b) after CMP treatment. The respective Ra roughness values are 1.183 and 0.770 nm, Scanning size is 1×1μm^2

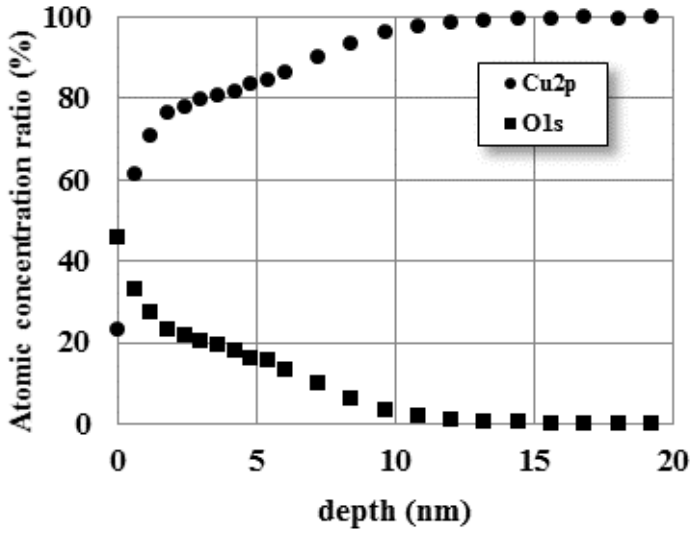

Fig. 2 XPS depth profile of a Cu deposited film after CMP treatment.(●) are Cu 2p peaks, (■) are O 1s peaks

B. Bonding Procedure

Fig. 3 shows a schematic illustration of the bonding apparatus (MWB-08AX, Mitsubishi Heavy Industries) used for the SAB method. The Cu surface was activated by the Ar fast atom beam (FAB). The FAB source generates a neutralized atom beam with energy of about 1 keV. The bonding procedure is as follows. As shown in Fig. 3, a Cu-coated wafer with mesa structures and a Cu-coated blank wafer face each other in the vacuum chamber. The electrostatic chuck (ESC) holds the upper wafer. The background vacuum pressure was about 2×10^{-6} Pa. The upper and lower wafers were both irradiated with an Ar FAB at the same time to remove the native oxide layer on the Cu surface. The two wafers were then put into face-to-face contact with a 100 kN load. The bonding conditions are shown in Table 1. The etching rate of Cu was about 1.7 nm/min when the FAB was operated by the conditions as shown in Table 1. Considering the results shown in Fig. 2, the Ar beam irradiation time for sufficiently removing the Cu native oxide layer was 7 min.

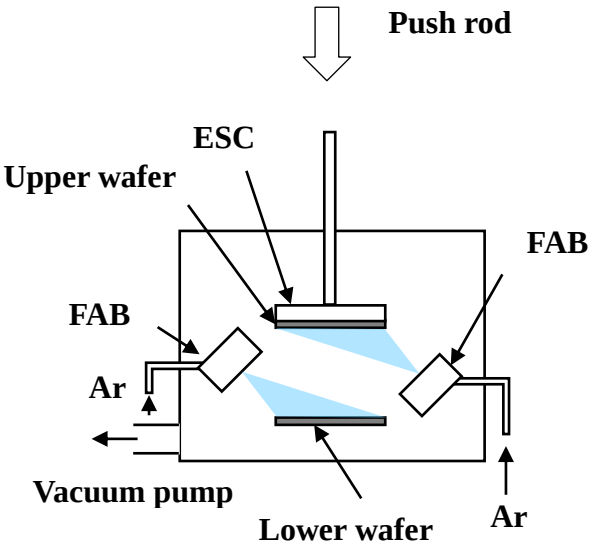

Fig. 3 Schematic illustration of bonding apparatus

TABLE 1 SUMMARY OF BONDING CONDITION

Source gas	Ar
Background vacuum pressure	about 2×10^{-6} Pa
Beam voltage	1.5 kV
Beam current	100 mA
Irradiation time	7 min.
Load at bonding	100 kN

III. RESULTS AND DISCUSSION

A. TEM Observation of the Bonded Interface

A cross-sectional TEM image of Cu/Cu bonding is shown in Fig. 4(a). The bonding interface is easily observed in this picture, but no voids or defects at the bonding interface can be observed. Additionally, as no intermediate layer is seen at the interface, the two Cu surfaces can be considered to be directly bonded. A high-resolution TEM image of the Cu/Cu bonding interface is shown in Fig. 4(b). In this picture, no micro-voids were observed and no intermediate layer could be seen. Considering the surface roughness as shown in Fig. 2(b), it is possible that micro-voids may form at the bonding interface; however, this picture shows one of the Cu surfaces tightly adhering to the other surface. It is possible that the contact area at the interface is broadened by plastic deformation of the two contacted surfaces under the applied load [13]. It is reported that the self-diffusion coefficient of atoms at the grain boundary is a few tens of orders of magnitude higher than that inside grains, and high atom mobility on the activated surface is expected to enhance atom self-diffusion at the bonding interface resulting micro-void-free bonding at the atomic scale [11, 12]. Moreover, the bonded lattice structure is confirmed at the bonding interface in this picture. Therefore, it is estimated that metallic bonding would be formed at the interface.

B. EDS Analysis of the Bonded Interface

The elemental composition was measured by EDS, which gives quantitative elemental information by spectroscopically analyzing the characteristic X-rays emitted from the specimen. All elements, in principle, can be detected. The result at each analysis position is shown in Table 2. The oxygen atomic percentages at all analysis positions are extremely low, revealing the absence of oxygen at the bonding interface, showing that the native oxide layer was removed sufficiently by the surface activating.

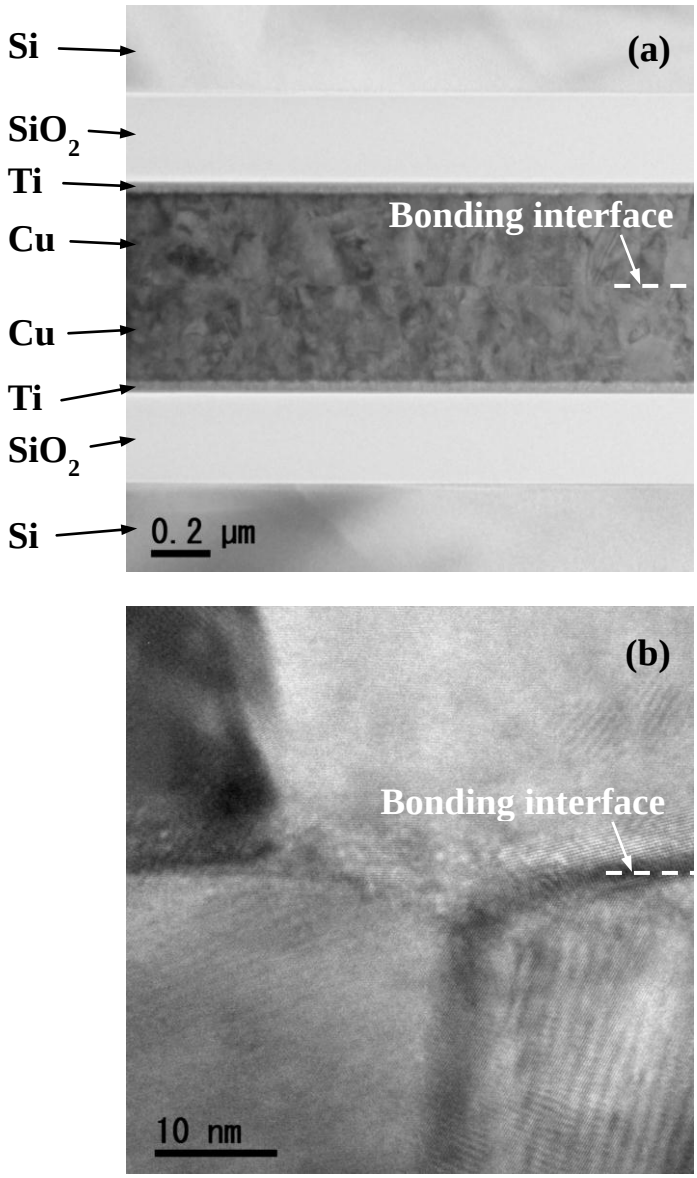

Fig. 4 TEM cross-section images of the bonded Cu/Cu films interface: (a) low magnification (b) high-resolution.

TABLE 2 ELEMENTAL QUANTITATIVE ANALYSES EXPRESSED IN ATOMIC PERCENT. POSITIONS 030, 031, 032, 033, AND 034 CORRESPOND TO THE POSITIONS INDICATED IN FIG. 5

(atom %)

Position No.	C	O	Al	Si	Ar	Cr	Fe	Ni	Cu	total
030	4.1	0.7	0.0	1.3	0.0	0.1	0.6	0.1	93.0	100.0
031	4.0	0.5	0.0	1.4	0.0	0.1	0.6	0.0	93.3	100.0
032	4.1	1.3	0.0	1.5	0.5	0.1	0.6	0.1	91.7	100.0
033	3.9	0.8	0.1	1.5	0.1	0.1	0.7	0.1	92.9	100.0
034	3.6	1.1	0.0	1.5	0.1	0.0	0.6	0.4	93.1	100.0

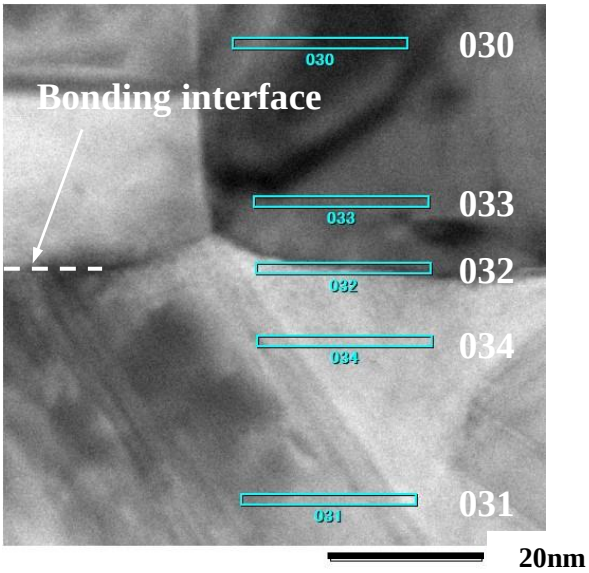

Fig. 5 TEM image of the bonding interface. The boxes and numbers 30 to 34 indicate the points where EDS analysis, given in Table 2, was carried out

C. EELS Analysis of the Bonded Interface

The oxidation state of Cu at the bonding interface was investigated by EELS, an analytical technique that measures the energy loss of high-energy electrons after they have passed through a specimen. Combined with TEM, EELS is capable of giving chemical information about a solid with a spatial resolution down to the atomic level. EELS analyses were carried out at each position of the bonding interface as shown in Fig. 6. Fig. 7 shows the EELS spectra of energy range 450 to 650 eV at each analysis position; only the sample background was visible. O-K edge spectra from CuO or Cu_2O have peaks at about 530, 531, 532 and 538 eV [15], however, those peaks weren't observed in those measured spectra. The three obtained spectra were clearly different from those of CuO and Cu_2O. Fig. 8 shows Cu-L edge spectra at each analysis position with pure Cu reference spectrum [14], showing that each measured spectrum has the same shape. Additionally, Cu-L edge spectra from CuO or Cu_2O have peaks at about 930 and 950 eV [14]; those peaks weren't observed in the measured spectra either. The absence of Cu oxide at the bonding interface was confirmed by EELS analysis combined with TEM.

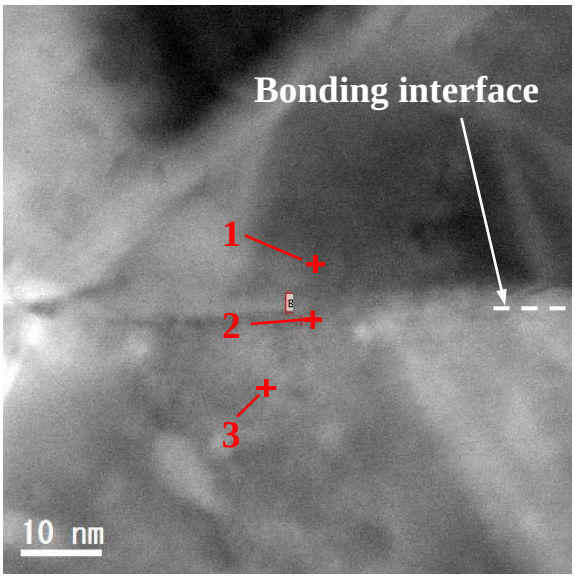

Fig. 6 TEM image of the bonding interface. The numbers 1 to 3 indicate the points where the EELS spectra given in Figure 7 and 8 were measured

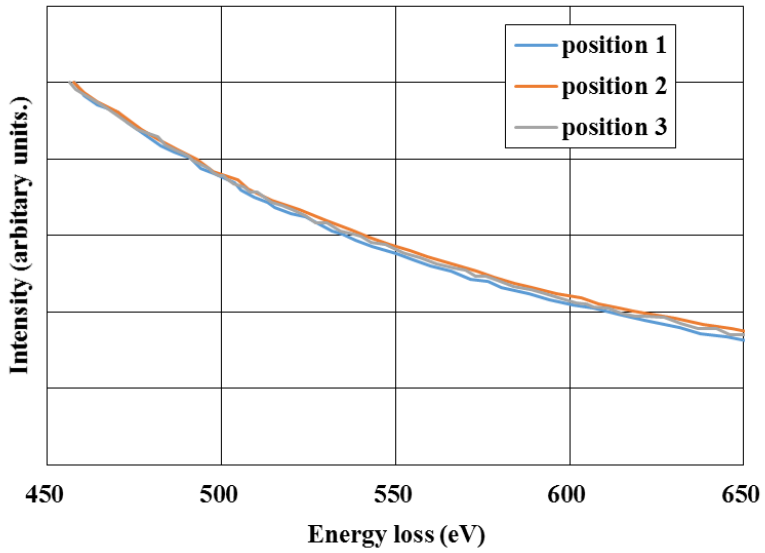

Fig. 7 EELS spectra (450–650 eV) at positions 1, 2, and 3 as indicated in Fig. 6

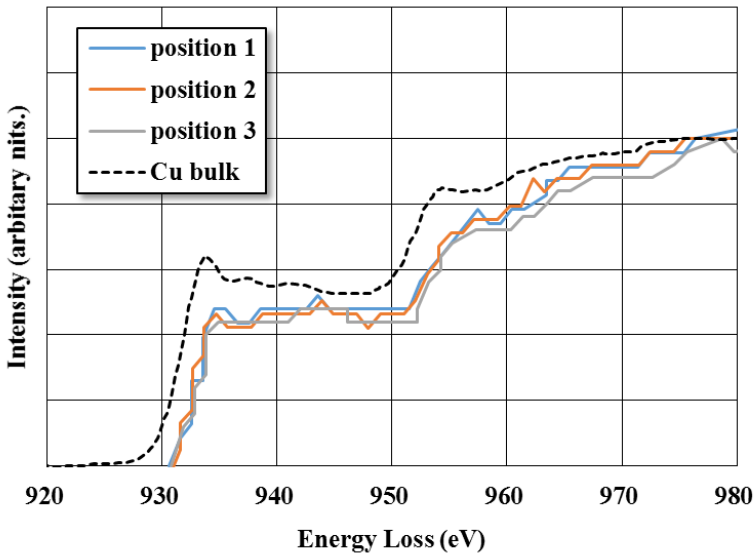

Fig. 8 EELS Cu-L edges spectra at positions 1, 2, and 3 as indicated in Fig. 6 and compared with bulk Cu reference spectrum

D. Tensile Test

The bonding strength was evaluated by tensile testing. The specimen for the tensile test was prepared by slicing the bonded wafer into 23×23 mm^2 pieces centered on the 7×7 mm^2 mesa structures as shown in Fig. 9(a). The specimen was glued to metal attachments as shown in Fig. 9(b). Fig. 10 shows the result by tensile test. The specimen fractured not in the interface of the bonded Cu/Cu, but in the interface between the thermal oxide layer and Ti film due to the mechanical weakness in the interface. The measured bonding strength was about 8 MPa. The bonding strength of the Cu/Cu bonded interface is therefore higher than 8 MPa. This value is lower than that in the similar interface reported in Ref. 17. Since the bonding strength in Ref. 17 was evaluated by the die shear test, it is impossible to compare them. To improve the bonding strength, we previously investigated the effect of annealing at a temperature lower than about 450 K after bonding [16].

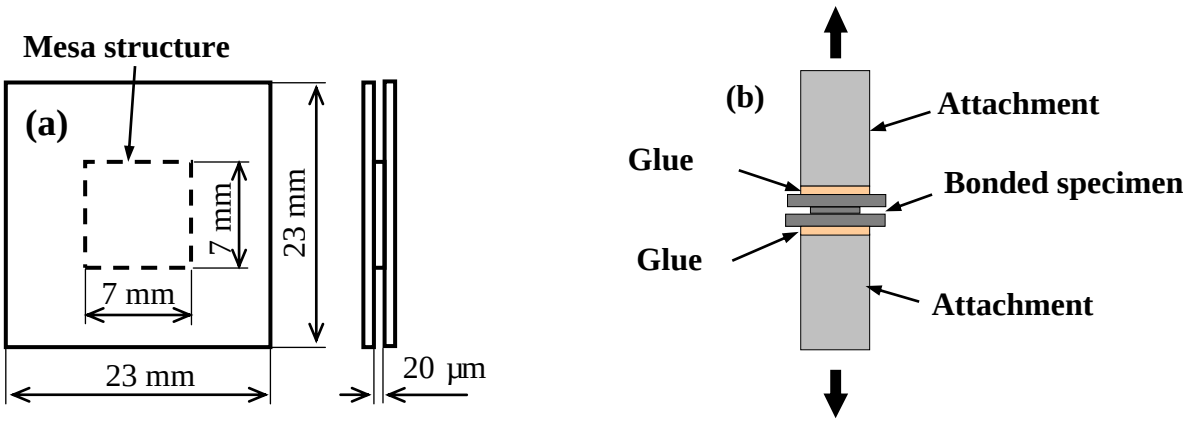

Fig. 9 (a) 23×23 mm^2 sliced piece from the bonded wafer, (b) Configuration for tensile test

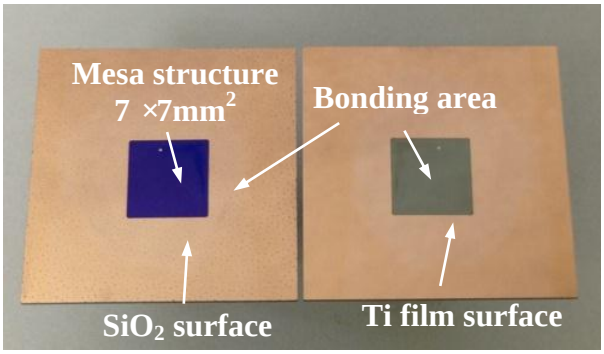

Fig. 10 Fracture image of Cu/Cu bonding. This bonding sample is fractured from the interface between the thermal oxide layer and Ti film

E. Electrical Characterization

The right side piece, as shown in Fig. 10, has a multilayer structure as shown in Fig. 11. The electrical conductivity through the bonded Cu/Cu interface on this piece was evaluated by placing metal tips on the Ti and Cu film surfaces, as shown in Fig. 11, so that current passed through the bonding interface. The current-voltage (I-V) characteristic of the Cu/Cu bonding is shown in Fig. 12. The resistance seems to be rather large; this would be due to the contact resistance between the metal tip and the metal film, or the impedance effect of the lead wires used in the I-V measurement. This subject should be considered in the future studies.

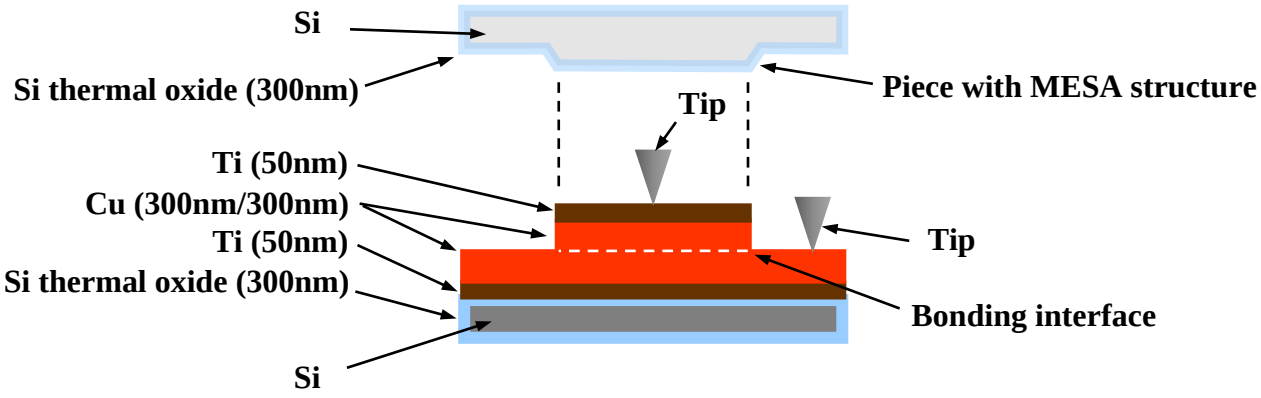

Fig. 11 Schematic diagram of the specimen for electrical characterization

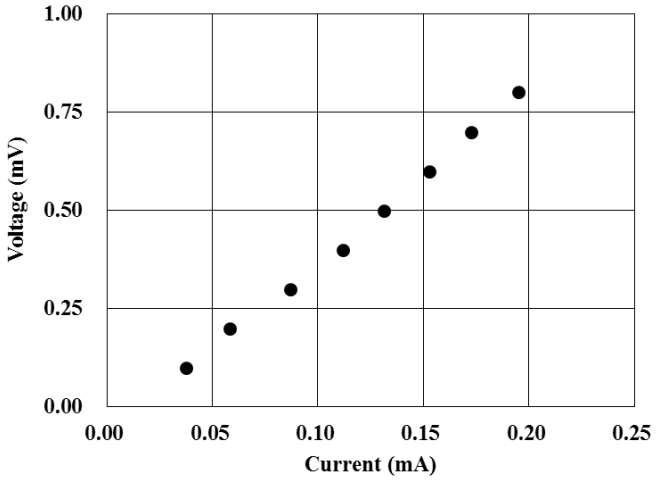

Fig. 12 I-V characteristic of the Cu/Cu bond describing the vertical conduction of the bonded piece after tensile testing

IV. CONCLUSIONS

The elemental composition and oxidation state of Cu at the bonding interface, in which Cu/Cu is bonded by the SAB method at room temperature, were investigated by EDS and EELS analyses combined with TEM, respectively. The absence of oxygen at the bonding interface was confirmed by EDS analysis, and the absence of Cu oxide was confirmed by EELS analysis. It was confirmed that the bonding strength of the Cu/Cu bonded interface was higher than 8 MPa by tensile testing, and the I-V characteristic of the bonded Cu/Cu interface was linear.

In this paper, we have shown that the SAB method at room temperature is a bonding technique that can fulfill both the bonding strength and the electrical characteristics of Cu/Cu direct bonding for 3D integration technology.

REFERENCES

[1] A. Fan, A. Rahman, and R. Reif, "Copper wafer bonding," Electrochem. Solid-State Lett., vol. 2, pp. 534-536, 1999.

[2] P. Gueguen, L. D. Cioccio, P. Gergaund, M. Rivoire, D. Scevola, M. Zussy, A. M. Charvet, L. Bally, D. Lafond, and L. Clavelier, "Copper direct-bonding characterization and its interests for 3D integration," J. Electrochem. Soc., vol. 156, pp. H772-H776, 2009.

[3] H. Takagi, R. Maeda, and T. Suga, "Wafer-scale spontaneous bonding of silicon wafers by argon-beam surface activation at room temperature," Sensors and Actuators, vol. A105, pp. 98-102, 2003.

[4] A. Shigetou, T. Itoh, M. Matsuo, N. Hayasaka, K. Okumura, and T. Suga, "Bumpless interconnect through ultrafine Cu electrodes by means of surface-activated bonding (SAB) method," IEEE Trans. Adv. Packag., vol. 29, pp. 218-226, 2006.

[5] H. Takagi, K. Kikuchi, R. Maeda, T. R. Chung, and T. Suga: "Surface activated bonding of silicon wafers at room temperature," Appl. Phys. Lett., vol.68(16), pp. 2222-2224, 1996.

[6] Y. Takahashi, H. Takagi, T. Suga, B. Gibbesch, G. Elssner, and Y. Bando, "Environmental effect on structural, mechanical and electrical properties of Al/Al interfaces joined at room temperature," J. Japan Inst. Metals, vol. 55, pp. 1002-1010, 1991.

[7] T. Suga, K. Miyazawa, and H. Takagi, "TEM observation of the Al and Cu interfaces bonded at room temperature by means of the surface activation method," J. Japan Inst. Metals, vol. 54, pp. 713-719, 1990.

[8] T. H. Kim, M. N. R. Howlader, T. Ito, and T. Suga, "Room temperature Cu-Cu direct bonding using surface activated bonding method," J. Vac. Sci. Technol., vol. A21, no. 2, pp. 449-453, 2003.

[9] T.H. Kim, M.M.R. Howlader, T. Itoh, and T. Suga, "Low temperature direct Cu-Cu bonding with low energy ion activation method," Proc., Int. Symp. on Electronic Materials and Packaging, 3rd IEEE, pp. 193-195, 2001.

[10] A. Shigetou, T. Itoh, and T. Suga, "Effect of exposure to vacuum condition in room-temperature direct bonding of CMP-Cu thin films by activated bonding(SAB) method," J. JIEP, vol. 9, no. 4, pp. 278-281, 2006.

[11] T. Shimatsu, R. H. Mollema, D. Monsma, E. G. Keim, and J. C. Lodder, "Metal bonding during sputter film deposition," J. Vac. Sci. Technol., vol. A 16, pp. 2125-2131, 1998.

[12] T. Shimatsu, and M. Uomoto, "Atomic diffusion bonding of wafers with thin nanocrystalline metal films," J. Vac. Sci. Technol., vol. B 28, pp. 706-714, 2010.

[13] Y. Takahashi, S. Aono, T. Kamitani, K. Inoue, and K. Nishiguti, "Development of estimation method of void spacing distribution during bonding and modelling interfacial contact process – Support System for Prediction of Solid State Diffusion Bonding (Part 1)," Quarterly J. Jpn. Weld. Soc., vol. 14, no. 4, pp. 666-673, 1996.

[14] R. D. Leapman, L. A. Grunes, and P. L. Fejes, "Study of the L23 edges in the 3d transition metals and their oxides by electron-energy-loss spectroscopy with comparisons to theory," Phys. Rev. B., vol. 26, pp. 614-635, 1982.

[15] L. A. Grunes, R. D. Leapman, C. N. Wilker, R. Hoffmann, and A. B. Kunz, "Oxygen K near-edge fine structure: An electron-energy-loss investigation with comparisons to new theory for selected 3d Transition-metal oxides," Phys. Rev. B., vol. 25, pp. 7157-7173, 1982.

[16] J. Utsumi and Y. Ichiyanagi, "Cu-Cu direct bonding achieved by surface method at room temperature," AIP Conf. Proc., 1585, pp. 102-107, 2014.

[17] A. Shigetou, T. Itoh, and T. Suga, "Direct bonding of CMP-Cu films by surface activated bonding (SAB) method," J. Mater. Sci., vol. 40, pp. 3149-3154, 2005.