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Su-Jin Kang [a] , Dong-Jin Kim [a] , Ji-Hoon Lee [a] , Sam-Kwon Choi [a] & Hwan Kyu Kim [b]

[a] Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon, Korea, 305-701

[b] Department of Macromolecular Science, Han Nam University, Taejon, Korea, 300-791

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NEW PI-SILICA HYBRIDS VIA SOL-GEL PROCESS FOR THIN FILM DIELECTRIC MATERIALS

SU-JIN KANG, DONG-JIN KIM, JI-HOON LEE, AND SAM-KWON CHOI
Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon, Korea, 305-701

HWAN KYU KIM*
Department of Macromolecular Science, Han Nam University, Taejon, Korea 300-791

Abstract: A new class of polyimide-silica hybrid materials for thin film microelectronics were successfully prepared by the sol-gel reaction of tetraethoxysilane (TEOS) in the solution of polyimide precursor in *N,N'*-dimethylformamide. The composite films were obtained by the hydrolysis and polycondensation of TEOS in the polyimide precursor solution, followed by heating at 270 °C. The chemical structures of polyimide-silica hybrid films were characterized by analytical techiques. X-ray diffraction showed that the polyimide-silica hybrid material has an amorphous structure. The hybrid material was quite stable at elevated temperatures (> 400 °C), with the associated weight loss of 10 wt % only around 600 °C. The dielectric constant of the polyimide-silica (50 wt%) composite measured by ellipsometry was 3.935 to 3.885 as a function of frequency in the range of 1kHz to 20 kHz.

INTRODUCTION

Due to advances in the design of new products coming from the microelectronics industry there are increasing demands for newly, readily processable polymer-based materials with low coefficients of thermal expansion (low CTE) and high thermal stability. Such materials which must also be capable of thin film processing and possess thermal and dimensional stability, such as CTE match to a Si wafer. In an effort to produce such materials, polymer-based composite materials produced with inorganic materials such as ceramics or glasses have been developed[1,2]. These composite materials can combine the low dielectric behavior and good processibility of polymers with the desirable characteristics of glasses such as a very good thermal and dimensional stability, and a lower coefficient of thermal expansion which is important for stress-free thin films on silicon substrates.

In an effort to combine the promising properties of both polymers and glasses, we have investigated polyimide-silica composite materials for use in thin film microelectronics made by the sol-gel reaction of tetraethoxysilane (TEOS) in the solution of polyimide

precursor in *N,N'*-dimethylformamide. The latter component of TEOS is used as the glass-like silica source for the sol-gel process. The composite films were obtained by the hydrolysis-polycondensation of TEOS in the polyimide precursor solution, followed by heating at 270 °C. We have used the disiloxane-containing polyamic acid (PIX-3400-8 (Hitachi)) instead of the PI, due to the higher solubility of a polyamic acid in aprotic polar solvents. In this paper, we report the synthesis and characterization of polyimide-silica hybrid materials via sol-gel processes for thin film microelectronics.

EXPERIMENTAL

1. Materials

Tetraethoxysilane (TEOS: Hüls) and a disiloxane polyimide precursor (PIX-3400-8 (Hitachi)) were used as received. N,N'-Dimethylformamide was dried over $MgSO_4$ and distilled over $MgSO_4$ under reduced pressure. Other chemicals were used as received.

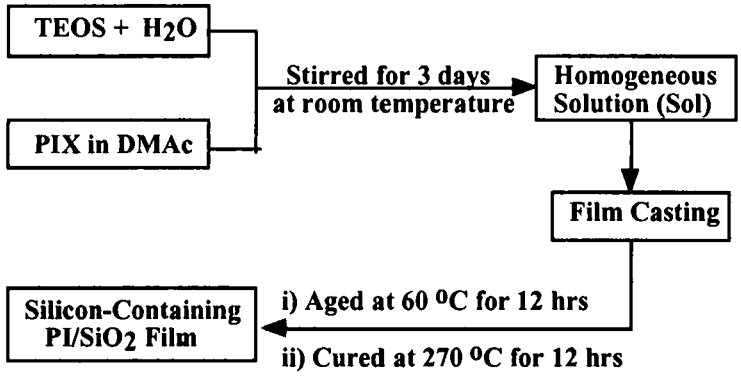
2. Preparation of Polyimide-Silica Hybrid via Sol-Gel Process

A disiloxane-containing polyimide precursor in NMP (6.0 g) and 40 mL of DMF were placed in a 100 mL three-necked flask provided with a stirrer and a reflux condenser. Known amount (4.0 g) of TEOS was added to the flask by using a syringe. Distilled water (1.362 g: [Si-OEt]/[H_2O]≈ 1) was added to the polyimide precursor solution to immediately form a heterogeneous mixture. The heterogeneous mixture was stirred for 5 minutes to obtain a homogeneous solution (sol). The sol solution was stirred for 4 days at room temperature. The solution was spin-coated at 3000 rpm for 30 seconds on various types of substrates such as a NaCl disc for IR analysis, or a silicon wafer for RI analysis. The films were aged at 60 °C for 12 hours under vacuum. To imidize polyamic acid and cure aged silica, the films were slowly heated up to 270 °C for 4 hours and then annealed at 270 °C at various times. The final films were analyzed by IR, solid state ^{29}Si NMR, TGA, and SEM (scanning electron microscopy).

RESULTS AND DISCUSSION

Polyimide-silica hybrid material has been synthesized by the sol-gel process starting from tetraethoxysilane (TEOS) in the presence of polyimide precursor in *N,N'*-dimethylformamide (DMF). Polyimide itself is insoluble in common organic solvents. The hybrid films were obtained by the hydrolysis and polycondensation of TEOS in the polyimide precursor solution, followed by heating to 270 °C. At 270 °C, polyimide

precursors were converted into polyimide with the loss of water. The solution was spin-coated on various types of substrates such as NaCl disc or a silicon wafer. The films were then aged at 60 °C for 12 hours under vacuum and finally annealed at 270 °C for various times, yielding yellow, transparent films, as shown in Scheme 1.



SCHEME 1. Preparation of silicon-containing polyimide/silica composites via sol-gel process.

The chemical structures of polyimide-silica hybrid film (containing a silica content of 50 wt. %) were characterized by IR, solid state ^{29}Si NMR, and SEM (scanning electron microscopy). IR data of the polyimide, prepared from the polyimide precursor which had been pyrolyzed at 270 °C for 12 hours, showed the disappearance of the amide carbonyl peak at 1650 cm^{-1} and the appearance of the imide carbonyl peak at 1720 and 1780 cm^{-1}. In addition, the IR spectrum of the film cured at 270 °C for 12 hours showed the formation of Si-O-Si bonds in silica (SiO_2) as well as disiloxane unit in polyimide around 1080 cm^{-1} and no silanol (Si-OH) groups around 3400 cm^{-1}. The formation of Si-O-Si bonds (Q_3 and Q_4) in silica (SiO_2) was proved by solid state ^{29}Si NMR spectroscopy[5], as shown in Fig. 1. A solid state ^{29}Si NMR spectrum of aged PI/silica shows the presence of dihydroxy (Q_2), monohydroxy (Q_3) and nonhydroxy silica (Q_4) states in the range of -90 ppm to -120 ppm. After cured at 270 °C for 12 hours, monohydroxy (Q_3) and nonhydroxy silica (Q_4) states as well as the presence of disiloxane unit around -8 ppm are present. It indicates that the formation of silicon-oxygen network structure from the sol-gel precusor of TEOS was developed like glass-like silica[6]. It should be noted that the presence of the disiloxane unit originated from disiloxane-containing polyamic acid may cause the chemical linkage between disiloxane-containing polyimide and the inorganic silicon-oxygen network to be less possible, while the

chemical linkage between oligosiloxane-containing polyimide and the inorganic silicon-oxygen network was formed[6].

Alternatively, after the sol solution was stirred at room temperature for the desired time, it was transferred into a vial, dried at 60 °C for 12 hours under vacuum, and then cured at 270 °C for 12 hours, leading to the formation of a yellow prestanding film. The uncured and cured hybrid materials were characterized by IR and TGA. Similar IR data was obtained from the cast film.

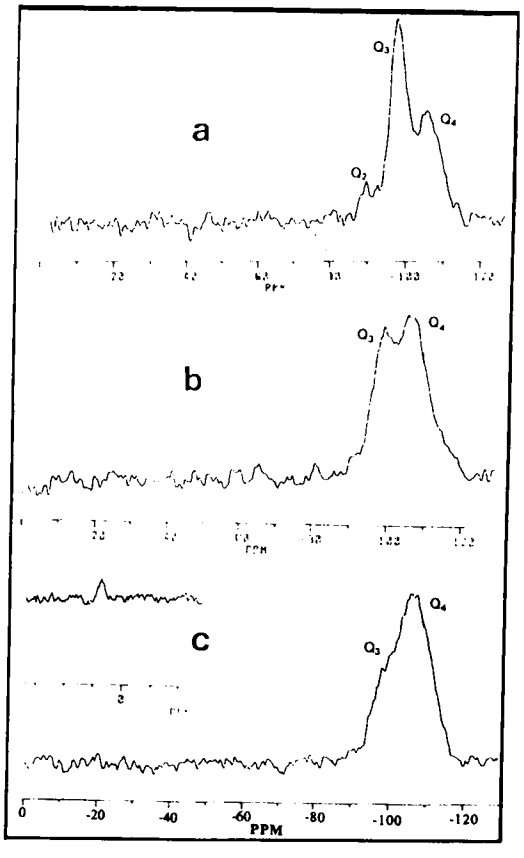


FIGURE 1. Solid state ^{29}Si NMR spectra of PI/silica aged at 60 °C for 12 hours (a); PI/silica cured at 260 °C for 12 hours (b); PI/silica cured at 260 °C for 12 hours (c).

TGA analysis of an uncured material showed two steps during the weight loss. The first weight loss (at 205 °C) resulted from concurrent condensation processes between terminated silanols (Si-OH) and terminated ethoxysilanes (Si-OEt), followed by a second weight reduction due to the decomposition of siloxane polyimide, when compared with

TGA traces of the cured siloxane polyimide and the cured PI- silica composite material. The polyimide-silica hybrid material cured at 270 °C for 12 hours was quite stable up to high temperatures (< 450 °C). The morphology of the fracture surface of the cured hybrid film was examined by SEM. Below the loading content of 20 wt % silica, a SEM photograph showed no microseparation between PI and silica. But, a SEM photograph containing 50 wt% silica showed the microphase separation (two different domains) between PI and silica, as shown in Fig. 2. One of these domains is rich in inorganic glass and the other in organic polymer region. The silica particles are well-dispersed in PI matrices and the diameters of the silica particles are in the range of 2 μm to 4 μm. The particle size was affected by both sol-gel processing temperature and the acidity of sol-gel process solution.

A number of physical and optical properties of a variety of polymers, glasses, and ceramics was summarized in Table 1. The dielectric constant of the polyimide-silica (50 wt%) composite measured by ellipsometry was 3.935 to 3.885 as a function of frequency in the range of 1kHz to 20 kHz, while the dielectric constant of the disiloxane polyimide (PIX, Hitachi) was 3.445 at the frequency of 1kHz. The dielectric constant of the polyimide-silica increases with the loading content of silica.

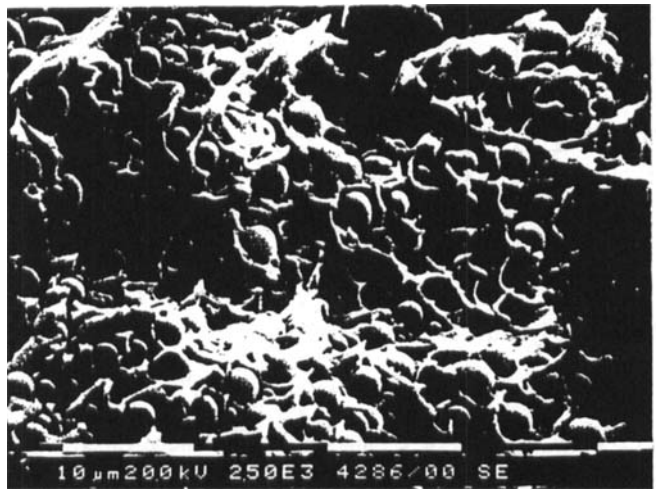


FIGURE 2. SEM photograph of PI/silica hybrid film cured at 270 °C for 12 hrs.

The polyimide-silica composites are optically transparent up to 50 % silica loading. TMA results showed that polyimide-silica composite material has two CTE values (3 ppm/°C below T_g and 30 ppm/°C above T_g). The moisture gain of the polyimide-silica composite was less than 0.5 %. These results of the lower CTE values and the lower moisture-up take were very important for preparing polyimide-silica composite material.

SUMMARY

The PI/silica composite materials combine the low dielectric behavior and good processibility of polymers with the desirable characteristics of glasses such as a very good thermal and dimensional stability, and a lower coefficient of thermal expansion which is important for stress-free thin films on silicon substrates. As a result of these unique properties, these composite materials are potential candidates for their application in thin films and for self-reinforced PWB materials.

TABLE 1. Physical and optical properties of organic and inorganic polymers.

Name	T_g (°C)	Moisture Gain (%)	CTE (PPM/°C)	Refractive index (ε_r)
Teflon	130	-	20.0	1.35 (2.1)
Epoxy Resins	<180	-	-	1.55 - 1.60
Polyimides	>250	1 - 4	8 - 60	1.63 (3.5)
Polyphenylene	>230	0.8	-	1.72 (3.55)
SiO_2, amorphorus	-	-	5.95	1.48 (3.8)
SiO2, crystal	-	-	0.5	1.55
Silicon, wafer	-	-	0.5	3.49
Diamond	-	-	2.3	2.40 - 2.46
Disiloxane PI/ SiO_2 composite	>230	<0.5	3 - 30	3.94 - 3.89*

* The dielectric constant of the polyimide-silica (50 wt%) composite was measured by ellipsometry as a function of frequency in the range of 1kHz to 20 kHz.

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