# Control and Enhancement of Anisotropic Thermal Diffusivity of Boron Nitride and Zinc Oxide Filled Polyimide Films *(invited)*

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To develop thermally conductive inorganic/organic composite films, various grades of hexagonal boron nitride (h-BN) and zinc oxide (ZnO) particles were hybridized with aromatic PIs having rigid or flexible main chains. Microphase-separated structures with "vertical double percolation (VDP)" morphology were spontaneously formed in the PI films composed of sulfur- and fluorine-containing PIs, in which two phases were separately aligned along the out-of-plane direction, and ZnO and MgO particles were preferentially precipitated in the fluorine-containing PI phase.[1–5]

Using thermal diffusivity (α) measurements along the out-of-plane ($\alpha_\perp$) and the in-plane ($\alpha_\parallel$) directions combined with SEM and WAXD measurements, we clarified that the PI films filled with large h-BN flakes exhibited a large difference (anisotropy) between $\alpha_\perp$ and $\alpha_\parallel$ due to the strong in-plane orientation of heat conducting h-BN plane, while smaller anisotropy was observed in composites with small flakes and aggregates, which orient more isotropically.[6] In addition, the effects of polymer chain rigidity/flexibility on the anisotropy in α (= $\eta$) and the void fraction ($v$) of h-BN/PI composite films were examined.[4,5] h-BN-filled composites of rigid rod PI exhibited smaller $v$ values than the flexible PI composites owing to the rigid chain with smaller free volume and dense packing between components.[5] The composites of highly anisotropic rigid PI matrix exhibited larger anisotropy in a than the flexible PI composites. Moreover, composite films were prepared by mixing two kinds of immiscible sulfur and fluorine containing PIs with needle-shaped n-ZnO particles.[7–9] These blend composite films exhibited significantly higher $\alpha_\perp$ than blend films containing pyramidal shaped p-ZnO particles due to the formation of vertical double percolation (VDP) structures. The n-ZnO particles confined in the VDP structures and partially oriented along the out-of-plane direction contributed to the enhancement of $\alpha_\perp$.

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