

Small-chip Attachment on Copper Leadframe with Sintered Nanosilver Paste

Jesus N. Calata, Hanguang Zheng, Guo-Quan Lu, Khai Ngo

Virginia Tech

213 Holden Hall (0237)

Blacksburg, VA 24061 USA

Luu Nguyen

Texas Instruments

2900 Semiconductor Drive

Santa Clara, CA 95052-8090 USA

Ph: 540-231-8423; Fax: 540-231-8919

Email: jcalata@vt.edu

Abstract

Sintered nanoscale silver paste provides a low-temperature alternative to solder for die attachment. Unlike solder, the sintered attachment does not melt upon reaching the original attachment temperature and therefore may be used at higher temperatures. Higher electrical and thermal conductivities mean less Joule heating and better heat dissipation characteristics and the porous microstructure imparts low elastic modulus for lower thermomechanical stress and enhanced reliability. The state of the technology has reached a point where it is now possible to obtain die-shear strengths comparable to solder at sintering temperatures between 250°C and 280°C with little or no applied pressure, depending on the chip size. In addition to attachments on silver or gold-coated surfaces, it is possible to form bonds on bare copper if done under inert or slightly reducing atmosphere. Because attainment of a strong bond depends on the paste being in contact with a clean (oxide-free or untarnished) surface, a study was made to determine if the attachment process will work on copper leadframes with either an anti-tarnish or anti-EBO (epoxy bleed-out) coating. Small mechanical silicon chips less than 3 mm x 3 mm in size were attached without pressure at temperatures as low as 260°C. The sintering atmosphere in the chamber was varied from pure nitrogen, to nitrogen + 4% hydrogen and to nitrogen + 1% oxygen. Attachments sintered in pure nitrogen or nitrogen with hydrogen produced die-shear strengths of at least 30 MPa and were just as strong as those bonded on bare copper. Sintering in nitrogen + 1% oxygen caused the die-shear strength to drop below 30 MPa but still above 20 MPa. In the presence of oxygen, the binder removal is due to oxidative combustion but the low level of oxygen caused incomplete binder burnout that interfered with the sintering while also causing some oxidation of the copper. On the other hand, the addition of hydrogen appeared to enhance the sintered microstructure accompanied by a slight increase in die shear strength. Sheared attachments that exposed the copper surface showed patches of silver still attached indicating formation of strong bond with the copper.

Key words

Anti-tarnish coating, copper leadframe, nanosilver paste, sintered silver attachment,

I. Introduction

Die attachment using sintered silver was shown to be feasible at temperatures comparable to solder reflow temperatures and at moderate applied pressures [1]-[4]. This was made possible by the use of nanoscale silver paste that can be sintered under 300°C without the need for high pressure as was done previously [5], [6]. Devices 3 mm x 3

mm or smaller generally do not require pressure for attachment. For larger devices, a pressure of 3 MPa is generally sufficient [7]. Die-shear strengths were obtained that are comparable to those of solder joints. Reliability of the joints was also shown to be an order of magnitude better [8]. Offsetting the higher cost of silver are higher electrical and thermal conductivities [9] and the capability to

withstand operating temperatures above the attachment temperature. Resistance to current induced electromigration was also shown to be better than those of solder or wirebonds [10]. These characteristics are attractive for applications where heat generation and dissipation can be a challenge. It also opens the door to wide bandgap devices that are able to operate efficiently at elevated temperature because now a die attach and interconnection material is available that can match their temperature capability [11].

However, the effort of achieving the attachment was done mainly on silver or gold-coated substrates. The coating prevented the base metal from oxidizing when exposed to air during heating, whether the metal was copper, aluminum or nickel. The strength of the silver attachment depends on the establishment of a direct bond between the sintered silver and the metallization. Since silver and gold are not susceptible to oxidation at the attachment temperature or in the case of silver revert to the metallic state upon heating, a clean silver to silver or silver to gold bond can be achieved. Unlike solder paste that contains a fluxing agent to remove the oxide, silver paste may not be used for attachment under conditions encountered in solder paste reflow.

Initial efforts to achieve sintered silver paste attachment on bare copper involved reducing the partial pressure of the sintering atmosphere to starve the chamber of oxygen [12]. However, this was not successful because it takes only a small amount of oxygen to cause copper to tarnish. Reduced oxygen partial pressure also had an unintended effect on the sintering process as it prevented the proper burnout and removal of the binder in the paste. This caused the retardation of the sintering process resulting in low bond strength. Increasing the oxygen content enhanced the binder burnout and sintering but the higher strength of the sintered silver was negated by increased oxidation of the copper that resulted in lower strength. An optimum condition exists but the die shear strength that was achieved remained below 10 MPa. An alternative method was a timed injection of oxygen or air into the nitrogen-purged atmosphere such that the oxygen would only be present just before the sintering temperature is achieved to burn off the binder. A bond strength of the order of 20 MPa was attainable but it also caused oxidation of the exposed copper. A reformulation of the nanosilver paste by the manufacturer was done to reduce the binder and allow sintering in the absence of oxygen. With the new formulation, it became possible to obtain die shear strength on copper exceeding 30 MPa. However, this feat was achieved on bare copper. Ogura, et al [13] performed die attachment on bare copper but the sintering temperature was 350°C in nitrogen. Die attachment on copper leadframe was done by Maruyama, et al [14] but there was no mention of any coating. Commercial processes that involve

attachment of chips on leadframes usually make use of copper leadframes with some form of coating to prevent tarnishing of the copper or bleed out of epoxy if it was used as the attachment material. The objective of this research was to demonstrate that it is feasible to achieve similar attachments on coated copper leadframes. Additionally, the attachments should be achieved at lower temperature and shorter total processing time, e.g., 1 hour or less.

II. Experimental Procedure

A. Materials

The paste that was used in the experiments was provided by NBE Technologies, LLC (Blacksburg, Virginia). It has a low binder content to accommodate oxygen-free sintering atmospheres to prevent oxidation of the copper. Commercial copper leadframes, with a section shown in Fig. 1, were provided by Texas Instruments (Santa Clara, CA) and came coated with a thin layer of either anti-tarnish or anti-epoxy bleedout (EBO) compound. During the course of the experiments, no distinction was made between the two and simply classified as coated substrates in contrast to bare substrates such as direct bond copper (DBC) substrates. The stock leadframes were cut into smaller pieces to allow fabrication of small numbers of attachments each time. The leadframe pieces were mounted using a liquid epoxy on alumina plates to impart flatness and rigidity during printing of the paste and placement of the chips. Mechanical chips measuring about 2.55 mm x 1.85 mm x 100 μ m thick were also provided by TI as the test chips.

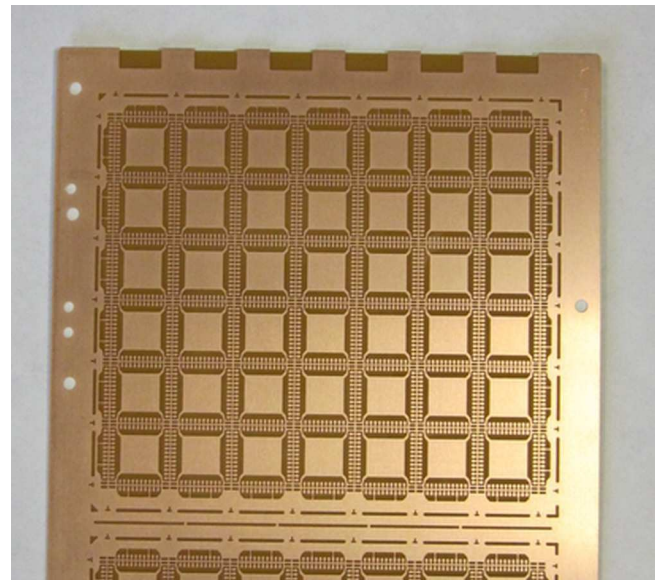


Fig. 1. Section of a coated copper leadframe that was used as the substrate for attachment of chips with sintered nanosilver paste.

B. Attachment and Testing

Before the nanosilver paste was printed, strips of 2-mil (50 μm) thick Kapton tape was laid down on opposite sides of the rectangular copper pattern to serve as the stencil. The leadframe was used as is to prevent unintentional removal of the protective coating by organic solvent such as alcohol or acetone or by scratching. A layer of the nanosilver paste was then applied to the surface and leveled off with a metal squeegee. The chip was dropped onto the coated copper square and the chip was pressed into the paste using a thickness control apparatus fitted with a micrometer to produce a wet thickness under the chip of around 40 μm .

For most of the attachments, drying and sintering were carried out in a controlled atmosphere chamber as shown in Fig. 2. The air in the chamber was purged and replaced with the desired sintering gas before starting the heating profile. Several gases were used during sintering, namely nitrogen, nitrogen + 4 % hydrogen, and nitrogen + 1 % oxygen. Heating profiles used are shown in Fig. 3(a) and Fig. 3(b). A modification to both profiles was also used to test the feasibility of performing low-temperature drying in both nitrogen and air since the leadframe has a protective coating. The drying stage was replaced by a separate drying below 100°C for up to 1 h and combined with another fast ramp profile to the sintering temperature to complete the attachment.

The die shear strength of the attachments were obtained using a Dage 4000 series tester from Dage Precision Industries. The microstructure of the sheared surfaces were examined in a scanning electron microscope (FEI Quanta 600 FEG environmental SEM) equipped with energy dispersive x-ray spectrometer (EDS).

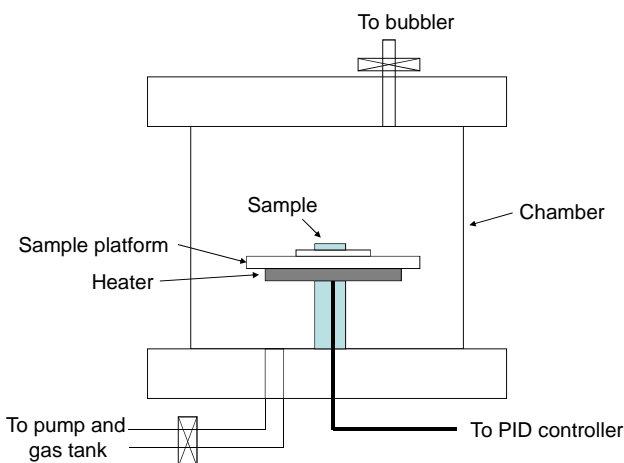


Fig. 2. Schematic diagram of controlled atmosphere chamber used to sinter the nanosilver paste die attachment under various nitrogen-based atmospheres.

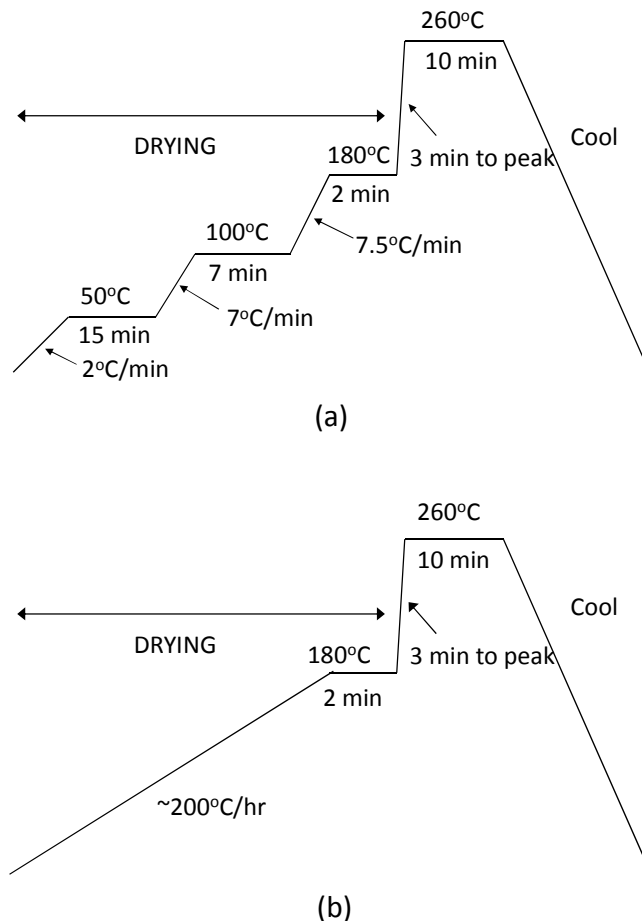


Fig. 3. Heating profiles used for sintering the nanosilver paste attachment on the copper leadframe with profile (a) having multiple drying steps and (b) with a single drying stage prior to the peak attachment temperature.

II. Results and Discussion

A. Die Shear Strength

Die shear test results for attachments sintered under different atmospheres are provided in Table I and plotted in Fig. 4. The results show that there is no significant difference between those processed using the three-step drying and one-step drying, which is just as well because it allows for simplification of the heating profile in a future implementation of the technique. The more important implication of the results is the sensitivity of the die shear strength to the composition of the atmosphere. The highest die shear strength was obtained when sintering was done in nitrogen containing 4% hydrogen. The lowest was obtained in nitrogen with 1% oxygen. At first, this may run counter to expectations based on the assumption that binder removal must take place before sintering can proceed. Because the particles are separated from each other by the organic binder, initiation of neck formation between particles that

precedes further densification cannot occur. A possible explanation for the differences in die shear strength is provided later in the discussion on the attachment microstructures.

Table I. Die shear strength of sintered nanosilver paste attachments formed under different gases and heating profiles.

Atmosphere	Die Shear Strength (MPa)	
	3-step drying	1-step drying
Nitrogen	33	31
Nitrogen + 4% H ₂	35	36
Nitrogen + 1% O ₂	25	19

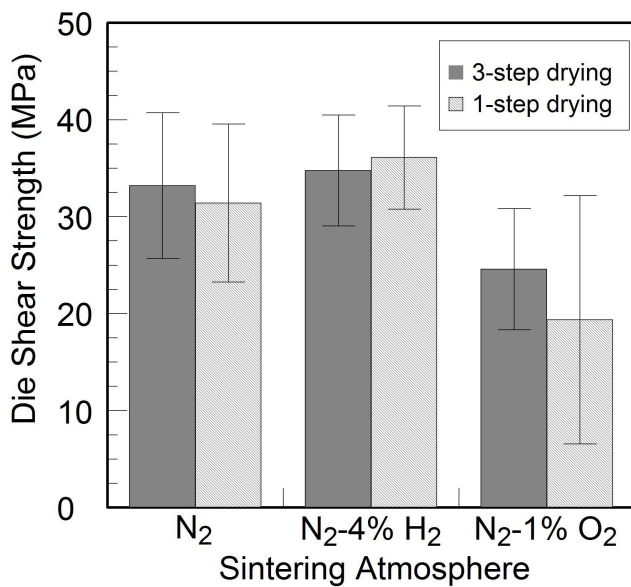


Fig. 4. Die shear strengths of attachments sintered using different profiles under different gases. Standard deviation is plotted as error bar.

Additional tests were also conducted to investigate the feasibility of replacing the drying stage of the heating profiles in Fig. 3 with a separate low-temperature drying in air to take advantage of the protective coating of the leadframe. Being able to carry out the drying in air would free up the controlled-atmosphere sintering furnace for increased throughput in a production environment. A drying temperature of 50°C was initially chosen where the temperature was slowly raised at 5°C/min and the attachment soaked for 1 h. This was followed by a separate single ramp heating of around 10 to 11°C/min to 260°C and sintering for 10 min in nitrogen. An average die shear strength of 23.7 MPa was obtained so the drying temperature was raised further to 70°C. Drying was also conducted in nitrogen as a baseline. The results are plotted in Fig. 5. A drying time of 30 min was sufficient to achieve

30 MPa under both atmospheres and increased further when dried for 1 h. The average strength for 1 h drying in air was obtained on a lesser number of samples due to cracking/breakage of chips during shearing and could be a bit misleading although the trend is obvious. No oxidation was observed on the leadframe after drying and was indirectly supported by the high die shear strength obtained relative to the attachments sintered in nitrogen + 1% O₂.

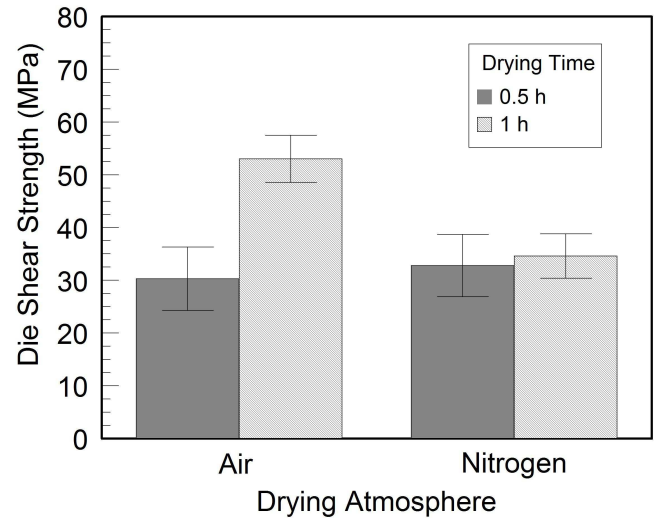


Fig. 5. Die shear strength of attachments dried at 70°C in air or nitrogen followed by sintering in nitrogen at 260°C.

B. Sintered Microstructure of Attachments

A low-magnification SEM image of the die attachment on the leadframe after shearing off the chip is shown in Fig. 6. The rectangular outline of the sheared device is clearly visible. Near the center of the attachment is an irregular crater exposing the copper. This sheared structure is typical of strong attachments as exemplified by the high die shear strengths of greater than 30 MPa obtained under nitrogen and nitrogen + hydrogen atmospheres.

The microstructures in Fig. 7 were obtained on the surface of the silver inside the sheared attachment area (not the crater). All of them are porous with the sintered particles forming a network surrounded by voids. While the structures of the silver sintered in N₂ and N₂ + 1% O₂ look similar, the attachment sintered in N₂ + 4% H₂ appears denser judging by the thickness of the silver network and the near-complete merging of the particles into strands or columns. The mechanism for the improved sintering behavior is not clear but a possible explanation could be a hydrogenation process catalyzed by metallic silver that decomposes the binder into smaller and more volatile or mobile molecules, thus enabling the particles to come into contact readily. In pure nitrogen, the binder would simply melt but because of its large size and length has less

mobility and slows down the sintering process.

The effect on die shear strength is reversed when a small amount of oxygen (1%) is present in the nitrogen, causing the bond strength to fall below 30 MPa. The low oxygen content could result in incomplete combustion that leaves behind a solid charred residue that hinders interparticle contact. This can be observed in Fig. 8 where a dark ring is formed around the matching inner edges of the attachment on the chip and the leadframe. The necks that form between particles are thinner and therefore will support less force than those formed in pure nitrogen. This is consistent with earlier work [12] that lowered the oxygen level by reducing the pressure of air although the effect was more severe because of the higher binder content of the paste that was used. Light oxidation of the copper may also have occurred as the dried paste was porous enough to allow the oxygen to diffuse under the die and react with the copper once the protective coating is degraded. The result is a weaker interface between the silver and the leadframe with the failure occurring primarily at the interface.

Finally, in the crater that exposed the copper after shearing, the image in Fig. 9 shows that patches of silver (light color), as confirmed by EDS, are actually attached to the copper indicating the formation of a bond where the silver particles come into contact with the copper surface, notwithstanding the initial presence of a coating. Since the copper remains unoxidized even after the coating disappears at higher temperature prior to the onset of sintering, development of strong silver to metallic copper bond will take place.

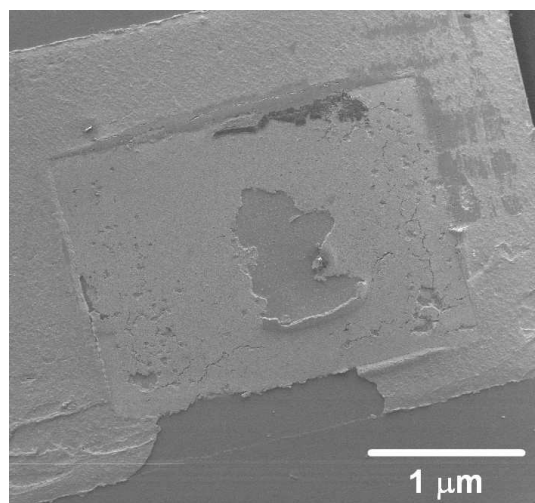


Fig. 6. Low-magnification SEM of nanosilver attachment sintered in $N_2 + 4\% H_2$ after shearing the chip from the leadframe. The irregular area inside the rectangular pattern is a crater exposing the copper underneath.

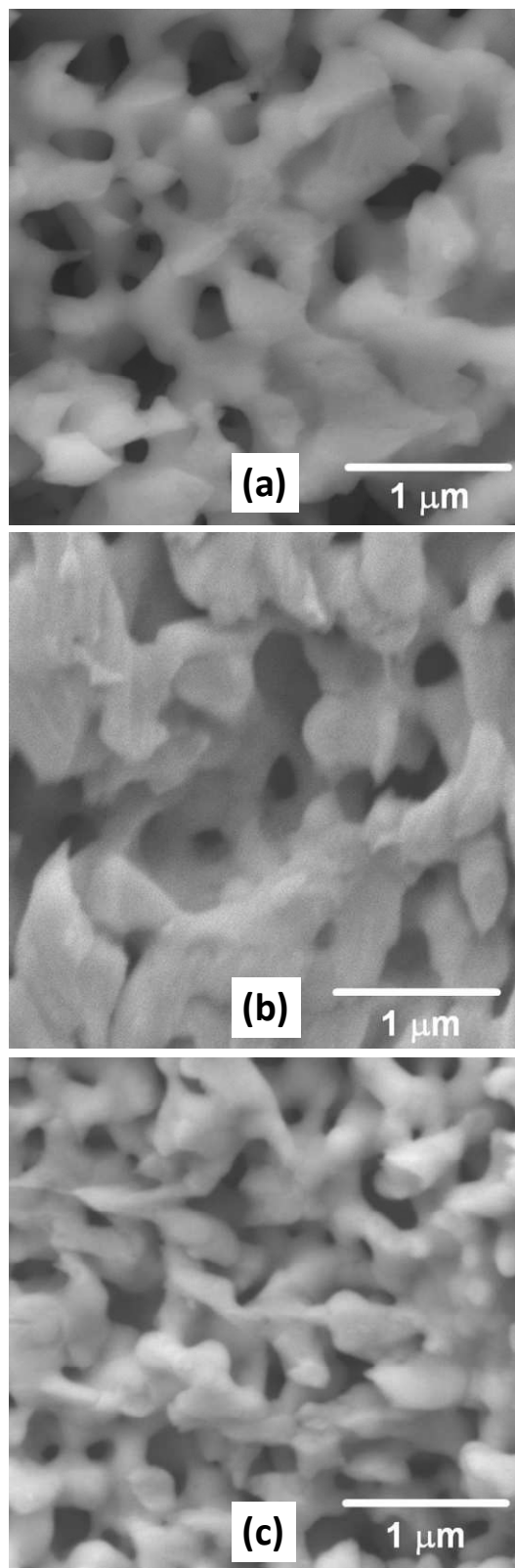


Fig. 7. Sintered microstructure of the silver attachments sintered under different atmospheres: (a) in N_2 , (b) in $N_2 + 4\% H_2$, and (c) in $N_2 + 1\% O_2$.

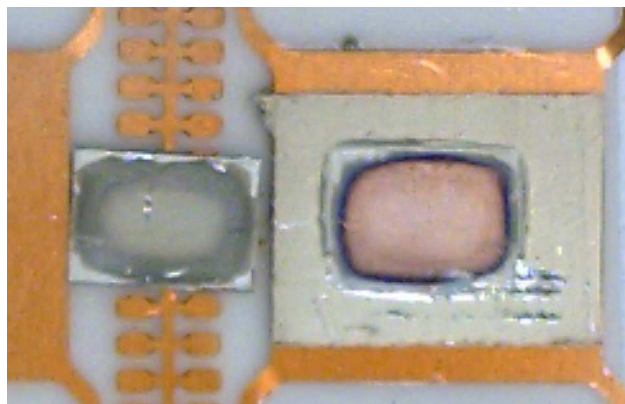


Fig. 8. Sheared attachment that was sintered in $N_2 + 1\% O_2$ showing a dark ring under the chip and on the silver remaining on the leadframe.

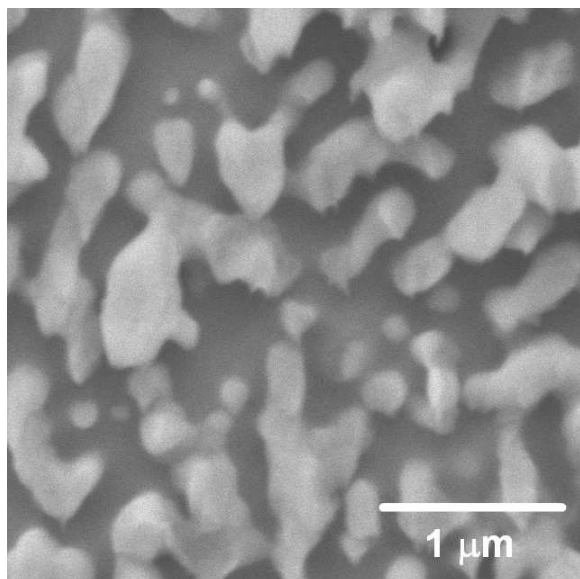


Fig. 9. SEM image of the crater exposing the copper after shearing the chip from the leadframe.

III. Conclusion

The research demonstrated the feasibility of small chip attachment on coated copper leadframe using sintered nanosilver paste similar to what can be obtained on bare copper substrate. Its process compatibility with the leadframe provides an alternative die attachment and interconnect materials to solder and epoxy. The coating on the leadframe makes it possible to perform drying separately that frees up the sintering furnace for increased throughput. The addition of hydrogen to the process atmosphere enhances sintering of the nanosilver paste that increases the bond strength. On the other hand, the presence of even a small amount of oxygen reduces the die shear strength due to incomplete binder burnout that hinders

sintering as well as causing oxidation of copper after the coating disappears at high temperature.

Acknowledgment

We would like thank Texas Instruments (Santa Clara, CA) for providing financial support and materials in the performance of the research.

References

- [1] J. G. Bai, "Low-Temperature sintering of nanoscale silver paste for semiconductor device interconnection," Ph.D. Dissertation, Dept. Mat. Sci. Eng, Virginia Polytechnic Institute and State University, Blacksburg, VA, 2005.
- [2] J. G. Bai, Z. Z. Zhang, J. N. Calata, and G.-Q. Lu, "Low-temperature sintered nanoscale silver as a novel semiconductor device-metallized substrate interconnect material," *IEEE Trans. Compon. Packag. Manuf. Technol.*, vol. 29, Sep 2006, pp. 589-593.
- [3] J. G. Bai, J. N. Calata, and G.-Q. Lu, "Processing and characterization of nanosilver pastes for die-attaching SiC devices," *IEEE Trans. Electron. Packag. Manuf.*, vol. 30, Oct 2007, pp. 241-245, 2007.
- [4] M. Knoerr and A. Schletz, "Power semiconductor joining through sintering of silver nanoparticles: evaluation of influence of parameters time, temperature and pressure on density, strength and reliability," in *Proc. 6th Int. Conf. on Integr. Power Syst. (CIPS)*, 2010, pp. 1-6.
- [5] H. Schwarzbauer, "Method of securing electronic components to a substrate," U. S. Patent 4810672, March 7, 1989.
- [6] H. Schwarzbauer and R. Kuhnert, "Novel large area joining technique for improved power device performance," *IEEE Trans. Ind. Appl.*, vol. 27, Jan/Feb 1991, pp. 93-95.
- [7] T. G. Lei, J. N. Calata, G.-Q. Lu, X. Chen, and S. Luo, "Low-temperature sintering of nanoscale silver paste for attaching large-area ($>100 \text{ mm}^2$) chips," *IEEE Trans. Compon. Packag. Technol.*, vol. 33, Mar 2010, pp. 98-104.
- [8] M. Knoerr, S. Kraft, and A. Schletz, "Reliability assessment of sintered nano-silver die attachment for power semiconductors," in *Proc. 12th Electron. Packag. Tech. Conf. (EPTC)*, 2010, pp. 56-61.
- [9] X. Cao, T. Wang, K. D. T. Ngo and G. Q. Lu, "Characterization of lead-free solder and sintered nano-silver die-attach layers using thermal impedance," *IEEE Trans. Compon. Packag. Manuf. Technol.*, vol. 1, April 2011, pp. 495-501.
- [10] J. N. Calata, G.-Q. Lu, K. Ngo and L. Nguyen, "Electromigration of sintered nanoscale silver films at elevated temperature," *J. Electron. Mater.*, submitted for publication.
- [11] V. R. Manikam and K. Y. Cheong, "Die attach materials for high temperature applications: a review," *IEEE Trans. Compon. Packag. Manuf. Technol.*, vol. 1, April 2011, pp. 457-478.
- [12] H. Zheng, L. Xu, J. Calata, K. Ngo, S. Luo, G.-Q. Lu, "Effect of oxygen partial pressure on sintering nanoscale silver die attachment on copper substrate," in *Proc. Int. Conf. on Electron. Packag.*, 2011, pp. 241-245.
- [13] H. Ogura, M. Maruyama, R. Matsubayashi, T. Ogawa, S. Nakamura, T. Komatsu, H. Nagasawa, A. Ichimura and S. Isoda, "Carboxylate-passivated silver nanoparticles and their application to sintered interconnection: a replacement for high temperature lead rich solders," *J. Electron. Mater.*, vol. 39, Aug 2010, pp. 1233-1240.
- [14] M. Maruyama, R. Matsubayashi, H. Iwakuro, S. Isoda and T. Komatsu, "Silver nanosintering: a leadfree alternative to soldering," *Appl. Phys. A: Materials Science and Processing*, vol. 93, Nov 2008, pp. 467-470.