



Vertical filler alignment of boron nitride/epoxy composite for thermal conductivity enhancement via external magnetic field



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ABSTRACT

Anisotropic boron nitride (BN) was vertically aligned along the direction of heat transport using a magnetic field. Iron oxide nanoparticles deposited onto the BN surface act as a magnetically responsive material allowing particle alignment. The amount of iron oxide deposited, and therefore the magnetic response, is easily controlled by modulating the precursors. The polarization of paramagnetic iron oxide in the magnetic field leads to the formation of vertical particle arrangements. The thermal conductivity of the synthesized vertically aligned composite increased from $1.765 \text{ W m}^{-1} \text{ K}^{-1}$ to $3.445 \text{ W m}^{-1} \text{ K}^{-1}$ with 30 vol% filler loading that is a 1.96-fold increase compared with a randomly oriented composite. The filler content affected both particle dispersion and arrangements, with homogeneously dispersed fillers aggregating due to induced dipole interactions into column-like structures with favorable thermal transport properties.

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1. Introduction

Microelectronic packaging is playing an increasingly important role in the advancement of electronic and electric technologies as electronic devices, communication equipment, and lighting apparatuses become ever denser and more powerful [1–3]. These improvements in size and performance result in more heat being generated in smaller volumes. Increasing temperatures are known to cause exponential decreases in mean lifetimes, resulting in device failure and inducing power leakages that lead to degraded performances [4]. Efficient heat dissipation is therefore crucial to maintain device operating temperatures at desired levels. Traditionally, heat sinks are used in flip chip assemblies of microprocessors to remove heat from the device. However, the heat dissipation capacity of a heat sink decreases due to interfacial thermal resistance caused by the poor thermal contact between the heat sink and the device, arising from a mismatch in surface roughness. In this context, thermal interface materials (TIMs) have been introduced to fill the gap between asperities and thereby minimize thermal contact resistance [5].

TIMs are based on polymer resins that are loaded with thermally conductive filler material. Polymers are normally used because of

their high resistivity and low dielectric constant. Epoxy resins in particular are some of the most widely used polymers in present-day microelectronic packaging because of its excellent adhesive properties and processability. However, because of their low thermal conductivity, epoxy resins do not dissipate the heat generated in such devices effectively [6,7]. Several studies have been devoted to improving the thermal conductivity of polymers, with thermally conducting fillers such as AlN, BN, Al_2O_3 , and SiC having emerged as a cost-effective solution to thermal management issues [8–10]. Generally, extremely high filler loading, typically larger than 50 vol %, is required to achieve high thermal conductivity when these conventional composite fabrication methods are used. However, one of the major drawbacks of composites with such high filler loading is the degradation of the mechanical properties of the polymer, with the rigid (typically ceramic) filler particles acting as defects in the polymer matrix. Moreover, these high filler loadings reduce the processability of the material—one of the major advantages of polymers—because the viscosity of the composite increases with the filler volume fraction [11]. In order to achieve both high thermal conductivities and reasonable mechanical properties, a novel approach is required based on low filler loading.

Recently, particle alignment has been shown in a variety of industrial applications, notably in biology, microfluidics, and electronics [12–14]. Yoshihara et al. achieved molecular orientation along the injection direction and studied its effect on thermal conductivity [15]. However, this method is not broadly applicable

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because of the very particular synthesis method, namely extrusion from a processable melt mix thermoplastic matrix. Although extrusion is a widely used compounding method, it has several drawbacks, two major ones being a limited filler content and particle breakage. Indeed, because of the very high shear forces generated in the process, relatively soft particles can be damaged and cracked. Moreover, the viscosity of the paste increases sharply with filler content, restricting the latter. Furthermore, the method described cannot produce true particle arrays because their alignment is fixed to the injection direction. Garcia et al. reported hybrid laminates with aligned carbon nanotubes fabricated in-situ using chemical vapor deposition [16]. However, this procedure is not suitable for compounding due to prohibitive manufacturing costs and to the thermal damage inflicted at high temperatures on the composite. An alternative approach for effective filler alignment is therefore highly desirable, which would be both applicable to composites and flexible in terms of the alignment direction.

Among the different particle array methods, magnetic field alignment is particularly attractive in this regard since the external magnetic field affords total control over the alignment direction, but also because the procedure is inexpensive and does not damage the composite. In this study, boron nitride was chosen as a thermally conducting filler due to its high thermal conductivity, chemical stability and electrical insulation properties. 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 with an in-plane thermal conductivity of $600 \text{ W m}^{-1} \text{ K}^{-1}$, almost 20 times higher than its through-plane thermal conductivity [17]. Therefore, controlling the orientation of BN in the polymer matrix is critical in optimizing the performance of its composites. Magnetic alignment requires the filler to respond to the external magnetic field. Although BN is not an intrinsically magnetic material, magnetically responsive BN can be prepared from commercial BN by surface modification using superparamagnetic iron oxide nanoparticles (magnetite). Iron oxide nanoparticles interact with poly(vinyl pyrrolidone) (PVP)-coated BN surfaces through electrostatic interactions between the positively charged nanoparticles and the negatively charged PVP. This magnetically actuable BN is the tool that will allow the properties of anisotropic materials to be manipulated through the magnetic field.

2. Experimental section

2.1. Synthesis of Fe_3O_4 -decorated BN

BN surface treatment was performed using a sodium hydroxide solution. Indeed, BN particles have few surface functional groups and strong chemical resistance. Therefore, surface treatment was required to open the particles to chemical or physical bonding. Generally, hydroxide ions attack and break structural defects on the particle surface and replace them with hydroxyl functional groups. However, due to the strong chemical resistivity (quasi chemical inertness) of BN, the surface chemical bonds are particularly resistant, such that very high concentrations of sodium hydroxide and strong reaction conditions are required to permeate BN structural defects. The BN particles were suspended in a 5 M NaOH solution at $120 \text{ }^\circ\text{C}$ for 48 h to attach hydroxide functional groups onto their surface [18]. The particles were then rinsed with deionized (DI) water and the basic solution was filtered several times to restore a neutral pH. The BN hydroxide (BN–OH) particles were left in a furnace at $80 \text{ }^\circ\text{C}$ for 5 h, allowed to cool to room temperature, and then stored in desiccators.

Next, iron oxide nanoparticles were synthesized on the BN surface by hydrolysis of an aqueous solution. First, 1.5 g of PVP was

dissolved in 100 ml DI water and 0.5 g of BN powder was added with magnetic stirring to homogenize the aqueous dispersion. A few hours later, a certain amount (see Table 1) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added into the BN dispersion, which was then stirred at $90 \text{ }^\circ\text{C}$ overnight. When a feeding ratio of iron precursor to BN is changed for 0.1–2, the Fe_3O_4 coated BN particles are denoted as BN– Fe_3O_4 (0.1), BN– Fe_3O_4 (0.5), BN– Fe_3O_4 (1), BN– Fe_3O_4 (1.5), and BN– Fe_3O_4 (2), respectively. The feeding ratio was the weight ratio between $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and BN particle when all of the precursor was converted to iron oxide. At this stage, the positive Fe ions are attracted to the negatively charged PVP leading to the formation of gel-like $\text{Fe}(\text{OH})_3$ [19]. This $\text{Fe}(\text{OH})_3$ was aged at $90 \text{ }^\circ\text{C}$ for 4 h producing FeOOH particles, which were reduced by hydrazine monohydrate to form strongly magnetic Fe_3O_4 nanoparticles. These were finally washed in DI water; in contact with water, the hydrophilic PVP dissolves quickly and leaving the BN– Fe_3O_4 behind [20]. Finally, the products were washed with DI water, filtered several times, and vacuum-dried at $80 \text{ }^\circ\text{C}$ for 5 h to remove the solvent. Scheme 1 illustrates the fabrication procedure of iron oxide-coated BN.

2.2. Fabrication of the aligned BN/epoxy composites

For this study, a mixture of bisphenol-A to DDM (4,4'-diaminodiphenylmethane) was prepared with a 1:0.4 equivalent weight ratio. First, 3.184 g of DDM was placed in a four-neck round-bottom flask equipped with a reflux condenser and was preheated to $120 \text{ }^\circ\text{C}$. Then, 30 g of bisphenol-A resin was added and the mixture was heated in an oil bath at $120 \text{ }^\circ\text{C}$ for 15 min under N_2 atmosphere. Bubbles were removed by placing the mixture in a vacuum oven for 30 min at room temperature.

Samples were prepared containing 10, 20, 30, and 40 vol% BN and BN– Fe_3O_4 thermally conducting particles. Each epoxy/filler mixture was homogenized using a magnetic stirrer, poured into polytetrafluoroethylene (PTFE) molds, degassed in a vacuum oven at $50 \text{ }^\circ\text{C}$ for 1 h, then sandwiched between two strong magnets, and finally cured in a convection oven at $120 \text{ }^\circ\text{C}$ for 3 h. The strength of magnetic field between Teflon mold is 0.4 T.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a VG Microtech ESCA2000 system equipped with a Mg $K\alpha$ X-ray source (1253.6 eV) and a hemispherical analyzer. During curve fitting, the same Gaussian peak widths were used for each spectrum. X-ray diffraction (XRD) patterns were collected using a D8-Advance, Bruker-AXS diffractometer at a scan rate of 1°s^{-1} over a 2θ range of $5\text{--}70^\circ$ with Cu $K\alpha$ radiation (0.154056 nm). Field-emission scanning electron microscopy (FE-SEM, Carl Zeiss, Sigma) was used to inspect particle morphologies before and after iron oxide coating and to investigate film cross-sections. The samples were sputtered with a thin layer of platinum before FE-SEM observations to avoid charge accumulation. Energy

Table 1
The amount of iron salt, density and Fe_3O_4 /BN weight ratio of BN and various BN– Fe_3O_4 particles.

	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ [g/1 g of BN]	Density [g/cm ³]	Fe_3O_4 /BN ratio [g/BN 1 g]
Raw BN		2.2851	0
BN– Fe_3O_4 (0.1)	3.5022	2.3455	0.0498
BN– Fe_3O_4 (0.5)	7.0044	2.3921	0.0898
BN– Fe_3O_4 (1)	10.5066	2.5113	0.1989
BN– Fe_3O_4 (1.5)	14.0088	2.6345	0.3232
BN– Fe_3O_4 (2)	17.5110	2.6434	0.3327

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