

Enhanced Thermal Conductivity in Polyimide / Metallic Oxide Composites with Controlled Phase Separation Morphology and Anisotropy of Particles

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Abstract—Thermal conductivity along the out-of-plane direction in polyimide (PI) blend films containing ZnO and MgO particles with different sizes and anisotropic shapes was investigated. Microphase-separated structures with “vertical double percolation (VDP)” morphology were spontaneously formed in the films composed of a sulfur- and a fluorine-containing PI, in which two phases were separately aligned along the out-of-plane direction, and particles were preferentially precipitated in the fluorine-containing PI phase. The blend film exhibits 460–650% enhancement of thermal conductivity at 27 vol% of particles, which indicate that the VDP structure with selective incorporation of particles with isotropic or anisotropic shapes functions as an effective thermal conductive pathway.

Keywords: Polyimide film, Thermal conductivity, Microphase-separation, Vertical double percolation

I. INTRODUCTION

A representative super engineering plastic, 'polyimide' (PI), has been widely used in electronic, automobile, and aerospace applications owing to their high thermal stability, good mechanical properties, chemical and environmental stability, and favorable electrical properties. Upon strong demands from micro- and power-electronic industries, functional composite materials consist of μm -size ceramic particles such as Al_2O_3 , AlN , h-BN and thermally stable polymers have been widely investigated for enhancement of thermal conductivity with high electric resistivity for thermal interface materials (TIMs) and insulating layers in MPUs and power-ICs. (Fig. 1(a)). However, improvement is still limited due to large interfacial contact resistance between inorganic particles and polymer matrix. In this study, we report a significant enhancement in thermal conductivity in phase-separated polyimide/polyimide (PI/PI) blend films composed of a sulfur- and a fluorine-containing PI even at a low particle loading based on a selective confinement technique of ZnO and MgO particles. (Fig. 1(b)). In addition, effect of anisotropic shapes (six-sided pyramidal and needle-like) of ZnO particles on the out-of-plane thermal conductivity of phase-separated PI blend films will be discussed.

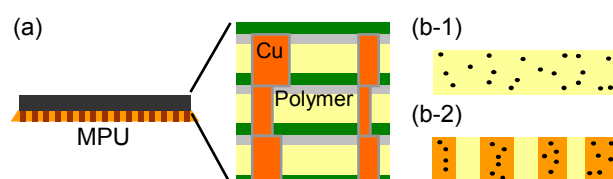


Figure 1. (a) Illustrations of a MPU chip and the inside. Schematic designs for polymer thermal interface materials (TIM) with (b-1) homogeneously dispersed and (b-2) selectively incorporated fillers.

II. EXPERIMENTAL

ZnO nano-pyramidal particles (ZnO-nP) were obtained by refluxing zinc acetate in oleylamine at 240°C for 40 min.[1] MgO μm -sized particles (MgO- μP) were obtained from Ube Materials Industries Ltd. PI blend films containing different affinities to inorganic ions were prepared, *i.e.*, BPDA-SDA (SD) as a sulfur-containing PI and BPDA-TFDB (TF) as a fluorine-containing PI (Fig. 2) [2]. Each precursor solution of these PIs, *i.e.*, poly(amic acid)s in *N,N*-dimethylacetamide (DMAc), was blended with ZnO-nP and MgO- μP . A translucent mixture solution was obtained after stirring for 4 h at room temperature. PI blend/particles hybrid (PI blend) films of 25–35 μm in thickness were obtained by spin-coating of the solution onto Si wafers, followed by drying at 70°C for 1h and thermal imidization at 350°C for 1.5 h under nitrogen flow. For reference, a monophase "homo-PI" film (TF/particles hybrid film) was also prepared. Thermal diffusivity along the out-of-plane direction ($\alpha_{\perp}$) in PI films was measured with an AC temperature wave analyzer (*ai-Phase mobile*) at room temperature. Thermal diffusivity (α) has the most prominent influence on the thermal conductivity (λ) because λ is the product of thermal diffusivity, heat capacity, and density. Microphase-separated morphologies were observed by an optical microscope and a scanning electron microscope (SEM) on the surfaces of the resultant blend-PI films, whereas the surfaces of the homo-PI films were very flat and homogeneous without phase separation.

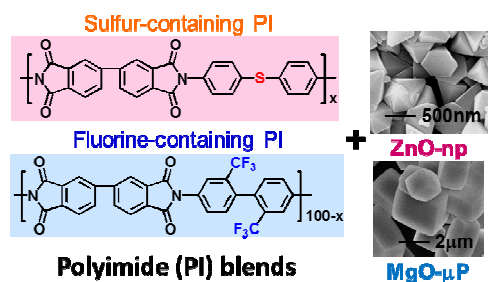


Figure 2. Molecular structures of the PI blend: BPDA-SDA/BPDA-TFDB (SD/TF) and photos of ZnO and MgO particles.

III. RESULTS AND DISCUSSION

Cross-sectional SEM images of PI blend films clearly indicates formation of micro-phase separated structure, in which two phases are separately aligned along the out-of-plane direction to the film plane (Fig. 3, inset). The average size of each phase was estimated as 50–100 μm . This type of phase separation has been designated "vertical double percolation" (VDP) morphology. Fourier transform infrared attenuated total reflectance microscope spectroscopy (Micro FT-IR ATR) was used for characterizing chemical composition of ZnO-nP or MgO- μP -rich phase and -poor phase [3]. The prominently absorption band around 1050–1200 cm^{-1} , which is attributed to $-\text{CF}_3$ of BPDA-TFDB phase revealed that particle-rich phase and -poor phase are mainly composed of TF and SD, respectively. Accordingly, ZnO-nP and MgO- μP are preferentially precipitated in the TF phase, and VDF morphology shown in Fig. 1(b-2) was spontaneously formed. It is expected that the continuous TF phases containing higher amount of ZnO-nP / MgO- μP function as an effective thermal conductive pathway along the vertical direction of the films.

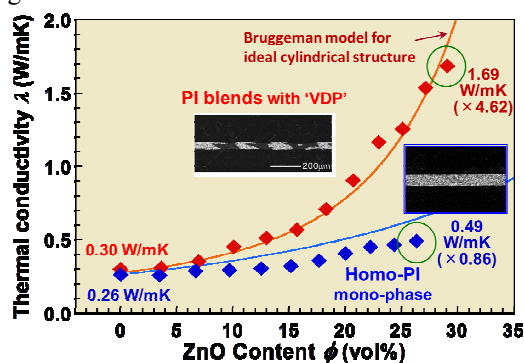


Figure 3. Relationship between the out-of-plane thermal diffusivity ($\alpha_{\perp}$) and the morphology of PI nanohybrid films containing ZnO-NP in the blend PI and the homo-PI system. The lines are the $\alpha_{\perp}$ values calculated for an ideal PI blend model (red line) and a Homo-PI model (blue line) based on the Bruggeman theory.

Fig. 3 shows the observed values of $\alpha_{\perp}$ in the PI blend and the homo-PI films with different molar ratios of ZnO-NP. In the cases of homo-PI, ZnO-NP was homogeneously dispersed in films, and the $\alpha_{\perp}$ slightly increased with increasing the ZnO-NP content: $15.3\sim 24.4\times 10^{-8} \text{ m}^2/\text{s}$ ($\times 1.59$ times). On the contrary, PI blends films exhibited higher absolute values and enhancement of $\alpha_{\perp}$ than those of homo-PIs, and the PI blends films with 27 vol% of

ZnO-nP showed the highest $\alpha_{\perp}$: $18.5\sim 78.8\times 10^{-8} \text{ m}^2/\text{s}$ ($\times 4.62$ times).

The phase-separated PI blend films exhibited significantly higher $\alpha_{\perp}$ than those of mono-phased homo-PI films with homogeneous dispersion of particles. The significantly enhanced $\alpha_{\perp}$ can be explained by the following two factors. Firstly, particles were highly concentrated in TF phase of the blend films according to the initial design strategy, while the SD phase functioned as the excluding domain for particles. Secondly, VDF morphology leads to the preferential location of particles along the out-of-plane direction. The TF phase with higher particle content forms effective thermal conductive pathway along the vertical direction of the films, while the SD phase with much lower particle content endows flexibility and toughness to the hybrid films. These phenomena clearly demonstrate the effectiveness of VDF morphology. Moreover, the resulting PI blend films kept their high thermal stability (*i.e.* degradation temp. $> 400^\circ\text{C}$) and good flexibility.[4] Moreover, it should be noted that the PI blend films containing large-size MgO- μP exhibited higher thermal conductivity than those with ZnO-nP between 0 and 24 vol%, whereas similar conductivities were observed over 24 vol %. This demonstrates that 'filler size effect', which effectively reduces interfacial contact resistance, is significant at lower filler contents, whereas the effect becomes insignificant over the particle content at which thermal conductive pathways resulting from effective percolation within VDF morphology are formed. In the presentation, the thermal conduction behaviors of PI hybrid films containing hBN particles with highly anisotropic shapes will be also discussed.[5]

IV. CONCLUSIONS

Two types of PI, sulfur- and fluorine-containing PIs, were blended with pyramidal ZnO and cubic / needle-like MgO particles. Under the optimized conditions of spin-coating and thermal curing, microphase separated structures with VDP morphology were spontaneously formed in the blend films, in which two phases are separately aligned along the out-of-plane direction, and filler particles were selectively confined in the fluorine-containing PI phase. PI blend films with VDP morphology exhibited more than 460–650 % enhancement of thermal conductivity in the out-of-plane direction at 27 vol% loading of ZnO and MgO particles, whereas monophase PI films with homogeneously dispersed particles exhibited only 90–150 % enhancement. These results indicate that the VDP structure with selectively localized particles functions as an effective thermal conductive pathway which goes over the percolation threshold.

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