Thermolytic Acidolysis of Polyamic Ester Containing t-Butyl Unit

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Abstract: Thermolytic acidolysis of polyamic esters (PAEs) in solid and solution states were elucidated. The polyamic esters were synthesized by direct polycondensation using a condensing agent, and inherent viscosities were ranged 0.34-0.81 dL/g. The polymer films of PAEs with t-butyl ester were readily acidolized by contacting with various organic acids, but those of the methyl, ethyl, and isopropyl ester were intact. The solution acidolysis revealed that the polyamic ester with t-butyl ester was solubilized in 2.38 wt% of tetramethylammonium hydroxide (TMAH) aqueous solution after treated with p-toluene sulfonic acid for 3 minutes at 50°C. In solid state, acid catalyzed thermolysis temperature of PAE with t-butyl ester was shifted to lower temperature, but those of the other chemical reactions, such as loss of water and polyimide decomposition were unchanged. The effluent gas at 1st decomposition of the PAE was identified as isobutene. It implied that the thermolytic acidolysis was proceeded via the formation of polyamic acid and isobutene.

Introduction

Photosensitive polyimides (PSPIs) are attracting interest since they can be simplified semiconductor fabrication. Most of photosensitive polyimides are negative type and consist of polyamic acid salt or polyamic ester with crosslinkable side chain* such as acrylate, methacrylate or vinyl group. The PSPIs with crosslinkable group have their own drawbacks: needs of organic solvent as developer which can swell the crosslinked patterns, lower resolution due to the contraction of swollen pattern during drying, lower sensitivity, and residual scum in developed area, etc.

On the contrary, positive PSPI can be developed by aqueous solution of diluted organic base, which does not give a swelling pattern. Thus one can get better resolution and higher sensitivity. Conventional positive PSPI* consists of polyimide (or its precursor) and naphthoquinone azide (NQ), which is very popular photosensitive material for i-line resist. Since the naphthoquinone azide is not a chemical amplified (CA) photosensitive materials, NQ has to be added more than 10 wt% to the polyimide in order to give enough photosensitivity. The large amount of NQ can degrade the dielectric, mechanical, and thermal properties of polymeric film.

We have researched the chemically amplified positive PSPI containing photoacid generator (PAG). Primary conclusion is that the polyamic ester (PAE) is one of the candidates for the positive PSPI. Polyamic esters are known as the polymer with excellent storage stability in polar solvents and detailed studies have been published. In general, polyamic esters can be prepared from diacid chloride of diester of tetracarboxylic acid with diamines at room temperature. However, there are numerous synthetic methods of direct polycondensation from diacid and diamines by using various condensing agents. Since chloride ion can diffuse to and corrode the metal (Al) line and/or can alter the dielectric constant of insulating materials such as SiO₂.

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and polymeric low dielectrics, the ion contents of chloride is severely controlled to be less than 1000 ppb for 16M DRAM. Therefore, it is very important to prepare chlorine-free polymer for semiconductor industry.

Prior to study the lithographic performance of the polyamic ester with PAG, it is essential to investigate the thermolytic acidolysis18 and structural dependency of the PAE.

This article reports the synthesis of polyamic ester by ion-free manufacturing procedure and acidolysis of the polyamic ester in solution and solid state. These are very important to understand the lithographic processing condition such as selecting acid sensitive group, screening of PAG, and optimizing of post exposure baking (PEB).19

Experimental

Materials. N-Methyl-2-pyrrolidone (NMP) supplied by Junsei Chemical Co. Ltd., GC 99% was purified by vacuum distillation with CaH₂ and stored over 4 Å molecular sieves at 0 °C. Triethylamine (TEA) supplied by TCI, >99% was purified by simple distillation with CaH₂ and stored over 4 Å molecular sieves. 4,4’- Oxydianiline (ODA) supplied by Mitsui Toatsu Chemical Industries Ltd. was purified by recrystallization from THF. Other reagents and solvents were obtained commercially and used as received.

Characterization. H-NMR and 13C-NMR spectra were taken on Bruker AMX 300MHz and 500MHz spectrometers using tetramethylsilane as an internal standard. Infrared spectra were measured as KBr pellets on a Bio-Rad Digi-Lab Division TS 20/80 FT-IR Spectrometer. Thermal analysis was carried out by using a DuPont model 9900 TGA and model 910 DSC under nitrogen at atmosphere. The inherent viscosities (ηsp) of the polyamic esters were determined at 30 °C by using a Cannon Fenske Viscometer at concentration 0.5 g/dL solutions of NMP.

Monomers Synthesis.

Synthesis of the Di-tert-butyl Ester of Pyromellitic Acid20 (Scheme I): Potassium tert-butoxide (43.6 g; 0.2 mol) was dissolved in 800 mL of THF, pyromellitic dianhydride (PMDA) (44.9 g; 0.4 mol) was added. After stirring for 12 hrs, the resulting suspension was filtered off and washed with THF and ether, and dried to give the potassium salt of desired product. The salt was carefully neutralized in aqueous solution with dilute HCl. The precipitated product was filtered, washed with distilled water, dried, and recrystallized several times from ethanol/water. This process yields 48.3 g of pure p-di-tert-butyl ester of pyromellitic acid as a white powder.

Synthesis of the Dimethyl Ester of Pyromellitic Acid: PMDA (15.03 g; 0.07 mol) was slowly dissolved with gentle heating in 60 mL of dry methanol under dry nitrogen in 200 mL flask. After stirring was complete, as indicated by dissolution of PMDA, the solution was cooled and distilled water was added. The methanol was stripped under vacuum until crystallization was initiated. After overnight refrigeration, the crystals were filtered and dried under vacuum oven at 40 °C. 6.2 g (32% yield) of the pure p-dimethyl ester of pyromellitic acid was isolated.

The typical example of the syntheses of the various diacid esters of PMDA is described20 as shown in Scheme II.

Diethyl Ester of Pyromellitic Acid: yield 63%,
Disopropyl Ester of Pyromellitic Acid: yield 72%.

Synthesis of Condensing Agent. Diphenyl

Scheme II. Synthesis of various esters of pyromellitic acid.
They were cast on slide glass and dried at 70 °C for 90 min. After one drop of pre-prepared solution of acid in distilled water (3 x 10⁻⁴ mol/L) was placed on PAE films and was heated up to 50 °C for 10 minutes. The resulting film was washed with distilled water and treated by 2.38 wt% tetramethylammonium hydroxide (TMAH) base developer whether it is developable or not.

**In Solution State:** A 25 mL of 10 wt% solution of PAE-I in diglyme with 3 x 10⁻³ g p-toluenesulfonic acid (PTSA) was mixed at 50°C and the small portion of solution was sampled as time interval by re-precipitation into methanol, dried under vacuum oven. The powder sample was analyzed by IR.

**In Solid State:** The polyamic ester (PAE-I) film were cast on the slide glass from the 10 wt% polymer solution with or w/o PTSA (5 wt% to polymer) in diglyme and dried under reduced pressure at room temperature for 3 days. And the film was measured by TGA and DSC under a nitrogen atmosphere and heating rate of 20°C/min.

**Results and Discussion**

**Synthesis.** In order to prepare chlorine-free polyamic esters, we have adopt the direct polymerization method using diphényl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate as condensing agent, which was developed by Ueda et al.² The polycondensation method using this special condensing agent is very useful to get a polymer with ion contamination free and minimization organic impurities at very mild condition. Organic impurities in polymer were often encountered from direct polycondensation by using DCC as condensing agent.

The six polyamic esters containing methyl, ethyl, isopropyl and t-butyl ester were synthesized by direct polycondensation method, as presented in Table I.

The polymerization was performed at room temperature and the inherent viscosities of polymers were ranged 0.34–0.81 dL/g and reached to the maximum in a 12 hrs. After purified by successive precipitation from methanol 3 times, we have confirmed that the
Table I. Inherent Viscosities of Synthesized Polyamic Esters

<table>
<thead>
<tr>
<th>Ester Groups of Polyamic Ester</th>
<th>Diamine</th>
<th>Polymer Code</th>
<th>Yield (%)</th>
<th>$\eta_{in}$ (dL/g)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-buty1</td>
<td>HF-BAPP</td>
<td>PAE-I</td>
<td>99</td>
<td>0.81</td>
</tr>
<tr>
<td>t-buty1</td>
<td>MDA</td>
<td>PAE-II</td>
<td>78</td>
<td>0.33</td>
</tr>
<tr>
<td>methyl</td>
<td>ODA</td>
<td>PAE-III</td>
<td>84</td>
<td>0.44</td>
</tr>
<tr>
<td>ethyl</td>
<td>ODA</td>
<td>PAE-IV</td>
<td>79</td>
<td>0.37</td>
</tr>
<tr>
<td>isopropyl</td>
<td>ODA</td>
<td>PAE-V</td>
<td>91</td>
<td>0.63</td>
</tr>
<tr>
<td>isopropyl</td>
<td>MDA</td>
<td>PAE-VI</td>
<td>82</td>
<td>0.34</td>
</tr>
</tbody>
</table>

* The inherent viscosities determined at 30°C at concentration 0.5 g/dl solutions of NMP.

The results were tabulated in Table II.

As shown in Table II, the polyamic esters from methyl (PAE-III), ethyl (PAE-IV), isopropyl (PAE-V, PAE-VI) were not dissolved out from the standard developing solution, which means that there were no acidolysis or negligible acidolysis, at most, were taken place. On the contrary, the area of acid contacted polyamic esters films containing t-buty1 unit was completely dissolved out in 2 minutes. These suggested us a possibility of the formation of polyamic acid from the polyamic t-buty1 ester by acidolysis and diffusion of the contacted organic acid into the polymer film.

The dissolution rate was varied with acids, thickness of polymer film and chemical structure of polymer backbone, even though, we could not get a noticeable tendency yet. The results with weak acetic acid were rather surprising since the pK$_a$ value of acetic acid is only 4.76. The strong organic acids such as PTSA, MeSO$_2$H, CF$_3$-SO$_2$H and CF$_3$COOH are frequently used as counter part of the photoacid generator.

We further investigated the acidolysis of PAE-I in the solution with various reaction time. The p-toluene sulfonic acid was added to 10 wt% of polyamic ester solution in diglyme and heated to 50°C, which is rather mild condition. The IR spectra of the re-collected by re-precipitation from methanol were presented in Figure 1. Also, IR spectrum of polyamic acid (PAA) was depicted for comparison. The acidolyzed polymer (Figure 1, line B) showed major differences from the IR spectrum of untreated polyamic ester (Figure 1, line A), in the range of 1670 cm$^{-1}$ and 1133 cm$^{-1}$, which represent for characteristic bands of amide I and t-buty1 ester, respectively. The amide I band is reduced in IR spectrum of

Table II. The Results of Simple Acidolysis in Film State

<table>
<thead>
<tr>
<th>Acid</th>
<th>PKa</th>
<th>PAE-I (t-buty1)</th>
<th>PAE-II (t-buty1)</th>
<th>PAE-III (methyl)</th>
<th>PAE-IV (ethyl)</th>
<th>PAE-V (isopropyl)</th>
<th>PAE-VI (isopropyl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTSA</td>
<td>1.7</td>
<td>O</td>
<td>O</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>MeSO$_2$H</td>
<td>-</td>
<td>O</td>
<td>O</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CF$_3$SO$_2$H</td>
<td>-</td>
<td>O</td>
<td>O</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CF$_3$COOH</td>
<td>0.25</td>
<td>O</td>
<td>O</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>4.76</td>
<td>O</td>
<td>O</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

O: developable, x: not developable.

Thermolytic Acidolysis of Polyamic Ester Containing t-Butyl Unit.

Figure 1. The IR spectra of PAE-I (A), that of after acidolysis in solution (B) and that of PAA (C).

Figure 2. The residual content of t-butyl moiety in PAE-I after acidolysis in solution at 50°C.

Figure 3. TGA thermograms of PAE-I (A) and PAE-I with PTSA (B) and isobutene evolution (A-1 and B-1) at the given temperature on Mass spectra.

Acid treated PAE-I due to the strong interaction with newly formed carboxylic acid by hydrogen bond. And the relative intensity of 1133 cm⁻¹ was also reduced owing to the de-protection of t-butyl ester. The t-butyl contents were measured by calculating the relative intensity at 1133 cm⁻¹ (C-O-C, stretching) to 1502 cm⁻¹ (C=C stretching) as an internal reference in the corresponding IR spectra. As shown in Figure 2, the t-butyl group was de-protected very quickly in 1~3 minutes and the rate was slowed after then. And the re-collected polymers after 3 minutes acidolysis could be dissolved in TMAH solution.

Thermolytic acidolysis of the polyamic ester in solid states were also investigated by using TGA and DSC. The p-toluene sulfonic acid was added to the polymer by casting of the polymer solution with PTSA from diglyme and drying in vacuum at room temperature for 3 days.

As can be seen from the TGA thermograms (Figure 3), there are 3 different weight losses of polymer. The polyamic t-butyl ester (PAE-I) without PTSA showed 1st weight loss about 107~177°C, 2nd weight loss between 177~318°C and 3rd weight loss above 530°C represented that the decomposition of t-butyl group, the imide formation of the polymer and polyimide decomposition, respectively. While, the acid (PTSA) were added to the polymer, the temperature of 1st weight loss, decomposition of t-butyl group, was shifted to lower temperature range of 70~129°C from 107~177°C as shown in Figure 3 (dotted line, curve B), but the other temperature of weight loss, the 2nd and the 3rd, were similar to that of polyamic t-butyl ester (PAE-I) without PTSA. Which strongly imply that the added acid (PTSA) catalyzed the thermolytic acidolysis of t-butyl ester very effectively, but catalytic effects on the imide formation and thermal decomposition of PI were not that much effective.

To confirm the thermolytic acidolysis of the t-butyl group we have analyzed the effluent...
maximum thermolytic acidolysis were taken placed at 184°C and 107°C for untreated and PTSA added sample, respectively.

From the all the results and discussions, we can concluded that the t-butyl ester group in PAE can be thermolytically acidolized to form the carboxylic acid and isobutene which is stable and volatile gas, which gives driving force to proceed the reaction forward. While, the methyl, ethyl, isopropyl polyamic esters do not provide this kind of pathway, thus they are not good candidates to be a functional group of PSPI.

This simple experiment we present in this article is very useful and can be expanded as fundamental data for optimization of the PEB condition, which is very essential for chemically amplified PSPI. The detailed lithographic performance of polyamic ester will be presented elsewhere.

**Conclusions**

Thermolytic acidolysis of polyamic esters (PAEs) in solid, and solution states were elucidated. The polymer films of PAEs with t-butyl ester were readily acidolized by contacting with various organic acids, but those of the methyl, ethyl and isopropyl ester were intact. The solution acidolysis revealed that the polyamic ester with t-butyl ester was solubilized in 2.38 wt% of TMAH aqueous solution after treated with p-toluene sulfonic acid for 3 minutes at 50°C. In solid state, acid catalyzed thermolysis temperature of PAE with t-butyl ester was shifted to lower temperature, but that of the other chemical reaction, such as loss of water and polyimide decomposition were unchanged. The effluent gas at 1st decomposition of the PAE was identified as isobutene. All the evidences we have discussed, suggested that the formation of isobutene was originated from the acidolysis of the polyamic ester, not from the imidization via formation of t-butyl alcohol. It can be concluded that the thermolytic acidolysis of the PAE with t-butyl ester was proceeded via formation of polyamic acid and isobutene. This simple method will be very effective and useful to design the structure of chemically amplified photosensitive
polymide, to select of acid for PAG and to optimize the PEB condition for lithography.

References

(22) CRC Handbook of Chemistry and Physics, 60th Ed., D 165 (1980).