Advanced Packaging

Particle Atomic Layer Deposition

Tailoring particle surface chemistry with atomic precision

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Increasing miniaturization and circuit density is an ongoing trend in electronics.[1] Consequently, today's electronics generate large amounts of heat. If heat is not properly dissipated, the operational lifetime and reliability of the electronics can be drastically reduced. Therefore, effective thermal management is critical. In many applications, it is important to couple a circuit with a heatsink via a highly thermally conductive material, which is usually a composite consisting of a filler in a matrix of epoxy, paste, or grease.

Filled-epoxy manufacturers say that the higher the cured thermal conductivity, the better. The mode of material application needs to remain consistent with current standard manufacturing practices. Users cannot tolerate large changes in viscosity, temperature, or application methods without having to modify their process equipment.

Boron nitride (BN) has a very high thermal conductivity of approximately 400 W/mK at 300 K, which is much higher than other thermal filler materials such as fumed silica (SiO_2, ~1.5 W/mK) and alumina (Al_2O_3, ~30 W/mK), and typical base epoxy matrices (~0.2 W/mK).[3,4] While these properties make BN a desirable choice as a filler material in thermal management applications, the loading of BN particles in composites is limited by the inertness of the BN surface and resulting viscosity of the composite matrix. The resulting viscosity increase limits particle loading in the epoxy and therefore the composite material's thermal conductivity. Higher loadings are needed as the microelectronics industry develops faster and denser integrated circuits that produce more heat.

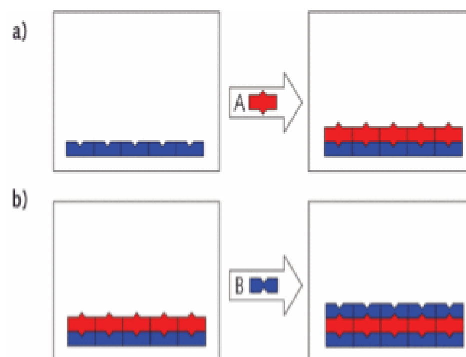

Figure 1. *Schematic representation of the digital processing control provided by the self-limiting reaction sequence of two precursors.*

Ultra-thin films can alter the chemical nature of the BN surface without adversely affecting the thermal conductivity of the BN particles. Al_2O_3 and SiO_2 are attractive coating materials because many epoxy

systems have been developed and optimized for use with Al_2O_3 or SiO_2 particles. The oxide film should be thin to minimize the effect of the coating on the thermal conductivity of the BN particles. In addition, SiO_2 could be selectively deposited only on the edge planes of the platelet-style BN particles. This could allow for better alignment of the BN platelets and higher package thermal conductivity.

Wet chemical processing and chemical vapor deposition (CVD) techniques can not easily control the deposition of ultra-thin films on particles, and uneven coatings often result because of limited conductance through convoluted pathways in particle beds. CVD approaches can also cause particle agglomeration unless the particle bed is effectively agitated or fluidized. In contrast, atomic layer deposition (ALD) is an ideal technique for depositing ultra-thin films with precise thickness control and high conformality; techniques have been developed for the deposition of Al_2O_3 and SiO_2 using sequential surface reactions.[5,6] Self-limiting surface reactions control the deposition at the atomic level in this approach. Consequently, uniform and conformal deposition will occur on high-aspect-ratio porous structures or particle beds.

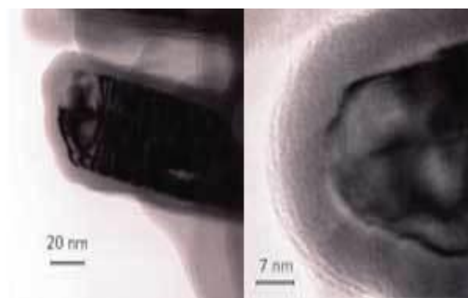

Figure 2. *TEM images of alumina-coated BN particulates (J.D. Ferguson et al., Thin Solid Films 371, 95 2000).*

ALD is a technique similar to CVD; however, self-limiting surface reactions are used to control the deposition of the film layer on the particle surface (Figure 1). Initially, the surface of a particle has a specific chemical functionality. The surface is then exposed to an ALD precursor (species A) that can react with that surface functionality, but not with itself. The reaction continues until all surface functional groups have been completely reacted with the precursor. At that point, species A is removed from the reactor and the surface is exposed to the second ALD precursor, species B, which will only react with the functional groups on the surface that resulted from the deposition of species A. Again, species B will continue to deposit until all active sites on the surface are functionalized to regenerate the original surface functionality, and prepare the particle for another cycle beginning with species A. Each reaction step is self-limiting, and only allows for one monolayer of the reactant to deposit. Film thickness can, therefore, be digitally controlled at the atomic scale by controlling the number of reaction cycles performed. Although ALD reaction kinetics vary depending on particle and coating chemistries, manufacture material cost is relatively insensitive due to the high-volume scale of existing fluidized bed reactor (FBR) systems. BN platelet particles are commonly used as fillers to increase the thermal conductivity of electronic plastic packages, but there are two limitations in the ability to improve performance. The first is poor surface wetting of the BN particles with the resin, which results in high viscosity and limited loadings. The second is poor interfacial adhesion of the BN particles to the polymer in the cured composite BN/epoxy matrix, which limits peel strength and thermal conductivity. Both of these limitations result from an inert BN surface that is difficult to modify by conventional CVD and wet chemical methods. A desirable designed BN filler particle maintains a high bulk thermal conductivity while the BN particle surface is controlled - but ultra-thin so as not to significantly reduce bulk thermal conductivity - to allow improved wetting and interfacial adhesion in polymer systems. The filler particle should contain Al-OH or Si-OH surface functional groups for improved wetting by

polymer coupling agents/resins prior to curing, and for greater interfacial adhesion in the cured composite. Moreover, the ideal technique should provide a means to coat individual primary BN particles and not agglomerates thereof (Figure 2). In some applications, it may also be desirable to selectively coat (i.e., functionalize) only edges and not basal planes of BN particles. Such a designed filler particle may provide for increased wettability and interfacial adhesion of the BN edges within a polymer matrix while maintaining high thermal conductivity via direct BN basal plane stacking.

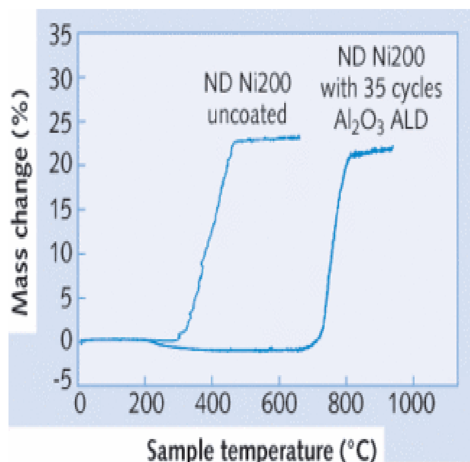

Figure 3. *Thermogravimetric analysis of increased oxidation resistance of 200-nm Ni particles after ALD coating with alumina (35 cycles).*

Controlling film thickness with conventional coating processes such as wet solution chemistry, physical vapor deposition (PVD), CVD, or plasma-enhanced chemical vapor deposition (PE-CVD) can be difficult. Unlike an adapted ALD technique, * these conventional processes have a tendency to agglomerate the particles and create additional particulate matter. PVD is a line-of-sight technique requiring ultra-high vacuum conditions, which works well for flat substrates but not with multidimensional structures such as particles, due to fluidization issues under high-vacuum conditions.

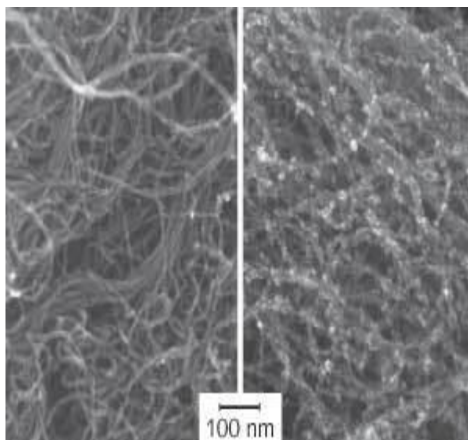

Figure 4. *TEM images of multi-walled CNTs before (left) and after 35 cycles of ALD coating with alumina (right).*

The general applicability of adapted ALD offers a level of process flexibility to produce customized composite particles for a variety of niche packaging applications, reducing composite design cycle time by providing engineers with a development tool to dial-in additive surface functionality while maintaining particle bulk properties. For example, an electronics packaging adhesive that requires high

thermal conductivity and electrically insulating properties may incorporate BN. If the incumbent adhesive has been designed for alumina-particle additives, then alumina-coated BN of the same size will typically exhibit similar rheological characteristics, and thus lend itself to a copy-exact manufacturing strategy. Further, the electrical properties of the adhesive could be altered by replacing the BN with other similarly coated alumina particles.

This technique can also be used to impart increased oxidation resistance to metal particles in multi-layer chip capacitors (MLCCs) and low-temperature co-fired ceramic packages (LTCC).[7] Base metals such as copper and nickel are used in the fabrication of MLCCs, and must be processed in an inert or reducing atmosphere to prevent oxidation. Improving the oxidation resistance of nickel, for example, allows the use of higher partial pressures of oxygen and/or higher temperatures during the organic binder burn-out phase of the MLCC firing process. This promotes complete removal of the organic and prevents the formation of carbon that may lead to defects in the resulting MLCCs. LTCCs currently use silver, gold, and other precious metals, but the ability to impart oxidation resistance to copper and nickel may allow the use of these less-expensive metals as conductors in LTCC packages.

Thermogravimetric analysis shows that one company's** 200-nm nickel begins rapid oxidation in air at around 300°C, but after 35 cycles of alumina ALD deposition, the temperature at which rapid oxidation begins increases to more than 650°C (Figure 3). The alumina film increases the overall particle mass by just 5%, while extending the oxidation temperature by over 325°C. The oxidation protection level of the film can be tuned (within certain limits) by varying the number of ALD reaction cycles. Other performance enhancements can be obtained by using different ALD chemistries.

Carbon nanotubes (CNTs) can also be functionalized by ALD coatings. Coatings on CNTs grow in two morphologies: conformal, where the ALD film covers the entire surface of the tube but is not chemically bonded to it; and decorated, where the film is chemically bonded to the surface but grows outward only from defect sites on the tube in an island growth fashion (Figure 4). The decorated coating is of particular interest, as the alumina islands on the CNT surface may allow for better compositing with a polymer matrix, leading to products with enhanced structural, thermal, and electrical properties.

Summary

This adapted ALD is an exciting technology that provides a mechanism to engineer additive surface chemistry with atomic precision. Moreover, this approach is directly scaleable to new material sets given the maturity of FBR systems. This ability to design and cost-effectively manufacture micro- and nanoscale particles will significantly reduce composite design cycle time for an array of electronic and structural applications.
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**NanoDynamics, Inc.

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