Nano- And Micro-Filled Conducting Adhesives For Z-axis Interconnects

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We take a look at micro-filled epoxy-based conducting adhesives modified with nanoparticles for z-axis interconnections, especially as they relate to package level fabrication, integration, and reliability. A variety of conducting adhesives with particle sizes ranging from 80 nm to 15 µm were incorporated as interconnects in printed wiring board (PWB) or laminate chip carrier (LCC) substrates. SEM and optical microscopy were used to investigate the micro-structure, and conducting and sintering mechanisms. Volume resistivity of nanoparticle-modified adhesives is in the range of 10^{-5} to 10^{-6} ohm-cm. The present process allows fabrication of z-interconnect conductive joints having diameters in the range of 55-300 microns. There was no delamination of conductive joints after 3X IR-reflow (assembly precondition), pressure cooker test (PCT), and solder shock. The processes and materials used to achieve smaller feature dimensions, satisfy stringent registration requirements, and achieve robust electrical interconnections are discussed.

The needs of the semiconductor marketplace continue to drive density into semiconductor packages. The high end of this market appears to be standard Application-Specific Integrated Circuits (ASICs), structured ASICs, and Field-Programmable Gate Arrays (FPGAs). These devices continue to need increasing signal, power, and ground die pads, and a corresponding decrease in pad pitch is required to maintain reasonable die sizes. Traditionally, greater wiring densities are achieved by reducing the dimensions of vias, lines, and spaces, increasing the number of wiring layers, and utilising blind and buried vias. However, each of these approaches possess inherent limitations, for example those related to drilling and plating of high aspect ratio vias, reduced conductance of narrow circuit lines, and increased cost of fabrication related to additional wiring layers. One method of extending wiring density beyond the limits imposed by these approaches is a strategy that allows for metal-to-metal z-axis interconnection of subcomposites during lamination to form a composite structure. Conductive joints can be formed during lamination using an electrically conductive adhesive. As a result, one is able to fabricate structures with vertically-terminated vias of arbitrary depth. Replacement of conventional plated through holes with vertically-terminated vias opens up additional wiring channels on layers above and below the terminated vias and eliminates via stubs which cause reflective signal loss.

During the past few years, there has been increasing interest in using electrically conductive adhesives as interconnecting materials in the electronics industry. Conductive adhesives are composites of polymer resin and conductive fillers. Metal–to-metal bonding between conductive fillers provides electrical conductivity, whereas a polymer resin provides better processability and mechanical robustness.

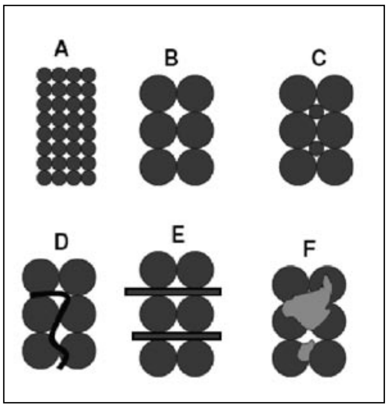
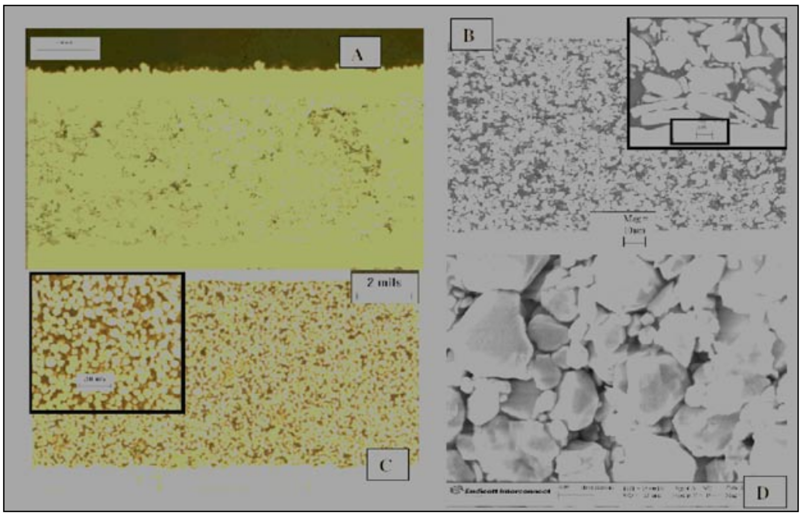


Figure 1 – A variety of adhesive-filled microvia structures. Adhesive consists of polymer and (A) nano particle, (B) controlled size micro particle, (C) nano-micro particle mixture, (D) nano tube/wire – micro particle mixture, (E) micro particle-sheet/flake (2D), and (F) micro/nano –low melting point particles

Figure 2 – Micrographs for the cross-sectional view of adhesives (A) Low melting point (LMP) alloys, (B) Silver micro particles, (C) Cu micro particles, and (D) mixture of silver nano and micro particles



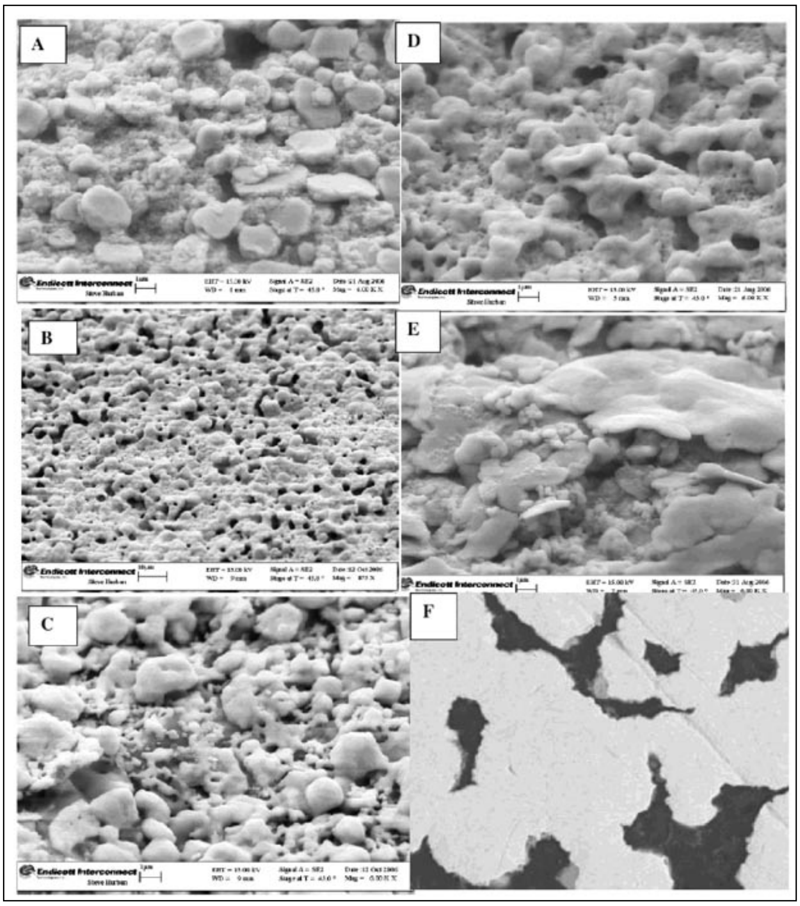
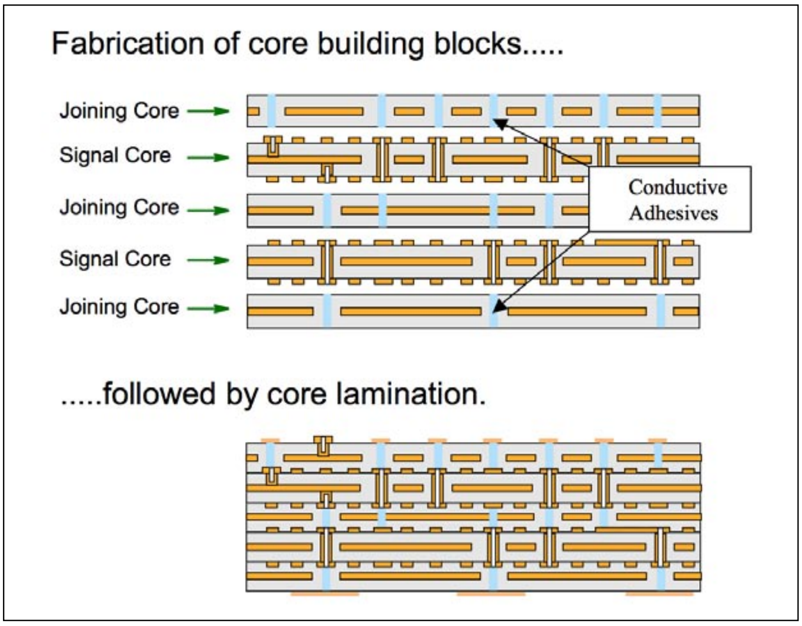


Figure 3 – SEM micrographs for the polymer nano-micro-composite filled silver based conducting adhesives; (A) un-sintered at 200°C, (B)-(D) sintered at (275 +10)°C, (E) un-sintered at 300°C, and (F) sintered micro-composites at 365°C

Conductive adhesives usually have excess filler loading that weaken the overall mechanical strength. Therefore, reliability of the conductive joint formed between the conductive adhesive and the metal surface to which it is mated is of prime importance. Conductive adhesives can have broad particle size distributions. Larger particles can be a problem when filling smaller holes (e.g., diameter of 60 µm or less), resulting in voids. Several nano-and micro-filled adhesives have been reported for advanced packaging applications. For example, Xiao et al describes epoxy or silicone based conductive adhesive joints and their thermal and mechanical stabilities. Jeong et al reported the effect of curing behaviours, solvent evaporation and shrink, on conductivity of adhesives. They also described conductivity of micro filled adhesives upon addition of nanoparticles. Lee reported on the addition of nano-sized silver particles to micro-sized flakes, and the effect on resistivity for these mixed-sized silver particle-filled conductive adhesives. Goh et al mentioned the effect of annealing on the morphologies and conductivities of sub-micrometer sized nickel particles used for electrically conductive adhesive. Inoue et al investigated the variations in electrical properties of a typical isotropic conductive adhesive (ICA) made with an epoxy-based binder that are caused by differences in the curing conditions. Coughlan et al described electrical and mechanical analysis of conductive adhesives where the main properties of joint resistance and adhesive strength were examined before and after different environmental treatments. Fu described cluster effects of nano fillers in conductive adhesives. Sancakter et al reported pressure-dependent conduction behaviour with particles of different sizes, shapes, and types. The effects of external pressure on the filler resistance were measured. Jiang et al reported on surface functionalised nano silver-filled conductive adhesives. Li reported that self-assembled monolayers (SAMs) protected silver nano-particle-based conductive adhesives. Although several composites are available for the advance of semiconductor technology, there is potential scope for improvement of the existing materials, so that low processing temperature, flexible, reliable processes and material can be developed for Z-axis interconnections. Furthermore, all studies

Figure 4 – Parallel lamination of subcomposites (cores) to form laminate chip carrier having four signal wiring planes with a stripline transmission line structure



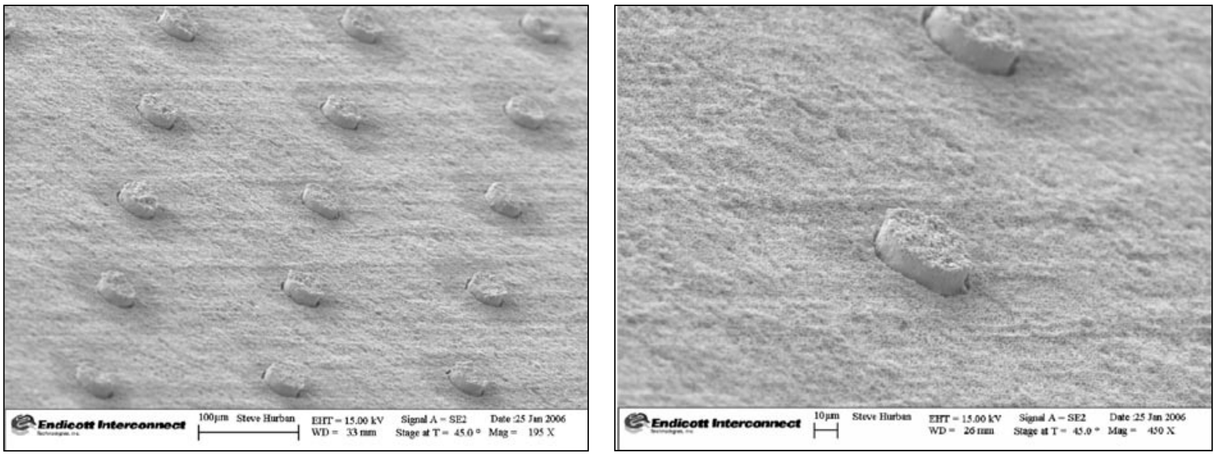


Figure 5 - SEM micrographs of adhesive-filled joining core; (A) 55 micron hole diameter, and (B) higher magnification

have described materials property and reliability assessment at a macroscopic level but have never described device level fabrication, integration and reliability issues. Conductive adhesives without device level integration will be of less importance for Z-axis interconnects.

The objective of this present study is to investigate the effect of nanoparticle addition to microcomposites. Nanoparticles of silver were chosen because of their higher electrical conductivity and chemical stability. Nanoparticles were mixed with microparticles to improve the sintering behaviour of the adhesives. The paper presents a reliability assessment of nanocomposite joints conducted by testing samples exposed to pressure cooker tests (PCT), IR-reflow, and solder shock. The work was extended to the development of a z-axis interconnect construction for a laminate chip carrier and printed wiring board (PWB). The structure employs an electrically conductive medium to interconnect thin cores (subcomposites). The cores are processed in parallel, aligned, and laminated to form a composite. The net effect is a composite laminate having vertical interconnections with small diameter holes that can terminate arbitrarily at any layer within the cross section of the package. There is no requirement for PTHs to be formed at the composite level. This effort is an integrated approach centring on three interrelated fronts: (1) materials development and characterisation; (2) fabrication of z-interconnect, and (3) reliability of the interconnect package.

Experimental procedure

A variety of silver, copper, and low melting point (LMP)-based nano and micro particles and their dispersion into epoxy resin were investigated in order to achieve uniform mixing in the adhesive. In a typical procedure, epoxy-based conductive adhesives were prepared by mixing appropriate amounts of the conducting filler powders and epoxy resin in an organic solvent. For conductivity measurements, a thin film of this paste was deposited on a substrate and cured at different temperatures ranging from 150°C to 365°C. For reliability assessments, two paste films were laminated together.

In the fabrication of a high-density laminate chip carrier, a joining core consisting of a single metal reference plane and no circuit traces for signal transmission (0S/1P) was constructed using a copper power plane, 35 µm thick, sandwiched between layers of a dielectric material composed of silica-filled allylated polyphenylene ether (APPE) polymer. Through holes in the joining cores, formed by laser drilling, and having diameters ranging from 50 to 75 µm, were filled with an optimised electrically conductive adhesive. The adhesive-filled joining cores were cured and cross sectioned to evaluate hole fill quality. Adhesives were characterised by Scanning Electron Microscopy (SEM) and optical microscopy to ascertain particle dispersion and interconnection mechanism. A Keithley micro-ohmmeter was used for electrical measurements.

Nano-micro and micro filled conductive adhesives

Nanoparticle generally refers to the class of ultra fine metal particles with a physical structure or crystalline form that measures less than 100 nanometers (nm) in size. They can be 3D (block), 2D (plate), 1D (tube or wire) structures. In general, nanoparticle-filled conductive adhesives are defined as containing at least some percentage of nanostructures (1D, 2D, and/or 3D) that enhance the overall electrical conductivity or sintering behaviour of the adhesives. Figure 1 represents a theoretical comparative model for a variety of possible structures based on powder filling a microvia. In this instance, the volume of the microvia is constant for all six cases. Conductivity is achieved through metal-metal bonding. Increasing the number density of particles increases the probability of metal-metal contact. Each contact spot possesses a contact resistance. For microparticles, the number density of particles will be much less than for nanoparticles. Therefore, microparticle-filled vias will tend to have a lower contact resistance, although the probability of particle-particle contact will be less. In the case of a nano-micro mixture, the micro-scale particles could maintain a low contact resistance, whereas nano-scale particles can increase number of particle contacts. Nano- and microparticle mixtures could be nanoparticle-microparticle, nanoplate (2D)-microparticle, nanotube (1D)-microparticle, or any combination of these three cases. Another possibility is use of low melting point (LMP) filler. The LMP filler melts and reduces interparticle resistance. Hence, conductive adhesives can be categorised as nano, micro, nano-micro, or LMP based systems.

Figure 2A shows a cross section of a LMP-based adhesive. LMP melts and produces a continuous metallic network. In the silver adhesive, the average filler diameter is in the range of 5 µm. Filler loading was high and adjacent particles united mutually and necking phenomena between fillers occurred; namely, a conduction path was achieved, as shown in Figure 2B. A similar result was observed when silver particles were replaced by 4 µm Cu particles (Figure 2C). A variety of silver filled adhesives with a mixture of nano and micro particles were studied. In nano-micro mixtures, nano particles occupy interstitial positions to improve particle-particle contact for conductivity. For the silver nano particles (~80 nm size), the fillers can self sinter and make a continuous conduction path. A high surface area of silver nanoparticles needs an excess amount of solvent in order to make high loading silver paste. Figure 1D represents micro structures of nano-micro silver filled adhesives.

Sintering

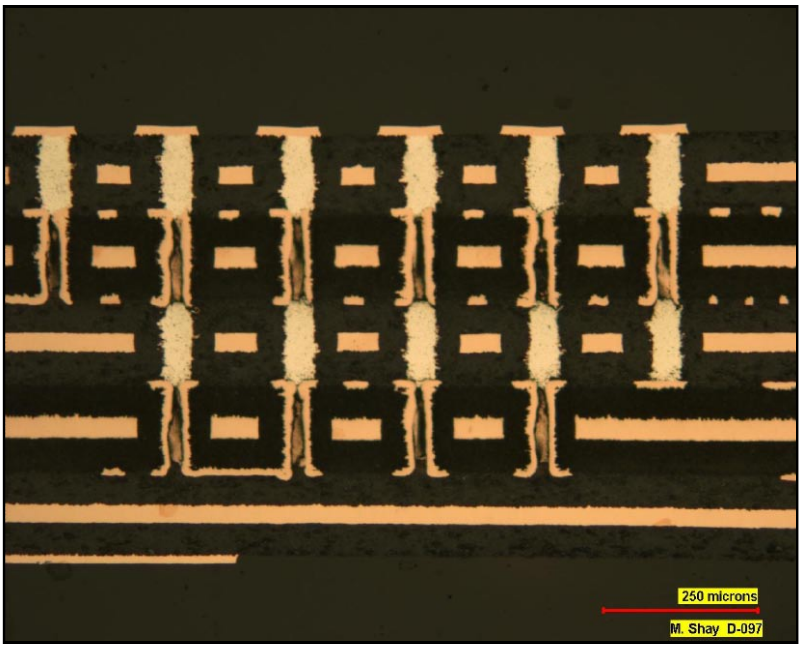
It is well known that change in grain size has a direct impact on the electronic properties of a system. In view of this, a systematic investigation of electrical resistance behaviour of silver nanocomposites has been carried out, and the results of such an investigation are presented here. Figure 3 shows SEM images of the specimens collected from nanoomposites with different sintering temperature, from lower temperature (Figure 3A) to higher (Figure 3E). As can be seen, the main components are a mixture of nanoparticles and microparticles. The nanoparticles may contact with the adjacent ones, but the nano aggregation lengths are short, less than 10-fold of the microparticle diameter on average (Figure 3A). As the sintering temperature increases, particle diffusion becomes more and more obvious. The aggregation length becomes much longer, resulting in the formation of one-dimensional jointed particle assemblies developing into a smooth continuous network (Figures 3B-D). Conductivity measurements show that the resistance drops 30-50% from 200°C to 265°C. In contrast, the nanocomposites synthesised with a nano-micro mixture show a much different morphology as can be seen in Figures 3E. The nanoparticles are less (low concentration approximately 84% metal). They are not following the same sintering mechanism as observed for the nanocomposite shown in Figures 3B-D. Instead, most of the particles maintain their identity, as if they didn't sinter with temperature. Figure 3 shows nanocomposites sintered at lower temperature and higher temperature. The observation suggests that the sintering mechanisms are different for the nanocomposites synthesised in the two different mixtures. Based upon the morphologies observed above, we suggest a sintering mechanism for the nanocomposites at low temperature as follows.

In the high-concentration region, nanoparticles are highly reactive due to immediate particle to particle contact. Moreover, the diffusion (sintering) of nanoparticles should be higher than that of the corresponding bulk solid. With the increase of size, the particles need higher temperature for diffusion to make a uniform metallic network. Figure 3F shows sintering at 365 oC for a microcomposites where minimum particle size in the range of 5 microns. However, in the low-concentration region (metal concentration approximately 84%), the polymer plays an important role. In this region, the amount of polymer is sufficient to prevent metallic diffusion/sintering (Figure 3E) even for 80 nm particle.

Core fabrication

Nanocomposites were used for hole fill applications to fabricate z-axis interconnections in laminates.

Figure 6 – Photograph of nanocomposite filled z-interconnect chip carriers with vias having 55 micron diameter shown in cross section



Conductive joints were formed during composite lamination using electrically conductive nanocomposites. Z-axis interconnection was achieved using joining cores. Through holes in the joining cores, formed by laser or mechanical drilling and having diameters ranging from 50 µm to about 300 µm, were filled with an nanocomposite based electrically conductive adhesive. The adhesive-filled joining cores were laminated with circuitised subcomposites to produce a composite structure. Lamination was used to cure the adhesive in the composite and provide Z-interconnection between the circuitised subcomposites. A variety of joining core structures such as 0S/1P (P= Power, S= signal), 0S/2P, etc. were used for hole fill applications. The cores can be structured to contain a variety of arrangements of signal, voltage, and ground planes. In addition, signal, voltage, and ground features can reside on the same plane.

By alternating 2S/1P and 0S/1P cores in the lay-up prior to lamination, the conductive nanocomposite electrically connects copper pads on the 2S/1P cores that reside on either side of the 0S/1P core. Two signal layers are added to the composite structure each time one adds an additional 2S/1P core and an additional 0S/1P core. A structure with four signal layers composed of five subcomposites (two 2S/1P cores and three 0S/1P cores) is shown schematically in Figure 4. Although this particular construction comprises alternating 2S/1P and 0S/1P cores, it is possible to place multiple 0S/1P cores adjacent to each other in the stack.

Figures 5 shows SEM micrographs of a joining core having paste-filled holes with a diameter of 55 µm as a typical representative example. A photograph of a composite laminate structure is shown in cross section in Figure 6. Proper preparation of the subcomposites is crucial to obtaining robust, reliable joining between dielectric layers and between the conductive paste and the opposing copper pad. Sufficient flow of the dielectric materials must be achieved during lamination to allow for complete encapsulation of circuitised features and achieve good dielectric-to-dielectric bonding. Package level and sub-composite level reliability of conductive joints in the test vehicle were further examined by IR-reflow (3X, 225°C), PCT and solder shock. No intrinsic failure mechanisms were observed. There was no cracking or delamination at the paste joints. Conductive joints are stable even after multiple IR-reflow (3X), and PCT followed by a 15 seconds solder dip.

Conclusions

A variety of micro-filled conducting adhesives modified with nano particles were used for a z-axis interconnection applications. High aspect ratio, small diameter holes anywhere in the range of 55 to 300 microns were successfully filled. Addition of nanoparticles reduces sintering temperatures of micro-filled conducting adhesives. Excess polymer (16% or higher) based adhesives were less sensitive to sintering. Conductive joints were stable after 3x IR-reflow, PCT, and solder shock. The nanocomposite-filled joining cores were laminated with circuitised subcomposites to provide stable, reliable z-interconnections among the circuitised subcomposites.

Optimised Copper Inks For Aerosol Jet Printing For Printable Electronics

Applied Nanotech Holdings announced that its subsidiary, Applied Nanotech (ANI), established a strategic development program with Optomec, a global leader in the emerging field of printed electronics for solar, display, electronic packaging and flexible electronics applications. As a part of the commitment, ANI will install a dedicated Optomec M3D Aerosol Jet printer at its facilities in order to adapt its copper ink to Optomec's patented ultra high resolution printing technology. By utilising ANI's copper ink, the Optomec printer will offer the solar, display, flexible circuit and PCB manufacturers contact-free deposition of high quality, low cost metal lines. According to Applied Nanotech, the Optomec printing solution is able to produce much finer lines than is currently possible with traditional screen printing and inkjet printing equipment. The combined ANI/Optomec copper ink printing solution will provide an alternative to silver inks facilitating lower cost, coupled with the promise of higher reliability. Furthermore, ANI's copper inks do not require expensive vacuum installation or inert gas environment lowering the cost of the capital for manufacturing equipment. According to Optomec, the company's customers have a rapidly growing appetite for Aerosol Jet proven materials as they deploy their systems in production applications for solar cells, displays, and printed electronics manufacturing. According to Applied Nanotech, today the metallic conductive ink technology is based on expensive silver inks. The electronic printing industry is actively looking to replace silver inks with copper inks that can be deposited at low temperature in air. These proprietary copper inks based on copper nanoparticles are available today at Applied Nanotech and the collaboration with Optomec will provide a total solution to the flexible electronics industry.

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