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In situ formation, surface characteristics, and interfacial adhesion of poly (imide siloxane)/tantalum oxide hybrid films

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Abstract

A new poly(imide siloxane)/tantalum oxide (PIS/TaO_x) hybrid material has been successfully fabricated through the in situ formation of TaO_x within a PIS matrix by sol–gel process. The hybrid thin films are prepared from 4,4-oxydiphthalic anhydride (ODPA), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (*p*-BAPP), α,ω-bis(3-amnopropyl)polydimethyl siloxane (APPS) and *p*-aminophenyltrimethoxysilane (APTS). The coupling agent APTS is employed to provide covalent bonding between the PIS and the TaO_x and to control the block chain length of poly (amic acid siloxane). The effect of TaO_x content in the PIS/TaO_x hybrid thin films on surface characteristics, thermogravimetric analysis, thermal expansion coefficient, dynamic mechanical properties and the adhesion strength between the PIS/TaO_x hybrid films and copper foil are investigated. The presence of TaO_x on the hybrid film surface can improve the adhesion strength between the PIS/TaO_x hybrid film and copper foil. Furthermore, by incorporating TaO_x into the PIS matrix, the PIS/TaO_x hybrid film possesses lower thermal expansion coefficient and retains good mechanical and thermal properties as well.

Keywords: Poly(imide siloxane); Tantalum oxide; In situ; Sol–gel; Adhesion strength

1. Introduction

Polyimide (PI) is a low dielectric material, excellent mechanical property and thermally stable polymer. They have become one of the most widely used polymers in semiconductor integrated circuit (IC) packaging [1–6]. On the one hand, PI modified with siloxane segment is usually used for adhesion application between PI and copper [5,7,8]. On the other hand, a thin passivation/adhesion promoting layer of metals such as Cr and Ta are pre-coated to improve the adhesion between PI and copper as well as to prevent the formation of copper oxide in the interface [9–12].

In the previous references, the adhesion strength between PI and copper can be enhanced by incorporating the siloxane segment into the PI matrix and pre-coating a thin layer of Ta onto the PI surface by chemical vapor deposited (CVD) method [13,14]. However, this method is expensive and inefficient. In this study, a new type of poly(imide siloxane)/tantalum oxide (PIS/TaO_x) hybrid film is synthesized by in situ sol–gel process. *p*-Aminophenyltrimethoxysilane (APTS) is applied to control the polyimide/siloxane (PIS) block chain length as well as to improve the mechanical property of PIS. Moreover, tantalum ethoxide ($Ta(OEt)_5$) is also incorporated into the PI matrix to enhance the adhesion strength between PIS and copper. Here, it is intended to correlate the properties, thermal and dynamic mechanical properties and surface characteristics as well as adhesion strength, with the PIS/TaO_x hybrid films' composition.

2. Experiment

2.1. Materials

High-purity octamethylcycloterasilxane (D4), and 1,3-bis(3-aminopropyl)-tetramethyldisiloxane (DSX) is obtained from Tokyo Chemical Industry. Tetramethylammonium hydroxide pentahydrate (TMAHP, 98%) is acquired from Lancaster. 4,4'-oxydiphthalic anhydride (ODPA, 98%) from Chris-kev is dried in a vacuum oven at 85 °C overnight. 2,2-bis[4-(4-Aminophenoxy)phenyl]propane (*p*-BAPP, 98%) from Aldrich Chemical Company is dried in a vacuum oven at 85 °C for 8 h prior to use.

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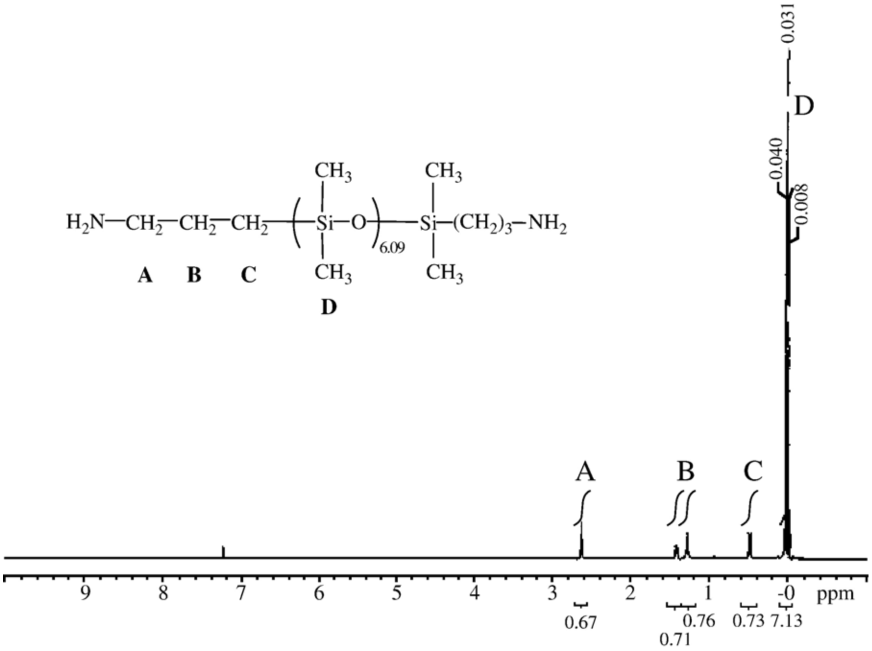

Fig. 1. NMR spectrum of 625 g/mol APPS.

p-Aminophenyltrimethoxysilane (APTS, 90%) from Gelest is used as supplied. *N*,*N*-dimethyl formamide (DMF) is from Tedia Company. The tantalum additive is tantalum ethoxide (Ta(OEt)$_5$), obtained from Lancaster. Other additive includes acetylacetone (acac) is available from Tokyo Chemical Industry.

2.2. Synthesis of α,ω-bis(3-aminopropyl)polydimethylsiloxane (APPS) oligomer

The catalyst, tetramethylammonium siloxanolate (TMAS), is made by reacting stoichiometrically amount of TMAHP and D4

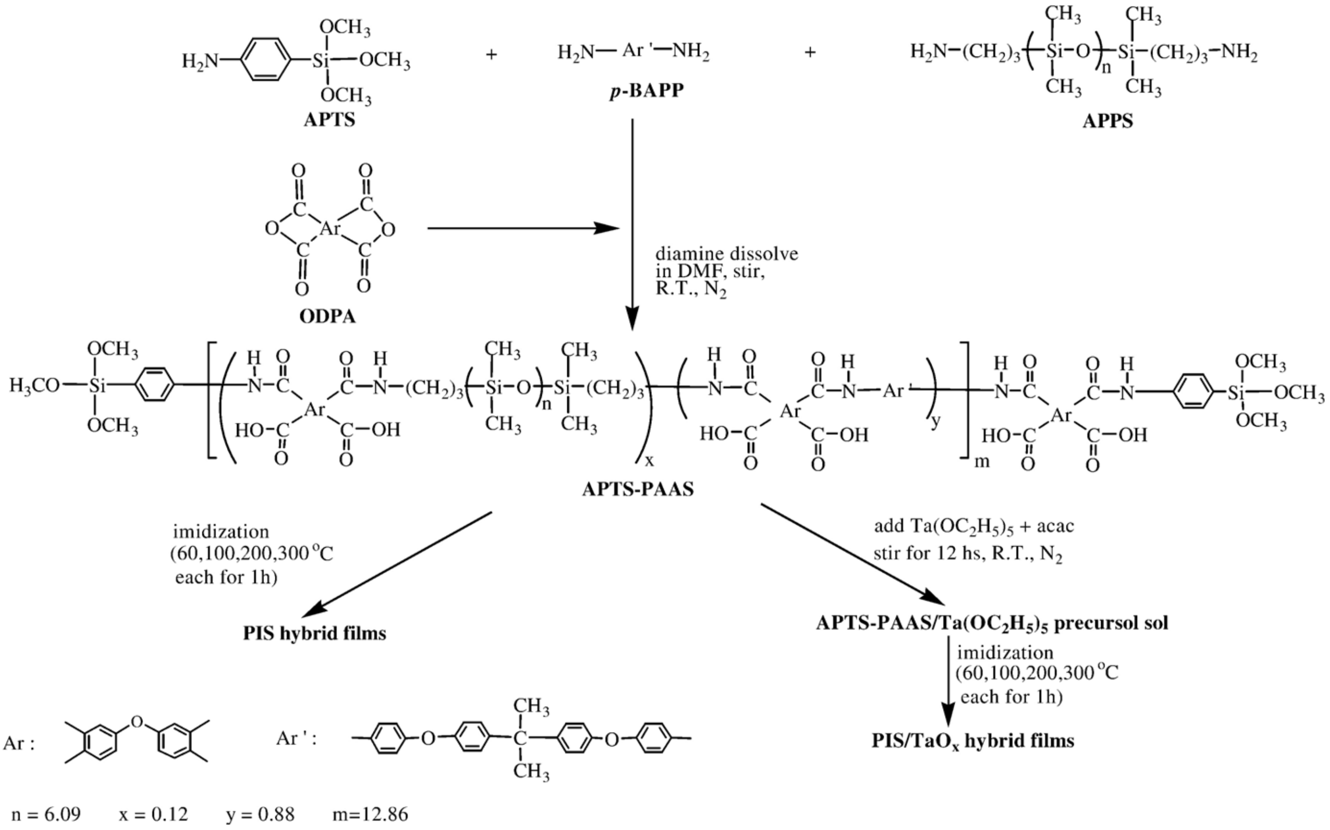

Fig. 2. The chemical structure and reaction process of PIS and PIS/TaO$_x$ hybrid films.

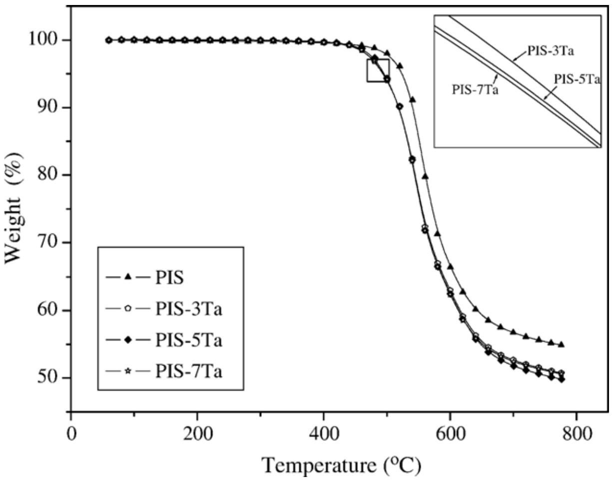

Fig. 3. Dynamic thermogravimetric curves of PIS and PIS/TaO$_x$ hybrid films.

stirring at 60 °C under argon atmosphere for about 48 h. The APPS oligomer is prepared from the mixture of stoichiometric DSX and D4 at 80 °C under nitrogen atmosphere, and then adding 1.0 wt.% of TMAS and stirring for 48 h and then raising temperature to 150 °C to decompose the catalyst. After cooling down, the reactant is heated at 105 °C under vacuum condition to remove the residual of D4 [8,15–17]. The number average molecular weight of 625 g/mol is determined by using proton nuclear magnetic resonance (NMR) spectroscopy as shown in Fig. 1.

2.3. Synthesis of poly(imide siloxane)/tantalum oxide (PIS/TaO$_x$)

Poly(amic acid siloxane) (PAAS) solutions are made by reacting stoichiometrically amount of *p*-BAPP, APPS, APTS (APTS is used to control the chain length with block molecular weight of 10,000 g/mol), ODPA and suitable amount of DMF under a nitrogen atmosphere and stirring for 2 h. After this period, modified PAAS solutions are made by adding the mixture of Ta(OEt)$_5$ and acac (molar ratio of Ta(OEt)$_5$ to acac is fixed to 1:5 [18]) and stirring for 12 h. The chelating agent acetylaceton (acac) is employed to control the sol–gel reactivity of tantalum alkoxides. The metaloxide concentration are approximately 3, 5, 7 wt.% within the PIS matrix, assuming complete imidization, complete conversion of the Ta(OEt)$_5$ to the tantalum pentoxide, and no residual solvent. The reaction is shown in Fig. 2.

Table 1
Characteristic analysis of PIS and PIS/TaO$_x$ hybrid films

Sample code	Decomposition temperature T_d (°C)[a]	CTE (μm/m °C)[b]	DMA test		Peel strength (N/cm)[e]
			E′ (MPa)[c]	Tg (°C)[d]	
PIS	513.3	94.2	1530	230.7	3.37
PIS-3Ta	486.9	86.6	1485	231.3	4.68
PIS-5Ta	486.3	88.2	1495	232.0	7.96
PIS-7Ta	484.9	84.5	1620	232.8	2.70

[a] Temperature at 5% weight loss.

[b] The coefficient of thermal expansion are determined over a range of 55–200 °C.

[c] Storage modulus of hybrid films are measured at 60 °C.

[d] The maximum in tan δ curve is designated as glass transition temperature.

[e] Averages of five measurements.

The precursor of PAAS is coated on a dust-free glass plate with a 650-μm doctor blade. The gel film is then heated at 60, 100, 200 and 300 °C each for 1 h. Consequently, the PIS/TaO$_x$ hybrid films have an average final thickness of 65–75 μm.

2.4. Measurements

Thermogravimetric analysis (TGA) is performed with a TA Instruments TGA-Q500 at a heating rate of 20 °C/min from 60 °C to 800 °C under nitrogen. The in-plane thermal expansion measurement is carried out in the range of 50–350 °C by using a DuPont 2940 probe, which provided 0.05 N tension force on the film, at a heating rate of 5 °C/min. The coefficient of thermal expansion (CTE) values on the temperature scale are between 55–200 °C. The dynamic mechanical analysis (DMA) is carried out from 60 °C to 250 °C with a TA Instruments DMA 2980 at heating rate of 3 °C/min and 1 Hz frequency. X-ray photoelectron spectrometer (XPS) is obtained by using a PHI Quantera SXM spectrometer working in the constant analyzer energy mode with a pass energy of 280 eV and AlKα radiation as the excitation source. XPS analysis is done at room temperature and pressure below 10^{-8} Torr. The take-off angle used in the XPS measurement is 45° and sputter rate 3.97 nm/min. The PIS and PIS/TaO$_x$ hybrid films are adhered to Cu foil substrates, which preheat at 360 °C for 2 min and apply 50 kg/cm^2 pressure for 5 min. The adhesion of the samples by using 180° peel test method (Model HT-8116 Hung TA) and peel rate is 50.8 mm/min.

3. Results and discussion

A novel material poly(imide siloxane)/tantalum oxide (PIS/TaO$_x$) hybrid thin film has been successfully prepared through the in situ formation of TaO$_x$ within a PIS matrix by sol–gel

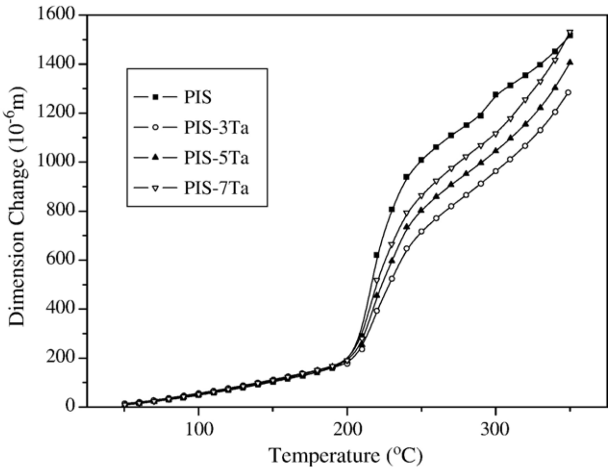

Fig. 4. Thermal expansion of PIS and PIS/TaO$_x$ hybrid films.

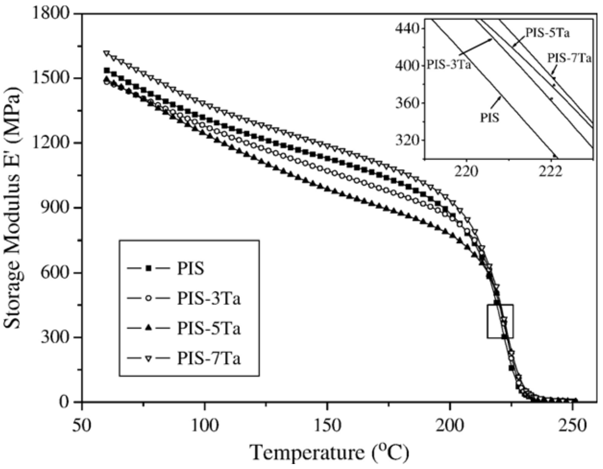

Fig. 5. Storage modulus curves of PIS and PIS/TaO$_x$ hybrid films.

process. The dynamic thermogravimetric curves of PIS and PIS/TaO$_x$ hybrid films are measured at a heating rate of 20 °C/min under nitrogen atmosphere as shown in Fig. 3. The decomposition temperatures (T_d), at 5% weight loss, are listed in Table 1. The result indicates that hybrid film starts to decompose around 450 °C and losses of 5% weight between 484 to 513 °C. According to the previous studies, the decrease in thermal stability could be attributed to the metallic compounds, which can oxidatively degrade polyimide films [19–21]. Besides, there could be some residue of acetylacetone still remaining in the hybrid films. Those residues will decrease the thermal stability of hybrid films. Although the introduction of TaO$_x$ causes a decrease in thermal stability, all the hybrid films still possess a pretty good thermal stability.

Fig. 4 shows the coefficients of thermal expansion (CTE) of PIS and PIS/TaO$_x$ hybrid films. The CTEs of hybrid films listed in Table 1 are calculated in the range between 55 °C and 200 °C. All the PIS/TaO$_x$ hybrid films exhibit about 8–10% lower CTEs as compared with PIS. The tendency of decreasing CTEs of hybrid films is more remarkable at an elevated temperature (>200 °C). This property will enhance the reliability for adhesion application between PIS films and copper. Moreover, the hybrid film with lower CTE value also can avoid delaminating between the hybrid film and copper foil.

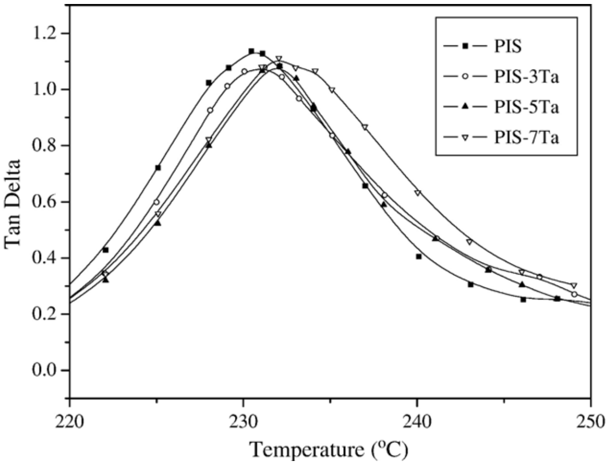

Fig. 6. Tan delta curves of PIS and PIS/TaO$_x$ hybrid films.

The dynamic mechanical properties of PIS/TaO$_x$ hybrid films as a function of temperature are shown in Figs. 5 and 6. Fig. 5 shows the storage moduli of PIS/TaO$_x$ hybrid films. It can be seen that the storage modulus of hybrid films with 3 wt.% and 5 wt.% TaO$_x$ are decreased. However, the storage modulus of hybrid films with 7 wt.% TaO$_x$ increases as compared with that of pure PIS. The glass transition temperatures, Tgs, of all the PIS/TaO$_x$ hybrid films are taken from the maximum of tan δ curves in Fig. 6. The Tg of the hybrid films are increased with increasing TaO$_x$ content. This result could be attributed to the filler effect of TaO$_x$, thereby affording stiffer hybrid films.

Fig. 7 shows the X-ray photoelectron spectrometer (XPS) results of PIS/TaO$_x$ hybrid films. The chemical composition of PIS-7Ta hybrid film is shown in Fig. 7(a). On the top-right side is the enlarged result of Ta 4_f for the PIS-7Ta hybrid films. Fig. 7(b) demonstrates the composition-depth results after sputtering for 30 s. It can be seen that PIS-7Ta contains the compound of Ta–O (24.1 eV) on the hybrid film surface [22], while the signal of Ta–O is not found after sputtering. It is implied that the migration of Ta–O species from the bulk to the surface of the polymer is observed. This phenomenon will enhance the adhesion strength between hybrid film and copper. Besides, the spectrum of the PIS-3Ta hybrid film has the same tendency.

The adhesion strength between the PIS/TaO$_x$ hybrid films and copper is measured by 180° peel tests. Table 1 presents the adhesion strength between the PIS/TaO$_x$ hybrid films and copper foil. The adhesion strength of pure PIS is 3.37 N/cm, while the adhesion strengths of the PIS/TaO$_x$ hybrid films are 4.68, 7.96 and 2.70 N/cm for PIS-3Ta, PIS-5Ta and PIS-7Ta, respectively. The improvement of adhesion strength with small incorporation of TaO$_x$ could be attributed to the existence of TaO$_x$ on the hybrid film surface. Once the content of TaO$_x$ increases up to 7 wt.%, the hybrid film becomes brittle and will crack within the polymer film. However, the delamination at the interface is not found during the peel test. It is also found that the incorporation of TaO$_x$ into the hybrid film matrix makes a loss in flexibility of the hybrid film. Therefore, the mobility of

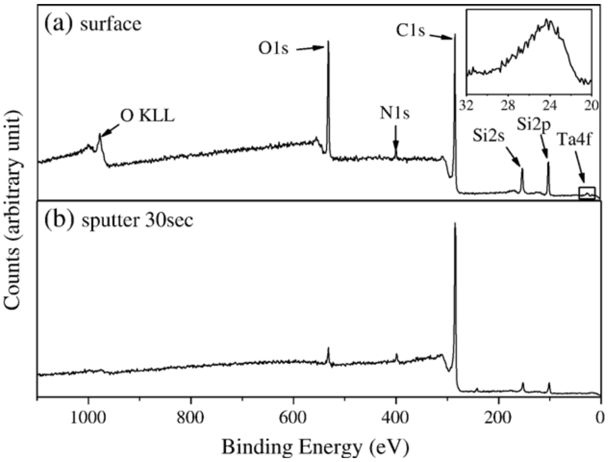

Fig. 7. XPS survey spectra of PIS-7Ta hybrid film (a) on PIS-7Ta hybrid film surface (b) sputter after 30 s.

polymer chain is diminished and the hybrid film with high TaO_x content can't afford a larger load without fracture during the peel test.

4. Conclusion

The poly(imide siloxane)/tantalum oxide (PIS/TaO_x) hybrid films have been successfully fabricated by in situ sol–gel process. The improvement of adhesion strength could be attributed to the presence of TaO_x on the hybrid films surface. However, further addition of TaO_x causes a failure or crack within the polymer substrate instead of interfacial failure during the peel test. Owing to the increase of rigidity, the hybrid film is too brittle to afford a larger load without fracture. This result also indicates that the adhesion strength is higher than the mechanical strength of the hybrid film. Based on X-ray photoelectron spectroscopic (XPS) data, Ta–O compound primarily presents on the surface of the hybrid film. This result enhances the adhesion strength between the hybrid film and copper foil. Moreover, by incorporating TaO_x into the PIS matrix, the hybrid films possess lower thermal expansion coefficient at elevated temperature and they still maintain good thermal and mechanical properties as well.

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