Effects of Vertical Double Percolation Morphology and Particle Size on Thermal Diffusivity of Polyimide Blend/Metal Oxides Hybrid Films

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Introduction

With miniaturization of devices and increased circuit density, microelectronics components generate large amounts of heat. In case that heat is not dissipated efficiently, workable time of components should be shortened, which becomes a significant problem from individual devices to electronic modules and systems. Thermal interface materials (TIM, Fig.1) are widely used to transfer heat across jointed solid surfaces such as between CPUs and heat sinks or heat spreader. Thermally stable polymers are quite important in electronic applications such as TIM, low-dielectric insulators, and heat spreaders. Polyimides (PIs) exhibit high thermal stability with good mechanical and insulation properties. Thereby, PIs have been widely used as interlayer dielectrics and substrates for flexible circuit boards. However, thermal diffusivity along the out-of-plane direction ($D_{\perp}$) of polymers including PIs is much lower than those of ceramics and metals. Recently, hybrid materials consisting of polymer matrix and homogeneously dispersed inorganic fillers have been investigated to enhance the thermal conductivity. However, improvement in thermal conductivity is still limited due to the following two factors: (i) large interfacial thermal resistance between polymer surfaces and fillers, and (ii) limited total amount of fillers to maintain their insulation properties. We have previously reported that immiscible PI blend films containing zero-valent silver nano-particles significantly enhance the out-of-plane thermal diffusivity [1−2]. Furthermore, we have recently reported that immiscible PI blends containing selectively dispersed zinc oxide (ZnO) particles (~0.5 μm) show much higher thermal conductivity than PIs containing homogeneously dispersed ZnO [3−4] (Fig. 5, HOMO ZnO and Blend ZnO [4]). Under well-controlled preparation conditions, thermal conductive pathways were spontaneously formed along the out-of-plane direction by selective incorporation of particles in one phase, which is called 'vertical double percolation (VDP)' morphology [4].

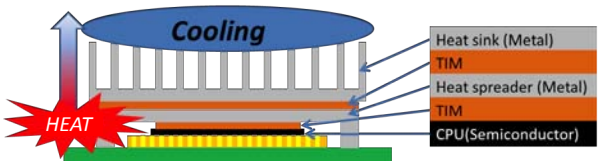

Figure 1. Schematic illustration of CPU unit.

Experimental

Magnesium oxide (MgO) particles (~1.2 μm, provided by Ube Material Industries) were chosen as a new thermal conductive filler. The thermal diffusivity of MgO is comparable to ZnO (~55 W/m·K). A PI blend prepared from TF and SD PIs (Fig. 2) was used as a matrix. Hybrid films were obtained by thermal curing of PI precursors containing metal oxide particles (ZnO, MgO) at 350°C for 1 h. The volume ratios of SD, TF and metal oxide particles (Fig. 3) were set to $100-x$: $100-x$: $2x$ (x = 0~29.8). The $D_{\perp}$s of PI hybrid films were measured at room temperature with an AC temperature wave analyzer (ai-Phase mobile 1, ai-Phase Co. Ltd.) [5-6]. Top surface images of PI blend films were taken with an Olympus SZX12 microscope, and cross-sectional images of the films were observed using a SEM (Miniscope TM3000, Hitachi High-Tech).

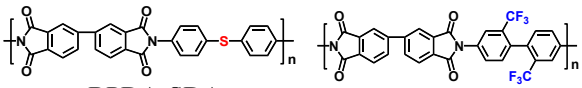

Figure 2. Molecular structure of PI blend: BPDA-SDA/BPDA-TFDB.

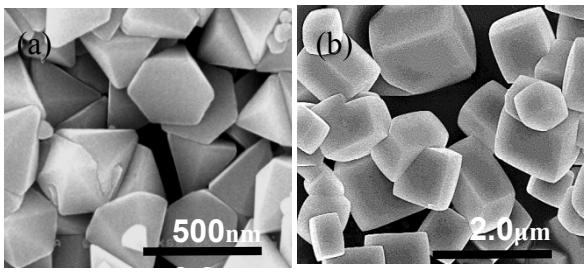

Figure 3. SEM images of (a)ZnO nano-pyramidal particles and (b)MgO micro-cube particles.

Results and Discussion

Firstly, relationships between $D_{\perp}$ value and phase separation morphology of PI blend films containing MgO particles were investigated (Fig. 4, *i.e.* 'HOMO MgO' and 'Blend MgO'). In the case of 'HOMO MgO', the MgO particles are homogeneously dispersed in PI matrix, and their $D_{\perp}$ values were increased as the MgO contents increased. In contrast, 'Blend MgO' (e.g. Fig. 5(b)) exhibited significantly larger $D_{\perp}$ values compared to 'HOMO MgO'. This is because heat transfer is interfered mainly at interfaces between polymer matrix and filler particles due to phonon scattering, which causes thermal resistance with lowered $D_{\perp}$. Comparing to homogeneously dispersed system, filler particles incorporated in the VDP system ('Blend MgO') easily come into contact with neighboring particles because they are highly concentrated in one phase. Thus, interface area is substantially

reduced when particles make contacts with other particles. Therefore, highly filled phases act as effective 'thermal conductive pathways' in the PI blend films. This result agrees well with our previous study [4].

Secondly, $D_\perp$ values of PI blend films containing MgO particles are compared with those of PI films containing homogeneously dispersed MgO and ZnO particles (Fig.4, 'HOMO MgO' and 'HOMO ZnO'). The average diameter of MgO particles is 2−2.5 times larger than that of ZnO. PI films with MgO exhibited larger $D_\perp$s than those with ZnO in homogeneously dispersed system. This is because large particles have smaller total surface areas than small particles. Thereby, ZnO particles cause larger interfacial thermal resistance between PI matrix and particles compared with MgO. As a result, the PI films containing MgO exhibited larger $D_\perp$ values than those with ZnO.

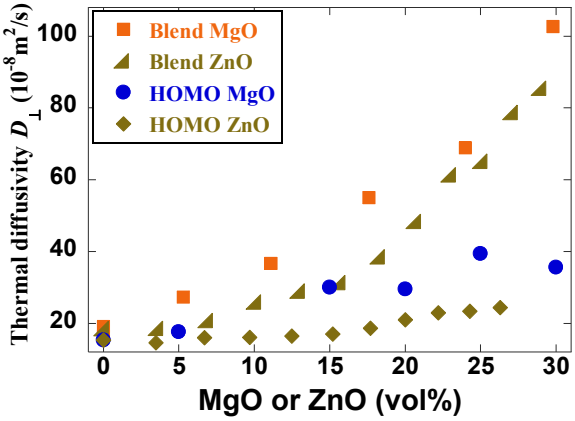

Figure 4. $D_\perp$ values of Blend and HOMO films with different vol% of ZnO [4] or MgO particles.

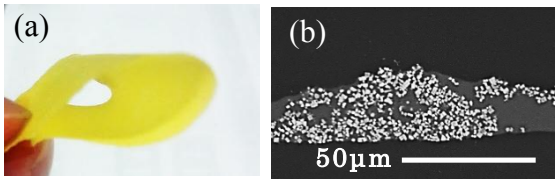

Figure 5 PI blend films containing MgO particles
(a) macroscopic image of 24 vol%,
(b) cross-sectional SEM image of 29.8 vol%

Thirdly, difference in $D_\perp$ values between 'Blend MgO' and 'Blend ZnO' films is examined. The PI blend films containing MgO exhibited significantly larger $D_\perp$ values than those with ZnO between 0 and 24 vol% of filler contents, whereas similar $D_\perp$ values were obtained over 24 vol%. This indicates that particle size of fillers has a significant effect on $D_\perp$ at relatively lower filler contents, which is explainable in terms of total amount of interfacial thermal resistance. At lower filler contents, use of large particles can reduce interface areas, which effectively lowers thermal resistance. Therefore, the $D_\perp$ of films containing larger particles are substantially increased. On the other hand, the effect of larger particles is limited over 24 vol% because close contact among conductive fillers (MgO and ZnO) are attained in these blend films at higher concentrations due to the formation of 'VDP structure' with effective thermal conductive pathways. In these films, particle density in one phase is almost saturated.

Conclusion

The effects of particle size and spatial distribution of thermally conductive fillers were investigated to examine the relationships between phase separation morphology and thermal diffusivity in the out-of-plane direction ($D_\perp$) in PI films prepared from fluorine-containing (TF) and sulfur-containing (SD) PIs. Two types of thermally conductive particles with different diameters: MgO and ZnO were used, and measured $D_\perp$ values were compared between a) homogeneously dispersed (HOMO) and b) selectively dispersed (Blend) systems. The $D_\perp$ values of 'Blend MgO' were much larger than those of 'HOMO MgO' due to the formation of effective thermal conductive pathways (*i.e.* VDP structure). 'Blend MgO' exhibited larger $D_\perp$ values than those of 'Blend ZnO' at lower filler contents (< 24 vol%), though no apparent difference was observed at higher filler contents. The effect of larger particles is less significant at higher filler contents in the VDP systems due to the saturated particle density in one phase. We believe that investigation of the PI blend system which forms VDP structure provide valuable information to develop new polymer/inorganic hybrid materials with enhanced thermal conductivity.

Reference

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