OPTICAL SURFACE PROPERTIES
OF POLYIMIDES CROSS-LINKED THIN FILM*

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Novel cross-linked polyimide thin films have been prepared by thermal imidization of poly(amic acid) precursors. Optical surface properties of these polyimides are investigated and compared with bulk optical characteristics obtained from the group contribution theory. The refractive index of the surface and the surface absorption coefficient values were evaluated by means of ellipsometry. The results reveal that the investigated samples present small absorption at the surface and the surface refractive indices are easily influenced by the diamines used in synthesis.

Key words: polyimides, refractive index, surface absorption coefficient.

1. INTRODUCTION

Polyimides are important industrial materials because of their excellent properties. They are extensively used in the electronics industry as insulators in complex devices, owing to their high thermal resistance and low dielectric constant. Beside the electrical properties, their optical properties have been extensively investigated due to the potential applications in the field of optical communications [1].

Conventional aromatic polyimides are often categorized as an insoluble, intractable, and infusible material because of their rigid backbone structure. These disadvantages make them extremely difficult to process and greatly limit their commercial uses. Various attempts have been developed to overcome these deficiencies, including the use of noncoplanar or alicyclic monomers and the introduction of flexible segments into the polymer backbone [2, 3]. The strategies of these methods are the reduction of chain crystallinity, inter-molecular


charge-transfer and electronic polarization interactions. An alternate successful approach involves the incorporation of pendant groups onto the rigid polyimide backbone [4]. These works have shown that the presence of bulky groups could effectively prevent the coplanarity of aromatic rings and reduce the packing efficiency of molecular chains without sacrificing thermal properties. As compared to the conventional polyimides, partially aliphatic polyimides offer a unique combination of qualities because they present lower dielectric constant, good transparency and higher flexibility and implicitly better processability. Most applications demand specific characteristics such as those required by absorption, refractivity, wetting and adhesion for coatings, certain types of composite materials or nanostructures [5]. Thus, it is necessary to obtain uniform, defect-free films with correct thickness for polyimides [6]. Because of the nature of these materials, it is often necessary to make measurements on samples consisting of complicated/multilayer stacks, including anisotropic, inhomogeneous, absorbing films. Recently, different ellipsometric techniques have been proposed to fulfil this task. However, in the case of complex structures, despite showing strong potentialities, ellipsometry seems to be very sensitive to the choice of a proper physical model, the optical and geometrical parameters of the sample under investigation, and a good initial guess in the fitting procedure. This method also is used to determine the optical constants at the wavelength of interest, important for developing lithography at shorter wavelengths.

In this paper new partially aliphatic polyimides have been developed by combining of imide units, aromatic rings, a cycloaliphatic anhydride with flexible and asymmetrical structure, maintaining a compromise between processability and the physical and thermal characteristics. To enhance their new properties, 5 – (2,5 – dioxotetrahydrofurfuryl) –3– methyl – 3 – cyclohexenyl – 1,2 –dicarboxylic acid anhydride (epiclon) has been used as raw material for polyimides [7]. The products have been characterized from the view point of their chemical structure, thermal behaviour and solution properties. Also, the conformational characterization in dilute solution [8], hydrophobicity/ hydrophilicity balance, surface free energy [9] and electrical properties [10] for these polymers, in comparison with their corresponding poly(amic acid)s, were studied. In this work, polyimide cross-linked thin film has been prepared by thermal imidization of their precursors. Their optical surface properties have been investigated in correlation with the chemical composition.

2. EXPERIMENTAL

The precursors of the polyimides – the poly(amic acid)s– have been obtained by the polycondensation reaction of equimolar amounts of 5-(2,5-dioxotetrahydrofurfuryl) –3– methyl– 3 – cyclohexenyl–1,2 dicarboxylic acid
anhydride (epiclon) with two diamines: 1,4- (p-aminophenoxy)benzene (1) and 1,4-bis(p-aminophenoxy)benzene (2) [11].

The reactions were carried out in N-methylpyrrolidinone (NMP) as a solvent, under inert atmosphere. The concentration of the reaction mixture was adjusted to 20% total solids. The polymer solution was heated at 250°C during three hours to perform thermal imidization, leading to the corresponding cross-linked partially aliphatic polyimides PI1 and PI2 (Scheme 1).

Refractive index, $n_2$, and surface absorption coefficient, $k_2$, of the polyimide films were evaluated by means of PCSA ellipsometer at 657 nm at 25°C. The method allows evaluation of these parameters from the correlation between the incidence angle, $\alpha$, the amplitude of reflected and incident electric field ratio, $\Psi$, and their phase difference, $\Delta$, according to equation (1).

$$\tan \Psi \cdot e^{i\Delta} = \rho = \frac{r_p}{r_s}$$

where $r_p$ and $r_s$ are the complex Fresnel reflection coefficients of the sample for p- (in the plane of incidence) and s- (perpendicular to the plane of incidence) polarized light, illustrated in Fig. 1. These coefficients contain desired information related to material optical properties and physical dimensions. Ellipsometry measures this complex ratio as a function of wavelength.

Variable angle ellipsometry performs measurements as a function of wavelength and angle of incidence [12]. Because ellipsometers measure ratios of two values they are accurate and reproducible, even at low light levels, and no reference material is necessary. Because ellipsometers measure a phase difference $\Delta$ (as well as an amplitude ratio), they are sensitive to ultrathin films (< 1 nm). Using ellipsometry results in high sensitivity to multiple film parameters, and eliminates the “period” problem associated with interference
oscillations in thick films. Ellipsometry does not measure optical constants, it measures the change in polarization expressed as $\Psi$ and $\Delta$. To extract useful information about a material structure, it is necessary to perform a mathematical model dependent analysis of the ellipsometric data.

3. RESULTS AND DISCUSSION

The dependence of the ellipsometric parameters $\Psi$ and $\Delta$ on the incidence angle $\alpha$ is important in electing the correct mathematical model for determination of the optical constants. The measured values are presented in Table 1.

The shape of dependence between $\Psi$ or $\Delta$ and incidence angle from Fig. 2 determines the election of equations (2) and (3) for the evaluation of the refractive index and the surface absorption coefficient.

Table 1

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\Psi$</th>
<th>$\Delta$</th>
<th>$n_2$</th>
<th>$k_2$</th>
<th>$\Psi$</th>
<th>$\Delta$</th>
<th>$n_2$</th>
<th>$k_2$</th>
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<td>19.273</td>
<td>0.728</td>
<td>1.615</td>
<td>0.097</td>
<td>28.611</td>
<td>3.222</td>
<td>1.612</td>
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<td>0.023</td>
<td>22.345</td>
<td>9.839</td>
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<tr>
<td>75</td>
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<td>4.241</td>
<td>1.611</td>
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<td>13.177</td>
<td>1.619</td>
<td>0.106</td>
</tr>
<tr>
<td>70</td>
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<td>1.607</td>
<td>0.046</td>
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<td>174.344</td>
<td>1.619</td>
<td>0.079</td>
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</table>
5 Optical surface properties of polyimides cross-linked thin film

Fig. 2 – Ellipsometric parameters dependence on the incidence angle.

\[
\frac{n_1' \tan \alpha}{n_2} = \tan \Psi \cdot e^{i\Delta}
\]

where \( n_1 \) is the refractive index of the air, and \( n_2' \) is the complex refractive index, related to refractive index of the polymer, \( n_2 \), and surface absorption coefficient, \( k_2 \) (equation (4)).

\[
n_2' = n_2 - ik_2
\]

The resulted values for the optical constants are listed in Table 1, revealing that the investigated samples present small absorption at the surface and the surface refractive indices are easily influenced by the diamines used in synthesis. Thus, PI2 sample presents very small differences regarding the refractive index values, but relatively higher values for the surface absorption coefficient. The results concerning the refractive index obtained by means of ellipsometry are in accord with those obtained from the group contribution theory, where \( n_2 = 1.615 \) for PI1 and \( n_2 = 1.611 \) for PI2 [10]. Optical properties of these compounds combined with their electrical properties recommend them as interlevel dielectric layers in the fabrication of semiconductor chips and multichip packaging structures.
4. CONCLUSIONS

Polyimide cross-linked thin films were obtained from thermal imidization of the poly(amic acid)s precursors. Optical constants of these materials were investigated by means of ellipsometry. The results reveal that the investigated samples present small absorption at the surface and the surface refractive indices are easily influenced by the diamines used in synthesis. Thus, the optical properties induced by the partially aliphatic anhydride (epiclon) combined with the electrical ones recommend them as good insulators for electronic applications.

REFERENCES