Novel Low-Dielectric-Constant Copolyimide Thin Films Composed with SiO_2 Hollow Spheres

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Received 11 October 2008; accepted 22 March 2009
DOI 10.1002/app.30467
Published online 9 November 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A series of copolyimide/SiO_2 hollow sphere thin films were prepared successfully based on bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]methane and 9,9-bis(4-(4-aminophenoxy)phenyl)fluorene (molar ratio = 3 : 1) as diamine, and 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) as dianhydride, with different wt % SiO_2 hollow sphere powder with particle size 500 nm. Some films possessed excellent dielectric properties, with ultralow dielectric constants of 1.8 at 1 MHz. The structures and properties of the thin films were measured with Fourier transform infrared spectra, scanning electron microscope, thermogravimetric analysis, and dynamic mechanical thermal analysis. The polyimide (PI) films exhibited glass-transition temperatures in the range of 209– 273°C and possessed initial thermal decomposition temperature reaching up to 413–477°C in air and 418–472°C in nitrogen. Meanwhile, the composite films were also exhibited good mechanical properties. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1133–1137, 2011

Key words: dielectric properties; polyimides; thin films

INTRODUCTION

Polyimides (PIs) as high performance polymers were more and more focused by academic and industrial research groups.[1] Especially, low-dielectric-constant PIs were widely used in microelectronic industry, aerospace, electrical insulation, and semiconductor industries for the excellent thermal stability and good mechanical properties (for example, replacing silicon dioxide with dielectric constants ranged of 3.9–4.2 as the interlevel dielectric in integrated circuit productions).[2] Much work had been done for preparing low-dielectric-constant PIs. Usually, the dielectric constants of most nonfluorinated PIs were in the range of 2.9–3.5. Introducing fluorinate groups could obviously decrease the dielectric constants. They were in the range of 2.5–3.2. In 2004, Hsiao and Chang[3] indicated that PIs with trifluoromethyl possessed good dielectric properties; however, the dielectric constants were still not low enough for the application in developing microelectronic industry. Nanocomposite PI was another significant kind of PIs with low-dielectric constant. Wang et al.[4] claimed that they had already synthesized another kind of nanoporous PI with low-dielectric constant. In 2005, Zhang et al.[5] had successfully prepared novel silica tube/PI composite films with variable low-dielectric constant in the range of 2.9–3.8. By the year of 2003, Kohei et al.[6] noted that diamine or dianhydride monomer with fluorene groups could be used to reduce the dielectric constants of PIs.

In our previous work, low-dielectric-constant PIs were successfully prepared based on bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]methane (BDAPM) and different common dianhydrides. The PI contained —CF_3 groups possessed low-dielectric constant about 2.8 at 1 MHz. Then a series of copolyimide films exhibited lower dielectric constants were synthesized by copolymerization with different molar ratios of BDAPM and 9,9-bis(4-(4-aminophenoxy)phenyl)fluorine (BAOFL) as diamine. The PI films showed the lowest dielectric constants about 2.3 at 1 MHz with the molar ratio of BDAPM : BAOFL = 3 : 1.[7,8]

Also, we had prepared PI/SiO_2 films based on BDAPM as diamine, and 4,4′-(4,4′-isopropylidenediphenoxy) bis(phthalic anhydride) (BDAPA) as dihydride, composed SiO_2 hollow sphere with different wt %. Obviously, PI/SiO_2 composite showed lower dielectric constants than pure PIs. In 2006, Chen et al.[9,10] developed a method for the fabrication of monodisperse hollow silica spheres. However, SiO_2 hollow spheres powder prepared by Chen's method should be calcined before used for the polystyrene remained in SiO_2 hollow spheres could bring huge influence to polymerization.

Here, we report a series of copolyimide/SiO_2 hollow spheres thin films with ultralow dielectric constants and good mechanical properties. The novel copolyimide/SiO_2 thin films were synthesized based on BDAPM and BAOFL with molar ratio 3 : 1, and BDAPA as dianhydride, then composed with SiO_2 hollow sphere from 1–5 wt %. The dielectric

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properties, mechanical properties, morphologies, and thermal stabilities of the PI films were also examined.

EXPERIMENTAL

Materials

2,6-Dimethylphenol, 9,9-bis(4-hydroxyphenyl) fluorene, *p*-chloronitrobenzene, anhydrous potassium carbonate, hydrazine monohydrate, and 5% palladium on activated carbon (5% Pd/C) were used as received. BPADA were recrystallized from acetic anhydride and dried *in vacuo*. 1-Methyl-2-pyrrolidinone (NMP), and *N*,*N*-dimethylformamide (DMF), were purified by distillation under reduced pressure before they were used. The other chemical reagents (all from Shanghai Chemical Reagents, Shanghai, China) were used as received.

Preparation of the SiO_2 hollow spheres

The SiO_2 hollow spheres powder prepared by Chen's method should be calcined at 500°C for 6 h before used for removing the remained polystyrene which could bring huge influence to polymerization.[9,10] And the particle size for the SiO_2 hollow spheres was 500 nm.

Preparation of the PIs

In our previous work, we have proposed a processing method of PIs with low-dielectric constant based on BDAPM and BAOFL consisting in literature.[7,8,11] PIs were prepared by a conventional two-step polymerization method. Molar equivalents of diamine and dianhydride were dissolved in dried NMP with a 10% solid concentration under a nitrogen atmosphere at room temperature for 24 h; then, added the SiO_2 hollow sphere powder, stirred for another 24 h; after that, the solutions were then spread on glass plates, which were placed in an 80°C vacuum oven for 2 h to remove the solvent, and the films were heated sequentially from 80 to 200°C for about 8 h for imidization.

Characterization

The structures of the PIs were confirmed by IR with a Nicolet Magna IR650 (Madison, WI), whereas differential scanning calorimetry (DSC) measurement was deduced from a TA Instruments Q20 under a nitrogen purge at heating rate of 10°C min^{-1} from 30 to 350°C. The thermal stabilities of PIs were recorded on a TA Instruments Q50 under a nitrogen purge and an air purge. The scanning rate was 20°C/min. Dynamic mechanical analysis, was performed on a Mark V dynamic mechanical thermal analyzer. The run conditions were a frequency of 1 Hz and a heating rate of 3°C/min from −100 to 300°C in nitrogen. The dielectric constant values were tested using a Hioki 3532-50 impedance analysis instrument (Hioki E. E. Corporation, Ueda Nagano, Japan) with the films plated aluminum on both surfaces at 25°C. Scanning electron microscopy (SEM) observation was performed on a Sirion field-emission SEM. The morphologies of the cross-sectional surface of the copolyimide/SiO_2 films were determined from SEM images. The composites were fractured first in liquid nitrogen and mounted on conductive glass by means of a double-sided adhesive tape. A thin layer of gold was sputtered onto the cross-sectional surface before SEM observation.

RESULTS AND DISCUSSION

The PI synthesized from BDAPM and BAOFL with molar ratio 3 : 1 composed with SiO_2 1 wt % was designated PI- $SiO_2$1%; that with 2 wt % was designated PI-SiO_2 2 wt %. The rest were designated PI-$SiO_2$3 wt %, PI-$SiO_2$4 wt %, PI SiO_2 5 wt % and the PI synthesized without SiO_2 was designated PI.

IR spectra of the copolyimide/SiO_2 films

Figure 1 shows the IR reflectance spectra of the PI films. As representative examples, from the IR reflectance spectra of the pure PI, PI-SiO_2 3%, and PI-SiO_2

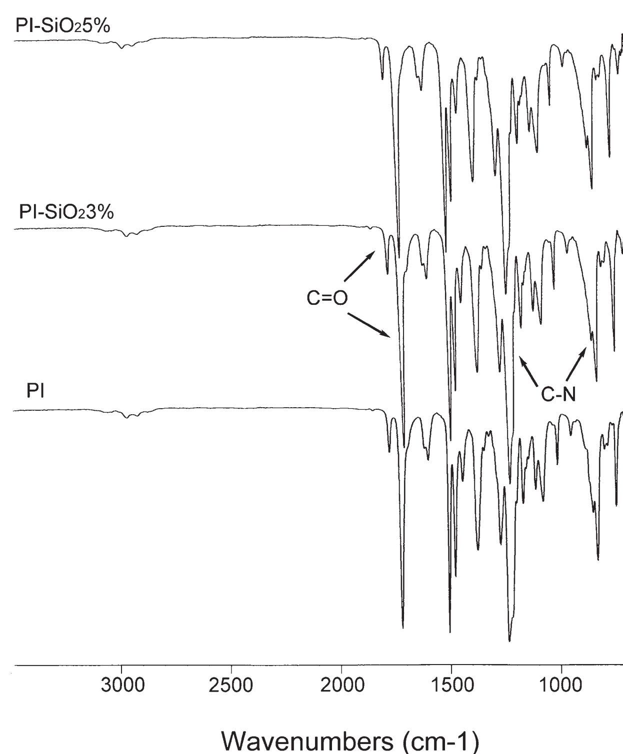

Figure 1 IR reflectance spectra of the copolyimide/SiO_2 films.

5%, absorption bands at about 1720 cm^{-1} and 1780 cm^{-1} represent the symmetric and asymmetric stretching of C=O in imide groups and those at about 1377 cm^{-1} and 725 cm^{-1} represent C—N stretching and C—N bending, respectively, in imide groups as well. The existence of imide groups was indicated. There were no obvious absorption bands of —OH between 3000–3500 cm^{-1}, which proved the PI precursors were almost fully imided. It was proved the successful synthesis of PIs.

Dielectric properties

The dielectric constants of the PI composite films were tested at different frequencies from 1 k–1 MHz at 25°C. The dielectric loss tangent value was in the range of 0.001–0.009. Figure 2(a) presented the relationships between dielectric constants and frequencies. The dielectric constants of all the copolyimide/SiO_2 films stably reduced with increasing frequency. From Figure 2(b), it was clear that with increasing of the content of SiO_2 hollow spheres, the dielectric constants at 1 MHz of these films first decreased gradually, then gained enhancement stably. It was noticed that the dielectric constant of the composites reduced from 2.3 of the pure PI to 1.8, then increased to 2.7. The copolyimide/SiO_2 films, PI-SiO_2 3% exhibited the lowest dielectric constant values about 1.8. The dielectric constant of air was 1.0, so the air voids stored in the SiO_2 hollow spheres were the main reason of the reduction of dielectric constants.[12] Meanwhile, some air voids might exist in the gaps on the interfaces between the SiO_2 hollow spheres and the PI matrixes.[13] Therefore, the reduction of the dielectric constant was contributed by the whole air voids created by incorporating the SiO_2 hollow spheres, including the air volume stored within the SiO_2 hollow spheres, the air voids came from the gaps on the interfaces between the SiO_2 hollow spheres and the PI matrix.[14,15] With the increasing of SiO_2 hollow spheres content, the amount of air voids contained by SiO_2 hollow spheres increased at very beginning. And it resulted

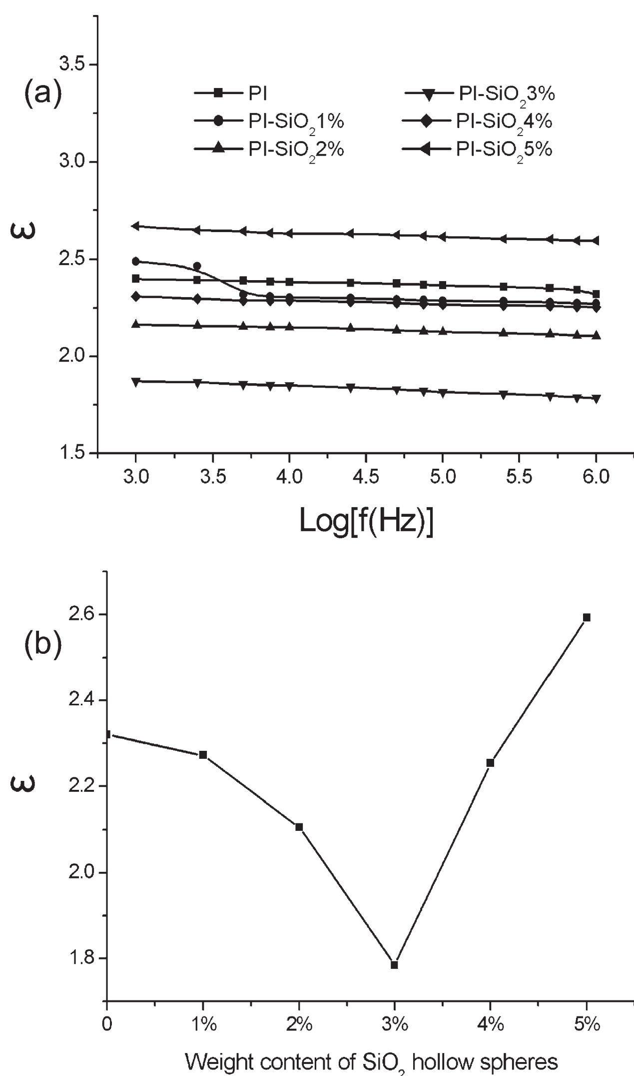

Figure 2 (a) Relationships between the dielectric constant (ε) and frequency (*f*) for the copolyimide/SiO_2 films at 25°C. (b) Relationships between the dielectric constant (ε) and the weight content of SiO_2 hollow spheres for the copolyimide/SiO_2 films at 25°C.

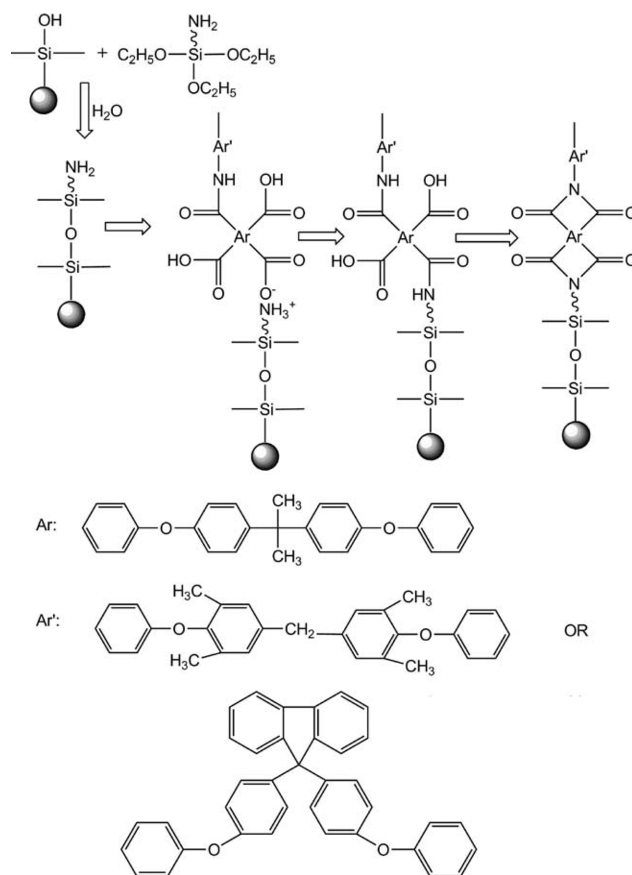

Figure 3 Preparation of the copolyimide/SiO_2 films.

the dramatic decreasing of the dielectric constants for PI composite films. On the contrary, after exceeding this characteristic content 3%, too much SiO_2 hollow spheres incorporated, which caused the aggregation and poor dispersion of SiO_2 hollow spheres. The dielectric constant of SiO_2 was about 3.9–4.2. With the increasing of the SiO_2 hollow spheres, the dielectric constants of films were more and more influenced. Therefore, it caused the stable enhancement of dielectric constant.

Morphology

Figure 3 showed the schematic linking formation of the PI with the SiO_2 hollow spheres. The KH-550 had been chemically grafted onto the SiO_2 hollow spheres. These surface-linking KH-550 contained amine groups, would further react with the poly(amic acid) during the reaction process, and thus increase the interfacial adhesion between SiO_2 hollow spheres and PI matrix.[16]

Figure 4 showed the SEM images of the cross-sectional surface of copolyimide/SiO_2 films. It could be clearly observed the morphology of PI-SiO_2 3% and PI-SiO_2 5%. The similar phenomena could be observed from the SEM image of the cross-sectional surface of the copolyimide/SiO_2 films, in which the SiO_2 hollow spheres were uniformly dispersed almost as individual particle in the matrix as shown in Figure 4.

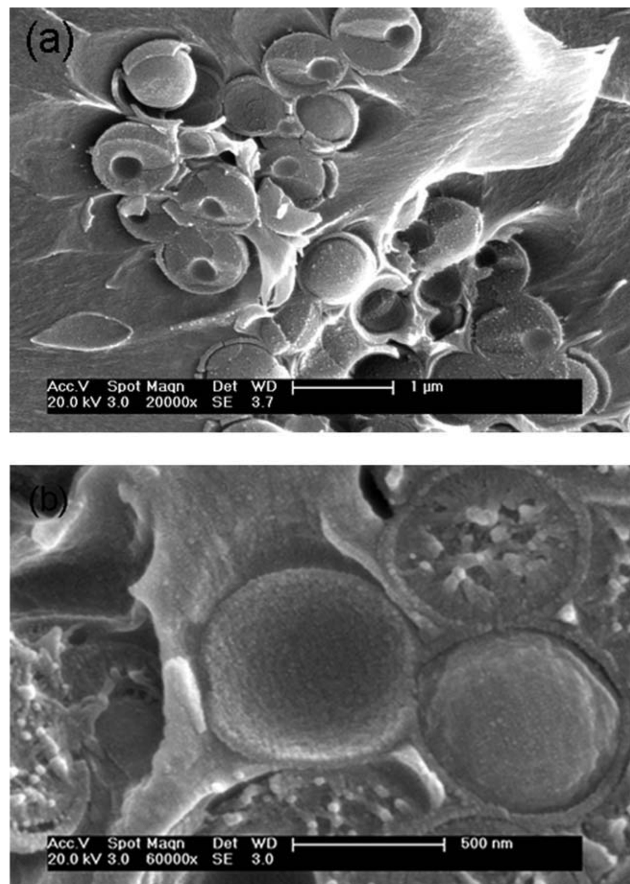

Figure 4 SEM images of the cross-sectional surface of copolyimide/SiO_2 films.

TABLE I
Thermal Properties of Copolyimide/SiO_2 Films

Sample	T_g[a] (°C)	T_{d5}[b] (°C) In air	T_{d5}[b] (°C) In N_2	Char yield[c] (%)
PI-SiO_2 1%	209	413	418	48.5
PI-SiO_2 2%	211	425	439	44.2
PI-SiO_2 3%	221	454	453	45.1
PI-SiO_2 4%	245	428	428	43.3
PI-SiO_2 5%	273	477	472	43.4

[a] T_g determined by DSC in nitrogen at heating rate of 10°C min^{-1}.
[b] Temperature at 5% weight loss determined by TGA in nitrogen and in air at heating rate of 20°C min^{-1}.
[c] Char yield at 700°C in nitrogen.

The SEM images of SiO_2 hollow spheres dispersed in copolyimide/SiO_2 films showed clearly its coarse surface covered with a thin layer of the PI. These results also confirmed the effective surface treatment of the SiO_2 hollow spheres, and revealed that the SiO_2 hollow spheres had good bonding interfaces with the matrix.[17] All these phenomena proved the assumption for the cause of dielectric properties.

Thermal properties

Table I contained the data for thermal properties of the copolyimide/SiO_2 films examined by DSC and TGA. The temperatures at 5% weight loss reduced stably, and showed values reaching up to 418– 472°C in nitrogen and 413– 477°C in air, respectively. This presented that the copolyimide/SiO_2 films containing

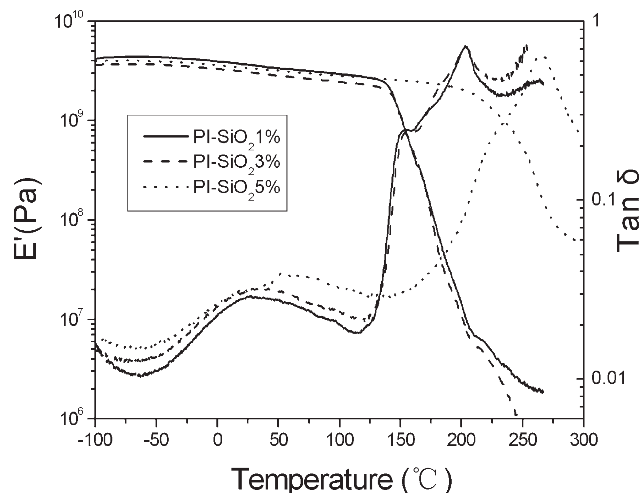

Figure 5 Dynamic mechanical spectra of the copolyimide/SiO_2 films.

TABLE II
Dynamic Mechanical Analysis of the Copolyimide/SiO_2 Films

Sample	α		β	
	T_g(°C)	tan δ	$T_β$(°C)	tan δ
PI-SiO_2 1%	201	0.73	31.6	0.029
PI-SiO_2 3%	201	0.72	33.9	0.032
PI-SiO_2 5%	265	0.65	58.5	0.039

The dynamic mechanical thermal analysis data were collected at 30°C/min in nitrogen at 1 Hz. α relaxation is the glass-transition temperature; β relaxation, occurs below the T_g and is associated with local band rotations and molecular segment motions along the polymer backbone, and the magnitude segments contributing to the relaxation; $T_β$, the peak value temperature of the β relaxation.

different SiO_2 hollow spheres contents possessed the good thermal stability. The static glass-transition temperatures increased gradually and were in the range of 209–273°C, a bit higher than dynamic glass-transition temperatures mentioned above. In the same way, with the increasing of the SiO_2 hollow spheres content, PI-SiO_2 5% possessed the highest static glass-transition temperature.[18] And there was no obvious tend of the char yield. Various factors, such as the shape, the way of piling, etc, could lead to the irregular results in nitrogen.

Mechanical properties

Figure 5 presented the dynamic mechanical properties of the copolyimide/SiO_2 films. As representative examples, PI-SiO_2 1%, PI-SiO_2 3%, and PI-SiO_2 5% were investigated. The dynamic glass-transition temperatures were 201°C, 201 °C, 265°C, respectively. In general, the mechanical properties of the PI films were excellent, exhibited very high tensile strength and modules.[15] Tan δ showed temperature dependence of the mechanical loss for the PI films. From figure, it was clear that there were wide ranges of α relaxation peaks represented glass-transition temperatures in the lines of tan δ for all the films. This result was expected as the SiO_2 hollow spheres resulted in ring formation which decreased the stiffness of the polymer backbone and enhanced the main-chain mobility.[10] PI-SiO_2 5% possessed the highest dynamic glass-transition temperature. Evidently, the behaviors were in agreement with the results of the dielectric constants for the films.[14] Table II contained the data of dynamic mechanical analysis of the PI films. Typical behaviors of PIs were exhibited: the storage modulus was lost above the softening point. Below the softening point, the storage modulus of the PI films was consistent with conventional PIs. Below dynamic T_g, the β relaxation, associated with local bond rotations and molecular segment motions along the polymer backbone, was proportional to the concentration of segments.[18] In general, these motions were considered to be a primary function of the PI, and their presence and magnitude were ascribed to several material properties.[16] PI films with higher temperatures and lower tan δ values possessed higher energy barriers for molecular motion. All of these were attributed to the rotation of these bonds hindered by the rigid and bulky fluorene groups, ultimately causing an increasing chain stiffness of PI chains.

CONCLUSIONS

In summary, novel copolyimide/SiO_2 thin films with low-dielectric constants were prepared successfully. The low-dielectric constants (about 1.8 at 1 MHz) of the films, required for the mentioned applications in introduction, were the most important property in this study. The low-dielectric constant was ascribed to the effect of air stored in the hollow spheres, pores, and interfaces between the SiO_2 hollow spheres and the PI matrix in the composite. It might be possible to further reduce the dielectric constant of the composite by choosing a matrix with a smaller dielectric constant, or obtain PI materials with tunable dielectric constants. The structures and morphologies of the films were investigated. And these films had good mechanical properties under the glass-transition temperatures. Moreover, all the films possessed good thermal stabilities.

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