Optical Anisotropy of Uniaxially Drawn Silver-Dispersed Fluorinated Polyimide Films and Its Application to a Thin Film Polarizer

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ABSTRACT

Anisotropy in optical transmittance in the visible and near-infrared region was observed for uniaxially drawn and silver-dispersed polyimide films. The films were prepared in a one step operation, that is thermal curing and simultaneous uniaxial drawing of poly(amic acid) films dissolving 6 ~ 25 mol% of silver nitrate. The polyimide chains having a rod-like structure were oriented along the drawing direction during curing accompanying with the precipitation of silver nano-particles having elongated shapes. An anisotropy in transmittance of 100 : 1 was obtained for a 15μm-thick film at 850nm with an transmittance of 80% perpendicular to the drawing direction, and its optical properties were retained after annealing at 300°C for 1h. This film can be used as a thin-film polarizer inserted into a groove formed in silica-based waveguides.

INTRODUCTION

Polyimide films containing metal/metal oxide particles generated *in-situ* have been studied extensively by Taylor *et al.* in an attempt to synthesize materials with unique electrical, magnetic, thermal, or adhesive properties.[1] They have incorporated silver salts and organosilver complexes in aromatic polyimides and obtained highly reflective silver-containing polyimide films.[2-4] Recently, we have prepared five kinds of Cu, Al, Pd, Ag, and Au-containing fluorinated polyimide films [5]. The precipitation of zero-valence Ag and Au particles were confirmed by x-ray diffraction and transmission electron micrograph. And the increase in refractive indices were observed. On the other hand, Stookey[6] reported that a large anisotropy in optical transmittance was observed in a stretched inorganic glass containing silver particles. In this study, we intend to generate silver nanoparticles having elongated shapes in a thermally stable polymeric material in one operation (Fig.1). When the polyimide molecular chains are highly oriented by uniaxial

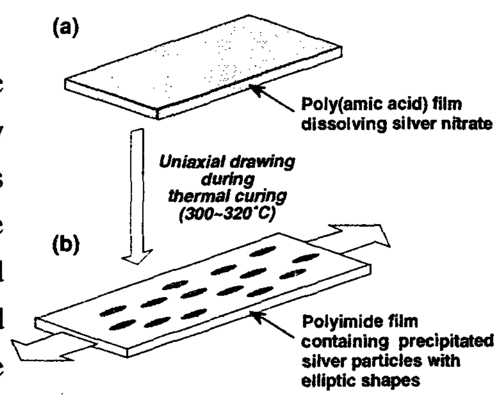
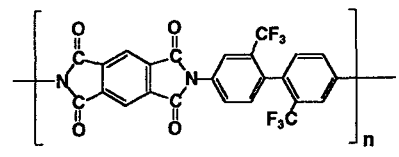


Fig.1 Method of preparing polyimide films having optical anisotropy.

drawing during curing, the shapes of the precipitated silver particles are expected to be elongated along the drawing direction. The fluorinated polyimide, PMDA/TFDB [7], was used as a matrix polymer, and silver nitrate ($AgNO_3$) was used as a source material of silver particles.



PMDA / TFDB

Figure 2 shows the absorption spectra of the silver-doped poly(amic acid) (PAA) and polyimide films cured at various temperatures in air. Since they were not uniaxially drawn, no optical anisotropy was observed in the film plane. An absorption peak is clearly observed at 430nm for the film cured at 200°C. This peak wavelength coincides with that of the surface plasmon resonance of Ag colloids reported in the literature.[8,9] This indicates that $AgNO_3$ incorporated into polyimide was reduced to Ag by the thermal treatment at 200°C, and nanometer sized Ag particles were generated in the film. As the curing temperature increases, the absorption band at 430nm grows and looks slightly displaced to longer wavelengths, suggesting that the silver particles increased in size. The different feature observed for the 350°C film can be understood from their appearance ; a reflective surface with silvery color was formed on the surface. This indicates that Ag particles were concentrated near the air-side surface.

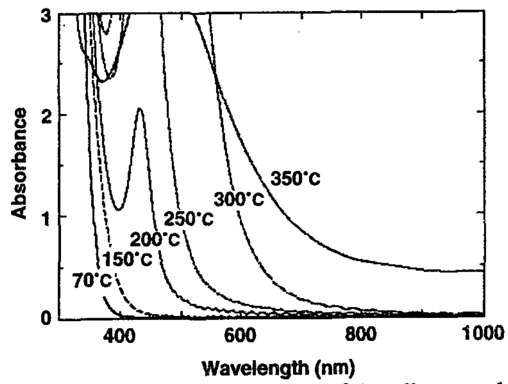


Fig.2 Absorption spectra of Ag-dispersed polyimide films with various curing temp.

For preparing uniaxially drawn silver-dispersed polyimide films, PAA films peeled from the substrate were cut into rectangular forms by 15mm x 5mm and loaded in a thermal mechanical analyzer (TMA: Shinku-Riko TM-7000). Figure 3 shows the transmittance spectra of the silver-dispersed polyimide films uniaxially drawn during curing with varying the load of TMA from 5g to 18g. A constant load was applied along the longer axis of the film by TMA during thermal curing. The film was thus heated to 320°C at a heating rate of 10°C/min, kept for 1 h, and then cooled to room temperature. The spectrum of a dopant-free polyimide was also shown for comparison. As expected above, all the uniaxially-drawn and silver-dispersed films exhibited distinct anisotropy in optical transmittance in the visible and near-IR region. The transmittance parallel to the drawing direction is considerably lower than that perpendicular to the direction. In addition, the optical anisotropy (dichroic ratios) increased as the load increased. On the other hand, the non-silver-dispersed film uniaxially drawn with a load of 20g showed much higher transmittance in a wide range (400-1600nm), but no optical anisotropy.

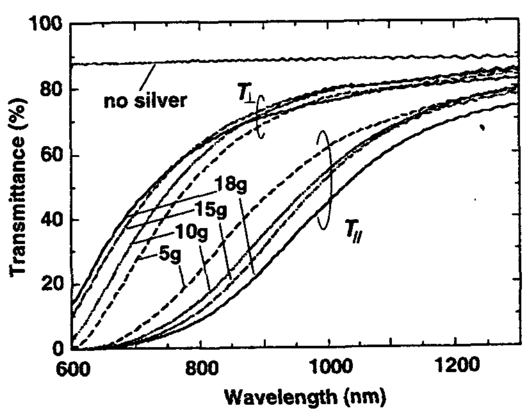


Fig.3 Absorption spectra of Ag-dispersed polyimide films with different tensile loads.

Figure 4 shows the WAXD patterns of a uniaxially drawn silver-dispersed polyimide films. The significant anisotropy in the diffraction patterns show a uniaxial orientation of polyimide chains accompanying with orientational crystallization. The precipitation of zero-valence silver particles is also identified. Figure 5 shows the polarization absorption spectra of PI films with varying the staying time at the highest curing temperature (Tf : 330°C). The difference in transmittance between the two polarization directions and the wavelength dispersion of optical anisotropy shows a significant dependence on the staying time at Tf. The films cured for 16-18min at the Tf give the highest optical anisotropy under the curing condition. Figure 6 shows the dependence of curing atmosphere on the in-plane birefringence (Δn) measured at 1307nm and the dichroic ratio (D) at 670nm. The uniaxial orientation of polyimides and the optical anisotropy should be reflected to Δn and D, respectively. Although a large Δn was obtained under nitrogen, the value of D is much smaller than that obtained in air, which suggests that oxygen play an important role in the formation (crystallization) of silver-nanoparticles. Hence, the optical anisotropy should be determined by size, aspect ratio, degree of orientation of longer axis, and anisotropic distribution of the silver particles precipitated in a film. In order to obtain polyimide films having large optical anisotropy, the curing conditions, the drawing loads, the atmosphere during curing, and the kinds of dopant should be optimized.

In the conventional processes using glasses, metal nano-particles are formed or embedded in a matrix glass, and then elongated by uniaxial drawing with the glass plate. However, in the present method, the precipitation and elongation of silver nano-particles take place in one step operation. From the facts that an absorption peak of silver nano-particles was observed even for an isotropic film cured at 200°C,

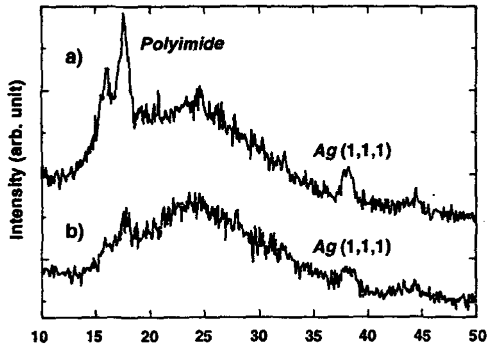


Fig.4 WAXD patterns. a) parallel and b) perpendicular to the drawing direction.

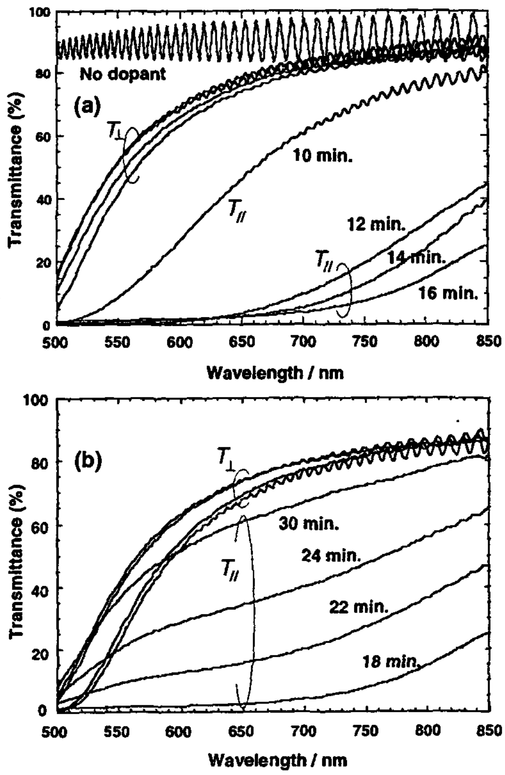


Fig.5 Polarization absorption spectra of PI films with varying the staying time at the highest curing temperatures (330°C).

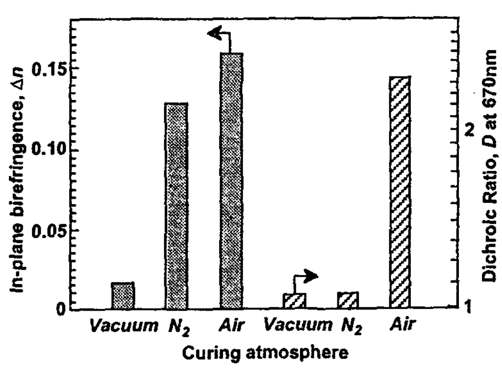


Fig.6 The dependence of curing atmosphere on the birefringence and the dichroic ratio.

and it grew considerably at higher temperatures, a following mechanism is suggested : a) silver particles with spherical shapes begin to precipitate from polyimide around 200°C. b) the precipitation become vigorous, and the particles begin to coagulate or sinter between 250-300°C. c) precipitated silver spherical particles are elongated along the drawing direction between 300-320°C accompanying with the significant elongation of the polyimide film. Highly oriented polyimide molecules provide an anisotropic environment for the growth of silver-nano-particles. The melting temperature of bulk silver is higher than 900°C, however it have been reported that sintering of silver nano-particles begins at 150°C.[10]

Figure 7 show the transmittance spectra of a film that exhibits the largest extinction ratio of ca.20 dB (100 : 1) at 870nm. In particular, the transmittance for the polarization parallel to the drawing direction ($T_{//}$) is less than 0.5% in the whole visible region. Although the polyimide films were cleavable along the drawing direction, they showed good flexibility and tractability. In addition, no change was observed in the transmittance, the optical anisotropy, and the flexibility after annealing at 300°C for 1 h. Figure 8 shows a schematic configuration of an optical waveguide circuit with thin-film polyimide polarizer. The thickness of the films (~15μm) is sufficiently thin for decreasing excess loss caused by inserting films into a groove.[11] Inorganic glass plates with such small thicknesses are generally difficult to handle and insert into a thin groove. In conclusion, uniaxially drawn and silver-dispersed fluorinated polyimide film is a promising material for thin-film polarizer incorporated into optical waveguide circuits that function at the visible and near-infrared wavelengths .[12]

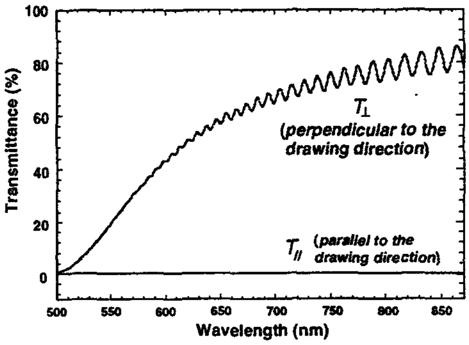


Fig.7 Polarized transmittance spectra of PI film having a large *D* of ca.100.

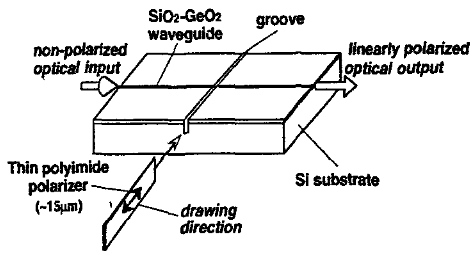


Fig.8 Configulation of an optical wave-guide with thin polyimide polarizer

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