Preparation and sintering characteristics of nano-silver wrapped tin paste

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Research article

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Abstract

Nanosilver paste, an interconnect solder is a common choice in the electronics packaging industry, however higher sintering temperatures and lower sintering strength limit its application. At present, core-shell nano-slurry has been studied and applied to chip interconnection. Based on the mechanism of heterogeneous flocculation, we have developed a new nano-silver wrapped tin paste (Sn@Ag paste), and according to the decomposition temperature of the organic dispersant in the slurry, A corresponding sintering process with a maximum temperature of 300 ° C was developed. The Sn@Ag core-shell structure makes Sn have good dispersibility and oxidation resistance, and the sintered product of the slurry is a mixture of a solid solution of Ag and an Ag₃Sn phase. Among them, the hard and brittle phase Ag₃Sn acts as a dispersion strengthening effect in the Ag matrix phase, and the solid solution of Ag acts as a replacement solid solution strengthening. With the increase of doping Sn content, the sintering strength is significantly improved. When the Sn content is 5%, the joint shear strength reaches the highest value of 50Mpa, which is higher than the pure nano silver paste by 10 Mpa. This new nano-silver wrapped tin paste technology has the characteristics of low temperature sintering and high temperature service, so it is expected to be widely used in semiconductor power devices.

1. Introduction

At present, high-temperature power device chip bonding often uses nano silver paste sintering method, and the joint formed by sintering of nano silver paste has good electrical and thermal conductivity^[1], but there are also the following problems:

- (1) The sintering temperature of the nano silver paste is in the range of 250 ° C to 350 ° C. This high heating temperature is not compatible with other packaging materials^[2].
- (2) The intermetallic compound is not formed after the nano silver paste is sintered, and the joint shear strength is low.

Therefore, it is imperative to improve the sintering performance of nano silver paste. There are two general methods. One method is to use a short-chain organic surfactant as a dispersing agent in the preparation of the nano-silver. Generally, such organic matter has a relatively low thermal decomposition temperature and can lower the sintering temperature. However, this makes the dispersibility of the nano-silver worse, increasing the risk of agglomeration of the nanoparticles; the other method is to reduce the particle size of the nano-silver particles, and the melting point of the nanoparticles decreases with the decrease of the particle size, thereby lowering the sintering temperature. However, this makes the production process complicated and costly^[3], which is not conducive to large-scale industrial applications. Adding low-melting alloy elements is a good way to improve the sintering performance of nano-silver solder paste. In the alloy, the melting points of tin, indium and gallium are relatively low, but the cost of indium and gallium is relatively high. We choose nano tin as the alloying element. Considering

that tin is easily oxidized, and the core-shell material can prevent the oxidation of tin, and at the same time ensure the uniform distribution of tin, a core-shell composite material is used.

The preparation method of the metal core-shell structure is generally classified into a solid phase method, a gas phase method, and a liquid phase reduction method. Among them, the solid phase method (mainly ball milling) is difficult to avoid the oxidation of the surface of the nanoparticles, and it will inevitably introduce impure substances during the preparation of the material; the gas phase reaction equipment requires more precision; The liquid phase reduction method is limited by the inherent properties of the metal, resulting in limited application conditions^[4]. Heterogeneous flocculation method refers to the method of preparing a core-shell material by attracting and agglomerating particles with different natures of charge. The method has the advantages of mild reaction conditions and less equipment input, there are many applications in improving the performance of ceramic materials, and there are few applications on electronic package interconnection materials. Therefore, we chose heterogeneous flocculation to prepare Sn@Ag core-shell nanoparticles, which is a new attempt. The key is to choose a suitable surfactant, adjust the moderate pH of the solution, and determine the size of the corresponding core-shell particles.

The sintering process of nano-silver package tin paste is divided into four stages of dissolution, diffusion, solidification and reaction. As the sintering temperature increases, nano-tin diffuses into the nano-silver. When the Sn melts, the diffusion speed will increase. The liquid phase Sn will contact the solid phase Ag, and the liquid will rise or penetrate along the gap, thus rapidly uniform diffusion in the body and leads to a lattice change of the matrix; after the solidification process, the reaction forms an intermetallic compound IMC phase. Finally, an Ag-based replacement solid solution and a uniformly distributed Ag₃Sn are obtained. The Ag-based replacement solid solution will act as a solid solution strengthening, and Ag₃Sn acts as a second phase to diffuse and strengthen the shear strength of the joint ^[5, 6]. Therefore, we studied the preparation process of nano-silver-coated tin paste, and analyzed its sintering properties and sintering mechanism.

2. Experiment

2.1 Preparation of nano silver package tin paste

In order to apply the hetero-flocculation method to prepare Sn@Ag core-shell material. Firstly, nano-silver and tin are adsorbed by anionic and cationic surfactants respectively. The isoelectric point of nano-silver is higher, the anionic surfactant can be strongly adsorbed on the nano-silver particles, and the isoelectric point of nano-tin is lower. Cationic surfactants have a large adsorption capacity on nano tin particles; secondly, it should be noted that the "nuclear layer" particles are usually much larger than the size of the "shell" particles, which is beneficial to the completion of the coating process, so determine the nano silver particle diameter is 20 nm, the nano tin particle diameter is 100 nm; then when the total length of the hydrophobic chain of the surfactant (the total number of carbon atoms) is constant, the more

asymmetric the length of the two hydrophobic chains, the better the solubility of the mixed system [7], so, Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) are selected as the compounding surfactant. Taking ethanol as a solvent, consider comprehensively to determine the pH of the solution is 7.

The nano silver paste adsorbed by SDS was slowly added to the nano tin slurry adsorbed by CTAB, and the two attracted each other by the action of electrostatic attraction. As the adsorption amount increased, the surface charge changed from a positive value to zero. The electrostatic repulsion between the colloidal particles is reduced, the thickness of the electric double layer is reduced, and finally the bridging effect occurs and flocculation, thereby forming a slurry of the nano-silver-coated tin core-shell structure. Further adding nano silver paste, the adsorption of nano-silver with negative charge increases, and the charge of the particles increases from zero to a higher negative value, so that the colloidal particles are redispersed, as shown in Fig. 1. Through previous experiments, it was determined that the tin content was 5%, so we prepared a Sn@Ag slurry with Ag and Sn mass ratio of 19:1.

The boiling points of sodium lauryl sulfate and cetyltrimethylammonium bromide were 250 ° C and 300 ° C, respectively, and the maximum sintering temperature was determined to be 300 ° C in order to sufficiently decompose during the sintering process.

2.2 Development of sintering process

In order to improve the sintering effect of the Sn@Ag paste, the substrate and the chip were replaced with a copper plate to produce a sandwich structure. As shown in Fig. 2, the upper surface is a copper plate with a diameter of $\varnothing 2.8$ mm, and the bottom is a copper substrate with an area of 12×12 mm². The upper and lower copper plates are bonded together by Sn@Ag paste.

Although the Sn@Ag slurry sintering process can also be divided into three stages (Fig. 2 Process A), it is different from the pure nano silver paste sintering process [3] (Fig. 2 Process B). The first step was maintained at 80 ° C for 10 minutes, exceeding the solvolysis temperature to allow the ethanol to fully decompose. The second step was heated to a temperature of 250 ° C for 10 minutes to reach the decomposition temperature of the surfactant, so that sodium lauryl sulfate was sufficiently decomposed. The last step is heated to 300 ° C, which reaches the boiling point of cetyltrimethylammonium bromide, so we chose 300 ° C as the highest sintering temperature, followed by a 50 minute isothermal process, which is to ensure CTAB Completely decomposes and allows the tin and silver to fully diffuse and react. The heating rate of the sintering process was 10 ° C / min. Sintering is carried out in air rather than in a vacuum. The final cooling process is a slow cooling in air.

3. Results And Discussion

3.1 Sintering strength of Sn@Ag paste

For comparison with Sn@Ag paste, we first performed a sintering experiment on pure nano-silver and tested the shear strength of the joint using a shear tester (DAGE 4000), as shown in Fig. 3. Under the sintering temperature of 300 °C and the sintering pressure of 6 MPa, the shear strength of the pure nano-silver joint was 40 Mpa, and then the shear strength of the sintered joint of Sn@Ag slurry with 5% tin content was tested, Joint shear strength at the same temperature and pressure reached 50 MPa, which is 10 Mpa higher than that of pure nano silver paste joint.

3.2. Form of Sn@Ag paste sintering

Figure 4 SEM image of Sn@Ag paste and pure nano silver paste

Figure 5 (a) is a 10,000x SEM image of the Sn@Ag slurry joint. In comparison with the dark sintered morphology of pure nano-silver, it can be found that the sintered morphology of the Sn@Ag paste is light and dark, in which the light-colored regions are sintered to be denser. The composition analysis of the denser region A is shown in Fig. 5(b) on the right. It shows that the content of the Ag atom is three times that of the Sn atom, which is the same as the atomic ratio of the compound Ag_3Sn . Therefore, it can be inferred that the final product of the sintered Sn@Ag paste is composed of Ag and Ag_3Sn , and this mixture promotes the sintering performance of the Sn@Ag paste.

3.3 Strengthening mechanism

Through experiments and references, it is concluded that the improvement of the shear strength of sintered Sn@Ag pulp may be due to the following two mechanisms: (1) dispersion strengthening; (2) displacement solid solution strengthening.

3.3.1 Dispersion strengthening

The formation of Ag_3Sn is produced by a series of processes such as melting, diffusion, reaction, and solidification. The resulting Ag_3Sn grain size is on the order of nanometers and is evenly distributed throughout the matrix, as shown in Fig. 7. The morphology and distribution of Ag_3Sn grains conform to the characteristics of the dispersed strengthening phase, and Ag_3Sn has hard and brittle properties. Therefore, we can infer that the Ag_3Sn grains act as an ultrafine second phase insoluble in the matrix in the Sn@Ag paste [9], which acts as a dispersion strengthening. Figure 8 is a conceptual second phase dispersion strengthening model which, as shown, prevents the growth of the grains and limits the movement of dislocations. When the joint is subjected to shearing force, Ag_3Sn acts to prevent shearing.

Figure 6 XRD pattern of sintered Sn@Ag paste and pure nano silver paste

3.3.2 Replacement solid solution strengthening

According to the phase diagram of the Ag-Sn binary alloy, the equilibrium phase formed after sintering the Sn@Ag slurry has a solid solution of Ag and the intermetallic compound IMC, as shown in Fig. 9 shows the SEM image of the Sn@Ag slurry sintered layer. Figure. 9(b) demonstrated, Ag is uniformly distributed throughout the sintered layer in the SEM image. Figure. 9(c) demonstrated, Sn is uniformly distributed over the lattice of the Ag matrix, replacing the position of the silver atoms. Therefore, Sn is dissolved in Ag to form an Ag-Sn replacement solid solution.

For the Ag-Sn displacement solid solution, the Sn atom acts as a solute atom, replacing the lattice position of Ag, resulting in lattice distortion of Ag, which pinches dislocations and makes slippage difficult to continue. These increase the resistance to dislocation movement, resist the shear force, strengthen the strength of the Ag matrix, and thus replace the solid solution strengthening. The radius of tin and silver ions is similar. After replacement, the strength of the solder can be increased gently, and the toughness and plasticity are not affected [10].

4. Conclusion

(1) In order to reduce the sintering temperature and increase the sintering strength of the nano-silver, we have developed a nano-silver-coated tin paste. When the Sn content is 5% and the sintering temperature is 300 °C, the joint performance is the best. This Sn@Ag paste also improves the oxidation resistance and the dispersibility of tin in the silver matrix.

(2) The sintering strength of Sn@Ag slurry increased significantly with the increase of Sn content. When the Sn content reached 5%, the shear strength of the joint was the highest, 50 MPa, which was 10 Mpa higher than that of the pure nano-silver sintered joint. However, when the content of nano tin is less than or more than 5%, the shear strength of the joint becomes small.

(3) Analysis of the sintered joint of nano-silver solder paste shows that the shear strength is improved because the equilibrium phase produced after sintering is Ag-Sn replacement solid solution and intermetallic compound Ag_3Sn , which respectively act as replacement solid solution strengthening and the role of diffusion strengthening.

Therefore, the newly developed nano-silver-coated tin paste technology not only reduces the sintering temperature, but also improves the sintering strength, and meets the characteristics of low-temperature sintering and high-temperature service, so it has the potential to be widely used in power semiconductor devices.

Declarations

Availability of data and materials

All datas and materials are availability.

Competing interests

All authors declare no competing financial interests.

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Authors' contributions

All authors approved the final version.

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Figures

Figure 1

Preparation process of Sn@Ag core-shell nanomaterials

Figure 2

Nano-silver tin paste (TDSP) sintering process

Figure 3

Shear Tester Dage 4000

Figure 4

SEM image of Sn@Ag paste and pure nano silver paste

Figure 5

Microstructure and composition analysis of Sn@Ag paste (a) 10000 times SEM image of Sn@Ag paste; (b) Partial EDS analysis

Figure 6

XRD pattern of sintered Sn@Ag paste and pure nano silver paste

Figure 7

SEM image of Sn@Ag sintered layer

Figure 8

Diffusion enhancement model

Figure 9

SEM image of Sn@Ag slurry sintered layer