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NONLINEAR OPTICAL PROPERTIES OF FULLERENE (C_{70}) THIN FILMS

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NONLINEAR OPTICAL PROPERTIES OF FULLERENE (C_{70}) THIN FILMS

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C_{70} fullerenes evaporated onto rubbed polyimide substrates at greater than 150°C were found to orient almost parallel to the rubbing direction, as confirmed by atomic force microscopy and polarized absorption analysis. The directions of maximum absorption, including both linear and nonlinear absorption components, also appeared to be aligned with the rubbing direction. The third-order electrical susceptibility of the evaporated C_{70} fullerenes thin films was measured using a z-scan method and found to be $\chi^{(3)} = Im\ \chi^{(3)}$: $10^{-6} \sim 10^{-8}$ esu at a wavelength of 500 nm.

Keywords: C_{70} fullerene; third-order optical susceptibility; z-scan

1. INTRODUCTION

Functional π-conjugated organic materials exhibit interesting optical and electrical properties that are strongly dependent on molecular orientation or stacking, which in turn are dependent on substrate materials and preparation temperatures. C_{70} fullerene is a functional material that exhibits many potentially useful optical and electrical phenomena related to the locations of the π-electrons. C_{70} fullerenes are ellipsoidal with D_{5h} symmetry and 5 chemically distinct carbon sites. C_{70} thin films exhibit two broad absorption peaks in the visible wavelength range.

The purpose of this study is to investigate the orientation of C_{70} fullerenes in thin films prepared on substrates at various temperatures based on the third-order susceptibilities ($\chi^{(3)}$) obtained by a z-scan method.

2. EXPERIMENTAL

C_{70} molecules were evaporated onto four different types of surface-treated substrates: a clean glass plate (BK7), an indium tin oxide (ITO) plate, and two polyamide rubbed plates (RN1199 and LP-52). The polyimide plates were prepared by spin-coating polyimide films onto a clean glass plate and then rubbing the polyimide surface. Substrates were maintained at room temperature, 120℃, 150℃, 180℃ and 200℃ during preparation. Prepared films were nominally 50 nm thick, as controlled using a quartz oscillator. Samples were evaluated by atomic force microscope (AFM), absorption spectra analysis and third-order optical susceptibility $\chi^{(3)}$ measurements. Susceptibility measurements were made by a z-scan method at fundamental incident laser wavelengths of 500 nm, corresponding to C_{70} resonance, and 600 nm, far from C_{70} resonance as seen in Figure 1.

Figure 2 shows the optical system used to measure nonlinear absorption and nonlinear refraction, which were employed in the caluculation of $\chi^{(3)}$. Nonlinear absorption is measured with an open aperture, and nonlinear refraction is measured with a closed aperture [1].

3. RESULTS AND DISCUSSION

3.1. Atomic Force Microscopy

Figure 3 shows AFM images of thin films fabricated by evaporation of C_{70} molecules onto ITO plate at three different temperatures. As shown in the figures, the microcrystalline size increased with substrate temperature, and the growth occurred in all directions.

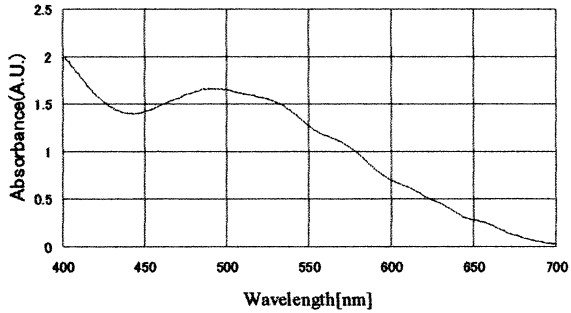

FIGURE 1 Absorption spectra of C_{70} thin film on a clean glass plate.

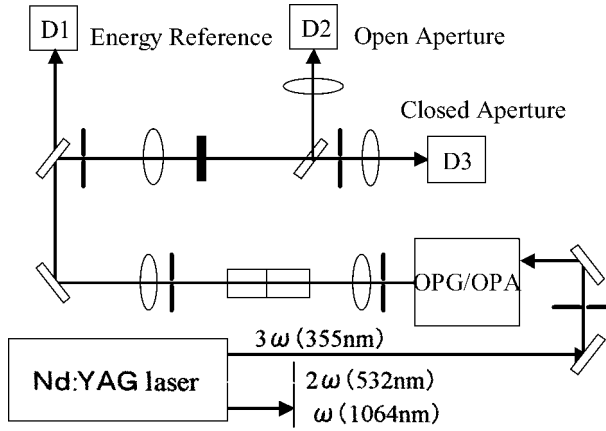

FIGURE 2 Optical system used to measure nonlinear absorption and refraction.

Figure 4 shows an AFM image of one of rubbed substrates (RN1199). The distance between rubbing lines varied between about 0.5 and 0.7 μm. The LP-52 rubbed plates had similar rubbing line separations.

Figure 5 shows thin films fabricated by evaporation of C_{70} molecules onto RN1199 rubbed plates. At room temperature, microcrystals grew in all directions, whereas at 150℃, microcrystals grew aligned with the rubbing direction.

3.2. Polarized Absorption Characteristics

Figure 6 shows polarized absorbance characteristics of the RN1199 films shown in Figure 5 at a wavelength of 500 nm. The angles in the figure

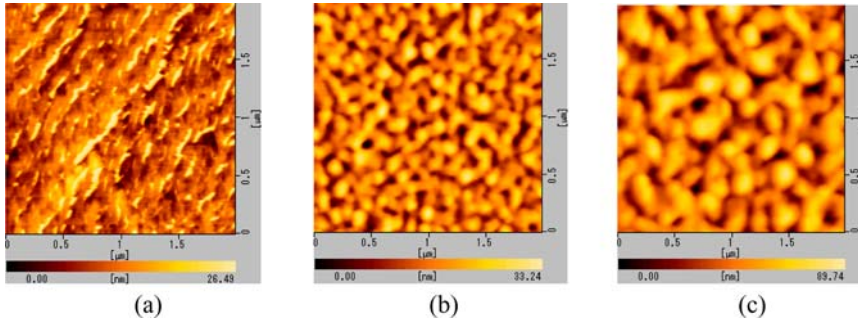

FIGURE 3 AFM images of C_{70} thin films evaporated onto ITO plates (2 μm × 2 μm) at (a) room temperature, (b) 150°C and (c) 200°C. (See COLOR PLATE XI)

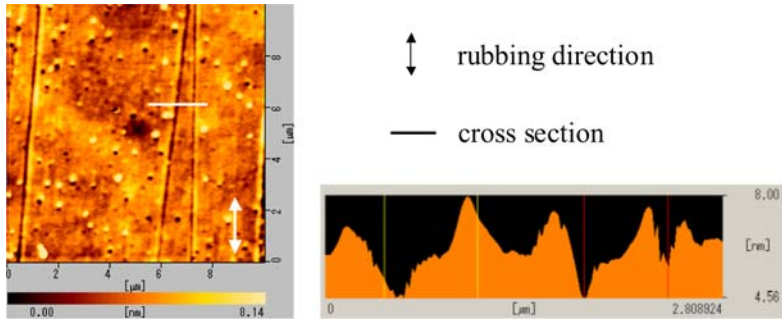

FIGURE 4 AFM image of rubbed polyimide substrate. (See COLOR PLATE XII)

represent the angle between the rubbing direction and the polarization. Measurements were made in increments of 30°. The thin film fabricated at room temperature exhibited the strongest absorption for light polarized in the rubbing direction. Absorbance at 30° and 90° was less intense, and absorbance at 60° was weakest. For C_{70} thin film deposited at 150°C, the maximum absorbance occurred with the rubbing direction parallel to polarization, and the minimum occurred when the two orientations were perpendicular. It is thought that microcrystal grains evaporated onto the rubbed plate at 150°C grew parallel to the direction of maximum

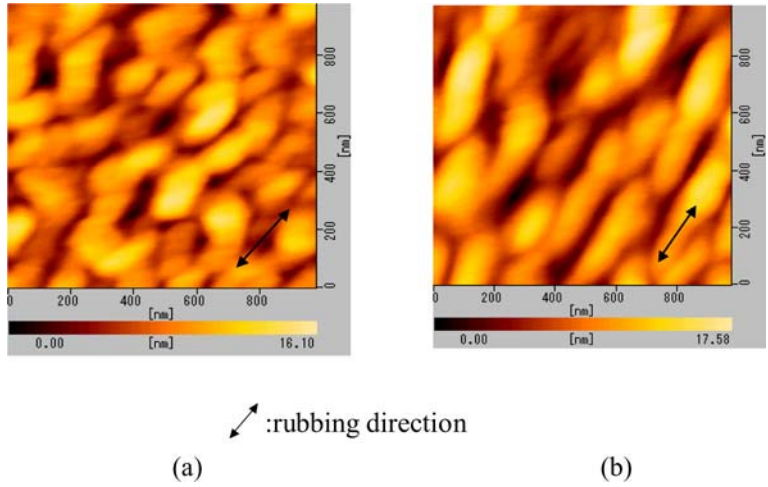

FIGURE 5 AFM photograph of C_{70} thin films evaporated onto RN1199 polyimide rubbed plates (2 μm × 2 μm) at (a) room temperature and (b) 150°C. (See COLOR PLATE XIII)

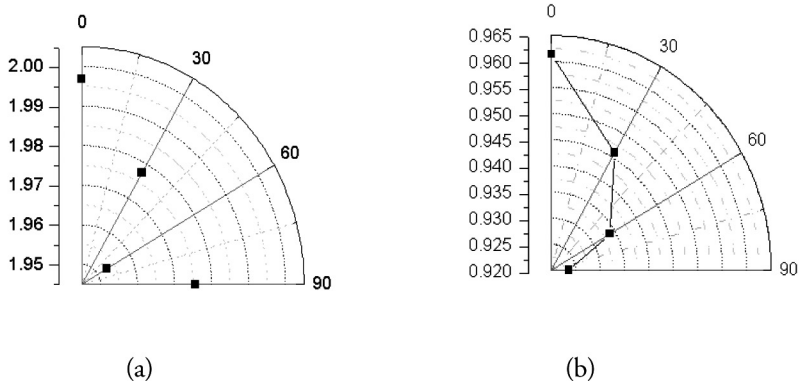

FIGURE 6 Polarized absorbance of C_{70} thin films evaporated onto RN1199 polyimide rubbing plates at (a) room temperature and (b) 150°C.

absorption, in agreement with the AFM images. Similar results were obtained for the LP-52 rubbed plate at 180°C.

3.3. Third-Order Susceptibility

Third-order susceptibilities ($\chi^{(3)}$) of metal-phthalocyanine has been found to depend on the microcrystal grain size [2,3], while that of C_{70} thin films has been found to depend on substrate temperature [4]. Microcrystal grain size increases with increasing substrate temperature. Table 1 shows values of Im $\chi^{(3)}$ for C_{70} thin films evaporated onto various substrates. For ITO plate substrates, $\chi^{(3)}$ increased with substrate temperature. Thus, it is clear that $\chi^{(3)}$ improves with increasing microcrystal size.

Figure 7 shows the linear and nonlinear absorption for angles of 0°, 30°, 60°and 90° and Table 2 shows the imaginary components of $\chi^{(3)}$ for C_{70} thin films on polyimide rubbed plates. The figure shows that the absolute values

TABLE 1 Estimated Values of Imaginary of $\chi^{(3)}$

Substrates	Im $\chi^{(3)}$
BK 7 (room temperature)	-2.5×10^{-7} [esu]
ITO (room temperature)	-1.9×10^{-7} [esu]
ITO (150°C)	-3.2×10^{-7} [esu]
ITO (200°C)	-5.5×10^{-7} [esu]

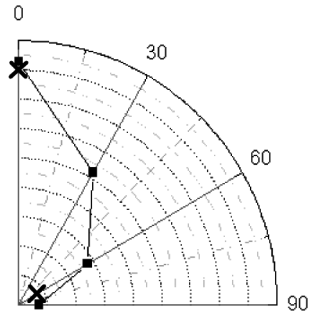

FIGURE 7 linear absorption (marked by ■) and nonlinear absorption (marked by ×).

TABLE 2 Estimated Values of Imaginary of $\chi^{(3)}$

Polyimide rubbing plates	Im $\chi^{(3)}$
0° (room temperature)	-7.1×10^{-7} [esu]
0° (150°C)	-2.0×10^{-6} [esu]
60° (room temperature)	-3.2×10^{-7} [esu]
60° (150°C)	-5.5×10^{-7} [esu]

of $\chi^{(3)}$ parallel to the rubbing direction is greater than that at 60° for C_{70} thin films evaporated onto rubbed plates. Both linear and nonlinear absorption therefore appear to be dependent on the growth direction of C_{70} thin films on polyimide rubbed plates.

4. CONCLUSIONS

Microcrystal grains of C_{70} thin films on ITO and polyimide rubbed plates were found to become larger with preparation temperature, and the imaginary component of third-order susceptibility was found to increase proportionally with microcrystal grain size. The maximum measured value of Im $\chi^{(3)}$ was 2.0×10^{-6} esu for C_{70} on polyimide rubbed plates maintained at 150℃ during deposition when oriented parallel with the polarization of incident light. C_{70} molecules evaporated onto RN1199 polyimide rubbed substrates heated to 150℃ formed microcrystals that grew parallel with the rubbing direction. For the rubbed substrates, the imaginary component of $\chi^{(3)}$ was found to be consistently highest in the rubbing direction.

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