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Synthesis and characteristics of polyimide/siloxane hybrid films for reliability adhesion

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Abstract

Polyimide/siloxane (PISi) hybrid films from 2,2′-*bis*[4-(3-aminodiphenoxy)phenyl]sulfone (m-BAPS), 3,3′-oxydiphthatic anhydride (ODPA) and *p*-aminopropyltrimethoxysilane (APrTS) have been successfully fabricated by an in-situ sol–gel process. The APrTS is used to introduce siloxane structure and to be the end-capped agent to control the polymer block chain length in the range of 5000–20 000 g/mol. The network structure of the PISi hybrid film is formed through the hydrolysis and condensation reactions. The PISi hybrid films with various polyimide block chain lengths are characterized with regard to the structure effect, mechanical properties, adhesion strength, adhesive melting flow and thermal stability. The result indicates that the more APrTS is contained, the shorter of the polyimide block chain length is formed and thus the lower inherent viscosity of APrTS-PAA is obtained. It is also suggested that the cross-linked density of the PISi hybrid film increases with the increase in the amount of APrTS. The network structure of the hybrid film reinforces the pure PI and makes the coefficient of thermal expansion (CTE) as well as adhesive melting flow decrease. Based on the dynamic mechanical analyses (DMA), the hybrid film with higher cross-linked density possesses superior mechanical property at elevated temperature. In addition, the introduction of APrTS causes an increase in thermal stability due to the network structure of hybrid film and the filler effect of the siloxane.
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Keywords: Polyimide; Sol–gel; Adhesive melting flow

1. Introduction

In the past three decades, polyimide has been used as reliable high-temperature polymer. They have been widely utilized for the semiconductor integrated circuit (IC) packaging and buffer coating layer applications [1–9]. This is attributed to the fact that polyimide possesses many outstanding properties such as high thermal stability, excellent mechanical properties, good chemical resistance and low dielectric constant. To meet the demand of highly miniaturized electronic devices, lead-on-chip (LOC) has become popular recently [10,11]. In the memory device package using LOC technology, the lead frame is laminated on the top of integrated circuit chip with a double-sided adhesive tape by hot press process in several seconds. The reliability of the interfacial adhesion between the polyimide film and the substrate is very crucial. Adhesion tapes such as polyamide-imide, polyamide and polyimide [12–14] tapes have been employed to improve the adhesion strength between the Alloy-42 lead frame (composed of 42% of Ni and 58% of Fe) and the polyimide passivation layer. However, some technical difficulties still remain such as thermal expansion and adhesive melting flow. In order to resolve these problems, a new type of material of low thermal expansion and adhesive melting flow is synthesized.

In this study, the polyimide/siloxane (PISi) hybrid film is applied to tapeless lead-on-chip packaging. The monomer of *p*-aminopropyltrimethoxysilane (APrTS) is incorporated into poly(amic acid) (PAA) matrix to form siloxane moiety and the amino group of APrTS also can be the end-capped

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agent to control the polyimide block chain length in the range of 5000–20 000 g/mol. Furthermore, the three dimension network structure of PISi hybrid film could be formed through the hydrolysis and condensation reactions of APrTS without adding extra acid/basic catalyst or water [15]. The primary aim of the work reported here will attempt to investigate the effect of various PI block chain lengths upon structure, mechanical and thermal properties. Besides, the adhesion strength and adhesive melting flow between the PISi hybrid film and Alloy-42 substrate are also discussed herein.

2. Experiment

2.1. Materials

3,3′-Oxydiphthalic anhydride (ODPA, 98%) from Tokyo Chemical Industry is purified by recrystallization from acetic anhydride and then dried in a vacuum oven at 125 °C over night. 2,2′-*bis*[4-(3-aminodiphenoxy) phenyl] sulfone (m-BAPS, 98%) from Chris-kev is subjected to a thermal treatment in a vacuum oven at 85 °C for 3 h prior to use. *p*-Aminopropyltrimethoxysilane (APrTS) from Tokyo Chemical Industry is used as supplied. *N*-methyl-2-pyrrolidone (NMP) from Tedia Company is dried over molecular sieves.

Table 1
The preparation and inherent viscosity of pure PAA and APrTS-PAA precursors

X[a]	m-BAPS/ODPA/APrTS[b]	Inherent viscosity[c]
5000	5.83:6.83:2	0.65
10, 000	12.57:13.57:2	0.71
15, 000	19.30:20.30:2	0.83
20, 000	26.04:27.04:2	0.92
Pure PAA	1:1:0	1.09

[a] Theoretical molecular weight of APrTS-terminated PAA precursor.
[b] The mole ratio of each reactant.
[c] At concentration of 0.5 g/dl of PAAs in NMP at 25 °C.

2.2. Synthesis

The synthesis of PISi hybrid film is carried out according to Fig. 1. The precursor of PISi is made by reacting stoichiometrically amount of m-BAPS, APrTS, ODPA and suitable amount of NMP under a nitrogen atmosphere. Table 1 shows the cross-linked APrTS-PAA with different

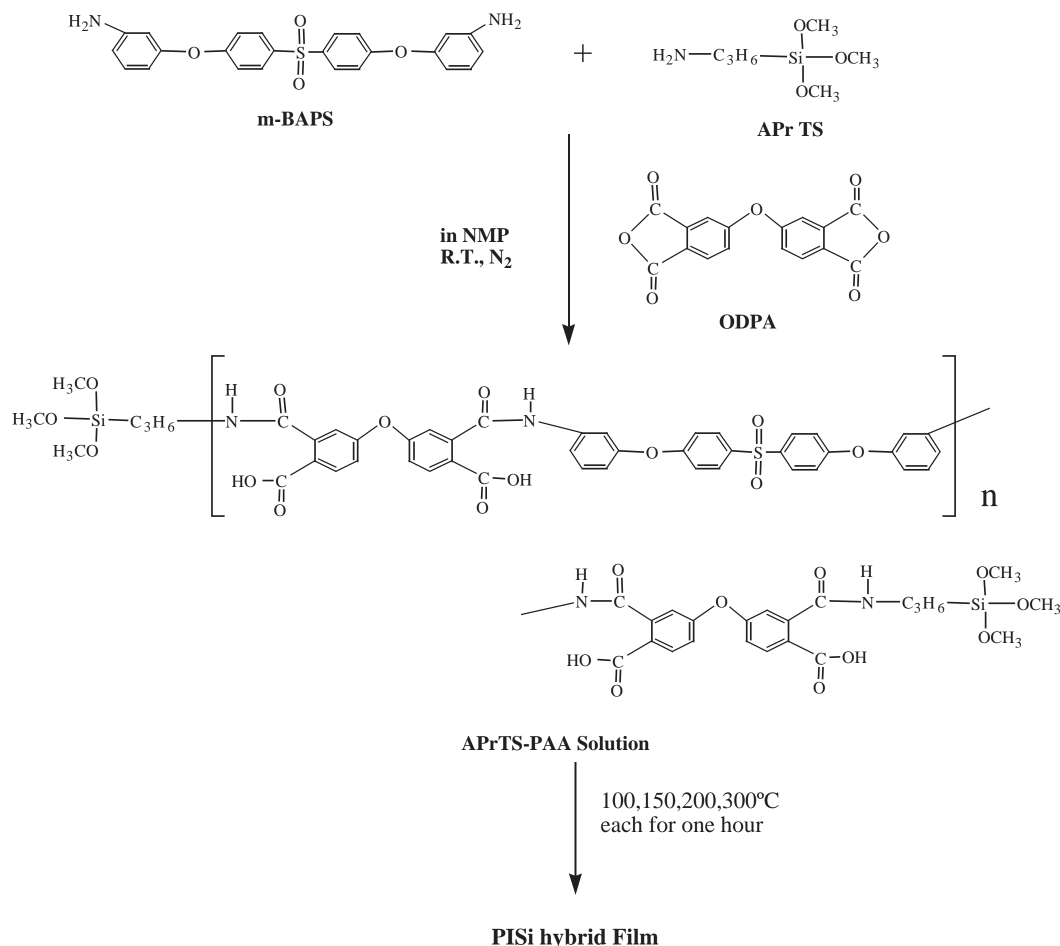

Fig. 1. The chemical structure and reaction process of PISi hybrid films.

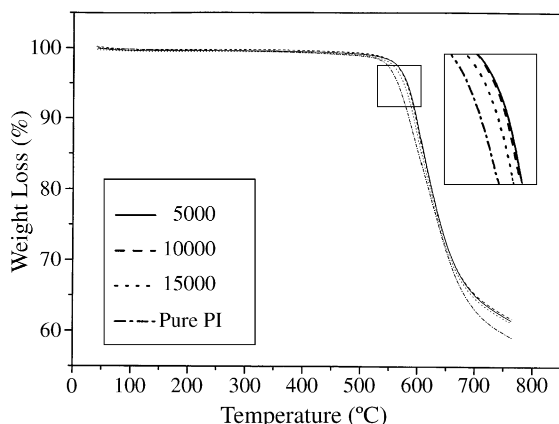

Fig. 2. The themogravimetric curves for pure m-BAPS-ODPA and PISi hybrid films.

molecular chain length and monomer molar ratio. The ODPA is added into the solution by five portions and it is better to ensure the complete dissolution of the prior portion before adding a fresh portion. After the dissolution of all ODPA, the reaction solution is further stirred for 2 h at ambient temperature. After this period, the precursor of APrTS-PAA is coated on a PET sheet by means of drawknife with a thickness of 250 μm. The APrTS-PAA gel film is then heated at 100 °C for 1 h in a forced-air convention oven to remove the solvent. After the first stage of curing, the freestanding APrTS-PAA hybrid film is transfer to a rectangle stainless frame clamp and imidized at 150 °C, 200 °C, 250 °C, and 300 °C each for 1 h. Consequently, the PISi hybrid films have an average final thickness of 30–40 μm.

2.3. Measurement

Thermogravimetric analysis (TGA) is carried out with a TA Instrument 2950 at a heating rate of 10 °C/min under nitrogen. The glass transition temperature (tanδ peak) and dynamic mechanical properties are measured using a TA Instruments DMA 2980 Dynamic Mechanical Analyzer at a heating rate of 3 °C/min from 60 to 330 °C. The samples size of 20×5 mm^2 is run at a frequency of 1 Hz with a tension clamp. The in-plane thermal expansion (CTE) measurement is carried out in the range of 30–330 °C by using a Du Pont 2940 probe, which provided 0.05 N tension force on the film, at a heating rate of 5 °C/min. The CTE values in the temperature scale between 30 and 220 °C are recorded. The samples for adhesion melting flow test are strips (5×15 mm^2) of the pure PI and PISi hybrid films. The hybrid films are laminated onto Alloy-42 substrates at 400 °C with 10 kg pressure applied for 2 s. The Alloy-42 is ultrasonically cleaned with dichloromethane three times, rinsed with D.I. water and dried with nitrogen. The peel test is performed by a homemade peel tester. The measurement of adhesion strength is carried by 90° peel test and the peel rate is 10 cm/min. The observation of melting flow is investigated by polarizing microscope.

3. Results and discussion

Polyimide/Siloxane (PISi) hybrid films are synthesized through self-catalyzed hydrolysis and condensation reactions by sol–gel method. The precursor solution of APrTS-PAA with different block chain length of 5000, 10 000, 15 000 and 20 000 g/mol, respectively, is prepared by adding suitable amount of APrTS monomer, which contains monofunctional amine group. The inherent viscosities of these precursors and pure m-BAPS-ODPA are 0.65, 0.71, 0.83, 0.92 and 1.09 dl/g, respectively, as shown in Table 1. Based on the result, it is indicated that the more APrTS is contained, the shorter polyimide chain length is formed and thus the lower inherent viscosity of precursor is obtained. It also can be seen that the pure m-BAPS-ODPA precursor (without APrTS content) possesses the largest inherent viscosity value. It is suggested that the incorporation of APrTS has the ability to control the PI block chain length. Meanwhile, after the imidization reaction, the cross-linked density of PISi hybrid films also increases with the increase in APrTS content.

The thermal degradation of pure PI and PISi hybrid films are displayed in Fig. 2. All the degradation graphs show one-step transition. According to Table 2, it can be seen that the thermal stability of pure PI film is inferior to PISi hybrid films. It is attributed to the fact that the addition of inorganic silica moieties and the cross-linked structure of PISi hybrid films could enhance the thermal stability of the PISi hybrid films.

Table 2 presents the glass transition temperature (Tg) of pure PI and PISi hybrid films measured by DMA. The pure PI exhibits the lowest Tg value of 241.9 °C, however, the hybrid films with 5000 g/mol chain length shows the highest Tg value of 250.5 °C. A tendency that the Tg increases with increasing the APrTS content is obtained. This result could be due to the three-dimension network structure of PISi hybrid films. The more APrTs is added, the shorter block chain length between the two cross-linked points is formed, which causes the higher cross-linked

Table 2
The thermal properties of pure m-BAPS-ODPA and PISi hybrid films

X	T_d (°C)[a]	Tg (°C)[b]	CTE (μm/m °C[c]
5000	589.3	250.5	47.3
10,000	588.6	247.5	49.2
15,000	583.9	246.1	50.5
20,000	582.0	245.0	53.0
Pure PI	574.5	241.9	54.3

[a] Measured by TGA at 10 °C/min under N_2 and determined at the temperature of 5% weight loss.
[b] Measured by DMA at frequency of 1 Hz and heating rate of 3 °C/min.
[c] Measured by TMA at heating rate of 5 °C/min and in the range of 30–200 °C.

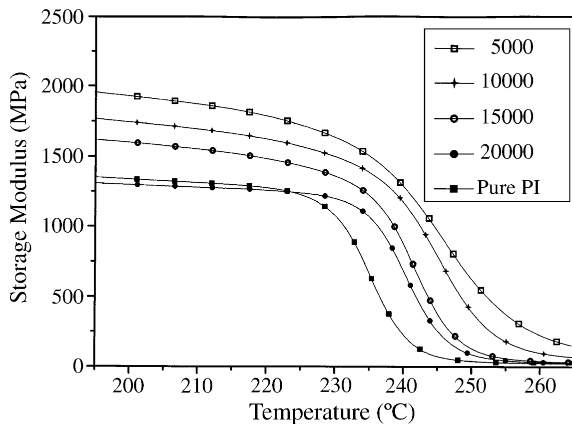

Fig. 3. The storage modulus of dynamic mechanical analysis for pure m-BAPS-ODPA and PISi hybrid films.

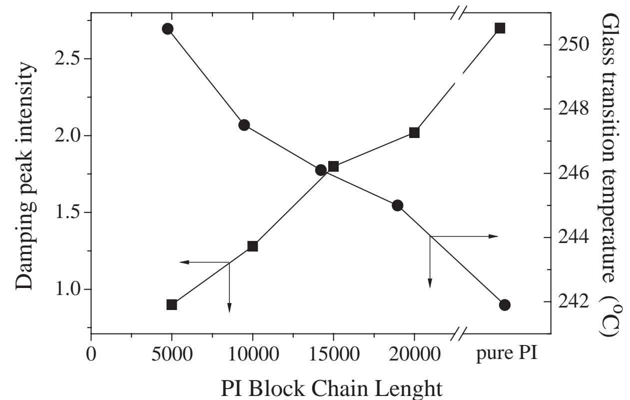

Fig. 5. The glass transition temperature (Tg) and damping peak intensity for pure m-BAPS-ODPA and PISi hybrid films.

density of the hybrid films. Therefore, the polymer chain mobility decreases and the higher Tg value is measured.

Table 2 lists the coefficients of thermal expansion (CTEs) of the PISi hybrid films. It is indicated that the CTEs of PISi hybrid films decrease with increasing the APrTS content. The pure PI has the largest CTE value due to the linear structure and higher flexibility. As the content of APrTS is increased, the CTEs value of PISi hybrid film is decreased. This is ascribed to the increase of cross-linked density and the rigidity of PISi hybrid films. Besides, the hybrid film with lower CTE value can prevent to delaminate between the PISi hybrid film and the Alloy-42 substrate.

Fig. 3 shows the storage modulus of pure PI and PISi hybrid films at different temperatures. The pure PI film has the lowest storage modulus, while the PISi hybrid films have higher storage modulus. Besides, the storage modulus of the hybrid films increase with increasing the APrTS content. The increase of storage modulus is ascribed to the addition of APrTS which is formed cross-linked structure and increases the rigidity of the hybrid films. From Fig. 3, it also shows that the mechanical properties of the PISi hybrid films could be improved by incorporating the APrTS into pure PI matrix. The enhancement of storage modulus is observed at both low and high temperatures. This property will enhance the reliability for applications at elevated temperature.

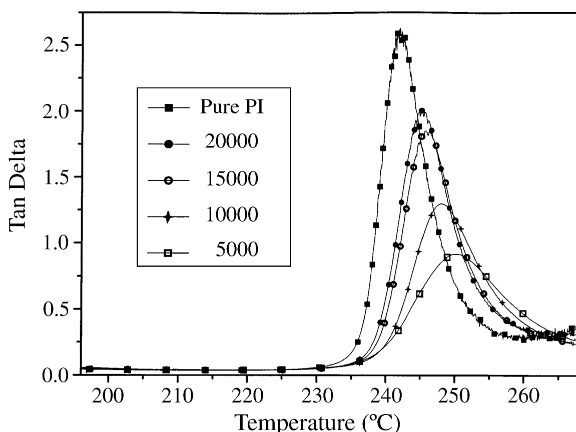

Fig. 4. The tan δ of dynamic mechanical analysis for pure m-BAPS-ODPA and PISi hybrid films.

Fig. 4 indicates that the pure PI has the lowest Tg value and the largest damping intensity. The damping intensity is equal to the Tan value and decreases with increasing the cross-linked density. Fig. 5 shows the Tg and damping peak intensity of pure PI and PISi hybrid films at different polyimide block chain length. The occurrence of damping is due to chain mobility, which produces the friction energy changing to the irreversible heat loss. Therefore, the lower damping value means the more rigid molecular chain and the lower intermolecular attraction force [16,17]. The polymer chain mobility and rigidity could significantly influence the adhesion strength and adhesive melting flow between the hybrid films and Alloy-42 substrate.

The adhesion strengths between the PISi hybrid films and Alloy-42 are presented in Table 3. It can be seen that the longer the polymer chain length is synthesized, the higher adhesion strength is obtained. This result could be due to the mobility of polymer chain. Generally, the polymer chain with higher mobility can facilitate the polymer (hybrid films) to diffuse to metal side. The hybrid film with block chain length of 20 000 g/mol has higher adhesion strength as compared with the pure PI. It is suggested that the silica moieties of the APrTS could enhance the adhesion strength between the hybrid films and Alloy-42 substrate.

The observation of adhesive melting flow between the PISi hybrid films and Alloy-42 is shown in Fig. 6. The left

Table 3
The adhesion strength of pure m-BAPS-ODPA and PISi hybrid films[a]

X	Adhesion strength[b] (N/cm)
5000	5.25
10,000	7.01
15,000	8.72
20,000	11.25
Pure PI	9.39

[a] The Alloy-42 substrates is at 400 °C and 10 kg pressure applied for 2 s.
[b] The peel rate is 10 cm/min.

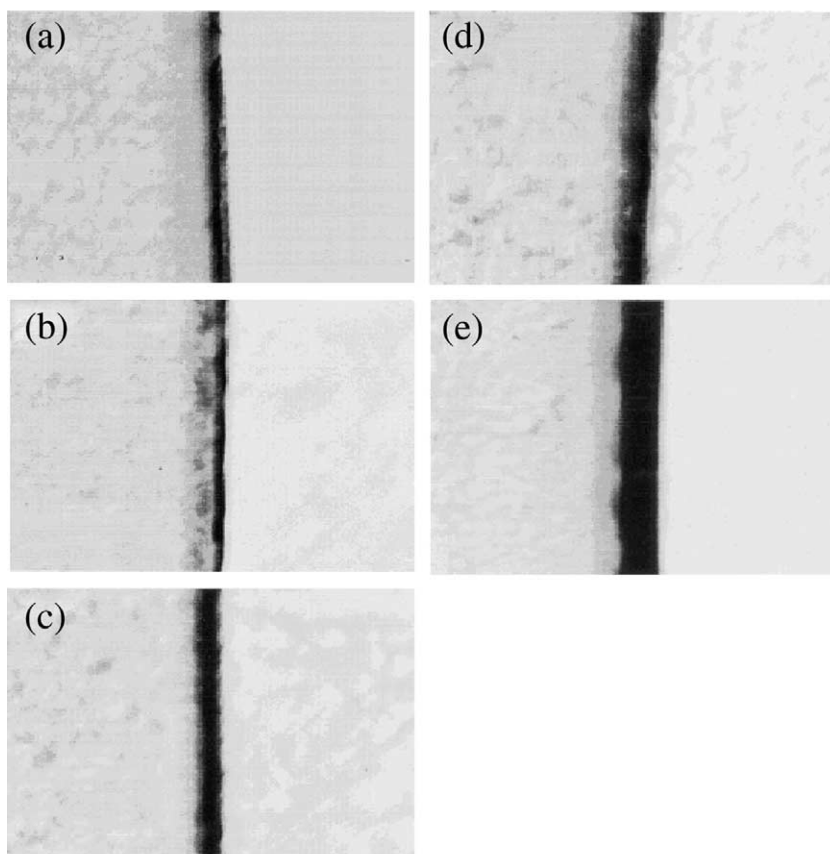

Fig. 6. The adhesion melting flow micrographs by polarizing optical microscope (× 500) for pure PI and PISi hybrid films.

side of the image is hybrid film adhered to Alloy-42 substrate and the right side is bare Alloy-42 substrate. The black striation in the middle of the image is the evidence of adhesive melting flow. It can be seen that the width of striation decreases with increasing APrTS content. The pure PI, without APrTS addition, shows broader striation as compared with PISi hybrid films. This result is attributed to the mobility of polymer chain. In general, the longer block chain length can facilitate hybrid film to flow at elevated temperature. On the contrary, it is restricted by the shorter block chain length. Based on the Fig. 6 and Table 3, a tendency that the higher adhesion strength causes more obvious adhesive melting flow is obtained. This property will limit the PISi hybrid films to practical applications. Therefore, how to obtain a good balance between the adhesion strength and the adhesive melting flow will be a subject in the future.

4. Conclusion

Siloxane-containing polyimide (PISi) hybrid films have been successfully fabricated by in-situ sol–gel process. This new silica-hybrid material successfully improves the adhesion strength and reduces the adhesive melting flow between the PISi hybrid films and Alloy-42 for the application of microelectronics packaging. The PISi hybrid films exhibit better mechanical and thermal properties as compared with the pure PI. As the content of APrTS increases, the molecule chain length between the two cross-linked points becomes shorter and the cross-linked density of the hybrid films increases. The addition of APrTS results in the increase of storage modulus, glass transition temperature and thermal decomposition temperature for the PISi hybrid films. Meanwhile, the thermal expansion of the hybrid films can also been reduced by incorporation of APrTS. The maximum adhesion value of 11.25 N/cm is obtained for the hybrid film with molecule chain length of 20 000 g/mol. Therefore, the introduction of APrTS into polyimide matrix can improve the reliability of hybrid films for applications at elevated temperature.

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