Laser Marking of Microporous Films

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Synopsis

The potential for microporous films as optical recording media is explored in this report. Irradiation of metallized films of microporous polypropylene and polyethylene with a HeNe laser produced marks having high contrast and which could be read without the aid of polarizing optics. The novel marking process involves melting, collapse of the microporous structure, and thinning of the film as the built-in strain relaxes.

INTRODUCTION

The development of media for optical recording has been a topic of active investigation for the past several years. The formation of pits or bubbles, phase transitions, alloy formation, and photochemical rearrangements are among the phenomena which have been used to produce detectable changes in both inorganic and organic materials when acted upon by focused laser irradiation.[1,2] For each of these approaches it is desirable that there be a threshold for writing and that there be high contrast between the mark and the background.

Almost universally, optical recording media consist of a thin film coated either from solution or by vapor deposition onto a substrate. The active layer absorbs light and undergoes a detectable physical or chemical change while the substrate provides mechanical support. The use of plastic films for optical media has received less attention. These have the potential of providing flexible media which may not require a substrate layer and which themselves participate in the marking process. Recently, Murthy and co-workers demonstrated the concept of laser marking by birefringence relaxation in stretched polymer films.[3] Thus, when stretched films of vinyl chloride-vinylidene chloride copolymer containing a polymethine dye were irradiated with a diode laser, local heating resulted in the loss of birefringence built into the film during stretching. Consequently, a clearly detectable mark could be seen with polarizing optics.

Microporous membranes offer another possibility for laser encoding of information. Such films are articles of commerce and find use in separations, controlled drug release, oxygen exchange, and battery separators. A recent publication describes the three-dimensional structure of one such microporous membrane, Celgard® 2500 as determined by electron microscopy.[4] As a result of extrusion, annealing, and stretching of the polyolefin, a microporous structure is formed with elliptical pores having their major axis parallel to the machine direction. It was felt that if such a film were to be coated with a

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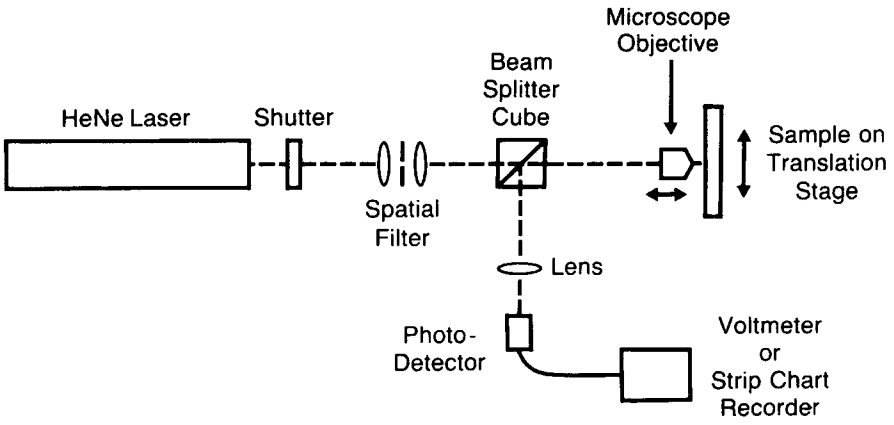


Fig. 1. Optical train used in marking studies.

suitable light-absorbing layer, then localized heating by a focused laser beam would result in collapse of the microporous structure or thinning of the film as the built-in strain is relieved. Either or both of these effects should result in a change in surface topography which is detectable without the aid of polarizing optics. This paper presents the results of studies which explore this possibility.

EXPERIMENTAL

The optical train used for the laser-marking experiments is shown in Figure 1. The laser was from Newport Research Corp. and rated at 5 mW, although actual output was closer to 8 mW. The maximum power which could be delivered to the sample was 6.3 mW. A mechanical shutter was used to control exposure times, the shortest available being 2 ms. The laser beam, on emerging from the spatial filter, had a diameter of 9 mm and was focused onto the sample by means of a 20X/0.54NA microscope objective which was mounted on a focusing collar. Samples of coated microporous media were taped to microscope slides and fastened to a motorized translation stage. The laser power at the sample plane was measured with a Scientech 362 power meter. Part of the light reflected from the sample was deflected by a nonpolarizing beam splitter cube onto a photodetector (Photamp Inc.) and the signal monitored with either a voltmeter or strip chart recorder.

RESULTS AND DISCUSSION

In a preliminary experiment, a sample of Celgard 2400 microporous polypropylene film was sputter-coated with 300Å of nickel and placed in contact with a mask having a 5-mm aperture. When irradiated with an unfocused incoherent infrared source (0.68 W/cm^2), the sample was marked in less than one second. The irradiated spot appeared dark in reflected light and bright when illuminated from behind. Rough measurements showed that the reflectance of the marked area was about 7% that of the nonirradiated background, while the transmittance of the irradiated spot had increased by a factor of 9. No marking occurred when a sample of film without the nickel coating was treated in the same fashion.

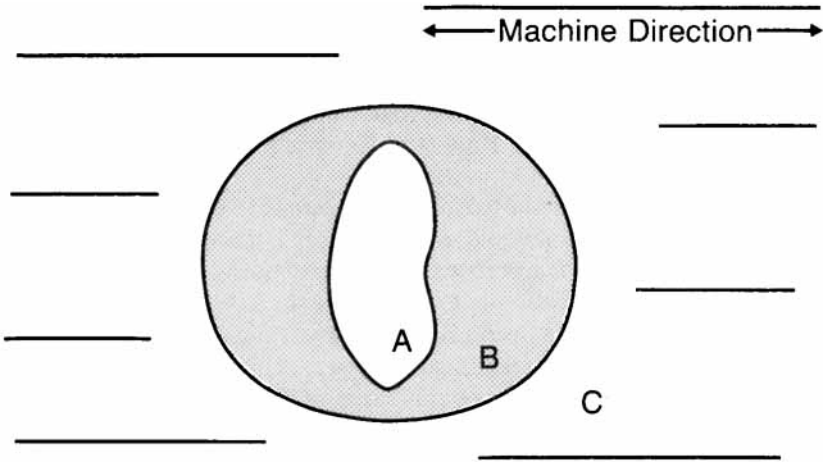
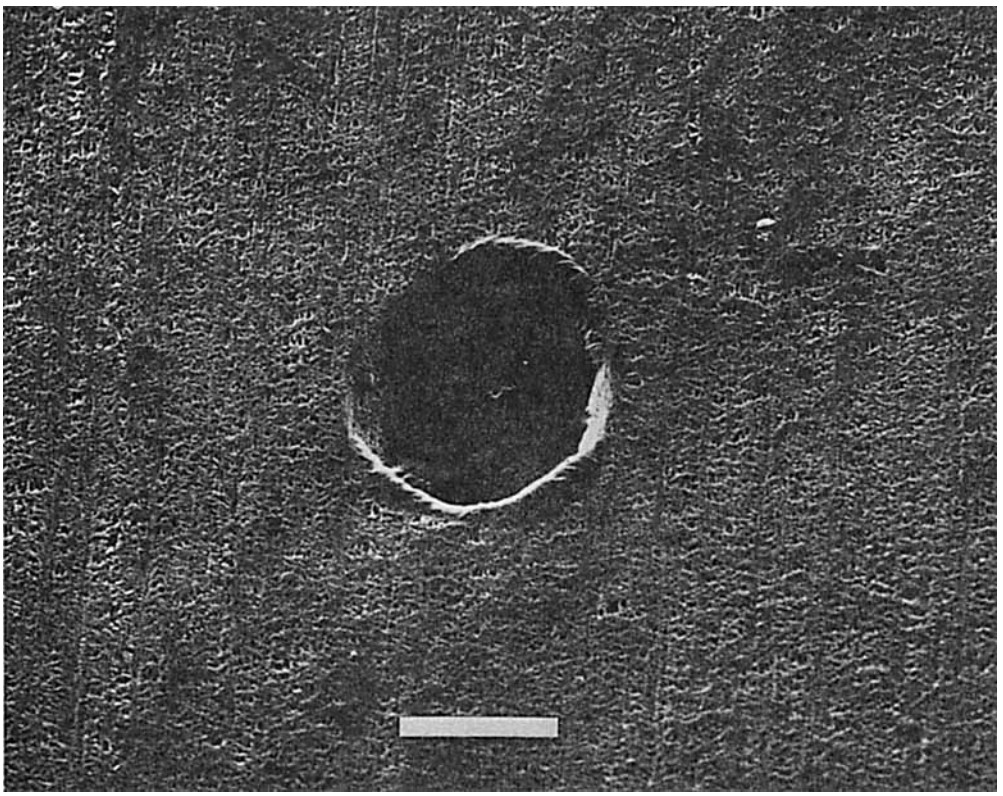


Fig. 2. Schematic of mark as seen by optical microscopy. (a) Transparent zone; (b) Translucent area: (c) Unmarked background.



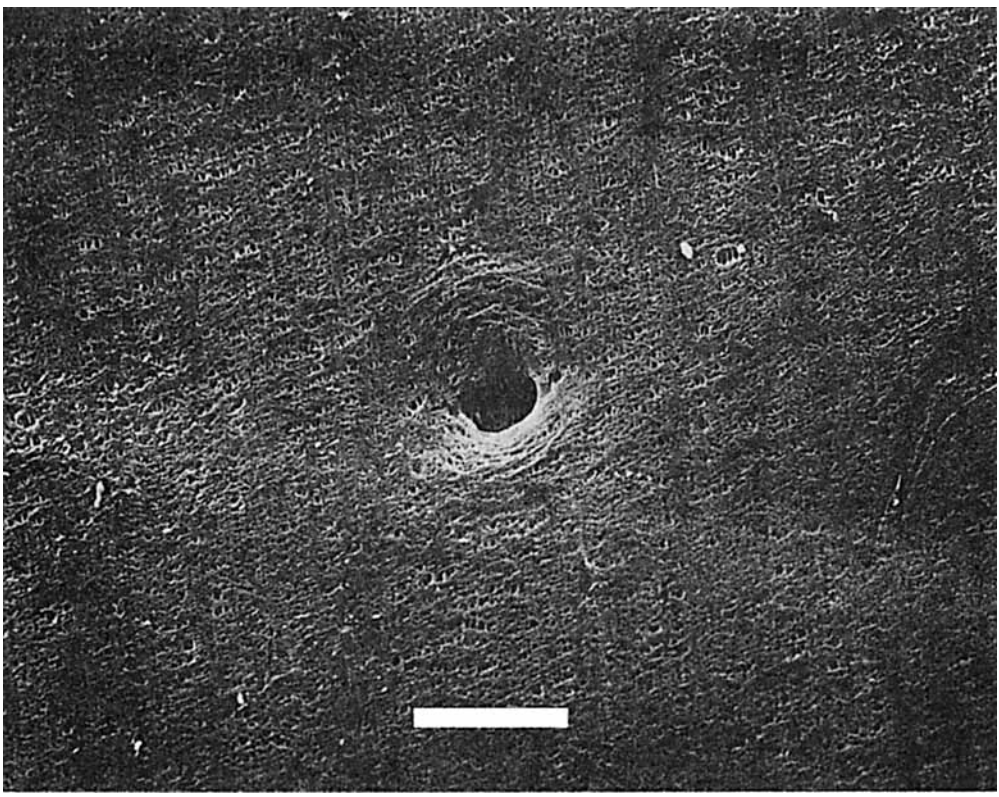
(a)

Fig. 3. SEM micrographs of marks formed in irradiated microporous polyethylene. Machine direction is vertical. Bars represent 20 μm. (a) 30 s exposure at 6.3 mW. (b) 2 ms exposure at 6.3 mW.

It was possible to produce smaller marks by focusing the light from a HeNe laser through a 20x microscope objective onto the coated side of the microporous film. Besides nickel, coatings of sputtered aluminum and palladium-gold (1 : 1) also served to capture the laser light and trigger the marking process, as did a dye/polymer layer (Oil Blue N in Emerez 1540) coated from 2-propanol solution.

Examination of the irradiated films by optical microscopy showed that of the metals tried, palladium-gold was the most adherent and resulted in the best defined marks. By transmitted light these marks revealed themselves as transparent spots, typically with an aspect ratio of about 1.6. The long dimensions decreased with decreasing exposure time, down to 10 μm at 250 ms exposure. The long transparent features were surrounded by slightly larger translucent marks which were roughly circular in appearance.

Since the Celgard film is made from polypropylene (softening point 165°C), it was of interest to see whether shorter marking times were possible with other materials. To this end, samples of an experimental variant of microporous polyethylene (softening point 130°C) designated K851, were also examined. Indeed, when a sample of this material was sputter-coated with 300 Å of PdAu and irradiated with a focused 5 mW HeNe laser beam, it was possible



(b)

Fig. 3. (*Continued from the previous page.*)

to produce marks with 2 ms pulses, the shortest exposure time available with our mechanical shutter.

The marks formed in irradiated K851 had the same general appearance as those formed in Celgard 2400, namely a transparent central feature (aspect ratio about 2.2) surrounded by an almost circular (aspect ratio 1.1) translucent area. This is illustrated in Figure 2. Closer examination of several irradiated samples showed that the short axis of the transparent feature and the long axis of the translucent feature were always oriented in the machine (stretched) direction of the film, regardless of the sample's orientation to the beam during laser irradiation. Further details of the marking process may be seen in the scanning electron microscopy (SEM) micrographs shown in Figure 3. The mark formed at 30 s exposure time is seen as a depression surrounded by rims. The aspect ratio of the depression is 1.2, with the long axis in the machine direction. The other SEM micrograph is of a partially developed mark with a completely melted feature whose long axis is in the transverse direction. This feature is surrounded by evidence of partial melting and of shrinkage in the machine direction.

Thus, as the microporous film is heated by the laser beam, it melts at the center of the focused spot where the beam is most intense and the opaque microporous structure is lost. At the same time, the surrounding area is heated sufficiently to permit relaxation of the stretched film. When this occurs, softened polymer and metal coating are pulled away from the hottest zone. The result is a transparent area of metal-free molten polymer surrounded by a translucent area which has been thinned by softening and contraction of the polymer.

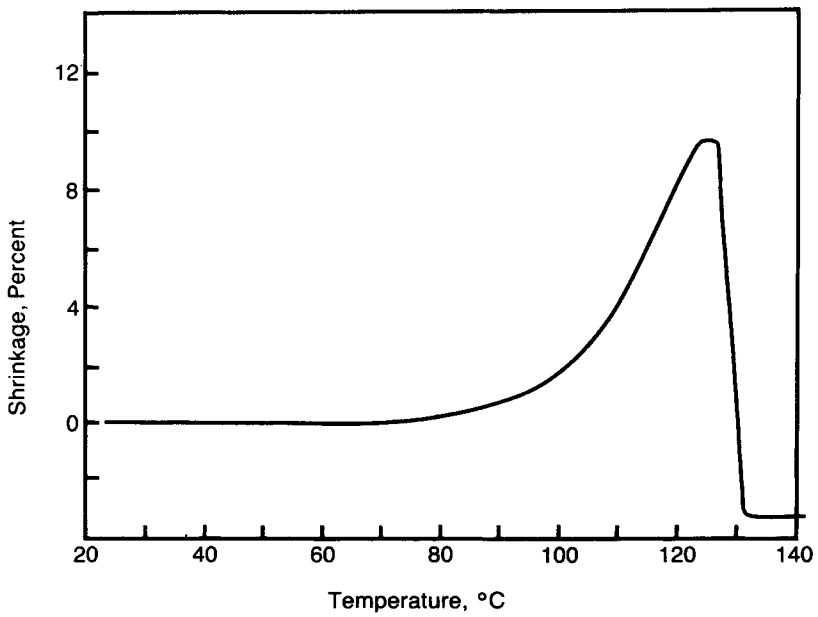


Fig. 4. Trace of fiber TMA run on sample of Microporous polyethylene coated with 300 Å PdAu.

Thermal analysis provided further insight into the marking process. Figure 4 shows the trace of a thermomechanical analysis on a sample of K851 coated with 300 Å of PdAu. The sample was mounted in the machine direction under a 1 g load. As seen from the figure, the sample began shrinking at about 68°C and continued doing so up to a maximum shrinkage of 9.7% which was reached at 125°C. At this temperature melting began and the sample length increased.

Differential scanning calorimetry (DSC) on an identical sample showed that 63.6 cal/g were absorbed in raising the temperature from 30 to 125°C and 42.1 cal/g in the interval 125 to 140°C. Since the coated film had an areal density of 1.20×10^{-3} g/cm^2, this corresponds to 0.32 J/cm^2 required to take the film from room temperature to greatest shrinkage before melting occurs. This value may be compared to a marking sensitivity on the order of 10^{-2} J/cm^2 reported for various thin film optical recording media.[5]

While it was not possible to obtain data at exposure times shorter than 2 ms with the apparatus available for these experiments, it was possible to reduce the laser power incident on the sample and thus get an idea of the threshold for marking. When this was done, it was found the lowest power at which a translucent mark formed (partial collapse of microporous structure) was at 1.4 mW with 15 s exposure, specifically 21 mJ energy. The laser energy for complete melting (transparent spot) was higher and depended markedly on the incident power. Thus, at 2.2 mW the shortest time for marking was 15 s, corresponding to 33 mJ, while at 2.0 mW the shortest marking time was 3 min corresponding to 360 mJ. The conditions described here are far from adiabatic and the best estimate for a marking threshold is that it is less than 12.6 μJ, corresponding to marking at 6.3 mW and 2 ms. It is likely that a more tightly focused beam and the use of a more powerful laser at shorter exposure times would lead to a lower threshold energy for marking than that indicated here.

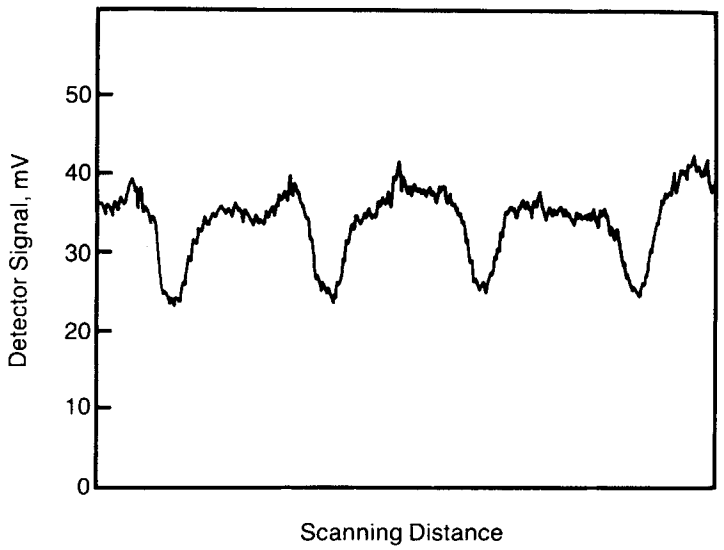


Fig. 5. Read signal scanning four laser-marked spots in metallized microporous polyethylene. The fine structure in the background is due to the micropores at the surface of the film.

It was of interest to examine the optical signal contrast which might be obtained upon marking. For this purpose contrast is defined by the quantity $(R_i - R_f)/(R_i + R_f)$ where R_i and R_f are the reflected light intensities before and after marking. In Figure 5 is shown a typical trace obtained from marks made at 5 mW power and 1 s exposure and read back with 1 mW power. The marks are clearly seen as negative-going peaks of reduced reflectivity. In addition to these, the background shows fine structure which is due to the surface of the microporous film. The contrast in this example is 0.23 and varied with the exposure time. With 6.3 mW power, the highest contrast obtained was 0.35 at 60 s exposure and decreased to 0.05 at 2 ms exposure.

CONCLUSION

The potential for microporous films as optical recording media has been demonstrated. These materials show a threshold for marking which involves both melting and shrinkage of the stretched films. The marks formed by this process may have high contrast, do not depend on polarized light for read out, and should have long storage life. It seems likely with better optics and shorter, higher power pulses that smaller marks and lower threshold energies than reported here could be demonstrated. A possible limitation of these materials for optical media is the low signal to noise ratio resulting from the surface pore structure. This would then limit them to use as low density media only.

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