

Tech Talk

Fine Lines in High Yield (Part CLVII)

Nanoparticles in Electronics

Karl H. Dietz (for CircuiTree Magazine, October, 2008)



Karl Dietz is the development manager at DuPont's Electronic Materials Laboratory, Research Triangle Park, NC. His responsibilities include application studies for printed circuit materials. Karl has 35 years of experience in a variety of R&D, manufacturing and quality control functions and holds a PhD. in organic chemistry from the University of Frankfurt, Germany. If you would like to participate in the exchange or if you have any questions, Karl Dietz can be reached at 919-248-5248, fax: (919) 248-5132, or via e-mail <Karl.h.dietz@usa.dupont.com>.

There is growing interest in the use of nanoparticles and their use in nanocomposites, not only in electronics but also in other fields such as engineering polymers, surfaces finishes, optics, and medical applications. A SciFinder Search (2002 – 2006) shows a dramatic increase in nanoparticle references (see Figure 1), a trend that is continuing to the present. This interest stems from the fact that more and more examples are found where the incorporation of nanoparticles into composites can significantly change material behavior and yield desirable mechanical, optical and electrical properties otherwise not achievable.

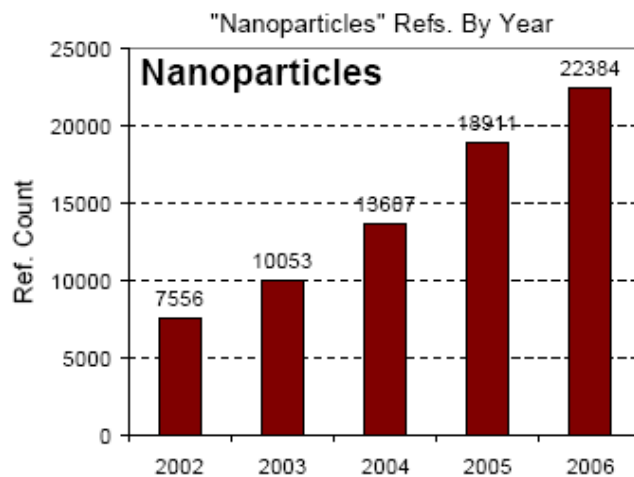


Figure 1: Growing Interest in Nanoparticles (SciFinder Search)


Since it is a challenge to form small particles and disperse them properly, the material property enhancements derived from nanocomposites have to be substantial and unique to warrant the effort.

Definitions of "nanoparticles" vary, but they typically describe sub-micron size particles which have sub-micron size in at least one dimension. The commercial availability of such particles is still limited. It includes fumed and colloidal silica, titania, alumina, certain clays, carbon black, noble metals, and soon carbon nanofibers.

There has always been a debate in electronic packaging about how to best achieve package reliability when materials of different CTEs (coefficient of thermal expansion) need to be used, leading to CTE mismatch and stress which can cause fractures. Most packaging engineers look



The miracles of science™




for materials with high fracture toughness, some look for low modulus materials. Having it both ways has not been possible which can be seen when modulus is plotted vs toughness for different material sets. A typical trade-off curve emerges that shows that modulus goes down as toughness increases. However, recent discoveries have shown that nanocomposites can break out of this trade-off dilemma in a very significant way, i.e. they exhibit both high toughness and modulus. These findings may translate into dielectric layers with improved reliability, a property that is especially critical for dielectric layers in packages close to the silicon chip which has a very low CTE.

Mainwaring and others (Ref. 1) report another remarkable example were the performance of a nanocomposite largely exceeds the prediction of conventional models such as Maxwell's law of mixtures. The Dk of a polyimide-alumina nanocomposite greatly exceeds the Dk of pure polyimide as well as pure alumina, and any volume fraction in between. Such behavior was successfully modeled by Vo & Shi who treat the polyimide-alumina interface as a separate, polarized third component.

It seems that the underfills used to release stress on solder joints between the low CTE chip and the higher CTE substrate would be a prime target for nanocomposites. These underfills are typically silica-filled epoxies. As the bump pitch gets finer and finer and the stand-off height between chip and substrate becomes lower, it becomes more difficult to achieve good flow and complete encapsulation with traditional underfills that feature micron-size filler particles. Likewise, pre-applied, no-flow underfills that contain large filler particles may not give reliable bump connections between the chip and the substrate. It is therefore not surprising to see development activities on underfills with nano-fillers. S. Rubinsztajn and others (Ref. 2 and 3) report on novel filler technology for no-flow and wafer level underfill materials using nano-filler technology. Reference 4 describes a novel no-flow underfill process and material whereby the underfill material does not contain an inorganic filler but a filler precursor. The inorganic filler itself can then be formed from the precursor during or after reflow of the solder bumps.

Soldermasks typically contain fillers that serve several functions, including serving as flame-retardants and acting as "crack-propagation stops" in the resin. Soldermasks for high end flip chip packages require good rheology to encapsulate very fine features and good resolution. The use of nano-size fillers is likely to improve these properties. A patent application (Ref. 5) describes a soldermask composition that requires no solvent, is UV-curable, contains a binder, acrylic monomers and photo-initiators as well as nanoparticle fillers. Soldermask compositions to be applied by inkjetting have been patented, containing inert filler particles with an average particles size of 300 nanometers and a typical particle size range of about 50 to 700 nanometers, for inkjet application with e.g. Printar's LGB809 printer.

Nano-metal or solder particles exhibit a unique characteristic: due to their high surface energy they melt (or sinter) at a lower temperature than the melting or reflow temperature of larger particles. This behavior is of particular interest in lead-free soldering where typical SAC alloys melt about 30-40°C higher than conventional tin/lead eutectics, and the higher processing temperature requires many process and material changes which have raised concerns about the reliability of electronic assemblies. While it is possible to lower the initial reflow temperature of lead-free nano-solder pastes, one has to keep in mind that repeat reflows, that may be necessary because of rework, will now only happen at the higher temperature that is characteristic for a given solder composition. The lower sintering temperature for nano-silver and nano-copper particles is a welcome property to form inkjetted conductors for printed electronic applications on certain organic dielectric platforms.



A Lead-Free Nano-Solder Project to study the application of nanotechnology to suppress non-lead solder reflow temperature is sponsored by iNEMI (International Electronics Manufacturing Initiative), and championed by Motorola Labs. Inkjetting of metallic nanoparticles for the formation of conductors is a very active field. A. Kamyshny and others from the Hebrew University of Jerusalem (Ref. 6) describe the inkjetting of an aqueous dispersion of silver nanoparticles, a composition that can be sintered at temperatures as low as 330°C to patterns with high conductivity. D. Kim and J. Moon of the School of Advanced Materials Engineering (Seoul, Korea), Ref. 7, describe the formation of highly conductive ink jet printed films of nanosilver particles for printable electronics. The influence of the metal particle size on the sintering temperature was studied and the resistivity as a function of sintering temperature was measured. S. Volkman and others of the University of California at Berkeley (Ref. 8) studied inkjetting of silver and copper conductors for printed RFID applications. They describe the formation of nanoparticles from metal salts by reduction with sodium borohydride. By optimizing the size of the nanoparticles and the organic encapsulant, they were able to inkjet metal conductors with low resistivity that could be annealed at 150°C. J. Sears and others of the Additive Manufacturing Laboratory (Ref. 9) studied a number of ways for maskless deposition of conductive inks and chose the M²D System (maskless mesoscale material deposition) which comprises pneumatic and ultrasonic atomizers, laser sintering, a heated stage positioning platform with a CAD/CAM interface. Furnace sintering was compared to laser sintering and low temperature photonic sintering. All methods yielded low resistance silver traces on substrates such as Kapton®, Mylar®, and rigid printed wiring board dielectrics.

Reference 10 describes the use of nano-filler particles in the formation of waveguides that are incorporated into printed circuit boards. The wave guide consists of a core polymer layer that is sandwiched between an upper and lower cladding layer. The nano-filler becomes part of the core polymer layer composition and its refractive index has to be close to that of the preferred polymer siloxane. The refractive index of the core composite is 0.5 to 5% larger than that of the upper and lower cladding.

References

1. P. Murugaraj, D. Mainwaring & N. Mora-Huertas, *Appl. Phys.*, 98, 054304 (2005)
2. Development of Novel Filler Technology for No-Flow and Wafer Level Underfill Materials, S. Rubinsztajn et al, *Journal of Electronic Packaging*, June 2005, Vol. 127, Issue 2, p. 77-85
3. Development of a Novel Filled No-Flow Underfill Material for Flip Chip Applications, A. Prabhakumar, S. Rubinsztajn et al, *Electronics Packaging Technology*, 200, 5th Conference (EPTC 2003), Vol.10, Dec. 2003, p.429-434
4. US Patent 6,943,058
5. Sachlev et al (IBM), US Patent Applic. No. 0138733 (2003)
6. Ink-jet Printing of Metallic Nanoparticles and Microemulsions, A. Kamyshny et al, *Macromolecular Rapid Communications (Wiley InterScience)*, Vol. 26, Issue 4, pg. 281-288
7. Highly Conductive Ink Jet Printed Films of Nanosilver Particles for Printable Electronics, D. Kim and J. Moon, *Electrochem. Solid-State Letters*, Vol. 8, Issue 11, pg. J30- J33 (2005)
8. Ink-jetted Silver/Copper conductors for printed RFID applications, S. Volkman et al, *Mat. Res. Symp. Proc.*, Vol. 814, Materials Research Society, 2004
9. Characterization of Conductive Inks Deposited with Maskless Mesoscale Material Deposition, Dr. James Sears et al, TMS, 2006 Annual Meeting, March 12-16, San Antonio, TX