Synthesis and Characterization of Low-Dielectric Photosensitive Polyimide/Silica Hybrid Materials

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ABSTRACT: Photosensitive polyimide/silica hybrid materials were synthesized by reaction between 4,4′-hexafluoroisopropylidene diphthalic anhydride (6FDA) and 4,4′-oxydianiline. The intrachain chemical bonding and the interchain hydrogen bonding between the polyimide and silica moieties were increased by the incorporation of 2-(dimethylamino) ethyl acrylate and 3-aminopropyl trimetho xysilane, respectively. The photoinitiator was bis(2,4,6-trimethyl benzoyl) phenylphosphine oxide (Irgacure-819). The various coupling agents were utilized included tetrakis (allyloxy) silane (TAL). Most silica hybrid films showed better volume shrinkage and temperature resistance. The cooperation of octavinyl POSS, as the coupling agent, can lower dielectric constant (k) down to 2.48 but with the poorer volume shrinkage and temperature resistance than the other silica hybrid films. The addition of tetramethyl orthosilicate and 3-methacryloxy propyltrimethoxysilane with silica content of 5.6 wt % can reduce k down to 2.26 but with worse volume shrinkage than the incorporation with TAL. The TAL hybrid film with degree of polymerization of 25 showed the best properties that optimized photolithography, dielectric constant ($k = 3.81$), volume shrinkage, and temperature resistance (Td5% $= 378°C$) with only 0.22 wt % silica content. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2422–2427, 2010

Key words: photosensitive polyimide; polyimide–silica hybrid; low-dielectric polyimide

INTRODUCTION

Polyimide films have been widely used in many applications because of their excellent heat resistance, stability, and electrical insulating properties. Some applications, however, require further property enhancements and the desired improvements can be obtained through incorporation of inorganic micro- and nano-fillers such as silica nanoparticles.

Organic–inorganic hybrid materials have been recognized as a new class of advanced materials because they can produce superior properties over the parent organic or inorganic materials.[1–5] These hybrid materials can be formed by sol–gel process via a number of approaches. For example, one method involves the hydrolysis of metal alkoxides to produce hydroxyl groups, followed by the polycondensation of the hydroxyl groups. These condensation reactions result in the formation of inorganic network that is covalently bonded to the organic oligomer or polymer.[6–10] Polyimide–silica hybrid materials have been widely studied recently because of their excellent thermal, mechanical, and electrical properties.[11–25] Incorporation of photosensitive functionality into hybrid materials is essential for patterned optoelectronic devices as it can save the extra step of adding photoresists.

However, the only limited polyimide/oxide hybrid materials have been demonstrated to be photopatternable. For example, Zhu et al. prepared the polyimide/silica hybrid materials based on intrinsic photosensitive dianhydride moiety of 3,3′,4,4′ benzophenone tetracarboxylic dianhydride.[26] Later, they extended a similar approach to prepare photosensitive polyimide/titania materials.[27] Although these were among the first few reports on photosensitive polyimide/inorganic hybrid materials, the patterned resolution (10 mm) and relatively large inorganic particle size (300 nm–2 mm) could be further explored. Ionic salt or ether-type photosensitive polyimides (PSPI) are widely used in microelectronic industries, including printed circuit boards and electronic packing.

However, their applications as photopatternable especially on optoelectronic devices (e.g., optical waveguides) are significantly limited because large volume shrinkage after curing (often up to 20–50%) is occurred from eliminating pendant photosensitive moieties. Such large volume shrinkage would cause a significant distortion on the patterned feature (usually rounded edge), reduced critical resolution, and

TABLE I
The Molar Ratios of Compositions on the Reaction Mixtures

Code	DP	Molar ratio of the composition								Film composition (%)	
		6FDA	ODA	APrTEOS	TAL	TMOS	MPTMS	MDAE	POSS	Polyimide	Silica
P0	9	5	4	0	0	0	0	0	0.00	100.00	0.00
P1	9	5	4	2	0	0	0	10	0.00	99.40	0.60
P2	9	5	4	2	6	0	0	10	0.00	97.60	2.40
P3	9	5	4	2	0	6	6	10	0.00	94.42	5.58
P4	9	5	4	2	6	0	0	0	0.83	96.37	3.63
P5	9	5	4	2	6	0	0	10	0.83	96.37	3.63
P6	25	13	12	2	6	0	0	10	0.00	99.78	0.22
P7	49	25	24	2	6	0	0	10	0.00	99.89	0.11
P8	99	50	49	2	6	0	0	10	0.00	99.95	0.05

induced large thermal stress after heat treatments.[28] Hence, the reduction of volume shrinkage has become one of the major issues for PSPI. Besides, better thermal and mechanical properties of organic polyimides are needed to success fully apply in heat resisted photopatternable especially optoelectronic functions. The approach to prepare photosensitive polyimide/silica hybrid materials could resolve the above problems of ionic salt photosensitive polyimide materials especially for optoelectronic devices.

In this study, novel ionic-salt type photopatternable fluorinated polyimide/silica hybrid materials with octavinyl POSS were developed to reduce the volume shrinkage and enhance physical properties over conventional PSPI. The volume shrinkage of photosensitive poly (6FDA-ODA)/MDAE was largely reduced by photocrosslinking MDAE with a coupling agents and the silica domain in the hybrid materials. The used coupling agents were TAL for the first times. The cooperation of tetramethyl orthosilicate (TMOS) and 3-methacryloxy propyltrimethoxysilane (MPTMS) that mention in Ref. 29 was compared. The effects of coupling agent, especially octavinyl POSS, and the silica content on the morphologies and physical properties of the obtained hybrid materials were discussed. These results indicate that the prepared low-dielectric photosensitive polyimide/silica hybrid materials may have the potential applications for electrical devices.

EXPERIMENTAL

Materials

4,4′-Hexafluoroisopropylidene diphthalic anhydride (6FDA, Fluka, 99%), 4,4′-oxydianiline (ODA, Fluka, 98%), 3-aminopropyltriethoxy silane (APr- TEOS, Aldrich, 99%), 2-methyl acrylic acid 2-dimethylaminoethylester (MDAE, Merk, 98%), tetra- kis(allyloxy) silane (TAL, Fluka, 96%), tetramethyl orthosilicate (TMOS, Aldrich, 99%), 3-methacryloxy propyl trimethoxysilane (MPTMS, Aldrich, 98%), dimethyl sulfoxide (DMSO, Aldrich, 99.5%), N,N-dimethyl

acetamide (DMAc, Aldrich, 99.8%), γ-butyrolactone (Aldrich, 97%), and octavinyl POSS (Hybrid plastics,99%) were used as received. The photoinitiator, bis(2,4,6-trimethylbenzoyl) phenyl phosphine oxide (Irgacure-819), was grateful provided by Ciba Specialty Chemical Thailand.

### Preparation of the photosensitive APrTEOS-capped poly(amide acid)–silica precursor (A-PAA)

APrTEOS-capped poly(amide acid)–silica precursor (A-PAA) was synthesized by the 4,4′-hexafluoro isopropylidenediphthalicanhydride (6FDA) with 4,4′-oxydianiline (ODA) in DMAc solutions and then coupled with 3-aminopropyltriethoxy silane (APrTEOS) by various the mole ratio of 6FDA: ODA: APrTEOS as in Table I. The DP is the degree of the polymerization which calculated from $(1 + r)/(1 - r)$ and r equal to mole of ODA/mole of 6FDA.

Preparation of the precursor solution (in scheme 1) of the hybrid films

The compositions for preparing photosensitive PI–silica films are listed in Table I. By using P2 as an example, 1.86 mL of the Tetrakis (allyloxy) silane (6 mmol) was added to the A-PAA solution and stirred for 15 min as shown in Scheme 1. Then, the deionized water and HCl solutions were added and allowed to react at room temperature for another 24 h. The amount of added water was equal to the total moles of the Si–OR groups for APrTEOS and Tetrakis(allyloxy)silane. After that, 1.5185 mL (6 mmol) of the MDAE and 136 mg of Irgacure-819 were added and stirred for 2 h to form the precursor of the P2.

Lithographic patterning

The prepared precursors of the P0–P8 were spread onto thin glass. The thin film was then soft baked at 50°C under vacuum for 20 min to partially evaporated solvent and then exposed to the UV light
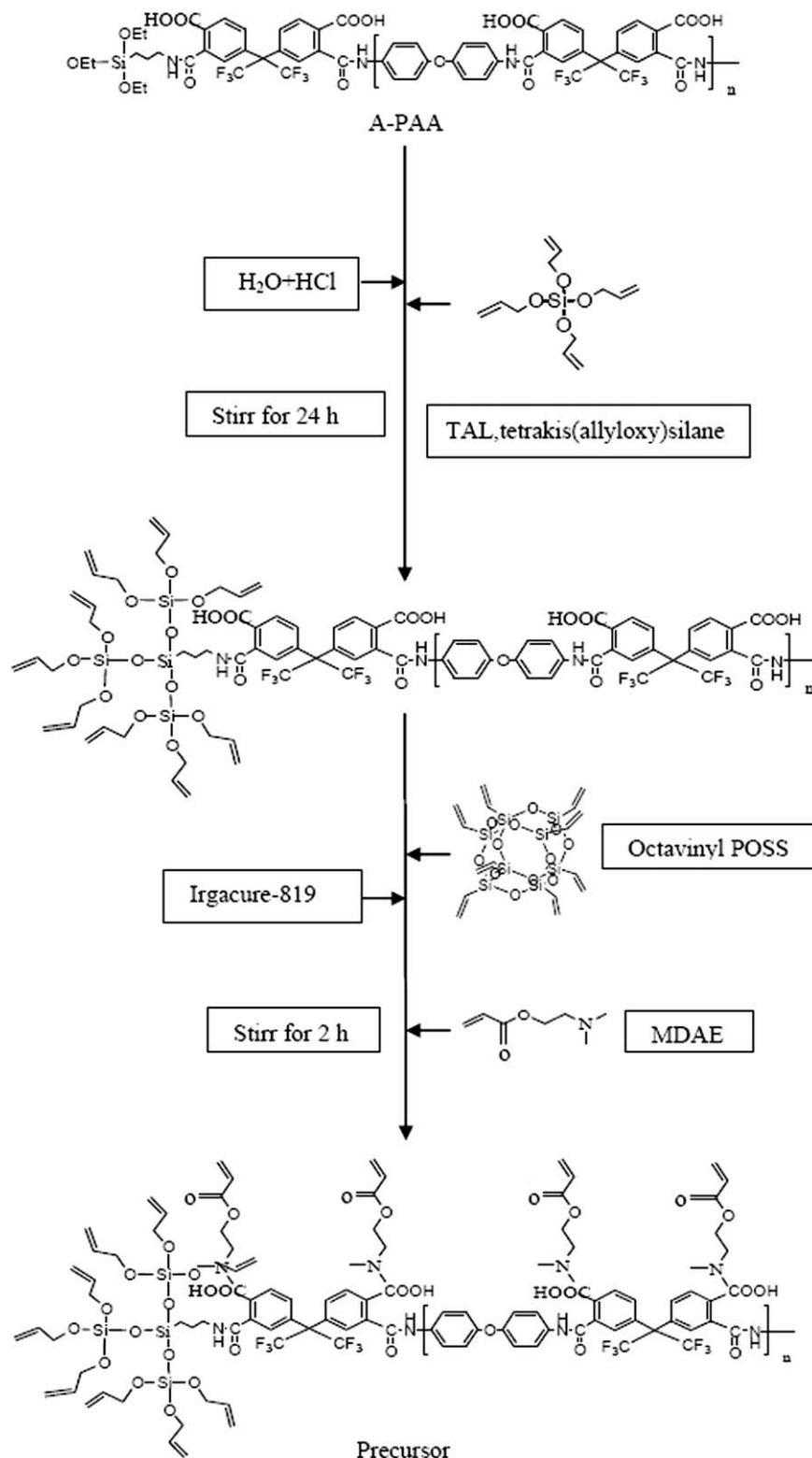
Scheme 1 Preparing precursor reaction scheme.

($\lambda = 360$ nm, 15W) through a transparent mask or a predefined Cr mask for 2 h. The films were developed by the mixture of DMSO/γ-butyrolactone in the weight ratio of 50/50. Finally, the developed pattern was cured by the multistep heating process of 150, 200, 250, and 300°C for 30 min each in high temperature oven. The thicknesses of the films at each temperature are recorded, and the volume shrinkages were calculated comparing to P0 that was the nascent polyimide.

Characterization

The Fourier transform infrared (FTIR) were recorded by Nicolet 6700^{TM} spectrometer in the range of 4000–400 cm^{-1} at a resolution of 1.0 cm^{-1}. The TGA were recorded by SDT Q 600 at a heating rate of 10°C from room temperature to 800°C under a continuous flow of nitrogen at 100 mL/min. The dielectric constants were recorded by Agilent E4980A LCR meter at frequency of 1 kHz and voltage of 1V. The thickness measurement utilized the micrometer and the confocal microscope (Olympus OSL3050) scanned the pictures of the films.

RESULTS AND DISCUSSION

The FTIR spectra of the prepared films after curing can be shown in Figure 1. The imide characteristic absorption bands of the prepared materials are further evidenced by the following absorption bands: 1778 cm^{-1} (C=O sym. str.); 1726 cm^{-1} (C=O asym. str.); and 1380 cm^{-1} (C—N str.). The Si—O—Si stretching bands around 1100 cm^{-1} of P5 and P4 are stronger than that of P2 and P1 which imply the higher silica content of P5 and P4. The C—NH (1660 cm^{-1}) characteristic absorption bands of the polyamic acid were completely disappeared from the spectra, indicating that the imidization reaction is complete. There are no free amine (3500 cm^{-1}) observed in the final spectra of the hybrid films.

The 5 wt % loss temperatures or degradation temperature (T_d) of the photosensitive polyimide films (P1) are lower than the T_d of the pure polyimide (P0), and the commercial pure polyimide (Kapton) due to the cooperation of MDAE which will be loss out during the curing process. The cooperation of TAL, TMOS, and MPTMS will dramatically increase the Td5% from 290°C (P1) to 368°C (P3) and 374°C (P2) due to the remaining of the MDAE according to the bond to silica content at the end of the chains. However, the T_d of the hybrid films (P2–P8) still lower than the nascent polyimide (P0, Kapton) due
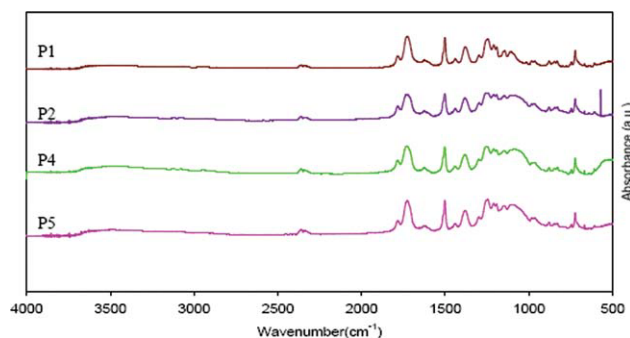

Figure 1 FTIR spectra of prepared thin films on thin glass. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Summary of the Properties of Hybrid Materials

Code	Thickness (μm)	5 wt % loss temperature (°C, in nitrogen)	Dielectric constant (K)
Kapton	77	577	4.25
P0	35	455	[a]na
P1	37	290	3.27
P2	28	374	2.58
P3	26	368	2.26
P4	22	286	[a]na
P5	52	248	2.48
P6	31	378	3.81
P7	30	380	3.90
P8	24	391	3.98

[a] na = Brittle, cannot prepare the measurement.

to the larger cooperation of less durable bond than the polyimide main chains (P0, Kapton). The Td5% of all the films can be summarized in Table II. Normally, the silica hybrid film will give higher T_d than the lower silica content. However, the increase of more silica by octavinyl POSS produced the contradict effect. The addition of the octavinyl POSS in P4 and P5 seems to slightly lower down the Td5% compared to the cooperated only TAL (P2) or the cooperated only TMOS and MPTMS (P3). The cooperation of MDAE with the octavinyl POSS (P5) gave the lower Td5% than the system cooperated only octavinyl POSS (P4) because of the higher weak bond of extra MDAE which cannot totally cooperated by the higher cross-linked that tighten all the materials together. The increase in DP of 25, 49, and 99 with P6, P7, and P8 with the same amount of cooperated TAL will gradually increased Td5% compare to P2 which have DP of 9 because of the more cooperation of imide bond in the photosensitive polymer. However, the more increase in Td5% due to DP, the less photosensitive properties of the hybrid films. Moreover, the less silica content (0.022%) of P6 (DP of 25) than the higher silica content (5.58 wt %) of P3 (with TMOS and MPTMS) did not decrease the Td5% of the hybrid film according to lower silica content but increased the Td5% and also remained the photosensitive patternable properties of the films.

Normally, the dielectric constant of the higher silica content hybrid films will be lower than the lower silica content which also vividly shown in Table II. The reduction of the dielectric constant according to POSS that result from the low dielectric constant of POSS molecules and the higher free volume by the incorporation of POSS in the main chain PI did not show the pronounce effects because the slightly reduction in dielectric constant of P5 (with octavinyl POSS) from P2 which use the same amount of TAL. The lowest dielectric constant (k) of 2.26 of the system of P3 (TMOS and MPTMS) with
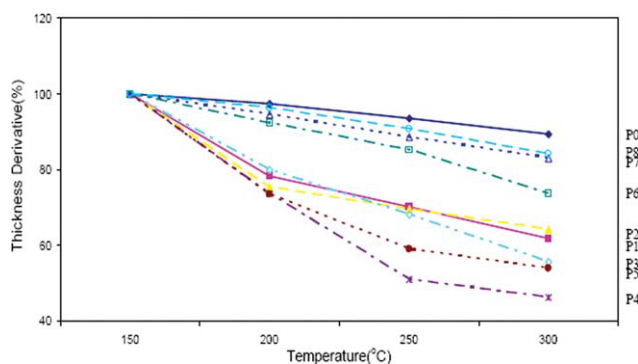
Figure 2 Thickness variation of P0–P8 in the curing process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the highest silica content of 5.58 wt % was observed but did not far from $k = 2.58$ of the system of P2 (TAL) with about half of the silica content of 2.4 wt %. This implied that if the equal amount of silica was attained, the system with TAL will have less dielectric constant than the system with TMOS and MPTMS.

If the thickness lost were compared, the least thickness lost will be pure polyimide (P0) because the lost came only from the solvent and the water that emit from imide bond only, and this thickness loss is the limiting thickness lost of all the samples. All the hybrid film P1–P8 will have more thickness loss due to the elimination of the fragile bond that did not bond to the main-chain polyimide. Figure 2 shows the thickness variation of P0–P8 at various curing temperatures and the higher curing temperature, the more thickness lost were observed. The cooperation of APrTEOS in every system will create more thickness loss regardless of the MDAE or the cooperation of TAL, TMOS, and MPTMS due to the weaker bond than the polyimide. When compared the system with the same amount of TAL and MDAE (P2, P6, P7, and P8) but with the different in degree of polymeriza-

tion (DP = 9, 25, 49, and 99 respectively), the higher the DP, the lesser the thickness loss. Although the higher degree of polymerization (DP = 49, 99) showed better volume shrinkage, they cannot be process as photopatternable compared with DP of 9 and 25. The system with only TAL (P2, P6, P7, and P8) has the lesser thickness loss than the system with TMOS and MPTMS (P3) and the octavinyl POSS system (P4, P5). The cooperation of octavinyl POSS will cause more thickness loss than the noncooperation. This also conformed to the common observation of Td5% and might be imply that the cooperation of octavinyl POSS will detrimental to the systems. Contradict to the Td5%, the cooperation of MDAE in octavinyl POSS system, P5 can create less thickness loss than the noncooperation of MDAE, P4, because the MDAE will increase more cross-linked in the system that results in the less thickness loss from the system at high temperature.

The photograph of the developed pattern of P6 can be shown in Figure 3(a). The fade areas are the unexposed to UV light that, after developed, the films were dissolved by solvent and wash away. The areas that exposed to the UV light are not dissolved by the solvent, when developed, and the films remained thicker after cure and give yellow color. If the sample P6 is observed under the confocal microscope, the patterns that formed can be seen in Figure 3(b).

The fade area which washed away by developing solutions will have lower level than the protected area which subjected to the UV light.

The film from the cooperation of TMOS and MPTMS (P3), that mention in,[29] has lowest dielectric constant but with the highest silica content. Moreover, the film P3 have the higher volume shrinkage than the DP of 9 (P1,P2) and even higher than DP of 25 (P6). The Td5% of P6 can compared with the MPTMS samples of[30] and better than P3 and P2. From experiments, the P6 (DP of 25) showed more
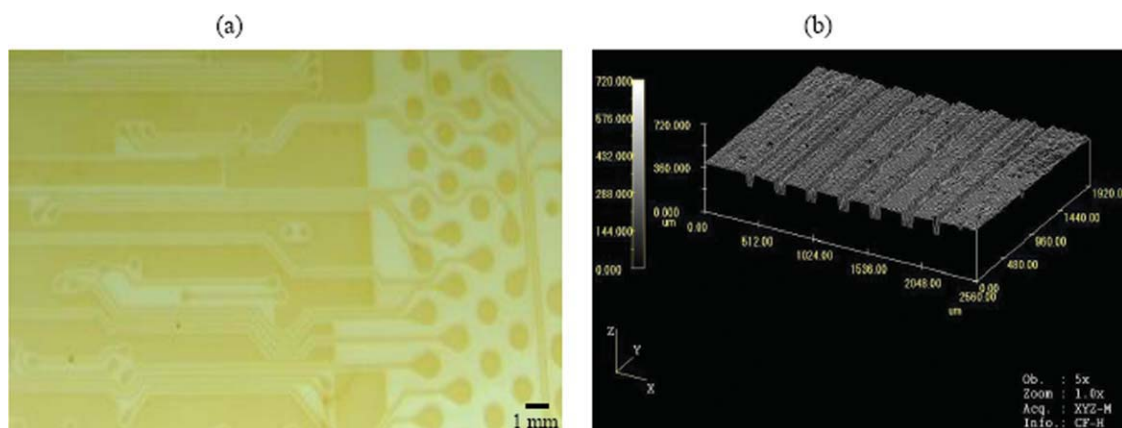

Figure 3 Photograph of P6 films (a) and scanning of P6 films by Confocal microscope (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

photopatternable and even showed lower volume shrinkage than the P2 (DP of 9), P3 and within the same vicinity as MPTMS samples of,[30] and if more silica is cooperated in DP of 25, the better dielectric properties will attain than P3 and P2 (DP of 9). The prepared photosensitive materials with TAL and having DP equal 25 could have potential applications for patterned electronic, and this method might be applicable to optoelectronic devices.

CONCLUSIONS

The low-dielectric photosensitive polyimide/silica hybrid materials were prepared successfully. The more cooperated of silica, the lower the dielectric constant. When the silica was cooperated, the dielectric constant of the thin hybrid film was dramatically reduced to 2.26. The volume shrinkage after curing process of photosensitive hybrid films could be reduced by the incorporation of TAL. The addition of Octavinyl POSS as the coupling agent can lower the dielectric properties but increase the volume shrinkage and the lower temperature resistance. Even with low silica content, the cooperation of TAL at the degree of polymerization of 25 gave the optimal properties than the high silica content of the cooperation of TMOS and MPTMS.

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