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Effects of precursor structure and imidization process on thermal expansion coefficient of polymide (BPDA/PDA)

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Effects of the drying condition on thermo-mechanical properties and morphology of PI(BPDA/PDA) were investigated. Polyamic acid and polyamic acid esters were used as precursors of the polyimide. Thermal expansion coefficients (TECs) of the polyimide films are strongly affected by precursor structures. The esters give larger TECs than the polyamide acid does. TEC of polyimide film from polyamide acid depends on imidization conditions. The lowest TEC is obtained when the film is dried at 100°C and the value increases with the drying temperature. The TECs of the polyimide films formed from polyamide acid esters do not depend on the drying temperature. In summary, interactions between the precursors and solvent (NMP) lead to large differences in higher order structures of the polyimides, which in turn affects the TECs. © 1997 Elsevier Science Ltd

(Keywords: polyimide; polyamide acid; polyamide acid ester)

INTRODUCTION

In electronics applications polyimide films have been widely used as a passivation layer of LSI devices[1,2]. The thermal stress between the silicon wafer and the polyimide passivation layer is a critical issue for LSI fabrication as silicon wafer size and with increasing of thickness of the passivation layer film are increased. Larger silicon wafers are desirable for improving productivity in which the nominal diameter is shifted from 125 mm to 200 mm or larger. Thicker passivation layers are necessary to protect the active area from alpha-rays which cause a soft error. Thermal stress causes deformation of the coated silicon wafer whereby the wafer becomes concave relative to the polyimide coated side. The deformation does not cause any problem when a small size silicon wafer is used. However, the deformation of a large silicon wafer with a thick passivation film will exceed the limit of photo-lithography process for making the bonding area. Low thermal expansion polyimides have a good potential for reducing the deformation caused by the thermal stress.

PI(BPDA/PDA) is the most widely used low thermal expansion polyimide[3-6]. A polyimide passivation layer with a controlled thermal expansion coefficient (TEC) is essential for better LSI fabrication. The effects of imidization process and film thickness on TEC and in-plane orientation have been reported. TECs were found to range from 0.3 ($\times 10^{-5}$ K^{-1}) to 1.5 ($\times 10^{-5}$ K^{-1})[7]. Film thickness[8-11] and ramp rate effects[12] on film properties of PI(BPDA/PDA) were significant. We have already reported the effect of drying temperature on TEC of the polyimide film when polyamic acid and polyamic acid esters were used as precursors[7]. The importance of interactions between the precursors and solvent on solution property, imidization reaction and resulting polyimide film have been clarified in several reports[7,13].

As a part of our ongoing series of studies on low thermal expansion polyimides, the mechanism to lower the polyimide TEC was investigated from the viewpoint of interaction between the precursors and the solvent, *N*-methylpyrrolidone (NMP).

EXPERIMENTAL

Reagent

N-methyl-2-pyrrolidone (NMP; 99% purity grade) was purchased from Tokyo Ohoka Kogyo Co. Ltd. and dehydrated using molecular sieves. Water content of the NMP was below 50 ppm in weight. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (*s*-BPDA) was purchased from Yuki Gosei Kogyo Co. Ltd. (Tokyo, Japan) and heated at 200°C for 2 h just before use to convert its carboxyl groups into anhydride. The anhydride melting point was 292°C. *p*-Phenylene diamine (*p*-PDA; 98% purity grade) was purchased from Tokyo Kasei Kogyo Co. Ltd. and purified by sublimation. The melting point was 145°C. Thionyl chloride purchased from Wako Chemical Co. (Tokyo, Japan) was distilled under nitrogen and stored in a sealed flask.

Sample preparation

Polyamic acid solution was prepared from *s*-BPDA and *p*-PDA as previously reported[14]. The concentration was 15% in NMP. The solution was heated for 8 h at 80°C to reduce the viscosity. Polyamic acid esters were synthesized from a

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3,3′,4,4′-biphenyltetracarboxylic dialkylester dichloride (alkylgroup: methyl, ethyl, *n*-propyl, and *n*-butyl) derived from a 3,3′,4,4′-biphenyltetracarboxylic dialkylester, and *p*-PDA. 3,3′,4,4′-Biphenyltetracarboxylic dialkylesters were prepared from *s*-BPDA and an alcohol. Details have been reported previously[15].

The polyamic acid solution was spin coated on a 4 silicon wafer and dried at the desired temperature, selected from 80, 100, 150, or 200°C for 1 h. Then the temperature was increased to 350°C for 70 min and the final imidization was carried out at 350°C for 30 min. The fully imidized samples were cooled to room temperature. All heat treatments, including cooling down, were carried out in a conventional oven filled with a nitrogen atmosphere.

Measurements

Linear thermal expansion coefficient. A film, 5 mm wide, 15 mm long (between chuks) and 20 μm thick, was used as a sample. The sample was placed in a thermo-mechanical analyser (TMA 1500, Shinku-Riko Co. Ltd., Tokyo, Japan) and heated to 350°C in order to remove absorbed water and any residual stress. After cooling to room temperature, changes in length of the polyimide film was measured while heating at a rate of 5°C min^{-1} in air. Since the TEC was temperature dependent, the average value between 50°C and 250°C was used as a representative value.

Decomposition of 1/2 compound (A). PAA (BPDA/PDA) solution in NMP was spin coated on a silicon wafer and dried under various conditions; the temperature ranged from 80°C to 130°C and times ranged from 0.5 to 3 h. The film was peeled off and cut into strings of 5 mm width. The strings (weighing 50 to 100 mg) were placed in a thermobalance (TGD 3000, Shinku Riko Co. Ltd.) and heated at 350°C for 1 h in a nitrogen atmosphere to complete the imidization reaction. During the heating, H_2O caused by the imidization reaction of the PAA and NMP which had remained in the film was evaporated. The residual amount of NMP after the drying process was calculated from total weight loss during imidization reaction.

Density. Tetrachloromethene/xylene mixed solution with the same density as the polymer film was prepared at 30°C by controlling the composition. The density of the solution was measured by DMA02C (Anton Paar Co. Ltd.) and the same temperature. Air was used as the reference.

X-ray diffraction pattern. The polyimide film (*ca.* 20 μm in thickness) prepared on Si wafer was peeled off and cut into strings of 5 mm width. Each X-ray specimen was prepared by stacking together many layers of strings to get a 5 mm total thickness. The out-of-plane diffraction pattern was measured by a wide-angle X-ray diffractometer (Rigaku Co., Tokyo, Japan) with nickel-filtered Cu $K_{\alpha 1}$ radiation.

RESULTS AND DISCUSSION

Thermal expansion coefficient of the polyimide films: effects of precursor structures

Figure 1 relates molecular weight of the leaving group and TEC of the resulting polyimide. Differences in TEC between the polyimide from PAA and TECs from PAEs were significant. The TEC of the polyimide from PAA was 0.5 ($\times 10^{-5}$ K^{-1}), while TECs of polyimides from the PAEs ranged from 1.8 to 2.2 ($\times 10^{-5}$ K^{-1}). TEC changed clearly between H_2O and CH_3OH. The difference in TEC was small when the leaving groups were changed from CH_3OH to C_4H_9OH, even though the molecular weight ranged from 32 to 72. These findings indicated that the type of precursor, i.e. PAA or a PAE had more influence on the TEC of the product polyimide than the molecular weight of the leaving group.

The TEC of a polyimide film is strongly affected by its chemical structure[16]. I.r. spectra of the polyimide films are shown in *Figure 2*. Peaks at 1710 cm^{-1} and 1770 cm^{-1} were assigned to out-of-phase and in-phase modes of $\nu C = O$ in the imide ring, respectively. The peak at 1350 cm^{-1} was assigned to the νC–N bond between the imide ring and the adjacent phenyl. All the spectra had these characteristic absorptions and they were identical regardless of the type of precursors used. The chemical structure of the polyimide films should be indistinguishable. The differences in TECs could be attributed to the differences in the higher order structure of the films.

Molecular compounds formation between polyamic acid unit and NMP have been reported[17–19]. Shibayev *et al.*[17] studied interactions between polyamic acid and solvents. They used pyromellitic dianilic acid as a model compound for polyamic acid [pyromellitic acid dianhydride (PMDA)/oxydianiline (ODA)] and reported the structure of pyromellitic dianilic acid–NMP molecular compounds that contained 2 or 4 NMP molecules per

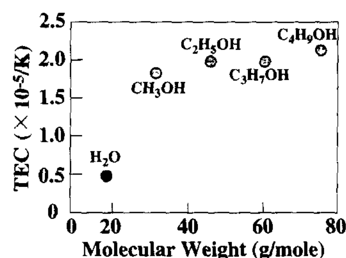

Figure 1 Effects of leaving group on thermal expansion coefficient of PI(BPDA/PDA)

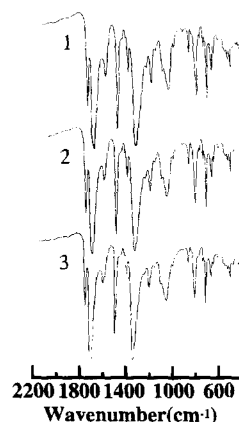

Figure 2 I.r. spectra of polyimides from PAA(BPDA/PDA) and PAE(BPDA/PDA). 1, From PAA; 2, from methyl ester; 3, from propyl ester

pyromellitic dianilic acid molecule. Two NMP molecules attached to amide groups and two NMP molecules attached to carboxyl groups of the model compound. Brekner and Feger[19] investigated the thermal imidization reaction of polyamic acid (PMDA/ODA) and clarified that PAA (PMDA/ODA) unit formed the same types of molecular compounds with NMP molecules. The 1/4 molecular compound between a PAA(PMDA/ODA) unit and NMP molecules decomposed to the 1/2 compound (A), i.e. the NMP molecules attached to the carboxylic groups of the PAA unit and two NMP molecules around 40°C, and the 1/2 compound (A) decomposed to the polyamic acid (PMDA/ODA) unit and two NMP molecules around 120°C. A highly crystalline nature was reported for both molecular compounds. The same types of molecular compounds would be expected for PAA(BPDA/PDA), and a different type of 1/2 molecular compound (B) in that two NMP molecules would attach to the amide groups of the PAE unit with the same degree of thermal stability as the 1/4 compound. For convenience we defined two kinds of 1/2 compounds; 1/2 compound (A) indicated that 1/2 compound between PAA and NMP and 1/2 compound (B) indicated that 1/2 compound between PAE and NMP. Formation of the crystalline molecular compound with NMP might have greater effects on higher order structure of polyimide films from PAA.

Figure 3 shows an Ahrrenius plot for the weight decrease caused by evaporation of NMP from spin coated PAA film on Si wafer. The plot was linear for the first order reaction and gave 20.5 kcal mol^{-1} as the activation energy. The activation energy calculated here was comparable to the value estimated for the bond energy of 1/2 compound (A) between pyromellitic dianilic acid and NMP[12]. The same type of 1/2 compound (A) should formed for PAA(BPDA/PDA). Effects of the presence of 1/2 compound (A) during the imidization reaction on TECs of the films were investigated.

Effects of drying temperature

The spin coated precursor film was placed in an oven at the desired drying temperature of 80, 100, 150, or 200°C for 1 h and imidized. TECs of polyimide films from PAA were affected by drying temperature (*Figure 4*). TEC was the lowest when the PAA film was dried at 100°C and the value increased with higher drying temperature. On the other hand PAE(methyl ester), which does not form 1/2 compound (A), gave comparable values ranging from 1.60–1.75 ($\times 10^{-5}\ K^{-1}$), independent of drying temperature. During the drying process the 1/4 compound composed readily and a certain amount of 1/2 compound (A) remained; the amount depended on the drying temperature. The remaining amount of 1/2 compound decreased with higher drying temperature because of thermal decomposition of the compound (*Figure 3*). The PAE which does not form 1/2 compound (A), gave higher and almost constant TEC values. These results pointed to the importance of the 1/2 compound (A) in lowering TEC.

The t.g.a. curves of the PAA solutions were measured for each imidization process. As expected, no or only a small amount of NMP remained after drying process at 150 or 200°C. A lot of NMP remained after drying at 80°C. The residual amount of NMP at the end of drying process at 100°C corresponded to quantitative formation of the 1/2 complex (A) and the TEC of the resulting polyimide film was the smallest. (*Figure 5*)

Figure 6 relates the amount of residual NMP in the PAA film after drying and TEC of fully imidized

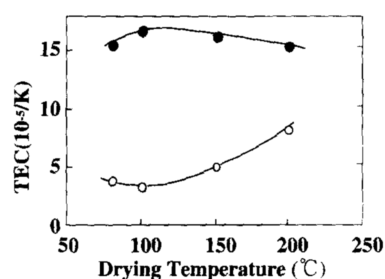

Figure 4 Effects of drying temperature on thermal expansion coefficient of PI(BPDA/PDA). ○, From PAA and ●, from PAE (methyl ester)

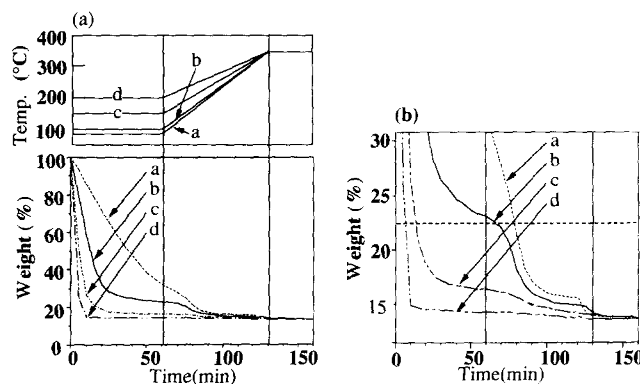

Figure 5 Weight change of PAA(BPDA/PDA) solution in NMP/15 wt% during imidization reaction when dried at: a, 80°C; b, 100°C; c, 150°C; d, 200°C

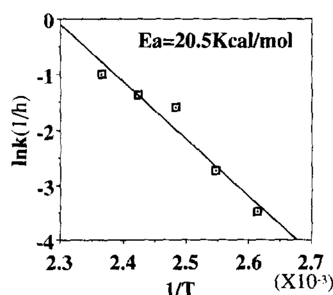

Figure 3 Activation energy of decomposition of PAA(BPDA/PDA)/NMP 1/2 compound

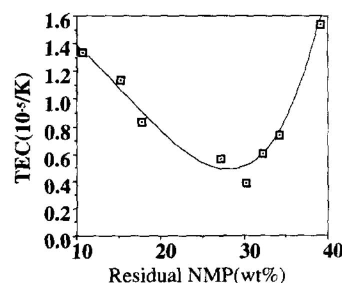

Figure 6 Effect of residual NMP in PAA film on thermal expansion coefficient of PI(BPDA/PDA) from PAA

polyimide films. Film thickness, drying temperature, and drying time ranged from 5 to 20 μm, 80 to 120°C and 0.5 to 3 h, respectively. TEC was a minimum when PAA film contained about 33% residual NMP, corresponding to quantitative formation of the 1/2 compound (A), and this was independent of film thickness and drying conditions. These results prove clearly that TEC of the polyimide film is controlled by formation of the 1/2 compound (A) during drying process.

Figure 7 shows displacement of the polyimide films caused by temperature change. TG was strongly affected by structures of the precursors and drying temperature. TGs varied in a trend similar to that of TECs. PAE (methyl ester) gave a lower TG than PAA. The former values were around 300°C and the differences were smaller compared with the latter. On the other hand, TGs decreased drastically with higher drying temperature when PAA was used as the precursor. Small shifts in TG of polyimide films from the PAE can be explained by diffusion controlled mechanism of thermal curing reaction of polymer[20,21] that pointed out, that the TG of thermally curable polymer increases with the increasing of initial cure temperature. The change in TG of polyimide from PAA is opposite to the mechanism, as mentioned after, effects of formation of the 1/2 compound (A) on crystalline nature of the polyimide can be the cause of the disagreement.

Film morphology

Figure 8 shows density of polyimide films. PAA and PAE (methyl ester) gave different densities. They ranged from 1.45 to 1.47 and 1.43 to 1.44, respectively. Formation of 1/2 compound (A) and aggregation of carboxylic group of PAA could be causes of the difference. The density of the film from PAA decreased on increasing drying temperature, unlike the density of the film from PAE (methyl ester) which increased with the temperature. A residual amount of 1/2 compound (A) and a plasticizing effect by NMP during the imidization reaction could be factors involved.

Figure 9 relates density and TEC to polyimide films from PAA and PAE (methyl ester). Overall, TECs decreased with increasing density. But they did not follow the density. TECs were insensitive to the density when PAEs were used as precursors; for PAA precursor, TEC changed abruptly when the density reached 1.45 and the drying temperatures that minimized TEC and that maximized density did not coincide. Crystallinity of the films is believed to be the cause of the results.

Figure 10a shows X-ray diffraction curves of the polyimide films from PAA. Diffraction peak around 20° is according to the plane distance of the imide rings. Since the diffraction intensities of films dried at 80°C and 100°C were larger than that of the film dried at 150°C, crystallinity of the former two films was more extensive than that of the film dried at 150°C. The position of the diffraction peak was 19° for the films dried at 80°C and 100°C, and 18.5° for the film dried at 150°C. The corresponding plane distance to the values of 2θ, 19° and 18.5° were 4.7 Å and 4.8 Å, respectively. *Figure 10b* shows X-ray diffraction spectra of the polyimide films from PAE (methyl ester). Since broader diffraction peaks with larger 2θ values were observed, the crystallinity of the films was smaller and the plane distance was larger compared with polyimide from PAA. Changes in diffraction intensity were small and the peak positions were identical (18°) for all drying conditions. The calculated plane distance for the polyimide films from the PAE is 5.0 Å.

Effects of the presence of the 1/2 compound (A) during imidization on the crystal structure was clear. Higher crystallinity and closer packing were attained when enough of the 1/2 compound (A) remained after drying. At the beginning of imidization reaction, the existence of the 1/2 compound (A) which has a highly crystalline nature, might be favourable for crystallization of polyimide film, and NMP molecules generated by

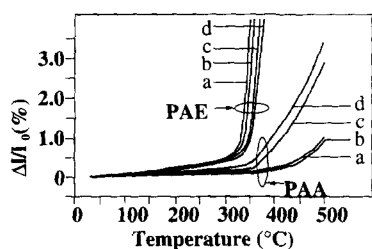

Figure 7 Elongation percentage ($\Delta l/l_0$) of PI(BPDA/PDA) from PAA and PAE (methyl ester) when dried at: a, 80°C; b, 100°C; c, 150°C; d, 200°C

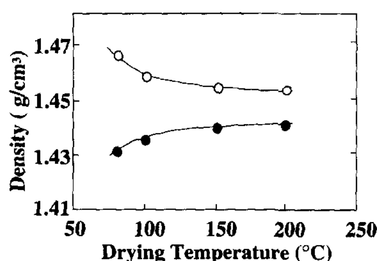

Figure 8 Density of PI(BPDA/PDA) films: ○, from PAA and ●, from PAE (methyl ester) for different drying temperatures

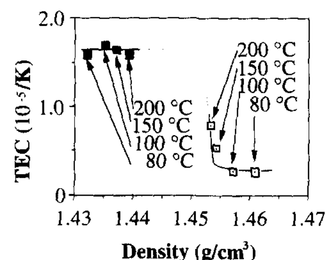

Figure 9 Density dependence of TEC of PI(BPDA/PDA) films: □, from PAA and ■, from PAE (methyl ester)

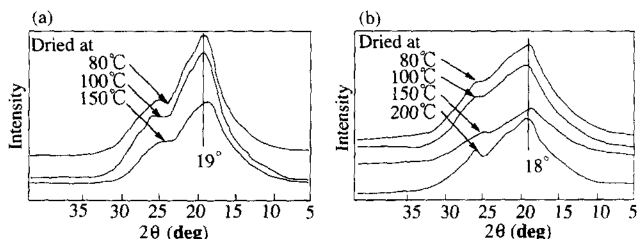

Figure 10 X-ray diffraction of PI(BPDA/PDA) films from (a) PAA and (b) PAE (methyl ester)

decomposition of the 1/2 compound (A) during imidization reaction might plasticize polyimide film and promote rearrangement of polymer chain to attain highly crystalline structure and closer packing.

There was a clear relation between crystal structure and TEC of the films. Films with higher crystallinity and shorter plane distance of imide rings had a lower TEC. Ordered structure with closer packing should increase intermolecular interaction and lower the motion of polyimide chains.

CONCLUSIONS

The effects of drying conditions on thermo-mechanical properties and morphology of PI(BPDA/PDA) were investigated. Polyamic acid and polyamic acid esters were used as a precursor of the polyimide. Thermal expansion coefficients (TECs) of the polyimide films were strongly affected by the structures of the precursors. The polyamic acid ester precursors (PAE) gave larger TECs than the polyamide acid (PAA), and the former were insensitive to drying conditions. TEC of polyimide film from PAA was strongly dependent on drying temperature. TEC was smaller when the film was dried at 100°C and TEC increased with increasing drying temperature. Formation of the 1/2 complex (A) between PAA and NMP was seen to be essential for controlling of TEC the polyimide films from PAA. TEC was minimized when the 1/2 compound (A) remained quantitatively in the film after drying. TG varied in a trend similar to that of TECs. The polyimide film from PAE had a lower TG than the polyimide from PAA. The polyimide films with lower TEC gave higher TG.

A clear relationship was observed between TEC and the crystal structure of the film. Polyimide films with higher crystallinity and shorter plane distance gave lower TECs.

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