Pulsed Ultraviolet Laser Ablation

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Abstract. The radiation transport involved in pulsed ultraviolet laser ablation of organic materials has been studied both theoretically and experimentally. A mathematical description of the absorption process that includes nonlinear effects such as chromophore saturation and multiphoton absorption is presented. This theoretical model accurately describes the observed polymer etch depth versus incident laser fluence relationship for various target materials, laser wavelengths, and pulse durations varying from nanoseconds to subpicoseconds. The theoretical analysis can also be used to explain observed nonlinearities in the transmission characteristics of polyimide subjected to intense KrF excimer laser irradiation.

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Irradiation of solid organic material with pulsed ultraviolet laser light of sufficient intensity causes clean etching of the substrate [1-3]. In the typical intensity range of $10^7$ W/cm$^2$ no visible plasma phenomena occur and the morphology of the etched solid surface indicates little or no oxidation or carbonization. Investigation of the molecular products of UV laser etching suggests that photochemical substrate decomposition plays a significant role at least for the shortest wavelengths investigated. Consequently this phenomenon of "cold" laser ablation has been termed "ablative photodecomposition" (APD) [3]. Excimer lasers are expected to have great utility in the microelectronics industry and in medicine because APD causes discrete removal of targeted material without significantly altering the adjacent bulk and allows for substrate processing on a submicron scale [1, 2, 4].

Ultraviolet laser ablation has been extensively studied for a variety of organic substrates, and several important features are now well documented. These include:

1. The process of APD has a threshold fluence, which depends mainly on the target absorption coefficient at the laser wavelength [5-9]. At fluences below this threshold only minuscule etching ($< 0.05\mu$m per laser pulse) is observed, if at all. Above threshold the etch depth per pulse increases rapidly with increasing laser fluence.

2. For fluences slightly above threshold the etch depth per pulse $d$ varies logarithmically with the laser fluence $F$ as:

$$d \sim \ln \left( \frac{F}{F_{th}} \right),$$

where $F_{th}$ is the threshold fluence [8, 10].

3. At higher laser fluences there are considerable deviations from the logarithmic relationship of (1) [7, 8, 11-13]. In many cases the observed etch depth fluence dependence becomes approximately linear [7, 8]:

$$d \sim (F - F_0)$$

where $F_0$ denotes a characteristic fluence usually not equal to the threshold fluence. For some materials $d$ approaches a constant value at greater fluences [12, 14].

4. Absorption of laser radiation leads to a temperature increase in the target material. Below the ablation threshold this temperature rise is directly proportional to the laser fluence per pulse, while above threshold the rate of temperature increase with increasing fluence becomes considerably slower [5].

5. APD is accompanied by an acoustic signal that increases abruptly at the ablation threshold [5]. This signal magnitude decreases with increasing laser wavelength [15].

6. Numerous molecular products are generated during APD. The nature and abundance of these decomposition substances depends sensitively on the material, laser wavelength, and laser fluence. For ArF (193 nm) excimer laser ablation of poly methylmethacrylate (PMMA), an abundance of the MMA monomer is found among the ablation products. In contrast, KrF (248 nm) excimer laser ablation of PMMA yields much less monomer in comparison with larger polymer fragments [6]. Ablation of PMMA with either laser also causes formation of low molecular weight products such as C$_2$ and ejection of solid polymer material [6]. Ablation of biological tissue yields primarily small molecules such as H$_2$, CO, CO$_2$, CH$_4$, and C$_2$H$_4$ [15, 16].

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7. The APD products leave the material surface with velocities of $10^8-10^9$ m/s [7, 17]. While the amount of substrate removed per pulse depends sensitively on incident laser fluence, the velocity distribution of ejected material varies only slightly with fluence.

8. The rapid onset of the etch process combined with the rapid ejection velocity result in the formation of an expanding plume of APD decomposition products during the laser pulse [6, 18, 19]. For ablation of certain materials such as PMMA, this plume can significantly attenuate laser radiation in the latter portion of the pulse and hinder ablation [6, 11, 12].

9. For certain materials irradiated with moderate fluence laser pulses ($F < 1.0 J/cm^2$), the absorption of several pulses is required before significant etching is observed [12]. The number of pulses required in this “incubation” process decreases with increasing pulse fluence.

Several attempts have been made to describe the APD phenomena theoretically [3, 10–12, 20–22]. There appears to be general agreement that at least for very short wavelength radiation ($\lambda \leq 200$ nm) direct photochemical bond breaking plays an important role in the ablation process. The simplest picture advanced early on describes APD as one-photon radiation (A < 200 nm) direct photochemical bond breaking of the material into highly volatile molecular fragments. This model can account for the clean rapid decomposition of the material into highly volatile products leaving the material surface with velocities of 103–104 m/s [7, 17]. While the amount of substrate removed per pulse depends sensitively on incident laser fluence, the velocity distribution of ejected material varies only slightly with fluence.

9. More complex models for the transfer of electronic energy into photodecomposition products are not well understood [28]. For radiation transport analysis of important quantities are the nature, distribution, and absorption cross-sections of the constituent chromophores, the picture for photoabsorption used in this work is that of individual chromophores homogeneously distributed throughout the substrate, each with a common appropriately averaged photoabsorption cross-section. This concept is further discussed in Appendix A.

The number of such chromophores within each imide monomer can be estimated to be on the order of ten. The measured small signal absorption coefficient of polyimide, $\alpha$, is roughly $1 \times 10^5$ cm$^{-1}$ at 248 nm [5]. KrF excimer laser ablation of this polymer starts at a fluence of 30–70 mJ/cm$^2$ [7, 10]. Using a threshold fluence of 50 mJ/cm$^2$, the number of absorbed photons per volume can be estimated as $N_{abs} \sim 1 \times 10^5$ cm$^{-3}$. Thus, at the ablation threshold about 3 photons are absorbed per monomer in polyimide. The number of absorbed photons per chromophore at fluences slightly above threshold approaches one. For bond cleavage, essentially a chemical reaction, the chromophore excited state lifetime is infinitely long compared to the 10–20 ns excimer laser pulse. Even in the case of excited electronic states within an intact molecule, chromophore excited-state lifetimes are finite and can be as long as microseconds [29]. If the excited chromophore state is nonabsorbing, laser irradiation of a substrate should cause saturation of the chromophores near the material surface. Saturation would allow a larger fraction of the incident pulse energy at higher laser fluences to penetrate deeper into the material and hence enhance the etching process [30]. Only close to the threshold fluence does the absorption coefficient for polyimide during ablation agree with the low-intensity value [10]. Transient absorption changes in polyimide at high laser intensities have recently been observed [31, 32].

Chromophore saturation has also been observed during ArF laser ablation of collagen, an important biological polymer [33]. While this saturation effect decreases the instantaneous absorption coefficient relative to the measured small-signal value that enters into Beer’s Law, other mechanisms such as multiphoton absorption and plume attenuation serve to increase total absorption. Both situations have been observed experimentally for different materials at sufficiently high fluences [5–8, 12].

The key to understanding the APD etch data is a careful analysis of the radiation transport at high laser intensity. In this paper a description of ablation is presented which takes into account the effects of chromophore saturation...