Optical Recording by a 823-nm GaAlAs Laser, Based on Stretched-Polymer Birefringence Relaxation

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Synopsis

A ~ 5-μm-thick stretched sheet of a vinyl chloride–vinylidene chloride copolymer containing a suitable polymethine dye providing an optical density of 1–2 at 823 nm has been used to record ~3-μm-diameter relaxed spots, produced with pulses of 250 μs or longer from a 5-mW GaAlAs laser operating at 823 nm. The spots have been observed under polarizing microscope. It is proposed that this demonstrates a principle that could be used for recording and retrieval of information by a laser beam, using a stretched polymer as the storage medium.

INTRODUCTION

In recent years, the use of polymers as an integral part of the optical information storage medium has attracted much attention. Generally, they are used as polymer–dye composites where the dye assists in absorbing the writing laser beam. A variety of mechanisms used for writing have employed such composites.[1-5] Recently, we published[6] a theoretical analysis and a few preliminary experimental observations on a new write–read concept: thermal relaxation of birefringence in stretched polymer/dye systems.

The principle is very simple: The writing laser beam causes local heating and thus partial or complete relaxation of birefringence in a partially oriented polymer film. One might hope that the power levels of the laser beam required to cause such relaxation would be lower than those required to cause melting or ablation. The polarization state of a readout beam will be different after passage through a recorded area and through an unrecorded area, because they differ in their birefringence. The change in polarization can be detected in a transmission or reflection mode.

The transmission mode operation is particularly easy to follow.[6] Suppose, for instance, that the birefringence of the stretched polymer is such that it acts as a half-wave plate. Then, the polymer will produce a light field when placed between crossed polarizers at an angle of 45° between the polarizer axes and the stretching direction. However, a relaxed area of the polymer will have no effect on the polarization state of the light and will appear dark between the crossed polarizers.

Presently, we report a demonstration of the feasibility of the concept. We have recorded on a dye–polymer system using a 5-mW GaAlAs laser and detected the recorded spots visually in the transmission mode under a polarizing microscope.

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EXPERIMENTAL

Poly(vinyl chloride) (Aldrich, high mol. wt.) and a vinylidene chloride–vinyl chloride copolymer (W.R. Grace and Co., Type 930) were investigated. Films of the two polymers were cast from 2–3% solutions of the polymer in 2-butanone and 1,1,2-trichlorethane, respectively, containing less than 5% by weight of the dye. They were less than 10 μm thick. They were annealed at 50°C for 2 min and carefully stretched up to 150–300% of the original length at this temperature by means of a mechanical stretcher. The stretched films were less than 5 μm thick and were sufficiently birefiringent to be seen clearly as a light field between crossed polarizers under a microscope. The thickness of the films was determined by weighing a known area of the film, using the published[7] densities of the two polymers.

The polymethine dyes employed were 1,1,5,5-tetrakis(*p*-dimethylaminophenyl)2,4-pentadien-1-ol perchlorate (λ_{max} at 820 nm, 630 nm) and 1,5-di(*p*-dimethylaminophenyl)-1,5-diphenyl-2,4-pentadien-1-ol perchlorate (λ_{max} at 823 nm, 525 nm), synthesized according to published procedures.[8] These dyes had decadic molar extinction coefficients in excess of 100,000 at the 823-nm wavelength of the GaAlAs laser and were very soluble in the polymers used. In the stretched polymers, they showed a weak dichroism (dichroic ratio ~ 1.2 at 823 nm). The combination of very high extinction coefficients and very high solubility permitted us to attain high near-infrared optical densities in the thin film easily. The films we used had absorbances of 1.0–2.0 at 823 nm, and about 0.5–1.0 at the visible peak, but were nearly transparent at shorter wavelengths in the visible. Even thinner films could easily be used with these dyes, and most of the writing laser beam energy would still be adsorbed.

The pulsed-diode laser recording system is shown in Figure 1. A CW laser diode (RCA C86014E) was operated in a pulsed mode, using the current-amplified TTL (transistor-transistor logic) pulses of a variable-length pulse generator (Global Industries 4001). The emission wavelength was 823 nm, and the light was linearly polarized to 87%. The elliptical beam was collimated and focused, using special laser diode optics (Melles Griot 06 GLC 002). The depth of focus was about 15 μm. The spot image was elliptical, and its size was approximately 4 × 1 μm. Detection of the transmitted light was accomplished by means of a photodiode (United Detector Technology PIN 125) operated in the photoconductive mode with a response time of 10 μs and observed on a 60-MHz oscilloscope (Tektronics 2215). A dichroic sheet polarizer (Melles Griot 03 FPG 001) was placed before the detector at 90° to the inherent polarization of the laser diode. Transmission through these crossed polarizers was greater than was originally hoped for, because

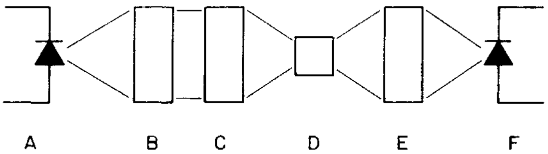

Fig. 1. (A) Laser diode; (B, C) Collimation and focusing optics; (D) sample held on an *x*-*y*-*z* translation stage; (E) dichroic sheet polarizer; (F) photodiode detector.

of the impure state of polarization of the laser doide and the inefficiency of the sheet polarizer at the wavelength of the laser diode. This can be readily improved by the use of high-quality polarizers.

This arrangement produced 5-mW pulses of time durations between 10 μs and about 25 ms, limited by the cooling requirements of the laser diode.

Sample position was controlled in three mutually orthogonal directions. The axis colinear with the laser light-propagation axis was controlled within 1 μm, and the perpendicular axes within 0.1 μm (Newport Research Corporation 420-0.5, Oriel 18320 and 18009). Overall control was accomplished with a custom-interfaced microcomputer (Franklin Ace 1000), making possible the production of the repetitive patterns necessary for survey work.

The recorded dots were examined and photographed under a polarizing optical microscope (Nikon Biophot).

RESULTS AND DISCUSSION

Poly(vinyl chloride) Film

Marking could be produced down to an exposure time of 2.5 ms. Shorter pulses produced no marks, which makes this polymer sheet unsuitable for practical use. All of the marks consisted of a central hole surrounded by a dark band. The size of the smallest hole, as seen through parallel polarizers, was 2.4 μm. The size of the marks increased with increased exposure time.

The sharply defined minimum in the required exposure time suggests that the minimum amount of heat generated during an exposure that is sufficient to burn a hole is not much larger and may even be smaller than the minimum amount required to relax the birefringence in this polymer. The rate of relaxation caused by shrinkage and redistribution of originally partially oriented polymer chains, which takes place when a stretched polymer is heated, is characteristic of the polymer. It appeared probable that a material that can shrink to a higher degree at a similar temperature could produce a noticeable relaxation of a birefringence already under conditions under which holes are not produced in poly(vinyl chloride). A survey of the properties of various linear polymers[9] revealed that the copolymer of vinylidene chloride and vinyl chloride has a higher degree of shrinkage compared to any other readily available commercial polymer.

Copolymer of Vinylidene Chloride and Vinyl Chloride

A copolymer of polyvinylidene chloride and polyvinyl chloride was then used to investigate the marking process. Marking with the laser beam resulted in holes for exposure times of 750 μs or longer whereas no holes were burned at 500-μs or 250-μs exposure times. We were pleased to note that the recording with these shorter pulses still produced noticeable marks. When viewed between parallel polarizers under a microscope, these dots had a central lighter region (~3.4 μm in diameter for 500-μs pulses and ~2.7 μm in diameter for 250-μs pulses) surrounded by a dark ring and appeared lighter than the rest of the polymer. Under these conditions the holes that were burned with longer exposures appeared bright within a dark band. Between crossed polarizers, all marks appeared dark on a light background (Fig. 2). For the marks obtained with 500-μs and 250-μs pulses, the contrast between marked and unmarked areas was better when viewed between perpendicular polarizers than between parallel polarizers. The spots appeared identical when viewed from either side of the film. The above is the theoretically expected[6] behavior for the central part of the recorded spot.

Pulses of 100-μs duration, and less, produced no detectable marks at all. In a separate experiment, the laser beam intensity was varied while the pulse length was kept constant at 10 ms. At 5-mW laser power, a hole was produced; at 3.5-mW laser power, marking by birefringence relaxation occurred; whereas at lower powers, no marking at all was detectable.

The threshold exposure time for obtaining birefringence relaxation was found to depend on the thickness of the films used, but no quantitative evaluation was performed. The parameter that limited the thickness of the sheets used in our experiments was the degree of birefringence that could be induced on stretching. As thickness of the film decreases, the birefringence induced upon stretching also decreases and so eventually it became difficult to identify the marked regions by inspection under a polarizing microscope although they probably still could be read by a laser beam if a high-quality set of polarizers were used. The attainable extent of stretching, which codetermines the birefringence induced, also depends on the quality and uniformity of the film. It is likely that with more sophisticated techniques of making uniform films, higher birefringence could be achieved at lower thickness.

There seems to be little doubt that there will always be exposure times

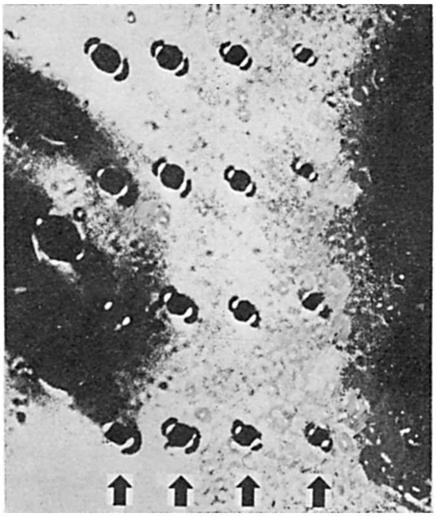

Fig. 2. A dyed stretched sheet of vinyl chloride–vinylidene chloride copolymer (2.5-μ thick) viewed between crossed polarizers. Four series of dark dots 25 μm apart (indicated by arrows) have been recorded by pulses of focused 823-nm GaAlAs diode laser light (5 mW). From left to right, the pulse lengths were 1000, 750, 500 and 250 μ sec. The larger black spots on the sides are holes in the sheets produced by longer pulses and are used as markers for microscopy. The irregularly placed gray dots are due to dust particles.

sufficiently short, and light intensities sufficiently weak to produce no noticeable recording. This threshold type of behavior is desirable for the readout process, as the reading beam will then not cause any recording and damage to the material.

The stretched sheets used in our experiments appear to remain birefringent indefinitely at room temperature, at least over a period of months. Other stretched-polymer sheets with which we worked in the past, primarily polyethylene, remained stretched for many years, and we expect that this will also be true of those used presently.

CONCLUSIONS

Optical recording with pulses of a focused beam of a 5-mW GaAlAs laser (823 nm) has been demonstrated, based on birefringence relaxation of spots on a stretched sheet of a commercially available kitchen-wrap polymer. A definite writing threshold has been found, both with respect to pulse length and beam intensity.

In order to make the process practical, pulse lengths shorter than the presently demonstrated 250-μs limit are required. It appears likely that they would work on a more fully optimized system, (a) employing thinner stretched films of a customized polymer produced in a dust-free environment and under better controlled conditions, and possibly kept at a slightly elevated rather than room temperature, (b) employing better optics producing a more strongly focused beam and possibly using a higher power laser, and (c) replacing viewing under a polarizing microscope by an actual laser beam readout.

Among the polymer properties, the most important are high affinity for the dye, high and uniform stretchability, high birefringence, high mechanical stability, low heat conductivity, fast relaxation rate at high temperatures, and zero relaxation rate at room temperature. For short enough pulses, the time available for birefringence relaxation within the hot spot will be determined by heat conduction to the cool environment and not by the length of the laser pulse itself.

The variety of possibilities offered by polymer and copolymer choice, polymer blending and doping, and control over molecular weight, makes us optimistic that a practically useful system can be developed.

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