Enhanced Thermal Conductivity Based on Vertical Double Percolation Morphology in Phase Separated Polyimide Blend Films Containing Metal Oxide Particles

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Introduction: Upon strong demands from micro- and power-electronic industries, functional composite materials consist of μm-size ceramic particles, such as Al₂O₃, AlN, h-BN, and thermally stable polymers have been widely investigated for enhancement of thermal conductivity and electric resistivity of thermal interface materials and insulating layers in power-ICs. However, improvement is still limited due to large interfacial contact resistance between particles and polymer matrix. In this study, we report a significant enhancement in thermal conductivity even at a low particle loading based on a selective confinement technique of ZnO and MgO particles in phase-separated polyimide/polyimide (PI/PI) blend films.

Methods: Two types of PIs, sulfur- and fluorine-containing PIs, were blended with pyramidal ZnO (0.3-0.5 μm) and cubic MgO (2-3 μm) particles. Since the thermal conductivities of ZnO and MgO crystallites are the same (55 W/m·K), 'filler size effect' can be primarily examined. Under the optimized spin-coating and thermal curing conditions, micro-phase separated structures with "vertical double percolation (VDP)" morphology were spontaneously formed in the blend films, in which two phases are separately aligned along the out-of-plane direction, and ZnO and MgO particles were selectively confined in the fluorine-containing PI phase.

Results & Discussion: PI blend films with VDP morphology exhibited more than 400 % enhancement of thermal conductivity in the out-of-plane direction at 24 vol% content of ZnO and MgO particles, whereas monophase PI films with homogeneously dispersed particles exhibited only 90-150 % enhancement compared with a pristine PI film. These results indicate that the VDP morphology with selectively localized particles functions as an effective thermal conductive pathway which goes over the percolation threshold. Moreover, PI blend films with larger-size MgO particles exhibited higher conductivity between 5 and 24 vol % than those with ZnO particles, whereas similar values were observed over 24 vol %. This demonstrates that 'filler size effect', which effectively reduces interfacial contact resistance, is significant at lower filler contents, but the size effect is insignificant at higher filler contents because mutual contact among particles induces effective percolation in the thermal conductive pathway.

References