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Influence of curing temperature on the optical properties of fluorinated polyimide thin films

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ABSTRACT

The influence of curing temperature (CT) on the optical properties of 6FDA/ODA poly(amic acid)-polyimide (PAA-PI) films was characterized by measuring ATR-FT-IR spectra, refractive index (RI) and birefringence of the films. The results showed that the infrared absorption intensity of characteristic peaks (IAICP) corresponding to the imide ring and the RI of PAA-PI films reached their maxima when the films had been cured at 270 °C, while the magnitude of birefringence ($|\Delta n|$) of the films reached its minimum as CT rose up to 330 °C. However, the RI decreased as CT was between 270 °C and 330 °C. Both the RI and $|\Delta n|$ of the film increased obviously when CT increased after 330 °C. We think this is due to the interchain crosslink reaction (ICCR) above 330 °C and can be an evident proof of ICCR. And the evidences supporting ICCR was also discussed via IR differential spectra.

1. Introduction

Polymeric materials are particularly attractive in integrated optical components and circuits for high speed optical communication [1–3], due to their high performance, rapid processibility and cost-effectiveness compared to silica. Of all optical polymers, fluorinated polyimides have been introduced to be the candidates for direct on-chip interconnection and optical devices, because they have low optical loss at the communication wavelengths, broad range of refractive index and excellent heat resistance [4].

Having controllable and invariable refractive index is fundamental and important for materials in optical applications. The refractive index of materials must be precisely controlled and stay invariable in the device fabrication process. However, the properties of polyimides are affected by special chemical structures, aggregation structures and progress of preparation [5,6]. Dramatic changes in the mechanical [7] and thermal [8] properties occur during thermal imidization as the poly(amic acid) precursors are transformed into the final polyimides. It has been found [9] that the thermal expansion coefficients of polyimide films decrease obviously while glass transition temperatures increase slightly as curing temperature rises because the free volume of polyimide decreases while intermolecular forces increase with the rise of curing temperature.

It is known [10] that the refractive index of a material is related to the free volume, polarizability of the material. In general, the high-temperature densification of aromatic polymers leads to an increase in refractive index due to the decrease of free volume. Actually, during thermal imidization of poly(amic acid), the accompanying occurred changes include not only high-temperature densification but also complicated chemical reactions such as cyclization, degradation and crosslinking as the curing temperature rises [5].

However, until now, only a few reports [11–13] have been devoted to characterize the optical behaviors of fluorinated polyimides and their precursor poly(amic acid)s cured at different temperatures. This paper will focus theoretically and experimentally on the optical properties by

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examining the FT-IR spectra, refractive index and birefringence of fluorinated poly(amic acid) and polyimide films on silicon wafer and presume the optimum thermal imidization temperature. Since the sample films were blends of poly(amic acid) and polyimide before the imidization process terminated, PAA-PI was used as the abbreviation for all poly(amic acid) and polyimide films cured at different temperatures and with different degree of imidization.

2. Experimental

2.1. Materials

4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99%, Aldrich) was used without further purification. 4,4′-oxydianiline (ODA, 99%, Aldrich) was sublimated under reduced pressure, and *N*-Methyl-2-pyrrolidone (NMP) which was used as a solvent for the preparation of poly(amic acid) was dried by refluxing over CaH_2 and purified by reduced distillation before being used.

2.2. Sample preparation

6FDA/ODA poly(amic acid) (PAA) (shown in Fig. 1) was prepared according to the literature [14]. PAA solid which had been dried under vacuum for 24 h at 35 °C was dissolved in mixed solvent of THF and DMF (volume ratio of THF to DMF was 3:2), and the concentration of PAA solution was 30 wt%. After being filtrated (0.45 μm, millipore filters) the PAA solution was spin-coated on a 2 inch-diameter silicon wafer, then dried in a vacuum oven at 70 °C for 1 h to remove most solvents. The initial thickness of PAA-PI films varied between 2 μm and 11 μm after being dried.

All the PAA-PI films were cured at 70 °C, 90 °C, 105 °C, 120 °C, 150 °C, 180 °C, 210 °C, 240 °C, 270 °C, 300 °C, 330 °C, 350 °C, 380 °C in a vacuum oven, respectively. Each curing process consisted of ramping the vacuum oven temperature at 1.5 °C/min from room temperature up to the specific temperature above, holding for 20 min, then cooling down to room temperature naturally for optical and spectroscopic measurements. All the measurements were carried out with the same sample, because no obvious difference in the refractive index and FT-IR spectra of PAA-PI films were observed between the sample undergoing multiple curing process and the one undergoing just one curing process if they have the same final curing temperature.

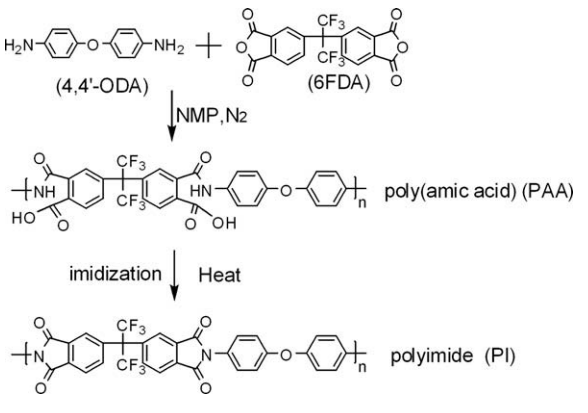

Fig. 1. Synthesis of fluorinated polyimide.

2.3. Characterization

Infrared spectra were recorded with a FT-IR spectrometer VERTEX70 from Bruker Optics (Ettlingen, German) through the attenuated total reflection (ATR) method. And the refractive index, birefringence of PAA-PI films which had been cured were directly measured through the METRICON 2010 prism couple thin film testing system. The temperature of environment was 22 ± 2 °C and the humidity was 30%.

3. Results and discussion

3.1. FT-IR spectra characterization of PAA-PI film

Fig. 2 shows the attenuated total reflection (ATR) FT-IR spectra of 6FDA/ODA PAA-PI film which underwent different curing process taking 70 °C (a), 90 °C (b), 120 °C (c), 150 °C (d), 210 °C (e), 270 °C (f), 330 °C (g), 380 °C (h) as their final curing temperature, respectively, while its initial thickness decreased from 11 μm to 7.6 μm. The tentative assignment of the prominent peaks involved in the thermal imidization process is given in Table 1 [15,16].

As shown in Fig. 2, the intensities of the characteristic peaks of amic acid groups (1647 cm^{-1}, 1612 cm^{-1}, and 1543 cm^{-1}) varied slightly with curing temperature below 120 °C. However, with the increase of curing temperature, these vibrational peaks decreased drastically, while the characteristic peaks of the imide ring at 1782 cm^{-1}, 1716 cm^{-1}, 1373 cm^{-1}, and 717.5 cm^{-1} appeared and became stronger from 120 °C up to 270 °C.

To monitor the thermal imidizaiton process of PAA-PI film, the imidizaiton degree was calculated from the relative absorption intensity (RAI) $I_{imide}/I_{1496\ cm^{-1}}$ in the ATR-FTIR spectra, where I_{imide} was the characteristic absorption peak area of the imide ring at 1782 cm^{-1}, 1716 cm^{-1}, 1373 cm^{-1}, and 717.5 cm^{-1}, and the absorption peak at 1496 cm^{-1}, corresponding to the C—C stretching of *p*-substituted benzene, was selected as an internal standard

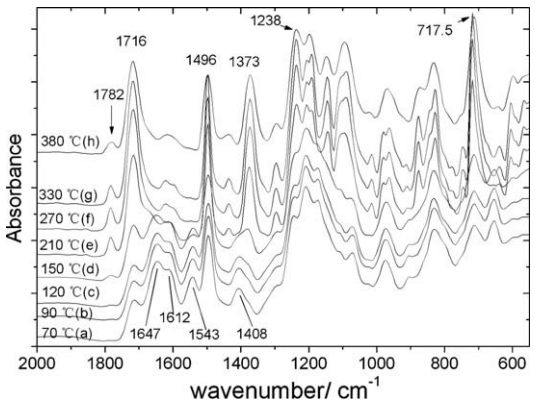

Fig. 2. ATR-FTIR spectra of PAA-PI films on silicon substrate cured at different temperature.