Characterization of Vapor Deposition Polymerized Polyimide Thin Films

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SYNOPSIS

Vapor deposition polymerized (VDP) polyimide (PI) thin films were prepared and characterized by using thermogravimetical analysis (TGA), scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared (FTIR), and bending-beam techniques. The film properties investigated were thermal stability, wet-etching characteristics, surface topology, imidization characteristics, internal stress upon curing and thermal cycling, and hygroscopic stress upon moisture diffusion. Markedly different characteristics are observed for the VDP-PI films when comparing with the conventional ones. They seem denser in film structure and have better mechanical properties, but are somewhat less stable in thermal resistance. © 1996 John Wiley & Sons, Inc.

Keywords: vapor deposition polymerization • polyimide • surface topology • characterization

INTRODUCTION

Polyimides (PIS) exhibit superb mechanical, thermal, and electrical properties. PI films have been very useful in microelectronic applications.1-2 Recently, PI thin films have been made successfully by vapor deposition polymerization (VDP).4-5 The VDP thin films can be made pin-hole free at least in the few hundreds angstrom scale.7 This will bring PIs to a more advanced utilization level, especially in thin film device applications.

The properties of the thin films may be different from those of the films obtained by using conventional methods. Especially, the PI film properties are well known to be process and thickness dependent, as reported in some studies.6-12 Different properties may lead to different applications and/or performance. Hence, it is important to have a basic understanding concerning the characteristics of the VDP thin films of PIs.

In this study, PI films of pyromellitic dianhydride-oxydianiline (PMDA-ODA) have been made using both the VDP and conventional methods. The resultant films were characterized using thermogravimetical analysis (TGA), scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared (FTIR), and bending-beam techniques. Comparison was made between the thermal stability properties, surface topologies, imidization characteristics, internal stresses during curing and thermal cycling, and hygroscopic stresses and diffusion rates upon water diffusion for the two different films prepared by the two different methods.

EXPERIMENTAL

VDP-PAA Thin Film Preparation

The polymer thin film forming monomers used were pyromellitic dianhydride, PMDA, and diamine, 4,4'-oxydianiline, ODA. These two monomers, 200 mg each, were evaporated from two separated boats to form a poly(amic acid) (PAA) thin film on substrate. The substrates used were silicon wafer and glass. The deposition process began at vacuum of 5 × 10⁻³ mbar. Figure 1 shows the scheme of the VDP apparatus. The resultant VDP-PAA film was subsequently annealed at elevated temperatures to convert to the VDP-PI counterpart.

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Conventional PAA Synthesis

The polycondensation of PMDA-ODA PAA was conducted as follows: in a four-neck round-bottom flask, ODA was dissolved in N-methyl pyrroldinone (NMP) solvent. Equal mol PMDA was then gradually added after complete dissolution of ODA. The reaction proceeded for 5 h by continuous stirring under a nitrogen atmosphere at 40°C. The resulting solutions had solid contents of 15 wt % and 1 wt %.

Thermogravimetrical Analysis

For TGA experiments, the VDP PAA films were scraped off the glass substrate and then placed in a platinum crucible. The conventional specimens were prepared by spin-casting the 1 wt % PAA solution on to a silicon substrate, and then prebaked at 80°C for 1 h. The solidified films were also scraped off and placed in a platinum crucible for measurement. The TGA experiments were done by using SEIKO Co. (Model 320) thermal analysis apparatus. The heating rate was 10°C/min. The gas used was air with a flow rate of 100 ml/min.

Wet Etching

The PAA films prepared by VDP were annealed at several different temperatures ranging from 150 to 400°C for 30 min, with a ramp rate of 2°C/min. All the resultant specimens were then immersed in an etching solution (Microposit Developer MF319, Shipley Co. Ltd.), which was diluted with deionized water to a 1 : 1 weight ratio before use.

Via-Hole Fabrication

Figure 2 shows the photolithographic process for making via-holes in the VDP PI films. The PAA films on silicon substrate were prebaked at 120°C for 30 min. A positive photoresist was then cast on the PAA films, followed by prebaking at 80°C for 30 min. A contact model mask was applied. The photoresist was exposed with a UV light (g-line), and then developed. The samples were postbaked at 120°C for 30 min. A Microposit Developer MF319 solution (Shipley Co. Ltd.) was used for etching the PAA films. The photoresist was then stripped by acetone. Finally, the samples were cured at 200°C for 30 min with a ramp rate of 2°C/min. SEM was then used for inspecting the resultant pattern.

Surface Topology

Surface topology of the specimens were also investigated using atomic force microscopy (AFM). The
specimens of the VDP PI films for AFM (Nanoscope II, Digital instruments, Inc.) were annealed at several different temperatures from 100 to 400°C for 30 min, with a ramp rate of 4°C/min. The AFM imaging was performed under ambient conditions. The AFM tip diameter of the Si3N4 cantilever, estimated from the AFM images, was 35 nm. In order to minimize tip-induced damage, the smallest contact force of 140 nN was used. The scan rate was set between 1 and 2 Hz.

**FTIR**

To investigate the imidization characteristics of the VDP thin films, the VDP-PAA films of 5000 Å were cured at several different temperatures. The curing time was 30 min and ramp rate 2°C/min. The curing process was performed in air. Transmission IR spectra were obtained using a Bomem DA 3.002 Fourier transform IR spectrophotometer with a resolution of 2 cm⁻¹. The degree of imidization was calculated from the resultant spectra according to ref. 13.

**Bending-Beam Stress and Diffusion Measurements**

By the use of bending-beam technique, the thermal stress and solvent diffusion in the VDP-PI thin film coated on substrate can be determined by measuring the variations of the bending curvature of the substrate with respect to temperature and time, respectively. Details regarding the technique and the corresponding bending-beam apparatus can be found in refs. 14 and 16. For the moisture diffusion experiment, the specimens were annealed at 400°C for 1 h.

**RESULTS AND DISCUSSION**

**Thermal Stability**

Figure 3 shows the TGA results of the VDP and conventional films. For the VDP films, the sample weight keeps on decreasing from the beginning, as shown in Figure 3(a). This may be attributed to the evaporation of the previously absorbed water in the sample. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. At temperatures above 185°C, weight loss becomes more marked, indicating the occurrence of imidization. At temperatures above 185°C, weight loss becomes more marked, indicating the occurrence of imidization. At temperatures above 185°C, weight loss becomes more marked, indicating the occurrence of imidization. At temperatures above 185°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more marked, indicating the occurrence of imidization. Above 148°C, weight loss becomes more...
compose drastically at very much the same high temperature. This is the temperature corresponding to the imide chain decomposition.

**Wet Etching Property**

The wet etching properties of the VDP films were examined after curing the specimens at several different temperatures ranging from 150 to 400°C. Regardless of film thickness, the films remained intact if they were cured at 250°C or above, for instance, the film integrity remains unchanged after immersing in the etching solution for a 48-h period. On the contrary, the as-deposited films is dissolved immediately when they were immersed into the etching solution. Table I lists the time required to dissolve the films. A drastic change in the dissolving time is observed when the curing temperature changes from 150 to 160°C. The dissolving time for the 2 μm film, for example, increases from 0.5 to 13 min as the curing temperature increases from 150 to 160°C. The films are still dissolvable after curing at temperature up to 200°C. However, a much longer dissolving time is needed.

**Surface Topology**

Figure 4 shows the SEM photograph of a VDP PI film with via-holes patterns obtained by using photolithography and wet-etching process. The VDP-PI film was previously cured at 200°C for 30 min. Good quality via-hole structure can be seen in the picture. The film surface is relatively smooth on a micrometer scale.

The surface topology of the VDP-PI films was further examined by using AFM. The AFM photographs are illustrated in Figure 5. The film surface is relatively smooth on the nanometer scale when curing at 200°C or below. The maximum thickness variation is 2 to 3 nm over a 1 × 1 μm scanning area. The surface becomes roughened when curing at the higher temperatures. The maximum thickness variation is 13 nm for the film cured at 300°C and 15 nm at 400°C. These films were cured in vacuum.

![Figure 4. SEM photograph of the VDP-PI thin film with via-holes pattern.](image)

For the films cured in air, the surface topology varies with the variation of curing temperature in a way similar to those cured under vacuum. These results are in consistent with those observed in the TGA experiment; for instance, some kind of decomposition occurs at the elevated temperatures before the imide chain decomposition.

**Imidization Characteristics**

Conventional PIs have been reported to fully imidize at 200, 250, or 300°C,15,18-20 For comparisons purpose, the temperature for complete imidization of the VDP films was chosen to be 300°C. Figure 6 shows the degree of imidization as a function of curing temperature for the VDP-PI films from the FTIR experiment. The imidization results are compared with those of the conventional PI films from a previous study.15

The VDP-PI films start to imidize very significantly at lower curing temperatures. The degrees of imidization are 44 and 85% for curing at 150 and 200°C, respectively, while they are below 20 and 50% for the conventional PI counterparts. At the elevated temperatures, the imidization characteristics of the two different films are markedly different. The de-

<table>
<thead>
<tr>
<th>Curing Temp.</th>
<th>As-Deposited</th>
<th>150°C</th>
<th>160°C</th>
<th>170°C</th>
<th>180°C</th>
<th>200°C</th>
<th>250°C</th>
<th>300°C</th>
<th>350°C</th>
<th>400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 μm</td>
<td>0.08</td>
<td>0.5</td>
<td>13</td>
<td>26</td>
<td>38</td>
<td>50</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.5 μm</td>
<td>0.01</td>
<td>0.15</td>
<td>11.5</td>
<td>40</td>
<td>66</td>
<td>300*</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Unit: minute.

* More than 50% of the film has been dissolved.
X: nondissolvable.
The degree of imidization remains unchanged for the conventional PI films from 300 to 400°C, while it goes beyond 100% for the VDP-PI ones cured at 350 and 400°C. As mentioned in the previous study, the calculation of the degree of imidization is based on a presumably unchanged internal standard absorption peak, which appears at 1500 cm\(^{-1}\) for the aromatic ring studied here. If some of the corresponding chemical bonds are broken during the curing process, the standard peak intensity will drop and the calculated results will be overestimated accordingly. The above TGA and AFM results reveal that the VDP-PI films decompose, at least partially, at 300°C and above. Probably, decomposition also takes place at some of the chemical bonds of the internal standard so that the calculated degree of imidization goes to a unrealistic number, for instance, over 100%. The films decompose more markedly at 400°C, as indicated by the AFM results. This may, therefore, explain why the degree of imidization goes even higher as the curing temperature further increases from 350 to 400°C.

**Internal Stress**

Figure 7(a) shows the stress as a function of temperature for an as-deposited VDP PI film of 2.3 μm on a 140 μm Si substrate. In the first cycle, the specimen was heated to 400°C at an average ramp
rate of 2°C/min and kept at 400°C for 1 h before cooling. After allowing the film to cool to room temperature, a second cycle was applied with a ramp rate of 4°C/min.

The stress curves of the two different cycles fall on top of each other during cooling. This indicates the film to be completely imidized in the first cycle, and no more significant decomposition has occurred in the second cycle. During the first heating cycle, the stress goes rapidly toward compressive at the lower temperature range. It goes toward compressive in a lesser rate as the temperature further increases to 100°C and above, indicating imidization. From 250 to 400°C, the resultant compressive stress almost remains unchanged. This may mainly result from the above-mentioned decomposition.

Figure 7(b) shows the stress pattern of the conventional PI film in a curing cycle. The conventional PI film exhibits a markedly different stress pattern upon curing. This is because the film is initially in the solution state. Hence, it exhibits no stress in the initial curing stage. Upon further heating, some solvent in the film has evaporated and the stress starts to build up. However, the stored stress is mostly released once the film is heated to a higher temperature. These phenomena continue until the temperature is greater than 180°C. At temperature above 180°C, a greater amount of solvent evaporates. In the meanwhile, the film is imidized to a greater extent. It can, therefore, store some stress upon further heating. Details regarding the reason why the stress pattern rises and falls can be referred to in ref. 21. Nevertheless, the stress pattern of the VDP-PI film can be realized to be very different from that of the conventional one.

The VDP-PI films show a higher thermal stress variation than that of the conventional ones. This indicates the VDP-PI films to have a higher biaxial modulus and/or coefficient of thermal expansion (CTE). The thermal stress properties of PI films have been reported to be thickness dependent.22,23 It would be more ideal if the above comparison could be made on the same film thickness basis. However, the thicknesses of the conventional PI films are much greater than those of the VDP-PI ones. According to ref. 24, thinner PI films exhibit smaller thermal stress variation. Hence, the above difference really exists between the two different films, and it
would be more marked if they are compared on the same film thickness basis. Therefore, the thermomechanical properties of the VDP-PI films can be realized to be significantly different from those of the conventional ones.

**Hygroscopic Stress and Moisture Diffusion**

Figure 8(a) shows the stress variation in the VDP PI film of 2.3 μm upon absorbing moisture in an enclosed chamber at 95% relative humidity. The internal stress changes from tensile to compressive as moisture diffusion proceeds. It takes the film 27 h to equilibrate. The measured hygroscopic stress is 35 MPa. For a conventional PI film of 4.2 μm, the hygroscopic stress is 7 MPa in water. The hygroscopic stress is the product of the hygroscopic strain and biaxial modulus of the film, and the hygroscopic strain is, in turn, proportional to the amount of absorbed water. Therefore, it may be that the biaxial modulus of the VDP-PI film is five times of that of the conventional PI one, if they both absorb the same amount of water. Or, vise versa, the amount of water intaken by the VDP-PI film is five times of that of the conventional PI, if they both have the same biaxial modulus. However, no matter which concept is correct, the VDP film can be concluded to be markedly different from that of the conventional PIs.

The diffusion coefficients of water in the two different films have also been determined from the above experiments. As shown in Figure 8(b), the diffusion of water in the VDP-PI film is much slower than that in the conventional one. The calculated diffusion constants are $1.3 \times 10^{-12}$ cm$^2$/s and $2.7 \times 10^{-9}$ cm$^2$/s in the VDP and conventional PI films, respectively. They are different by three orders in magnitude. The PI films prepared by using VDP seem to have a denser film structure.

**CONCLUSIONS**

To conclude, the VDP-PI films exhibit several characteristics markedly different from the conventional ones. The TGA, AFM, and FTIR results consistently show that the VDP-PI films are somewhat less stable at the elevated temperatures. They seem to possess some structures that are thermodynamically less stable than the imide chain. The stress behavior of the VDP-PI films upon curing, thermal cycling, or water diffusion is very different from that of the conventional ones. The higher thermal and hygroscopic stresses and much slower water diffusion rate, respectively, indicate a greater mechanical stiffness and a denser film structure for the VDP films.

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**REFERENCES AND NOTES**


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