Identifying the Development State of Sintered Silver (Ag) as a Bonding Material in the Microelectronic Packaging Via a Patent Landscape Study

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Sintered silver joint is a porous silver that bonds a semiconductor die to the substrate as part of the packaging process. Sintered Ag is one of the few possible bonding methods to fulfill the operating conditions of wide band-gap (WBG) power device technologies. We review the current technology development of sintered Ag as a bonding material from the perspective of patents filed by various stakeholders since late 1980s. This review addresses the formulation of sintered pastes (i.e., nano-Ag, hybrid Ag, and micron Ag fillers), innovations in the process and equipment to form this Ag joint. This review will provide the insights and confidence to engineers, scientists from universities and industry as well as investors who are developing and commercializing the sintered Ag as a bonding material for microelectronic packaging. [DOI: 10.1115/1.4033069]

Keywords: sintered silver, lead free solders, die-attach materials, nanosilver

1 Introduction

Sintered silvers are used in solar cells and flexible displays [1], printed electronics as circuitry wirings [2], and semiconductor packages as die attach joints [3–5]. These applications represent the different embodiments of sintered Ag albeit from different formulations of Ag pastes or Ag inks. This review will focus on the application of sintered Ag as a die or substrate-attach material. This Ag sintering technique is also known as "low-temperature joining technology" (LTJT). LTJT was developed in-house by Siemens Microelectronics in 1987 to bond large area power thyristors on molybdenum substrates [6]. Their initial formulation of sintered Ag pastes consisted only of micron-sized Ag flakes and cyclohexanol [6].

Since this early development in 1987, sintered Ag has evolved in paste formulations, processing routes and equipment as well as final applications in the semiconductor packages. One of the more recent applications of sintered Ag is to replace Pb-based solder as a die-attach material to comply with the restriction of hazardous substances directives. Unlike sintered Ag, these Pb–Sn based solder joint suffers from the deleterious effect of CuSn intermetallic, resulting in low fatigue strength [7–9]. In another application as a high performance substrate-attach material for power module, sintered Ag joints operates at the temperature of above 200 °C that is not feasible for Sn-based or Pb-based solders. Such elevated condition is common during the operations of WBG semiconductor, namely, gallium nitride (GaN) and silicon carbide (SiC) [10]. Other advantages of sintered Ag are their high electrical and thermal conductivities compared to the Pb-based solder joint.

This review aims to fill the gap in existing knowledge on the patent landscape of sintered Ag joints held by the various stakeholders. Most technical reviews neglected the patent information because of the inaccessible patent language to protect the core invention in as broad scope as possible, or only marginal improvement just to provide the "freedom to operate" to the assignee. Some patent owners also filed patents in certain miscellaneous areas to mislead their competitors of their true inventions. In addition, the sciences behind these patents are often not discussed in the patent applications, but a concurrent review of journal and conference publications in this review supports the inventive and scientific principles behind these patents in sintered Ag.

2 Patent Analysis of Sintered Ag as Bonding Materials

We used AcclaimIP database to analyze the patent trends of this field with "sintered silver" as the primary keyword. Patents and patent applications with the keyword "sintered" and "silver" separated by up to 1000 words were also retrieved from AcclaimIP database to be analyzed for their relevance to the bonding application. In addition, we also retrieved patents and applications using the Cooperative Patent Classification (CPC) of H01L2224/8384 and keywords silver within the claims. CPC-H01L2224/8384 classification is allocated to "bonding by sintering in semiconductor devices." Figure 1 shows the number of patent and patent applications of sintered Ag filed at the United States Patent and Trademark Office based on the assignees' filing dates. This trend in patenting activities suggested a growing belief and investment in sintered Ag as a bonding material for microelectronic packaging.

Regarding the technology relevance of the patents, we ensured that these patents are clearly related to using sintered Ag paste as bonding materials, and not related to other applications such as solar cells or printed electronics. If the company supplied Ag paste for applications in solar cells, printed electronics, or bonding materials in electronic sectors, we only selected the patents on bonding materials for this review. When finalizing the patents to be discussed, we also cross-referenced with companies known to be involved in the value chain of Ag paste as bonding materials market.

Figure 2 shows the main companies or universities patenting their discovery in sintered Ag as bonding materials based on their filing date. The key companies filing patents in this area are power module maker (e.g., Infineon Technologies, Hitachi, Bosch, and Semikron) and materials suppliers (e.g., Heraeus, Alphametals, and Henkel). Our analysis of sintered Ag as bonding materials

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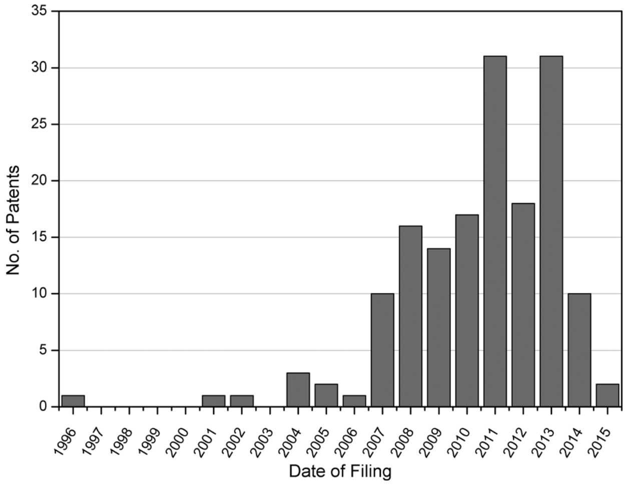

Fig. 1 An increasing number of patents filed and granted from 1995 till 2015 based on "sintered Ag in bonding applications" (refer to text for details)

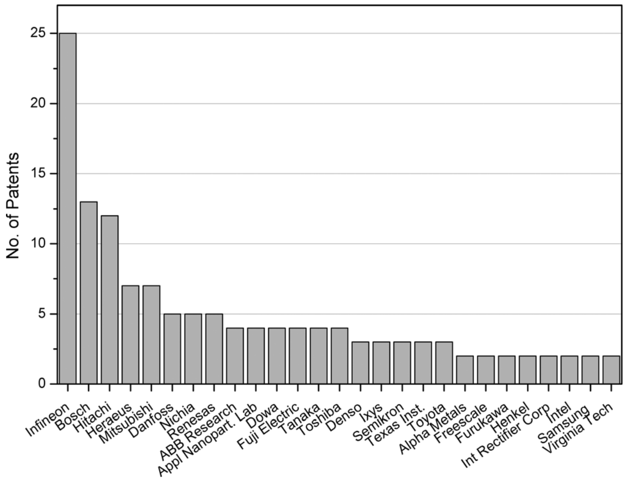

Fig. 2 Companies or universities patenting technologies related to sintered Ag as bonding materials

showed that semiconductor and end-user companies such as Infineon, Hitachi, Toyota, Mitsubishi, and Nissan also filed patents in materials compositions, process parameters, equipment besides their core business in the design of microelectronic packages.

Our analysis of the 150 patents related to sintered Ag suggested that these patents aim to address the following four main challenges limiting the adoption of sintered Ag as a bonding material in the microelectronic packaging:

2.1 Reliability of Pressure and Pressureless Sintered Ag Joints. Pressureless sintered Ag joint can be produced reliably only for small dies while pressure sintering will ensure the formation of reliable joints for large semiconductor dies. There is no consensus on what constitute a large or small die but typically, a big die has an area of more than 25 mm^2 [11,12] or 100 mm^2 [13]; the larger die being the current state of the art. Comparison of reliability between pressureless and pressure sintered Ag joint needs to consider the die size because a large die limits the access of oxygen to pyrolyze the binders in the Ag paste under the central region of the die [11]. Figure 3 shows the die shear strength of pressureless and pressure sintered Ag joints for different die sizes after thermal aging at between 250 °C and 300 °C [14–20]. At similar die sizes and duration of thermal aging, the pressure sintered Ag joints showed higher die shear strength than pressureless sintered Ag joints. Generally, pressure sintered Ag joints was also resistant to changes in die shear strength with extended thermal aging because of its compact and dense microstructure.

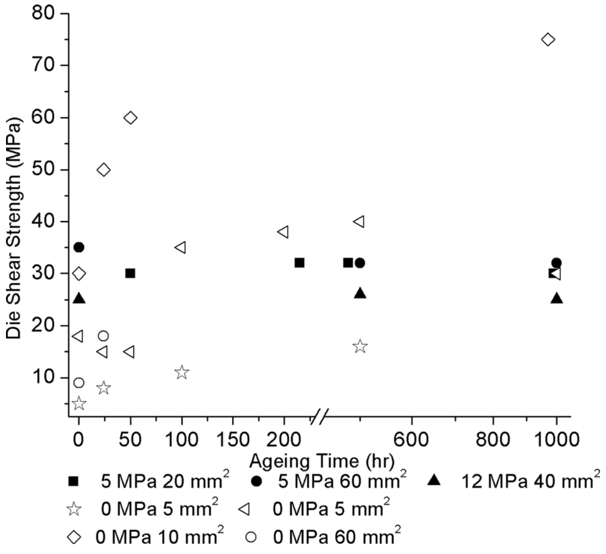

Fig. 3 Variation of die shear strength for pressureless and pressure sintered Ag joints of different die sizes, after thermal aging at between 250 °C and 300 °C for up to 1000 hrs [14–20]

Besides die size and sintering pressure, the reliability of sintered Ag joints depends on their grain size and interfacial properties that are controlled by factors summarized in Fig. 4 [2–5]. Comparison of similarly thermal cycled pressure and pressureless sintered Ag joints is a challenge to compile because researchers used different profiles of thermal cycles, failure criteria (i.e., percent of delamination and crack length), inspection tools, die sizes, and thickness. Die thickness is often not provided in the literature though it influences the thermomechanical stress during thermal cycles.

2.2 Process Control and Cost for Pressure Sintered Ag Joints. Pressure sintered Ag requires higher precision and accuracy of process control than pressureless sintered Ag joint because of physical and direct contact between the press and the semiconductor dies that may result in latent defects and reliability issues for the devices. The tolerance for the current sinter press was only ±5 μm in the absence of any dynamic control [21]. Sinter press is an additional and relatively new manufacturing step for microelectronic packaging industry, which is more accustomed to electrically conductive adhesive (ECA) and solder as a die-attach materials. Pressure sintering entails a steep learning curve in terms of the total cost of ownership (i.e., equipment, manpower and process development) and yield loss.

2.3 Different Metallizations for Sintered Ag. Sintered Ag paste can form good bonding on surfaces metallized with silver (Ag), gold (Au), platinum (Pt), or palladium (Pd) in the absence of any surface preparation. Reliability data on Pt or Pd metallization were not publicly available while pressureless Ag sintering on Au metallized substrates suffered from segregation and formation of void regions within the joint during thermal aging, leading to a reduced joint strength [16,17]. On the other hand, the preferred surfaces to be sintered in the production of the power module package are direct bond copper (DBC) and direct bond aluminum substrates. The native amorphous oxides prevent the diffusion of Ag atoms and sintering between Ag and aluminum or copper substrate. This situation necessitates a reformulation of Ag paste, modification of pressure sintering equipment, or additional plating cost to form a reliable Ag joint.

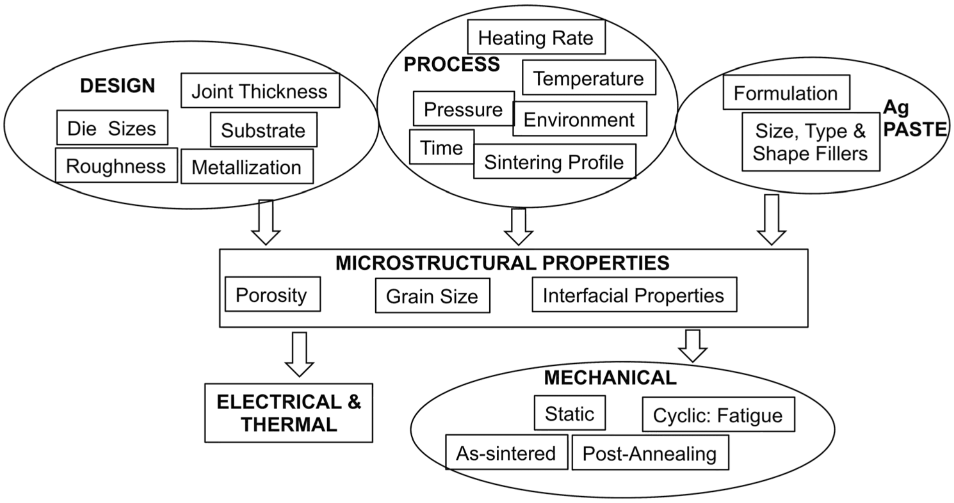

Fig. 4 Influence of the input factors (i.e., design, process and Ag paste formulation) on the microstructural properties (i.e., porosity, grain sizes, and interfacial properties) and the resulting mechanical, electrical and thermal properties of the sintered Ag joint

2.4 Sintering Environment for Ag Pastes. The preferred environment to sinter Ag paste is an inert atmosphere to prevent the oxidation of the Cu and Al substrates. The current state of the art in Ag paste formulation favors sintering in an oxidizing atmosphere to pyrolyze the binders and capping agents from the nano-Ag or reduce the Ag compounds in the Ag paste to form the Ag joint. Figure 5 shows the densification of nano-Ag paste under different environment; 1% O_2/N_2 sintered nano-Ag was denser than pure N_2 sintered nano-Ag while the hydrogen in the 4%H_2/N_2 also removed the binders from the nano-Ag paste by catalytic hydrogenation and hydrogenolysis during the pressureless sintering [22].

Since a discussion on all patents retrieved from this search was lengthy and counterproductive, we focus on the formulation in Ag pastes, processes, and equipment to sinter the Ag joints to address the four issues mentioned here.

3 Formulation of Ag Pastes

Based on the retrieved patents, the formulation for sintered Ag pastes can be divided into three main categories, namely, nano-Ag pastes, hybrid Ag pastes, and micron-Ag pastes. In addition, we included two subsections, namely, inert additives used in a micron Ag pastes and Ag sintering at interfacial substrates.

3.1 Nano-Ag Paste. Amongst the different process parameters mentioned in Fig. 4, sintering temperature, pressure, and time constitute the iron triangle of a reliable sintered Ag joint. In this iron triangle, a reduction of one parameter (i.e., pressure) requires the increase of other two parameters (i.e., temperature or time) to form a reliable sintered Ag joint [23–26]. The relationship between these three parameters is typically represented in a three-dimensional process mapping, similar to Fig. 6, for each formulation of Ag paste [21].

As the application of pressure on the semiconductor dies during joint formation poses a reliability risk, many innovations aim to reduce this pressure further without increasing the temperature or time significantly from current die attaching norms. Hence, all three parameters can only be reduced simultaneously by reducing the sizes of silver particles to the nanometer range, as shown in Fig. 7.

The increase in surface area and curvature of the Ag nanoparticles provide the driving force for sintering at lower temperature and lower pressure than the micron sized Ag fillers. In one study, Ag nanoparticles with the diameter of 26 nm have an estimated surface area of 23.81 m^2/g [27]. Figure 8 illustrates the contribution of surface curvature of the nanosized grains and applied external pressure in densifying the materials [28]. The intersection of these two parameters (i.e., curvature and pressure) depends on different materials system and formulations; the influence of surface curvature dominates the densification behavior below this grain size and vice versa for grains larger than this critical dimension. It should be noted here that grain size and particle size can be used interchangeably in Fig. 8, though these two terms refer to different concepts in the sintering literature. The governing equation for this sintering phenomena is based on the Mackenzie–Shuttleworth model, shown here [29]

$$\frac{d\rho}{dt} = \frac{3}{2}\left(\frac{\gamma}{r} + P_{\text{applied}}\right)(1-\rho)\left(1 - \alpha\left(\frac{1}{\rho}-1\right)^{\frac{1}{3}}\ln\frac{1}{1-\rho}\right)\frac{1}{\eta}$$

$d\rho/dt$ is the densification rate while $(\gamma/r + P_{\text{applied}})$ is the driving force for densification. P_{applied} is the applied sintering pressure; γ is the surface energy; r is the particle radius; α is the geometrical constant; ρ is the density, and η is the densification viscosity. The driving force is illustrated graphically in Fig. 8.

Since these Ag nanoparticles are reactive in air atmosphere, they can self-sinter or agglomerate in the absence of capping agents or dispersants. Current innovations focus on the formulation of capping agents or dispersant, binders, and solvents in the nano-Ag to optimize the sintering characteristics with different substrates, joint designs, and sintering environment. Binders are added to prevent cracking of the printed Ag paste during handling while solvents are added to adjust the viscosity of the Ag paste to be printable or dispensable. The main ingredients for the nano-Ag paste have been summarized and reproduced here in Table 1 for readers' convenience [3].

An analysis of the patents on nano-Ag paste formulation put the upper limit of their filler size at 100 nm though some like Hitachi cited their Ag filler size to be in the range of 1–50 nm, possibly to provide the additional driving force to sinter the joint without pressure [30]. Tanaka Kikinzoku also specified the use of sub-100 nm size nanoparticles for printed wire applications in 2005 [31] but later broadened the range of metal nanoparticles to 5 till 1000 nm for the bonding applications [32]. Their chemistry also changed from the high boiling solvents containing sulfur, amino, ether, or hydroxyl group in their initial patent application [31] to

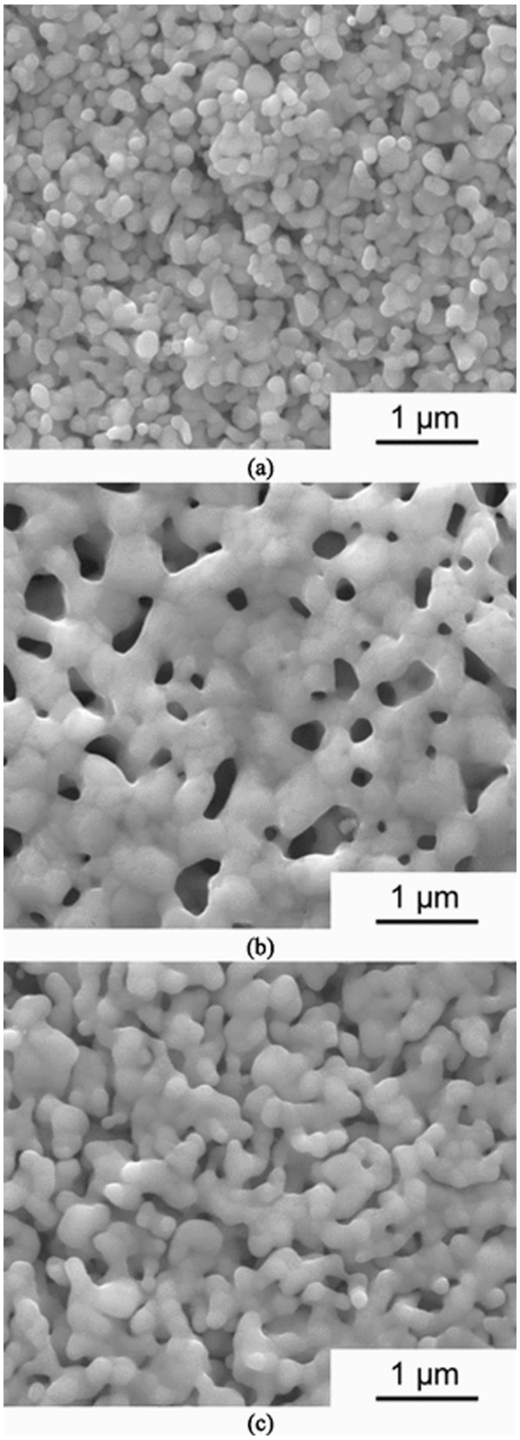

Fig. 5 Scanning electron micrographs of pressureless sintered nano-Ag paste at 280 °C under three different environments, namely, (*a*) N_2, (*b*) 1% O_2/N_2, and (*c*) 4%H_2/N_2 [22]

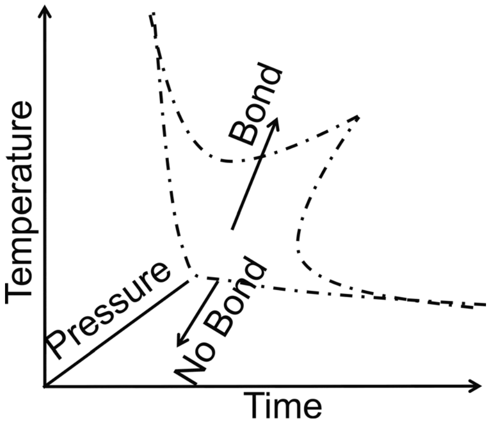

Fig. 6 Process mapping for a typical sintered Ag paste in terms of sinter pressure, temperature, and time demarcating the "bond" and "no bond" regions [21]

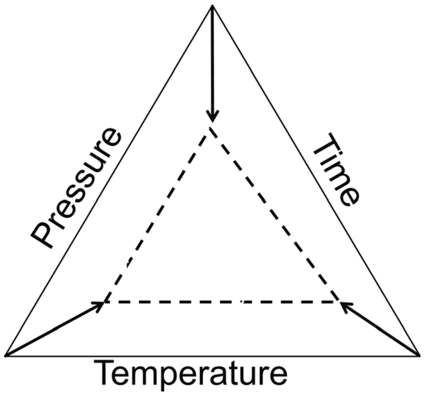

Fig. 7 The "iron triangle" of sintering temperature, pressure and time to produce a reliable pressured sintered Ag joints; the smaller triangle utilizes the surface curvature and surface energy of the Ag nanoparticles to reduce these three parameters simultaneously

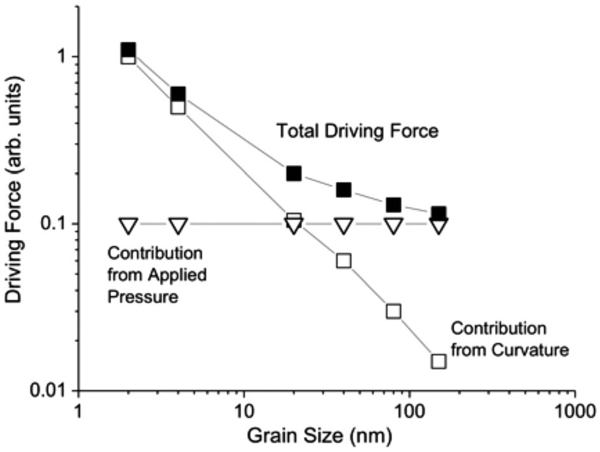

Fig. 8 Driving force for the consolidation of nanopowder as a function of grain size [28]

the low boiling point solvents containing the hydroxyl groups (i.e., alcohol) for their bonding applications [32]. This change is to lower the sintering temperature to be closer to the solder die attach process at 250 °C.

Another compound added to the formulation of nano-Ag paste is the oxygen-containing metallic compounds (e.g., Ag carbonate or Ag peroxide) to pyrolyze the binders locally instead of relying on the oxidizing environment to remove them during sintering [33]. This approach was similar to the sintering agents used in the micron-sized Ag paste [34]. These residual binders posed a reliability risk to the sintered Ag joints but an oxidizing environment would also oxidize the substrate to pose another interfacial delamination risk to the packaged semiconductor [11].

One major innovation in this area is the advent of nano-Ag laminate to provide an easier control of the thickness of sintered Ag joint because the thickness of die attach joint was more critical than the sizes of the semiconductor dies in determining the

Table 1 Main additives of nano-Ag paste [3]

No.	Component	Example
1	Dispersant/ passivating layer/organic shell/capping agent	Menhaden fish oils, poly (diallydimethyl ammonium chloride), polyacrylic acid, polystyrene sulfonate, triethylene glycol, methyloctylamine, dodecylamine, hexadecylamine, myristyl alcohol, 1-dodecanol, 1-decanol stearic acid, oleic acid, palmitic acid, and dodecanethiol
2	Binder	Ethyl cellulose, polyvinyl alcohol, polyvinyl butyral, and wax
3	Solvents/ thinner	isobornyl cyclohexanol, texanol, terpineol, butyl carbitol, toluene, xylene, ethanol, and phenol

reliability of the Ag joints [4,35] (Note: laminate, sheet, film, and preform are used interchangeably in this review.) The use of Ag laminate was reported as early as 1987 in a patent by Siemens [36], and this approach had been pursued by others [32,37–41]. Unlike Ag joint formed from Ag paste, the die shear strength of the Ag joints formed from Ag laminate did not depend on the joint thickness and area [15]. Furthermore, the degradation of die shear strength of the Ag laminated joint after thermal cycling test could be reduced easily by increasing the thickness of the die attach materials to more than 50 μm [15]. Others demonstrated that Ag nanoporous sheet can be sintered on the electroless nickel/immersion gold (ENIG) finished Cu disk without any cleaning flux to produce a Ag joint of similar strength as the Pb–5Sn joint [42]. This result could be achieved regardless of the sintering environment in nitrogen or ambient air atmosphere [42], unlike the results of Zheng et al. mentioned in Sec. 2.4 [22].

Others pursued the Ag foil approach; a Ag foil was sandwiched between two layers of nano-Ag paste to bond with the semiconductor dies and substrate to form the sintered Ag joint [43]. Such "sandwich foil" approach would be less accommodating than the Ag nanoporous sheet proposed by Kim and Nishikawa [42] in relieving the thermal (cycling) stress because the former was a rolled Ag foil of 100% density sintering with nano-Ag pastes at the interfacial regions. While this outcome only demonstrates the proof of principle for bonding with Ag laminates and their repeatability in production volume is still questionable, it does show the advantages of Ag laminates over the Ag paste approach to overcome the key challenges mentioned earlier.

Generally, an additional pressure (i.e., 1–10 MPa) was applied to form a reliable Ag joint despite the self-sintering ability of the nanometer-sized Ag fillers [37]. Hence, several groups added thermosetting resin such as epoxy or polyimide to the formulation of nano-Ag paste to avoid the use of pressure during sintering [44,45]. This approach was also used in the ionic polymeric film embedded with sinterable Ag nanoparticles for die attach application [46]. The Ag-embedded polymer was subjected to ultraviolet or microwave degradation before a final sintering step was carried out to form the sintered Ag joint [46]. This class of polymeric-based nano-Ag paste or film is known as "sintered Ag adhesives" in the market. Sintered Ag adhesive is an adhesive with nanofillers such as nano-Ag particles and a polymeric matrix to provide the adhesion to eliminate the preheating or solvent drying step and pressure during sintering. However, the use of polymeric matrix would slightly compromise the electrical performance of this adhesive Ag joint because of their lower sintering temperature at less than 200 °C [47].

Others produced a polymer-free and pressureless Ag joint with a die shear strength of 10 MPa, despite sintering in an inert environment [48]. As shown in Fig. 9, their success in pressureless sintering is based on careful mixtures of two Ag nanoparticles (labeled as "2" and "3") and one micron sized Ag fillers (labeled "1") of different surface modifications and dimensions, but mathematically related to optimizing the densification step during sintering [48]. However, the patent did not disclose the volumetric ratios of these three components.

Similar pressureless micron-nano sintered Ag paste system has also been successfully demonstrated by other researchers [13]. Another researcher suggested the mass ratios of 65:23:12 for nanoparticles with mean diameter of 168 nm:59 nm:20 nm to achieve a high density for the sintered Ag joint in the absence of any pressure [49]. Although these composite pastes are known as the nanometallic paste in the literature, these formulations are more aptly known as hybrid Ag pastes because of their different sizes in Ag fillers, which will be discussed in Sec. 3.2.

3.2 Hybrid Ag Pastes.

It should be noted here that not all hybrid Ag pastes produce pressureless Ag joints as other sintering aids and optimized sintering profile are needed. In the case of pressure sintered Ag joints, the hybrid Ag paste are typically produced by a dual particle system with ratios of 3:1 for micron to nano-Ag particles [50]. Some researchers specified a volume ratio of 7:3 for micron to nanosized fillers to be used in their Ag paste [51,52], while others used an equal weight percentage of micron and nanosized Ag fillers [53]. This volumetric ratio is based on the "real" maximum packing densities of 64–65% for the monosized particles in a random close pack arrangement [49,54]. This volumetric ratio will translate to $(0.36/0.64)/0.64 \approx 1:3$ for nano to micron-Ag ratios to achieve the maximum density [50].

In the absence of pressure during sintering, the packing density alone can reach 87% and 95% for bimodal and trimodal mixture systems of Ag nanoparticles, respectively [49]. The relationship between mono, bimodal, and trimodal mixtures of Ag nanoparticles, sintering pressure, and shear strength are shown in Fig. 10 [49,50]. Clearly, a trimodal system achieved higher shear strength than bimodal or mono system Ag paste and this trend is magnified in the presence of sintering pressure.

Besides high packing density, the densification of a hybrid Ag paste is also derived from the reduced capping agents of the nano-Ag used in the formulation; micron-Ag fillers do not need any capping agents to prevent self-sintering. The reduction can be as high as 30 wt. % for some hybrid Ag paste that translated to 20% reduction in porosity [50]. However, the optimum percentage of

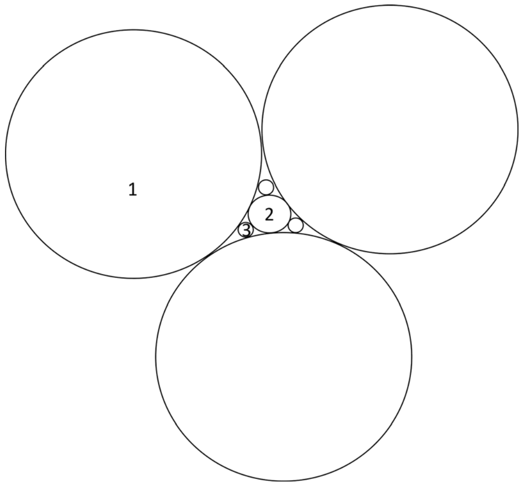

Fig. 9 Dimensional relationship of the diameters for the two Ag nanoparticles (2 and 3) and another micron-sized Ag filler (1) used to produce pressureless nano-Ag paste [48]

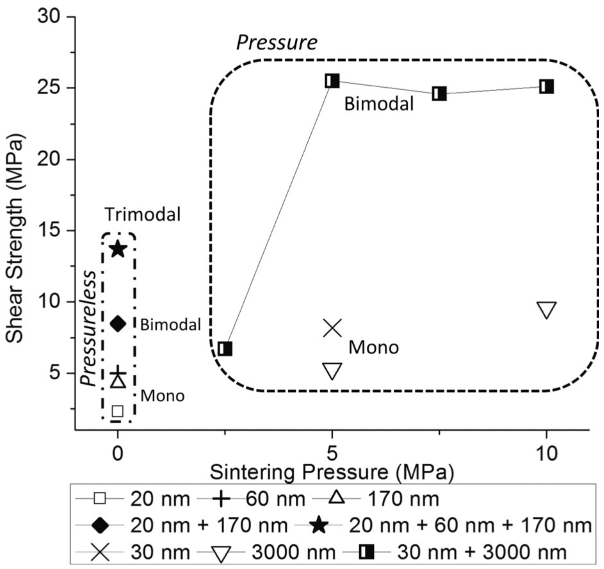

Fig. 10 Shear strength of mono, bimodal, and trimodal hybrid Ag paste formulation for pressure and pressureless sintering at 350 °C [49,50]

micron, submicron, and nano-Ag fillers also depends on the filler shapes and sizes, solvents, and sintering profile [55]. In general, the increase in densification resulted in better mechanical and electrical properties for Ag joints made from a hybrid of micron-Ag and nano-Ag fillers (ratios of 3:1) [50] or micron mixed with submicron Ag fillers (ratios not disclosed) [55] than a pure micron-Ag joint.

3.3 Micron-Ag Paste. Compared to nano-Ag and hybrid-Ag paste, the micron-Ag paste has a long history in development, application, and proven reliability record in the field [56]. Similar to nano-Ag technology, development also focused on reducing the pressure and temperature during sintering by optimizing filler size and their crystallographic properties, paste formulation, and sintering profile. One of the first patents in sintering micron Ag paste used pressure of 9–15 MPa to sinter Ag flakes of 15 μm (in diameter) at temperature of 180–250 °C [6]. In the case of filler size, Heraeus patent application in this area blended sub-micron-sized Ag compound fillers (sizes between 0.2 and 5 μm) with solvents and binders to form the sintered Ag joint at the temperature below 400 °C [57]. Heraeus claimed that sintering temperature can be lowered to 240 °C with a minimum pressure of 0.5 MPa [57]. Nichia suggested Ag filler size of 0.3–15 μm in their formulation while maintaining the sintering temperature in the range of 150–320 °C [58]. Instead of claiming the range of filler size in their patent, Henkel cited a minimum tap density of 4.9 g/cc or higher to ensure good work life of their micron-Ag paste and densification of the Ag joint during sintering [59]. Tap density affects the rheology of the Ag paste to ensure good printing or dispensing of the Ag pastes on the substrate or wafer before the die-placement step.

In the case of crystallographic properties of the Ag fillers, one company suggested the use of metallic particles possessing at least 50% degree of crystallinity and “some anisotropic in their crystallographic directions” [60]. This anisotropic property serves as the initiation sites for sintering amongst the Ag particles [60]. Others also specified the use of hollow Ag particles to control the sintering properties as well as to reduce weight and cost [61]. This sort of specifications for the Ag filler properties are seldom discussed in the literature and instead, the sintering quality is often attributed to the capping agents and binders of the Ag paste and their interaction with the faying substrate [62]. However, a study to deconvolute the influence of Ag crystallographic properties from their binders properties on the quality of sintered Ag joint may not be straightforward because of the simultaneous oxidation of binders and commencement of sintering amongst the Ag fillers.

Instead of relying on the surface curvature and energy of Ag nanoparticles to reduce the sintering pressure shown in Fig. 8, micron Ag paste relied on the Ag compounds (i.e., Ag oxide, Ag lactates, Ag citrates, Ag formats, and Ag carbonate) and sintering agents (i.e., organic peroxides, inorganic peroxides, inorganic acids [34], and aluminum [63]) to form the sintered Ag joints without any sintering pressure. These sintering agents burn the organic binders in the Ag paste and reduce the Ag compounds in-situ to form the bonds amongst the micron Ag particles and substrates [34]. Typically, the Ag oxide is less than 15 at. % of the available Ag fillers, as measured by X-ray photoelectron spectroscopy, to enable good bonding amongst the adjacent Ag fillers [64]. The sintering agents also lower the sintering temperature to less than 200 °C, and inorganic acids clean the faying substrate in-situ during the sintering process [65]. Others included colophonium as a surface activating agent for direct sintering to the Cu surfaces [66].

3.4 Inert Additives in the Micron Ag Pastes. Some researchers added a mixture of metallic coated silicon dioxide or ceramic oxide or carbide in their micron-Ag paste to improve their mechanical properties [67]. These additives act as barriers to grain growth [68] or crack propagation within the die attach materials and control the coefficient of thermal expansion mismatch between the semiconductor die and substrate [43]. This composite approach in the formulation of micron-Ag paste also reduced the internal stress within the die-attach region of power module by 30% [69]. As a comparison, grain sizes in a sintered nano-Ag joint increased from 100 nm to 300 nm when the sintering pressure and temperature increased from 4 MPa and 210 °C to 12 MPa and 300 °C, respectively [70]. Such threefold increase in the grain size has a serious implication on the internal stress and mechanical properties of the sintered nano-Ag joints though such data are not publicly available.

The inclusion of inert additives into the micron-Ag pastes may adversely affect their electrical and thermal conductivities. In the case of electrical conductivity, an addition of 36 vol. % from silicon carbide additives to the average 20 vol. % of pores found in a typically sintered Ag joint could reduce its conductivity by half to 20 MS/m [69]. Nonmetallic fillers are assumed to be voids because of their low electrical conductivity. If such assumption is made and correlated to Ag joint of similar porosity (i.e., density of 55%) in the literature, the measured electrical conductivity of the sintered Ag joint was approximately 16 MS/m at 20 °C and it decreased further to 10 MS/m at 200 °C [71]. The reduced electrical conductivity was still better than those measured for $Pb_{92.5}Sn_5Ag_{2.5}$ solder joint that only has an electrical conductivity of 5 MS/m [72].

In the case of thermal conductivity, the inclusion of inert additives is not as harmful as its reduction in electrical conductivity because these nonmetallic fillers (i.e., SiC and BN) have reasonable thermal conductivities [69]. Porosity of the Ag joint appears to be the only factor in determining the thermal conductivity because voids trap heat [71]. The pores reduce the thermal conductivities as much as 15% of its thermal conductivity for a Ag joint with 10 vol. % of porosity [73]. In a recent study, a silver joint of 15 vol. % porosity reported a thermal conductivity of approximately 160 W/mK [71,73]. This result compares favorably with those shown in Fig. 11 that demonstrates the relationship of thermal conductivity of pure sintered Ag as a function of density and testing temperature [74]. Such thermal conductivity is more than six times of those measured for $Pb_{92.5}Sn_5Ag_{2.5}$ solder joint at 25 W/mK.

Therefore, the inclusion of inert additives into the micron Ag paste not only improves its mechanical properties but only slightly reduce its electrical conductivity and thermal conductivity of the sintered Ag joint. Instead, the development of such composite

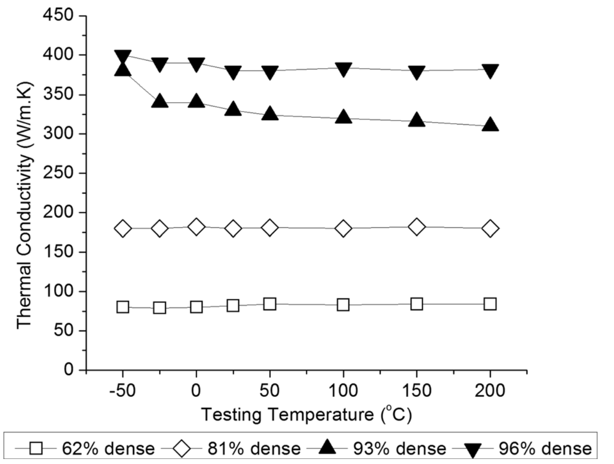

Fig. 11 Thermal conductivity of sintered Ag joints as a function of density and temperature [74]

micron-Ag paste should focus on controlling the porosity of sintered Ag joints to achieve the desired outcome.

3.5 Ag Sintering at Interfacial Substrates. Section 2.3 discusses the inability of Ag paste to sinter on surfaces like copper, nickel, or aluminum, which have tenacious oxides. In the literature, copper substrates were typically cleaned with diluted acids to remove the copper oxides to ensure good sintering in their studies. Such practices would deem unacceptable in a large-scale production. Hence, Namics used glass frits containing the $\mathrm{Ag_20}$, $\mathrm{V_20_5}$, and $\mathrm{Mo0_3}$ to react with the nano-Ag fillers to form calcined films to bond on the Cu present on the DBC substrate [75]. Others carried out a diffusion Sn–Ag soldering on the sintered nano-Ag joint to promote the interfacial bonding between semiconductor dies and DBC [76]. Although this two-step approach is not straightly sintered Ag joint per se, this combination approach produced an intermetallic joint of AgSn to enhance the joint strength. Others like Toyoda also used a Au-based (e.g., Au–Sn, Au–Sb, and Au–Ge) back-metallized light-emitting diode chip to form an alloy with the nano-Ag paste during their joint formation at 300 °C [77]. Toyoda's approach was more akin to the ternary alloy soldering than sintering. These process innovations had the cost advantages compared to the specialized equipment used to remove the copper oxides "in situ" before microjetting and sintering the Ag paste onto the die pad area on the substrate [78] or the semiconductor wafer [79].

Another approach to increase the adhesion at the interfacial regions is to vaporize and condense the nanocrystalline Ag on the substrate or dies to be used as bonding materials [80]. Variation of this approach was demonstrated recently [81] based on patents owned by Nichia [58,82,83]. This approach may pose some reliability concern because of the thickness of the die attach materials (i.e., 1–500 nm) limiting the performance of these Ag joints [84]. Others reduced this reliability issue by embedding the Ag particles into the wafer backside via etching before sintering with Ag-filled adhesive applied on the substrate [85]. Such innovative approach remained to be discussed in the open literature but such approach is appealing because of its ease in scaling to production volume and the increase in interfacial strength.

4 Processing and Equipment to Sinter Ag Joints

4.1 Main Processing Routes of Pressure Sintering. Closely related to the formulation of the Ag paste are the processing conditions and related equipment to sinter these Ag joints. The process of applying pressureless sintered Ag paste is similar to the current ECA used as die-attach adhesives in the microelectronic packaging industry. In the case of pressure sintered Ag joints, the process consists of three main stages: (1) Ag paste printing or dispensing on wafer or substrate, (2) die placement, and (3) pressure sintering the dried Ag paste to form the Ag joint. Figure 12 summarizes the common steps of the four main processing routes for pressure and pressureless sintered Ag joints.

4.1.1 Route 1 (Substrate Printing > Preheat > Die Placement > Pressure Sintering). Amongst the different processing routes illustrated in Fig. 12, route 1 is the most common route used by many companies and researchers. Route 1 was part of the original claims in the Siemens AG patent filed in 1989 [6], and this approach was automated by using a conveyor belt to transfer the semiconductor dies to the DBC in two stages [86]. The first stage of this process adheres this semiconductor die temporarily on the support strip before bonding with the sintering tools in the next step. Meanwhile, others also improved processing route 1 to include different pressing rams to suit their designs of power modules [87]. Many innovations in these patents are incremental in nature and product-specific, and they do not incorporate fundamental changes in the four main steps, i.e., Ag paste printing, preheating, die-placement, and pressure sintering.

Preheating was carried out in a conventional box oven at a temperature between 50 °C and 100 °C to remove the solvents from the Ag paste [88,89] while die-placement is also carried out by a standard die-bonder to place the semiconductor dies on the preheated Ag paste. The preheated Ag paste has certain tackiness to

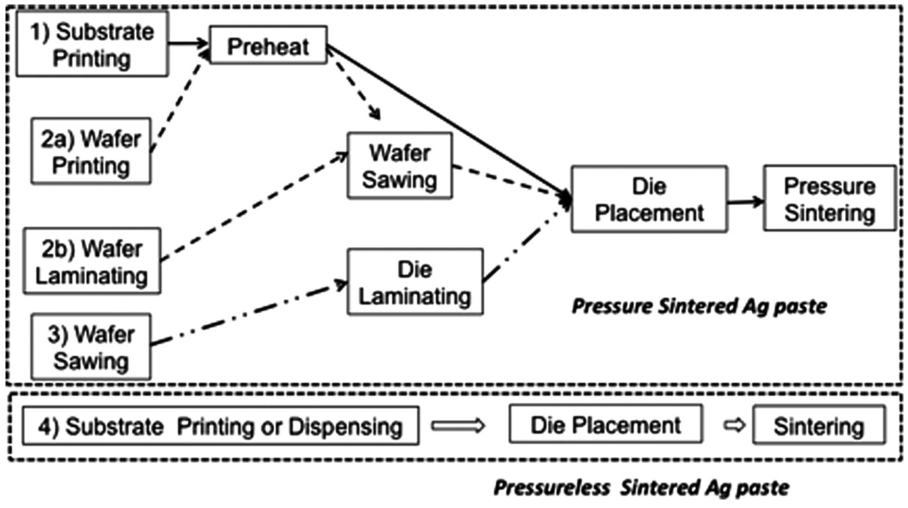

Fig. 12 Common processing route for pressure and pressureless sintered Ag joints [4]

hold the Ag-metallized dies before being sent to a pressure sintering step [90]. Others suggested a precompressed stage to smoothen this preheated Ag paste to provide a stronger but temporary holding force for the semiconductor dies before the next step in pressure sintering the dried Ag paste [91].

Pressure sintering represents a new and robust step to control the porosity and hence the reliability of the Ag joints. The innovations and related issues in pressure sintering will be discussed in Sec. 4.3. What is the range of porosity for a reliable sintered Ag joint? Some researchers suggested the range of porosity to be less than 20% for their fully sintered Ag joints while the preheated Ag paste has a porosity of between 60% and 80% in their patent applications [92]. Another company targeted the porosity of their sintered Ag joint to be as small as 5%, instead of 20% porosity mentioned earlier, to form a reliable sintered Ag joint [93].

As suggested in Figs. 4 and 11, porosity (or density) affects the mechanical properties, thermal and electrical conductivities of the Ag joint. Figure 13 shows the relationship between sintering pressure and density of nano-Ag and micron-Ag paste [26,94]. At similar sintering pressure, temperature, and time, nano-Ag paste densified to higher values than micron-Ag because of the higher surface energy of the Ag nanoparticles compared to the micron-sized Ag particles [94]. Figure 13 also suggests that the maximum density of Ag joint can be achieved without damaging the substrate because compression testing of DBC substrates showed cracking only under 30–50 MPa pressure [95]. The sintered Ag joint of 20% porosity was achieved by four times reduction in sintering pressure to produce the Ag joint with 5% porosity [93]. This information suggests that the sintering pressure could be as high as 20 MPa to achieve the 5% porosity to produce a reliable sintered micron-Ag joint, based on Fig 13.

Besides density, the pore shape plays a role in determining the reliability of the sintered joint [24,96]; pore shape can be quantified by the form factor (F) which is calculated based on the following equation: $F = 4\pi A/P^2$. F is the form factor; A is the measured pore area; and P is the measured pore perimeter [97]. A round pore produces a form factor (F) of 1 while an increasing irregular pore will result in F becoming 0. Sintered Ag joints with small round pores tend to have a higher die shear strength than those with large irregular pores because of the stress concentrators in the latter [13].

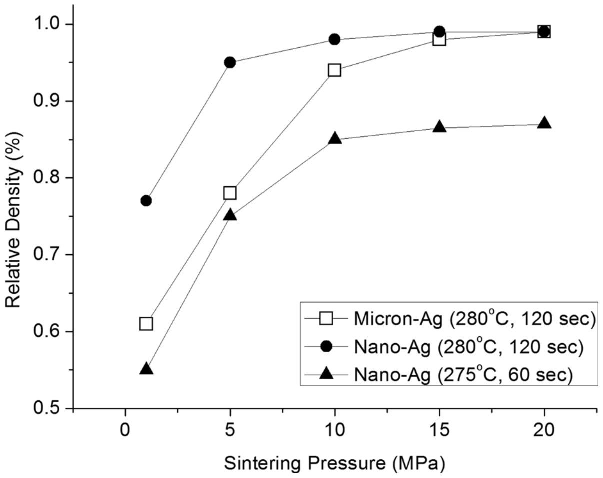

Fig. 13 Relative density of nano-Ag and micron-Ag joint as a function of sintering pressure. Density of pure-Ag is 10.49 g/cm^3 [26,94].

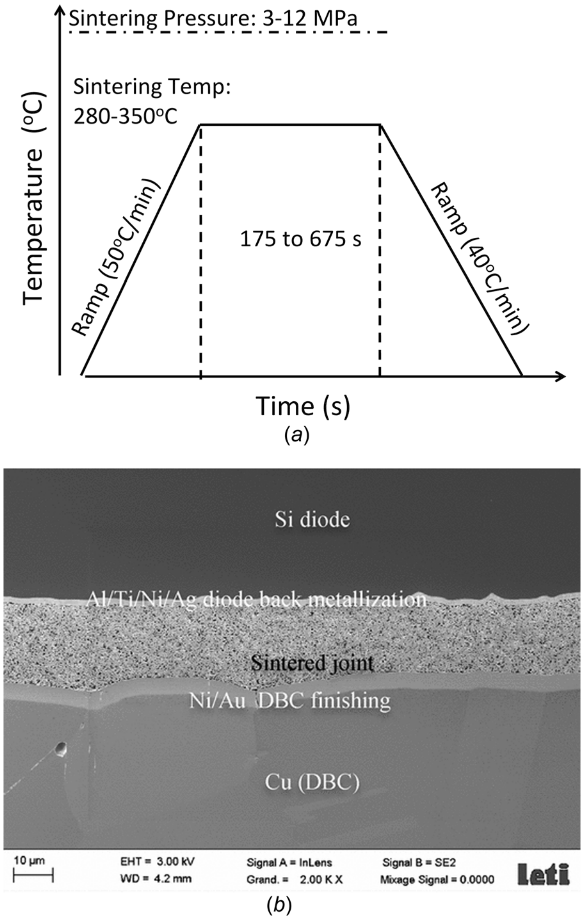

Fig. 14 (*a*) Sintering profile and (*b*) microstructures of the sintered Ag joints produced by lamination and pressure sintering (route 3) [15]

4.1.2 Wafer Printing > Preheat (Wafer) > Die Placement > Pressure Sintering (2a). Wafer Laminating > Wafer Sawing > Die Placement > Pressure Sintering (2b). Routes 2a and 2b use the wafer instead of the substrate as the starting material to be printed or laminated. Similar to other steps, the equipment used are the standard DEK solder printer or die attach film laminator found in a typical microelectronic packaging company. Preheating of Ag-wafer (route 2a) is similar to route 1; it is carried out in a conventional box oven. The preheated Ag-printed wafer or Ag laminated wafer is mounted on a frame and diced in a typical wafer saw machine before die-placed to a substrate. Some process development is needed to find a suitable film to hold the preheated Ag paste or Ag laminate on the wafer backside during the wafer-saw and die-placement stages because some of the dried Ag paste or Ag laminate may remain on the mount and not transfer completely to the substrate, causing uneven thickness of Ag die-attach materials during the pressure sintering. Hence, one company dispensed tacking agent to hold the Ag-laminated dies on the die pads during the die placement stage [98]. As mentioned in Sec. 4.3, the dynamic insert control technology is able to pressure sinter multiple Ag-laminated dies of different thicknesses within a tolerance of ±100 μm [21].

Nevertheless, route 2a had been claimed by various parties [99–103] while route 2b was also pursued by several groups [92,101] with their commercialization partners [98]. Similar to route 1, most of innovations in these patents are incremental in nature with claims on the different operating ranges, and they are likely to be filed to provide the freedom to operate to the assignees. Some researchers compacted the preheated Ag paste before wafer sawing to enhance the transfer of the dried Ag from the wafer sawing stage to the die-placement stage [102]. Such compacting step can pose a significant risk to the production yield and reliability of these semiconductor dies while the beneficial effects of higher density could be controlled better from the sintering profile, Ag paste formulation, or the final pressure sintering step.

4.1.3 Route 3 Wafer Sawing > Die Laminating > Die Placement > Pressure Sintering. Route 3 of Fig. 12 was pioneered by Alpha Metals [104]. After the wafer-sawing step, a thermal-heated flip-chip bonder picks up the sawn dies and able to laminate or stamp the sawn dies on the nano-Ag sheets because of the adhesiveness of the Ag film in the presence of the heated bonder [15]. Then the bonder will die-place and pressure-sinter the Ag-laminated dies one by one on specific locations of the substrate. Each Ag laminated die goes through similar pressure and sintering profile and hence, the low throughput compared to other batch-like process routes in Fig. 12. Figure 14 shows a typical sintering profile and the microstructure of the sintered Ag joint produced by this route [15]. The main advantage of this route is the ease of switching to different die sizes within one power module or package.

4.1.4 Route 4: Substrate Printing or Dispensing > Die Placement > Sintering. Route 4 (Fig. 12) was the pressureless sintered Ag joint pursued by various materials suppliers mentioned earlier in Sec. 2.1 [48]. Pressureless sintered Ag joint used similar die-bonder as ECAs, to dispense the Ag paste. Typically, some process development was carried out to suit the high viscosity of Ag pastes and such work are limited to design of showerhead (i.e., locations, numbers, and diameters of nozzles) and other process parameters used in the dispensing process. Alternatively, Ag pastes are stencil-printed on the substrate with a DEK solder printer. The die-placement step is also carried out with a standard die bonder while sintering is carried out according to the recommended temperature profile in a conventional box oven filled with N_2 or ambient atmosphere. Breakthroughs in the pressureless sintered Ag joints comes from Ag paste formulation and associated sintering profile to form a densified Ag joints for large dies ($>100\ \text{mm}^2$) in N_2 atmosphere, or alternative sintering method such as electrical sintering.

This electrical-based sintering approach imposed an over-voltage of at least 5 V within a bond gap of 100 μm to initiate the sintering of the Ag nanoparticles to form this Ag joint [105]. They listed this "over-voltage" approach to form the printed electronics as well as bonding of electronic module in their patent. Figure 15 shows their layout of the silicon die and printed Ag paste to accommodate the voltage electrode to sinter the printed Ag paste [105]. This layout overcame the limitations of current assisted sintering technology (CAST) that only sintered the copper disk with Ag paste to demonstrate their proof of principles [106]. In principle, this electrical-based sintering was similar to the spark plasma sintering (SPS) reported in the literature though the maximum voltage for the latter's techniques was 2 V [71]. An additional advantage of the former system over the SPS or CAST was the complete absence of pressure, and yet of comparable bonding quality [105]. However, this electrical-based approach needed an additional step to remove any excessive unsintered Ag paste after the sintering of Ag joint.

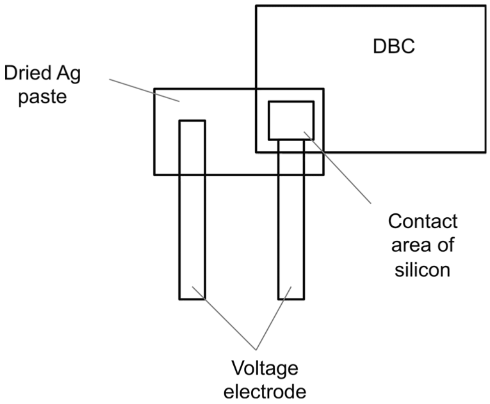

Fig. 15 Top view of electrode arrangement to sinter the silicon dies on the DBC [105]

4.2 Other Process Routes for Pressure Sintering.

As shown in Fig. 4, the porosity of the sintered Ag joint is one of the most critical parameters to ensure the reliability of the sintered Ag joint. Realizing the importance of this parameter, Bosch suggested the following sintering process: (1) print, (2) dry, (3) pressure sinter, (4) print a second layer, (5) dry, and (6) pressure sinter with the semiconductor dies [107]. The first sintering process was carried out at a higher pressure to reduce the porosity before the second step was carried out together with semiconductor dies at lower pressure. Such variable pressure created a dense Ag layer at the interfacial region with the substrate followed by a porous central region at the interface region closer to the semiconductor dies.

Such microstructure was not as reliable as the Ag joint created by similar variable pressure approach by Toyota [108]. Toyota used a variable pressure to impose a higher pressure to increase the density of the sintered joint to increase bond strength after the pyrolyzation stage of binders and capping agent [108]. While Toyota patent lacked the details of what constitute a high or low-pressure sintering, the patent described several possible mechanisms such as elapsed time and thickness reduction to detect the burnt-off of the organics before the initiation of the second stage of high-pressure sintering. Similar two-step pressure sintering was also proposed elsewhere [109]. A well-tuned variable pressure

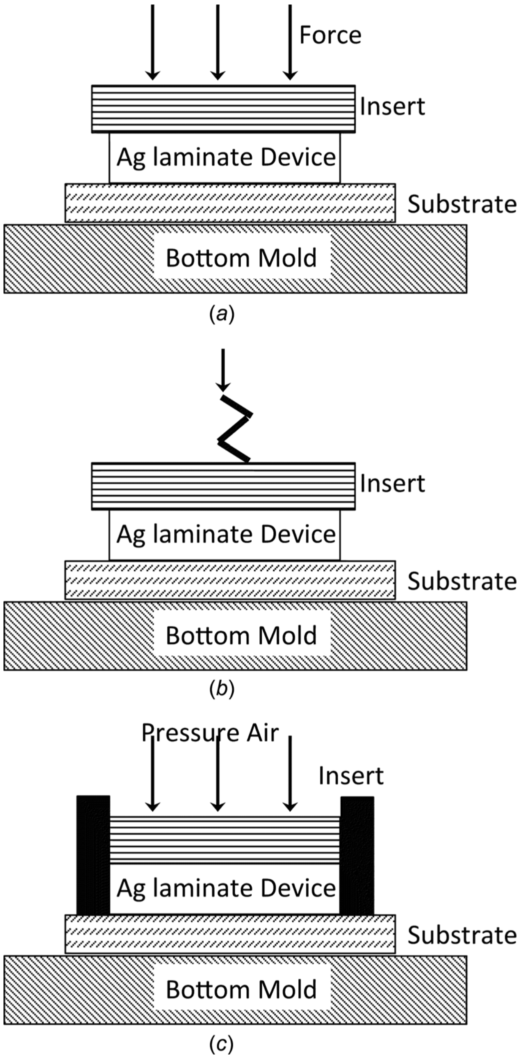

Fig. 16 Evolution of inserts used in the sinter press (*a*) static insert, (*b*) spring loaded insert, and (*c*) DIT [21,110]

sintering can create a dense Ag layer at the interfacial region with substrate or semiconductor dies to sandwich a porous central region of the sintered silver; this microstructure is similar to the bonding of nanoporous Ag sheet on the ENIG-finished substrate [42]. Such microstructure of variable porosity relieves the stress of the Ag joint during thermal cycling or other high-temperature storage tests [42].

4.3 Challenges and Solutions During Pressure Sintering.

Pressure sintering represents the new process step in the packaging of semiconductor dies. Process development works in research laboratories and universities often use hydraulic presses from Carver or even tensile tester working in a compression mode to pressure sinter the semiconductor dies with Teflon or high temperature silicone as a cushion to avoid direct contact from the press. Commercially, Boschman and Locatelli are developing sinter press dedicated to this process step [110,111]. In spite of many innovations in sintering the Ag joint, direct contact between the press insert and semiconductor dies is unavoidable during pressure sintering. Figure 16 shows the evolution of inserts used in the sinter press, namely, (a) static insert, (b) spring loaded insert, and (c) dynamic insert. The spring-loaded inserts were able to pressure sinter the Ag-laminated dies of different thicknesses placed on the die-pads but they suffered from high maintenance and replacement cost because of the typical sintering temperatures between 250 °C and 350 °C. Dynamic insert technology (DIT) used the gas as actuating force to compensate for the height tolerance of individual dies laminated/printed with Ag paste up to ±100 μm in z-axis during pressure sintering [21]. DIT could program the sintering pressure on an individual die as well as group sintering for the entire substrate.

This approach with fluidlike actuating force is pursued by other equipment as well as power module maker, in different forms and shapes. ABB Research pressured isostatically the semiconductor dies and DBC substrate to reduce this direct contact in a chamber filled with liquid [112]. While this arrangement was designed to provide uniform pressure over an uneven contour of the power module, uneven thermal expansion of various parts and components in the power module could result in movements and cracks in the final sintered semiconductor components.

Instead of using liquid to distribute pressure during sintering of the Ag joint, others filed a patent using pressure-transmissive materials such as gas, putty, gel to achieve the same task [113]. This approach was expected to have a better throughput than those proposed by ABB Research [112] because of the simultaneous sintering of several semiconductor dies in one processing cycle.

Instead of batch-sintering, International Rectifier Corporation (IRC) used a “colletlike” fixture to pressure sinter the semiconductor dies individually [114]. The throughput might be lower in this IRC process, but the yield could be improved with better control during pressure sintering of individual semiconductor die. These equipment used either gas or liquid to distribute the pressure during the formation of the sintered Ag joints [112,114], while others only used gas as the actuating force for their pressure sintering [115]. Again, these equipment relied on the parameter optimization of sintering time, pressure, and temperature, mentioned in Fig. 4, to sinter the Ag joint to achieve the appropriate density and mechanical properties for its intended application.

While not exactly a pressure sintering equipment, several companies researched on the use of ultrasonic or microwave to enhance the sintering via plastic deformation of the Ag nanoparticles during pressure sintering [32,113]. There may be technical challenges like shielding of the ultrasonic module from the high temperature press or even reliability concern on the performance of semiconductor dies after packaging. The efficacy of such technologies only begins to be explored now, and it is not publicly reported. This additional driving force for sintering may reduce or eliminate the sintering pressure completely. Separately, some researchers introduced ultrasonic energy to compact the Ag paste before pressureless sintering [116]. This compacted nano-Ag joint had higher density and shear strength than uncompacted Ag joint, if an ultrasonic agitation, of at least 40 W for 60 s, was carried out prior to the thermal sintering.

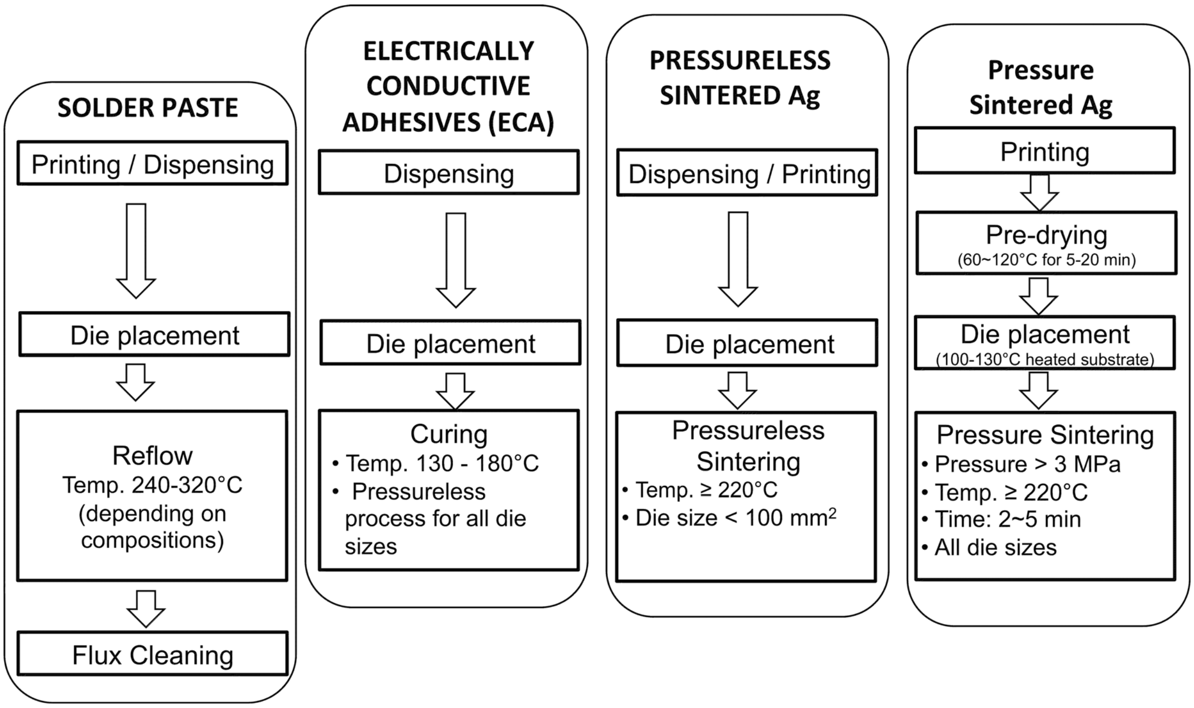

Fig. 17 Typical process flows and parameters of solder paste, ECAs, pressureless, and pressure sinter Ag pastes as die attach materials

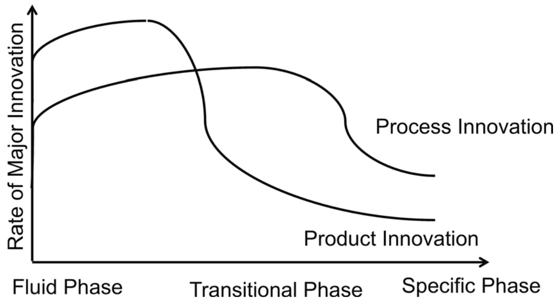

Fig. 18 Three phases of innovation namely: fluid, transitional, and specific phases, as described by Utterback [120]

5 Conclusions and Recommendations

In this review, we explored the patent landscape of sintered Ag paste from their formulation, process, and equipment to produce these sintered Ag joints. Based on our analysis of the applicable patents, current Ag paste formulation aims to sinter on substrates that are prone to oxidation such as Cu and Al in the ambient environment by including the peroxides or other endothermic reducing Ag compounds in their formulations. Recent patent applications also showed patenting of Ag laminates in addition to the Ag pastes in their specifications.

There is also the continuing interest to produce the pressureless Ag joint of similar reliability as the pressure sintered Ag joints because of the obvious cost advantage as a drop-in solution for the microelectronic packages. Figure 17 compares the common process flows for solder paste, ECAs, pressureless [13], and pressure sintered Ag paste [25,117] as die attach materials with their typical process conditions.

The development of pressure sintering equipment will continue to garner interest unless a reliable pressureless Ag joint is successfully demonstrated in mass-production. The analysis of pressure sintering equipment also showed a trend of applying the pressure via air or fluid-like cushioning to compensate the varying thickness of the semiconductor dies placed on the die pads.

Amongst the analyzed patents, we did not come across any patents addressing the issue of Ag migration in the sintered Ag joint though journal publication suggested the use of parylene coating on the semiconductor dies after Ag sintering [118]. Silver migration is influenced by the electric field, temperature, and partial pressure of oxygen in the semiconductor package [119]. The operating range of electric field and temperature of the semiconductor package are determined by the circuit and package design while oxygen can be reduced by deposition of diffusion barrier like parylene or siloxane coatings.

Our patent analysis also suggested that sintered Ag technology is reaching the end of the fluid phase of the Utterback's Three Phases of Innovation (Fig. 18) [120]. There was a steady increase of patents in product innovations (i.e., Ag paste formulation) while the process innovation (i.e., process and equipment) to realize the Ag joints only began to rise in the end stage of fluid phase. There is plenty of room for process innovations while the major constituents of the Ag pastes were fixed, as shown in Table 1 and elsewhere [4]. Various stakeholders were still searching for the best design of microelectronic packages and processes to realize the full potential of sintered Ag joint at this stage of development.

Meanwhile, this continuous adoption of sintered Ag technology beyond the traditional power module makers augured well for the development of this sintered Ag joint as it reflected their confidence in this technology. Central to their trust in this technology is the materials science knowledge underpinning the sintering process of Ag joint.

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References

[1] Layani, M., and Magdassi, S., 2011, "Flexible Transparent Conductive Coatings by Combining Self-Assembly With Sintering of Silver Nanoparticles Performed at Room Temperature," J. Mater. Chem., **21**(39), pp. 15378–15382.
[2] Peng, P., Hu, A., Gerlich, A. P., Zou, G., Liu, L., and Zhou, Y. N., 2015, "Joining of Silver Nanomaterials at Low Temperatures: Processes, Properties, and Applications," ACS Appl. Mater. Interface, **7**(23), pp. 12597–12618.
[3] Siow, K. S., 2012, "Mechanical Properties of Nano-Ag as Die Attach Materials," J. Alloys Compd., **514**(c), pp. 6–14.
[4] Siow, K. S., 2014, "Are Sintered Silver Joints Ready for Use as Interconnect Material in Microelectronic Packaging?," J. Electron. Mater., **43**(4), pp. 947–961.
[5] Khazaka, R., Mendizabal, L., and Henry, D., 2014, "Review on Joint Shear Strength of Nano-Silver Paste and Its Long-Term High Temperature Reliability," J. Electron. Mater., **43**(7), pp. 2459–2466.
[6] Siemens, 1987, "Method of Securing Electronic Components to a Substrate," U.S. Patent No. US4810672B2.
[7] Zuruzi, A. S., Lahiri, S. K., Burman, P., and Siow, K. S., 2001, "Correlation Between Intermetallic Thickness and Roughness During Solder Reflow," J. Electron. Mater., **30**(8), pp. 997–1000.
[8] Pang, H. L. J., Tan, K. H., Shi, X. Q., and Wang, Z. P., 2001, "Microstructure and Intermetallic Growth Effects on Shear and Fatigue Strength of Solder Joints Subjected to Thermal Cycling Aging," Mater. Sci. Eng. A, **307**(1–2), pp. 42–50.
[9] Che, F. X., and Pang, J. H. L., 2012, "Characterization of IMC Layer and Its Effect on Thermomechanical Fatigue Life of Sn-3.8Ag-0.7Cu Solder Joints," J. Alloys Compd., **541**, pp. 6–13.
[10] Buttay, C., Planson, D., Allard, B., Bergogne, D., Bevilacqua, P., Joubert, C., Lazar, M., Martin, C., Morel, H., Tournier, D., and Raynaud, C., 2011, "State of the Art of High Temperature Power Electronics," Mater. Sci. Eng. B: Solid-State Mater. Adv. Technol., **176**(4), pp. 283–288.
[11] Wang, T., Zhao, M., Chen, X., Lu, G. Q., Ngo, K., and Luo, S., 2012, "Shrinkage and Sintering Behavior of a Low-Temperature Sinterable Nanosilver Die-Attach Paste," J. Electron. Mater., **41**(9), pp. 2543–2552.
[12] Schmitt, W., 2010, "Novel Silver Contact Paste Lead Free Solution for Die Attach," 6th International Conference on Integrated Power Electronics Systems (CIPS), Nuremberg, Germany, Mar. 16–18.
[13] Fu, S., Mei, Y., Li, X., Ning, P., and Lu, G. Q., 2015, "Parametric Study on Pressureless Sintering of Nanosilver Paste to Bond Large-Area (≥100 mm^2) Power Chips at Low Temperatures for Electronic Packaging," J. Electron. Mater., **44**(10), pp. 3973–3984.
[14] Egelkraut, S., Frey, L., Knoerr, M., and Schletz, A., 2010, "Evolution of Shear Strength and Microstructure of Die Bonding Technologies for High Temperature Applications During Thermal Aging," 12th Electronic Packaging Technology Conference (EPTC), Singapore, Dec. 8–10, pp. 660–667.
[15] Khazaka, R., Thollin, B., Mendizabal, L., Henry, D., Khazaka, R., and Hanna, R., 2015, "Characterization of Nanosilver Dry Films for High-Temperature Applications," IEEE Trans. Device Mater. Reliab., **15**(2), pp. 149–155.
[16] Paknejad, S., Dumas, G., West, G., Lewis, G., and Mannan, S., 2014, "Microstructure Evolution During 300 °C Storage of Sintered Ag Nanoparticles on Ag and Au Substrates," J. Alloy Compd., **617**, pp. 994–1001.
[17] Fang, Y., Johnson, R. W., and Hamilton, M. C., 2015, "Pressureless Sintering of Microscale Silver Paste for 300 C Applications," IEEE Trans. Compon. Packag. Manuf. Technol., **5**(9), pp. 1258–1264.
[18] Chen, S., Fan, G., Yan, X., LaBarbera, C., Kresge, L., and Lee, N. C., 2015, "Achieving High Reliability Via Pressureless Sintering of Nano-Ag Paste for Die-Attach," 16th International Conference on Electronic Packaging Technology (ICEPT), Changsha, China, Aug. 11–14, pp. 367–374.
[19] Morita, T., Ide, E., Yasuda, Y., Hirose, A., and Kobayashi, K., 2008, "Study of Bonding Technology Using Silver Nanoparticles," Jpn. J. Appl. Phys. Part 1, **47**(8 PART 1), pp. 6615–6622.
[20] Chua, S., Siow, K., and Jalar, A., 2016, "Microstructural Studies and Bonding Strength of Presssureless Sintered Nano-Silver Joints on Silver, Direct Bond Copper (DBC) and Copper Substrates at 300 °C," J. Alloy Compd. (submitted).
[21] Wang, L., 2015, "Low Temperature Hermertic Packaging With Ag Sintering Process," 16th International Conference on Electronic Packaging Technology (ICEPT), Changsha, China, Aug. 11–14, pp. 1317–1320.
[22] Zheng, H., Berry, D., Ngo, K. D., and Lu, G. Q., 2014, "Chip-Bonding on Copper by Pressureless Sintering of Nanosilver Paste Under Controlled Atmosphere.," IEEE Trans. Compon. Packag. Manuf. Technol., **4**(3), pp. 377–384.
[23] Hausner, S., Weiss, S., Wielage, B., and Wagner, G., 2015, "Joining of Copper at Low Temperatures Using Ag Nanoparticles: Influence of Process Parameters on Mechanical Strength," International Brazing & Soldering Conference (IBSC 2015), Long Beach, CA, Apr. 19–22.

[24] Fu, S., Mei, Y., Li, X., Ning, P., and Lu, G. Q., 2015, “Parametric Study on Pressureless Sintering of Nanosilver Paste to Bond Large-Area ($\geq$100 mm^2) Power Chips at Low Temperatures for Electronic Packaging,” J. Electron. Mater., **44**(10), pp. 3973–3984.

[25] Schmitt, W., 2010, “New Silver Contact Pastes From High Pressure Sintering to Low Pressure Sintering,” 3rd Electronic System-Integrated Technology Conference (ESTC), Berlin, Germany, Sept. 13–16.

[26] Knoerr, M., and Schletz, A., 2010, “Power Semiconductor Joining Through Sintering of Silver Nanoparticles: Evaluation of Influence of Parameters Time, Temperature and Pressure on Density, Strength and Reliability,” 6th International Conference on Integrated Power Electronic Systems (CIPS), Nuremburg, Germany, Mar. 16–18.

[27] Wei, Z., Zhou, M., Qiao, H., Zhu, L., Yang, H., and Xia, T., 2009, “Particle Size and Pore Structure Characterization of Silver Nanoparticles Prepared by Confined Arc Plasma,” J. Nanomater., **2009**, p. 968058.

[28] Skandan, G., 1995, “Processing of Nanostructured Zirconia Ceramics,” Nanostruct. Mater., **5**(2), pp. 111–126.

[29] Mackenzie, J. K., and Shuttleworth, R., 1949, “A Phenomenological Theory of Sintering,” Proc. Phys. Soc. Sect. B, **62**(12), pp. 833–852.

[30] Hitachi Ltd., 2008, “Method for Mounting an Electronic Part on a Substrate Using a Liquid Containing Metal Particles,” U.S. Patent No. US7393771B2.

[31] Tanaka Kikinzoku, 2005, “Metal Paste and Film Formation Method Using the Same,” U.S. Patent No. US20050127332A1.

[32] Tanaka Kikinzoku, 2010, “Method of Bonding,” U.S. Patent No. US7789287B2.

[33] Applied Nanoparticle Laboratory Chip, Nihon Superior, 2015, “Oxygen Source-Containing Composite Nanometal Paste and Joining Method,” U.S. Patent No. US20150037197A1.

[34] Heraeus, 2015, “Metal Paste With Oxidizing Agents,” U.S. Patent No. US8950652B2.

[35] Herboth, T., Fruh, C., Gunther, M., and Wilde, J., 2012, “Assessment of Thermo-Mechanical Stresses in Low Temperature Joining Technology,” 13th International Conference on Thermal, Mechanical and Multi-Physics Simulation and Experiments in Microelectronics and Microsystems (EuroSimE), Cascais, Portugal, Apr. 16–18, pp. 1/7–7/7.

[36] Siemens, 1987, “Method for Fastening Electronic Components to a Substrate Using a Film,” U.S. Patent No. US4856185A.

[37] Virginia Tech Intell Prop, 2012, “Nanoscale Metal Paste for Interconnect and Method of Use,” U.S. Patent No. US8257795B2.

[38] Heraeus Deutschland, 2015, “Contacting Means and Method for Contacting Electrical Components,” U.S. Patent No. US8925789B2.

[39] Henkel, 2015, “Metal Sintering Film Compositions,” U.S. Patent No. WO/2015/034579.

[40] Alpha Metals and Setna Rohan, 2014, “Sintering Powder,” U.S. Patent No. WO/2014/068299.

[41] Int Rectifier, 2012, “Porous Metallic Fim as Die Attach and Interconnect,” U.S. Patent No. US20130256894A1.

[42] Kim, M. S., and Nishikawa, H., 2014, “Silver Nanoporous Sheet for Solid-State Die Attach in Power Device Packaging,” Scr. Mater., **92**, pp. 43–46.

[43] Alpha Metals, 2015, “Composite and Multilayered Silver Films for Joining Electrical and Mechanical Components,” U.S. Patent No. WO/2015/031801.

[44] Hitachi Chem., 2015, “Silver Paste Composition and Semiconductor Device Using Same,” U.S. Patent No. US20150217411A1.

[45] Hitachi, 2014, “Bonding Method and Bonding Material Using Metal Particle,” U.S. Patent No. US8821768B1.

[46] Virginia Tech Intell Prop, 2005, “Nano-Metal Composite Made by Deposition From Colloidal Suspensions,” U.S. Patent No. US20050127134A1.

[47] Meschi Amoli, B., Hu, A., Zhou, N. Y., and Zhao, B., 2015, “Recent Progresses on Hybrid Micro–Nano Filler Systems for Electrically Conductive Adhesives (ECAs) Applications,” J. Mater. Sci. Mater. Electron., **26**(7), pp. 4730–4745.

[48] Applied Nanoparticle Laboratory and Toyota Motor, 2013, “Three-Metallic-Component Type Composite Nanometallic Paste, Method of Bonding, and Electronic Component,” U.S. Patent No. US8497022B2.

[49] Morisada, Y., Nagaoka, T., Fukusumi, M., Kashiwagi, Y., Yamamoto, M., Nakamoto, M., Kakiuchi, H., and Yoshida, Y., 2011, “A Low-Temperature Pressureless Bonding Process Using a Trimodal Mixture System of Ag Nanoparticles,” J. Electron. Mater., **40**(12), pp. 2398–2402.

[50] Kiełbasiński, K., Szałapak, J., Jakubowska, M., Młozniak, A., Zwierkowska, E., Krzemiński, J., and Teodorczyk, M., 2015, “Influence of Nanoparticles Content in Silver Paste on Mechanical and Electrical Properties of LTJT Joints,” Adv. Powder Technol., **26**(3), pp. 907–913.

[51] Samsung Electro Mech., 2014, “Power Module Using Sintering Die Attach and Manufacturing Method Thereof,” U.S. Patent No. US8630097B2.

[52] Samsung Electro Mech., 2012, “Conductive Metal Paste Composition and Method of Manufacturing the Same,” U.S. Patent No. US20120219787A1.

[53] Baker Hughes Inc., 2011, “Method and Apparatus for Joining Members for Downhole and High Temperature Applications,” U.S. Patent No. US20120292009A1.

[54] Brouwers, H., 2006, “Particle-Size Distribution and Packing Fraction of Geometric Random Packings,” Phys. Rev. E, **74**(3), p. 031309.

[55] Suganuma, K., Sakamoto, S., Kagami, N., Wakuda, D., Kim, K. S., and Nogi, M., 2011, “Low-Temperature Low-Pressure Die Attach With Hybrid Silver Particle Paste,” Microelectron. Reliab., **52**(2), pp. 375–380.

[56] Göbl, C., and Beckedahl, P., 2008, “A New 3D Power Module Packaging Technology Without Bondwires,” International Exhibition and Conference for Power Electronics, Intelligent Motion, Renewable Energy and Energy Management (PCIM Europe 2008), Nuremberg, Germany, May 27–29, pp. 561–566.

[57] Heraeus, 2009, “Process and Paste for Contacting Metal Surfaces,” U.S. Patent No. US20090134206A1.

[58] Nichia, 2015, “Method for Producing Conductive Material, Conductive Material Obtained by the Method, Electronic Device Containing the Conductive Material, Light-Emitting Device, and Method for Producing Light-Emitting Device,” U.S. Patent No. US8968608B2.

[59] Henkel, 2015, “Sinterable Silver Flake Adhesive for Use in Electronics,” U.S. Patent No. US8974705B2.

[60] Henkel, 2015, “Sinterable Metal Particles and the Use Thereof in Electronics Applications,” U.S. Patent No. WO/2015/126807.

[61] Kaken Tech, 2015, “Conductive Paste and Die Bonding Method,” U.S. Patent No. US20150115018A1.

[62] Scola, J., Tassart, X., Vilar, C., Jomard, F., Dumas, E., Veniaminova, Y., Boullay, P., and Gascoin, S., 2015, “Microstructure and Electrical Resistance Evolution During Sintering of a Ag Nanoparticle Paste,” J. Phys. D: Appl. Phys., **48**(14), p. 145302.

[63] Heraeus 2015, “Metal Paste With Co-Precursors,” U.S. Patent No. US8950653B2.

[64] Hitachi Chem., 2011, “Adhesive Composition and Semiconductor Device Using the Same,” U.S. Patent No. US20130183535A1.

[65] Henkel, 2014, “Silver Sintering Compositions With Fluxing or Reducing Agents for Metal Adhesion,” U.S. Patent No. US20140030509A1.

[66] Infineon Tech., 2008, “Module Including a Sintered Joint Bonding a Semiconductor Chip,” U.S. Patent No. US8253233B2.

[67] Robert Bosch, 2013, “Starting Material and Process for Producing a Sintered Joint,” U.S. Patent No. US20130216848A1.

[68] Zhang, H., Nagao, S., and Suganuma, K., 2015, “Addition of SiC Particles to Ag Die-Attach Paste to Improve High-Temperature Stability; Grain Growth Kinetics of Sintered Porous Ag,” J. Electron. Mater., **44**(10), pp. 3896–3903.

[69] Heuck, N., Langer, A., Stranz, A., Palm, G., Sittig, R., Bakin, A., and Waag, A., 2011, “Analysis and Modeling of Thermomechanically Improved Silver-Sintered Die-Attach Layers Modified by Additives,” IEEE Trans. Compon. Packag. Manuf. Technol., **1**(11), pp. 1846–1855.

[70] Zabihzadeh, S., Van Petegem, S., Duarte, L. I., Mokso, R., Cervellino, A., and Van Swygenhoven, H., 2015, “Deformation Behavior of Sintered Nanocrystalline Silver Layers,” Acta Mater., **97**, pp. 116–123.

[71] Alayli, N., Schoenstein, F., Girard, A., Tan, K. L., and Dahoo, P. R., 2014, “Spark Plasma Sintering Constrained Process Parameters of Sintered Silver Paste for Connection in Power Electronic Modules: Microstructure, Mechanical and Thermal Properties,” Mater. Chem. Phys., **148**(1–2), pp. 125–133.

[72] Indium Corp., 2015, “Indium Corp. Indalloy® 151 Pb-Sn-Ag Solder Alloy,” MatWeb LLC, Blacksburg, VA.

[73] Youssef, T., Rmili, W., Woirgard, E., Azzopardi, S., Vivet, N., Martineau, D., Meuret, R., Le Quilliec, G., and Richard, C., 2015, “Power Modules Die Attach: A Comprehensive Evolution of the Nanosilver Sintering Physical Properties Versus Its Porosity,” Microelectron. Reliab., **55**(9–10), pp. 1997–2002.

[74] Wereszczak, A. A., Vuono, D. J., Wang, H., Ferber, M. K., and Liang, Z., 2012, “Properties of Bulk Sintered Silver as a Function of Porosity,” Oak Ridge National Laboratory, Oak Ridge, TN, Report No. ORNL/TM-2012/130.

[75] Namics, 2015, “Conductive Paste and Method for Producing a Semiconductor Device Using the Same,” U.S. Patent No. WO/2015/108205.

[76] Infineon Tech, 2014, “Semiconductor Device Including Diffusion Soldered Layer on Sintered Silver Layer,” U.S. Patent No. US8736052B2.

[77] Toyoda Gosei Co., 2014, “Method for Mounting Luminescent Device,” U.S. Patent No. US8852970B2.

[78] Ixys, 2014, “Solderless Die Attach to a Direct Bonded Aluminum Substrate,” U.S. Patent No. US8716864B2.

[79] Ixys, 2014, “Power MOSFET Having Selectively Silvered Pads for Clip and Bond Wire Attach,” U.S. Patent No. US8653667B2.

[80] Infineon Tech, 1999, “Pressure Sintering Method for Fastening Electronic Components on a Substrate,” U.S. Patent No. US5893511B2.

[81] Kuramoto, M., Kunimune, T., Ogawa, S., Niwa, M., Kim, K. S., and Suganuma, K., 2012, “Low Temperature and Pressureless Ag-Ag Direct Bonding for Light Emitting Diode Die-Attachment,” IEEE Trans. Compon. Packag. Manuf. Technol., **2**(4), pp. 548–552.

[82] Nichia, 2015, “Semiconductor Device and Production Method Therefor,” U.S. Patent No. US8927341B2.

[83] Nichia, 2014, “Light Emitting Semiconductor Element Bonded to a Base by a Silver Coating,” U.S. Patent No. US8836130B2.

[84] Heuck, N., Palm, G., Sauerberg, T., Stranz, A., Waag, A., and Bakin, A., 2010, “SiC Die-Attachment for High Temperature Applications,” Mater. Sci. Forum, **645–648**, pp. 741–744.

[85] Texas Instruments Inc., 2015, “Embedded Silver Nanomaterials Into Die Backside to Enhance Package Performance and Reliability,” U.S. Patent No. US20150069600A1.

[86] Infineon Tech, 2010, “Apparatus and Method for Producing Semiconductor Modules,” U.S. Patent No. US7851334B2.

[87] Semikron Electronics, 2009, “Power Semiconductor Substrates With Metal Contact Layer and Method of Manufacture Thereof,” U.S. Patent No. US20090008784A1.

[88] Heraeus, 2010, “Controlling the Porosity of Metal Pastes for Pressure Free, Low Temperature Sintering Process,” U.S. Patent No. US2010/0051319A1.

[89] Zhao, S. Y., Li, X., Mei, Y. H., and Lu, G. Q., 2015, "Study on High Temperature Bonding Reliability of Sintered Nano-Silver Joint on Bare Copper Plate," Microelectron. Reliab., **55**(12), pp. 2524–2531.

[90] Siemens AG, 2004, "Heat Conducting Adhesive Joint With an Adhesive-Filled Porous Heat Conductor," U.S. Patent No. US6823915B2.

[91] Danfoss Power Solutins, 2012, "Method for Producing a High-Temperature and Temperature-Change Resistant Connection Between a Semiconductor Module and a Connection Partner," U.S. Patent No. US20120037688A1.

[92] Infineon Tech, 2014, "Pre-Sintered Semiconductor Die Structure," U.S. Patent No. US8835299B2.

[93] Gobl, C., and Faltenbacher, J., 2010, "Low Temperature Sinter Technology Die Attachment for Power Electronic Applications," 6th International Conference on Integrated Power Electron Systems (CIPS), Nuremberg, Germany, Mar. 16–18.

[94] Kraft, S., Zischler, S., Tham, N., and Schletz, A., 2013, "Properties of a Novel Silver Sintering Die Attach Material for High Temperature–High Lifetime Applications," SENSOR 2013, Nurenberg, Germany, May 14–16, pp. 242–247.

[95] DeVoto, D., Mihalic, M., and Paret, P., "Reliability of Bonded Interfaces," National Renewable Energy Laboratory, Golden, CO, NREL Report No. APE028.

[96] Siow, K. S., Tay, A. A. O., and Oruganti, P., 2004, "Mechanical Properties of Nanocrystalline Copper and Nickel," Mater. Sci. Technol., **20**(3), pp. 285–294.

[97] Chawla, N., and Deng, X., 2005, "Microstructure and Mechanical Behavior of Porous Sintered Steels," Mater. Sci. Eng. A, **390**(1), pp. 98–112.

[98] Alent Alpha, and Fico Besi, 2013, "Argomax Ultra Fast Sintering," Alpha, South Plainfield, NJ, accessed Mar. 2, 2016, http://www.alphadieattach.com/UFS-Ultra-Fast-Sintering.asp

[99] Infineon Tech, 2014, "Semiconductor Device and Method," U.S. Patent No. US8828804B2.

[100] Infineon Tech, 2014, "Device Including a Semiconductor Chip and a Carrier and Fabrication Method," U.S. Patent No. US8637379B2.

[101] Alpha Metals, 2012, "Sintering Materials and Attachments Methods Using Same," U.S. Patent No. US20120114927A1.

[102] Semikron Electrinic, 2012, "Power Semiconductor Component With Metal Contact Layer and Production Method Therefor," U.S. Patent No. US8110925B2.

[103] Ixys, 2012, "Solderless Die Attach to a Direct Bonded Aluminum Substrate," U.S. Patent No. US8716864B2.

[104] Alpha Metals, 2011, "Sintering Materials and Attachment Methods Using Same," U.S. Patent No. US20120114927A1.

[105] Valtion Teknillinen, 2015, "Method for Manufacturing Conductors and Semiconductors," U.S. Patent No. US9011762B2.

[106] Mei, Y., Cao, Y., Chen, G., Li, X., Lu, G. Q., and Chen, X., 2013, "Rapid Sintering Nanosilver Joint by Pulse Current for Power Electronics Packaging," IEEE Trans. Device Mater. Reliab., **13**(1), pp. 258–265.

[107] Robert Bosch, 2015, "Two-Step Method for Joining a Semiconductor to a Substrate With Connecting Material Based on Silver," U.S. Patent No. US20150123263A1.

[108] Toyota, 2010, "Bonding Method," U.S. Patent No. US7770781B2.

[109] Valeo Electronique, 2008, "Method of Assembling a Member on a Support by Sintering a Mass of Conductive Powder," U.S. Patent No. US8444913B2.

[110] Boschman, 2014, "Advanced Molding and Sintering Systems: Sinterstar Innovate F-XL," Boschman Technologies B.V., Duiven, The Netherlands.

[111] Locatelli Meccanica, 2016, "Hydraulic Presses," Locatelli Meccanica S.r.l., Subbiano, Italy.

[112] ABB Research, 2005, "Method for Mounting Electronic Components on Substrates," U.S. Patent No. US6935556B2.

[113] Freescale Semiconductor Inc., 2015, "Packaged Semiconductor Devices and Methods of Their Fabrication," U.S. Patent No. US9099567B1.

[114] Int Rectifier, 2014, "Sintering Utilizing Non-Mechanical Pressure," U.S. Patent No. US20140224409A1.

[115] Infineon Tech, 2012, "Method for Producing a Composite and a Power Semiconductor Module," U.S. Patent No. US20130203218A1.

[116] Li, Y., Jing, H., Han, Y., Xu, L., and Lu, G., 2016, "Microstructure and Joint Properties of Nano-Silver Paste by Ultrasonic-Assisted Pressureless Sintering," J. Electron. Mater., (epub ahead of print).

[117] Krebs, T. H., 2012, "mAgic—Novel Sintering Materials for Die Attach on DCB," PowerGuru (epub ahead of print).

[118] Riva, R., Buttay, C., Allard, B., and Bevilacqua, P., 2013, "Migration Issues in Sintered-Silver Die Attaches Operating at High Temperature," Microelectron. Reliab., **53**(9), pp. 1592–1596.

[119] Mei, Y., Lu, G. Q., Chen, X., Luo, S., and Ibitayo, D., 2011, "Migration of Sintered Nanosilver Die-Attach Material on Alumina Substrate Between 250 and 400 in Dry Air," IEEE Trans. Device Mater. Reliab., **11**(2), pp. 316–322.

[120] Utterback, J. M., 1996, *Mastering the Dynamics of Innovation*, 2nd ed., Harvard Press, Boston.