Microstructural evolution of sintered silver at elevated temperatures

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ABSTRACT

Reduction in the sintering temperature of metal powders by lowering particle size into the nanoparticle range has resulted in a new class of porous sintered joining materials. Especially promising are sintered silver based materials which can be used to form bonds between wide-bandgap semiconductor die and circuit boards for use in high temperature applications. This work shows that for these materials the exterior sintered silver surface oxidizes preventing surface morphology changes, while the interior pore surfaces of the porous silver remain largely oxide-free. These pore surfaces facilitate fast atomic movement resulting in grain growth and changes in the internal microstructure. Morphology changes in the temperature range 200–400 °C are presented both as statistical averages of grain size and, uniquely in this type of study, by tracking individual pores and grains. It is shown that the internal structure will undergo changes during high temperature storage in contrast to the stable outer surface. A new technique, utilizing the electromigration effect to check the relative surface mobility of atoms in the interior pores and exterior surfaces was used to support the conclusions deduced from thermal ageing experiments. Finally, we speculate that the stability of the exterior surface could be reproduced in the interior if the chemistry of the paste was altered to allow formation of a passivating layer on the interior pores during the final stages of the sintering process, resulting in formation of a stable die attach material for applications of up to 400 °C, for which there is an urgent need.

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1. Introduction

The operating temperature of electronic materials in hybrid automotive, aerospace, space exploration, and deep oil and gas exploration can reach 300 °C and beyond [1]. Current high temperature die attach materials such as high temperature solders or Solid Liquid Inter-Diffusion (SLID) bonding materials suffer from high homologous temperatures and Pb content in case of high temperature solders or rapid reduction in mechanical strength by increase in temperature in case of SLID systems [2]. Therefore, there is a requirement for new joining materials that can be processed at low temperatures but that retains joint strength at high temperatures.

One of the potential solutions involves utilization of the unique properties of nanoparticles. By reduction in particle size, the ratio between surface area and volume increases, contributing to a rise in surface energy and a melting point that is considerably lower than that of the bulk material [3]. For example, in the case of silver the melting point of bulk silver is 961 °C, while melting point of 2.4 nm silver particles is 350 °C [4]. This feature of nanoparticles has been researched in the past decade in order to decouple the processing temperature from operating temperature of high-temperature electronic packaging materials, with silver receiving special interest because of its desirable

mechanical, electrical and thermal properties [4–9] as well as the noble metal nature of silver that prevents excessive oxide formation. In this case, the attachment or interconnects can be formed at considerably lower temperatures than the melting point of the bulk material which determines the ultimate operating temperature. The high surface energy available and noble metal surface of silver also allows sintering to take place without pressure being placed on the die; an added benefit for manufacturers, but one which leads to the final sintered structure containing 20–30% of pores.

Although many studies have been performed on the sintering behaviour of nanoparticles [10,11], and also the mechanical properties of their sintered structures [8,9,12,13], there exists few detailed studies on the high temperature behaviour and stability of sintered silver at temperatures above 300 °C as a high temperature die attach (excepting [14,15]), while previous studies below 300 °C concentrate on bulk mechanical properties and statistical averages of microstructural properties [8,9,16–20]. In the present work, we determine the nature and speed of microstructural changes in sintered silver throughout the 200–400 °C temperature range and investigate the atomic migration mechanisms that lead to these changes. Tracking of changes in individual grains and pores is found to be complicated by the fact that any exposure of the internal pore surfaces to air leads to rapid oxidation and freezing of the microstructure in its original state, similarly to the original exterior surface of the material. Therefore, we have utilised optical microscopy and a glass substrate to prevent the internal pore surfaces

from oxidizing while enabling in-situ observations to take place. These microstructural changes would in most cases lead to unreliability and weakening strength [9,17–19] so that these studies are an innovative technique for understanding long term mechanical reliability and strength preservation of sintered silver for applications in the range 200–400 °C.

2. Experimental

In these studies, two commercially available silver nanoparticle pastes produced by NBE Tech under the names of NanoTach® X and NanoTach® N have been utilised. NanoTach® N is recommended for small size die of 3×3 mm, while NanoTach® X is recommended for attachment of 10×10 mm die in a pressure-less sintering process. The composition of NanoTach® X is shown in Table 1 below. The assemblies, listed in Table 2, were all sintered using the recommended temperature profile from the paste manufacturer under zero applied pressure.

In a previous study [19], samples were cross sectioned after sintering, and aged at 300 °C for 24, 100 and 500 h to track properties such as porosity and average pore size. In that study the evolution of individual pores and grains could not be tracked continuously. In the current experiments, in order to track changes occurring inside the sintered silver microstructure and investigate them continuously, samples were assembled by manual deposition of the NanoTach® X paste onto glass slides followed by placement of approximately 150 μm thick, 10×10 mm Menzel–Gläser cover-slips on top of the paste. To investigate the grain growth mechanisms of the sintered silver, these samples have been placed on a cartridge heater at 250, 300, 350 and 400 °C and the grain evolution has been observed in-situ for up to 7 h using an optical microscope (See Fig. 1), while one sample has been placed inside a furnace at 200 °C for 5 h. This experiment is referred to as sample set 1.

Observation of high temperature behaviour of sintered silver structure through the cover-slip provides information on microstructural changes similar to those occurring inside non-sectioned samples which have not been exposed to air. The presence of the cover-slip planarizes the initial microstructure and may affect parameters such as local porosity. However, comparison with samples that have been aged at 300 °C and then cross-sectioned [19] show qualitatively similar results indicating that the same mechanisms are active. The optical images were then analysed using Image J 1.46r coupled with the image processing toolbox in Matlab with a methodology [21] that allowed the microstructural evolution of sintered silver at high temperatures to be studied statistically (e.g. average grain size). In this method the optical images of the sintered structures have been segmented using an Image J predesigned function to separate the grains and their sizes have been measured using Matlab to calculate the average grain sizes.

The second set of samples was prepared by deposition of the paste into wire shaped gaps with approximate dimensions of 1 mm by 1 mm cross-section and 3 mm length for the first sample and approximately 150 μm by 150 μm cross section and 4 mm length for the remaining samples of this set. The first sample was stored at 300 °C in air and the remainder were stored at 300 and 400 °C inside a vacuum of 5 mPa and at 450 and 500 °C in air to study microstructural evolution of the free surfaces.

Table 1
NanoTach® X composition.

Components	Weight percent
Silver	70–85
Silver oxide	0–10
Cellulose	1–8
Alpha terpineol	5–20
Menhaden fish oil	0–2
Isopropanol	<1
Ethanol	<1

Table 2
Sample sets.

Sample set no.	Purpose of experiment	Paste type and surface dimensions
1	Observation of microstructure evolution on a surface not exposed to air using optical microscope.	NanoTach® X 10×10 mm $\times$ 100 μm
2	Observation of exterior surface evolution under different atmospheres using SEM.	NanoTach® X 150×150 μm $\times$ 4 mm and $1 \times 1 \times 3$ mm
3	Observation of interior microstructure evolution after cross sectioning using SEM.	NanoTach® N 2.5×2.5 mm $\times$ 30 μm
4	Observation of exterior surface evolution after acid cleaning using SEM.	NanoTach® X $r = 2$ mm
5	Comparison of exterior and interior atomic migration patterns during electromigration using SEM.	NanoTach® X $175 \times 175 \times 812$ μm

The third sample set consisted of a single sample selected for thermal ageing after being first cross sectioned and polished in an attempt to observe evolution of the interior of sintered silver continuously. After the sintering step using NanoTach® N followed by cross sectioning, the sample was mounted using a hot mounting resin (LevoFast) from Struers, which consisted of melamine with minerals and glass filler. The sample was mechanically polished using successively finer grades of silicon carbide cloth before final polishing with water based suspensions of 3 and 0.25 μm monocrystalline diamonds. The hot mounting resin was selected to withstand high temperature storage. The assembly was stored at 300 °C in air in an oven for 1, 4, 5, and 20 h consecutively (30 h in total), and observed under a Scanning Electron Microscope (SEM) to track changes.

The fourth set of samples was prepared by sintering of the NanoTach® X paste inside glass sample holders, which were designed for surface cleaning of the samples by perchloric acid (effective for removing organic contamination on silver without causing damage from the utilised concentration [22,23]) before high temperature storage. After manual deposition of paste into the holder and sintering, the samples were stored for 30 min inside an aqueous solution containing 20% concentration of perchloric acid and then stored in deionised water before placement into the furnace for high temperature storage at 300 °C inside ~40 mPa vacuum for 5 h.

The fifth set of samples were prepared using the NanoTach® X paste with the same dimensions as the third set for electromigration studies [24]. These samples were subjected to high current densities of 2.4×10^8 A/m^2 for periods ranging from 20 to 25 days before cross sectioning in order to compare atomic migration patterns on the surface and interior of the porous material.

The free surfaces of the sintered silver were observed using a Hitachi S4000 SEM coupled with Electron Dispersive X-ray (EDX) for elemental analysis.

3. Results and discussion

3.1. Observation of microstructural evolution in the absence of air

Fig. 2 shows optical images from sample set 1 of three samples stored at constant temperatures of 250, 350 and 400 °C showing the continuous evolution of microstructure adjacent to the cover-slip. Fig. 3 is a more detailed examination of the 350 °C sample clearly showing coarsening of the microstructure. Using image processing software, the average grain sizes from the images were calculated and plotted in Fig. 4. For the 400 °C sample, the grain sizes go through three grain growth phases, each having a lower slope than the