ポリイミド分子鎖と六方晶ＢＮ粒子の配向異方性が複合材料の熱伝導率異方性に及ぼす効果

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Abstract: A series of inorganic/organic composite films exhibiting high thermal diffusivity (D) was prepared from five different grades of flake-shaped hexagonal boron nitride (hBN, **Fig.1**) [1] ceramic particles and aromatic polyimides (PIs. **Fig.2**). Thermal diffusivities along the out-of-plane ($D_{\perp}$) and in-plane ($D_{//}$) directions of hBN/PI films were measured and analyzed in terms of size, shape, volume loading and orientation of hBN particles, as well as molecular structures of rigid and flexible PI matrices. hBN/PI films filled with large and high-aspect-ratio particles exhibited large anisotropy in $D_{\perp}$ and $D_{//}$ due to the strong in-plane alignment of heat-conducting basal (100) plane of hBN particles, while smaller anisotropy was observed in films filled with small flakes and aggregates, which are less likely to align in the in-plane direction during film processing The anisotropic property observed in hBN/PI films exhibited strong correlation with the orientation of hBN particles estimated using SEM image analyses and wide-angle x-ray diffraction. Moreover, composites of hBN and rigid PI exhibited higher anisotropy in $D_{\perp}$ and $D_{//}$ than flexible PI-composites, reflecting the effect of the rigid and densely packed PI chains that align in the in-plane direction.

Keywords: Polyimide, hexagonal boron nitride, thermal diffusivity, composite films

Experimental

hBN flakes with different agglomeration states (**Table I**) were dispersed in polyamic acid (PAA) solutions of *s*BPDA-ODA (OD) precursor. Each hBN/OD film containing 10 to 60 vol% hBN was prepared by spin-casting of the corresponding hBN/PAA slurry on a Si substrate followed by thermal curing up to 350°C. Following the same procedure, hBN/PI films of rigid *s*BPDA-PDA PI (PD) and F(8.0) particles were also prepared at 10 to 50 vol%.

Table 1. hBN grades of various sizes

Grade	**F(0.7)**	**F(8.0)**	**F(18.0)**	**A(4.0)**	**A(12.0)**
D_{50}*	0.7	8.0	18.0	4.0	12.0
Particle shape	Flakes			Aggregated flakes	

* median particle size

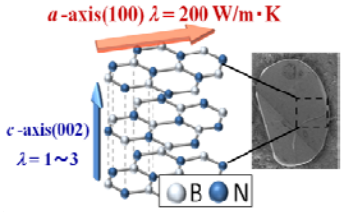

Fig.1 Crystal structure of hBN

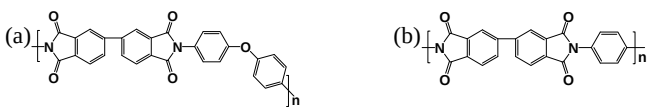

Fig.2 Chemical structures of (a) *s*BPDA-ODA PI (OD) and (b)*s*BPDA-PDA PI (PD)

The $D_{\perp}$ and $D_{//}$ values were measured by the temperature wave analysis (TWA) [2] method and the laser-heating angstrom method [3], respectively. The degree of orientation of hBN particles was estimated by cross sectional images of scanning electron microscopy (SEM) and transmission wide-angle X-ray diffraction (WAXD) patterns.

Results and Discussion

Fig.3 shows orientation indices of hBN particles in hBN/OD films, estimated by $\boldsymbol{I}_{(002)}/(\boldsymbol{I}_{(002)}+\boldsymbol{I}_{(100)})\times 100$, where $\boldsymbol{I}_{(002)}$ and $\boldsymbol{I}_{(100)}$ are (100) and (002) peak intensities, respectively. A high degree of in-plane orientation of (100) plane was observed in films filled with large flake-shaped particles, F(8.0) and F(18.0), while small platelet-shaped F(0.7) and aggregate-filled films showed nearly isotropic orientation. The F(18.0) and F(8.0) films exhibited large anisotropy in $D_{\perp}$ and $D_{//}$, while smaller anisotropy was observed in films containing F(0.7) particles and aggregates. The anisotropic D values observed in the hBN/OD films showed strong correlation with the orientation of hBN particles estimated by SEM and WAXD.

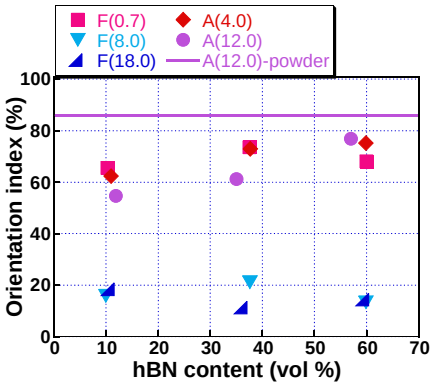

Fig.3 Orientation indices of hBN/OD films

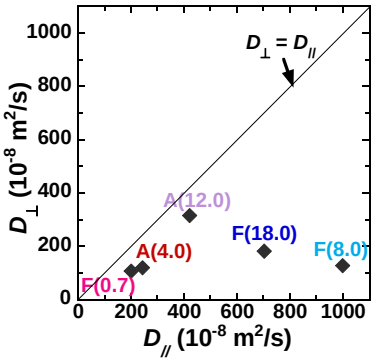

Fig.4 $D_{\perp}$ and $D_{//}$ values of 60vol%-hBN/OD films

The results for $D_{\perp}$ and $D_{//}$ measurements are shown in **Figs. 5** and **6**, respectively. PD-composites showed lower $D_{\perp}$ values compared to OD-composites, and a reversed trend was observed in $D_{//}$. In addition, the onset of $D_{\perp}$ increase appeared at higher concentration in PD composites. It can be attributed to the fact that densely packed PD chains are aligned strongly in the in-plane direction, while OD chains are more randomly oriented because of the flexible ether linkage. Therefore, addition of only a small volume of BN particle to the PD matrix was not enough to loosen the aggregated PI chains. In the in-plane direction, however, the strong in-plane alignment of PD chains effectively enhanced the D values at all concentrations.

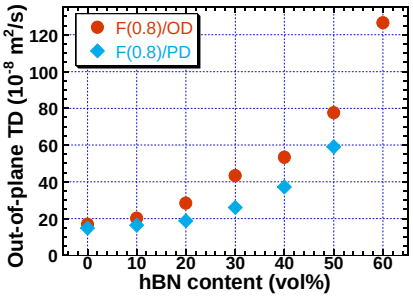

Fig.5 $D_{\perp}$ of F(8.0)/OD and F(8.0)/PD

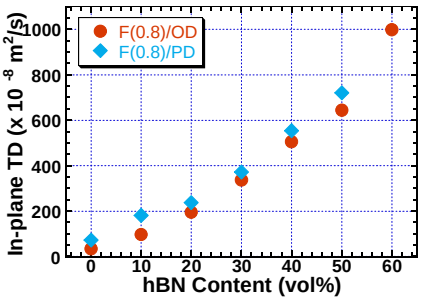

Fig.6 $D_{//}$ of F(8.0)/OD and F(8.0)/PD

References

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