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Thermal and mechanical properties of epoxy composites with a binary particle filler system consisting of aggregated and whisker type boron nitride particles

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This study aims to investigate packaging materials based on polymer matrices for microelectronics. A binary filler system consisting of whiskers and aggregated particles of boron nitride (BN) was employed to improve the thermal conductivity of the epoxy resin. To prevent filler breakage during commercial mechanical mixing, a wetting method was used during sample fabrication. The polar functionalities introduced on the BN particles by sodium hydroxide treatment allowed the permeation of the epoxy resin because of a secondary interaction, which allowed the fabrication of a composite without voids. The maximized filler packing density and filler dispersion of the two kinds of fillers caused changes in the thermal conductivity. According to our results, the composite containing a 70:30 volume percent of the filler fraction of aggregated and whisker-type BN particles showed the maximum thermal conductivity. This is ascribed to the maximized formation of conductive networks combined with minimization of the heat resistance along the heat flow path. The filler composition and shape also resulted in composites with a higher storage modulus.

1. Introduction

As devices become increasingly smaller and faster, heat dissipation in microelectronic packaging has become a critical issue [1,2]. The operation of all electronic devices produces heat as an unwanted by-product. According to a previous study, the reliability of devices exponentially depends on the operating temperature of the junction. Even a small difference in the operating temperature can result in the reduction of the lifespan of the device by half. Therefore, it is crucial to dissipate the heat generated from devices as quickly and as effectively as possible to maintain the operating temperatures of the device at a desired level [3]. Traditionally, in typical flip chip assemblies of microprocessors, heat sinks are used to remove heat from the device. However, the heat dissipation capacity of a heat sink decreases due to the interfacial thermal resistance arising from a mismatch between the surface roughness of the device and the heat sink resulting in poor thermal contact. Thermal interface materials (TIMs) have been introduced to fill the gap between asperities and minimize thermal contact resistance [4]. Extensive research has been carried out to develop novel TIMs based on thermosetting or thermoplastic polymers. In particular, epoxy resin, an electrical insulator, has been widely used because of its excellent processability. However, epoxy cannot sufficiently dissipate heat because of its low thermal conductivity (~0.2 W/m K). To effectively solve the thermal dissipation problem, the use of epoxy composites with different ceramic fillers has been investigated. The properties of these epoxy/ceramic filler composites depend on the nature of the ceramic fillers, including their chemical and physical composition, size, shape, and dispersion in the matrix. Some thermally conductive fillers, such as boron nitride (BN), have been considered as attractive candidates on account of their advantageous properties, such as high temperature stability, large thermal conductivity, high mechanical strength, extreme hardness, corrosion resistance, and oxidation resistance. These properties make BN an interesting material for many applications, such as in refractories, as lubricants, in grinding, optical coatings, and ceramic composites [5–7].

The orientation of the filler can affect the thermal conductivity of the composite and is particularly important for non-spherical anisotropic fillers. Generally, BN occurs as two-dimensional hexagonal flakes exhibiting an in-plane thermal conductivity of 600 W/m K; almost 20 times higher than the through-plane thermal conductivity. Unfortunately, due to gravity, most fillers lie along a direction perpendicular to the heat transport direction. Therefore, it is widely accepted that significant enhancement in the thermal

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conductivity can be achieved by controlling the alignment of the fillers and the direction of their thermal conductivity along the heat transport direction. Recently, some novel methods to control the filler orientation have been reported. However, these methods result in the enhancement of the thermal conductivity only at low filler loadings because a large amount of the filler causes an increase in the viscosity, interfering with the filler orientation. The proposed methods show significant enhancements; however, the thermal conductivities are marginal compared to that expected from systems with a high filler loading fraction [8,9].

The preferred method to control the filler orientation is to control the shape and direction of the filler. In the present case, we have used aggregated BN (A-BN) and whisker-shaped BN (W-BN) as shape controlled particles. Nearly spherical A-BN particles were obtained by the thermomechanical aggregation of hexagonal BN (H-BN), while the W-BN particles were obtained by the crystal growth of small BN flakes [10]. Since the A-BN particles were formed by the random aggregation of H-BN, the in-plane direction of the constituent H-BNs were lie on the outer direction of the particle. In the case of W-BN, when H-BN powder containing a sufficient amount of oxygen was heated between 1750 and 2100 °C in a nitrogen atmosphere containing carbon, numerous BN sheets were produced, stacking together to form the BN whiskers. The radial direction of the W-BN particles was perpendicular to the bottom because the W-BN particles were laid by gravity. Because the dominant crystalline direction of these particles was almost parallel to the heat dissipation direction of the TIM, we expected that these shape controlled fillers might effectively enhance the thermal conductivity.

Most commercial process of blending used for polymer composites reinforced with fillers involves extrusion. Extrusion is used extensively for mixing, compounding, or for the reaction of polymeric materials. The versatility of the extrusion equipment allows the operating parameters to be configured specifically for the formulation involved. In addition, the configurations of the extruder screws themselves may be varied using forward conveying elements, reverse conveying elements, kneading blocks, and other designs in order to achieve particular mixing characteristics. Despite its wide use, extrusion has several major drawbacks, such as particle breakage [11]. Due to the high shear forces generated during the process, relatively soft particles can undergo damage and cracking. In the present case, shape controlled BN particles were used as thermally conductive fillers. A-BN and W-BN were processed to obtain small aggregations of H-BN by mechanical force. The H-BN particles are plate-like with flat surfaces, which correspond to the basal planes of the hexagonal crystal structure. The basal plane of BN is molecularly smooth and is devoid of surface functional groups that enables chemical bonding or other interactions. In contrast, a few functional groups, such as hydroxyl and amino groups, are found on the edge planes of the pellets. These functional groups allow the dispersion of the BN filler to form chemical bonds with other molecules in organic solvents. Due to their intrinsic nature, BN, A-BN and W-BN are held together only by weak physical aggregation. When the physical aggregation is broken, the advantage of the controlled shape is lost. Hence, to maintain the shape and properties of the fillers, it is essential to use a composite fabrication method, which does not involve mechanical milling.

In our previous study, we reported a new operationally facile composite fabrication method, i.e., the wetting method. This method avoids the use of an added solvent and mechanical mixing of the filler and the matrix [12,13]. To prepare a composite by the wetting method, it is necessary to increase the wettability by modifying the surface of the filler to enable the effective absorption of epoxy. Gravitational force can be considered is critical for driving the drop movement after the epoxy drop has wetted the tilted BN surface; however, the surface wettability is also an important factor in achieving the homogeneous distribution of epoxy in the composite structure because the epoxy partly penetrates in the direction lateral to the gravitational force. To increase the wettability, we used sodium hydroxide treatment to introduce hydroxyl groups. According to our previous study, sodium hydroxide treatment was suitable for treating the BN surface to accomplish enhanced wettability with epoxy.

Theoretically, thermal resistance is caused by phonon scattering. Polymer composites with high thermal conductivities can be obtained by adding fillers with high intrinsic thermal conductivities. However, as discussed by Bigg, when the intrinsic thermal conductivity of the filler is 100 times greater than that of the polymer matrix, the improvement in the thermal conductivities of the polymer composites is insignificant. Experimentally obtained thermal conductivity values are much lower than those estimated by the rule of mixture approach [14]. On the contrary, the aspect ratio of the filler is a more important parameter for dictating the thermal conductivity of a composite; the fillers with large aspect ratios easily form interconnections, which are termed as a conductive network. The formation of random bridges or networks of conductive fillers facilitates phonon transfer leading to high thermal conductivities. This implies that a hybrid filler system with a large formation of networks is necessary to prepare next generation heat dissipation materials. Therefore, to maximize the abundance of thermally conducting paths, the polymer composites were filled with hybrid fillers consisting of particles of different sizes at near-maximum packing loading determined experimentally. In addition, surface modification and the wetting method were used to attempt to minimize the particle damage.

2. Experimental

2.1. BN surface modification

BN particles consist of only a few functional groups and surface treatment is necessary to enhance the wettability to enable epoxy penetration into BN film. Hence, the BN particles were suspended in a 5 M sodium hydroxide (NaOH) solution at 130 °C for 48 h to introduce hydroxy groups onto the surfaces of the BN particles. Generally, NaOH is used for the hydroxyl functionalization of ceramic particles. Particles were dipped into a solution of NaOH, and were rinsed with deionized water and filtered several times until a neutral pH was observed. The BN particles treated with NaOH (BN-OH) were then treated in a furnace at 80 °C for 5 h, cooled to room temperature, and then stored in desiccators.

2.2. Composite preparation

In this study, the composites were fabricated by a novel wetting process. The two types of BN particles at various volume ratios (10:0, 7:3, 5:5, 3:7, 0:10) were homogeneously dispersed in ethanol using ultrasonication. The mixture was poured into a glass mold and placed on a silicon oxide membrane (0.2 μm, Anodisc, Whatman, USA). The mixture poured into the glass mold was filtered via vacuum filtration. After filtration, the BN film was dried at room temperature as slowly as possible to prevent cracking of the surface. The BN film was then peeled off of the SiO_2 membrane. Subsequently, epoxy containing the curing agent (equivalent weight ratio = 1:0.4) was placed on the BN film. The BN film was kept in a furnace maintained at 80 °C for a few hours to maintain the fluidity of the epoxy and enable effective penetration. The epoxy easily penetrated into the fabricated BN film because of its