Material Removal Rates of Biocompatible Polymers During Laser Ablation

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Excimer laser ablation is an effective method for machining polymeric materials for use in biomedical devices. Application of this technique, however, requires knowledge of laser material interactions. Process viability is strongly influenced by such ablation characteristics as the removal rate and the presence of thermally affected zones surrounding an ablated area. Furthermore, the selection of laser parameters can significantly influence debris generation and the extent of downstream cleaning which is needed. This paper discusses the qualitative features of excimer ablation of polymers and presents estimates of the ablation thresholds and ablation rates for several biocompatible polymers as a function of pulse fluence. The basic experimental apparatus is summarized along with details of the experimental approach. Experimental data are shown in graphical form and are accompanied by a discussion of the implications of these results for manufacturing applications.

Introduction

For more than twenty-five years, the interaction of materials with intense laser beams has been a topic of intense study [1–8]. Discussion of ablation processes has included both theoretic analyses and summaries of empirical results [9–13]. The ability of laser ablation systems to provide a high degree of control in material removal with minimal damage to surrounding material has driven this interest. The improvement of industrial excimers has contributed much to the evolution of these processes. These lasers operate at repetition rates and pulse energies which have made the use of ablation economically competitive, particularly for the ablation of organic polymers.

The focus of this paper is on the ablation of polymeric films using a xenon chloride (XeCl) excimer with a projection optical system. In particular, recent experimentation on a test bench version of an ablation tool is reported. The materials considered have been the topic of previous research, but this work presents empirical guidelines for process development on such tools.

Laser ablation of polymers is a complex process, and the presentation of heuristic rules for predicting process behavior is an important step toward developing viable processes which can successfully compete with alternate technologies.

Experimental Apparatus

In order to evaluate ablation characteristics of materials and to develop reliable processes, a prototype projection tool was developed. The tool utilizes a Lambda Physik 3000 (XeCl) excimer. This laser is routinely operated at 250 Hz, with pulse energies ranging between 300 and 400 mJ. Because of their low coherence, excimers are useful for projection systems, where an entire field can be illuminated at once without laser speckle being generated on the target. This enhances the potential throughput of the system, particularly for applications where the necessary fluence can be achieved over a large field.

The optical path of the testbed is similar to that of ablation tools previously developed by Tamarack Scientific; however, the testbed is designed to allow a variety of experimental optical systems to be evaluated. The layout, as seen in Figure 1, begins with a series of turning mirrors which transport the raw beam from the laser to an anamorphic lens which shapes the beam. The beam is then directed through a homogenizer, which divides the beam into 49 beamlets. The homogenizer directs these beamlets so that they overlap in the mask plane, greatly increasing beam uniformity. When properly tuned, this system results in variation of less than five percent about the mean for the usable illuminated area.

The image which will be ablated on the target material is defined by a mask held in the mask plane by a vacuum chuck. Fluence at the mask plane is on the order of 30 – 40 $mJ \cdot cm^{-2}$; thus, for reasons of process reliability and mask durability, multilayer dielectric masks are typically preferred. The experiments reported in this paper utilized such a mask.

The beam is directed by a turning mirror from the mask into the 5x projection lens. The position of this mirror is controlled by piezoelectric actuators mounted on orthogonal axes on the mirror mount. In a process known as ‘dithering’, the orientation of the mirror is adjusted slightly between pulses to allow precisely defined motion of the image on the target[14]. This process allows the creation of a wide variety of feature profiles in addition to the “native” taper, which is observed to be a weak function of fluence.

The projection lens focuses the mask pattern on the target material and increases beam intensity by a factor of 25 over the value in the mask plane. Fluences at the surface of the substrate typically cover a range 600 to 1200 $mJ \cdot cm^{-2}$.

The target material is held in the focal plane by a vacuum chuck, mounted on a three axis translation stage. The vertical travel allows the stage to be adjusted to ensure proper focusing of the image.

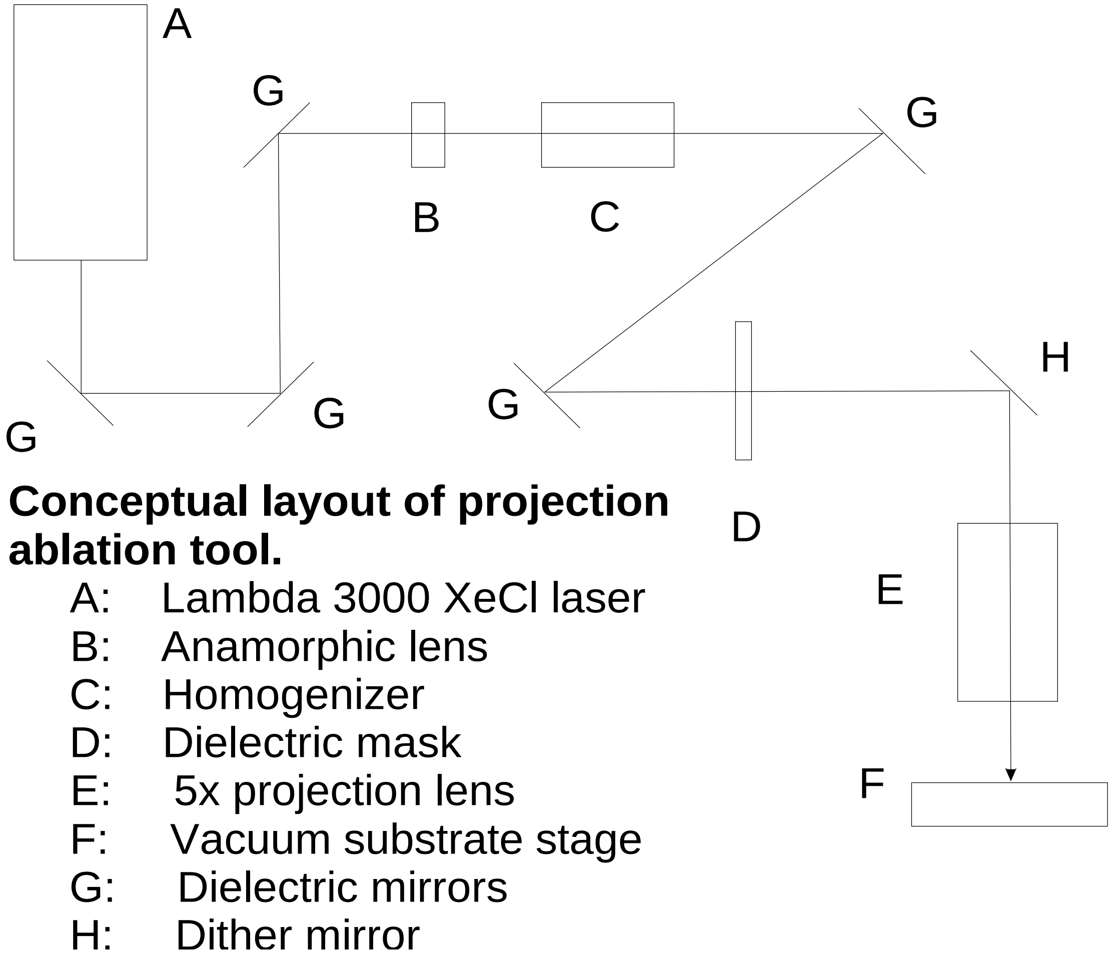

Figure 1. Optical layout of excimer projection ablation testbed

Results

The ablation rates reported below are calculated from the number of pulses required to ablate through a polymeric film. Thus, these are not instantaneous rates, but rather are integrated over a number of pulses.

The four materials for which ablation rates are estimated are summarized in Table 1. These films are widely available, and have a wide range of mechanical and chemical properties. (In order to allow consistency in system setup between materials, the thickness of potential samples was restricted to less than 10 mils. Future studies could relax this limit.)

Material	**Trade Name**	**Thickness, mm**
Polyester	Mylar	75
Polyimide	Kapton	50
Polycarbonate/PET blend	Bayfol CR6-2	175
Polyvinyl chloride	KGC 200	100

Table 1 : Materials evaluated

The same mask was used to evaluate all of the materials. A pattern consisting of circles with a diameter on the mask of 130 μm was chosen so that the resulting holes on the film would be clearly visible, and so that breakthrough would be unambiguously defined. In practice, significantly smaller features can be generated, with features on the order of 1 – 5 μm easily attainable.

A plot of the observed material removal rates is provided in Figure 2. For all four of these materials, the ablation threshold is below the typical operating range of the tool, and within this range the logarithm of the material removal rate varies approximately linearly with fluence. Qualitatively, it is observed that the polyester and polyimide films were machined at a significantly higher rate than the polycarbonate/PET blend and the PVC film. As discussed by Duley, a normalized etching rate, β, can be calculated to facilitate comparison of results[15]. Estimates of β based on these experiments are seen in Table 2. The values observed in these experiments are noticeably larger than those reported by Duley. This difference is expected, because these experiments cover a relatively small range of fluences above the ablation thresholds, where the value of β should be largest. Furthermore, the effective etch rate is influenced by mechanical processes associated with punch–through as well as by radiative ablation. This factor will also tend to raise the value of β.

Material	**b, mm×mJ^{-1}×cm^{2}**
Polyester	8×10^{-3}
Polyimide	4×10^{-3}
Polycarbonate/PET blend	3×10^{-3}
Polyvinyl chloride	6×10^{-5}

Table 2. Normalized etch rates

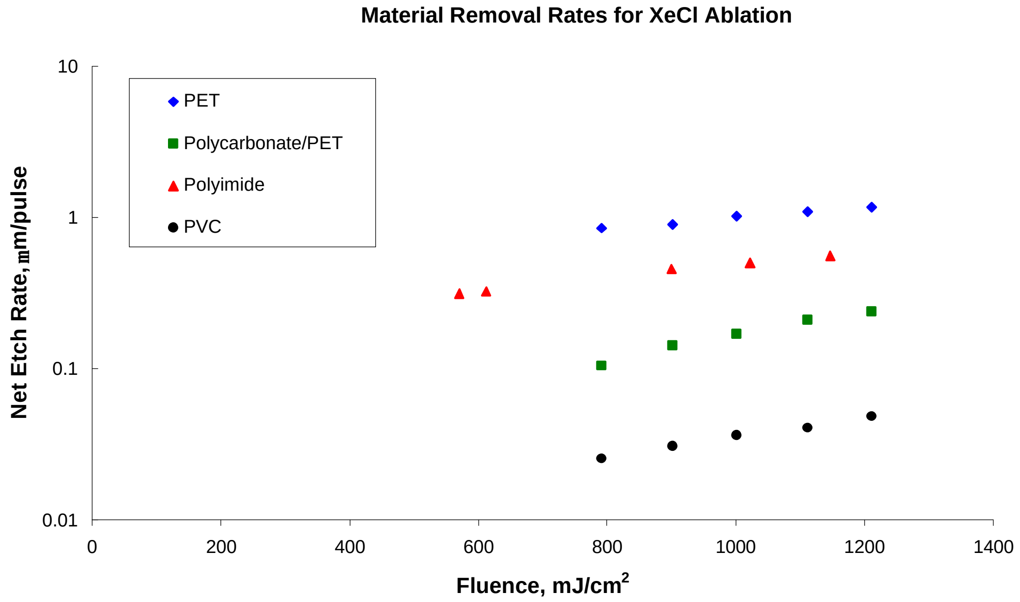

Figure 2. Observed material removal rates as a function of fluence for four polymeric materials.

Conclusions

Excimer ablation of polymers is an attractive method of generating precisely defined features in polymeric films at high throughputs. The design of such processes, however, requires reliable estimates of the effective etching rate. This paper presents such results for four materials of potential interest for the manufacture of small scale devices. In particular, it is shown that appreciable etching rates can be seen at the fluences typical of projection ablation tools.

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References

1. Duley, W.W. (1996) UV Lasers: Effects and applications in materials science, Cambridge University Press, Cambridge

2.. Miller, J.C. (1994) "History, scope, and future of laser ablation," in Fundamentals and Applications of Laser Ablation, J.C. Miller, ed., Springer–Verlag, Heidelberg

3. Dabby, F.W. and Paek, U.-C. (1972) "High–intensity laser–induced vaporization and explosion of solid material," IEEE J. Quantum Electronics, **8**, 106-111

4. Ready, J.F. (1971) Effects of High Power Laser Radiation, Academic Press, Orlando

5. von Allmen, M. (1987) Laser–Beam Interactions with Materials, Springer–Verlag, Heidelberg

6. Duley, W.W. (1983) Laser Processing and Analysis of Materials, Plenum Press, New York

7. Knight, C.J. (1979) "Theoretical modeling of rapid surface vaporization with back pressure," AIAA J., **17**, 519–523

8. Paek, U.C., and Kestenbaum, A. (1973) "Thermal analysis of thin film micromachining with lasers," J. Appl. Phys., **44**, 2260–2268

9. Srinivasan, R. (1993) "Ablation of polymethyl methacrylate films by pulsed (ns) ultraviolet and infrared (9.17 μm) lasers: a comparative study by ultrafast imaging," J. Appl. Phys., **73**, 2743-2749

10. Shannon, M.A. (1993) Laser–Material Interactions: A study of laser energy coupling with solids, Ph.D. thesis, University of California at Berkeley (also published as Report LBL–34889, Lawrence Berkeley Laboratory)

11. Kilgo, M.M. (1995) The influence of ambient medium density on laser ablation processes, Ph.D. thesis, University of California at Berkeley (also published as Report LBNL–39195, Lawrence Berkely National Laboratory)

12. Braren, B., Casey, K.G., and Kelly, R. (1991) "On the gas dynamics of laser–pulse sputtering of polymethylmethacrylate," Nucl. Instr. and Meth. B, **58**, 463–472

13. Zweig, A.D. and Deutsch, T.F. (1992) "Shock waves generated by confined XeCl excimer laser ablation of polyimide," Appl. Phys. B, **54**, 76-82

14. Sheets, R. (1990) "Method and Apparatus for Effecting Selective Ablation of a Coating from a Substrate, and Controlling the Wall Angle of Coating Edge Portions," U.S. Patent No. 4,940,881

15. Duley, W.W. (1996) UV Lasers: Effects and applications in materials science, Cambridge University Press, Cambridge, pp 175–176

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