A study on dielectric characteristics of fluorinated polyimide thin film

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Abstract

In this work, the effects of fluorination of polyimide thin films on surface and dielectric characteristics were studied using X-ray photoelectron spectroscopy (XPS) and dielectric spectrometry, respectively. The thermal and mechanical properties of the film were characterized by thermogravimetric analysis (TGA) and tensile strengths, respectively. The fluorine content of the polyimide thin film was increased with increasing treatment concentration, resulting in decreasing dielectric constant of the film. It was found that the replacement of fluorine led to the decrease of the local electronic polarizability of polyimide, or to the increase of the free volume, which can be attributed to the relatively large size of fluorine. Nevertheless, the fluorination did not significantly affect thermal or mechanical properties of the polyimide film under mild conditions in this system.

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1. Introduction

Polyimides exhibit a number of outstanding properties, such as excellent thermal stability in air, solvent resistance, and mechanical and electrical behavior. These materials have been considered for use in numerous applications that require robust organic materials, including composites and precursors for high-performance aerospace materials, as well as membranes for gas separation [1,2].

Thermally stable and highly insulating polyimides are in great demand for several technological applications. One of the most important applications of polyimides is as interlevel dielectric insulators (ILD). In order to achieve maximum possible device speed through smaller dimensions, insulating materials with dielectric constants as small as possible are preferred. The development of polyimides with an increasingly low dielectric constant has been the focus of several recent investigations, so measurement of the electrical properties of polyimide thin films is a necessary technology [3–5].

In recent years, many authors have undertaken research in the area of fluorinated polyimides. This involves design of materials by the controlled manipulation of individual atoms or molecules for specific applications, such as low-dielectric materials for ILD [6–9].

Fluorination is one of the methods for decreasing the dielectric constant of polyimides. The incorporation of fluorine increased in the fractional free volume of polyimide, and the electronic polarizability of the fluorinated polyimide decreases due to the low polarizability of the fluorine atom [10]. The dielectric constant values are strongly influenced by the fluorine content: the dielectric constant is decreased as the fluorine content increases. This can be attributed to the following three effects: changes in hydrophobicity, changes in free volume, and changes in total polarizability. The lowest dielectric constant is due to a combination of all three factors [11–16].

In the light of the studies, we investigate the changes in dielectric characteristics of fluorinated polyimide thin films before and after fluorination. Also the changes in surface, thermal, and mechanical properties of the film are studied in the fluorination condition.

2. Experimental

2.1. Synthesis and fluorination

Polyimides are made from the condensation polymerization of a dianhydride and a diamine. The monomers
used were pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA). All monomers were obtained from Aldrich Chemicals and were purified by recrystallization before use. Also, the solvent N-methyl-1-pyrrolidinone was supplied by Aldrich Chemicals. The structures of monomers and solvent are shown in Fig. 1.

Typically, the synthesis of polyimides includes two-step polymerization. First, 8 wt% of the diamine was dissolved in NMP in a flask under nitrogen purging. Second, a stoichiometric amount of the dianydride in powder form was slowly added to the diamine solution, resulting in a solution called polyamic acid (PAA). Third, the PAA solution was cast onto glass slides using an applicator (Sheen Instrument, S220403).

The coated polyamic acid was dried under vacuum at 80°C for 24 h and thermally imidized under nitrogen with successive heating cycles, as shown in Fig. 2. And Fig. 3 shows the two-step polymerization to prepare the polyimide.

The polyimide thin films were subjected to fluorination under different conditions. The fluorination reaction was performed in a batch reactor made of nickel with an outer electric furnace. After evacuation, the fluorine gas was introduced into the reactor at room temperature, and then the reactive gases were purged from the reactor with nitrogen gas. In the case of the reaction at room temperature, the reactor is cooled and evacuated in a cooling bath prior to being charged with fluorine. The fluorine pressure was varied between 0 and 50 kPa, namely, F0, F5, F10, F30, and F50. Also, the nominal reaction time was fixed to 10 min.
2.2. Thermal conversion and X-ray photoelectron spectroscopy

The thermal conversion of polyamic acid to polyimide was confirmed by Fourier transform IR (FT-IR) spectroscopy (MIDAC, M2000). The scans were shown from 400 to 4000 cm\(^{-1}\) and required 40 s to complete.

The X-ray photoelectron spectroscopy (XPS) measurement of polyimide surfaces was performed using a VG Scientific ESCA LAB MK-II spectrometer equipped with a MgK\(_\alpha\) X-ray source. The base pressure in the sample chamber was controlled in the range from 10\(^{-8}\) to 10\(^{-9}\) Torr.

2.3. Thermogravimetric analyses and tensile strengths

To investigate the thermal stability of the polyimide thin film, the thermogravimetric analyses were performed in nitrogen using a TGA 951 Dupont thermal analyzer, at a heating rate of 10 °C/min from room temperature to 850 °C.

The tensile strength of the polyimide thin film was measured according to ASTM D412 using an UTM (Universal Testing Machine, Instron 1125). All tests were conducted at a crosshead displacement rate of 500 mm/min.

2.4. Dielectric constants of polyimide thin film

The dielectric characteristics were measured using a dielectric spectrometer (Novocontrol GmbH, Model CONCEPT 40). The diameter of electrode and the film was 20 mm. To ensure good electrical contact between the electrodes and the polyimide thin film, the films were sputter-coated beforehand with a thin layer of silver for 20 s on both sides. The dielectric constants of the film were determined over the frequency range of 10\(^{9}\)–10\(^{7}\) Hz at temperatures between −100 and 100 °C at heating rate of 5 °C/min.

3. Results and discussion

3.1. Thermal conversion from polyamic acid to polyimide

Fig. 4 shows the thermal conversion of the polyamic acid to polyimide by FT-IR spectroscopy. Polyimides are synthesized by a conventional two-step procedure through ring-opening polyaddition and subsequent thermal cyclodehydration, as shown in Fig. 3. The ring-opening polyaddition in NMP at room temperature yields polyamic acids. The FT-IR spectroscopy confirms the formation of polyamic acid.

The characteristic absorption bands of the polyamic acid appear near 3400–2400 (O–H in carboxylic), 3500–3100 (N–H in amide), 1660 (C\(=\)O in amide), 1535 (C\(=\)N in amide), and 1513 cm\(^{-1}\) (C\(=\)C in C\(_6\)H\(_5\)) [1,6,17].

After thermal imidization, the thermal conversion to polyimides is performed by successive heating of the polyamic acid to 290 °C in vacuum. The FT-IR spectroscopy confirms the formation of polyimides. The characteristic absorption bands of the fully cured polyimide appear near 1780 (C=O in phase), 1720 (C=O out of phase), 1513 (C=C in C\(_6\)H\(_5\)), 1370 (C–N in imide), 1100 ((OC)\(_2\)NC in imide), and 725 cm\(^{-1}\) (imide ring deformation) [1,6,17].

3.2. Surface properties

Fig. 5 shows the XPS survey scan spectra with the polyimide thin film. The XPS spectra of nontreated polyimide thin film show carbon, nitrogen, and oxygen (binding energy 285, 404, and 532 eV, respectively) peaks. In the case of the fluorinated polyimide thin film, the XPS spectra newly show fluorine (binding energy, 694 eV) peaks. From the results of XPS spectra, Table 1 represents the F\(_1\)/C\(_1\) ratios of the polyimide thin film.

<table>
<thead>
<tr>
<th>Chemical composition of polyimide thin film</th>
<th>C(_{1s})</th>
<th>N(_{1s})</th>
<th>O(_{1s})</th>
<th>F(_{1s})</th>
<th>F(<em>{1s}/C</em>{1s}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>74.6</td>
<td>5.2</td>
<td>20.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F5</td>
<td>51.7</td>
<td>3.9</td>
<td>14.5</td>
<td>29.9</td>
<td>57.8</td>
</tr>
<tr>
<td>F10</td>
<td>49.3</td>
<td>3.7</td>
<td>13.6</td>
<td>33.4</td>
<td>67.7</td>
</tr>
<tr>
<td>F30</td>
<td>46.2</td>
<td>3.7</td>
<td>13.8</td>
<td>36.3</td>
<td>78.6</td>
</tr>
<tr>
<td>F50</td>
<td>45.3</td>
<td>3.1</td>
<td>12.0</td>
<td>39.6</td>
<td>87.4</td>
</tr>
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</table>
polyimides before and after fluorination. As experimental results, the $F_{1.5}/C_{1.5}$ ratios of the polyimides are increased with the treatment concentration, which can be attributed to the increase of carbon–fluorine functional groups of polyimide surfaces by the fluorination. At the fluorination treatment, fluorine diffuses only slightly and slowly inside the polyimide and then the diffusing fluorine atom produces active radicals from the hydrocarbon backbone during the reaction time because of the highest electronegative character of fluorine atom. The active radicals lead to an introduction of strong carbon–fluorine (C–F) covalent bonds on the polyimide thin films [12–14,18].

From the result of the XPS spectra, Fig. 6 shows the expanded scale of $C_{1.5}$ XPS spectra for the polyimide thin film. As a result, the $C_{1.5}$ spectra of the nontreated polyimide thin film reveal the presence of four peaks corresponding to C–C groups (284.6 eV), C–N groups (285.6 eV), C–O–C groups (286.2 eV), and C=O groups (289.2 eV). In the case of fluorinated polyimides, the $C_{1.5}$ spectra of fluorinated polyimide thin film newly show C–F (288.7 eV), CF$_2$ (in trifluorobenzene, 290.5 eV), and CF$_3$ groups (291.1 eV). The results are explained by the extreme electronegativity of fluorine, which is always electron-withdrawing inductively when bonded to carbon, and the bonds is strongly polarized in $\delta^+\text{C} \rightarrow \text{F}^-$. Consequently, C–F bonds have relatively stronger than other C–X bonds. Therefore, the intensity of carbon–fluorine groups is increased as a function of the treatment gas [11–14,19–21].
Table 2
Thermal stability parameter of polyimide thin film

<table>
<thead>
<tr>
<th>IDT (°C)</th>
<th>F0</th>
<th>F5</th>
<th>F10</th>
<th>F30</th>
<th>F50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>590</td>
<td>594</td>
<td>592</td>
<td>588</td>
<td>544</td>
</tr>
</tbody>
</table>

3.3. Thermal and mechanical properties

Fig. 7 shows the TGA thermograms of each of the polyimide thin film before and after fluorination. From the TGA curves of the film, the thermal stability is also given by the initial decomposition temperature (IDT), as listed in Table 2. In general, high thermal stability of polyimides is due to the presence of rigid backbone structures. The IDT of non-treated polyimide thin film shows near 590 °C. But the IDT of fluorinated polyimide is slightly decreased as compared to that of F0 in the range of 540–600 °C for polyimide containing pyridine ring. Also, they left more than 55% char yield at 850 °C in nitrogen. The TGA data indicate that the polyimides have fairly high thermal stability than other polymers [1,6,22].

The mechanical properties of the polyimide thin films prepared by the thermal imidization method are listed in Fig. 8. The polymer exhibits ductile behavior with an elongation, up to 38% and good tensile strength up to 115 MPa. Also, the mechanical properties of the fluorinated polyimides were almost similar to those of the nontreated polyimide. Therefore, the fluorination does not lead to a significant change in thermal stability or mechanical properties of the polyimide film under a mild condition in this system [1,9,23].

3.4. Dielectric characteristics of polyimide thin film

The dielectric constant of polyimide thin film was calculated by using the equation [24]

$$\varepsilon_r = \frac{C \times D}{\varepsilon_0 \times A}, \quad (1)$$

where $\varepsilon_0$ is the permittivity of free space ($8.85 \times 10^{-14}$ F/cm), $\varepsilon_r$ the permittivity of polyimides, $C$ the capacitance, $D$ the film thickness, and $A$ the electrode area.

Fig. 8 shows the dielectric constants of the fluorinated polyimide thin film. As results, the maximum dielectric constant of F0 is 3.10 and those of the fluorinated polyimides are largely decreased in the range of 2.80–2.50 with increasing $F_{18}/C_{18}$ ratios of the polyimides.

Above mentioned the XPS studies, the fluorination introduces new carbon–fluorine functional groups onto polyimide surfaces. Generally, the high ionization potential of fluorine and its relatively low polarizability imply very weak intermolecular interactions. This is explained by the electrons of fluorine being very tightly held and close to the nucleus [18,19]. Therefore, the electronic polarizability of the fluorinated polyimides is decreased as the number of fluorine atoms substituted for hydrogen is increased, due to the lesser electronic polarizability of a C–F bond relative to that of a C–H bond [10,21]. And the free volume also increases due to the relatively large volume of fluorine compared with hydrogen, which reduces the number of polarizable groups per unit volume, from which the dielectric constant of the fluorinated polyimides is decreased as the fluorination concentration increases.

4. Conclusions

In this work, it is found that fluorination introduces carbon–fluorine functional groups, such as C–F and CF₂ groups, onto the polyimide surfaces. And the $F_{18}/C_{18}$ ratios of the fluorinated polyimides are increased as a function of the treatment concentration. Consequently, the carbon–fluorine groups lead to a decrease of the dielectric constant of the fluorinated polyimides, which can be attributed to the changes in free volume and electronic polarizability. Nevertheless, the bulk materials properties including the thermal stability and mechanical behavior of the films studied do not significantly change in the evolution fluorination.
Fig. 9. Dielectric constants of polyimide thin film with fluorination concentration: (a) F0, (b) F5, (c) F10, (d) F30, and (e) F50.

References
