

# Ablative photodecomposition of polymers

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Recently it has been observed that far-UV (193 nm) laser radiation can cleanly etch organic polymer films. In contrast to etching of the film by lower energy radiation, which leaves the walls of the etch region uneven due to melting, far-UV radiation ablates the material with minimum damage to the remaining sample. A model has been developed to explain the photochemical etching due to 193-nm laser light. The predictions from this model are (1) the reacted material ablates without melting the remainder of the sample; (2) the average perpendicular velocity of the ejected material is  $\sim 1000\text{--}2000$  m/s; (3) the angular spread is small and peaked in the direction normal to the surface; and (4) the material ablates layer by layer. Items 1, 2, and 3 are in excellent agreement with the experimental results. A model has also been developed to simulate the ablation of solids by the thermal (in contrast to the photochemical) process. The predicted pit shape and angular distribution are quite different from those obtained from the photochemical model. The effect of impurity or solvent molecules is also discussed.

## I. INTRODUCTION

There has been considerable development in the use of laser radiation to remove material from a solid. Of particular interest is the observation that short pulses of far-UV radiation ablate organic material cleanly, i.e., the remaining sample exhibits a precisely defined pit.<sup>1-12</sup> On the other hand, irradiation by longer wavelength (e.g., visible or infrared) laser light results in a damaged or melted sample after the ablation has taken place.<sup>9</sup> The ablation process by far-UV radiation has potential as a "dry" etching step in the semiconductor industry and in certain medical applications. Obviously two different physical phenomena are occurring. For the ablation by UV radiation it has been proposed that a photochemical reaction occurs such that the product molecules have a larger specific volume than the original sample.<sup>1-3</sup> A volume explosion then results that ejects the material from the solid. Of importance here is that one photon of UV radiation has sufficient energy to break one chemical bond. In contrast there is not sufficient energy in one photon of visible or infrared radiation to dissociate a chemical bond. Laser light in the IR to visible range thus primarily heats the sample. Eventually some of the atoms or molecular fragments will have sufficient energy to eject or evaporate from the solid.

The questions that still remain are (1) how, after the photochemical bond breakage, to explain the ablation of the material from the sample, and (2) why does the photochemical process cleanly etch materials while the thermal process melts and damages the sample? In this study, we present two microscopic models, one to describe the photochemical process and one for the thermal process. Each model makes specific predictions regarding the experimental observables of pit shape, angular distributions, and energy distribution of the ablated material. For the photochemical process, we examine the effect of mixtures of compounds in which one of the components does not photochemically ablate as a pure substance.

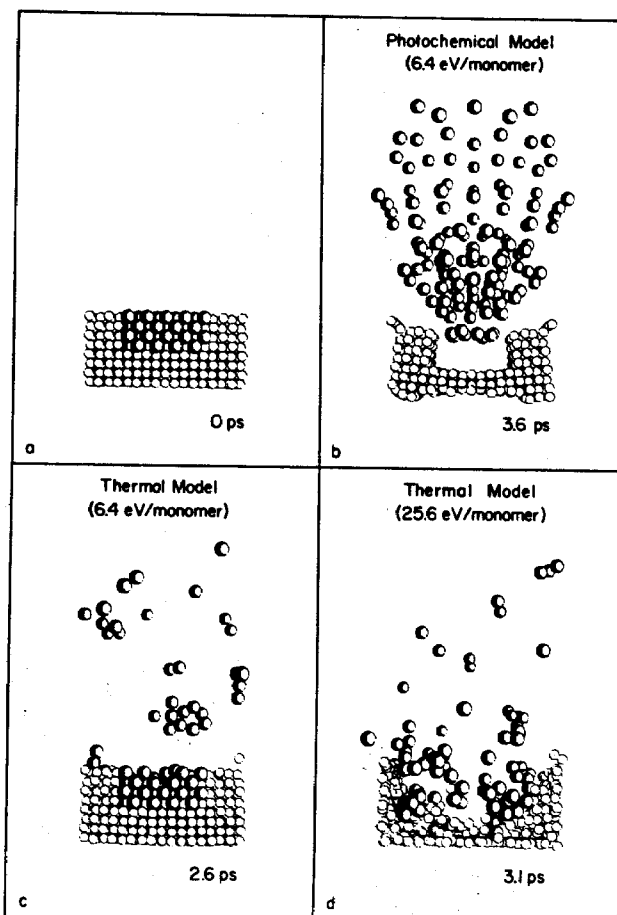


FIG. 1. Side view of the movement of the species as a function of time. The radii of the circles are arbitrary although the smaller, plain circles represent the nonirradiated species and the larger, shaded circles the irradiated species. There is a slight perspective in the drawings (1 ps =  $10^{-12}$  s): (a) initial configuration, (b) photochemical model (6.4 eV/monomer), (c) thermal model (6.4 eV/monomer), and (d) thermal model (25.6 eV/monomer).

## II. DISCUSSION

In the photochemical model the polymer or organic material is described by structureless monomer units held together by strong attractive interactions. After the laser light strikes the sample, a few of the monomer units react photochemically. The interaction describing the reacted species is a repulsive potential. The energy of the reacted species is 193 nm (6.4 eV) greater than that of the unreacted species. The motion of the particles subsequent to this photochemical reaction is followed by integrating the classical equations of motion. The details of this procedure are given elsewhere.<sup>13,14</sup>

A sideview of the initial configuration of units is shown in Fig. 1(a). The smaller circles represent the unreacted sample and the larger shaded circles the photolyzed units. The position of the units at 3.6 ps is shown in Fig. 1(b). The important prediction of this photochemical model is that the ablation occurs without melting the surrounding solid. It also predicts that the average perpendicular velocity of the ablated material is 1000–2000 m/s and that the angular spread is within  $\sim 30^\circ$  of the surface normal. Both of the last two predictions are in agreement with experimental results.<sup>15</sup> The model also predicts that the material ablates layer by layer.

We model the thermal process by assuming all units interact *via* the attractive potential.<sup>14</sup> We assume that the laser radiation is absorbed into vibrational modes and accordingly each reacted unit is given kinetic energy. The direction of the velocity vector is randomly chosen. The final positions of the units are shown in Figs. 1(c) and (d) for initial kinetic energies of 6.4 and 25.6 eV, respectively. For 6.4 eV of kinetic energy [Fig. 1(c)], only  $\sim 30\%$  of the energized units eject. An equivalent amount of energy deposited as kinetic energy is not as efficient in removing the material as the process that occurs in the photochemical model. This difference in energy threshold has been observed in biological samples.<sup>9</sup> If the equivalent of four photons of energy (25.6 eV) are given to each unit then a substantial pit results [Fig. 1(d)]. Here, however, the sample is melted and damaged. In addition, parts of

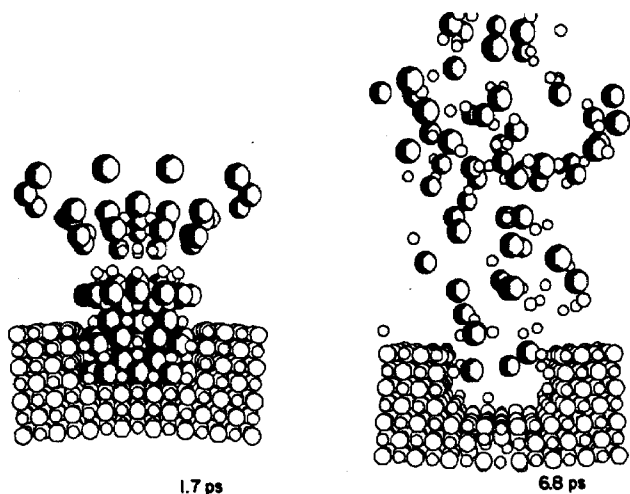


FIG. 2. Photochemical ablation of a mixture. The symbolism is the same as in Fig. 1. The smaller circles represent the solvent or nonphotosensitive component. In this case, the attraction between the solvent molecules and the reacted species is relatively weak and the volume increase is large.

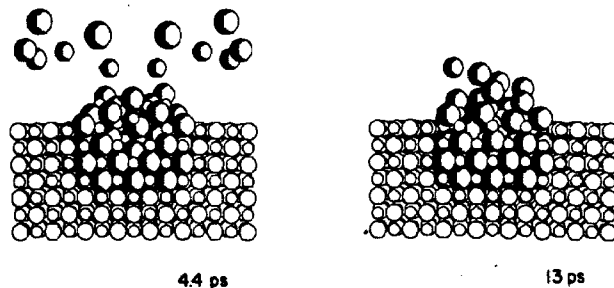


FIG. 3. Photochemical ablation of a mixture. Here the attraction between the solvent molecules and the reacted species is stronger than in Fig. 2 and the explosive force is not as large.

the sample that were not irradiated are also sputtered. Thus we can obtain ablation by this thermal mechanism but it does not result in a cleanly etched pit. The predicted angular distribution of the ablated material in the thermal model is very broad, extending out to  $60\text{--}70^\circ$  from the surface normal.

These microscopic models appear reasonable for describing the photochemical and thermal processes in homogeneous materials. In nature, both phenomena can also occur in very complex mixtures such as corneal tissue<sup>5</sup> or aortal walls.<sup>9</sup> The extension of the thermal model to more complex matrices seems straightforward. The extension of the photochemical model is more involved. Several factors could be important for photochemical ablation of a mixture. If all the compounds photochemically ablate as pure substances then the mixture will presumably also ablate. If some of the components do not ablate as pure substances, then the properties of the mixture are not obvious. The relatively concentrations of the ablative versus nonablative components will be important. In addition the attractive interaction between the nonablative component and the photochemically reacted material will influence whether the material can escape the solid.

The photochemical model has been examined for a two-component system. One component is photochemically sensitive, i.e., it ablates as a pure substance. The other component which will be referred to as the solvent does not photochemically ablate. The two components are present in equal concentrations. The photosensitive component is allowed to react and expand its volume as described above. The solvent is weakly attracted to both the reacted and unreacted material. Depending on the strength of this attractive interaction and the power of the volume explosion, two different processes can occur. First, almost everything in the irradiated region ablates (Fig. 2). Second, only a small amount of material near the surface ablates (Fig. 3). In neither case does only the photochemically active material ablate leaving the solvent behind. The complete ablation should occur for high concentrations of photosensitive material, large volume changes and/or weak interactions between the solvent and the reacted material. For low concentrations of photosensitive material or strong attractive forces between the solvent and the reacted material, the ablation should be suppressed.

The question of how homogeneous the material must be can also be examined by only photochemically exciting part of the central region of monomers. The end results, if only

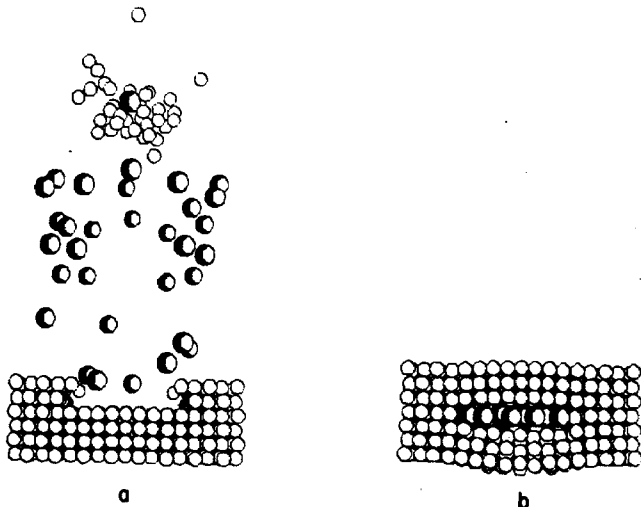


FIG. 4. Partial photochemical excitation: (a) only the monomers in the second layer were excited and (b) only the monomers in the fourth layer were excited.

the monomers in the second layer are excited, are shown in Fig. 4(a). The effect of only exciting the monomers in the fourth layer is shown in Fig. 4(b). The volume explosion is capable of ejecting a small amount of material above it as seen in Fig. 4(a). However, if there is too much tightly bound material, the reacted molecules remain in the solid.

These theoretical attempts at examining the effects at either heterogeneous materials or partially excited samples are relatively crude. They do, however, point out that there are processes and systems that have not been explored experimentally. It is time to design well-defined systems to study the photochemical ablation phenomena.

### III. CONCLUSIONS

Microscopic models are presented here for the photochemical and thermal ablation of polymeric and biological sam-

ples. The models make specific predictions about pit shape, angular distribution, and energy distribution of the ablated material. The photochemical process results in a cleanly etched pit while the thermal model results in melting and sample damage. The precise wavelength regime in which the photochemical, thermal, or possibly even both processes are operative will undoubtedly depend on the characteristics of individual materials.

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