

Characterization of Molecular Chains Alignment of Pulsed UV-Laser-Induced Polyimide Film Surface

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ABSTRACT

We have studied the molecular orientation in laser-induced periodic sub-micrometer structure on polyimide surface by polarized reflect IR absorption spectroscopy. The dichroism has been observed for 1722cm^{-1} and 1231cm^{-1} absorption bands. We found that the molecular chains in LIPSS tend to orient perpendicular to the laser-induced periodic lines.

INTRODUCTION

Following the success of the application of laser in the preparation of micro- and nano-structure pattern on the surface of metallic, semiconductive and inorganic insulating materials, the study has been extended to the laser-induced periodic structure on polymer surface(LIPSS) recently. The approach of studying LIPSS of polymers was initially using unpolarized laser to form ripple structure, but the periodic liner structures would not be formed or orient at random and the lines were rough and ruleless[.Subsequently, polarized laser beam was used for making LIPSS and cleaner, integrate lines of periodic structures were produced on surfaces of a lot of polymers, such as, amorphous polymer like poly(ethersulphone), polyetheretherkoton, polystyrene and polyimide; and semicrystalline polymer like poly(ethelene terephthalate). Under the influence of polarized laser beam, the direction of these structures runs either perpendicular or parallel to the plane of polarization. The formation of the periodic lines has been thought as a result of the repeated heating and cooling in polymer surfaces following intensity distribution caused by interference of reflected surface electromagnetic waves and incoming polarized laser beam^{1,2}. We think this process may lead to the local orientation of the polymer molecular chains. To justify our suggestion, polarized reflection infrared spectroscopy was applied to study the molecular orientation in the periodic sub-micrometer pattern formed on the polyimide surface.

EXPERIMENT

In our experiment, Spectra-Physics Quanta-Ray GCR-4 Nd:YAG laser was used at its fourth harmonic mode with a wavelength of 266nm. The fluence of laser beam was 30 mJ/cm² at a repetitive rate of 10Hz and pulsewidth of 5ns. To obtain periodic sub-micro lines structure in a large size, a X-Y moving table with an angle adjustable platform was used, and the polyimide film, which was inclined at 20°, was exposed under atmospheric condition by scanning in speed X of 5nm/s and Y of 0.005nm/s, respectively.

The polyimide used in this study was prepared from the polycondensation between 4,4'-diamino-3,3'-dimethyl diphenylmethane and benzophenone-3,3'-4,4'-tetracarboxylic acid dianhydride³. The polyimide solution was spin-coated on glass substrates, The substrates were subsequently heated at 150°C for 1h to evaporate the solvents.

The polarized reflection infrared spectra were recorded using a Bio-Rad FTS 6000 Fourier-transform Infrared spectrometer equipped with an IR polarizer and mercury cadmium telluride detector. Spectra were measured at 4 cm⁻¹ resolution, The number of scans were 400 times.

RESULTS AND DISCUSSION

A molecular-chain oriented polymer shows a different absorption or reflection IR spectrum when the orientation of the polymer relative to the direction of linearly polarized light is changed, because an interaction between a polarized electric field of the radiation and a dipole moment associated with the vibration becomes maximum or minimum when an angle between those two are 0° and 90°, respectively. In this study, the reflection polarized IR spectroscopy was applied to evaluate the molecular chain orientation of the polymer film surface because of two points. First, the existence of the periodic sub-micrometer lines on the polymer surface would lead to the difference of the transmittance IR absorption at the different location with different film thickness. Secondly, the height of the sub-micrometer lines is about 70nm, which is much smaller than the thickness of the film (1 μm). The molecular chain orientation may occur only on the surface area and may not be fully reflected in a transmittance spectrum. The easiest way to obtain the surface information of a material is through a specular reflection measurement. However, true specular reflection spectra have derivative-like spectral patterns and it is generally not advantageous to use them for qualitative or quantitative purposes. In this study, a reflection spectrum was transformed into an absorption spectrum through the Kramers-Kronig transformation.⁶

Figure 1 shows the polarized IR spectra after the Kramers-Kronig transformation of the polyimide in both the irradiated and non-irradiated areas. Spectrum a is from the irradiated area with IR polarization direction perpendicular to the direction of the sub-micrometer lines. Spectrum b is from the non-irradiated area with the polarized direction identical to spectrum a. Spectrum c is from the irradiated area with the IR polarized direction parallel to the sub-micrometer lines direction. Spectrum d is from the non-irradiated area with the identical polarized direction to spectrum c. Spectrum e is the dichroic spectrum, which is the difference between the net perpendicular absorption and the net parallel absorption after the subtraction of the absorption of the non-irradiated area. Absorption at 1722cm^{-1} and 1231cm^{-1} exhibits clear dichroism. Absorption at 1722cm^{-1} is from C=O stretching while that at 1231cm^{-1} is from C-C-C structure between the two phenylene and the methylene groups. C=O stretching exhibits strong response when the IR polarization direction is parallel to the sub-micrometer lines direction, while C-C-C absorption shows strong response when the IR polarization direction is perpendicular to the sub-micrometer lines direction. These results indicate that the C=O groups in polyimide show higher tendency to orient in the direction parallel to the sub-micrometer lines while the C-C-C linkages tend to orient in the direction perpendicular to the sub-micrometer lines, i.e., the molecular chains in LIPSS on polyimide surface orient in part in the direction perpendicular to the sub-micrometer lines. Figure 2 is model of this orientation. We think that this orientation is caused by the induction of the alignment of dipole moments in polyimide molecular chains by the directional electric field associated with the polarized pulsed laser beams during the melting and cooling process. The polar carbonyl groups are subjected to the orientation in the electric field direction.

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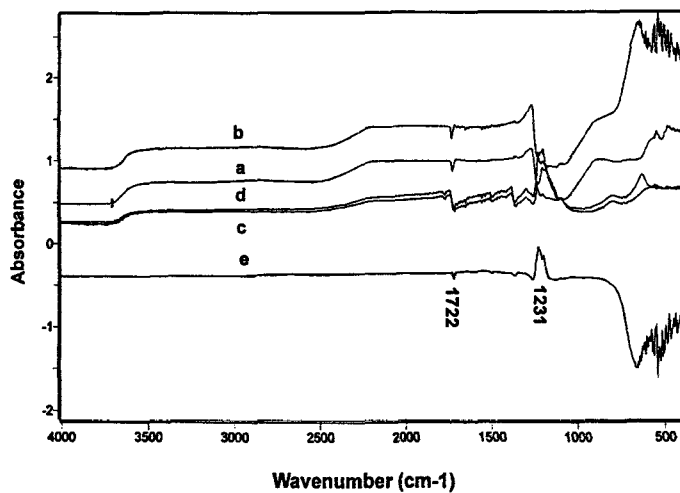


Fig.1 Polarized reflection FT-IR spectra of polyimide obtained after a Kramers-Kronig transformation. a.irradiated area (A_{\perp}), b.non-radiated area (B_{\perp}),c. irradiated areas (A_{\parallel}), d. non-radiated area (B_{\parallel}), (e) dichroic spectrum($\perp - \parallel$),after a and c are subtracted from b and d, respectively.

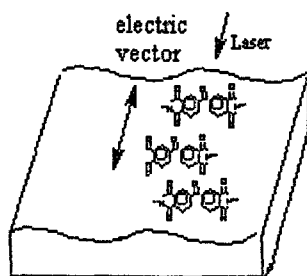


Fig.2 Molecular orientation pattern of polyimide