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OPTICAL DATA STORAGE AND METALLIZATION OF POLYMERS

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INTRODUCTION

The utilization of polymers as media for optical data storage offers many potential benefits and consequently has been widely explored. The imaging process should produce stable images which have high contrast (readily discernible differences between the image and the background) and high resolution (which allows higher storage density). There are two basic lithographic mechanisms - "photon mode" processes, wherein absorption of a single photon causes an incremental change in the image intensity and "thermal mode", which relies on heat to effect a detectable change in the storage medium. For a photon mode process the spatial resolution is diffraction limited; stray photons falling outside the desired area degrade the resolution and image quality. Hence, photon mode processes must rely on short wavelength radiation (ultraviolet, x-ray, and electron beam) to achieve high resolution. These approaches are employed in much photoresist technology.

An alternative writing mechanism is to use heat to effect physical or chemical changes. Thermal processes selectively raise the temperature to some critical point at which image formation commences. Because of their non-linearity (i.e., the extent of the storage medium's response is not simply proportional to the amount of input energy), thermal lithographic techniques are inherently high in both contrast and stability. Since a single photon provides insufficient energy to induce the marking event, thermal methods are not diffraction limited; consequently, there is no *a priori* reason to employ short wavelength radiation. However, it is anticipated that thermal diffusion away from the directly heated regions may smear the image, and therefore conventional thermal imaging methods are regarded as low resolution techniques.

This report describes new developments [1-6] in thermal imaging wherein high resolution lithography is accomplished without thermal smearing. The emphasis has been on the use of poly(ethylene terephthalate) film, which simultaneously serves as both the substrate and the data storage medium. Both physical and chemical changes can be induced by the application of heat and thereby serve as a mechanism for high resolution optical data storage in polymers. The extension of the technique to obtain high resolution selective metallization of poly(ethylene terephthalate) is also described.

EXPERIMENTAL

All polymers used in this study were obtained from commercial sources. Typical experiments were carried out using polymer sheets produces by extrusion through a slit die; for this reason surface quality and smoothness were mediocre. Heating was accomplished by exposing polymer films (typically 0.005" thick) to 10.6 μm infrared radiation from a Coherent Model 42 CO_2 laser. The output of the laser was at least two orders of magnitude more intense than necessary for the present experiments; hence, substantial attenuation of the beam was required. The intensity profile of the laser beam was nonuniform; thus, reliable estimates of actual power requirements were not possible.

To create an image, the laser beam flood illuminated a mask comprised of gold patterned on a GaAs wafer. The mask lay on top of the polymer, whereby radiation was selectively prevented from impinging on the polymer surface by reflection. In an alternative arrangement, an image was produced by reflecting the laser light from aluminum surfaces onto the films.

For the metallization experiments the film surface was covered with gold, aluminum, or copper prior to irradiation. Both vacuum deposition of the metal, as well as physical lamination of a metal foil against the polymer, were used. When using vacuum deposition, the polymer surface was uniformly covered with non-continuous islands of the metal. This allowed irradiation through the metal-covered layer in order to heat the polymer. For the films covered with a metal foil, the irradiation of course had to be done through the back side.

RESULTS

Laser Induced Crystallization.

Crystalline - amorphous phase transformations are a potential basis for thermal lithographic techniques. The conversion of an amorphous polymer to the crystalline state alters the optical properties, introducing opacity and birefringence, and thus producing an image. A number of studies have employed the crystallization of small molecule species residing on or in a polymeric matrix. The advantage of using a polymer as the active medium is that it can simultaneously serve as the substrate. The polymer film must be initially amorphous, but yet highly crystallizable, in order to produce a high contrast image. Few polymers crystallize extensively above room temperature, while still crystallizing sufficiently slowly to be obtainable in the amorphous state. Among these few poly(ethylene terephthalate) was determined to be unique in its ability to provide high resolution data storage.

Laser induced crystallization was accomplished in PET, for example, by heating the film over roughly 10 μm wide regions with infrared radiation reflected from a piece of aluminum. The localized heating causes the PET to be brought above its crystallization temperature. The crystalline image thus produced appears opaque (white) to the naked eye, while the high birefringence associated with the crystal phase produces a very distinct image when viewed through crossed polarizing filters. The imaging is not accompanied by any alteration of the surface topography of the films. The crystalline images produced by the irradiation were stable to 245°C, at which point melting commences.

In an alternative arrangement a mask was used to define the image. The gold coating comprising the mask image was for convenience placed in physical contact with the polymer film. This arrangement reduces the temperature of the regions shielded from the radiation, since the gold functions as a heat sink. By this method high resolution (*circa* one micron) images, with both good contrast and edge acuity, were routinely obtained. Unfortunately the available masks did not contain images any smaller than this, so that the ultimate limits on the resolution could not be assessed.

The crystalline images produced by the infrared radiation extend completely through the film thickness. There was no evidence of any gradient or accumulation of crystallinity toward the front (irradiated) side of the films. With the mask in contact with the film, higher power levels were necessary to induce crystallization, presumably to compensate for reflection losses at the interfaces (measured to be 30%) and heat conduction to the gold.

The efficiency of the marking process can not be quantified with the present experimental apparatus, primarily because of the non-uniformity of the laser intensity profile. Dose-response curves exhibit the non-linearity expected for a thermal method. This non-linearity contributes to the contrast and edge acuity achievable. Non-linearity of the response is a principle attraction of thermal imaging processes.

The resolution of a thermal process is expected to be governed by the diffusion of heat away from the directly irradiated regions. Modeling of the heat flow in these experiments has been carried out; the results indicate that the material is not in thermal equilibrium as the lithography transpires. This is the reason for the absence of image smearing by thermal diffusion.

An obvious advantage of using a physical change such as crystallization as the writing mechanism is that such a process is reversible, potentially allowing for multiple read/write cycles. This reversibility has in fact been demonstrated. Thermally crystallized images could be erased by reapplication of the laser radiation. The erasure is reversible, with the crystalline image reproduced by exposure again to an appropriate level of the laser radiation. The crystallization and melting can be successively executed by simple adjustment in the intensity or duration of the irradiation.

An initially crystalline, and thus opaque, PET film can be written on by using the laser to locally melt the polymer. A disordering process such as melting can be accomplished significantly faster than the reverse operation of ordering the polymer segments into a crystalline phase; therefore, in principle induced melting of a crystalline film is potentially a faster marking process than crystallization of amorphous polymer.

Ablation

Although lacking reversibility, a chemical change induced by heat can also serve as a lithographic method. When the PET is exposed to higher levels of the infrared radiation, a different process than crystallization occurs. The more intense irradiation promotes significant chemical bond rupture in the PET, with the byproducts of this decomposition expelled as fragments or vapor. This ablation at the PET surface creates a three dimensional image. These images, since they result from a chemical change, are not erasable. The dimensions of the images obtained by ablation were less than 1 μm, with exceptional edge acuity. Although marks slightly less than 1 μm in width were also produced, the masks used to image the laser light have defects at this scale. The ultimate resolution achievable with this technique can not be determined with the presently available equipment.

The depth of the laser etching is proportional to the irradiation time. A correspondence was also found between this depth and the weight loss measured for the films. Similar to the radiation induced crystallization, there is minimal thermal diffusion, as evidenced by the steepness of the walls of the troughs produced by the laser etching. The existence of a threshold for thermal ablation, below which there is no change in the film's appearance, facilitates attainment of high resolution imaging.

The use of thermal ablation as an imaging method was also carried out with several other polymers. High resolution images could be obtained with polycarbonate and poly(ether ether ketone). Using polysulphone, poly(methyl methacrylate), and polychlorotrifluoroethylene, some deformation transpired upon exposure to the laser radiation. Images were achieved in the latter two materials, although an optimal process might involve radiation of a different wavelength. The ablation of two thermosetting polymers, poly(cyanurate) of bisphenol A dicyanante and Epon 28 epoxy was accompanied by some charring of the film. The efficiency and imaging quality varied widely, with the best overall results achieved with PET.

Metallization

It is known that PET will adhere to metals, and particularly to metal oxides, when raised above its melting point while in contact with the metal. Actually, for amorphous PET it is only necessary to heat the polymer above the glass transition temperature for bond formation to transpire. Localized metallization of PET can therefore be effected by its irradiation through a mask. The underside of the PET is maintained in contact with the metal, for example in the form of a thin film or a deposited layer, during exposure to the infrared light. After irradiation the metal in the unexposed regions is readily brushed or stripped away, leaving behind a metallized pattern. Alternately if the deposited layer is discontinuous, the irradiation can be done through the metal layer itself. The bonding to PET is superior for copper and aluminum than for gold. Attempts to remove the former two metals invariably resulted in cohesive failure of the polymer. In all cases the adhesion of the metal to the polymer film passed a standard "Scotch tape test". All indications are that the metallization process is governed by the same factors as the lithography processes described above. Hence, it is expected that the achievable resolution of the film metallization should be better than one micron.

SUMMARY

In anticipation of smearing by thermal diffusion, it is generally believed that photon processes are necessary for high resolution lithography. The present results with infra-red laser irradiation of PET, however, indicate that thermal methods have potential for high resolution optical data storage applications. Both radiation induced crystallization and ablation have been demonstrated to produce high resolution optical images in the polymer film. The two processes prevail at different levels of radiation intensity. While only the former process is reversible, ablation may offer advantages with regard to contrast and resolution. Although the resolution limits of these methods are presently unknown, one micron marking has been routinely demonstrated. These techniques can be readily extended to achieve metallization of polymer films, with the attributes of selectivity and high resolution retained. Particularly noteworthy is the simple one-step nature of the metallization process. No chemical reagents or extraneous washes are necessary.

A familiar commercial application of optical data storage is the compact disk (CD). Information takes the form of a series of pits in the surface of a polymer film, each depression having the same depth but being of different lengths and separations. The variation in the reflection of a light beam as it traverses alternately the smooth CD surface and the pits provides the data transcription. The pits in a CD are created by a stamping process; a master engraves onto the polymer substrate a negative relief. The lithographic methods described herein have the potential to be a "drop-in" replacement for the manufacture of CD's and similar technologies. The non-contacting aspect of the present laser marking techniques, however, will enable one to circumvent the manufacturing limitations of a physical stamping process.

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REFERENCES

1. M.F. Sonnenschein, A.M. Kotliar, and C.M. Roland, Poly. Eng. Sci. 30, 1165 (1990).

2. M.F. Sonnenschein and C.M. Roland, Appl. Phys. Lett. 57, 425 (1990).

3. C.M. Roland, J.P. Armistead and M.F. Sonnenschein in Thermal Marking of Amorphous Poly(ethylene terephthalate); Shalaby, S.; Clough, R., Eds.; ACS Symposium Series; Amer. Chem. Soc.: Washington, D.C., 1991.

4. M.F. Sonnenschein and C.M. Roland, U.S. Patent #4,975,358, 1990.

5. M.F. Sonnenschein and C.M. Roland, U.S. Patent #5,043,251, 1991.

RELATED LITERATURE

1. The Effects of Radiation on High-Technology Polymers, Reichmanis, E.; O'Donnell, J., Eds.; ACS Symposium Series; Amer. Chem. Soc.; Washington, D.C., 1989; Vol. 381.

2. Symposium on Polymers in Microlithography; Poly. Mater. Sci. Eng., 1989, 60, 40.

3. Reichmanis, E.; Thompson, L.F. Chem. Rev. 1989, 89, 1273.

4. Electronic and Photonic Applications of Polymers; Bowden, M.J.; Turner, S.R., Eds.; Advances in Chemistry; Amer. Chem. Soc.: Washington, D.C., 1988; Vol. 218.

5. Symposium on Polymer in Information Storage Technology; Polymer Preprints, 1988, 29, 195.

6. Polymers for High Technology - Electronics and Photonics, Bowden, M.J.; Turner, S.R., Eds.; ACS Symposium Series; Amer. Chem. Soc.; Washington, D.C., 1987; Vol. 346.

7. M.D. Croucher and M.A. Hopper, Chemtech 1987, 17, 426.