

Large-scale production of boron nitride nanosheets-based epoxy nanocomposites with ultrahigh through-plane thermal conductivity for electronic encapsulation

Zhijian Sun^{a, c, 1}, Michael Yu^{a, 1}, Jiaxiong Li^{a, c}, Macleary Moran^a, Mohanalingam Kathaperumal^{b, c}, Kyoung-Sik Moon^{a, c}, Madhavan Swaminathan^{b, c}, Ching-Ping Wong^{a*}

^a School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States.

^b School of Electrical and Computing Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States.

^c 3D Microsystems Packaging Research Center, 791 Atlantic Dr. Atlanta, Georgia 30332, United States.

Corresponding author: cp.wong@mse.gatech.edu (C.P. Wong)

¹ Zhijian Sun and Michael Yu contributes equally.

Abstract—

Recent advances in two-dimensional (2D) nanomaterials have generated great interest in the investigations of these materials for wide ranging applications in the micro- to nano-scale electronics, healthcare, and energy storage areas. In particular, 2D materials such as boron nitride nanosheets (BNNS) have been studied extensively due to their unique material properties that include a large specific surface area, high thermal conductivity (~ 750 W/mK), and wide bandgap (~ 5.5 eV), along with the associated electrical insulation. In this paper, we prepared BNNS by liquid exfoliation of hexagonal boron nitride (h-BN). Liquid exfoliation is an enhanced method to achieve large-scale and low-cost production, which is more suitable for large volume applications. In this paper, we have combined low-energy ball milling and sonication methods to produce BNNS on a large scale.

BNNS have a high in-plane thermal conductivity due to their 2D morphology but a lower through-plane thermal conductivity. Also, the thermal interface resistance between BNNS is also an important factor that impedes the through-plane thermal conductivity. Thus, we employed a vacuum filtration method to obtain thick BNNS cakes. These cakes have a high x-y/in-plane thermal conductivity and a low z/through plane thermal conductivity. After slicing the cake vertically, it is rolled over to convert the strong x-y plane thermal conductivity to the z-plane. The now high thermal conductivity z-plane allows for effective 3D electronic packaging. Following this, BNNS are infiltrated into epoxy resins to fabricate epoxy nanocomposites with a low filler loading. This paper presents detailed studies on the coefficient of thermal expansion (CTE), electrical resistivity, thermal stability, and thermomechanical properties of the synthesized BNNS-epoxy nanocomposites. This study reveals the promising applications of high performance, thermally conductive epoxy nanocomposites in advanced packaging technologies such as 2.5D/ 3D packaging.

Keywords: 2D Materials, Boron Nitride, Epoxy Nanocomposites, Thermal Conductivity, Semiconductor Packaging

I. INTRODUCTION (*HEADING 1*)

As modern technology rapidly advances every year, the components that make up these electronic devices need to be improved simultaneously. This results in a demand for the increase of on-chip power density¹. The increase in more integrated circuits leads scientists to advanced packaging techniques. Complex electronic packaging involving the integration of multiple functional dies is promising in the future of microelectronics, but thermal management and heat dissipation become more and more of an obstacle¹⁻⁵. Because of this, thermal interface materials (TIMs) are one approach being explored in chip packaging to improve the efficiency of heat transfer within the device. Within a chip, the interfaces of the die, heat spreader, and heat sink are not smooth. The raw connection of their surfaces result in microgaps that increase thermal resistance. Flowable TIMs can fill in the interfaces and effectively connect either a die to a heat spreader or a heat spreader to a heat sink. Current TIMs that are in use or are being explored include phase change materials, thermal greases, and thermal pads³. In TIMs, there is an ongoing struggle for a balance between high thermal conductivity and strong thermal connectivity in material selection. Metals have a high thermal conductivity but create a poor connection between chip components; meanwhile, soft materials generally create an effective connection but have a low thermal conductivity⁶. Epoxy is a flowable polymer resin that can be used as a TIM⁷. Because of its low thermal conductivity, highly thermally conductive nanofillers are utilized to create an epoxy composite material that fulfills

both requirements of creating an efficient heat transport path and eliminating microgaps that increase thermal resistance⁸⁻¹⁰. Along with TIMs, other components that increase heat transfer efficiency include underfills, die attach films, and epoxy molding compounds. Fillers in a polymer matrix can increase the thermal conductivity of a composite material by reducing phonon scattering within the nanocomposite network. Dispersion of fillers is a key factor in controlling thermal conductivity¹⁰. Effective filler dispersion reduces agglomeration which would adversely increase phonon scattering, reducing the thermal conductivity. Among the current popular fillers in epoxy composite materials for use in advanced packaging, graphite is at the forefront because its monolayer form, graphene, has an ultrahigh in-plane thermal conductivity of up to 6000 W/mK^{11,12}; however, for 3-D electronic packaging applications, graphene is unsatisfactory because of its low electrical resistivity¹³. With the 3-D integrated architecture stacking of chips in advanced packaging, electrical insulation becomes immensely important¹⁴. Within the stacking sequence, preventing current from flowing from one layer to another and causing a short circuit is essential to maintain routine device operation. As such, h-BN is explored as a filler in an epoxy matrix for both its thermal conductivity and electrical insulation. h-BN is also known as “white graphene” because of its properties which are similar to that of graphite. h-BN can be exfoliated to boron nitride nanosheets (BNNS), and these, like graphene, have a high thermal conductivity (up to 2000 W/mK)¹⁵. As mentioned before, one key difference between the two materials is attributed to their electrical properties. Graphene is a zero-energy semiconductor while BNNS is a wide bandgap semiconductor, resulting in more electrically insulative properties¹⁶. In addition, BNNS has higher thermal stability and chemical inertness¹³. The combination of the high thermal conductivity and electrically insulative properties of BNNS give it its desirability for use as a filler in epoxy composite materials.

Although BNNS has a strong in-plane thermal conductivity, it exhibits a low through-plane thermal conductivity. One workaround to achieve high thermal conductivity in the z-direction of a chip stacking architecture involves the processing of BNNS. After manufacturing a block of BNNS, rotating it 90° would align each hexagonal layer vertically to achieve effective thermal conductivity in the z-dimension. Creating strongly interconnected layers within BNNS during synthesis can improve the structural integrity of the BNNS-epoxy composite after rotation. In addition to this novel approach, the exfoliation of h-BN to BNNS may increase the thermal conductivity of the resulting composite even further. BNNS, as compared to h-BN, has additional benefits for use as a filler in epoxy composites. This BNNS-epoxy composite is

promising in the fields of advanced electronic packaging, especially those involving integrated architectures requiring electrical insulation.

II. EXPERIMENTAL

A. Materials

Hexagonal BN platelets were obtained from Momentive™ performance Materials. Sodium dodecyl sulfate (SDS) was purchased from Sigma-Aldrich. Deionized (DI) water was produced from a Barnstead Smart2 Pure Water Purification system (Thermo Scientific). Epoxy resin was obtained from EPON™, and the hexahydro-4-methylphthalic anhydride hardener was obtained from Lindau chemicals, Inc. The catalysts are 1-cyanoethyl-2-ethyl-4-methylimidazoles which were purchased from Sigma-Aldrich. All the chemicals were used as received.

B. Method

The preparation of boron nitride nanosheets follows the method reported in our previous work¹⁷. The h-BN powder was dissolved in SDS-water (0.05wt%) solution, loaded in a sealed polyethylene bottle, and then ball-milled for 24 hrs. The milled samples were sonicated for 4 hrs to further exfoliate h-BN powders into BNNS. The BNNS were collected by filtration and washed repeatedly by ethanol and water. Finally, they were dried at 50 °C in an oven.

Then the BNNS were dispersed in ethanol and sonicated for 30 mins to ensure the dispersion uniform, followed by vacuum filtration. The BNNS cake was rotated 90° and sliced up. The sliced BNNS was immersed into epoxy solution (epoxy resins: hexahydro-4-methylphthalic anhydride:1-cyanoethyl-2-ethyl-4-methylimidazoles = 1:0.8:0.01 weight ratio) for 1 hr. Then the samples were transferred to vacuum oven for degas at 50 °C for 2 hr. After that, the samples were cured at 155 °C for 1hr in oven. The final samples were polished before thermal conductivity measurements.

C. Characterizations

Scanning Electron Microscope (SEM) images of the fillers were taken by Hitachi SU8230 FE-SEM. Atomic Force Microscopy (AFM) images of the fillers were taken by Veeco Dimension Edge Atomic Force Microscope. The thermal conductivity values of epoxy composites were measured by C-THERM Transient Plane Source (TPS) Flex.

III. RESULTS AND DISCUSSION

A. Characterization of BNNS fillers

h-BN is exfoliated to produce BNNS directly. The spheroid morphology of h-BN shown in Figure 1 (a) and (b) indicates

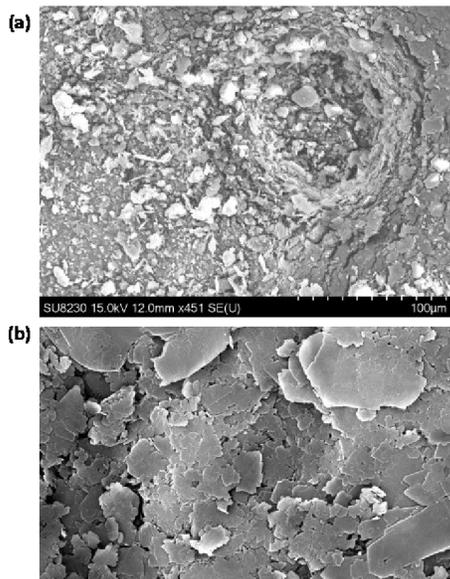


Figure 1. (a) The SEM of h-BN in 100 μm and (b) 10 μm.

that h-BN has many spherical particles, representing h-BN aggregation. After exfoliation, the h-BN becomes the 2D nanosheets presented in Figure 2 (a) and (b). The diameter of BNNS is around 5 μm. In addition, from AFM results shown in Figure 3 (a) and (b), the BNNS has a thickness of

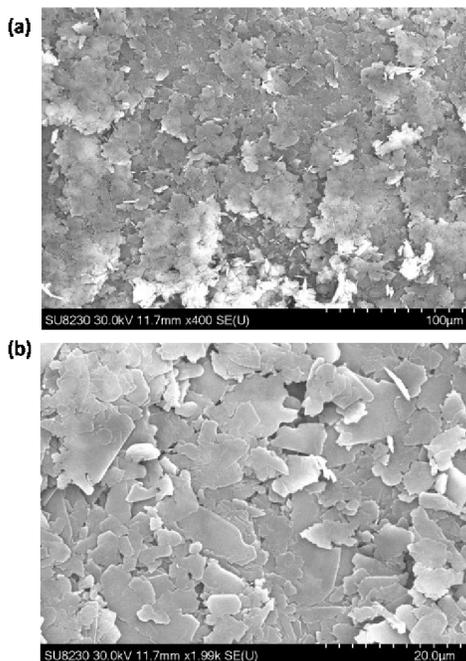


Figure 2. (a) The SEM of BNNS in 100 μm and (b) 20 μm.

only 30 nm after exfoliation, which supports that BNNS has been successfully produced with a low thickness.

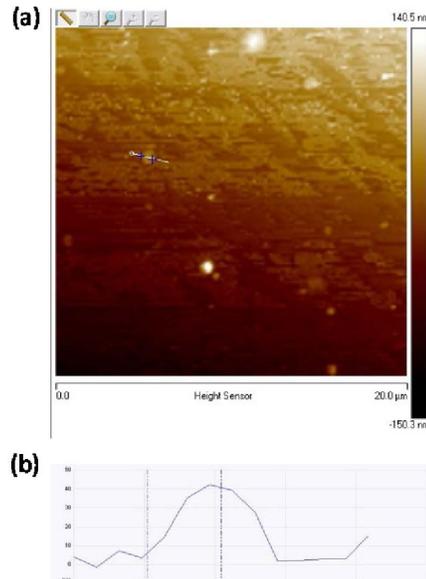


Figure 3. (a) AFM image of BNNS and (b) corresponding cross section of BNNS.

B. Thermal properties of BNNS/Epoxy composites

Through-plane thermal conductivity is especially important in 3D semiconductor packaging. The heat not only needs to dissipate in the in-plane direction, but it also needs to dissipate in the through-plane direction such as in TIMs applications. Unfortunately, BNNS has a high in-plane thermal conductivity but a low through-plane thermal conductivity due to its 2D morphology. Therefore, it is highly desirable to develop a facile method to fabricate BNNS polymer composites with a high through-plane thermal conductivity. Through vacuum filtration, the BNNS stack densely by each other. After rotation and slicing without any chemical modification, the highly organized vertically aligned thermally conductive network provides prolonged phonon pathways, yielding a much higher through-plane thermal conductivity. From Figure 4, the neat epoxy has a thermal conductivity of around 0.2 W/mK, while the addition of h-BN fillers increases the thermal conductivity of the epoxy composite to 1.0 W/mK. After exfoliation, due to the large aspect ratio of BNNS, the thermal conductivity of BNNS-epoxy composites is 1.9 W/mK at 51 wt% filler loading, which is an 82.5% enhancement as compared to h-BN epoxy nanocomposites, and it is an 850% enhancement as compared to neat epoxy.

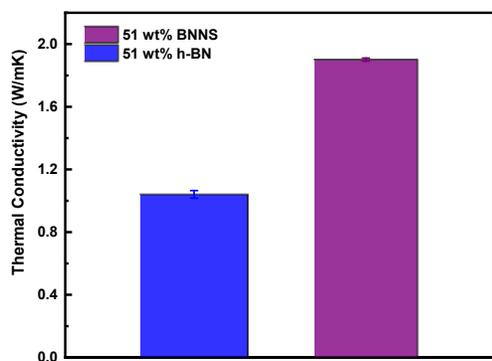


Figure 4. The thermal conductivity of h-BN and BNNS epoxy composites.

IV. SUMMARY

In summary, we have used low cost and large-scale methods to synthesize BNNS by employing ball-milling and sonication. The SEM and AFM results proved the successful liquid phase exfoliation of h-BN through a smaller measured diameter and thinner thickness as compared to h-BN powders. High through-plane thermal conductivity epoxy nanocomposites were achieved with an innovative process. First, vacuum filtration was employed to create thick BNNS cakes. Next, taking advantage of the high in-plane thermal conductivity of BNNS, the cakes were rolled over to change the high thermal conductivity orientation from the x-y plane to the z-plane. The BNNS-epoxy nanocomposites have a high thermal conductivity of 1.9 W/mK, which is an 850% improvement as compared to neat epoxy. This study reveals the promising applications of high-performance, thermally conductive yet electrically insulating epoxy nanocomposites in advanced packaging technologies such as 2.5D/ 3D packaging.

ACKNOWLEDGMENT

This work was supported by the Industry Consortium at the Georgia Tech Packaging Research Center (PRC). This work was performed in part at the Georgia Tech Institute for Electronics and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (Grant ECCS-2025462).

REFERENCES

(1) Shahil, K. M. F.; Balandin, A. A. Thermal Properties of Graphene and Multilayer Graphene: Applications in Thermal Interface Materials. *Solid State Communications* **2012**, *152* (15), 1331–1340.

(2) Wang, Z.-G.; Lv, J.-C.; Zheng, Z.-L.; Du, J.-G.; Dai, K.; Lei, J.; Xu, L.; Xu, J.-Z.; Li, Z.-M. Highly Thermally Conductive Graphene-Based Thermal Interface Materials with a Bilayer Structure for Central Processing Unit Cooling. *ACS Applied Materials & Interfaces* **2021**, *13* (21), 25325–25333. <https://doi.org/10.1021/acsami.1c01223>.

(3) Dai, W.; Ma, T.; Yan, Q.; Gao, J.; Tan, X.; Lv, L.; Hou, H.; Wei, Q.; Yu, J.; Wu, J.; Yao, Y.; Du, S.; Sun, R.; Jiang, N.; Wang, Y.; Kong, J.; Wong, C.; Maruyama, S.; Lin, C.-T. Metal-Level Thermally Conductive yet Soft Graphene Thermal Interface Materials. *ACS Nano* **2019**, *13* (10), 11561–11571.

(4) An, D.; Cheng, S.; Xi, S.; Zhang, Z.; Duan, X.; Ren, Y.; Li, J.; Sun, Z.; Liu, Y.; Wong, C.-P. Flexible Thermal Interfacial Materials with Covalent Bond Connections for Improving High Thermal Conductivity. *Chemical Engineering Journal* **2020**, *383*, 123151.

(5) An, D.; Duan, X.; Cheng, S.; Zhang, Z.; Yang, B.; Lian, Q.; Li, J.; Sun, Z.; Liu, Y.; Wong, C.-P. Enhanced Thermal Conductivity of Natural Rubber Based Thermal Interfacial Materials by Constructing Covalent Bonds and Three-Dimensional Networks. *Composites Part A: Applied Science and Manufacturing* **2020**, *135*, 105928.

(6) Dai, W.; Ma, T.; Yan, Q.; Gao, J.; Tan, X.; Lv, L.; Hou, H.; Wei, Q.; Yu, J.; Wu, J.; Yao, Y.; Du, S.; Sun, R.; Jiang, N.; Wang, Y.; Kong, J.; Wong, C.; Maruyama, S.; Lin, C.-T. Metal-Level Thermally Conductive yet Soft Graphene Thermal Interface Materials. *ACS Nano* **2019**, *13* (10), 11561–11571.

(7) Li, J.; Ren, C.; Sun, Z.; Ren, Y.; Lee, H.; Moon, K.; Wong, C.-P. Melt Processable Novolac Cyanate Ester/Biphenyl Epoxy Copolymer Series with Ultrahigh Glass-Transition Temperature. *ACS Applied Materials & Interfaces* **2021**, *13* (13), 15551–15562.

(8) Loeblein, M.; Tsang, S. H.; Pawlik, M.; Phua, E. J. R.; Yong, H.; Zhang, X. W.; Gan, C. L.; Teo, E. H. T. High-Density 3D-Boron Nitride and 3D-Graphene for High-Performance Nano-Thermal Interface Material. *ACS Nano* **2017**, *11* (2), 2033–2044.

(9) Chen, J.; Huang, X.; Sun, B.; Wang, Y.; Zhu, Y.; Jiang, P. Vertically Aligned and Interconnected Boron Nitride Nanosheets for Advanced Flexible Nanocomposite Thermal Interface Materials. *ACS applied materials & interfaces* **2017**, *9*.

(10) Liu, Z.; Li, J.; Liu, X. Novel Functionalized BN Nanosheets/Epoxy Composites with Advanced Thermal Conductivity and Mechanical Properties. *ACS Applied Materials & Interfaces* **2020**, *12* (5), 6503–6515.

(11) Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. Superior Thermal Conductivity of Single-Layer Graphene. *Nano Letters* **2008**, *8* (3), 902–907.

(12) Chen, S.; Wu, Q.; Mishra, C.; Kang, J.; Zhang, H.; Cho, K.; Cai, W.; Balandin, A.; Ruoff, R. Thermal Conductivity of Isotopically Modified Graphene. *Nature materials* **2012**, *11*, 203–207.

- (13) Lim, W. H.; Hamzah, A.; Ahmadi, M. T.; Ismail, R. Analytical Study of the Electronic Properties of Boron Nitride Nanosheet. In *2017 IEEE Regional Symposium on Micro and Nanoelectronics (RSM)*; 2017; 42–45.
- (14) Wu, F.; Chen, S.; Tang, X.; Fang, H.; Tian, H.; Li, D.; Peng, X. Thermal Conductivity of Polycaprolactone/Three-Dimensional Hexagonal Boron Nitride Composites and Multi-Orientation Model Investigation. *Composites Science and Technology* **2020**, *197*, 108245.
- (15) Golam, R. M.; Alper, K.; Babak, A.; Reza, S.-Y. 2D Boron Nitride Nanosheets for Polymer Composite Materials. *NPJ 2D Materials and Applications* **2021**, *5* (1).
- (16) Wang, J.; Ma, F.; Liang, W.; Sun, M. Electrical Properties and Applications of Graphene, Hexagonal Boron Nitride (h-BN), and Graphene/h-BN Heterostructures. *Materials Today Physics* **2017**, *2*, 6–34.
- (17) Sun, Z.; Li, J.; Zhang, M.; Yu, M.; Moon, K.; Wong, C. Large-Scale and Low-Cost Production of Graphene Nanosheets-Based Epoxy Nanocomposites with Latent Catalyst to Enhance Thermal Conductivity for Electronic Encapsulation. In *2021 IEEE 71st Electronic Components and Technology Conference (ECTC)*; 2021; 607–612.