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MODELING THE ABLATION OF POLYMERS BY LASER BEAMS

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Abstract

The removal of polymer surface atoms by intense UV laser beams is modeled with an effective process of solid-gas phase transformation accounting for the decomposition of the polymer. Ablation dynamics is driven by the incident laser beam intensity and the contributions from reflections off the side walls.

1. Introduction

The very large integrated circuits of a high end mainframe computer are usually placed on top of thermal conducting modules. These modules are built by very thin layers of ceramic materials containing the necessary wiring to interconnect different circuits on the same, or different, modules. There are severe technological restrictions on the thickness of the ceramic layers: too thin layers can not be manipulated without the appearance of cracks and other defects.

A new technology involves depositing a thin layer of a polymer on top of the ceramic module. The polymer then is used as a media to make wiring connections [1], allowing for more complex module connections and reducing the number of lines inside the ceramic module. The wiring lines on the polymer are then drawn by means of an intense, but very short, ultraviolet laser pulse [2][3]. The duration of the pulse is short enough so that only a small amount of heat is dissipated towards the bulk of the polymer. The surface temperature of the polymer then becomes higher than the decomposition temperature and the polymer breaks up into monomers and other by-products [2]. Polymer fragments and debris resulting from the decomposition are removed from the surface by an expanding shock wave produced by the high temperatures [4]. Typically a few hundred angstroms to several microns of material are removed by each laser pulse. This entire

process is usually referred as ablation [2][3]. The wiring lines produced by the ablation process are then filled by a conducting material using a variety of techniques [1][5].

In order to achieve a good filling of the holes, the angles of the side wall and the topography of the bottom of the holes have to conform with severe tolerances. Same techniques may require shallow angles while others perpendicular walls [1].

The possibility of producing reproducible profiles etching polymers yields a new stage not only for high resolution pattering in the electronic industry but also in other applications as tissue removal in surgery [6].

In this lecture we present a study of the shape of holes produced by the ablation of polymers. We will concentrate on the ablation of polyimide (commercial DuPont Kapton^{TM}) and lasers with 308nm wavelength. Kapton is a class of polymer that meets many requirements in the electronic industry and is chosen for its chemical and mechanical stability [7][8]. As performance requirements for very large scale integrated (VLSI) circuit continue to increase, polyimide films will play a leading role in insulating and protective layers.

We start with a thermal model which we then simplify to a surface evolution equation describing the main features of the ablation process. We find that the relevant parameter controlling the shape of the holes is the flatness of the intensity profile resulting from laser optics. The reflection of the laser beam off the side walls produces holes with non-flat bottoms.

2. Thermal ablation and photo ablation

It is experimentally found that in order to start an ablation process, the laser has to deposit a minimum energy on the surface. The minimum energy deposited is referred to as the threshold fluence (values for polyimide can be found in [9]).

When a large amount of energy is deposited on a surface, ablation is a likely process to occur. At high energy fluxes the thermal relaxation processes within the material are not fast enough to dissipate the energy absorbed. Under this condition, a transition phase between the solid state to a gas phase becomes possible in a localized region of the material, ejecting polymer fragments with large translational, vibrational and rotational energies [4][10]. The ablated material is ejected from the surface at speeds with Mach numbers in the range 3-10. The shock wave produced by the gas is clearly visible.

The subsequent thermal history of the ejected material is still a controversial subject. It has been argued that the plume of polymer fragments produced during the ablation absorbs a negligible amount of the applied radiation at very small energy fluences ($< 1 J/cm^2$). However, there is some experimental evidence that the laser beam energy is partially absorbed by the ejected material [4][9][11].

Lasers used in polymer ablation have wavelengths in the range 193-308nm, the ultraviolet (UV) region of the electromagnetic spectrum. The photons from UV lasers have energies of order 3-6eV, which are comparable to typical electronic transitions present in organic compounds. These highly energetic photons may break individual polymer bonds leading to what is called photoablation. For short laser wavelenghts, individual bond breaking may be an important part of the entire ablation process [2][3][9]. Unfortunately, the relative importance of thermal-ablation vs. photo-ablation is still not fully understood.

Another interesting aspect of polymer ablation is the difference in behaviour of the first few laser pulses. For fluences slightly larger than the threshold fluence, it has been observed that the first pulses remove a smaller amount of material than subsequent pulses [11][12]. However, the etch rate reaches an assymptotic value at later pulses depending on the duration of the laser pulse [11][12]. This cumulative effect, or incubation process,

indicates that the degradation of the polymer has to occur before proper ablation. This phenomena will not be considered in the present paper.

3. Polyimide ablation model

We will consider the following simplified thermal mechanism: heat transport inside the material and no radiation absorbed by the ablated material. We will also assume a temperature for decomposition and a latent heat necessary to produce the phase transition. The heat transport equation in the material is

$$\rho C_p \frac{\partial T}{\partial t} = \nabla(\kappa \nabla T) + \alpha I(\vec{x}, t), \tag{1a}$$

where α is the absorption coefficient for light, $C_p(T), \rho(T)$ and $\kappa(T)$ are the density, specific heat capacity and thermal conductivity of polyimide. The incoming energy flux is given by $\vec{I}(\vec{x}, t)$. Initially the polyimide is located below the plane $z = 0$ and due to the laser pulses its final upper surface will be below the original plane.

There are two characteristic lenght scales in the heating process: the absorption scale L_α and the diffusion length L_d, where

$$L_\alpha = \alpha^{-1} \quad \text{and} \quad L_d = \sqrt{\frac{\kappa \tau}{\rho C_p}}. \tag{1b}$$

Here τ is the duration of the pulse, or pulse width. For polyimide etching at $308nm$ we have $L_\alpha = 0.1\mu$ and $L_d = 0.05\mu$, for $\tau = 30ns$.

An estimate of the heating contribution to the threshold laser intensity can be obtained by ignoring heat dissipation:

$$I_h = \frac{\rho C_p}{\alpha \tau}(T_a - T_o) \sim 6\ 10^5 W/cm^2, \tag{2a}$$

where T_a is the melting temperature and T_o the ambient temperature. However, there is a more relevant contribution to the threshold fluence resulting from the minimum photon flux required to overcome the various polymer relaxation processes [9]. The threshold laser intensity is determined by the energy absorbed in the layer α^{-1}

$$I_T = \frac{\lambda}{\alpha \tau} \tag{2b}$$

where $\lambda = \sim 8\ 10^3 \mathrm{J/cm}^3$ is the ablation latent heat. The value of λ corresponds to two photon absorptions per monomer [9].

A widely accepted model for the ablation, referred to as Beer's law which predicts that $\Delta\xi_{etch} = \alpha^{-1}\ln(\mathcal{F}/\mathcal{F}_T)$, where $\Delta\xi_{etch}$ is the ablation depth, $\mathcal{F} = \int_o^\tau I(t)dt$ is the energy fluence and $\mathcal{F}_T = \tau I_T$ is the threshold fluence. The fluence threshold $\mathcal{F}_T$ is the maximum energy that can be dissipated by relaxation processes into the bulk material before ablation can take place [9]. This model ignores thermal dissipation and also assumes that the ablated material absorbs laser energy as efficiently as the underlying polymer. However, there is large amount of evidence indicating that the heuristic Beer's law is only a simplified approximation to the observed etching process [2][3][9][13].

Here we consider other alternative: that the fragments are transparent at the excitation wavelenght, which is simulated by an instantaneous disappearence of the irradiated

layer. For fluences higher than the threshold value, our model indicates that the remaining energy of the laser beam δE is spent ablating a volume δV of polymer at a rate

$$\frac{\delta E}{\delta V} \approx \frac{(\mathcal{F} - \mathcal{F}_T)}{\Delta \xi_{etch}} = \lambda. \tag{3}$$

It has been shown that the linear dependence indicated in Eq. (3) is enough to describe small fluence experimental data [13].

To complete the description of the two dimensional ablation process, we need to describe the energy balance at the moving boundary between the ablated and unablated materials. Note that the penetration depth per pulse is given by $\Delta \xi_{etch} = (\mathcal{F} - \mathcal{F}_T)/\lambda \sim L_\alpha(\mathcal{F}/\mathcal{F}_T - 1)$. For fluences larger than the threshold fluence, the total etch is much larger than L_α and L_d. Excluding the presence of a mushy region at the ablation front and ignoring the details of the temperature inside the material, the following surface condition is derived

$$\lambda \frac{d\xi}{dt} = \vec{I}(\vec{x}, t).\vec{n} - \vec{q}_T(\xi), \tag{4}$$

where ξ is the normal coordinate to the moving interface, with normal vector $\vec{n}$, $\vec{q}_T(\xi)$ is the heat flux accounting for the heating of the polymer, and $d\xi/dt$ is the ablation velocity.

When the energy transfer to the surface is faster than the relaxation mechanisms present in the polymer, the heat flux $\vec{q}$ is not longer given by $-\kappa \nabla T(x, z, t)$ and we will assume that is given by the threshold value $I_T\ \vec{n}$. It is easily seen that a Stefan model will reach a traveling wave solution if absorption by the ablated material is ignored, thus our choice of a constant heat flux. Note that at this stage we have transformed the ablation process to a surface evolution problem, and that the derived surface condition implies that no energy is absorbed by the ejected material while an amount $\mathcal{F}_T$ is released to the bulk of the polymer during every pulse.

The energy flux on the surface is computed by

$$\begin{aligned} \vec{n}.\vec{I}(x, z, t) &= \mathcal{R}(\theta)\vec{I}_L(x, t)\vec{n}(\theta) \\ &+ \int_{\mathcal{C}} \mathcal{R}(\theta)(1 - \mathcal{R}(\phi))\vec{n}(\theta).(\vec{I}_L(x, t) - 2\vec{n}(\phi)(\vec{n}(\phi).I_L(x, t))d\phi, \end{aligned} \tag{5}$$

where $\mathcal{R}(\theta)$ is the reflectivity at incident angle θ and $I_L(x, t)$ is the incident laser intensity profile. Integration is performed over those angles which contribute to the fluence at point (x, z) which surface slope is given by

$$\cos\theta = \left(1 + \left(\frac{\partial z}{\partial x}\right)^2\right)^{-1/2} \tag{6}$$

The normal coordinate to the ablation front is expressed as function of the axial coordinate by the relation $\partial\xi/\partial z = \cos\theta$. We are making one further assumption: that the ablated surfaces are relatively smooth and that the reflection off them is according to geometric optics [14]. This treatment would not be valid at lengths comparable to the laser wavelength. We use the following optical parameters for polyimide: $\alpha_e = 11.2\mu m^{-1}$ and real permeability $\epsilon_e = 3.0\epsilon_o$. The values were obtained by fitting experimental data provided by B. Braren and F. Doany.

The final model then results in

$$\frac{1}{C_a}\frac{\partial z}{\partial t} = \begin{cases} I(z, x, t)/I_T - \sqrt{1 + (\partial z/\partial x)^2} & I > I_T \\ 0 & I \leq I_T \end{cases} \tag{7}$$

Here $C_a \sim I_T/\lambda \sim 2-3\ 10^{-3}\mu m/ns$ is a scale surface velocity during the pulse. The current model predicts a linear dependence on the fluence and agrees with the model proposed in [13].

This model is only valid in the low fluence region. High fluences show a saturation of the linear dependence of the ablation rate, possibly involving new physical phenomena occurring in the ejected fragments [11][12]. For nanosecond pulses, saturation occurs above $2-6J/cm^2$, while in the picosecond time-scale saturation of the linear dependence occurs at only $0.5J/cm^2$. Other mechanisms that could play a relevant rol are bleaching of the polymer, plasma formation, nonlinear and multiphoton absorption and the blocking of the laser beam by the ejected material [12]. Fig. 1 shows the etch depth curve for polyimide as a function of the laser fluence.

4. Numerical results

We discretize Eq.(7) using centered second-order accurate difference scheme in space and uniform meshes. For the time discretization, we used explicit fourth order Runge-Kutta integration. A major complication in the code is the tracing of rays which are reflected off the side walls. The reflected energy is redistributed but inforcing total energy conservation.

The linear dependence indicated in Eq.(7) was used even for large fluences by introducing an effective penetration depth which depends upon fluence,

$$\alpha = \frac{1}{\Delta\xi_{etch}(\mathcal{F})}\left(\frac{\mathcal{F}}{\mathcal{F}_T} - 1\right). \tag{8}$$

We choose $\mathcal{F}_T = 70mJ/cm^2$ to fit the etch rate values published in [3][9].

In Fig. 2 we show surface profiles obtained from three different laser intensity profiles for varying optical setups. It can be seen that reflections of the incident beam off the side walls introduce small modifications to the profile (less than 5%) for the steeper intensity profile in accordance with the small reflectivity of polyimide. However, the effects of side wall reflection is important for non-uniform laser profiles. The difference between the maximum and minimum of the bottom of the hole may be as large as 20%. The contribution from laser beam reflections off the side walls becomes more relevant as the number of pulses is increased, modifying both, the hole depth and wall slope as shown in Fig. 2.

We have also been able to reproduce conical structures, observed when impurities, which are not ablated, shield the underlying polymer surface [15]. Equations (6) and (7) indicate that the limiting cone angle results $\phi = 2\sin^{-1}(\mathcal{F}_T/\mathcal{F})$ if the contribution from reflections is not considered [15].

5. Conclusions

The ablation dynamic model proposed in this lecture, which is consistent with a thermal decomposition picture of the polymer ablation, is a suitable starting point to describe the two-dimensional etching of polymers by laser beams. We obtained that reflections of the laser beam off the side walls of the holes contribute to produce deeper profiles. The present model allows, in principle, to analyze and modify the observed etching profiles. An improvement of the current model is desirable by including the ejected fragment dynamics and the thermal history of the polymer surface.

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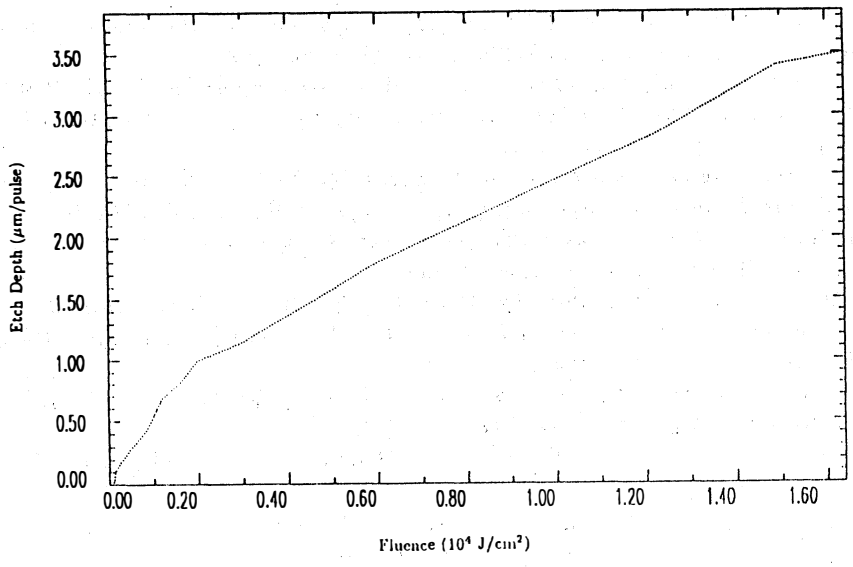

Fig. 1: Etch curve for polyimide at 308 nm.

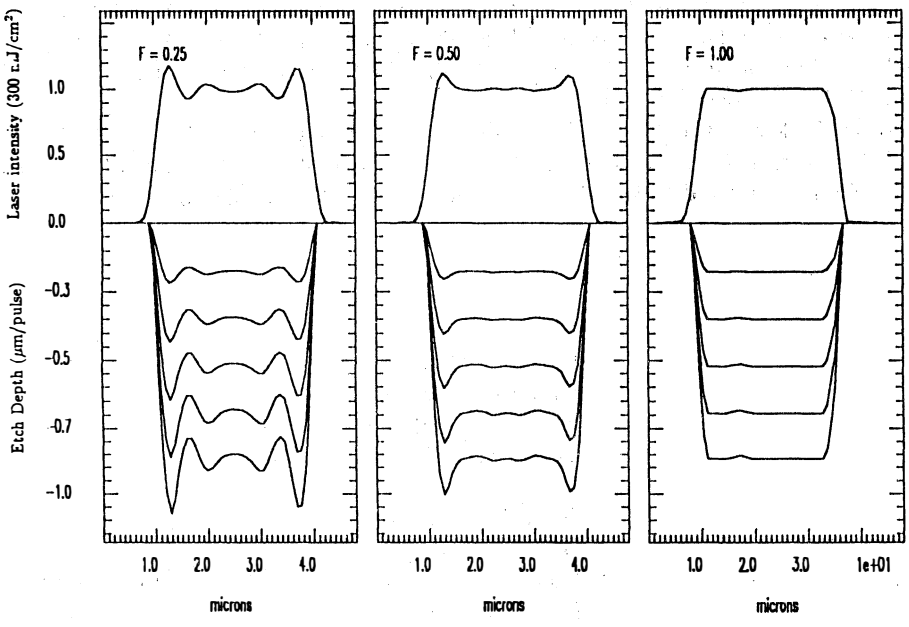

Fig. 2: Laser intensity profiles and the ablated surfaces for 300 mJ/cm² laser pulses.