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DOI
10.1109/ICEPT50128.2020.9201937

Publication date
2020

Document Version
Final published version

Published in
2020 21st International Conference on Electronic Packaging Technology (ICEPT)

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***Abstract*—Nano-metal sintering is a promising technology for the next generation of semiconductor packaging due to its positive effect on reliability enhancement. Compared with the silver sintering, copper-based sintering technique has more potential to be applied in die attachment field as its superiorities on lower cost, higher melting temperature without electromigration. In this study, Taguchi method is applied to study and analyze the effect of nano-/micro- particle ratio on sintering properties. Sintering temperature is also taken into account since it depends on the particle size a lot. The results show that both sintering temperature and nano-micro- ratio play significant role on influencing shear strength. The best combination is 300 nm with 1 um mixing (1:1) with over 35 MPa shear strength with 300°C sintering temperature. The fracture surface result shows that the crack propagated in the sintering body. Furthermore, the cross-section inspection reveals dense bonding and clearly sintering necking, and the porosity is lower than 12%. 227.8 W/m*K thermal conductivity and 6.0 uΩ•cm electrical resistivity are measured for the sample, which indicates the great potential for the packaging application in high power situation.**

Keywords*—Nano copper, sintering technology, electronics packaging

I. INTRODUCTION

Wide bandgap (WBG) semiconductors such as silicon carbide (SiC) and gallium nitride (GaN) compared with the silicon possess higher broken-down voltage, lower on-resistance, higher operational temperature, and faster switching speed, as shown in Figure 1a. Therefore, they have been thought to be the potential candidates to replace the silicon-based semiconductors in high-frequency and high-power application fields [1-3]. To bring the superiority of WBG semiconductor into full play, it is necessary to enhance the performance of packaging technology and at the same time lower down the manufacturing cost. Generally, a standard structure of power device contains a die attachment layer directly below the dice, which is significant for the electrical conduction and heat dissipation. The conventional packaging strategies utilize multi-component soldering for die-attachment, leading to the problem of low service temperature and brittleness due to the intermetallic (IMC) precipitation [5].

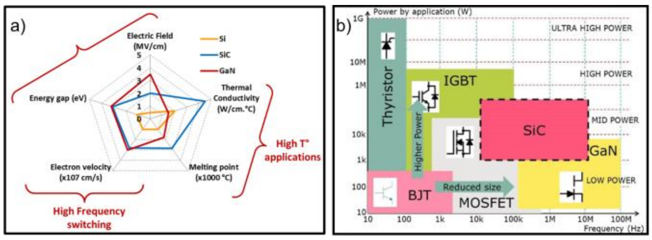

Fig. 1. a) Properties comparison between Si and WBG semiconductors [3]; b) typical power devices and their service power range [4].

Recently, the development of micro and nano technology provides new approaches for the next generation of packaging interconnection technology. For example, the nano silver sintering technology possesses low process temperature (250~300°C), high service temperature (over 450°C) and high thermal conductivity (200W/mK) [6] at the same time. Nano copper sintering is even a better choice as it possesses the similar properties as nano silver material but with relatively lower cost and without the problem of electron migration. However, plenty of research also found that nano particles of copper the size of which is below 100 nm were not easy to be synthesized in mass production and they are quite easy to be oxidized if not proper protection method is applied [7]. Thus, the copper paste containing nano single-sized copper particle is facing the serious costing issue. For these reasons, orthogonal experiment is applied to study the effect of the micro-/nano-copper mixing ratio and sintering parameters on the shear strength. The sintering experiments are conducted at the temperature between 260~300°C in hydrogen and argon mixing atmosphere. The fracture surfaces of the tested samples are observed and the porosity of the sample are extracted from the SEM image captured at the cross-section. Finally, the thermal conductivity and electrical resistivity of the samples are measured as well to check the feasibility of this material for the application of power electronics packaging.

II. MATERIALS AND PROCEDURE

A. The copper particle and paste

In this study, three different nano-sized copper particles (NPs, 100nm, 300nm, 500nm) with three different micron-sized copper particles (MPs, 1μm, 5μm and 20μm) are selected to be studied. Such copper particles are purchased from the same suppliers. To fabricate the metallic paste, ethylene glycol(EG) is used as solvent due to its low boiling point and appropriate viscosity. The mass ratio of the copper paste is over 80 wt.%. The copper paste prepared for this study is shown in the Figure 2.

Fig. 2. Copper paste in this study.

B. Test vehicles

To mimic the die attachment (DA) scenario, a 5mm×5mm×1mm oxide free copper(OFC) plate is used as dummy dice and an another 10mm×10mm×1mm OFC is used as a substrate as shown in the Figure 3a. Copper paste is printed onto the top surface of the copper substrate with same size of the dummy dice. Then the dummy dice is attached to the copper paste surface via sintering process. Such sample is used for the die shear test and cross-section observation. For the purpose of thermal conductivity test, a cylinder disc with Φ10 mm diameter and 1mm thickness is prepared by a special mold. Same sintering process parameters are applied when preparing this sample, and the schematic diagram of the disc sample is shown in Figure 3b.

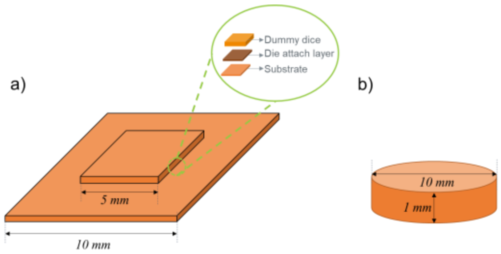

Fig. 3. Schematic diagram for a) the die-attached sample, and for b) the cylinder-shaped sample.

C. Experimental procedure

To begin with, the copper particle samples are observed by scanning electron microscope (Zeiss Germini SEM 300) to check the size distribution and morphology of each group. Then the particle samples smaller than 1 μm are washed by acid solution to remove the surface oxidation. The as-washed particles are examined by X-ray diffraction (XRD) to check the existence of oxide phase and the particle groups without oxidation are used to prepare copper paste in the next steps. Next, the EG solvent is weighted and poured into the sample jar. Then the different copper particles are weighted and added into the sample jar by sequence with the nano particles ratio and micro-/nano- particles size shown in the Table I. The mixed sample is stirred by the mechanical stirring and then milled by the three roll milling machine. Finally the as-milled paste is further homogenized by the planet agitator at 1500 rpm for 2 min and the paste is then stored in the nitrogen box ready for the shear test.

TABLE I. DESIGN OF EXPERIMENT BY USING TAGUCHI METHOD

Sample No.	Different factors on sintering properties			
	Factor 1: NPs ratio	*Factor 2: NPs size*	*Factor 3: MPs size*	*Factor 4: Sintering temperature*
1	30%	100 nm	1 μm	260℃
2	30%	300 nm	5 μm	280℃
3	30%	500 nm	20 μm	300℃
4	50%	100 nm	5 μm	300℃
5	50%	300 nm	20 μm	260℃
6	50%	500 nm	1 μm	280℃
7	70%	100 nm	20 μm	280℃
8	70%	300 nm	1 μm	300℃
9	70%	500 nm	5 μm	260℃

The well prepared copper paste is then set to the 10mm × 10mm copper substrate by the stencil printing method. The printing thickness is 0.1 mm. Next, the sample is dried in the oven at 150°C for 20 min. After drying, the 5mm × 5mm copper plate is placed onto the paste surface manually and the whole sample is then placed into the hot pressure machine for the sintering process. The sintering experiments are conducted at the temperature 260, 280 and 300°C in 5% hydrogen and argon mixing atmosphere for 30 min, assisted with 10 MPa pressure. Nine sandwiched-like samples and 4 disc samples are prepared for each group.

Eight of each as-sintered sandwiched-like samples are then sheared to test the bonding strength by using Dage 4000 shear tester with 100μm/s shear rate. The fracture surface of the sheared samples are observed via Zeiss Aixon Scope A1 Microscope. One sandwiched sample of each group is selected for the porosity measurement. The cross-section sample is sawed and the surface is polished by ion milling(Hitachi) before SEM observation. Then ImageJ is utilized to figure out the pores area and to calculate the porosity. In the end, for thermal conductivity and electrical resistivity measurement, the disk shaped samples are prepared by the mold shown in the Figure 4. The laser flash analysis is used to obtain the material thermal diffusion coefficient (NETZSCH LFA467 HyperFlash) and the material density is obtained by using the Archimedes method.

The thermal conductivity is calculated by multiply the density with thermal diffusion coefficient and specific heat capacity. Finally four point probe method is used to measure the electrical resistivity.

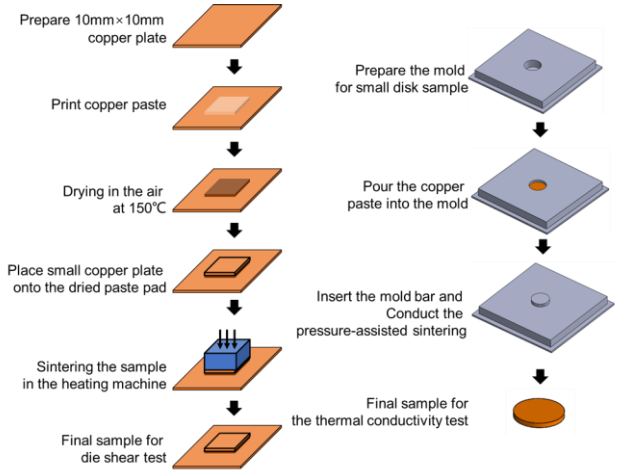

Fig. 4. Flow chart of sample preparation for the sintering die-attached sample and sintering cylinder sample.

III. RESULTS & DISCCUSION

A. Copper Particles Characterization

All groups of copper particles are first characterized by SEM to check the size and morphologies, as shown in Figure 5, in which the first three photos are for the NPs, and the rest of them are for the MPs. From the pictures it indicates that all the particles are dispersed well with granular shape except for the 100nm ones. Thus an ultrasonic dispersion process is necessary before using 100nm particles to fabricate paste.

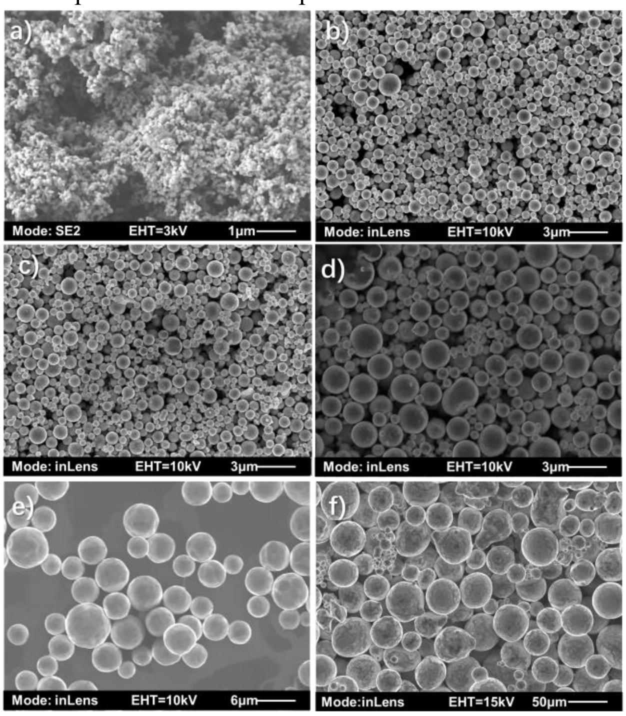

Fig. 5. SEM photos for the copper powders with a) 100nm, b) 300nm, c) 500nm, d) 1μm, e) 5μm and f) 20μm sizes.

Nano sized copper particle is easy to be oxidized when exposed in the air. For this reason, before the paste preparation, the copper particles which are smaller than 1 μm are washed by acid solution to remove the surface oxidation layer. The Figure 6 below shows the X-ray diffraction (XRD) results of the as-washed particles. It reveals that there is no peak for the oxides phase at around 35° after washing. The copper paste is then prepared by utilizing the particle after treatment.

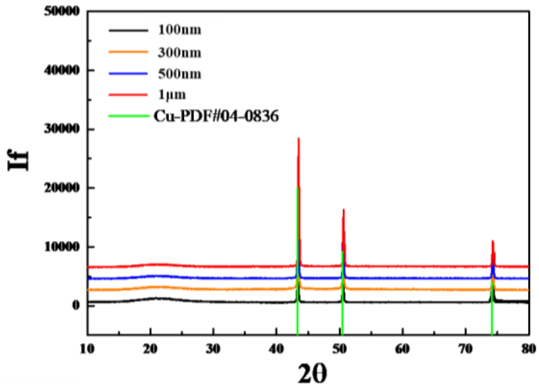

Fig. 6. The XRD results of the washed copper particles.

B. Die Shear Test

All groups of copper paste are printed onto the 10mm×10mm copper substrates and then placed with 5mm×5mm dummy die to fabricate the sandwiched structure. The sintering experiments are conducted at the temperature among 260, 280 and 300°C in 5% hydrogen and argon mixing atmosphere for 30 min with 10 MPa pressure. The shear tests results are summarized into the Figure 7. From the chart, the sample 1, 5 and 9 are the three ones with the lowest shear stress. The reason is the low sintering temperature (260°C) which cannot provide enough driving force for the bonding formation. By increasing the sintering temperature to 280 and 300°C, the shear stress is also enhanced to over 12.5 MPa. The best shear stress comes from the sample 8 with 300°C sintering temperature and 70 wt.% nano sized particle ratio.

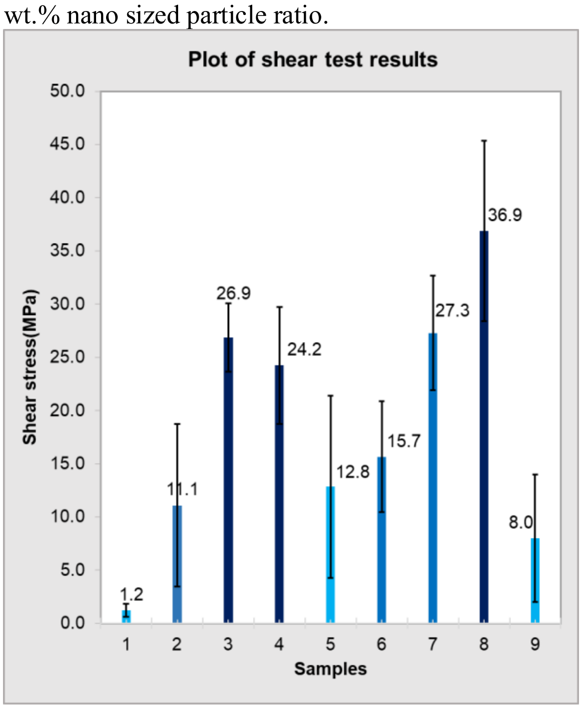

Fig. 7. Shear test results of different sample groups.

To further analyze the shear test results, the Taguchi method is applied. By conducting the design of experiment, the effect of different factors on the sintering property is extracted. From the results shown in Figure 8, it can be obtained that the sintering temperature and NPs to MPs ratio play the most significant role in the sintering process. The higher the sintering temperature and the larger the nano to micron ratio, the higher the sintering bonding strength is. Among them, the effect of specific size of the NPs and MPs are not pronounced. The 300nm particles is probably better choice when mixing with micron sized particle than 100 nm ones. The 20μm particles is quite suitable when combining with 100nm particles. But when 300nm particles are applied, 1μm particles are better.

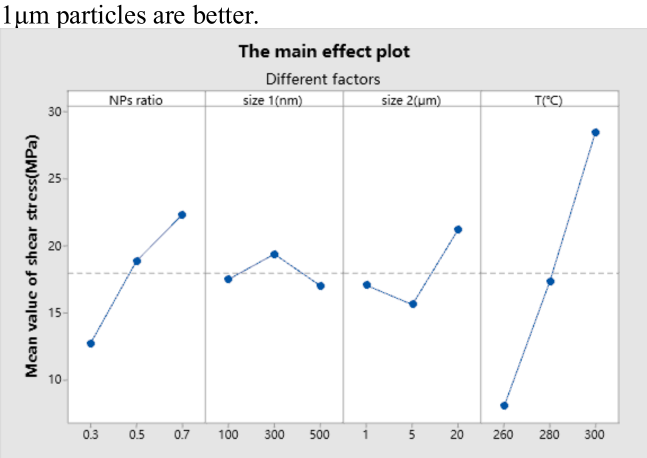

Fig. 8. Main effect factors diagram by using Taguchi method

The fracture surfaces are observed then by optical microscope. From the Figure 9 below, it can be seen that the samples with low shear stress (Figure 7a, b, e, f, g, i) show either the smooth fracture surface of copper substrate, or the complete upper surface of the entire copper sintering layer, which indicates the weak joint formation between copper sintering layer and the other two plate. Whereas the ones with high bonding stress (Figure 7c,d and h) shows incomplete sintering layer, which refers to the crack propagation into the sintering layer during the shear test and thus indicates a cohesive mode.

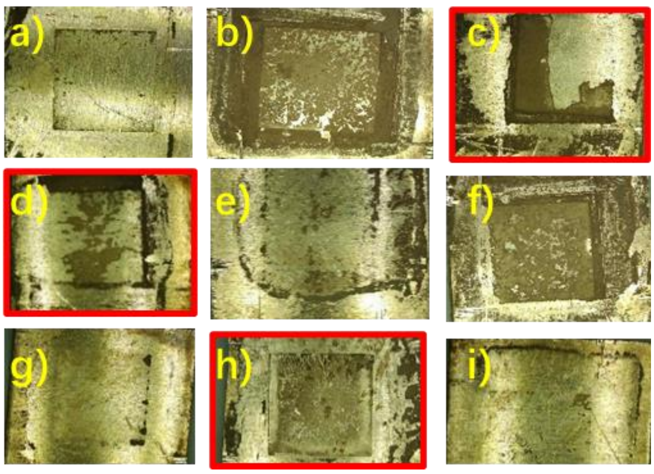

Fig. 9. Fracture surface photos obtained by OM.

To further study the ratio effect on porosity, the cross-section is observed by SEM for the sample 1, 2 and 3 to represent the samples with relatively low, medium and high stress. Sample 1 (Figure 10a) shows lots of un-sintered copper particles and huge pores and that might be the reason for the low shear stress. Perhaps the low sintering temperature cannot provide enough driving force for the particle mass transportation and therefore no obvious necking formation can be observed. In Figure 10b and 10c, more dense structures with obvious necking formation can be found and that is thought to be because the higher sintering temperature and reasonable mixing ratio. The best shear results is from sample 8 with 70wt.% 300 nm and 30wt.% 1μm sintered at 300℃, the porosity is around 11% by calculation.

C. *Cross-section Analysis and Porosity Measurement*

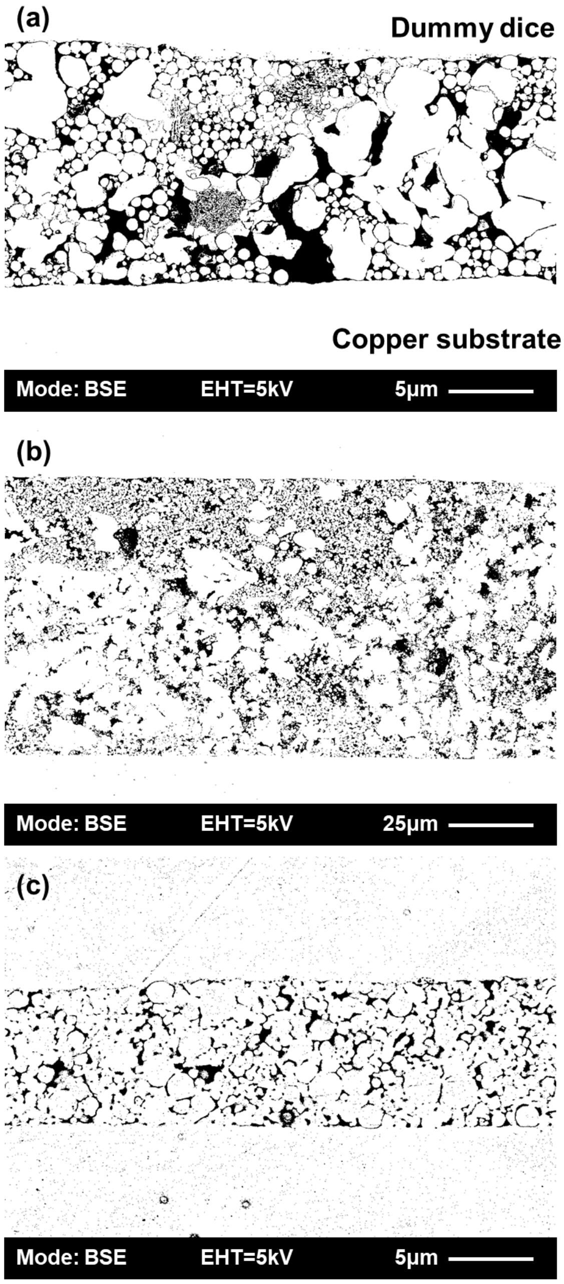

Fig. 10. SEM photos for the cross-section of a)sample 1,b)sample 2 and c)sample 3.

D. *Thermal conductivity and electrical resistivity*

Thermal conductivity and electrical resistivity are also measured for sample 8. The thermal diffusion coefficient and density of sample 8 are measured as 109.78 mm^2/s and

$5.54 g/cm^3$ respectively. It is reported that, the specific heat capacity is around 386 J/(kg*K). Therefore, the thermal conductivity is around 227.8 W/m*K calculated by using the following equation:

$$\lambda = \alpha \cdot \rho \cdot c \qquad (1)$$

where α is thermal diffusion coefficient, ρ is density and c indicates the specific heat capacity. Such value is quite high enough to transfer the heat from the dice to the heat sink.Moreover, by conducting four-point probe method, the electrical resistivity is measured as 6.0 uΩ•cm which is only 4 times higher than that of the bulk copper.

IV. Conclusion

In this study, design of experiment is conducted by using Taguchi method. The nano-/micro- particle ratio as well as sintering temperature effect on sintering properties are studied. The results show that the most pronounced factors are sintering temperature and nano-micro- ratio. The best NPs and MPs combination is 300 nm with 1 um mixing (1:1) sintered at 300°C, which shows over 35 MPa shear strength with. The fracture surface of such samples shows that the crack propagated in the sintering body and thus refers to a cohesive mode of failure. Furthermore, the cross-section inspection reveals dense bonding and clearly sintering necking. 227.8 W/m*K thermal conductivity and 6.0 uΩ•cm electrical resistivity are measured for the sample, which indicates the great potential for the packaging application in high power situation.

Acknowledgment

This work was supported by the Key-Area Research, Development Program of Guang Dong Province (2019B010131001) and the National Natural Science Foundation of China (No. 51706029).

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