Compressive properties and microstructure evolution of sintered nano-silver

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Abstract. In this work, the compressive properties of sintered nano-silver applied to the third generation semiconductor at room temperature are tested at a loading rate of $10^{-2} \text{s}^{-1}$. The compressive stress-strain curve shows obvious elastic and plastic stage, and with the failure of the pore wall and sintering neck, the damage accumulates gradually until failure. The microstructure is analyzed statistically by scanning electron microscope. A finite element model for porous structure is developed by matching scanning electron microscope analysis. The elastic modulus of pore wall and sintering neck is obtained by combining the macro experimental data with the Ashby model. The local failure process of sintered nano-silver is simulated numerically. It is noted that the failure path is determined by large pore and pore spacing.

1. Introduction

The commonly used lead-free solder (SnAgCu) can hardly match the high temperature working environment of the third generation semiconductor [1, 2]. It is urgent to find alternative packaging materials suitable for high operating temperature. After sintering, solidified nano-silver can withstand temperature up to 961 °C [3], and it has excellent electrical and thermal conductivity. A small amount of organic matter in the nano-silver paste can prevent the aggregation of silver nanoparticles during storage. During the sintering process, the volatilization of organic matter leads to the formation of a large number of pores in the solidified nano-silver, which causes discrete of mechanical properties of structural parts welded by nano-silver paste [4]. Therefore, the macro [3-7] and micro mechanical properties [8-10] of sintered nano-silver have attracted wide research interest in semiconductor industry.

Due to the mismatch of thermal expansion coefficient between the chip and substrate, the sintered nano-silver suffers from compressive stress in the actual working environment. At present, the researches of sintered nano-silver of compressive experiments mainly based on nanoindentation technology [8, 9, 11] and using micro-compression specimen [12]. However, the macro and micro mechanical properties of sintered nano-silver are not completely consistent due to existence of internal pores. There are few reports on the experiments and numerical simulations of the mechanical properties of sintered nano-silver under macro pressure. In the current study, rectangular specimens were prepared for compressive experiments at room temperature, and the microstructure of sintered nano-silver was analyzed by scanning electron microscope (SEM). The simulation of local failure of sintered nano-silver was realized by finite element analysis of porous structure using ABAQUS.
2. Experimental method and analysis
The sintered nano-silver adopted in this work is provided by INDIUM company, and the silver nanoparticles are irregular polygons before sintering, as shown in Figure 1 (a). According to statistical analysis, the particle size is approximately 359.26 nm [4]. The nano-silver paste was injected into the pouring tank to prepare the compressive specimen, and heated at 300 °C for 50 minutes by QUICK 870 heating table, and cooled to room temperature in the air environment. The size of compressive specimen is 3×3×4.5mm, as shown in Figure 1 (b).

![Figure 1 Morphology of nano-silver paste before and after sintering: (a) silver nanoparticles; (b) compressive specimen.](image)

During the sintering process, the silver nanoparticles (About 91% of silver content) in the nano-silver paste are stacked, and the adjacent silver nanoparticles are fused with each other to form the three-dimensional porous solid. The fusion of two adjacent particles forms a sintering neck, as shown in Figure 2 (a). Generally, a plurality of nanoparticles is interconnected to form a supporting structure (pore wall), which is similar to the block in the concrete structure, as shown in Figure 2 (b). Sintering neck and pore wall can conduct force and electricity. Most of the cured structures show ductile failure in the process of tension as observed by SEM. It is noted that the cross section for SEM scanning in Figure 2 was prepared through tension. Therefore, it shows that the curing degree is reasonable at this sintering temperature. In addition, a small amount of interface failure occurs, which is characterized by the smooth fracture surface, as shown in Figure 2 (b). Some of the silver nanoparticles inside the pores have become sphere under the effect of surface tension, as shown in Figure 2 (c). It should be noted that there also exist larger defects, which are not the focus of present study and will not be described in this work.

![Figure 2 Microstructure and Energy Dispersive Spectrometer (EDS) of sintered nano-silver: (a) sintering neck; (b) boundary of particles; (c) pores and unmelted particles; (d) element distribution.](image)
EDS analysis results of the local cross section is shown in Figure (d). It shows that the internal organic matter of nano-silver paste basically combusts completely after sintering at 300 °C for 50 minutes. Thus, the contents of carbon and oxygen are relatively low, as shown in Figure 2 (d). This also confirms that the selected sintering temperature can make the organic matter burn completely, and beneficial to the silver nanoparticles solidify to form an impregnable structure.

The Nano Measurer 1.2 was used to analyze the maximum pore diameter in Figure 2 (a). Here the maximum diameter is defined as the distance between the maximum distance on the edge of the pore. A total of 113 pores are counted, the largest diameter is 2.16 μm and the minimum diameter is 0.03 μm. The average diameter is 0.36 μm, and the porosity is 57.87% as calculated by Image J (Threshold = 114). It should be noted that the porosity in this work represents only meso porosity and does not include macropores.

3. Experimental results and numerical analysis

3.1. Experimental results

![Figure 3 Compressive experiment of sintered nano-silver: (a) stress-strain curve; (b) damage stage; (c) destruction stage](image)

The compressive experiments were conducted for three specimens at a loading rate of $1 \times 10^{-2}$s$^{-1}$ at room temperature. The average stress-strain curves of the three specimens are shown in Figure 3. There are obvious elastic and plastic segments in the deformation process, as shown in Figure 3 (a). In the plastic segment, the internal damage occurs due to the failure of sintering neck, and the fracture occurs after approaching the critical strain. In this work, the strength corresponding to 0.2% residual strain is taken as the yield strength, which is 44.06MPa, and the corresponding elastic modulus is 882.95MPa. The maximum strength is 49.07MPa, and the corresponding plastic strain is 0.037. The damage starts to sprout [13] because the sintering neck gradually begins to break as shown in Figure 3 (b), and the failure occurs when the plastic strain reaches the critical plastic strain (About 0.28), as shown in Figure 3 (c).

3.2. Qualitative analysis of failure by finite element method

The elastic modulus of the whole specimen is analyzed in this work, which includes the influence of defects. From the microscopic analysis, it can be observed that there are a lot of pores in the sintered nano-silver. Therefore, it is necessary to make the elastic modulus equivalent when establishing the finite element model.

The elastic modulus $E$ of porous materials can be obtained by determine porosity $P$ and Poisson's ratio $\nu_0$ [13]. Ashby et al. [14] proposed the elastic modulus of porous materials as:

$$E = cE_0(1 - P)^n$$

where $E_0$ is the elastic modulus of solid material; $n \approx 2$ [13]; $c$ can be obtained by [15]:

$$c \approx \frac{1}{2(1-\nu_0^2)}$$
Combined with the results of SEM, a code of random porous model was developed using Python, and the local microstructure of sintered nano-silver was analyzed by finite element model. The model size is consistent with Figure 4 (a), which is 4.5 (height) × 6 (width) μm. In this work, the pore is assumed to be a circle. The radius of pores is generated by random function:

\[ r_i = r_{\text{min}} + \text{random} \times (r_{\text{max}} - r_{\text{min}}) \]  

where \( r_i \) is the radius of the \( i \)th circle; \( r_{\text{min}} \) and \( r_{\text{max}} \) are the minimum and the maximum radius of the generated circle, respectively. In this work, \( r_{\text{min}} = 0.03 \mu m \) , \( r_{\text{min}} = 2.16 \mu m \), and the porosity is 57.87%.

Equation (4) is used to control that the \( i \)th and \( i+1 \)th circle do not intersect:

\[ D > r_i + r_{i+1} \]  

The elastic modulus of the sintering neck with removing porosity is 7558.2MPa from Equation (1) and (2). In this work, the failure mode of microstructure is analyzed qualitatively by finite element method, therefore, the constitutive model of sintering neck is assumed to be an ideal elastic model. The finite element model is shown in Figure 4 (a).

The finite element analysis shows that the failure path of sintered nano-silver is dominated by the pores with larger size in the microstructure, as shown in Figure 4 (b). Smaller minimum distance between pores may cause higher risk of fracture, where the failure of sintering neck and pore wall is the key factor. A large number of internal pores lead to different stress states and failure modes of sintering neck and pore wall in compressive process, which are verified by finite element analysis and experimental results, as shown in Figure 4 (b), (c) and (d).

4. Conclusion
In this work, we found that the internal pores present multi-scale distribution, the pore wall and sintering neck work together to bear the compressive stress, which is confirmed by the microstructure and finite element analysis of the sintered nano-silver. The internal microstructure of sintered nano-silver is established by random porous model according to SEM image. The failure path is determined by the large pores and the interval between the neighboring pores.
Authorship contribution statement
Yao Yao and He Gong designed the experiment, performed the experiments and wrote the manuscript. He Gong and Hongcheng Wu analyzed experimental data. He Gong and Hongcun Guo wrote the numerical code. Yao Yao supervised the research.

Acknowledgment
The authors would like to acknowledge the financial support by the National Natural Science Foundation of China (No. 11772257); Natural Science Foundation of Shaanxi Province (No. 2020JM-103); Innovation Foundation for Doctor Dissertation of Northwestern Polytechnical University (No. CX201948) and Fundamental Research Funds for the Central Universities (No. G2019KY05212).

Conflict of Interest: The authors declare that they have no conflict of interest.

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