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XPS study on early stages of heat deterioration of silicon-containing aromatic polyimide film

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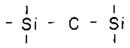
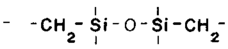
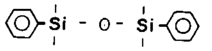
Early stages of heat deterioration of some silicon-containing aromatic polyimide thin films with disiloxane groups (I) in their main chains were studied with XPS. It was found that the thermal decomposition of silicon-containing aromatic polyimides takes place at lower temperatures than those not modified with silicon. The low thermal stabilities observed are explained by the easier decomposition of silicon–carbon bonds (e.g. silicon–methylene, silicon–aryl) than other bonds (e.g. carbon–carbon, carbon–oxygen). Particularly, silicon–methylene bonds (II) readily undergo thermal oxidative decomposition and start to decompose at 350 °C under aerobic conditions. This starting temperature of thermal decomposition is lower by 100 °C than that of the corresponding polyimide not modified with silicon. In the case of polyimide incorporating silicon–aryl bonds (III) instead of silicon–methylene bonds, the decrease in the thermal decomposition temperature is as small as 50 °C, and decomposition under aerobic conditions starts at 400 °C.


$-\overset{|}{\underset{|}{Si}}-C-\overset{|}{\underset{|}{Si}}-$

I


$-CH_2-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-CH_2-$

II



III

Keywords: XPS, TG, aromatic polyimide, silicon, silicon–carbon bond, heat deterioration, dissociation energy

INTRODUCTION

Polyimides have been used in various fields of the electronic industry because of their superior thermal stabilities and mechanical properties. Interlayer insulation films, buffer coating fi" alpha-ray shielding films for semiconductors and/or printing wiring boards, and oriented films for liquid crystal displays are typical applications of polyimides. A variety of new polyimides developed for such applications are available in the market. Polyimides with disiloxane groups in their main chains have been developed in order to increase the reliability of semiconductor devices utilizing their good adhesive properties to silicon wafers.[1] However, introduction of disiloxane groups has given rise to a problem of reduction in thermal stability. Polyimides affording both adhesiveness and thermal stability are in strong demand. With the development of such polyimides in mind, we studied the relationship between the chemical structure of polyimides and their thermal stabilities. Some silicon-containing aromatic polyimides have been synthesized and their thermal properties are investigated. Among many methods of analyzing thermal properties used so far,[2-7] thermal analysis[2-4] and mass spectroscopy[5] have been employed in the present experiment. In addition, X-ray photo-electron spectroscopy (XPS), which is applied in a recent report on the thermal decomposition of polyimides above 500 °C,[8] has been used for the analysis of silicon-containing aromatic polyimides at 200–450 °C.

EXPERIMENTAL

Synthesis of polyamic acid

Polyamic acids were prepared according to the literature.[9] Monomer compositions of these model polyamic acids are shown in Table 1. Each model polyamic acid was spin-coated on silicon wafers and dried at 100–200 °C min^{-1}. The polyamic acid layer turned into polyimide films (200–700 nm thick) by further stepwise heating at 200, 300, 350, 400 and 450 °C/30 min. The polyimide

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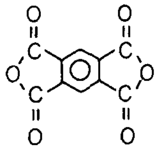
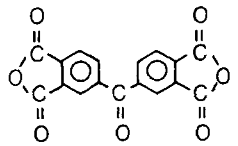
Table 1 Monomer compositions of polyamic acids

Polyamic acids	Monomers: Dianhydrides (mol %)	Diamine (mol %)	Silicon-containing compounds (mol %)
A	PMDA (50), BTDA(50)	DDE (100)	None
B-1	PMDA (50), BTDA(50)	DDE (98)	BAPDS (2)
B-2	PMDA (50), BTDA(50)	DDE (95)	BAPDS (5)
B-3	PMDA (50), BTDA(50)	DDE (90)	BAPDS (10)
C-1	PMDA (49), BTDA (49)	DDE (100)	SXDA (2)
C-2	PMDA (47.5) BTDA (47.5)	DDE (100)	SXDA (5)
C-3	PMDA (45), BTDA (45)	DDE (100)	SXDA (10)
D	PMDA (45), BTDA (45)	DDE (100)	TP-SXDA (10)

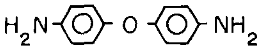
PMDA: Pyromellitic acid dianhydride



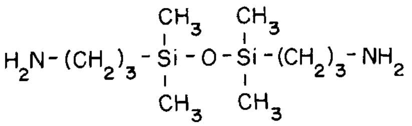
BTDA: Benzophenone tetracarboxylic acid dianhydride



DDE: 4,4′-diaminodiphenyl ether

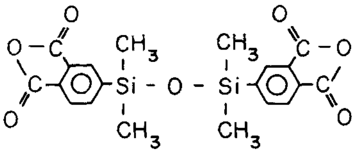


BAPDS: 1,3-Bis(3-aminopropyl)-1,1,3,3,-tetramethyldisiloxane

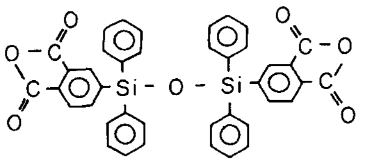


$$H_2N-(CH_2)_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3-NH_2$$

SXDA: 1,3-Bis(3,4-dicarboxyphenyl)-1,1,3,3-tetramethyldisiloxane dianhydride



TP-SXDA: 1,3-Bis(3,4-dicarboxyphenyl)-1,1,3,3-tetraphenyldisiloxane dianhydride



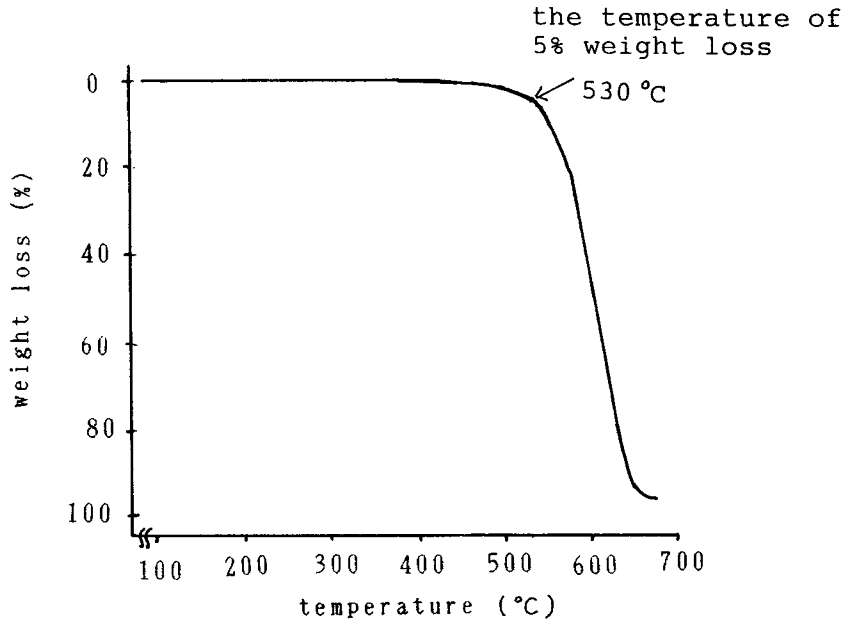


Figure 1 TG curve of polyimide A after heating under aerobic conditions (heating conditions: 200 °C/30 min and 350 °C/30 min).

films formed on silicon wafers were used as such for XPS measurement. In thermal analyses, polyimide films peeled from the surfaces of silicon wafers were used.

Measurement

Thermal weight loss curves (TG curves) were determined using a DuPont Model 9900 thermal analyzer. Measurement was carried out under aerobic conditions at a heating rate of 5 °C min^{-1} in the temperature range from room temperature to 700 °C. For each run 10 mg of polyimide sample were used.

Mass spectroscopy measurement was carried out using a Hitachi Model M-2000 gas chromatograph–mass spectrometer equipped with a Nihon Bunseki Kogyo Model JRP-3 thermal decomposer at a decomposition temperature of 400 °C under a nitrogen atmosphere and at an ion source temperature of 50 °C.

XPS spectra of films were obtained with a Perkin–Elmer Model ESCA-5400 spectrometer. Magnesium-Kα radiation (1257.6 eV) generated by a 400 W X-ray generator with path energy of 84.45 eV was used. Measured area was 3 mm × 10 mm.

Bond dissociation energy was calculated according to MOPAC's AM1 method using a Silicon Graphics Computer Systems IRIS 4D/70GT.

RESULTS AND DISCUSSION

Conventional aromatic polyimide (polyimide A)

The TG curve of polyimide A after heating under aerobic conditions is shown in Fig. 1. The temperature corresponding to the weight loss of 5 % is around 530 °C. This shows the excellent thermal stability of polyimide A.

Changes of C_{1s}, O_{1s} and N_{1s} XPS spectra of polyimide A after heating under aerobic conditions are shown in Fig. 2. No change in XPS spectra is observed up to 450 °C, indicating that the chemical structure of polyimide A does not change in this temperature range.

BAPDS-modified aromatic polyimide (polyimide B)

Although aromatic polyimides have an excellent thermal stability, they have the drawback of poor adhesive properties to base materials such as silicon wafers. This causes reduction of the reliability of semiconductor devices using these polyimides. Therefore, attempts have been made to improve adhesion of aromatic polyimides by incorporating disiloxane groups in their main chains. Some of such polyimides are now commercially available; an aromatic polyimide containing BAPDS is a typical example.

Figure 3 shows the TG curves of polyimide **A** and polyimides **B** (**B-1** to **B-3**) after heating under aerobic conditions. The temperature corresponding to the weight loss of 5 % gradually decreases with the increase of the BAPDS content. This demonstrates the effect of BAPDS on the thermal stability of polyimides **B**. However, it is difficult to correlate TG curves with the change in the chemical structure of polyimides **B**. Therefore, XPS spectra were measured to obtain the information on their structural changes on heating.

Corresponding changes of C_{1s}, O_{1s}, N_{1s} and Si_{2p} XPS spectra of polyimide **B-2** after heating under aerobic conditions are shown in Fig. 4. The Si_{2p} peak shifts from 100.9 to 101.9 eV on heating at 350 °C. This indicates that the silicon–carbon or silicon–oxygen bonds decompose at 350 °C and that progressive silicon oxidation occurs at this temperature. Accordingly, thermal stability of polyimide **B-2** is lower at least by 100 °C compared with that of polyimide **A**. At 400 °C, the peak-shift of Si_{2p} to higher energy is observed, indicating further oxidation of silicon. The peak intensity drop of C_{1s} at 288.0 eV (C=O) from 13 % to 11.9 % at 400 °C indicates the cleavage of imide rings in polyimide **B-2**. The cleavage of imide ring and oxidation of silicon proceed further at 450 °C, where the Si_{2p} binding energy of silicon is 102.6 eV, which is very close to the Si_{2p} binding energy in silicon dioxide (SiO_2), 103 eV. In other words, almost all the silicon atoms in polyimide **B-2** are bonded to oxygen at 450 °C. The O_{1s} peak shifts from 531.7 to 532.2 eV by elevating the temperature from 400 to 450 °C. It can be deduced from this peak shift that the heating at 450 °C decreases C=O bonds and increases C—O bonds in number.

Figure 5 shows the variation of relative concentrations of the elements with the heating conditions of polyimide. The concentrations were calculated from the peak intensities in the XPS spectra. No change in the relative concentration of elements is observed for polyimide **A** from 300 to 450 °C. This indicates that polyimide **A** is thermally stable up to 450 °C. On the other hand, the change in the relative concentration of the elements starts from 350 °C in polyimide **B-2**. Reduction of carbon concentration is observed together with increase of silicon and oxygen concentrations. These results support facile thermal oxidative decomposition of the silicon–carbon (or silicon–oxygen) bonds in BAPDS over other bonds. This leads to the reduction of thermal stability of polyimide **B** containing BAPDS.

In order to find which is most easily decomposed among silicon-methylene, silicon-methyl and silicon–oxygen bonds, gaseous components in the thermal decomposition of polyimide **B-2** were probed by mass spectroscopy. The mass spectrum of the gaseous products obtained when

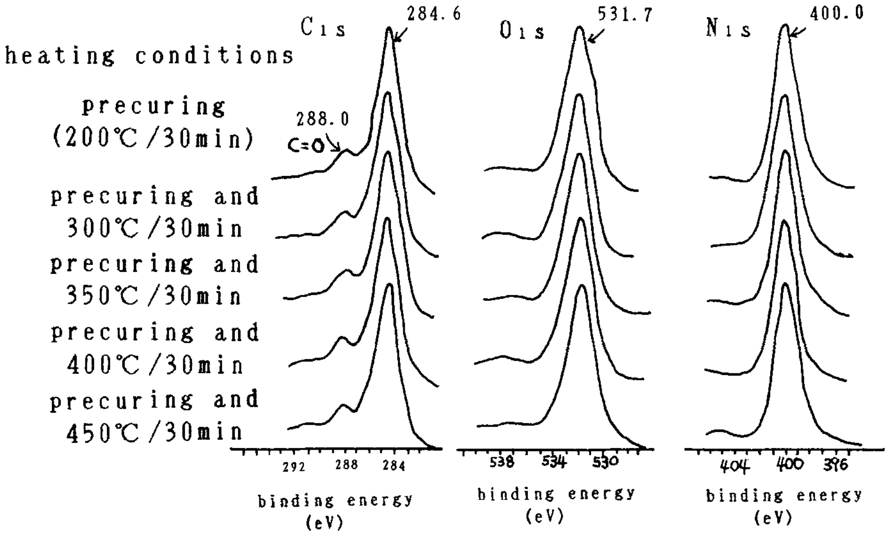


Figure 2 Changes of C_{1s}, O_{1s} and N_{1s} XPS spectra of polyimide A after heating under aerobic conditions.

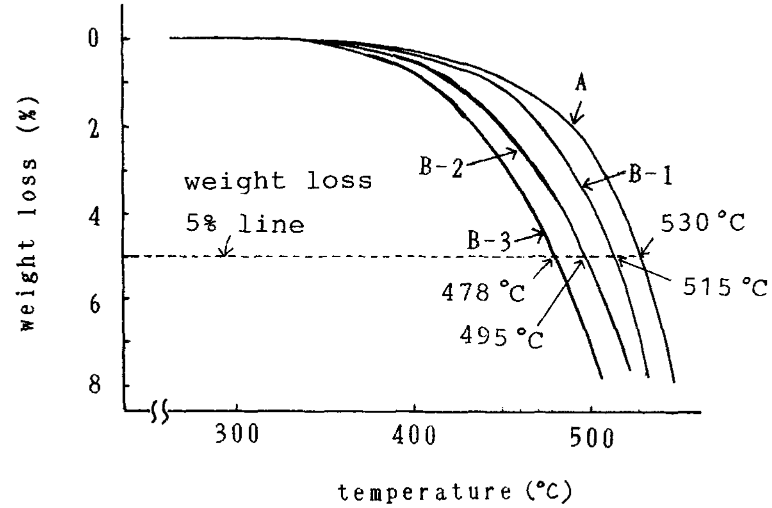


Figure 3 TG curves of polyimide A and polyimide B (B-1 to B-3) after heating under aerobic conditions (heating conditions: 200 °C/30 min and 350 °C/30 min).

polyimide **B-2** was heated at 400 °C is shown in Fig. 6. Fragment peaks observed can be mainly assigned to products due to the cleavage of silicon–methylene bonds. No fragments due to the silicon–methyl bonds are observed. Accordingly, the silicon–methylene bonds decompose more easily than the silicon–methyl bonds.

Dissociation energies of the chemical bonds in BAPDS, SXDA and PT–SXDA are given in Table 2. Dissociation energies of silicon–carbon and silicon–oxygen bonds were calculated. A considerable degree of consistency is found between the calculated value and the literature value[10] for Si—CH_3 and C—H bonds. Dissociation energies decrease in the order: silicon–oxygen > carbon–carbon > silicon–methyl > silicon–methylene bonds. These results are consistent with the mass spectroscopic data. The chemical bond most susceptible to thermal

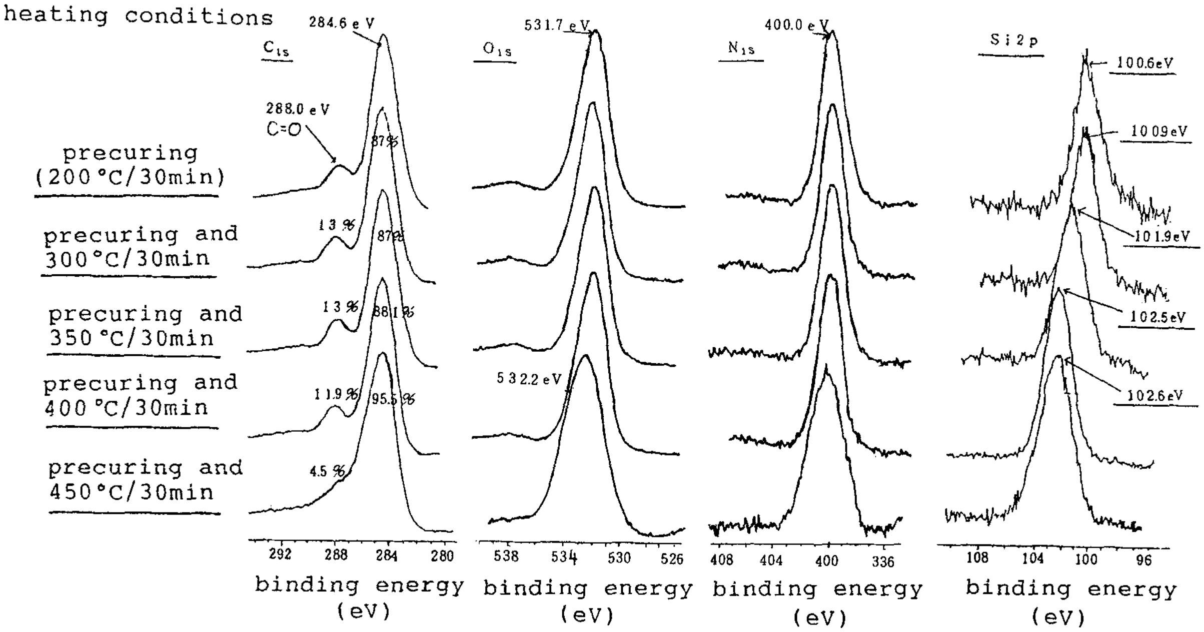


Figure 4 Changes of C_{1s}, O_{1s}, N_{1s} and Si_{2p} XPS spectra of polyimide **B-2** after heating under aerobic conditions.

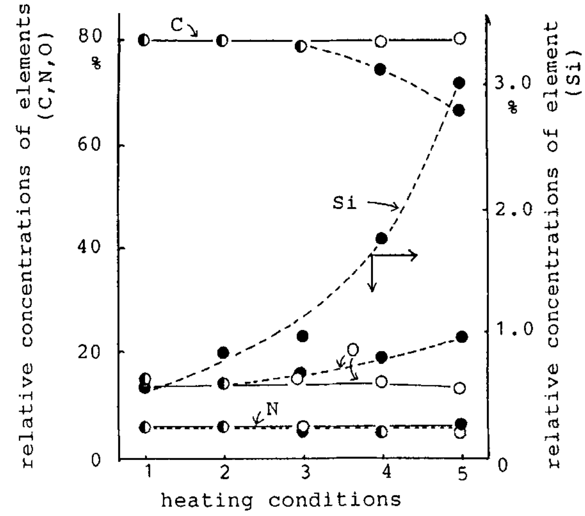


Figure 5 Variations of relative concentrations of elements vs heating conditions of polyimides. ○—○ polyimide **A**; ●---●, polyimide **B-2**. Heating conditions: 1, 200 °C/30 min; 2, 200 °C/30 min and 300 °C/30 min; 3, 200 °C/30 min and 350 °C/30 min; 4, 200 °C/30 min and 400 °C/30 min; 5, 200 °C/30 min and 450 °C/30 min.

decomposition is the silicon–methylene bond. The fragments of CO at *m/z* 28 and CO_2 at *m/z* 44 in the mass spectrum are formed probably by the decomposition of imide rings, which supports the XPS spectrum data.

Corresponding changes of C_{1s} and Si_{2p} XPS spectra of polyimide **B-2** after heating under a nitrogen atmosphere are shown in Fig. 7. The Si_{2p} peak-shift to higher energy is observed at 400 °C. More specifically, the peak position of Si_{2p} is 102.0 eV at 400 °C and 102.8 eV at 450 °C. This means that the thermal stability of polyimide **B-2** under a nitrogen atmosphere is higher by 50 °C than that under aerobic conditions. Oxygen atoms in air accelerate the thermal decomposition of silicon–methylene bonds. On the other hand, the C_{1s} peak is practically unchanged up to 450 °C, indicating that the imide rings remain intact.

SXDA-modified aromatic polyimide (polyimide C)

It was found that BAPDS-modified polyimides exhibit a high adhesive property to base materials including silicon wafers. This is an excellent property for improving the reliability of semiconductor devices. Disiloxane groups in these polyimides lead to the high adhesive property. However, they have reduced thermal stability compared with the unmodified polyimide. The presence of silicon–methylene bonds in BAPDS is the cause of the low thermal stability. Therefore, we prepared SXDA-modified aromatic polyimide (polyimide C) having silicon–aryl bonds instead of silicon–methylene bonds in the polymer main chains, and evaluated its thermal stability. As is apparent from Table 2, the dissociation energy of the Si—C(aryl) bond (88.6 kcal mol^{-1}, 371 kJ mol^{-1}) is larger than that of the Si—CH_2 bond (72.8 kcal mol^{-1}, 305 kJ mol^{-1}), and, therefore, improved heat resistance is expected for polyimide **C**. Polyimide **C** shows an excellent adhesive property to base materials, similarly to BAPDS-modified polyimides.

TG curves of polyimides **C** (**C-1** to **C-3**) after heating under aerobic conditions are given in Fig. 8 in comparison with polyimide **A**. The starting temperature for weight loss decreases with the increase of SXDA content. This indicates that the presence of SXDA causes the reduction of thermal stability. However, the degree of reduction is smaller than that of BAPDS.

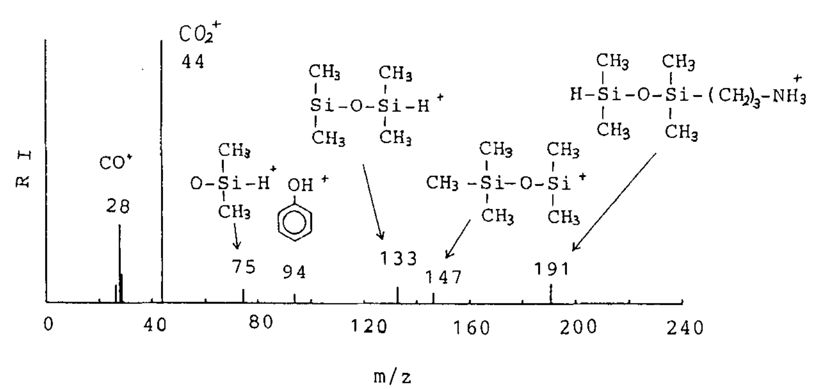


Figure 6 Mass spectrum of the gaseous products when polyimide **B-2** was heated at 400 °C.

Table 2 Bond dissociation energies

Bonds	Bond dissociation energy (kcal mol^{-1})	
Si—C(CH$_2$) bond in BAPDS	72.8	
Si—C(CH$_3$) bond in BAPDS	79.4	(79)[a]
Si—O bond in BAPDS	114.4	
Si—C(aryl) bond in SXDA and TP-SXDA	88.6	
Si—C(CH$_3$) bond in SXDA	79.6	
Si—O bond in SXDA	114.9	
C—H	103.8	(104)[a]
C—C		(88)[a]
C—O		(91)[a]

[a] Ref. 10.

Variations of C_{1s}, O_{1s}, N_{1s} and Si_{2p} XPS spectra of polyimide **C-2** after heating under aerobic conditions are shown in Fig. 9. The spectra start to change from 400 °C, which is higher by 50 °C than that of polyimide **B-2**. The Si_{2p} peak shifts from 101.0 to 102.0 eV at 400 °C. This means that the silicon–carbon bonds start to decompose at this temperature. The improvement in the thermal stability of polyimide **C-2** compared with **B-2** results from the substitution of the silicon–methylene bonds with silicon–aryl bonds. The peak shifts to 102.9 eV at 450 °C, showing that a progressive silicon oxidation occurs. On the other hand, C_{1s}, O_{1s} and N_{1s} XPS spectra are practically unchanged up to 450 °C, indicating that the imide rings remain intact. Further, no gaseous products were detected when polyimide **C-2** was heated at 400 °C. This also supports the superior thermal stability of SXDA-modified polyimide to BAPDS-modified polyimide.

TP-SXDA-modified polyimide (polyimide D)

It can be seen from Table 2 that the dissociation energy of the Si—C(aryl) bond (88.6 kcal mol^{-1}, 371 kJ mol^{-1}) is larger than that of the Si—CH$_3$ bond (79.4 kcal mol^{-1}, 332 kJ mol^{-1}). Accordingly, use of TP-SXDA in which all of the methyl groups in SXDA are substituted with aryl groups is supposed to improve thermal stability further. Thus, TP-SXDA-modified polyimide (polyimide **D**) was prepared to evaluate its thermal stability.

The TG curve of polyimide **D** after heating under aerobic conditions is given in Fig. 10 in comparison with those of polyimide **A**, polyimide

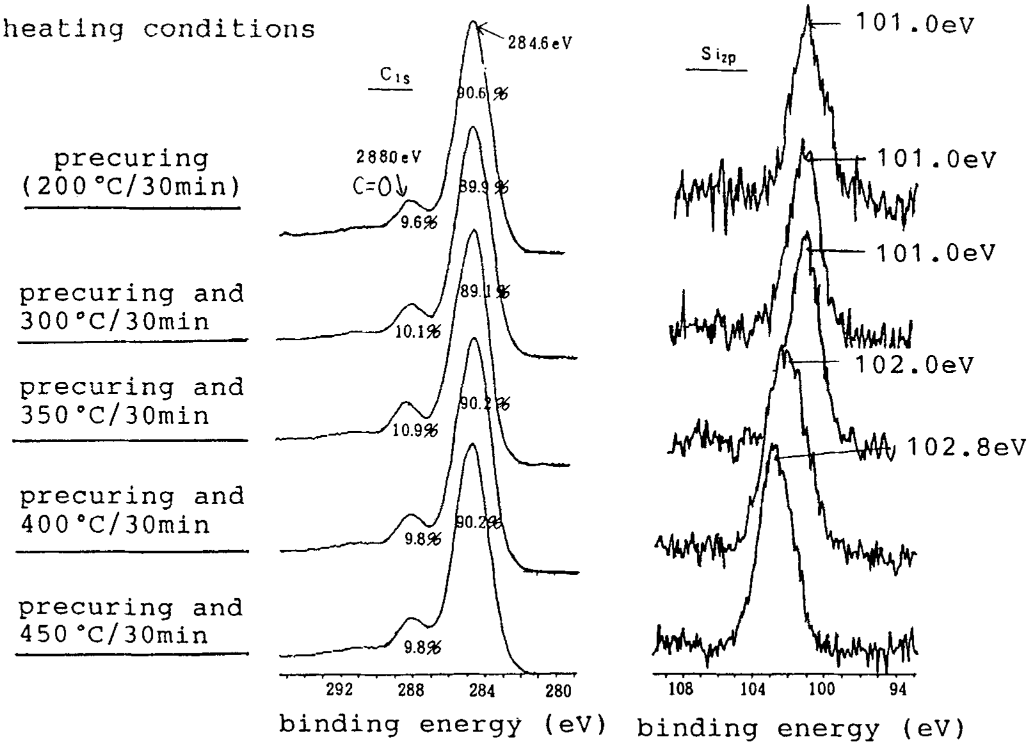


Figure 7 Changes of C_{1s} and Si_{2p} XPS spectra of polyimide **B-2** after heating under a nitrogen atmosphere.

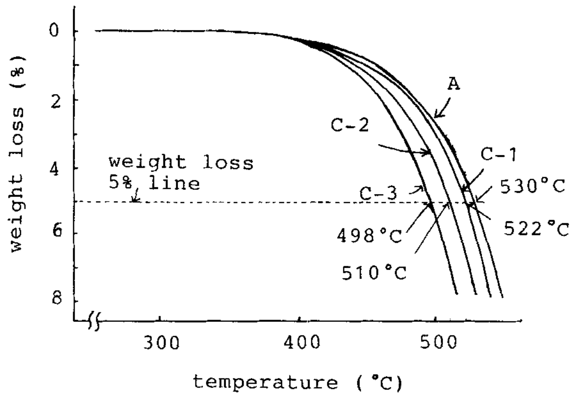


Figure 8 TG curves of polyimide **A** and polyimide **C** (**C-1** to **C-3**) after heating under aerobic conditions (heating conditions: 200 °C/30 min and 350 °C/30 min).

B-3 and polyimide **C-3**. The temperature of 5 % weight loss of polyimide **D** is essentially equal to that of polyimide **C-3**. Accordingly, the thermal stability of sillicon–methyl and that of silicon–aryl bonds are essentially equal.

Changes of Si_{2p} XPS spectra of polyimide **B-3**, polyimide **C-3** and polyimide **D** after heating under aerobic conditions are shown in Fig. 11. The change of Si_{2p} binding energy for polyimide **B-3** is observed at 350 °C similarly to polyimide **B-2**. Polyimide **C-3** shows the change of Si_{2p} binding energy at 400 °C, as does polyimide **C-2**. Polyimide **D** also shows the change of Si_{2p} binding energy at 400 °C, but the magnitude of the change is smaller than that of polyimide **C-3**. These results suggest that polyimide **D** has a thermal stability a little greater than that of polyimide **C**. Little difference between their TG curves can be interpreted as follows: The conversion from SXDA to TP-SXDA is effective only for the improvement of thermal stability of the side chains of this polymer.

CONCLUSION

Early stages of heat deterioration were studied with XPS for three types of silicon-containing aromatic polyimide (polyimides **B**, **C** and **D**) thin films having disiloxane groups in their main chains.

1. Thermal stability of aromatic polyimide having disiloxane groups in the main chains is lower by 50–100 °C than that of unmodified aromatic polyimide. This is because the silicon–carbon bonds

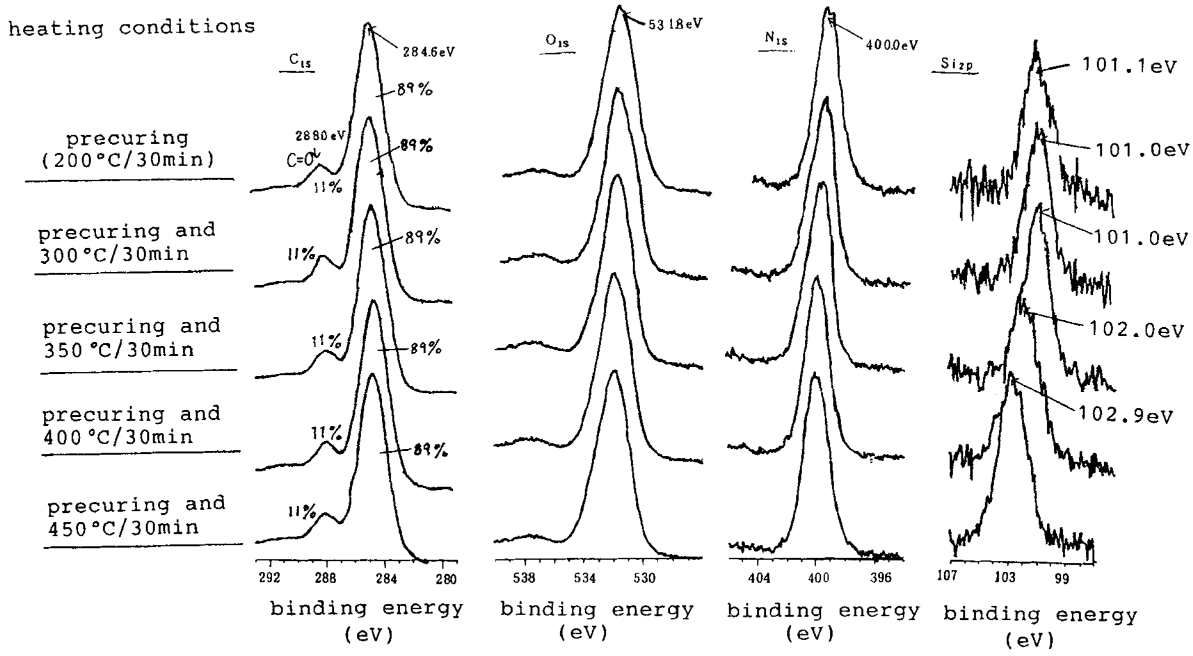


Figure 9 Changes of C_{1s}, O_{1s}, N_{1s} and Si_{2p} XPS spectra of polyimide **C-2** after heating under aerobic conditions

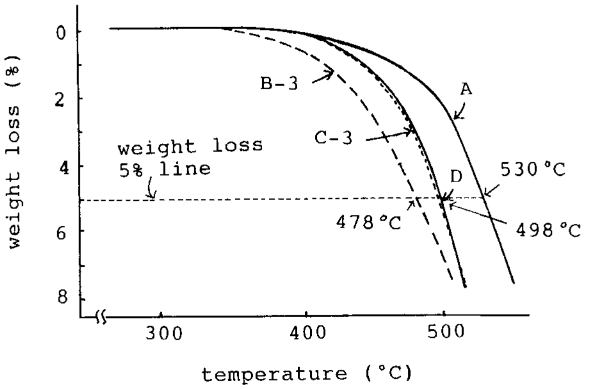


Figure 10 TG curves of polyimide **A**, polyimide **B-3**, polyimide **C-3** and polyimide **D** after heating under aerobic conditions (heating conditions: 200 °C/30 min and 300 °C/30 min).

are liable to decompose by heating more easily than the other bonds (e.g. carbon–carbon bonds, carbon–oxygen bonds).

2. Thermal stability of BAPDS-modified aromatic polyimide (polyimide **B**) is significantly lowered with the increase in the BAPDS content. Polyimide **B** starts to decompose under aerobic conditions at 350 °C, lower by 100 °C than the unmodified aromatic polyimide. This decrease in the thermal stability is due to the presence of silicon–methylene bonds in the main chain which are susceptible to thermal decomposition.

3. Although the thermal stability of SXDA-modified aromatic polyimide (polyimide **C**) is reduced with the increase of the SXDA content, the degree of reduction is smaller than in the case of polyimide **B**. This polymer starts to decompose at 400 °C under aerobic conditions. The higher thermal stability of polyimide **C** compared with polyimide B is explained by the higher thermal stability of silicon–aryl bonds than silicon–methylene bonds.

4. The thermal stability of TP-SXDA-modified aromatic polyimide (polyimide **D**) with silicon–aryl bonds both in the main and side chains is essentially equal to that of polyimide **C**.

XPS proved to be an effective method of analyzing early stages of heat deterioration of polyimide films.

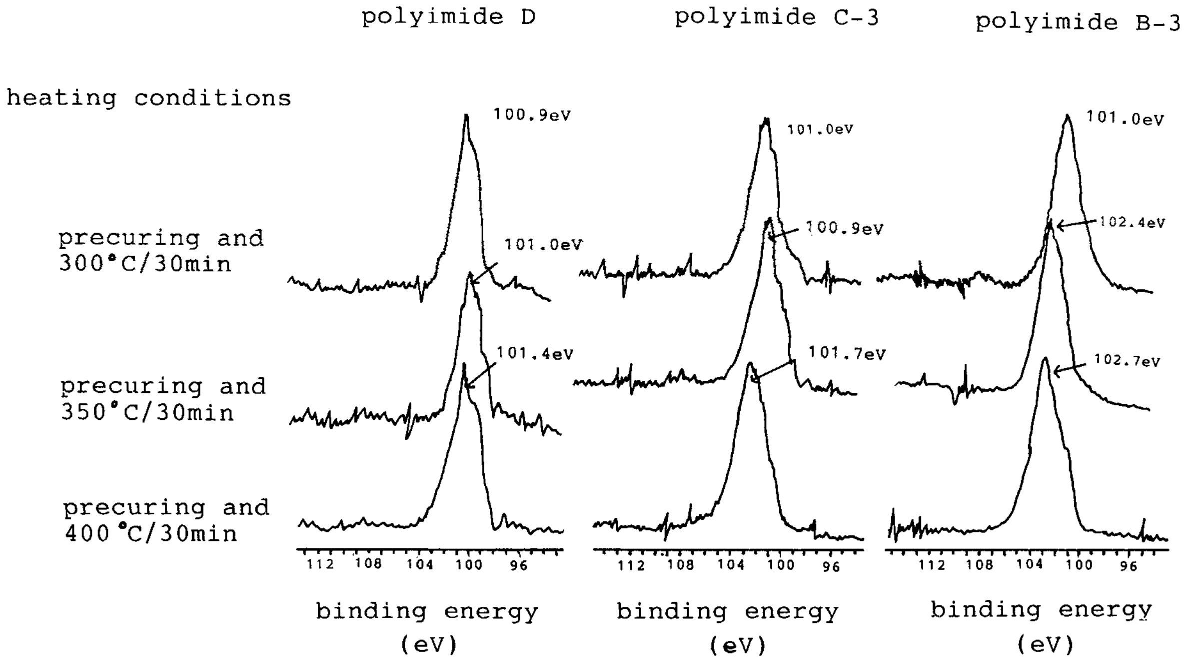


Figure 11 Changes of Si_{2p} XPS spectra of polyimide **B-3**, polyimide **C-3** and polyimide **D** after heating under aerobic conditions.

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