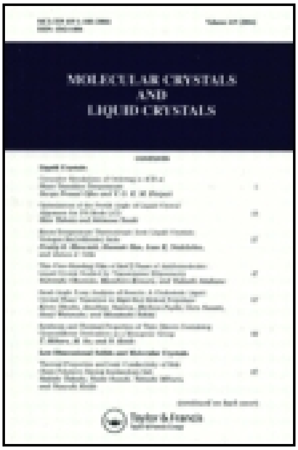

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Measurement of Refractive Index and Thickness of Fluorinated Copolyimide Films by Spectroscopic Reflectometry

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Measurement of Refractive Index and Thickness of Fluorinated Copolyimide Films by Spectroscopic Reflectometry

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Various fluorinated copolyimide films were prepared on a Si wafer from copoly(amic acid) solution of pyromellitic dianhydride (PMDA) or bis(3,4-dicarboxyliphenyl)hexafluoropropane dianhydride (6FDA) and a diamine mixture of 4,4'-oxydianiline (ODA) and 2,2'-bis-(trifluoromethyl)benzidine (BTBz). Refractive index and thickness of polyimide films were measured by means of spectral reflectance measurement. A gradual increase of the refractive index was observed in the course of imidization for PMDA series polyimides and almost no change or a slight decrease for 6FDA series polyimides. Film thickness decreased about 30% after imidization. The refractive indices of final polyimides depended on the fluorine content as well as the structure of the copolyimide.

Keywords fluorinated polyimides; refractive index; thickness; spectroscopic reflectometry

INTRODUCTION

Recently, thin films of fluorinated polyimide have attracted an attention with regard to possible applications to optical interconnects and waveguides due to their excellent thermal stability, high optical transparency, low-loss property and good processibility.[1-3] It is critical to measure characteristics of a thin film such as thickness, roughness, and optical constants for the application, designing and synthesis of the materials as well as devices. Optical techniques are one of the preferred methods because they are accurate, nondestructive, and require little or

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no sample preparation time. Spectral reflectance measures the thickness and refractive index of a thin film at the same time from the reflectance spectrum over a range of wavelengths, and in general, is much simpler and less expensive than ellipsometry.[4,5] In this study, we synthesized a series of fluorinated copolyimides and measured their refractive indices and thickness by means of spectroscopic reflectometry. The refractive index and thickness changes during the thermal imidization and those of final polyimides are discussed with respect to the fluorine content of the copolyimide. Another objective of this study is to demostrate the spectroscopic reflectometry as a simple and convenient method to measure the refractive index and thickness of thin films.

EXPERIMENTALS

The structures of copolyimides used in this study are shown in Figure 1. Their corresponding copoly(amic aicd)s were synthesized by reacting either pyromellitic dianhydride (PMDA) or bis(3,4-dicarboxyliphenyl) hexafluoropropane dianhydride (6FDA) with a various molar mixture of aromatic diamine of 4,4'-oxydianiline (ODA) and 2,2'-bis(trifluoromethyl)benzidine (BTBz) at 5 °C. The concentration of the copoly(amic acid) was about 10 wt.% in NMP. Copoly(amic acid) was spin-coated on a Si wafer which was pretreated with an adhesion promoter (trimethoxy aminopropylsilane). The films were dried at 60°C in vacuum for overnight and were imidized stepwisely at 100, 150, 200, 250, 300, and 350 °C for 30min at each temperature.

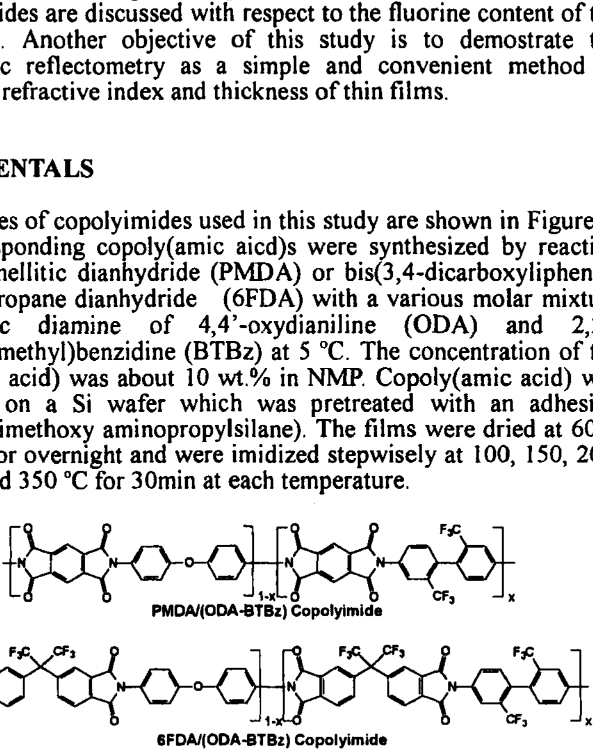

FIGURE 1. Structure of polyimides.

The spectroscopic reflectance was measured by using a fiber-optic UV-visible spectrophotometer (Guided Wave, Model 260) with random polarized light source. The thickness and refractive index were calculated from the measured reflectance spectra in the wavelength range of 350 nm to 1000 nm. The numerical fitting was carried out by a commercial software (FilmSpectrum, SCI, Encintas, CA, U.S.A.). The Lorentz oscillator model was used for estimating the change of the optical constants of polyimides as a function of wavelength.

RESULTS AND DISCUSSION

To confirm that the spectroscopic reflectometry is an accurate method to determine a refractive index and thickness of thin film, we measured methylsilsesquioxane (MSSQ) film of which the optical constant was well known. The determined refractive index and thickness for MSSQ film by reflectance spectra were in good agreement with those measured by ellipsometry within a few percent error.

In Figure 2, change of refractive index as a function of imidization temperature is shown. For PMDA series, the refractive index increased with the imidization temperature, especially for the samples of lower BTBz content. However, in the case of 6FDA series, the refractive index changed little during the imidization. This is probably attributed to the enhancement of molecular packing during the structural change from poly(amic acid) to polyimide in the case of PMDA series. However, in the case of 6FDA series, compact molecular packing is not favored due to the bulky trifluoromethyl substituents and kinked structure even in the fully imidized structure, which resulted in little change during the imidization and inherently low refractive index values compared to the PMDA series.

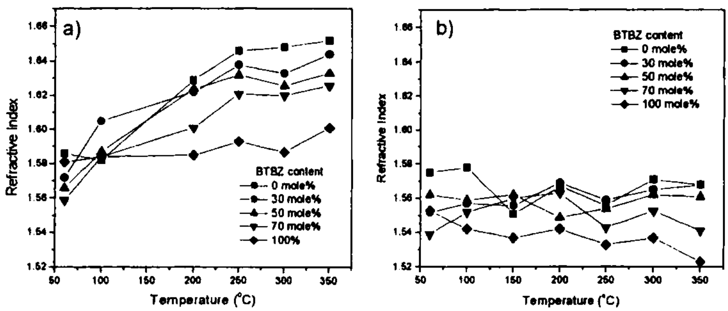

FIGURE 2 Refractive index and thickness change of copolyimides as a function of imidization temperature for a) PMDA and b) 6FDA series.

For PMDA series, the refractive index and thickness changed rapidly until the temperature reached at 200°C. The change of refractive index and thickness may be attributed to the structural change during the imidization as well as the evaporation of the residual NMP. FT-IR study showed that the degree of imidization was ca. 10% at this temperature. After that, refractive index and thickness showed steady state value and changed little for further imidization (see Figure 3). From this result, it was thought that molecular packing occurred rapidly at the initial stage owing to the presence of imide structures and did not change much as the imidization proceeded further.

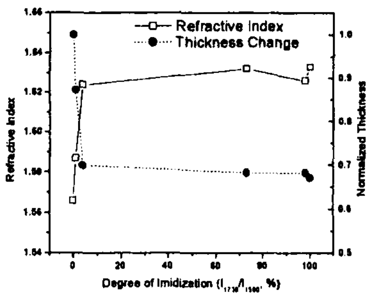

FIGURE 3 Refractive index and thickness change as a degree of imidization for PMDA series with 50 mole% BTBZ.

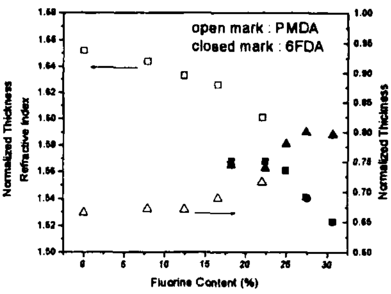

FIGURE 4 Refractive index and thickness change as a function of florine content calculated for the PMDA and 6FOD series.

In Figure 4, the dependence of refractive index and degree of film shrinkage on the fluorine content of the copolyimides is shown for PMDA and 6FDA series. As the fluorine content increased, the refractive index and film shrinkage decreased in S-shape. It was reported that the fractional free volume of polyimides increased as the fluorine substitution increased.[6]

In summary, as the fluorine content in polyimides increased, refractive index and film shrinkage ratio decreased probably due to the decreased packing density by the bulk trifluoromethyl substituents and the kinked structure.

Further investigations on the relationship between the optical properties and structure of fluorinated polyimides and the measurement technique by using spectral reflectometry is on the progress and the details of the experiment and results will be published elsewhere.

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