New Bonding Technique Using Copper Oxide Materials

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As a bonding technique between semiconductor elements in a semiconductor device and external substrates, a reduction bonding technique has been developed that uses CuO particles several micrometers large. This technique has the following features. (1) CuO particles can be reduced in about 200°C H2 atmosphere. (2) Pure Cu particles about 50 μm in diameter form at this time. (3) The formed Cu particles form a sintered Cu layer. (4) Bonding can be achieved above 350°C. Bonding requires pressurization. The bonding strength (shear breaking strength) of this sintered Cu layer and Ni electrodes used by many semiconductor devices was evaluated. Consequently, bonding strengths were about 20 MPa at pressurization of 1.2 MPa and a heating temperature of 350°C. Moreover, in the bonded interface of a sintered Cu layer and Ni electrodes, the sintered Cu layer formed the hetero-epitaxial layer between Ni electrodes. For this reason, we confirmed that the bonded interface of a sintered Cu layer and Ni electrodes was in a strong bonding state on the metal object.

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1. Introduction

In semiconductor devices used in trains, wind power equipment, automobiles, etc., the current density tends to increase as equipment is miniaturized.1) As this happens, the operating temperature for semiconductor devices becomes an elevated temperature. For this reason, the semiconductor devices are demanded to have long-term high reliability in high temperature environments.2) Moreover, in new devices such as silicone carbide (SiC), bond material needs to be developed that resists high temperature.3) As a bond material for high temperature environments of semiconductor devices, the solder material containing much lead has mainly been used. However, from the viewpoint of environmental protection, a bond material needs to be developed that complies with the RoHS command that no harmful lead be used.

To achieve this, a silver-nano-particle bonding technique has been examined.4–7) This bonding technique, which does not use lead, can carry out bonding at a temperature lower (about 300°C) than the melting point of silver. This bonding temperature is lower than the bonding temperature of lead solder material (about 350°C). Furthermore, the resulting bonding layer has high radiation and high heat resistance, which are features of silver. For this reason, this bonding technique has been considered suitable for a high temperature environment. Furthermore, a part of the protection coat material used to stabilize a silver nano particle discharges a residue into the bonding layer, without its effect being eliminated during the bonding process. We were anxious about this residue corroding the bonding layer.

To solve these problems, a bonding method using a low-cost silver oxide particle has been reported.8,9) This technique has the following features.

(1) It is a bonding method using the silver oxide particles several micrometers large to which high-boiling-point alcohol is added.
(2) Adding this alcohol accelerates the reduction reaction at low temperature.
(3) Silver nano particles form at this time.
(4) The formed silver nano particles do not have an organic substance.
(5) The silver nano particles formed from the silver oxide particle are sintered immediately.
(6) This method forms the bonding layer of pure silver similarly to the silver nano particle bonding method.

This technique may be able to reduce material cost below that of the silver nano particle bonding method. However, silver tends to produce ion migration, so we were anxious about the reliability declining. Furthermore, we were also anxious about the cost of bond material rising due to a sharp rise in the raw material price.

Additionally, copper is comparatively low cost and has high conductivity and high productivity equivalent to those of silver. Furthermore, it also has excellent ion migration resistance, and if copper nano particles are used for bonding, many problems will become solvable. On the other hand, the copper nano particle has a problem: it is oxidized easily if left at room temperature.10) To solve this problem, there is a method for coating the copper nano particle surface with silica11) or a polymer.12) However, to remove these coats, they must be heated at 400°C or more. For this reason, this method was unsuitable for the bonding process of 350°C or less required for semiconductor mounting. On the other hand, a synthetic process of copper nano particles using CTAB (cetyl trimethyl ammonium bromide) of a low-molecule organic material has been reported.13) However, oxidization of copper particles has not been preventable.

On the basis of this situation, a silver oxide reduction bonding technique is applied in which reducing atmosphere is used. Developing a reduction bonding method using copper-oxide material may make many problems mentioned above solvable.

2. Reduction Characteristics of Copper Oxide

We conducted thermal analyses (thermogravimetry-differential thermal analysis (TG-DTA)) on Cu2O and CuO particles (all were commercial reagents) and investigated the reduction temperature. The weight reduction curve of TG-DTA showed that 10% of the reduction rates was set as the reduction start temperature (T (10%)), and 100% of the reduction rates was set as the reduction end temperature.
The results are shown in Fig. 1 and listed in Table 1. The analyses were performed in a mixed gas of 3% hydrogen and 97% nitrogen. Different $T$ for $T\, (100\%)$ and $T\, (10\%)$ are also listed in Table 1. The $T\, (10\%)$ and $T\, (100\%)$ for the Cu$_2$O were large. On the other hand, $\Delta T$ was larger for Cu$_2$O than CuO. Consequently, we confirmed that CuO was easier to reduce than Cu$_2$O. Using these results, we were able to compound a copper oxide material with CuO junctions.

3. Experimental Procedure

3.1 Composition of CuO particle for bonding

CuO particles for bonding were synthesized on the basis of a metal salt-base reaction. An aqueous solution of NaOH (1 M) (19 mL) was added to 981 mL of 0.0102 M Cu(NO$_3$)$_2$ aqueous solution under vigorous stirring at 20°C, which resulted in a Cu$^{2+}$ concentration of 0.01 M in the final solution. The reaction time was 24 h, and a SEM image of these CuO particles is shown in Fig. 2.

3.2 Bonding strength

We investigated the bonding capability of synthetic CuO particles (bond material) with Ni. The bonding capability was evaluated as the bond strength under shear. Perspective views of the shearing test piece are shown in Fig. 3 (JIS Z3198-5). The test piece was a Cu disk that was about 2 µm thick and had electrolysis Ni plating on the surface. The bond material was painted onto each test piece within the black regions in the figure. The paint itself was approximately 100 µm thick. Bonding was accomplished by simultaneously applying heat and pressure (1.2 MPa) in a H$_2$ atmosphere, and the bonding time was 5 min. We used an SS-100KP bond tester (Seishin Shoji, maximum load: 100 kg) for the shear tests. The rate of shear was 30 mm/min, and the maximum load during fracturing was measured by applying a shearing force to the small Cu disk shown in Fig. 3 to fracture the bond. The shear strength was taken as this maximum load divided by the bond surface area (equivalent to the surface area of the disk).

3.3 Observation of bonding interface

A diamond paste (particle diameter: 0.25 µm) was used to finish buffing the cross-sectional samples used for the SEM observation that were first finished by buffing using polishing oil and then subjected to Ar-ion milling (at an accelerating voltage of 15 kV) for 180 s. We observed the interface using TEM to obtain more detailed images of the bond between the Cu and Ni. The samples used for observing the cross-sections of the bonds were milled using a focused ion beam (FIB; Hitachi FB-2000A). The milled thin film samples were mounted on a cutout mesh and observed using TEM (Hitachi H9000; acceleration voltage: 300 kV). Ion milling was also used when necessary to make the observation samples even thinner.

4. Results and Discussion

4.1 Results of bonding strength evaluation

Figure 4 shows the relationship between the bonding
strength and the bonding temperature for a synthetic CuO particle. The 250°C bonding temperature was not suitable for the bonding. However, the bonding strength rose as the bonding temperature rose to 300°C or more. The bonding strength was about 20 MPa at the bonding temperatures of 350°C and 400°C. We thus determined that the joint was excellent.

Figure 5 shows the state on the shearing side of the test piece after the shearing examination. We confirmed that the bond material was unreduced because of the black region at 250°C. We also determined that the unreduced material was not bondable based on the graph shown in Fig. 4. At 300°C or more, the bond material was changed into sintered copper. We confirmed that the bond material continued to reduce. Moreover, all the sintered copper remained on the shearing breaking side at 300°C or more. As for breaking while shearing, breaking predominantly happened during sintering of copper.

4.2 Observation of detailed bonding structure

Figure 6 shows SEM images of the cross-sections of the Cu sintered layer and Ni electrode (Ni plating). The bonding temperature was 400°C. The copper sintered layer shows a uniform porosity state in the SEM image (a), and image (b) shows the Cu sintered layer at the interface with the Ni electrode in more detail. We understood from this image that a high sintering density layer forms at the interface. We believe that this layer had been strongly bonded to the Ni electrode. Subsequently, a crystal direction analysis was conducted on this portion using electron backscatter diffraction (EBSD). Figure 6(d) shows the results of the analysis that support image (c). Image (d) shows that the Cu sintering layer of the interface had grown in this crystal direction to form a multi-crystal Ni electrode. These results prove that there is a good metal bond and that the sintering Cu and Ni electrode interface is in a strong bonding state.

A TEM image of the interface of the sintering Cu and Ni is shown in Fig. 7. The low-magnification TEM image (a) shows that the crystal growth of the sintering Cu is in the same direction as the crystal direction of the ground Ni electrode. Furthermore, the high-resolution image (b) confirms that the atomic arrangement of Cu and Ni is mostly in the same direction and that their diffraction patterns were mostly in agreement. Thus, Cu and Ni can be seen to have an epitaxial direction relationship. Therefore, Cu and Ni turned out to have a good metal bonding state. In addition, we confirmed that the synthetic CuO material also joins well with the Cu electrode.
4.3 State of diffusion of bonded interface

We were able to clarify the state of the crystal grain of the sintered Cu and Ni interelectrode. However, the diffusion was not clarified. We thus tried EBSD from the same viewpoint as TEM and the elemental mapping by using TEM-EDX. Figure 8(b) shows the EBSD crystal orientation map from the same view as in (a), which is a cross-section TEM image. In addition, the mapping data of (c) Cu and (d) Ni by using TEM-EDX is shown. As mentioned above, the crystal grew in the same direction for the Cu and Ni in the bonded interface.

On the other hand, neither Cu nor Ni is diffused mutually when (a), (c), and (d) are compared for the Cu-Ni crystal grain in the same direction. We determined that there was a clear distribution interface of Cu and Ni in the same crystal grain direction. The Cu was distributed in the grain boundary of the Ni electrode (Ni plating), and thus, Ni plating film is a stable thin film. We believe that Cu composed of a sintering layer was easier to diffuse than Ni composed of a plating film. Moreover, since the bonding structure integrity is ensured by the diffusion, a good metal-bonding is assumed to be realizable.

4.4 Reduction of CuO particles and sinter-bonding mechanism

We investigated the sintering behavior in the reduction process of CuO particles. Figure 9 shows the results from a SEM observation of CuO particles heat-treated in H2 at (a) 150°C, (b) 175°C, (c) 250°C, and (d) 300°C. SEM-EDX was used to confirm the compositions of the particles after each heat treatment.

At 150°C, the CuO particles formed a rectangular configuration. After heat-treating at 175°C, copper particles about 50 nm in diameter formed on the CuO particles. We believe that these copper particles carried out the reduction formation from the CuO particles. At 250°C, Cu was formed, and after 300°C heating, the entire structure went through Cu substance stratification. Copper is believed to be the sintering layer formed of the Cu particles formed when the CuO is reduced.
As mentioned above, the CuO particles turned out to form into approx. 50-nm-diameter Cu particles at 175°C during the reduction process, sintered under heat-treatment at 300°C, and became bulk Cu. The Cu particles sintered at the low temperature of 300°C or less are nanometer sized because they are produced using this reduction process. For the bonding method using CuO particles, we found out that metal-bonding can ensure that Ni is used as mentioned above.

Moreover, from the EBSD results shown in Figs. 6 and 8, the hetero-epitaxial bonding structure acquired when using Ni is believed to be a characteristic metal bonding structure acquired during the low temperature sintering of metal particles.

The interdiffusion of Cu and Ni has been widely researched. However, those investigations were done in a high temperature region exceeding 700°C. Moreover, the research on diffusion bonding of Cu and Ni clearly showed that a good bonding temperature was 700°C or more.

On the other hand, den Broeder and Nakahara heat-treated the Polycrystal diffusion couple of pure Cu and pure Ni and investigated the grain boundary diffusion region experimentally. Consequently, in the diffusion couple heat-treated at 600°C for 360 minutes, they clearly showed that diffusion of Cu to the inside of Ni phase is about 1 micrometer.

The above is the result of basing research on the bulk material of Cu and Ni. A high temperature is needed to bond Ni to Cu. However, although Cu is the nanometer-sized particulate like this research result in low temperature (400°C) and short time (5 min) conditions, Cu turned out to diffuse about 1 micrometer in the grain boundary of Ni (Fig. 8).

Because Cu particles are nanometer sized, the surface of particles is greatly revitalized. We think these particles exist in a condition similar to the liquid phase. When Cu particles in such a state come in contact with the bulk Ni, we think Cu particles diffuse to the grain boundary of the Ni membrane like the molten metal.

5. Conclusion

(1) The CuO in a copper oxide is easier to reduce than the Cu2O.

(2) The reduced CuO and sintered Cu layer can be bonded to Ni plating film. This Cu layer has a hetero-epitaxial orientation relationship with the Ni plating film, which is believed to cause high bonding strength with the Ni.

REFERENCES