High-resolution ablation of amorphous polymers using CO_2 laser irradiation

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Etching of various amorphous polymers by the application of CO_2 laser radiation (10.6 μm) is described. By passage of the radiation through a high-resolution mask in contact with the polymer surface, this ablation can produce images having submicron resolution and good edge acuity. The laser intensity required for ablation is compared for various thermoplastic and thermosetting polymers. Below the required level of intensity, no ablation is observed, but the laser irradiation can result in thermal crystallization. The energy necessary to induce ablation with infrared radiation is comparable to that required for UV decomposition.

The effect of high-energy radiation on polymers has focused mainly on the photochemistry induced using short-wavelength radiation. Day and Wiles[1] reported on the influence of wavelength and the presence of oxygen on poly(ethylene terephthalate) (PET) irradiation and detailed various reaction paths. Srinivasan and co-workers described in a series of papers[2-6] the effects of short-wavelength exposure (< 200 nm) on PET. Although the radiation was passed through a high-resolution mask, the resulting ablated images did not possess sharp edge acuity. Andrew et al.[7] compared the effect of UV radiation (308 nm) on PET to the use of a CO_2 laser (tuned to 9.6 μm), concluding that the UV etching was consistent with thermal degradation (that is, decomposition occurring in the ground electronic state). Photochemical studies of other thermoplastics such as poly(ether ether ketone),[8,9] poly(methylmethacrylate),[10,11] polycarbonate,[12,13] as well as a variety of thermosets,[14] are reported in the literature, along with several review articles.[15-18]

We have recently produced reversible, high-resolution images on amorphous PET via crystallization induced by CO_2 laser irradiation.[19] The process takes advantage of various mechanisms to avoid smearing of the images by thermal diffusion away from the irradiated regions. In this letter we describe the controlled ablation of PET and other polymers using 10.6 μm radiation from a CO_2 laser. The process produces distinct, high-resolution images and is consistent with a model offered for ablation of PET.[3-6]

Films of the amorphous polymer were placed in contact with either a dark or light field mask of gold on a GaAs wafer, patterned with images as small as 0.8 μm and as large as 500 μm. These masks were obtained from the NanoElectronic Fabrication facility at the Naval Research Laboratory. The reflecting gold surfaces of the mask shield regions of the film from the radiation, and also act as a heat sink to obviate thermal diffusion effects. A Coherent Model 42 CO_2 laser, operating at 10.6 μm, was employed as the light source. The laser beam was used to flood illuminate the masks. The spatial intensity profile of the radiation was not well defined. For this reason, laser powers reported herein are averages of the laser power over a cm^2 spot; hot spots within the beam may actually have been responsible for the observed ablation.

Ablation results were evaluated by inspection through a Zeiss transmission optical microscope using dark field optics and with an AMR Model 1000 scanning electronic microscope (SEM), as well as by IR spectroscopy (Analect and Nicolet FTIR microscopes). A Tencor instrument with 1.5-μm-diam stylus was employed to obtain topographic profiles, and a Perkin–Elmer AD2Z microbalance used for quantification of weight losses associated with the ablation.

Except for Ref. 7 previous studies of PET ablation have utilized the semicrystalline, biaxially oriented film, "Mylar." It is aparent from the results of others using UV radiation that ablation of the amorphous regions in semicrystalline PET requires less power than do the crystalline regions. The crystallites appear as a granular or furrowed texture when observed with SEM.[6,7] We obtained similar results using Mylar irradiated with 10.6 μm CO_2 laser radiation. From the absence of this texture when ablating amorphous PET with UV light, Andrew et al.[7] confirmed that the texture seen in Mylar was due to the crystalline phase.

Our studies suggest that many amorphous substances can be ablated with high resolution and good image edge acuity by infrared irradiation at sufficient powers. Figure 1 displays the microlithographic image (a) created on amorphous PET following irradiation with the CO_2 laser through the mask (b) for 30 s at 4.0 W. The images created possess an edge acuity similar to that of the lithographic mask (< 0.5 μm). This is demonstrated in Fig. 2 by the stylus trace (obtained using a Tencor instrument) of ablated images consisting of a series of bars 10 μm across separated by 15 μm spaces. Images 0.8 μm width having similar optical quality to Fig. 1 can be routinely obtained, although our masks tend to have more errors at this scale and the stylus of the Tencor instrument (1.5 μm diameter) does not permit an accurate depth profile to be obtained.

No deformation upon irradiation of the PET was observed, nor was any product of the photodecomposition evidenced on the surface. Srinivasan and Leigh[3] have previously suggested that such products produced from UV photodecomposition would possess kinetic energy sufficient to be volatile. The polymer surface following ablation is not measurably crystalline as determined by an absence
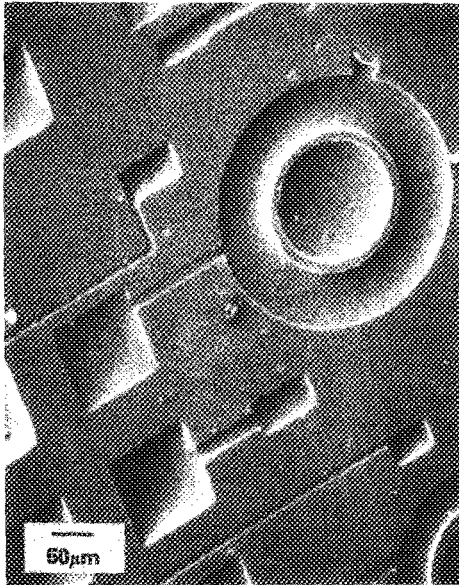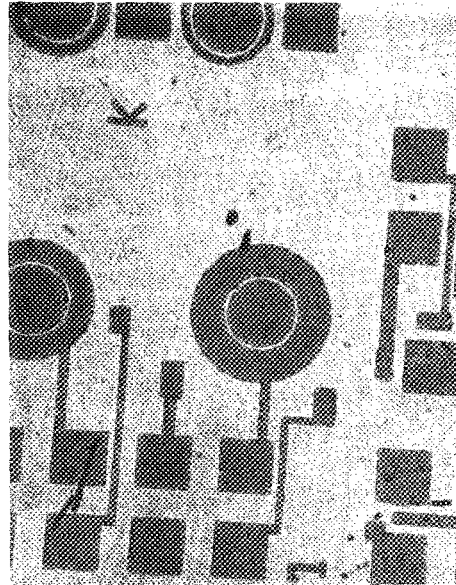
FIG. 1. (a) Scanning electron micrograph of positive image formed by irradiation of a 0.005-in.-thick film of amorphous PET with a CO_2 laser operating at 4 W. Imperfections are due to dust and mask errors. (b) Optical reflection micrograph of section of dark field mask used for production of the image.

of both optical birefringence and crystalline absorptions in Fourier transform infrared (FTIR) spectra of the film after irradiation. This result is consistent with the observations of UV-ablated PET.

Ablation was accomplished with a number of other amorphous polymers, although accompanying processes sometimes compromised the image quality. PET and polycarbonate were found to be the most efficiently ablated, with no other alteration of the films apparent. Poly(ether ether ketone) was found to be relatively resistent to ablation with 10.6 μm radiation, although high-resolution images were obtainable. Polysulphone, poly(methylmethacrylate), and polychlorotrifluoroethylene deformed and bubbled when exposed to the output of the CO_2 laser, although ablated images were achieved in the latter two materials. The ablation of two thermosetting polymers, poly-(cyanurate) of bisphenol A dicyanante and Epon 28 epoxy, required significantly higher powers (as much as 10 W/cm² with some dependence on the degree of cross linking) and was accompanied by some charring.

A dose response curve for the ablation of PET is given in Fig. 3. The proportionality of the image depth to the weight loss in the film indicates trivial weight loss due to

moisture desorption and oligomer volatilization. It is interesting to note that the total energy required for a given ablation depth in PET using a continuous IR source (Fig. 3) is similar to that necessary using a pulsed deep UV source.[5] This is consistent with the observations of Andrew et al.[7] that the decomposition mechanism of PET is independent of the wavelength of radiation. Of course the efficiency of the process will depend directly on the absorbance for a particular wavelength.

It was observed that infrared ablation, similarly to methods employing short-wavelength irradiation,[20] involves initial heating of the material to above its glass transition temperature. If the power is low enough, the polymer may thereafter begin to crystallize, with extended exposure to low power not resulting in ablation. If the energy is supplied sufficiently fast, however, crystallization is not observed; instead chain scission is induced with evaporation of the low molecular weight fragments. In this
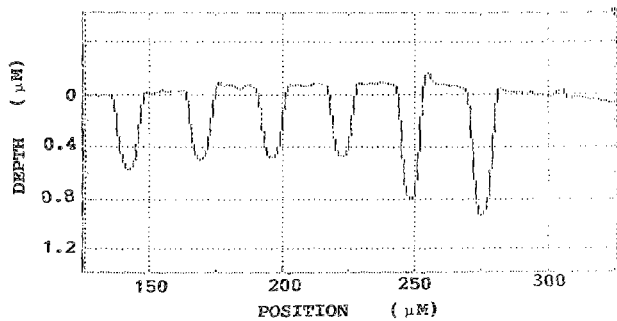

FIG. 2. Profile of microlithographic image consisting of 10 μm bars and 15 μm spaces (obtained using a Tencor instrument with a 1.5-μm-diam stylus installed).
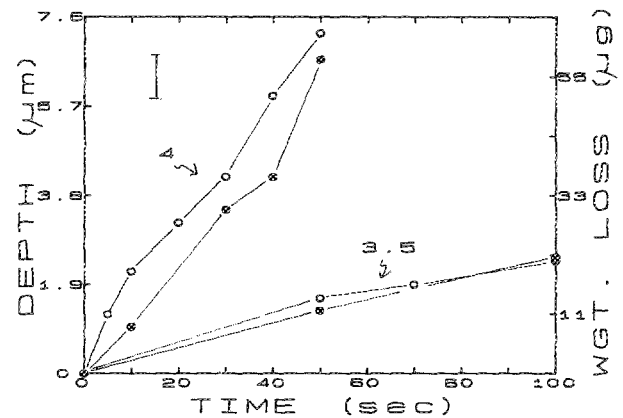

FIG. 3. Dose response curves for ablation of amorphous PET film by CO_2 radiation of the indicated power in watts per cm². The filled symbols refer to the image depth, representing the average of five samples, with the range in a typical set of measurements denoted by the error bar. The hollow symbols represent the weight loss in a film upon exposure to the radiation.

M. F. Sonnenschein and C. M. Roland

case, attainment of T_g simply provides sufficient mobility for the reactive sites. The photoproducts of the infrared decomposition have not been identified. Recent electron paramagnetic resonance spectroscopy experiments have shown that different radical intermediates are produced upon decomposition of PET by UV irradiation versus mechanical abrasion.[21] The detailed mechanisms underlying IR ablation remain to be investigated.

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