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To cite this article: Panpan Zhang et al 2018 J. Phys. D: Appl. Phys. 51 215305

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J. Phys. D: Appl. Phys. 51 (2018) 215305 (6pp)

https://doi.org/10.1088/1361-6463/aabe19

Effect of co-solvent on the structure and dielectric properties of porous polyimide membranes

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Received 29 September 2017, revised 12 April 2018 Accepted for publication 13 April 2018 Published 2 May 2018



Abstract

A series of porous polyimide (PI) membranes with 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-diaminodiphenyl ether (ODA) in the different ratio of co-solvent (N, N-dimethylacetamide (DMAC)/1, 4-butyrolactone (GBL)) were prepared by a novel wet phase inversion method. The influence of co-solvent on the structure and dielectric properties of membranes were investigated. PI membranes changed from finger-like structure to spongy-like structure with the increasing of the GBL content since the intermolecular interaction between PI induced by GBL. The proportion and size of finger-like structure gradually decreased with the increase of GBL content in DMAC/GBL co-solvent. Although PI membranes exhibited low dielectric permittivity ranges from 1.7-2.5, the dielectric breakdown strength (260.05 kV mm⁻¹) since the low proportion of macrovoids and defects. Moreover, when the ratio of GBL/DAMC was 84/16, the resultant PI membrane possessed a low dielectric constant (1.99) as well as relatively high breakdown strength ($100.53 \, \text{kV} \, \text{mm}^{-1}$). Therefore, porous PI membraness may be potential in many applications of electronics and microelectronics.

Keywords: dielectric materials, porous membranes, polyimide

(Some figures may appear in colour only in the online journal)

1. Introduction

With the increasing packing density of electronic devices utilized in the microelectronics industry, the insulating materials with low dielectric permittivity (low k) are urgently needed to replace the current wire insulator of silicon dioxide. It thereby reduces the resistance-capacitance (RC) delay, power dissipation, lineto-line crosstalk noise, and the capacitance between multilevel metal interconnects [1–3]. Polyimides (PIs), high-performance engineering materials, have been widely used as packaging materials and dielectric layers in the electronic and microelectronic industry, indicating suitable candidates for low-k dielectric materials because of their fantastic comprehensive performance, including good adhesion performances, outstanding thermal and mechanical properties [4–7]. However, the dielectric value of current PI is about 3.1–3.5, which is insufficient in meeting the requirement of interlayer dielectrics [8]. Therefore, it is necessary to scale down the k value of PI.

In general, there are two effective means of reducing the k value of PI. One is to decrease the polarizability through

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introducing lower polarizable chemical bonds such as C-O C-Si, and C-F in PI molecular; the other is to reduce the density of the PI by increasing the free volume or introducing pores into the membranes. Although many attempts at decreasing the polarizability of PI, the k value is still relatively high with the range of 2.3-3.0 [9–11]. Hence, porous PI material by introducing of pores is thought to be the most promising candidate for use as a next-generation of interlayer dielectrics [2, 12]. In recent years, porous PI membranes as low k materials have attracted more attention. The approaches to prepare porous PI membranes include introducing foaming agents and hollow microspheres, blowing porogen, agents, and ceramic components [13–16]. However, most of the methods require additives to generate pores, which are complex and unstable. In particular, phase inversion process is a simple method, which has been widely used for the preparation of synthetic polymeric membranes [17–21].

In this study, PI porous membranes were prepared using a simple wet phase inversion process and post thermal treatment. The influence of solvent composition on the morphology and dielectric properties of membranes was evaluated. A series of spongy-like and finger-like porous membranes were obtained. The dielectric permittivity, loss tangent, conductivity and breakdown strength of the membranes were investigated.

2. Experiential

2.1. Materials

The 4,4'-diaminodiphenyl ether (ODA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd (China). The solvent N, N-dimethylacetamide, DMAC (99.5%) and 1,4-butyrolactone, GBL (99.0%) were obtained from Tianjin Guangfu Fine Chemical Industry Research Institute (China) and Chemical Industry Development Co., Ltd (China), respectively. Deionized water (18.25 M Ω) was used as a nonsolvent gelation medium. All agents were analytical reagent (AR) grade and used as the raw materials without further purification.

2.2. Synthesis of polyamic acid

PI derived from ODA and BTDA were prepared by the following procedure. First, ODA (20 mmol, 4.00g) was dissolved in 40 ml GBL/DMAC co-solvent with different volume ratios (100/0, 84/16, 80/20, 75/25, 50/50, 25/75, 0/100) under dry nitrogen, followed by string for 30 min. Then BTDA (20 mmol, 6.44g) was added in several times, and the solution was stirred vigorously for 6h. Finally, a viscous and homogeneous polyamic acid (PAA) solution was obtained. Figure 1 depicts the synthesis route of PAA.

2.3. Preparation of porous PI membranes

Porous PI membranes were prepared using a wet phase inversion process. The PAA solutions were coated onto



Figure 1. The synthesis route of PAA.



Figure 2. Schematic diagram of the formation mechanism of porous PI membranes.

clean glass plates with a doctor blade, followed by immersing into a coagulation bath at 25 °C and kept for 3 h to form the porous structure. The deionized water was used as the coagulation bath. Then all the resulting membranes were dried under vacuum at 60 °C, followed by a thermal imidization at 100, 200, and 300 °C for each hour in a dry air-flowing oven. Finally, a series of PI membranes were prepared by the above-mentioned experimental steps. The figure 2 shows the schematic of the fabrication of the porous PI membranes.

2.4. Characterization and tests

The surface and cross-sectional morphologies of the PI porous membranes were investigated by scanning electron microscopy (SEM) (FEI Quanta 200FEG). The SEM samples were fractured in a liquid nitrogen atmosphere and sputtered with gold. The dielectric and electric breakdown properties of the membranes were measured by an impedance analyzer (Agilent4294A) and a dielectric withstand voltage test (YD2013, Changzhou Yangzi Electronic Co., Ltd), respectively. The dielectric samples were sputtered with gold electrodes on the two sides of the membranes.



Figure 3. SEM micrographs of cross section $(a_1)-(g_1)$, bottom surface $(a_2)-(g_2)$ and top surface $(a_3)-(g_3)$ of porous PI membranes obtained from GBL/DMAC co-solvent with different volume ratios: (a) 0:100, (b) 25:75, (c) 50:50, (d) 75:25, (e) 80:20, (f) 84:16, (g) 100:0.

3. Results and discussions

3.1. Morphology of porous PI membranes

The surface and cross-sectional morphologies of the porous PI membranes prepared using the mixture of GBL/DMAC with different ratios as solvents are shown in figure 3. The PAA solution with 20% of solid content was used as casting precursor. In figures $3(a_1)$ and (g_1) , it is easy to see that a finger-like

structure was formed as the porous PI membranes prepared from pure DMAC solvent, whereas a homogeneous spongylike morphology was obtained from pure GBL solvent. This phenomenon is due to that DMAC is mixed with water more favorably than GBL is, thus the membrane with DMAC undergoes fast phase-separation and shows the macro-void structure [22]. Moreover, the low interactions of GBL and water delay phase-separation process, which inhibits the formation of macro-void [21]. As the porous PI membranes prepared from DMAC/GBL co-solvent, the finger-like structure combined with the spongy-like structure was observed since the coexistence of the diffusion of GBL-water and DAMC-water in the system, as shown in figures 3(b1)-(f1). Moreover, the proportion of spongy-like structure gradually increased with the increase of GBL, which is caused by the intermolecular interaction between PAA induced by GBL. For PAA, DMAC is a 'good' solvent, whereas GBL is a 'bad' solvent. Thus, the addition of GBL tends to promote the aggregation of PAA molecules, which eventually reduced the intermolecular distance of PAA, contributing to the formation of spongy-like micro-voids [23, 24]. When a small amount of GBL is added, the slight aggregation of PAA molecules resulted in only a small number of micro-voids, as illustrated in figure $3(b_1)$. On the other hand, when more GBL was added as the ratio increased to 75:25, more PAA molecules aggregated in the system, thereby increasing the number of spongy-like microvoids. As for the PI membranes from pure GBL, the most significant aggregation of PAA molecules formed a completely spongy-like structure (figure 3(g)). Furthermore, the diffusion of GBL-water can suppress the formation of finger-like structure derived from the DMAC-water phase separation. As a result, the DMAC/water phase may not have enough time to grow macro-voids such as the finger-like structure with the increase of GBL content. In addition, it also can be found that all the PI membranes showed the porous top surfaces and the relatively less porous bottom surface. This is due to the initially precipitated surface layer which slows the precipitation from the top to bottom layer of the membrane [21]. Moreover, the surfaces of the membranes were slightly different because of the diverse inside-void structure and solvent system.

3.2. Dielectric properties of PI membranes

The dielectric permittivity, loss tangent and conductivity of the porous PI membranes were measured in the frequency range from 50 Hz to 1 MHz at room temperature, and the results are given in figure 4. In figure 4(a), the relative dielectric permittivity of membranes decreased slowly with an increase in frequency because of the reduction of the effective dipoles. At first, nearly all of the dipoles could keep up with the changing frequency at lower frequencies, but as the frequency rotation increased, they began to lag behind the frequency of the electric field, which led to the reduction of the effective dipoles [25]. Moreover, it can be noticed that porous PI membranes showed low values of dielectric permittivity ranges from 1.7-2.5. When the ratio of GBL/DAMC is higher than 16/84, dielectric permittivity of PI is lower than 2.0. In particular, the dielectric permittivity of membranes with pure DAMC solvent is only 1.78 at 100 Hz and room temperature, which is far lower than that of pure PI ($\varepsilon_r = 3.6$) [10]. The low dielectric permittivity of porous PI can be attributed to the existence of voids in the membranes. The Clausius-Mossotti equation was used to explain the relative dielectric permittivity of PI membranes [26]:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N}{3\varepsilon_0} (\alpha_e + \alpha_d) \tag{1}$$



Figure 4. Dependent (a) dielectric constant, (b) loss tangent, and (c) conductivity on frequency of porous PI membranes at room temperature.

where ε_r is the relative dielectric permittivity; ε_0 is the vacuum permittivity; N is the molecule number in unit volume; α_e and α_d are the electronic and distortion polarization in the molecule. According to equation (1), the introduction of pores significantly decreases the membrane density, namely, the molecule number (N), which directly lead to the remarkable reduction on the dielectric permittivity (ε_r) of PI membranes. In addition, it also can be seen that the dielectric permittivity decreased with the increasing content of DMAC in the DMAC/GBL co-solvent, which is due to the high effect of macro-void structure on reducing the density (N). The proportion of macro void increased with increasing DMAC (as shown figure 3), thereby causing

Table 1. Linear fitting results and Weibull parameters of porous I	PI membrane	es.
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PI membranes	Linear fitting results				Weibull parameters	
	Slope	ln(-ln(1 - P)) intercept	R	S/kV mm ⁻¹	β	$lpha/\mathrm{kV}~\mathrm{mm}^{-1}$
Pure DMAC	4.29	-17.21	0.9803	0.0665	4.29	55.24
25:75 (GBL:DMAC)	1.79	-6.18	0.9914	0.0290	1.79	31.58
50:50 (GBL:DMAC)	2.49	-6.81	0.9702	0.1005	2.49	15.41
75:25 (GBL:DMAC)	2.88	-11.35	0.9950	0.0169	2.88	49.71
80:20 (GBL:DMAC)	8.13	-35.61	0.9886	0.0384	8.13	79.84
84:16 (GBL:DMAC)	7.83	-36.10	0.9764	0.0796	7.83	100.53
Pure GBL	2.71	-15.07	0.9858	0.0479	2.71	260.05

the decreasing density and dielectric permittivity of the membranes.

Figure 4(b) shows the dielectric loss tangent of porous PI membranes for frequencies from 50 Hz to 1 MHz at room temperature. It can be seen that the loss tangent decreases slightly at first and then increases dramatically with increasing frequency. The dielectric loss tangent is mainly derived from interfacial polarization and relaxation polarization here. The dielectric loss tangent shows a slight decrease in the frequency range from 50 to 1000 Hz, which is attributed to that interface polarization lags behind the frequency changes of the electric field. The following increase in the frequency range from 10^4 to 10^6 Hz is due to the glass transition relaxation of the PI polymer matrix. In addition, it also can be noticed that all of the porous membranes exhibit low dielectric loss tangent, and even for GBL porous membranes, the value of loss tangent is still less than 0.006 at 100 Hz. The low loss tangent of membranes is ascribed to the introduction of air, which indirectly decreases the polarization of the whole PI membrane.

The conductivity of the porous PI membranes is given in figure 4(c). It is found that conductivity of porous PI increases obviously with increasing frequency. Moreover, the values of conductivity are no more than 10^{-9} S · m⁻¹. The results demonstrate that no conducting network was formed and confirm the excellent insulativity of porous PI membranes, which is meaningful for the application of this membrane in electronics and microelectronics.

3.3. Breakdown strength of PI membranes

The electric breakdown of the porous PI membranes was tested at room temperature. The two parameters Weibull distribution was used to analyze the dielectric breakdown [26]:

$$P(E) = 1 - e^{-(E/\alpha)^{\beta}}$$
⁽²⁾

where P(E) is the cumulative probability of a failure occurring at the electric field lower or equal to E. E is the experimental breakdown strength; α is a scale parameter referring to the breakdown strength with a 63.2% probability of failure; β is a shape parameter associated with the linear regressive to fit for



Figure 5. Weibull distribution of porous PI membranes.

distribution. The Weibull cumulative distribution function can be written as below by taking two logarithms:

$$\ln(-\ln(1 - P(E))) = \beta \ln E - \beta \ln \alpha.$$
(3)

Then we plotted $\ln(-\ln(1 - P(E)))$ versus lnE, the β and α values can be obtained from the slope and the ln(-ln(1 - P(E)))intercept, $\beta \ln \alpha$, respectively. The α and β are determined by least-squares linear regression. The linear fitting results and Weibull parameters of PI membranes are listed in table 1. As listed in table 1, the S values were in the range from 0.01–0.11 showing a smaller error, and the correlation coefficient (R) values were higher than 0.97, which means a good fitting on PI membranes. Figure 5 displays the Weibull distribution of PI membranes. It should be noted that the breakdown strength of the PI membranes is obviously different. The breakdown strength of PI membranes were 55.24 kV mm⁻¹ (pure DMAC), $31.58 \text{ kV} \text{ mm}^{-1}$ (GBL/DMAC = 25:75), 15.41 kV mm^{-1} (GBL/DMAC = 50:50), 49.71 kV mm^{-1} (GBL/ DMAC = 75:25), 79.84 kV mm⁻¹ (GBL/DMAC = 80:20), $100.53 \,\text{kV} \,\text{mm}^{-1}$ (GBL/DMAC = 84:16) and $260.25 \,\text{kV}$ mm^{-1} (pure GBL), respectively. In particular, the breakdown strength of PI with pure GBL was far higher than that of other membranes. It might be due to the macro-voids preferred to cause many defects thereby scaling down the breakdown strength of the membranes.

4. Conclusions

In conclusion, porous PI membranes with different GBL/DMAC solvents were prepared by a simple wet phase inversion method from BTDA and ODA. The morphology and dielectric properties of membranes were investigated. The morphology of PI porous membranes was strongly affected by the solvent ratio of GBL/DMAC in the coagulation process. As the increasing of the GBL/DMAC ratio, PI membrane changed from finger-like structure to spongy-like structure in the liquid-liquid phase-separation process. The porous PI membrane exhibited low dielectric permittivity ranges from 1.7-2.5 because of the low density of the PI membranes. In addition, the dielectric permittivity decreased with the increasing content of DMAC in the DMAC/GBL co-solvent. The difference of dielectric permittivity is originated from the various voids structures and ratios in the membranes. Moreover, the breakdown strength of PI was obviously diverse. The breakdown strength of PI membranes were $55.24 \,\mathrm{kV} \,\mathrm{mm}^{-1}$ (pure DMAC), $31.58 \text{ kV} \text{ mm}^{-1}$ (GBL/DMAC = 25:75), 15.41 kV mm^{-1} (GBL/DMAC = 50:50), 49.71 kV mm^{-1} (GBL/ DMAC = 75:25), $79.84 \, kV \, mm^{-1}$ (GBL/DMAC = 80:20), $100.53 \, kV \, mm^{-1}$ (GBL/DMAC = 84:16) and $260.25 \, kV$ mm⁻¹ (pure GBL), respectively. In particular, the PI from pure GBL yielded the highest breakdown strength among these membranes since the low proportion of macro-voids and defects. Moreover, the PI membrane derived from 84/16 co-solvent showed a low dielectric constant as well as higher breakdown strength than other co-solvent membranes. The results showed that the porous PI membranes have potential applications in electronics and microelectronics.

Acknowledgments

We thank National Natural Science Foundation of China (Nos. 51572058, 51174063, 51502057), the National Key R&D Program of China (2016YFB0303900), the Natural Science Foundation of Heilongjiang Province (E201436), the International Science & Technology Cooperation Program of China (2013DFR10630, 2015DFE52770), Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP20132302110031) and the Fundamental Research Funds for the Central Universities (No. HIT. MKSTISP.201628).

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