Nanoparticle Thin-Film Coatings Exhibit Anti-Fogging, Anti-Reflective, and Self-Cleaning Properties

The Pitch

A water-based coating technology that can be used to create transparent conformal thin-film coatings of nanoparticles with nanometer-scale control over thickness and porosity has been developed by researchers in the Departments of Materials Science and Chemical Engineering at the Massachusetts Institute of Technology (MIT). The coatings have a variety of technologically useful properties such as anti-fogging, anti-reflection, and self-cleaning, and are of interest to the military and automotive industries.

In recent years, nanoparticles of various materials with a wide range of sizes (from a few nanometers to hundreds of nanometers) have become commercially available. The ability to controllably manipulate nanoparticles into functional thin-film coatings, however, has proven to be very challenging, particularly in the search for nanoscale control over the placement and arrangement of the nanoparticles. By controlling the packing of nanoparticles in a thin-film coating, for example, it should be possible to manipulate important parameters such as porosity, surface texture/roughness, and mechanical durability.

The Technology

About 40 years ago, a research project demonstrated that oppositely charged "colloidal particles" could be assembled from aqueous solutions into uniform thin-film coatings through the use of a layer-by-layer sequential adsorption process. Building from this research, the MIT group has further refined the technique and established the processing framework needed to controllably manipulate a variety of nanoparticles into functional thin-film coatings.

Key to the development of useful coatings was gaining a fundamental understanding of the role nanoparticle surface charge and size play in the layer-by-layer assembly process and identifying a means to render the resultant all-nanoparticle thin-film coatings mechanically robust. In the former case, it turns out that there exists a narrow solution pH-processing window for creating high-quality coatings with layer thicknesses comparable to the diameters of the nanoparticles, which may account for the reason that this approach has been neglected over the past 40 years.

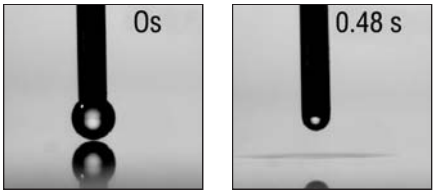

Figure 1. Images of a water droplet instantaneously wetting (<0.5 s) an anti-reflection coating. Sheet-like wetting of water droplets imparts anti-fogging characteristics to the coating.

The ability to render these coatings mechanically robust is clearly critically important for commercial applications.

Although the nanoparticle coatings can be assembled onto essentially any substrate, including substrates of complex shape and geometry, weak nanoparticle-nanoparticle interactions in the as-assembled thin films result in coatings that can be easily damaged with abrasion. The researchers have demonstrated that mechanically robust coatings can be created by familiar high-temperature calcination reactions (thermal treatment in the 500–550°C range) that essentially partially fuse the particles together. Clearly, such high temperatures are not suitable for plastic substrates. Thus, the researchers have also developed a lower temperature hydrothermal calcination process that produces similar or better results at temperatures as low as ~100°C. This latter development implies that commercially important plastic substrates such as those based on polycarbonate can be coated with the all-nanoparticle thin films.

The layer-by-layer deposition process provides control over the *z*-direction placement of nanoparticles of different sizes and over the level of nanoparticle aggregation within the film. As a result, it is possible to control the level and type of porosity within the film (from nano- to microporous) as well as surface roughness and texture. Thin-film coatings assembled with SiO_2 and TiO_2 nanoparticles, for example, exhibit extreme wetting behavior that is directly coupled to these important parameters. Both superhydrophobic and superhydrophilic coatings can be developed by controlling surface texture, porosity, and chemistry at the nano- and microscale. Superhydrophobic surfaces with advancing and receding water droplet contact angles in excess of 160° as well as stable superhydrophilic coatings with contact angles less than 5° in less than a second have been created by using this approach.

In the case of the superhydrophilic coatings, nearly instantaneous water wetting is observed as well as uniform water sheeting across the surface during drying. The net result is that the coating imparts anti-fogging characteristics to the substrate: light scattering water droplets do not form on the surface (see Figure 1). Since these effects are related to the wicking of water droplets into the nanoporous texture, the coatings are stable in time and do not require light activation as is the case for many TiO_2-based anti-fog coatings. The all-nanoparticle, thin-film coatings also significantly suppress light reflections from the substrate surfaces due to the low refractive index created by the presence of nanopores. Transmission levels can be higher than 99.6% in the visible region of the spectrum compared to the 94% level characteristic of uncoated glass. When TiO_2 nanoparticles are incorporated in the coating, an ultraviolet-light-activated self-cleaning effect is also observed. Thus, the coatings are multi-functional, exhibiting anti-fogging, anti-reflection, and self-cleaning properties.

Opportunities

Current efforts by the MIT researchers include the development of conformal Bragg reflectors, anti-fogging/anti-reflection coatings, transparent superhydrophobic coatings, and self-cleaning coatings. Partnerships aimed at developing the commercial potential of these coatings are welcomed. The technology is also available for licensing.

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Lightweight Metal–Graphite Composites Cool High-Power Electronics

The Pitch

Miniaturization in the electronics packaging industry has created a demand for innovative heat-removal materials that are lightweight, reliable, have high thermal conductivity, and are low cost. A family of metal-matrix composite materials has been developed that enables the electronic packaging engineer to specify thermal expansion to match the semiconductor package while maintaining the high thermal conductivity associated with aluminum- or copper-base plates and heat sinks. Metal Matrix Cast Composites, LLC (MMCC) has developed this family of lightweight, graphite, fiber-reinforced aluminum and copper alloys called MetGraf™, which can be made to match any coefficient of thermal expansion (CTE) over the range of 3–10 ppm/K (parts-per million-per degree Kelvin) by adjusting the metal-to-fiber ratio. By CTE-matching the semiconductor or semiconductor package, interfaces of low thermal conductivity can be eliminated, enabling the use of highly conductive adhesives or solders for improved heat dissipation and reliability. If the CTE-matching substrate also has high thermal conductivity, the same package can support higher thermal loads thus enabling faster and more powerful devices.

Materials currently used for high-performance electronic thermal management such as molybdenum/copper, tungsten/copper, aluminum/silicon carbide, and Kovar (an alloy of iron, nickel, and aluminum) have a narrow CTE range of ~7–10 ppm/K, are heavy, costly to machine, and have low (Kovar) to moderate thermal conductivity. However, while these materials can be designed to match the mid-range CTEs (7 ppm/K) of cofired ceramic (aluminum oxide) and beryllium-oxide–based electronic substrates, they have a limited range and cannot match emerging wide bandgap semiconductor materials such as SiC, GaN, Si, and AlN for substrates that require CTE values on the order of 4–5 ppm/K with greater heat sinking and dispersing capacity.

The market for matched CTE, high thermal conductivity, thermal management materials is estimated at ~$300 million, primarily consisting of applications in wireless communications, defense electronics, automotive and industrial electronics, space systems and satellites, military avionics, telecommunications, photonics, and semiconductor manufacturing. Materials selection depends on many factors, some of which include density, machinability, thermal conductivity, stiffness, and cost. In general, however, conventional materials are increasingly unable to meet the demands of many emerging technologies and thus system designers are forced to seek alternative solutions that can manage higher heat loads in smaller spaces.

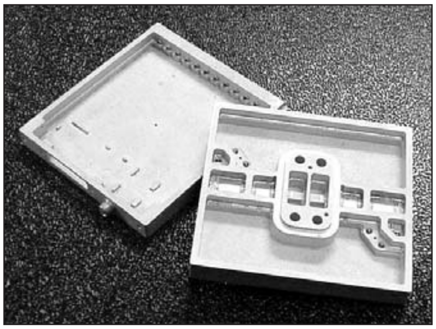

Figure 1. Au-plated aluminum graphite (Al MetGraf 7-200) transmit and receive modules.

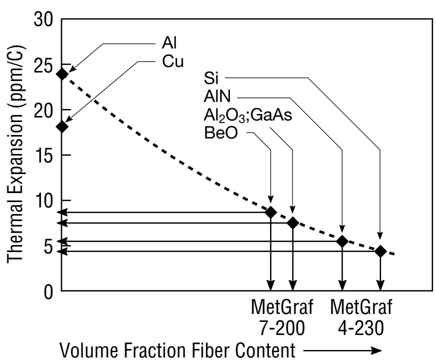

Figure 2. Thermal expansion of MetGraf as a function of the volume fraction of the graphite fiber content.

The Technology

A patented pressure infiltration process is used to infiltrate Al, Cu, and Mg alloys into graphite fiber preforms. This produces composite plate stock in various sizes that is easily machined to desired specifications, then plated with Ni, Au, or Ag for solderability. Au-plated Al-graphite transmit and receive modules for microelectronic packaging are shown in Figure 1. Low-cost, high-thermal-conductivity discontinuous graphite fibers are used that have a Young's modulus 4.5 times that of steel and 12.5 times that of aluminum with a negative CTE (graphite fibers shorten when heated). These properties act to constrain the expansion of aluminum or copper alloy matrices.

Materials with well-controlled properties are produced by designing the fiber architecture in a planar-isotropic array and controlling the volume fraction of fibers. Molten Al, Cu, or Mg alloys are then pressure-infiltrated into graphite fiber preforms (molds containing a graphite scaffold). Products with controlled expansion and high thermal conductivity are produced with CTE values 3–10 ppm/K. One of the Al-matrix products, designated MetGraf 7-200, has a CTE of 7 ppm/K from 20°C to 150°C plus an in-plane thermal conductivity of 200 W/mK. Another Al-matrix product, MetGraf 4-230, has a CTE of 4 ppm/K over the same temperature range with an in-plane thermal conductivity of 230 W/mK (Watts per meter Kelvin).

MMCC has developed a series of calibration curves for other CTE matches (see Figure 2). Copper-matrix products are manufactured with the same range of CTE values with in-plane thermal conductivity values of 300 W/mK. Both Al- and Cu-based materials are easily machined using standard tooling and are routinely plated with Ni and Ni + Au for ease of soldering to electronic packages.

This technology allows the continued development of high-power, high-frequency devices for computers, power supply, and high-frequency transmit and receive modules for advanced radar applications. In further advanced applications, MMCC is inserting high conductivity (>1500 W/mK) inserts into Cu- and Al-matrix composites for devices such as transmit and receive modules with extreme thermal load and cooling requirements but that still rely on CTE-matching to the device package to reduce or eliminate thermal stresses during heating or cooling.

Opportunities

The company is seeking new applications, contacts to further expand the market for these materials, collaborations, and investment to expand their marketing and manufacturing facilities.

Source: For information, contact James A. Cornie, Chief Technology Officer, MMCC, LLC, 101 Clematis Avenue, Waltham, MA 02453 USA; tel. 781-893-4449, fax 781-893-7230, and e-mail jcornie@mmccinc.com.

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Cost-Effective Solder Alternate for Electronics Protects Environment

The Pitch

To protect the environment, Europe, in 2006, mandated ridding electronics of lead, particularly the lead in solder. However, available lead-free solder technologies are costly. To address this problem, Aguila Technologies has developed innovative transient liquid phase sintering (TLPS) adhesives with enhanced thermal conductivity that are readily dispensable, re-workable, and provide at least twice the thermal conductivity of other commercially available polymeric adhesives. These new adhesives enable cost-effective manufacturing for a broad range of applications requiring die-attach (attaching a semiconductor chip to its packaging) by solder or adhesive bonding.

The Aguila bonding material (patent-pending) addresses several practical problems for die-attach operations including high effective thermal conductivity in the bond-line, low processing temperature (<200°C), dispensability, re-workability, and void-free assembly. It allows the use of adhesives in place of solders and enables reworking individual dies without having to scrap an already populated and functioning board. Initial applications are anticipated for wide bandgap semiconductor die-attach for radar transmit/receive (T/R) modules. The potential applications for this material also extend to other high-power radio frequency (RF) applications, light-emitting diode (LED) attachment, and other types of chips that require backside heat removal. The market for thermally conductive electronics adhesives currently exceeds $200 million and is growing.

The Technology

"Reduction of hazardous substances" or RoHS, refers to a directive from the European Union on the restriction of certain hazardous substances, including lead, in electrical or electronic equipment sold in the European Union after July 1, 2006. Aguila's lead-free, RoHS-compliant adhesive technology provides an effective bond-line conductivity of 16 W/mK. This is greater than a factor of two better than alternative, commercially available adhesives. For applications and industries not restricted by RoHS compliancy, the company's lead-containing adhesive provides conductivities greater than 40 W/mK. The high thermal conductivity of the Aguila TLPS adhesives results from the formation of robust metallurgical bonds at the interfaces of the surfaces to be joined (shown in Figure 1). Such metallurgical bonds are formed only when the TLPS adhesives are used in conjunction with metallized surfaces that are readily solderable.

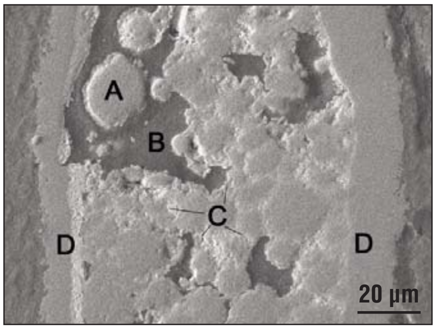

Figure 1. Cross-section of the bond-line on Ni /Au metallized surfaces showing phases: (A) high melting point filler; (B) low melting point interstitial; (C) intermetallics; and (D) adherend backside metallization.

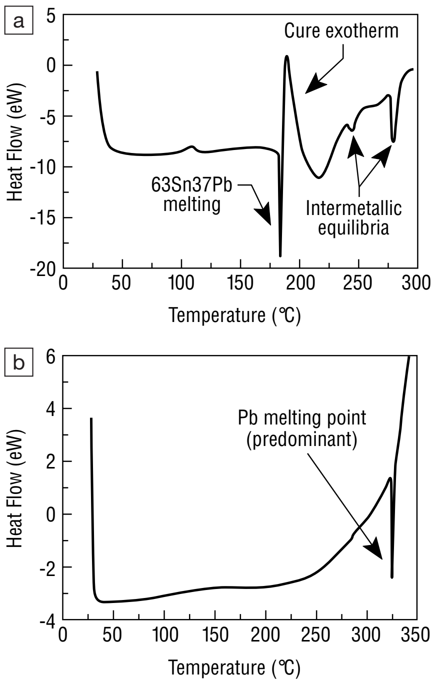

Figure 2: Differential scanning calorimetry (DSC) scans of the transient liquid phase sintering (TLPS) process before (a) and after (b) cure.

The transient liquid phase sintering process is made possible through the utilization of a polymeric binder containing flux (a paste applied with solder to aid it in flowing to a particular area) mixed with low- and high-melting point metallic powders in appropriate ratios. The binder is formulated to provide both a means for cross-linking as well as a fluxing functionality. During cure, the adhesives alloy with the backside metallization found on the joining surfaces while simultaneously undergoing cure and densification. In addition, the sintering and alloying process produces intermetallic compounds (ordered compounds composed of two or more metals) that are thermally stable at temperatures above the initial cure temperatures (as shown in Figure 2 for a Pb-containing solder). The cure results in the formation of metallurgical bond-lines that provide both enhanced thermal conductivity and also mechanically sound junctions at operating temperatures considerably above the glass transition temperature of the polymeric binder alone.

A further advantage of the Aguila die-attach adhesives is their ability to be reworked at relatively modest temperatures (<220°C). The die removal process was designed to ensure that surrounding devices and circuitry remain unaffected. The metallurgical nature of the bond-line enables new dies to be re-attached to the board without degradation of the mechanical, electrical, or thermal characteristics of the bond-line and assembly.

Opportunities

Aguila Technologies is seeking contracts, marketing partners, and licensees for their TLPS adhesive technologies.

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