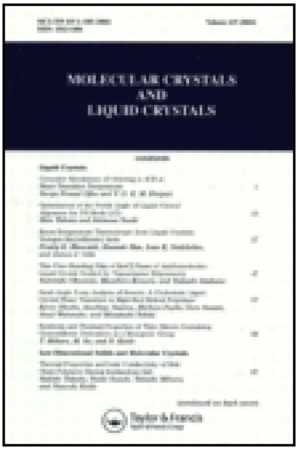

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Preparation and Characterization of Organic-Inorganic Hybrid Materials Via Sol-Gel Reaction for Interlayer Dielectrics

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Polyimides containing hydroxyl group, so-called poly(hydroxy-imide)s, were prepared by the thermal imidization in the presence of m-cresol. The poly(hydroxy-imide)s exhibited high resistance to thermal degradation, with 10% weight loss temperature starting at near 527 °C in air. The organic/inorganic hybrid materials were prepared with TEOS by acid-catalyzed sol-gel reaction of sol-gel polyimide precursors obtained from the coupling reaction of the poly(hydroxy-imide) with 3-(triethoxysilyl)propyl isocyanate. All of the cured hybrid films spin-coated on ITO glass are transparent. The initial decomposition temperature was recorded at 356°C. The dielectric constant of a hybrid material film was 3.24 at the frequency of 10kHz. The hybrid materials retained the coefficient of thermal expansion up to 3 ppm/°C below Tg and 30 ppm/°C above Tg.

Keywords: poly(hydroxy-imide); interlayer dielectrics; organic/inorganic hybrid materials; thermal expansion coefficient

INTRODUCTION

In recent years, as device dimensions minimize[1] to increase on-chip device densities, signal delays increase substantially, due to capacitive coupling and crosstalk between closely spaced metal lines. Signal transmission velocity depend on the inverse square root of the dielectric constant (ε_r) of the insulating medium. The potential application of polyimides may range from microelectronics to opto-electronics applications. They are particularly

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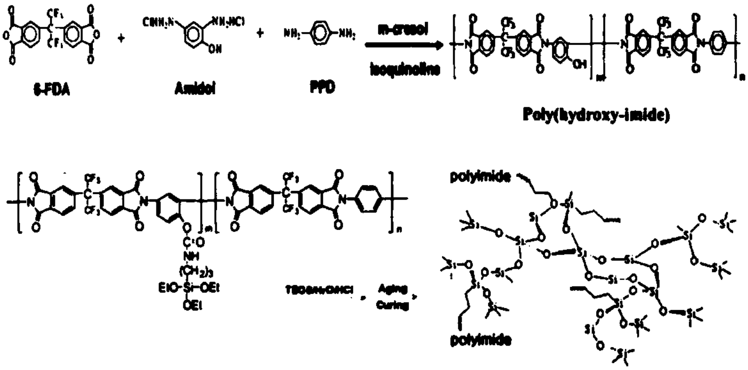
attractive materials as interlayer dielectrics in integrated circuit fabrication. Such materials must be capable of thin film processing and possess thermal and dimensional stability, their excellent thermo-oxidative stability, mechanical strength, electrical properties and solvent resistance, low dielectric constant and low thermal expansion coefficient(CTE) matching to a Si wafer.

In an effort to produce such materials, recently, our much attention has been focused on developing organic-inorganic hybrid materials containing molecular voids with low dielectric constants via sol-gel process. These hybrid materials can combine the low dielectric behavior and good processability of polyimides with the desirable characteristics of silica glasses such as low CTE and good dimensional stability. The sol-gel reaction involves the hydrolysis and condensation of metal alkoxides such as tetraethoxysilane(TEOS), forming the inorganic part of the hybrid materials.[2] The copolyimides containing hydroxy group used in this work were prepared through thermal imidization process, starting from dianhydride(6FDA) and the mixed diamines of amidol and p-phenyldiamine(PPD) in the presence of m-cresol (Scheme 1). The introduction of CF_3 groups into the polymer chain increases solubility and decreases dielectric constant and water-uptake.[3] Sol-gel polymeric precursors were prepared by the coupling reaction of copoly(hydroxy-imide)s with 3-(triethoxysilyl)propyl isocyanate, since the diamine of amidol provides chemical reaction sites between the polymer backbone and the silica. The silica particles as an inorganic material were generated via sol-gel reaction[4] of TEOS in the sol-gel precursor, acid catalyst and water. By varying the ratio of the metal alkoxide to the polymer, the thermal expansion coefficient of the hybrid materials could be improved. Also, we incorporated the molecular voids such as carboranes, adamantanes[4], and silsesquioxanes into the hybrid matrix. Our main aim is to investigate the dielectric constant and thermal properties of sol-gel derived organic/inorganic hybrid films.



SCHEME 1 Preparation of poly(hydroxy-imide)s and organic/inorganic hybrid materials.

RESULTS AND DISCUSSION

A synthetic route for the preparation of polyimides having hydroxyl group by thermal imidization is shown in Scheme 1. The resulting poly(hydroxy-imide)s were soluble in common organic solvents, including NMP, DMAc, DMSO, DMF and m-cresol. The chemical structure of the poly(hydroxy-imide)s was identified by FT-IR and ^{1}H-NMR analyses, as shown in Figure 1. IR spectrum of a poly(hydroxy-imide) showed several bands near 3300~3400 (for O-H str.), 1783 (for asym. C=O str), 1736 (for sym. C=O str), 1369 (for C-N str) and 721 cm^{-1} (for imide ring formation). Two broad peaks of 7.1-8.2 ppm and 10.36 ppm appeared in ^{1}H-NMR spectra were assigned to the phenyl group and the hydroxy group, respectively. The thermal property of the poly(hydroxy-imide) was evaluated by thermogravimetric and DSC analyses. The poly(hydroxy-imide) exhibited high resistance to thermal decomposition, with 10% weight loss temperature being recorded near 527 °C in air.

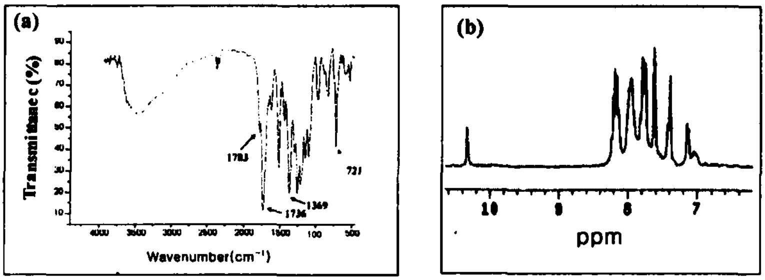


FIGURE 1 FT-IR (a) and ^{1}H-NMR (b) spectra of a poly(hydroxy-imide).

Hybrid precursors were synthesized through urethane linkage by the coupling reaction between the poly(hydroxy-imide) and 3-(triethoxysilyl) propyl isocyanate. Preparation of three-dimensional silica/polyimide networks was performed by the acid-catalyzed sol-gel reaction of a hybrid precursor with TEOS (see Scheme 1). After the addition of an aqueous acid solution was completed to the sol-gel precursors, the reaction mixture was stirred for 3 days at room temperature, providing a homogeneous solution (the sol). The sol was spin-coated on the ITO glass, yielding hybrid films. The hybrid films were dried in the vacuum oven at 60 °C for 12h and cured at 250 °C for 12h. After curing, the new absorption peak of the Si-O-Si band at 1070 cm^{-1} increased. The peak at 3400 cm^{-1} was indicated as the NH stretching band in urethane linkage. The thermal stability of the resulting hybrid materials was evaluated by TGA under air atmosphere. The initial decomposition temperature was recorded at 356 °C. (see Figure 2). The dielectric constants of a hybrid material and a poly(hydroxy-imide) film, measured at 10kHz, were 3.24 and 4.07, respectively. The hybrid materials exhibited low CTE up to 3 ppm/°C below T_g and 30 ppm/°C above T_g.

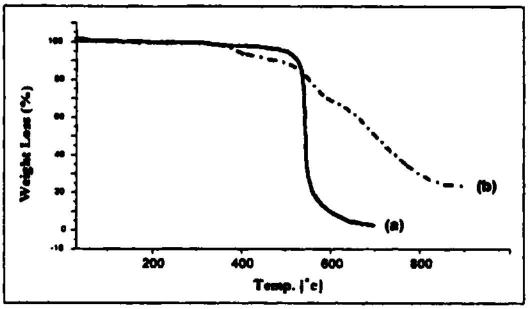


FIGURE 2 TGA thermogram of a poly(hydroxy-imide) (a) and a hybrid material (b).

In conclusion, the polyimide-based hybrid precursors were prepared by the coupling reaction of 3-(triethoxysilyl)propyl isocyanate with the poly(hydroxy-imide)s which were syntheisized through a thermal imidization process. The organic/inorganic hybrid materials was successfully obtained by the acid-catalyzed sol-gel reaction of polyimide-based hybrid precursors with TEOS under the various ratios of the metal alkoxide to the polyimide. They were initially decomposed at about 356°C. All cured hybrid films spin-coated on ITO glass have good transparency. The dielectric constant of a hybrid material film was 3.24 at the frequency of 10kHz. The hybrid materials retained low CTE up to 3 ppm/°C below T_g and 30 ppm/°C above T_g.

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References

[1] P. E. Cassidy, T. M. Aminabhavi and J. M. Farley, *J. Macromol. Sci.-Rev. Macromol. Chem. & Phys.*, ***C29***, 365 (1989).

[2] M. Bruma, J. W. Fitch, P. E. Cassidy, *J. Macromol. Sci.-Rev. Macromol. Chem. & Phys.* ***36***, 119 (1996).

[3] H. K. Kim, S. J. Kang, S. K. Choi, Y. H. Min, C. S. Yoon, *Chem. Mater.* ***11***, 779 (1999).

[4] Y. T. Chern, H. C. Shiue, *Macromolecules*, ***30***, 4646 (1997).