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Power Semiconductor Joining through Sintering of Silver Nanoparticles: Evaluation of Influence of Parameters Time, Temperature and Pressure on Density, Strength and Reliability

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Abstract

For decades soldering has been the technology of choice in die bonding. However, due to worldwide health regulations, the most common solder alloys, which contain lead, have been banned. Furthermore, standard solders cannot fulfil the reliability requirements of future power electronic devices. New interconnection technologies have to be developed. One of them is pressure sintering of silver flakes, which forms a highly reliable, highly thermally conductive bond. However, the level of pressure needed (30-50 MPa) requires a powerful pressing equipment and can lead to cracking of the devices and ceramic substrates. A promising development is the use of nano-scaled silver particles, which can be sintered using less pressure due to their superior sintering properties.

Preceding thermogravimetric and calorimetric analyses showed that the presence of oxygen eases the sintering of silver nanoparticles. In order to grasp the sintering characteristics of interconnection layers consisting of nano-scaled silver, sintering experiments were conducted in both air and nitrogen. Scanning electronic microscope pictures and density measurements with a laser profilometer show that sintering of the nano-scaled silver in air but under a chip, the case of real interest, is closer to uncovered sintering in nitrogen than in air. Densities remain lower and the microstructures more fine-grained. This is due to limitation of diffusion of organics out of and oxygen into the layer. The application of pressure can make up for this in terms of density. Hence, the increase in density of stencil printed layers of nano-silver when sintering at temperatures ranging from 200 to 300°C, pressures between 0 and 30 MPa, and for a time of up to 1800 s was measured. The density can be set to any value between 60% and 90% of bulk silver by adjusting sintering time and the levels of temperature and pressure. Samples for shear tests were built using dummy chips made of silver-coated copper. They show that after 60 s of sintering at 275°C and 5 MPa a good shear strength of 40 MPa had been established. If the remaining parameters are set correctly, even 5 s of sintering, a temperature of 225°C, or a pressure as low as 2 MPa is sufficient to generate bonds comparable to solder and high pressure sinter joints.

1 Introduction

Progress in power semiconductor technology results in ever-rising performance of the devices. At the same time, electronics and mechanics are increasingly being integrated leading to extreme operating environments that the new modules have to endure reliably. The integration of electrical motors and combustion engines in new hybrid cars is a widely discussed example these days.

At the moment, maximum temperatures of about 125°C are tolerable during typical operation of power electronic circuit boards. This limit is not set by the active elements made of silicon, though. Si-chips are theoretically able to operate as high as 200°C; the envisioned switch to silicon carbide would raise the bar to 500°C. However, today's interconnection materials are not suitable to reliably endure temperatures of 200°C, let alone 500°C. The state-of-the-art in die bonding, i.e. attaching a semiconductor chip to a circuit board, is soldering. The solder provides mechanical fixing and conduction of both current and heat. For decades the eutectic alloy of tin and lead, Sn63Pb37 (T_m=183°C), was used. Due to worldwide regulations banning poisonous materials from electronic products, such as the Restriction on Hazardous Substances (RoHS) issued by the European Union, substitutes for lead-containing solders have to be found. Basic lead-free solder alloys usually comprise a majority of tin (>96%) balanced with silver and copper. Their melting points are about 220°C. As a rule of thumb, solder materials can be reliably used up to a homologous temperature T_h of 80% of their absolute melting temperature, before creep effects lead to quick degradation. **Fig. 1** shows that SnAgCu solders are not suitable for temperatures exceeding 125°C. High temperature solders, which can be operated continuously at 200°C, do exist. Nevertheless, they may

not bridge the gap due to drawbacks such as high price (AuSn, AuGe, AuSi) or poor processability (BiAg, ZnAl). Moreover, they cannot meet the operating capabilities of SiC-devices, either. Therefore, other means of interconnection have to be found.

One approach is the silver sintering technology, which joins chips and substrates by sintering of a silver powder [1-5]. Usually, a screen or stencil printed layer of micron-scaled silver flakes is used as interconnection material. These silver pastes and power electronic modules containing sintered interconnects are already commercially available.

Due to the application of external pressures of 30 to 50 MPa, sintering takes place at a temperature of about 250°C. The bond formed is theoretically stable up to the melting point of silver at 961°C. However, when applying these pressures, even the slightest irregularities can lead to cracking of the brittle silicon chips and ceramic substrates. High scrap rates have to be expected. Recently, the process evolved to a new level due to the current research interest in nanotechnology: silver particles with a size of less than 50 nm are used instead of micron-scaled silver flakes [6, 7]. Their huge surface energy leads to improved sinterability. The particles even have to be passivated using organic capping materials to prevent them from sintering spontaneously at room temperature. Due to this fact, the pressure needed could be lowered one order of magnitude.

The purpose of this article is to show the impact of parameters such as time, pressure and temperature on the sintering behaviour of nano-scaled silver. Tracking the density of the silver layers monitored this. The suitability for die bonding was evaluated by means of shear tests.

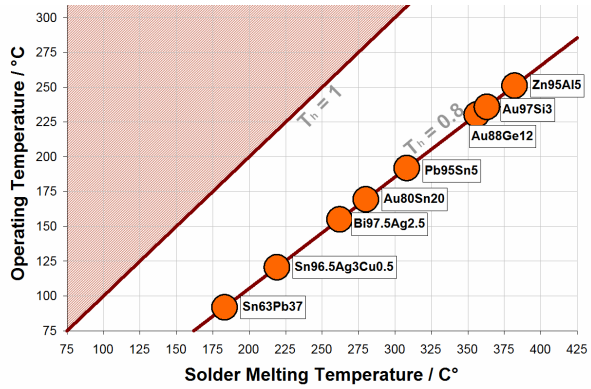


Fig. 1: Maximum operating temperatures of solders versus their melting temperatures. Red area shows two-phase region/liquid zone. Materials can only be reliably operated below the line T_h=0.8.

2 Experimental

Silver paste for die-attach containing spherical nano-scaled particles sized smaller than 50 nm was obtained from NBE Tech, LLC. The paste was stencil printed to copper substrates (dimensions 38 x 27 x 1 mm^3), which were electroplated with 5 µm silver, to form a square 14 x 14 mm^2 with a thickness of approximately 50 µm before drying. The specimens were then pre-dried for 30 min at 50°C followed by 30 min at 125° (heating rates 5 K/min). Sintering took place on a hot plate that was pre-heated to the desired sintering temperature. The hot plate was controlled by a K-type thermocouple to ±2 K and built into a pneumatic press type Schmidt Technology 23-100. For sintering, the specimens were laid onto the hot plate followed by immediate closing of the press. This resulted in high heating ramps of ca. 300 K/min on average. Thin silicone pillows cut to match the devices to be sintered were used to ensure an even distribution of pressure.

For density measurements, silicon dummy chips of size 10 x 10 mm^2 were put on the centre of the silver layers. The chips came without backside metallization. That means no connection to the sintered silver could be established due to SiO_2 covering their surface. The sinter layers (**Fig. 2a**) were scanned using a profilometer type NanoFocus µscan CF4 before and after sintering in order to determine the average thickness of the areas loaded with pressure. The density was calculated according to equation **(1)** and is shown as percentage of the density of bulk silver (10.49 g/cm^3).

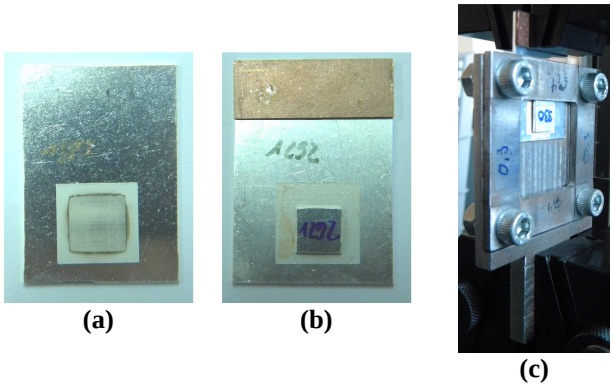
$$\rho = \rho_0 \cdot \frac{d_0}{d} \qquad (1)$$

The initial density ρ_0 was measured before by weighing and volume measurement with said profilometer for a series of ten samples. Furthermore, a thermogravimetric analysis was run to define the mass of organics remaining after the drying process. This was used to adjust the mass of the dried layers to only reflect the contribution of silver. This way, an initial density of 45.32% was identified. A total measurement error of 1% was calculated for density determination.

In order to evaluate the strength of the interconnection layers, dummy chips made of copper (dimensions 7.5 x 7.5 x 1 mm^3) and also coated with 5 µm of silver were sintered to the substrates (**Fig. 2b**). A special shear tool (**Fig. 2c**) was designed to conduct shear tests of the specimens with a Lloyd Instruments testing machine LRX plus. The samples were sheared at a fixed height of 0.1 mm above the surface of the substrate with a speed of 1 mm/min. A load cell capable of recording forces of up to 5 kN was used. Its measurement error was 0.5% FS. The results of several solder and sinter interconnection materials are shown in **Fig. 3** for comparison.

Three series of tests were conducted for both density measurements and shear tests to investigate the influence of the parameters time, temperature and pressure. The point of origin was defined as 60 s of sintering at 275°C with a pressure of 5 MPa. One of the parameters was varied while the remaining two were kept constant. Their respective intervals were 0..1800 s, 200..300°C and 0..5 MPa. In addition, two series of density measurements without covering the sinter layer with a chip were run in

air and nitrogen to examine the influence of the atmosphere. At least five samples per batch were evaluated during density and strength experiments.
A scanning electron microscope (SEM) Joel JSM-6610 was used to take pictures of the resulting microstructures.



(a) **(b)** **(c)**

Fig. 2: Pictures of specimens for density measurements **(a)** and shear tests **(b)**, and shear tool **(c)**.

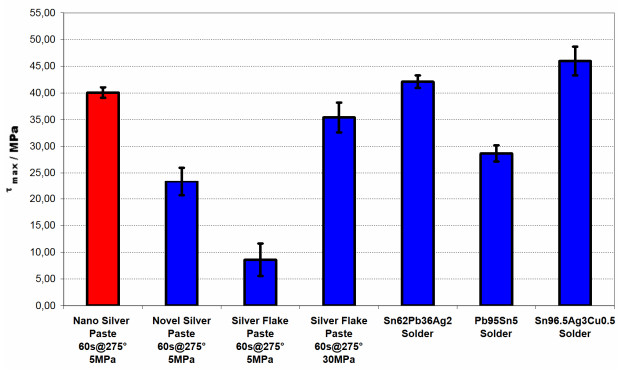


Fig. 3: Shear strength of different interconnection technologies. Red bar shows data of nano-silver paste used for the experiments of this article.

3 Results and Discussion

The comparison of the influence of the surrounding atmosphere in **Fig. 4** shows one distinctive challenge in sintering the nano-scaled silver particles. When the silver layers are sintered without being covered by a chip, an obvious influence of oxygen can be seen. About 10% more in relative density can be reached in air compared to nitrogen atmosphere. Also, the SEM pictures show a clear difference. While only the neighbouring grains have formed necks after 60 s in nitrogen (**Fig. 5b**), the sample sintered in air features bulky structures with grain sizes of 1 µm and above (**Fig. 5c**). This can be credited to the organics passivating the individual silver grains. The sintering of the silver nanoparticles is governed by the degradation kinetics of this capping layer that is much less stable in air than in atmospheres not containing oxygen [8]. Thus, sintering in inert atmospheres is slower. The real case of interest is sintering in air while a chip covers the silver layer, though. This severely constrains the diffusion paths for organics, oxygen and oxidation products. As the density measurements (**Fig. 4**) and SEM (**Fig. 5d**) show, this leads to a sintering behaviour that is closer to the one in nitrogen than to the one in air. Only after 600 s of sintering, a significant difference to nitrogen arises; the final value is at 61% approximately half way between uncovered sintering in air and nitrogen. When pressure is applied, the effect is more than compensated, leading to faster sintering and much higher densities. However, the microstructure is still very fine and thus very different to the uncovered sintering case (**Fig. 5e**). The external pressure has several effects: First of all, it increases the packing density by rearranging particles. This raises the coordination number, i.e. the average number of particle-to-particle contacts per grain. Furthermore, it exerts a mechanical force in addition to the thermal load on the organic passivation layer, which may consequently be locally destroyed. Finally, the pressure provides another driving force for sintering, which can be shown to be of the same order of magnitude as the one created by the surface energy of bare nanoparticles. Surface and grain boundary diffusion, but also sintering processes that are unique to nanoparticles such as plastic flow, mechanical rotation and amorphization can be expected to contribute to sintering [9-13].
Due to the findings displayed in **Fig. 4**, the impact of time, temperature and pressure on both density and strength of the nano-silver interconnection layer was investigated. **Fig. 6** shows the influence of sintering time at a constant temperature of 275°C and a constant pressure of 5 MPa on density and shear strength. The rising in density is very high during the initial seconds of sintering: 68% is reached after only 5 s; one minute of sintering returns 75% that continues to grow to about 88% after 30 min. The shear strength gains even faster returning 30 MPa after only 5 s. 60 s amount to 40 MPa. Further prolonging of the sintering time does not exhibit any significant rise in strength in these tests.

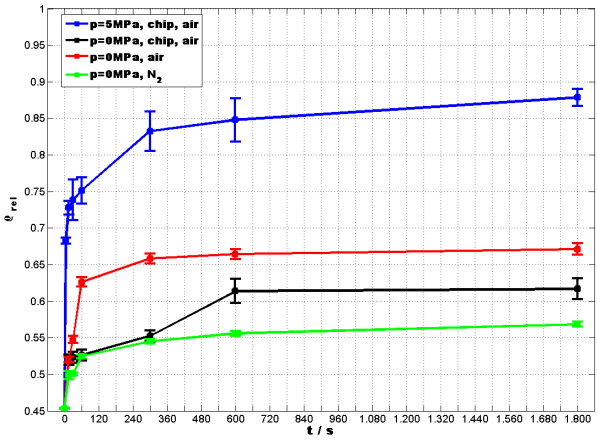


Fig. 4: Influence of sintering atmosphere on density of samples sintered at 275°C.

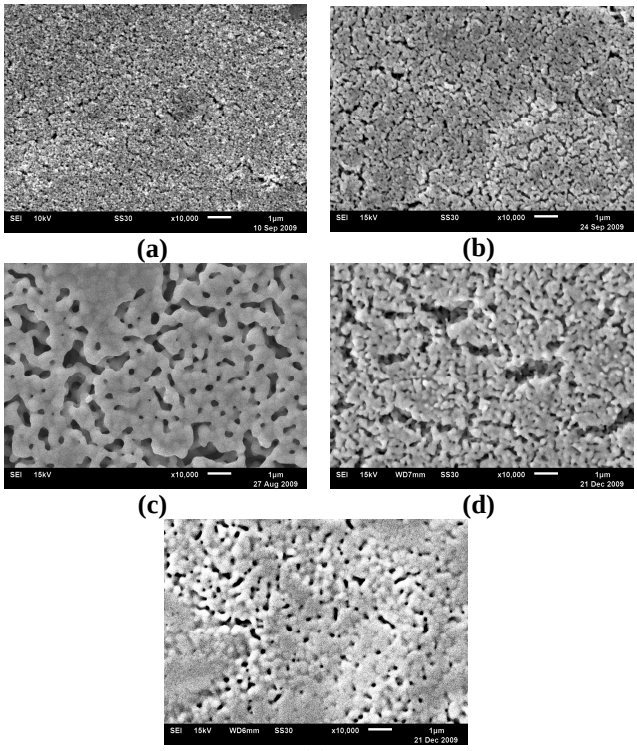


Fig. 5: SEM pictures of nano-silver layer after drying **(a)** and after sintering for 60 s at 275°C without chip in N_2 **(b)**, without chip in air **(c)**, with chip in air **(d)**, and with chip in air and a pressure of 5 MPa applied **(e)**.

The fast increase of both density and strength can be credited to the improved sintering capabilities and the given morphology of the nanoparticles. Once the protective capping of the particles is destroyed by means of temperature and pressure, the sintering can proceed very fast due to the huge driving forces provided by the surface energy and the external pressure. The gain in density slows down gradually due to the consumption of free surface energy. The abrupt stagnation of the shear strength after 60 s may be caused by the design of the samples. At a shear stress of 40 MPa a force of 2.25 kN is applied onto the side face of a copper dummy resulting in 330 MPa of compression there. This presumably leads to a deformation of the dummy that changes the load condition from pure mode II shearing to a mixture of mode I and mode II.

It was mentioned before that the sintering of the silver nanoparticles is governed by the depletion kinetics of the passivating organics. As for any chemical reaction, an exponential relationship to temperature is to be expected. This should be true in this case as well. However, due to the limited temperature interval that is of interest and that was thus investigated (200..300°C), the exponential relation between density and temperature can only be anticipated (**Fig. 7**); the graph appears rather linear. The minimum density measured at 200°C is approximately 65%. As temperature increases, it rises to about 80% at 300°C. Strength also climbs with temperature. However, its graph is not quite linear but flattens towards higher temperatures. 19 MPa are recorded as minimum value at 200°C, 41 MPa as maximum strength at 300°C. The course of shear strength towards higher temperatures can again be explained with the change in loading condition during shearing.

The applied pressure also has an important effect on density and strength. The density can be set from values of 58% at 0 MPa pressure to a maximum of 90% at 30 MPa in these tests. The shear strength increases rapidly from 7 MPa at 0.3 MPa pressure. The maximum is 47 MPa at 30 MPa of pressure. The graph shows that a certain minimum amount of pressure is necessary to establish considerable strength. Once the level is reached at about 2 MPa, resulting in a strength of 34 MPa, strength and density proceed almost in parallel (**Fig. 8**).

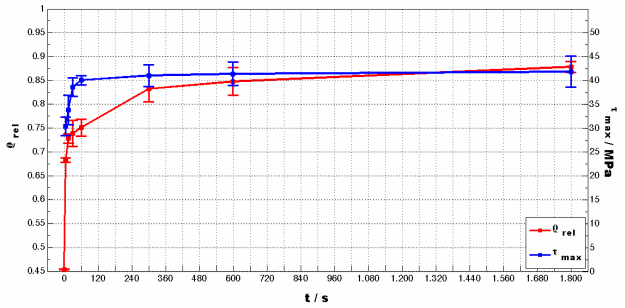


Fig. 6: Relative density ρ_{rel} and maximum shear strength τ_{max} of samples sintered at 275°C and 5 MPa versus sintering time.

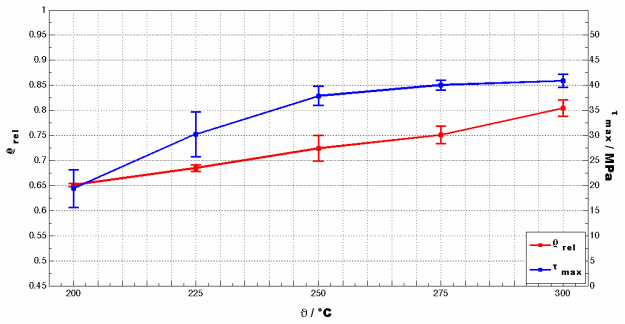


Fig. 7: Relative density ρ_{rel} and maximum shear strength τ_{max} of samples sintered for 60 s at 5 MPa versus sintering temperature.

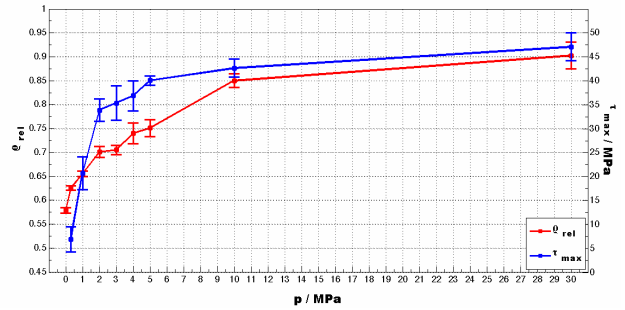


Fig. 8: Relative density ρ_{rel} and maximum shear strength τ_{max} of samples sintered for 60 s at 275°C versus sintering pressure.

Fig. 9 shows a summary of the test series as a plot of maximum shear strength versus density. The data of the three experiments is clustered, indicating that variations in time, temperature and pressure are viable and equivalent options to define the characteristics of the sinter layer. The density can be set at will between about 60% and 90%, resulting in shear strengths between 5 and 50 MPa in these tests.

As discussed before, the gain in strength with increasing time, temperature and pressure, i.e. density, flattens. This is presumably due to deformation of the copper dummy before the interconnection layer fails, leading to mixed-mode loading. Thus, in case of pure shear loading, higher values of strength can be expected for densities above 75%.

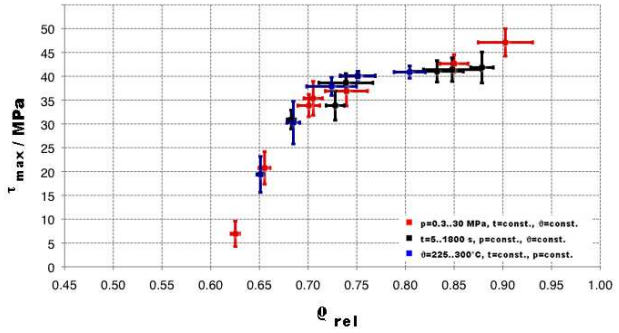


Fig. 9: Maximum shear strength τ_{max} versus relative density ρ_{rel} of test series displayed in Figs. 6-8

4 Conclusion and Outlook

Using density measurements and SEM pictures it was shown that the atmosphere has a crucial impact on the sintering characteristics of the nano-scaled silver particles. Placing them in between joining partners led to considerable worse sintering that was closer to sintering in nitrogen than in air. The application of pressure could more than compensate this constraint in sintering. However, the microstructure remained much finer than when sintering in air. The density could be set between 60% and 90% of bulk silver by variation of the parameters time, temperature and pressure. Shear tests were conducted to check the suitability of the sintered interconnection layers for die bonding. The strength rose with increasing density. The maximum strength recorded was close to 50 MPa. However, due to failing of the dummy chips used before failure of the sinter joint, the strength for densities greater than 75% was probably underrated in these tests.

Nevertheless, strengths that were good for die bonding could be shown. **Fig. 3** compared the shear strength of different joining technologies. The weakest solders returned less than 30 MPa. The experiments presented in this article show that sintering of nano-scaled silver can reach this value within 5 s, at a temperature of 225°C, or a pressure as low as 2 MPa, if the other parameters are set correctly.

Still, strength is only a necessary criterion for a stable interconnection. It is not sufficient to ensure reliability as other factors, e.g. aging, come into play. Joints consisting of sintered silver flakes were shown to have superior reliability qualities compared to solders since they are operated far below their melting point [14-16]. This can also be expected from the nano-silver material presented here. Power cycling and temperature cycling tests of interconnection layers made of nano-scaled silver are currently being run in our laboratory. The goal is to correlate reliability with sintering parameters and density.

5 Acknowledgements

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6 Literature

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