Development Status of Sintering of Silver Particles of Different Scales

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Abstract. Power devices developed based on emerging wide bandgap semiconductors have higher requirements for packaging materials, which need to be able to work in more demanding environments. Silver particle sintered materials could be sintered at lower temperatures, work at higher temperatures, and have excellent electrical and mechanical properties, meeting the requirements of new power devices. This article conducts a thorough analysis of the preparation of raw materials, sintering methods, and product properties for sintering silver particles of different sizes through a search of relevant literature. Combined with the current market requirements for packaging materials, the advantages, current problems, and future development trends of sintering silver particles at the nanometer, micrometer, and micro nano composite levels are explored, providing reference for further research and application of silver particle sintering.

Keywords: Silver sintering; Die-attachment; review.

1. Introduction

With the rapid development of electronic information technology, semiconductor devices are constantly moving towards high power, high integration, and miniaturization. The working energy density is also higher, which puts higher demands on the heat dissipation performance and reliability of semiconductor devices. Semiconductor power devices generally have characteristics such as high breakdown voltage, high saturation carrier mobility, high thermal stability, high thermal conductivity, and high-temperature service environments. In the power module of new energy vehicles, the working environment of power devices is more stringent, the load current density is higher, and they need to serve in harsh environments for a long time while maintaining stable performance. Emerging third-generation semiconductor materials have advantages such as high breakdown voltage, high junction temperature, high switching frequency, and low resistance, and are considered ideal alternative materials [1,2]. But they also generate more heat during service than traditional silicon-based chips, and the highest operating junction temperature of SiC based high-power chips currently available on the market can reach over 300 °C. Therefore, there are higher requirements for packaging materials, such as low-temperature connection, high-temperature service, excellent thermal fatigue resistance, high electrical and thermal conductivity, and moderate cost.

The widely used die-attach materials in the current market can only meet the requirements of low-temperature connection and cannot serve at high temperatures. Common die-attach materials such as conductive adhesives, tin based eutectic solder, and gold-based solder alloys generally have melting points below 300 °C. They are prone to melting at high temperatures above 300 °C, and the melting of solder inevitably poses a risk of device connection disorder and pad detachment. In addition, some researchers have attempted to develop Bi based and Zn based brazing materials, but these two types of brazing materials have poor performance and unavoidable defects, making it difficult to promote their use. Therefore, it is necessary to study new packaging materials.

Due to size effects, the melting point of nanomaterials significantly decreases with decreasing particle size. Their sintering temperature may be much lower than the melting point temperature of the metal. The main reason for this phenomenon is the release of surface energy during sintering. The sintered material has high reliability at high temperatures and has research value. Silver and copper have excellent electrical and thermal conductivity, but copper has poor oxidation resistance, which imposes strict requirements on the preparation, storage, and deoxygenation of particles during

sintering. Once copper is oxidized, its sintering performance will sharply decrease. Although silver is more expensive than copper, it has excellent antioxidant properties and a higher atomic migration rate. Meanwhile, its strength (tensile strength 125MPa) and ductility are excellent [3]. Silver nanoparticles can achieve low-temperature sintering in the atmosphere and are a promising packaging material.

Lea [4] first prepared a water-soluble sol containing stable silver nanoparticles using chemical reduction method for development technology. Schwarzbaum et al. [5] attempted to use sintered silver for packaging large-area power devices. Due to the use of micrometer sized flake silver powder, a pressure of 40 MPa needs to be applied during the packaging process, which can easily cause damage to the chip. Nanoscale silver particles have high sintering activity due to their size effect, and can be sintered under low or even no pressure conditions to achieve good bonding. Bai et al. [6] first investigated the thermal, electrical, and mechanical properties of nano silver paste. They used 30 nm nano silver powder for ultrasonic stirring to prepare a nano silver paste, which was sintered at 280 °C for 10 minutes to form a sintered body. The thermal conductivity was measured to be 240 W/m·K, the electrical resistivity was 2.6×105 Ω· cm, the thermal expansion coefficient was 19 × 10-6 K-1, and the shear strength was as high as 38 MPa. In this experiment, the thermal and electrical properties of the nano silver paste were similar to those of bulk silver, and the mechanical properties were good.

During the sintering process, silver nanoparticles are connected to form a sintered body similar to a block. In theory, the melting point of the sintered body after sintering can reach up to 961 °C, with a thermal conductivity of over 400 W/m·K [7], and excellent mechanical and corrosion resistance properties. It is currently one of the best materials for semiconductor device packaging. The sintering performance of silver particles is related to their surface energy, which depends on their size. Therefore, it is necessary to study the influence of silver particle size on performance.

This article discusses the current implementation schemes for sintering silver particles of different sizes at the nanometer to micrometer scale, analyzes the characteristics of various methods, compares their advantages and disadvantages, summarizes them, and proposes future research directions and prospects for silver particles in the field of packaging.

2. Case description

2.1. Nano-Sized Ag Sintering

Nanoscale silver sintering is the process of manufacturing and sintering nanosilver paste using nanoscale silver particles (with a diameter of 1-100nm). Its surface area to volume ratio allows it to sinter at lower temperatures (below 200 ℃) and pressures (below 5MPa). The product of nanosilver sintering usually has a porous structure, and with the increase of energy input, the porosity gradually decreases. When the energy input is constant, the sintering strength gradually decreases with the increase of particle size. However, copper has similar thermal and electrical conductivity to silver, and the price of nano silver is higher than that of nano copper, which limits the large-scale application of nano silver materials in power device manufacturing.

2.2. Micro-Sized Ag Sintering

Micro-silver sintering is the sintering process using flake-like silver materials at the micrometer scale (typically between 1-10 μm). The specific surface area of flake-like silver tissue is higher than that of spheres. Under the same volume, the sintering of silver flakes has a higher driving force, and compared with nanoparticles, silver flakes have a larger contact area, which can provide more diffusion channels. Interconnection can be achieved without excessive sintering pressure (0-10 MPa) and temperature (250-300 °C). During the interconnection process, the edge of the silver flake will form necking, and a large number of nanoparticles will be formed in the necking area. A large number of amorphous structures can be observed around the nanoparticles. These ultra-small nanoparticles

and amorphous structures can promote the interconnection of the silver flake due to their high surface energy, making the micro silver flake have excellent sintering performance.

2.3. Bimodal (Micro-Nano Hybrid) Ag Sintering

Composite silver particle sintering is the process of sintering using a mixture of micrometer and nanometer sized silver particles. Its sintering temperature is relatively low (< 250 ℃), and most of them use pressureless sintering or apply pressure within 3 MPa for assistance. Compared with sintering single sized silver particles, composite silver sintering reduces the need for solvents and also has higher shear strength (30-35 MPa). However, the preparation of composite silver paste involves the ratio and interaction of particles of different sizes, which may affect its uniformity and consistency. The research on composite silver paste also involves particle interactions, sintering process optimization, and other aspects.

3. Analysis and challenge

3.1. Nano-Sized Ag Sintering for die-attachment

There are various methods for sintering nano silver materials. Here, the author will describe a method for sintering nano silver materials. The average particle size of silver powder used in the experiment is about 50 nm, with a distribution concentrated between 30 nm and 80 nm. Firstly, modify the nano silver paste with organic amines. The modified Ag nano powder was mixed with organic solvent to form a uniform 85 wt.% nano Ag slurry by high-speed stirring. Silver paste uses a mixture of ethylene glycol, turpentine alcohol, and polyethylene glycol 200 as solvents, with an evaporation temperature as low as 250 °C. Modified silver nanoparticles are used to prepare the paste, and for comparison, the original silver nanoparticles are also used to prepare the paste. In this experiment, silver paste needs to be coated on the surface of the lower DBC substrate before sintering, and then the upper substrate is placed on top of the silver paste to form a three-layer adhesive structure. During the sintering process, the sample was heated to 250 °C at a stable rate of 16 °C/min. Subsequently, each type of silver paste was divided into three groups and incubated for different times (10 minutes, 30 minutes, 60 minutes), followed by natural cooling. [8]. The process was shown in Fig.1.

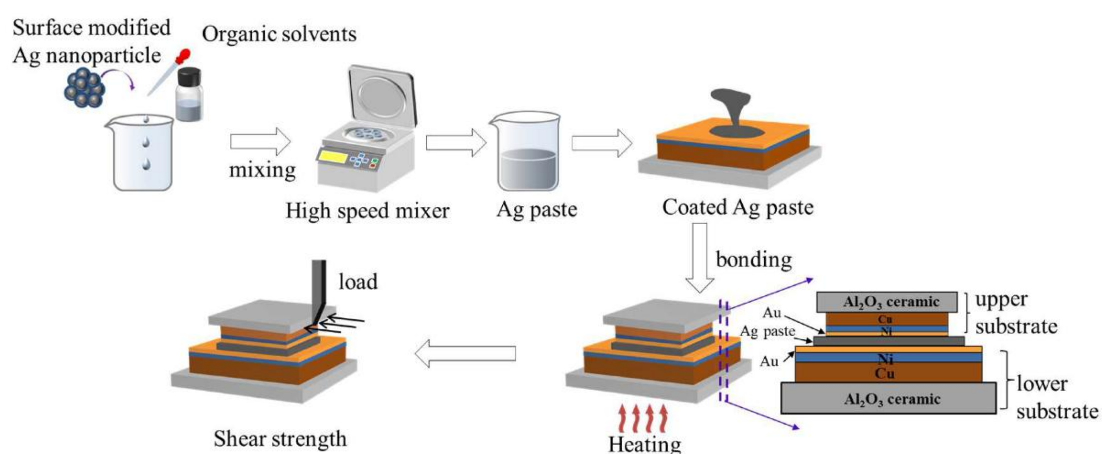

Fig. 1 Process diagram of pressureless sintering of nano silver paste [8]

This experiment indicates that the electrical resistivity of sintered products is related to the grain size and sintering density after sintering. Within a certain range, the smaller the grain size and the lower the density, the higher the electrical resistivity of the sintered product. After being kept at 250 °C for 30 minutes, one of the modified silver joints, named Ag-NOA joint, had a resistivity of 7.31 μΩ·cm, which was better than the original silver particle joint. After increasing the holding time to 60 minutes, the resistivity slightly decreased (5.3 μΩ·cm). The shear strength of sintered samples

is also related to the microstructure, porosity, and organic residues of sintered silver. After being held at 250 °C for 30 minutes, the adhesive strength of the Ag-NOA joint reached 61.8 MPa. The cross-section shows obvious plastic deformation characteristics. At 250 °C for 60 minutes, the shear strength slightly increased (69.3 MPa). [8]. This indicates that nano silver has excellent performance and is suitable for making sintered joints, among which modified nano silver powder has better sintering performance than unmodified one.

The sintering performance of nano silver is excellent, but there are still issues that need to be addressed, such as the potential loss risk of chips during sintering, the reliability of nano silver sintering materials, and the overall performance and reliability improvement of power devices [9].

3.2. Micro-Sized Ag Sintering for die-attachment

Micro silver sintering mostly adopts pressure sintering, but the methods used by different experimenters vary. Zehao Chen et al. [10] screen printed self-made micro silver paste onto a silver-plated copper substrate using a 0.12 mm thick steel mesh. After screen printing, the silicon wafer is covered on the slurry to form a sandwich structure. Then sinter the sample at a rate of 26 °C/min. For comparison, the experimenter set multiple sets of sintering processes with different parameters. There are five preheating temperatures set, respectively 70 °C, 90 °C, 110 °C, 130 °C, and 150 °C. Direct sintering experiments without preheating were also conducted as a control group to determine the optimal preheating conditions for homemade slurry. Subsequently, the sintering temperatures were set to five groups of 200 °C, 225 °C, 250 °C, 275 °C, and 300 °C, with sintering holding times of 5, 10, 15, 30, 45, and 60 minutes, respectively, to determine the effects of sintering temperature and sintering holding time. The microstructure of sintered silver flakes is shown in Fig. 2.

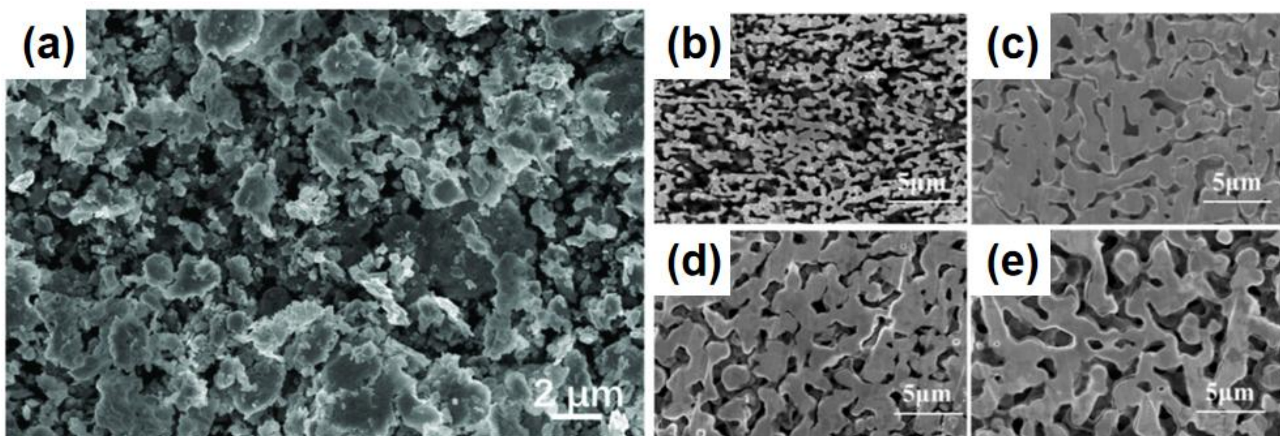

Fig. 2 The microstructure of the original silver sheet(a) and the structures obtained by sintering at 225 °C(b), 250 °C(c), 275 °C(d), and 300 °C(e), respectively. [10]

The optimal shear strength data obtained from the experiment for sintered micro silver paste is 42.78 MPa preheating temperature. This sample was preheated at a heating rate of 26 °C/min for 5 minutes at 130 °C, maintained at 10 minutes, and then sintered at 300 °C for 30 minutes. [10]. This reflects that micro silver sintering can produce materials with excellent mechanical properties at lower temperatures and in a shorter time. In addition, micro silver sintered materials have lower electrical resistivity and are suitable for connecting and packaging power devices.

For micro silver paste, the contact between particles must be considered during the sintering process, as its particle size is larger than that of nano silver paste, resulting in lower surface energy. Therefore, attention should be paid to the degree of sintering during the densification stage [10]. The solvent used in micro silver paste can also affect sintering, and factors such as wetting, viscosity, and volatility could affect the electrical resistivity and shear strength of sintered silver, which requires further research.

3.3. Bimodal (Micro-Nano Hybrid) Ag Sintering for die-attachment

For micro-nano hybrid silver slurries, most experiments currently use commercial silver particles for mechanical mixing preparation [11], such as surface modification of nano silver particles and mixing them with micro silver particles in different mass ratios. Mix ethylene glycol, turpentine alcohol, triethylene glycol monomethyl ether, and decanoic acid in a mass ratio of 3:3:3:1 to prepare an organic solvent. Prepare silver paste by mixing hybrid silver powder with organic solvent in a certain proportion. The mixing process is carried out by high-speed stirring with a mixer to obtain composite silver paste, which is then sintered. Usually, it is necessary to prepare silver pastes with different mass ratios for experiments to evaluate the electrical properties of the mixed silver paste, as shown in Fig. 3.

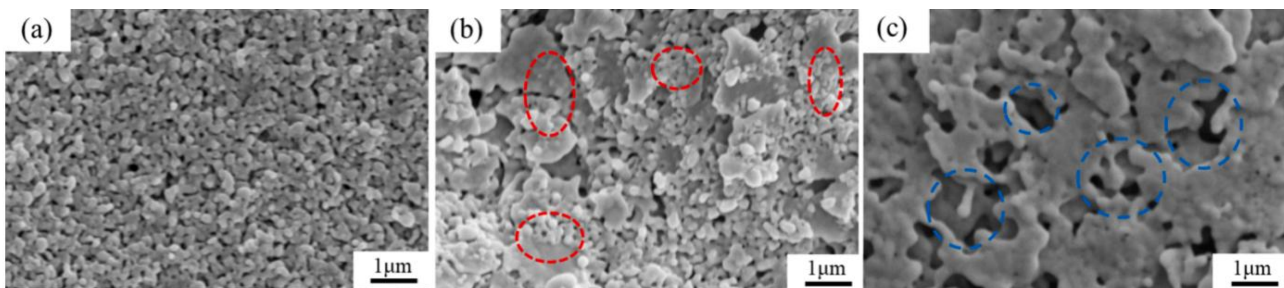

Fig. 3 Microstructure of different silver paste sintered films after 60 minutes at 250 ° C: (a) Micron silver (MS): Nano silver (NS)=0:1 (b) MS: NS=1:1 (c) MS: NS=1:0[11]

As shown in Fig. 4. The sintered film resistivity of micro nano hybrid silver paste (MS: NS=1:1) prepared by sintering at 250 °C for 60 minutes is 5.7 μΩ·cm, similar to that of nano silver paste (5.3μ Ω·cm), but the joint shear strength (47.32 MPa) is significantly lower than that of nano silver paste (65.65 MPa). Porosity is positively correlated with shear strength. A longer insulation time facilitates the complete sintering and diffusion of silver particles, thereby increasing the shear strength of the bonded joint and reducing the film resistivity at the same sintering temperature. The experiment showed that after being placed at 250 ° C for 500 hours, the shear strength of the nano silver paste joint decreased to about half of the initial value (33.38 MPa), while under the same conditions, the shear strength of the micro nano hybrid silver paste joint (45.78 MPa) approached the initial level, proving its stable mechanical reliability [11].

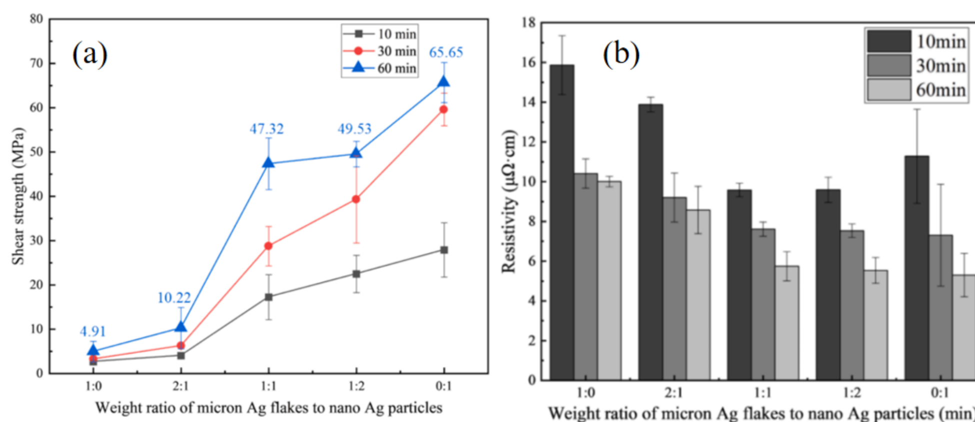

Fig. 4 Shear strength of joints sintered with silver paste of different mixing ratios (a) and electrical resistivity of films made with silver paste of different mixing ratios at different durations (b)[11]

Micro nano composite silver materials have certain development prospects, but research is needed to determine the optimal mixing ratio. In addition, the cost of silver is also one of the issues that the commercial application of this material needs to face.

4. Summary and Suggestions

Table 1. Comparation of various silver sinter paste

Type	advantages	disadvantages
Nano Ag	- low resistivity - high shear strength - Low sinter parameter	- low reliability - unstable sintering quality
Micro Ag	- stable mechanical properties - high stability and reliability - relatively low cost	- extra pressure assistance - significant solvent impact
Micro-nano composite Ag	- low sintering temperature - high reliability - good mechanical/electrical properties	- poor uniformity - difficult parameter control

The advantages and disadvantages of different silver sinter paste were shown in Table. 1. Nano sintered silver materials have the advantages of low electrical resistivity and high shear strength, making them suitable for packaging power devices. At the same time, the sintering of nano silver materials adopts a low-temperature and pressureless sintering environment, which makes the sintering conditions easier to achieve. Compared with other packaging materials, this is a market competitive advantage for nano silver sintered materials. However, due to the small size of nano silver particles, there are many pores in the sintered material, forming many defects. This makes the material prone to cracking during use, making it difficult for the sintered joint to be used stably for a long time. If it is to be widely applied, this problem must be solved. In addition, the properties of nanosilver sintered materials are unstable, and factors such as porosity in the material have a significant impact on its properties. Therefore, more in-depth research is needed to understand the influence of the structure of nanosilver materials on their properties, and to study appropriate sintering processes and parameters.

Compared with nano silver sintered materials, micro silver sintered materials have more stable and controllable mechanical properties. The stability and reliability of the material are relatively high, and it is not easy to crack. Compared with other packaging materials, micron sized sintered silver materials save expensive high-temperature alloy materials and reduce the overall cost of the device. The disadvantage of micro sintered silver materials is their poor adhesion, requiring additional pressure to assist sintering. However, this material is mainly used in power devices, and many electronic components in power devices are easily damaged under pressure, which is an unavoidable challenge in the application of micro sintered silver materials. The solvents used in micro silver paste also have a certain impact on the final sintered product, which may increase porosity, reduce the strength of the material, and its volatility and wettability may also affect the speed of the sintering process of the material. This requires further research to explore the influencing factors and find suitable solvents.

Micro-nano composite silver sintering combines the advantages of nano silver sintering and micro silver sintering. Micro-nano composite sintered silver materials can be sintered at low temperatures, and pressure assistance is not necessary. This material has high reliability and can be used stably for a long time. It also has excellent electrical and mechanical properties, making it highly promising in electronic packaging. However, in addition to these advantages, there have also been some issues with the sintering of micro nano composite silver. Micro nano composite sintered silver materials often exhibit segregation during the sintering process due to the presence of nano- and micro- sized silver particles in the composite silver paste, resulting in uneven final materials. In addition, due to the use of two or more silver particles of different sizes in the sintering of micro nano composite silver, the parameters applicable to the sintering of silver particles of different sizes are different, making it difficult to control the parameters of composite sintering. Even small changes can have a

significant impact on the results, which is one of the biggest problems faced by the promotion and use of this material.

Due to the immature development of silver particle sintering research direction, further research is needed on the influencing factors of sintering process and sintering product properties. From the current market environment, silver particle sintering has great prospects in the packaging of future power devices and is also a major research trend at present. In recent years, many researchers have devoted themselves to this direction of research. After solving the main problems, the promotion and application of silver particle sintering is an inevitable development result.

5. Conclusion

This article analyzes the common silver particle sintering methods and the properties of sintered materials from different scales. Among them, the sintering of nanoscale silver particles is usually carried out using low-temperature pressureless sintering, which is simple and easy to implement. The electrical and mechanical properties of the sintered products are excellent, matching the requirements of the packaging materials needed for power devices. However, the properties of the sintered products are difficult to control, and they are also prone to cracking and lack reliability. In summary, nanosilver sintering has excellent prospects, but it is currently difficult to popularize.The sintering of micrometer sized silver particles usually requires additional pressure to assist in promoting particle bonding. Micro silver sintered materials are stable and reliable, and their performance can also meet the requirements of packaging materials, but additional pressure can easily damage electronic components. The solvent used for micro silver paste can also affect the sintered material. From this, it can be seen that micro silver sintering has the potential for wide applications, but it is not yet mature and faces many problems.Micro nano composite silver sintering can be carried out at low temperatures, and the sintered material has high reliability and excellent electrical and mechanical properties. However, due to the use of silver particles of different sizes, the sintered material is uneven and the sintering parameters are difficult to accurately control. Micro nano composite silver sintering can obtain materials with excellent properties, but further research is needed to adjust the parameter settings.

In summary, silver particle sintering can be achieved at lower temperatures, and the resulting material has excellent electrical and mechanical properties, which can work at higher temperatures. It is feasible to use silver sintered materials as packaging materials in power devices, but the current related technologies and processes are not mature enough and still face many problems. The study of silver sintered particle size is meaningful, as it can promote the development of packaging materials and drive the development of power devices.

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