Analysis of Volumetric Thermal Expansion and Molecular Chain Orientation of Polyimide Films Based on Variable Temperature Measurement of Refractive Indices

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Abstract: Coefficients of volumetric thermal expansion (CVE) and the degrees of molecular chain orientation were quantitatively analyzed for six kinds of as-cast polyimide (PI) films formed on Si substrates based on variable temperature measurements of refractive indices. All the as-cast PI films exhibited remarkably smaller CVEs than those of the free-standing PI films, which is caused by tensile stress due to the mismatch in thermal expansion behavior between PI and Si substrate. The results of the molecular chain orientation analyses were consistent with the previous report.

1. Introduction

Polyimides (PI) have been widely used in electric and microelectronic industries, such as for insulation layers and flexible circuit boards due to their high thermal stability, low dielectric constant, good chemical resistance and mechanical properties. In these applications, control of coefficients of linear thermal expansion (CTE) of materials is crucial in terms of dimensional stability of integrated components. CTE mismatch between PI film and other inorganics, metals and ceramics, induces thermal stresses which may cause cracks or delamination. The CTEs and coefficients of volumetric thermal expansion (CVE) have been reported for free-standing PI films, though little is known for those of as-cast PI films formed on substrates. We have reported that the anisotropy in CTEs of PI films parallel and perpendicular to the film surface strongly correlates with the main chain orientation [1]. It is therefore important to analyze the chain orientation to evaluate and control the CTEs and CVEs of PI films. In this study, we investigated the CVEs and degrees of chain orientation for as-cast PI films based on variable temperature and polarization-dependent measurements of refractive indices.

2. Research Methodology

Six kinds of PI films (Fig.1) were prepared by spin coating of DMAc solutions of poly(amic acid) on Si substrate, followed by thermal imidization under nitrogen at 350 °C for 90 min. Refractive indices of the PI films were measured with a prism coupler (Metricon, model PC-2010) equipped with a home-built temperature controlling apparatus (Fig.2) [2]. All measurements were conducted during cooling from 150 °C to 60 °C for in-plane and out-of-plane refractive indices (n_{TE} and n_{TM}, respectively). Molecular polarizability was calculated by the density functional theory, and estimated degree of chain orientation is expressed by a polar angle which is defined as the angle between the axis perpendicular to the film surface and that along the PI main chain.

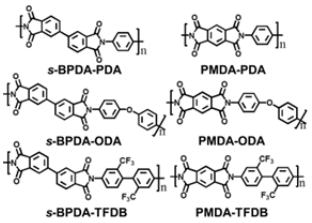

Figure 1: Molecular structure of polyimides

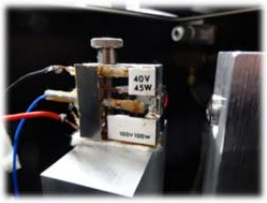

Figure 2: Photo of variable temperature apparatus for refractive index measurement

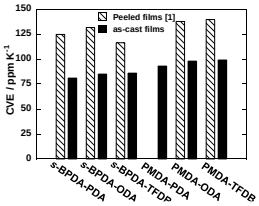

Figure 3: CVEs of free-standing and as-cast PI films

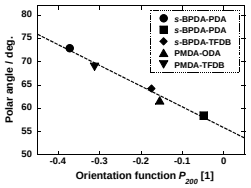

Figure 4: Relationship between the polar angle and the orientation function

3. Main Results and Conclusions

CVEs and polar angles of the PI films were calculated based on the refractive index measurements and the Lorentz-Lorenz and Vuks equations which relate refractive index, density, and polarizability of polymeric materials. Fig.3 indicates that all the as-cast PI films on Si substrates exhibited remarkably smaller CVEs than those of the free-standing PI films, which is caused by tensile stress due to the CTE mismatch between the PI and substrate. Moreover, the PIs having rigid structures with dense molecular aggregation exhibited smaller CVEs than those having bent linkages or bulky side chains. Fig.4 shows that the polar angles estimated in this study are in good linear relation with the orientation functions, P_{200}, estimated from optical birefringence [1].

4. References

[1] S. Sekiguchi, S. Ando, "Relationships among Orientation and Local Mobility of Molecular Main Chain and Thermal Expansion Behavior of Polyimide Thin Films," Polym. Prep. Japan, vol. 60(1), pp. 665, 2011.

[2] Y. Terui, S. Ando, "Control of Thermo-Optic Coefficients and Their Polarization Dependence in Polyimide Films Formed on Si Substrates," Proc. SPIE, vol. 5724, pp. 336-343, 2005.