Poly(Ethylene Terephthalate) Crystallization as a Method for Microlithography

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Thermal lithography on poly(ethylene terephthalate) (PET) is carried out by inducing crystallization through selective exposure of amorphous films to infrared radiation. The obtained images can be smaller than the wavelength of the CO_2 laser light. This circumvention of the diffraction limit is accomplished by taking advantage of the non-linear temperature dependence of the crystallization rate. The optical marking process is reversible through simple melting of the crystalline images. The complementary process, selective melting of an initially crystalline film, can also be accomplished. The use as a heat sink of a mask which forms the image pattern is demonstrated.

INTRODUCTION

There is much interest in the utilization of polymers as media for the storage of digital and image information (1–6). The desirable features of an optical recording method include efficiency and controllability of the marking process, good contrast existing between the mark and the background, and, ideally, the potential for erasure and rewriting. Higher resolution recording techniques (i.e., sub-micron) have an obvious attraction. "Photon-mode" processes, wherein absorption of a single photon effects a three dimensional marking event, are the basis of much photoresist technology (7–9). The spatial resolution is diffraction limited, hence UV, x-ray and electron beam radiation are primarily used.

Lithography can also be accomplished with thermal processes. These rely on the application of heat to induce some change in the recording medium. If a single photon is insufficient to effect the marking event, images smaller than the wavelength of the employed radiation can be obtained. Non-linearity of the response can provide both acuity and stability of the images, as well as circumventing the diffraction limit on resolution. The resolution of a thermal process is governed by the localization of the heating and by thermal diffusion. It can be shown that for the thermal diffusivities of organic polymers (about 10^{-3} cm^2s^{-1}), thermal energy conferred to the specimen will remain within the directly heated area only for very short durations (<100 ns) (10). The expectation, therefore, is that high resolution can be achieved with a thermal process only when an intense heat source is used to stimulate a rapid event. Ablation (decomposition and volatilization) or deformation produced by laser irradiation (11–13), often of dye-containing polymers (14–24), is the most frequent application of thermal marking.

Radiation-induced crystallization is another means to record thermally on polymeric media, offering the potential for reversibility via melting and recrystallization. Application of this approach may involve the crystallization of small molecules dispersed within a polymeric matrix (25, 26). The use of an infrared laser to induce local crystallization of initially amorphous poly(phenylenesulfide) has been reported (27). Thermal smearing resulted in very coarse images (>10^2 μm) extending well beyond the directly irradiated areas of the polymer film. In a similar fashion, crystalline spots (>10^3 μm in size) were introduced into films of poly(ether ether ketone) (28). It was asserted therein that doping with dyes would be necessary to achieve good resolution. Aside from thermal diffusion effects, the inherent resolution limit of lithography via polymer crystallization is the finite crystallite size. This report describes the utilization of laser induced crystallization and melting to obtain high resolution optimal imaging in poly(ethylene terephthalate).

EXPERIMENTAL

The poly(ethylene terephthalate), PET (Goodyear 1006 with an intrinsic viscosity equal to 1.04 (29)) was molded under pressure for 5 minutes at 285°C, then quenched in ice water to produce 50 micron thick amorphous films. Additive-free amorphous PET film (IV = 0.75 dl/g) from Eastman Chemicals

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(Kingsport, TN) was also used and gave comparable results. The initial absence of crystallinity in the precursor films was assured by measurement of the density (1.335 g/cc (30)), and an absence of both sharp reflections in wide angle X-ray scattering and significant optical birefringence (the commercial film showed some birefringence).

The films were written on by exposure to typically a few hundred milliwatts of 10.6 μm wavelength infrared radiation from a continuous-wave Coherent Model 42 CO_2 laser. The beam profile was somewhat ill-defined and non-constant; hence, the laser powers quoted herein are useful primarily in a relative sense and are only approximate from an absolute standpoint. Imaging was typically achieved by using the beam to flood-illuminate a mask comprised of gold patterned on a GaAs wafer. The mask lay on top of the polymer film, whereby irradiation was selectively prevented by the reflecting metal. In some cases the laser light was reflected from an aluminum surface onto the PET film in order to produce an image.

RESULTS

Laser-Induced Crystallization

In order to be written on via induced crystallization a material must be non-crystalline but readily crystallizable, a requirement as restrictive as it is obvious. Below the crystalline melting point, a highly amorphous state is usually not achievable in highly crystallizable polymers. An exception to this behavior is found with poly(ethylene terephthalate) (31). PET can be quenched from above its melting point (T_m = 250°C) into the glassy state (T_g = 70°C) without crystallization; nevertheless, crystallinities of as much as 80% are attainable when the material is maintained at temperatures between T_g and T_m (32). The ability to control the onset and extent of crystallization affords the capability to introduce into amorphous films optically distinct crystalline regions, which can serve as the microlithographic images. Similar considerations appertain to previous attempts at lithography utilizing polyphenylene sulfide (27) and poly(ether ether ketone) (28).

In *Fig. 1* is shown a PET film with a crystalline line produced by heating the film with infrared radiation reflected from a piece of aluminum. The width of this image is roughly equal to the CO_2 laser wavelength (10.6 μm). The high birefringence associated with the crystal phase produces the image through crossed polarizing filters. The crystallites are sufficiently large for significant light scattering, and consequently the line is also directly visible as an opaque image. Since the crystalline regions possess an intense phosphorescence (tau relaxation 0.5 s (33)) relative to the amorphous regions, the former can also be viewed with ultraviolet light. All of these means of observing the image reveal excellent definition, although the best image contrast is achieved through crossed polarizers. No alteration of surface texture as a result of the marking process was seen in scanning electron micrographs, although transmission optical microscopy revealed some texture indicative of spherulites.

Fig. 1. Crystallization line produced in PET by reflection of CO_2 laser radiation (one watt) from an aluminum surface positioned near the 0.13 mm thick PET film. The irradiation time was 30 seconds. The apparent width of the line here is approximate due to blurring of the image by the optical microscope.

The localized crystallization is a consequence of radiation heating of the PET to its crystallization temperature. The laser-induced crystallinity was found via calorimetry measurements to have a peak melting temperature of 245°C (with an onset at 231°C). In polymers a crystalline phase formed at high temperature will exhibit a melting point that is proportional to the crystallization temperature (34); however, this dependence is not observed at lower crystallization temperatures. For the PET employed herein, it was determined from calorimetry experiments that over the ranges from 110° to 140°C and from 210° to 230°C, the melting point (= 245°C ± 1°) did not vary with crystallization temperature. Between 140° and 210°C isothermal crystallization could not be achieved in the calorimeter, while beyond 100° and 230°C the crystallization rate was too slow to obtain data. The invariance of the melting point to crystallization temperature when the latter is below 230°C does not allow a determination from the melting point of the temperature prevailing during-laser induced crystallization. In differential scanning calorimetry conducted at 20°C per minute, crystallization of the PET was observed to commence at 140°C; however, crystallinity became detectable in a microscope through cross-polarizers after several seconds at temperatures as low as 120°C. Presumably the laser-induced crystallization transpires within this temperature range.

The regions crystallized with the laser were highly crystalline, as indicated from calorimetry measurements by the absence of any crystallization exotherms and by melting endotherms that were as high as 47 J/g. X-ray diffraction from the marked regions of the film provided no indication of any orientation of the crystalline phase.

While the marking event transpired over about a 30 s period, the actual efficiency of the marking process could not be quantified with the present experimental apparatus. No effort was expended toward optimizing this efficiency. A typical dose-response curve for various laser powers is displayed in *Fig. 2.* The strong non-linearity of the process, whereby images become apparent only beyond a certain threshold, is a main advantage of thermal lithography.

The CO_2 laser radiation encompassed a range of wavelengths centered within the major band at 10.6 μm. This region of the spectrum lies within 30 wavenumbers of the central frequency of an intense absorption associated with the O-CH_2 stretching mode for the trans conformation of the ethylene units in PET (35, 36). Assuming an absorptivity of 1 cm^{-1} and a heat capacity equal to 1.33 J/g-deg (30), a one watt laser could introduce sufficient energy to heat a 1 square micron area of 50 μm thick PET to a temperature sufficient for rapid crystallization in milliseconds. This theoretical writing rate could be increased by using a single frequency laser tuned to a known vibrational transition and by employing thinner films. In reality, the efficiency of the process is limited by the finite crystallization rate of the polymer. Upon exposure to the infrared radiation, crystallization invariably occurred over a time scale of seconds, rather than milliseconds. The crystallization rate can be amplified through the use of nucleating agents or by orientation of the film.

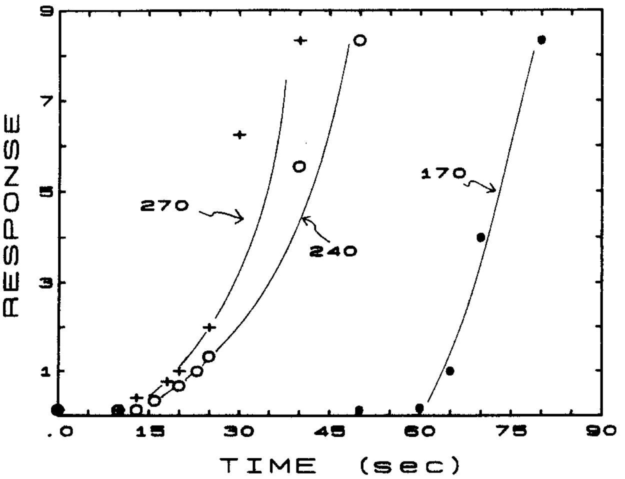

Fig. 2. The dose-response curve for PET amorphous film exposed to CO_2 laser of the indicated power (in m watts per cm^2). The nonlinearity allows marking at dimensions smaller than the wavelength of the radiation. The ordinate, expressed in arbitrary units, is proportional to the optical density measured for the crystalline mark. The limitation of the detector's response is being approached at the highest levels indicated herein.

From this perspective, melting is preferable to crystallization, and in fact images were obtained by selective melting of an initially completely crystalline film. Higher radiation intensities are necessary, however, so that more stringent control is required to employ melting as the lithographic mechanism. At sufficiently high laser powers, ablation of the PET commences (37).

Resolution

The ultimate resolution achievable by crystallization in a polymer film is limited by the size of the basic crystallite. In PET crystallized at low temperature, these can be very small (<.1 μm). *Prima facie* there is nothing surprising about thermal crystallization that happens to be accomplished using a laser; however, the spatial dimension of the image displayed in *Fig. 1* is extraordinary. A marking event that transpires over a 30 second time span is expected to be accompanied by diffusion of the heat be [illegible] few microns.

If the polymer film is approximated as a semi-infinite slab, the basic differential equation describing the flow of heat resulting from energy absorption is (38)

$$\delta^2 T/\delta x^2 - k^{-1}\partial T/\partial t = -A/K \qquad (1)$$

where T and t are temperature and time, respectively, A is the rate of heating (per unit volume per unit time), K the thermal conductivity, and k the thermal diffusivity. The radiation impingement is confined to a strip of width equal to $2L$, with $x = 0$ at the center of the irradiated area. From equation 1 the temperature rise within the irradiated region ($x < L$) is given by (38)

$$T_1 = kAt/K\{1 - 2i^2 erfc(L - x/2k^{1/2}t^{1/2}) - 2i^2 erfc(L + x/2k^{1/2}t^{1/2})\} \qquad (2)$$

while outside the directly heated region ($x > L$)

$$T_2 = kAt/K\{2i^2 erfc(x - L/2k^{1/2}t^{1/2}) - 2i^2 erfc(L + x/2k^{1/2}t^{1/2})\} \qquad (3)$$

where

$$i^n erfc(\Theta) = \int_\Theta^\infty i^{n-1} erfc(\varphi)d\varphi \qquad (4)$$

and

$$erfc(\Theta) = 1 - 2/\pi^{1/2}\int_0^\infty \exp(-\varphi^2)d\varphi \qquad (5)$$

The temperature elevation of the directly heated region relative to the neighboring, unirradiated material can be evaluated. For a given material the parameters K and k are fixed, while the resolution requirements determine L and x. The only primary variable is the irradiation time, with the largest temperature gradient (enabling the greatest definition and resolution of the imaging) achieved by decreasing the irradiation time. Using the appropriate values for PET (30):

$$K = 3.36 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ deg}^{-1}$$

$$k = 1.01 \times 10^{-1} \text{ cm}^2 \text{ s}^{-1}$$

the relative temperature rise can be calculated as a function of heating time for various resolutions. These results, displayed in *Fig. 3*, suggest that under adiabatic conditions the level of resolution obtained in *Fig. 1* is achievable only with the briefest of heating periods. In practice, however, the crystallization process had to be sustained for several seconds in order for observable markings to result. Much finer resolution is achieved than the limits deduced from elementary heat flow considerations which assume no heat losses.

While certain factors neglected in these calculations (e.g., divergence of the laser beam, and the temperature dependence of the polymer density) would serve to coarsen the image, a mitigating factor unaccounted for in *Eqs 1–3* is removal of heat by the film surroundings. Certainly cooling facilitates attainment of higher resolution. The principal point herein is that the resolution achieved with PET exceeds expectations based on calculations of this type, as well as prior studies with other polymers (27, 28).

Imaging was carried out on PET films on top of which had been placed a mask. The gold coating that defined the mask image was in contact with the polymer film, thus providing a heat sink. Using this technique, resolution half the wavelength of the employed radiation was achievable. Typical images obtained in this fashion are displayed in *Figs. 4a* and *4b*. With the mask present, higher power levels (*circa* 1.4 W/cm^2 and 4 W/cm^2, respectively) were necessary to induce crystallization, presumably in compensation for reflection losses at the interfaces (measured to be 30%) and heat conduction losses to the gold. The directly irradiated regions of the film may achieve a higher temperature with this procedure than when reflected light without a heat sink is used (as in *Fig. 1*). Consistent with a higher crystallization temperature, individual spherulites were apparent in the resulting crystalline images (*Fig. 4*).

The absence of a diffraction limitation on the resolution obtainable by a thermal process renders the

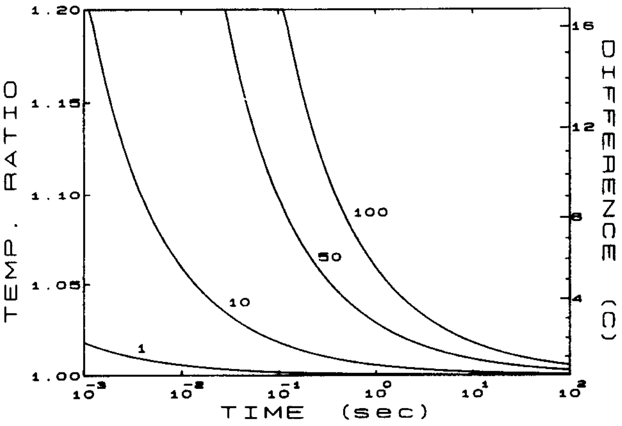

Fig. 3. The ratio of the temperature in the directly irradiated region to that in the outlying region, calculated from Eqs 2 and 3, respectively. These values are for distances from the boundary equal to 10% of the irradiated region's width (i.e., at x = 0.9L and x = 1.1L, where 2L is the width of the image and x = 0 at the centerline) for marks of various width, as denoted (in μm) along the curves. The corresponding temperature difference at a temperature of 120°C (the minimum temperature for rapid crystallization of the PET) is indicated on the right hand ordinate scale. These data suggest that, under adiabatic conditions, high resolution can only be achieved with a very fast marking process.

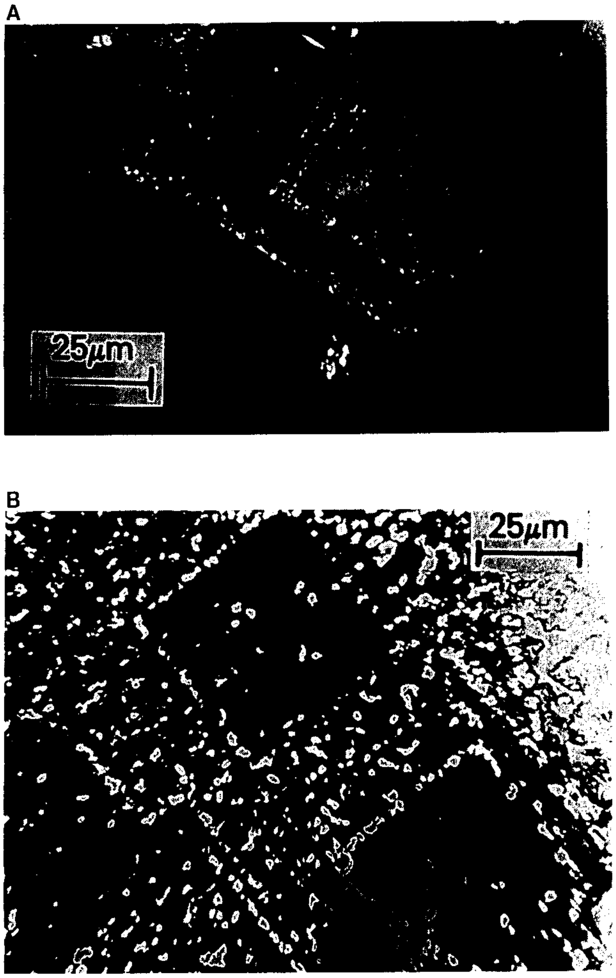

Fig. 4. (a) Amorphous PET film, 0.13 mm thick, was irradiated by flood illumination of a light field gold on GaAs mask for 20 s with 1.8 watts per cm² cw. The metallized side of the mask was in physical contact with the film. Images obtained on the PET film, identical in size to those on the mask, were in some regions as small as half the wavelength of the CO_2 laser emission. (b) Results from irradiation of 0.13 mm thick PET through a dark field mask for 30 s at 4.8 W/cm².

potential for imaging smaller than the wavelength of the radiation. Given the expected consequences of thermal diffusion, however, the high resolution of the PET laser writing process is unanticipated. This anomly is possibly related to the magnitude of the crystallization rate and its dependence on temperature. At the presumed low temperature of the laser writing, the extent of crystallization is controlled by spherulite growth rates, with facile nucleation due to the degree of super-cooling. The nuclei forming below 130°C require sufficient thickening before they become visible. It seems likely that the high resolution obtained with PET, which was not achievable with poly(phenylenesulfide) (27) or poly(ether ether ketone) (28), is related to the details of the temperature dependence of the spherulite growth rate. Further study of this aspect of the process is needed.

Reversibility

As mentioned above, melting of an initially crystalline PET film can also be used as a lithographic method. *Figure 5a* shows a crystalline film of PET on which the crystallization in a small region has been erased by exposure of the film to 8 watts of the CO_2 laser radiation for approximately 0.1 seconds. The resulting amorphous spot is transparent and non-birefringent, appearing dark against the birefringent crystalline background. A disordering process such as melting can in principle be accomplished significantly faster than the reverse operation of ordering the polymer segments into a crystalline phase. *Figure 5b* shows the "erased" spot after partial overwriting by exposure to less intense infrared light. The marking process appears to be completely reversible, with good clarity and definition maintained. The original uniformly white appearance of the film could be recovered consistently after repeated meltings and recrystallizations. No change in the surface texture of the films was evident in scanning electron micrographs after the multiple writings and erasures.

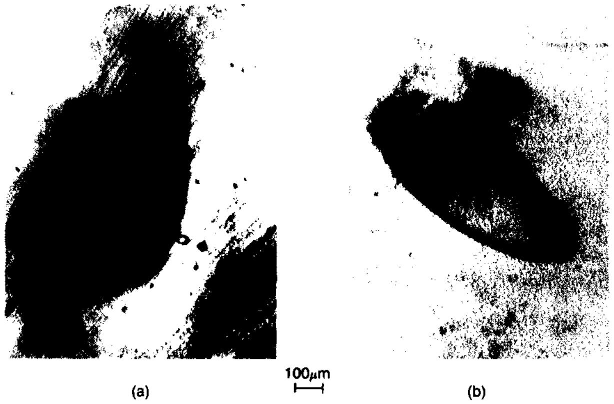

Fig. 5. (a) Amorphous spot produced by laser heating in a thermally crystallized PET film (as viewed through crossed polarizing filters). The dark area near the amorphous spot actually is blue in color through the polarizers. (b) The same spot after being partially overwritten through recrystallization via laser heating. After complete overwriting, the film is uniformly white, with no evidence of the original spot remaining.

SUMMARY

In anticipation of smearing by thermal diffusion, it is generally considered that photon processes are necessary for high resolution lithography. The present results with infra-red laser marking of PET, however, indicate that thermal processes have potential for high contrast, high resolution optical data storage applications. In addition to the possible reversibility of a writing mechanism based on thermally induced phase changes, the use of a polymer provides advantages with regard to the mechanical properties of the recording medium.

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