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Low Thermal Expansion Composites Prepared from Polyimide and ZrW_2O_8 Particles with Negative Thermal Expansion

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Inorganic/polymer composite films with adjustable small thermal expansion were prepared by incorporating sub- μm sized particles of zirconium tungstate (ZrW_2O_8) into aromatic polyimide (PI). ZrW_2O_8 particles exhibit negative coefficients of thermal expansion (CTE) between -4.8 to -8.7 ppm/K. The cross-sectional SEM images of ZrW_2O_8 /PI composite films indicate that filler particles are homogeneously dispersed in PI matrix without aggregation. The CTEs of these films are linearly decreased with increasing the volume fraction of ZrW_2O_8 . The CTE of a composite film containing 60 vol% of filler is as low as that of metallic copper (17 ppm/K). Assuming that the thermal expansion behavior is three-dimensionally isotropic, PI composite films containing more than 50 vol% of ZrW_2O_8 could achieve coefficients of volumetric thermal expansion smaller than 50 ppm/K.

Keyword: Polyimide / thin film / zirconium tungstate / thermal expansion / Organic-inorganic composite

1. Introduction

Polyimides (PIs) are representative super-engineering plastics exhibiting high thermal and chemical stability, flame retardancy, high electric voltage and radiation resistance, high mechanical strengths, and good flexibility [1]. PIs have been widely used in electric, electronic, and aerospace applications [2]. The authors have been exploring optical and photonic applications of fluorinated PIs for more than a decade [3]. Since PIs are generally used as buffer coatings and interlayer dielectric interconnects in micro- and opto-electronics, their larger coefficients of thermal expansion (CTEs) may lead to problems at interfaces with inorganic/metallic substrates, where thermal stress give rise to cracking or peeling. The incorporation of inorganic fillers into PIs is a versatile method to overcome these problems by cancelling or reducing the CTE mismatch at the interface.

Shi et al. first reported that cubic zirconium tungstate (ZrW_2O_8), which exhibits large negative CTE at -8.7 ppm/K [4], can be used to reduce the

thermal expansion of polyester and epoxy resin in 1997 [5]. Loadings of ZrW_2O_8 particles ranging from 0 to 30 vol % significantly reduce the CTEs from 94 to 56 ppm/K for polyester and from 54 to 18 ppm/K for epoxy composites. Sulliban and Lukehart [6] reported the preparation of ZrW_2O_8 /PI composites with up to 22 vol% filler loading in 2005. Since ZrW_2O_8 particles with unmodified surfaces showed poor interaction with PI matrix due to the hydrophobic nature of the PI, surface silylation improved the contact between the filler and PI. Although the composites showed reduced CTEs, the thermal expansion was not well controlled. In this study, high quality films of ZrW_2O_8 /PI composites with small and adjustable CTEs with high thermal stability will be prepared.

2. Experimental

2.1. Preparation of ZrW_2O_8 Particles

ZrW_2O_8 particles were synthesized using a solid-state reaction method [7,8]. Equimolar amounts of WO_3 and ZrO_2 (99.0%, Wako

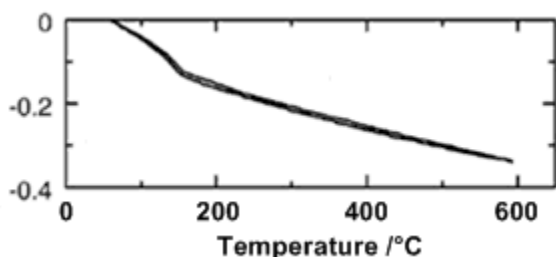
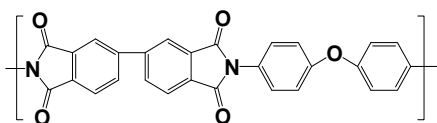


Fig. 1. Thermal expansion curve of ZrW_2O_8 particles prepared by the same method [7].

Chemical Co. Inc.) were mixed. The mixture was sintered at 1200°C for 8 h in air followed by quenching in liquid nitrogen. Fine particles were obtained by grinding with a planetary ball mill. Figure 1 shows the thermal expansion curve of ZrW_2O_8 particles prepared by the same method as this study [7]. The slope change observed at ca. 150°C corresponds to the phase transition from $\alpha\text{-ZrW}_2\text{O}_8$ to $\beta\text{-ZrW}_2\text{O}_8$. It has been reported that the average CTE between room temperature and 150°C is -8.7 ppm/K [4], and that between 150°C and 600°C is -4.8 ppm/K [9].

2.2. Materials for polyimide synthesis

The molecular structure of PI used in this study is shown in Scheme 1.



Scheme 1. BPDA-ODA polyimide

3,3',4,4'-Biphenyl-tetracarboxylic dianhydride (BPDA, Wako Chem. Co. Inc.) and 4,4'-diaminodiphenylether (ODA, Tokyo Chem. Indust., Co. Ltd.) were used after drying at 180°C without further purification. *N,N*-Dimethylacetamide (DMAc, anhydrous, Aldrich) was used as received.

2.3. Preparation of ZrW_2O_8 /PI composite films

A solution of precursor of PI, poly(amic acid) (PAA), was prepared by a conventional polycondensation method [1,2]. Equimolar amount of dianhydride was added to a DMAc solution of diamine, and stirred at ambient temperature for 24h. Then, ZrW_2O_8 particles dispersed in DMAc by super-sonic homogenizer (US-50, Nissei Corp.) was added to PAA solution and stirred for 12h with a high-power magnetic stirrer. The ZrW_2O_8 /PI composite films were prepared via spin-coating of mixture solutions onto silicon (Si) substrates, followed by drying at 70°C for 1h and thermal imidization at 350°C under a nitrogen atmosphere.

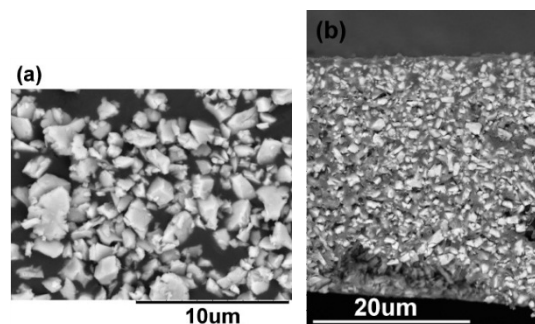


Fig. 2. SEM images of (a) ZrW_2O_8 particles and (b) PI/ ZrW_2O_8 (50 vol%) hybrid film.

2.4. Measurements

Wide angle X-ray diffraction (WAXD) patterns were measured with a Shimadzu XRD-6100 diffractometer. $\text{Cu-K}\alpha$ line ($\lambda=1.542$ Å) was used as a light source. The size distribution of ZrW_2O_8 particles was measured with a Nikkiso 9320HRA (X-100) laser diffraction particle size analyzer. SEM micrographs were observed with a Hitachi TM-3000 microscope. The surface was covered with sputtered Au. Thermal mechanical measurements (TMA) were conducted with a Shimadzu TM-60 analyzer. The tensile load was 5 g, and the heating rate was $10^\circ\text{C}/\text{min}$.

3. Results and Discussion

3.1. Characterization of ZrW_2O_8 Particles

Figure 2 shows the SEM micrographs of ZrW_2O_8 particles and the cross sectional view of ZrW_2O_8 /PI composite films. The mean-volume diameter and the mean-number diameter of the particles were 0.95 and 0.23 μm , respectively. In the composite film, ZrW_2O_8 particles are homogeneously dispersed without aggregation, though micro-voids are found near particles.

Figure 3 shows that the WAXD pattern of a ZrW_2O_8 /PI composite film fairly agrees with that of ZrW_2O_8 particle (α -phase), which indicates that the crystalline structure of ZrW_2O_8 particles was maintained after thermal imidization at 350°C .

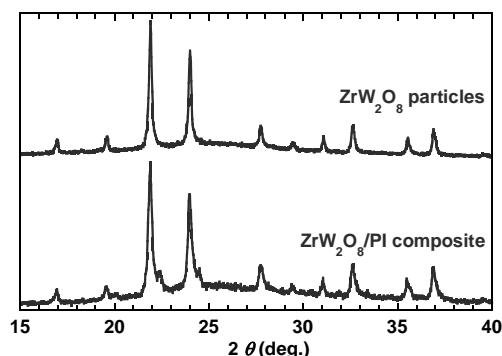


Fig. 3. WAXD patterns of ZrW_2O_8 particles and ZrW_2O_8 /PI composite film (50 vol%).

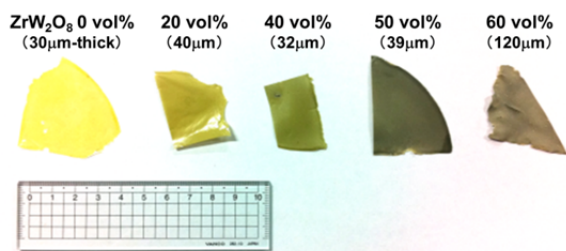


Fig. 4. Appearance of ZrW_2O_8/PI composite films with different fractions of ZrW_2O_8 particles.

3.2. Appearance of ZrW_2O_8/PI composite films

Figure 4 shows the color and appearance of the composite films prepared with different volume fractions of ZrW_2O_8 particles. The bright yellow color of pristine BPDA-ODA PI film (0 vol%) gradually change to khaki brown (60 vol%) through greenish yellow (20 vol%) and deep green (50 vol%). The greenish color could be partly generated by that of tungsten oxide (WO_3) because ZrW_2O_8 particles have grave white color. A small portion of ZrW_2O_8 particles could be thermally decomposed to WO_3 (bright green) and ZrO_2 (white) in the presence of moisture during thermal imidization.

3.3. Thermal expansion behaviors of composites

Figure 5 demonstrates the TMA curves of ZrW_2O_8/PI composite films with different ZrW_2O_8 fractions. Thermal expansion of all the composite films show high linearity between $80^\circ C$ to $180^\circ C$. Figure 6 shows the plots of CTE values of the composite films versus the ZrW_2O_8 content. Note that the CTE values are linearly decreased with increasing the ZrW_2O_8 fraction, which indicates that the linear thermal expansion, *i.e.* CTE, of composite films can be precisely controlled by varying the ZrW_2O_8 content. This figure displays a clear contrast to the relationship between ZrW_2O_8 fractions and CTE values observed for ZrW_2O_8/PI composite films reported by Sullivan and Lukehart [6]. In the present study, although no surface modification was conducted to ZrW_2O_8 surfaces, relatively good contact between the filler and PI matrix was achieved.

Furthermore, it should be noted that an incorporation of 60 vol% of ZrW_2O_8 particles into PI film significantly reduce the CTE of composite film as low as 17 ppm/K. This small CTE value is same as that of metallic copper (Cu) which is widely used as a conductive wiring material in integrated circuits and multi-layer wiring boards. Tani et al. [10] reported that the CTEs of ZrW_2O_8 /phenolic resin composites were reduced from 46 ppm/K to 14 ppm/K by incorporating

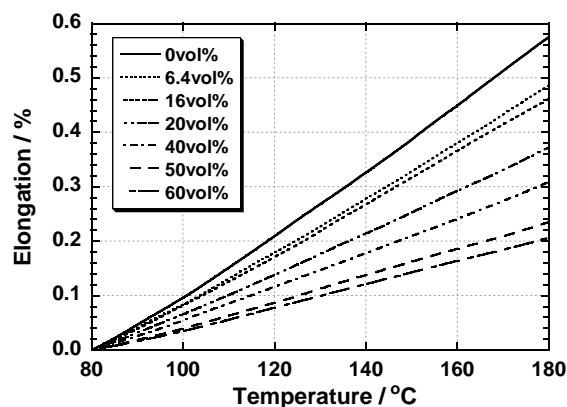


Fig. 5. TMA curves of ZrW_2O_8/PI composite films with different fractions of ZrW_2O_8 particles.

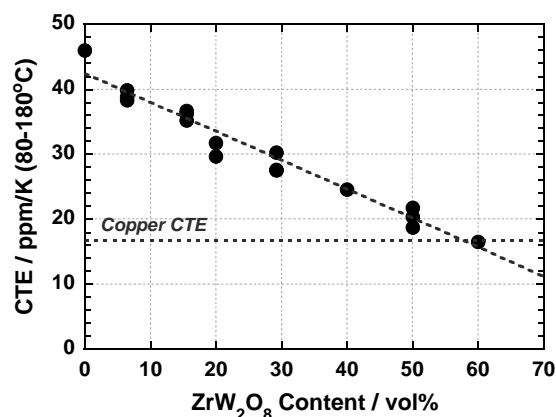


Fig. 6. CTEs of ZrW_2O_8/PI composite films with different fractions of ZrW_2O_8 particles.

ZrW_2O_8 particles up to 52 vol%. However, phenolic resin does not have sufficient thermal stability requisite for lead-free reflow-soldering processes in the latest semi-conductor industry (e.g. for several min at $270^\circ C$). A similar attempt was made by preparation of ZrW_2O_8 /cyanate ester composites, in which loading of up to 10 vol% of whisker-like ZrW_2O_8 nanoparticles results in a 20 % reduction in CTE for the thermosetting polymer matrix [11]. However, very active catalytic surface of ZrW_2O_8 whiskers seriously deteriorates the mechanical properties and thermal resistivity of the composites. Lind et al. [12] pointed out that surface modification of ZrW_2O_8 particles is effective to achieve good compatibility with polymer matrices. Hydroxyl ($-OH$) groups on ZrW_2O_8 surface can be reacted with 3-aminopropyltriethoxysilane, and the amine-terminated surface thus generated can be further modified by reaction with short PI oligomer chains. Use of compatibilizing agents, such as stearylamine, is another option for better contact between fillers and PI matrix and for reduction of micro-voids.

Assuming that the thermal expansion behaviors of the ZrW₂O₈/PI composite films prepared in this study are three-dimensionally isotropic, the films containing more than 50 vol% of ZrW₂O₈ could achieve coefficients of volumetric thermal expansion (CVE) smaller than 50 ppm/K, because CVE value is threefold of CTE value in isotropic substances. This indicates that thermally stable and stress-free dielectric layers and interconnects, which are perfectly compatible with copper wirings, can be fabricated using ZrW₂O₈/PI composites.

However, analytical method for precise measurements of CVEs of polymer thin films has not been established, and the CVE measurements for inorganic/polymer composite films should be fairly difficult. The material development of inorganic/PI composites exhibiting very low and adjustable volumetric thermal expansion is to be explored in parallel with the development of analytical methods for precise CVE measurements. In addition, deliberate efforts are to be devoted to reduce the CVE of PI matrices based on new design concepts for chemical structures and judicious control of molecular aggregation structures including degree of crystallinity and molecular orientation. The substantial reduction and adjustment of CVEs of polymeric materials is one of the most challenging subjects in future electronic & photonic materials engineering.

4. Conclusion

A series of ZrW₂O₈/polyimide (PI) composite films were successfully prepared by dispersion of sub- μ m-sized ZrW₂O₈ particles into DMAc solution of polyimide-precursor (PAA). The cross-sectional SEM images indicate that inorganic particles are homogeneously dispersed in the composite films without aggregation. The CTE of composite films is linearly decreased with increasing the volume fraction of ZrW₂O₈. The CTE of a composite film containing 60 vol%

fraction of ZrW₂O₈ (17 ppm/K) is as low as that of metallic copper. ZrW₂O₈/PI composite is a promising materials for reducing the CTE mismatch at the interface between polymer dielectrics and substrates composed of metallic, semi-conductors, and ceramics.

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