Materials Patternning with Excimer Laser Ablation

BY BODIL BRAREN

When lasers were introduced three decades ago, initial materials applications were limited due to the narrow range of laser wavelengths that were available. In those early days, infrared and visible lasers (CO$_2$, ruby, and Nd:YAG) were used for welding, cutting, and drilling of different metals.

With the invention of the UV excimer laser in the mid-seventies, a host of new possibilities for material processing emerged. Today, high resolution direct patterning—down to the micron level—is possible for a wide range of materials.

UV lasers offer distinct advantages for direct patterning. Most materials, especially organic polymers, have higher absorption at UV laser wavelengths than at longer wavelengths. The short pulse length, high absorptivity, and high energy density available with UV excimer lasers allow efficient ablation of material. An equally important advantage is the ability to pattern the light beam onto the substrate by projection systems, thereby allowing direct patterning and obviating the need for the solvents and other wet processing present in conventional photolithography.

**FUNDAMENTALS OF LASER ABLATION**

Excimer lasers are pulsed ultraviolet lasers in the wavelength range from 150-350 nm, depending on the gas fill. Typically the UV pulse has a full width at half-maximum (FWHM) of ~20 nsec. The energy output varies at different wavelengths but only 193 nm, 248 nm, and 308 nm lasers produce sufficient power for large area material processing.

In the last decade, excimer laser reliability has improved to meet the more demanding manufacturing needs of high repetition rate and power. Today there are lasers capable of providing a large uniform beam (10 cm$^2$) at 3 J/pulse. For laboratory use, excimer lasers are available with pulse lengths from 400 femtoseconds to several hundred nanoseconds.

**DIRECT PATTERNING**

A major challenge today is how to develop better optical systems to deliver the laser light onto the substrate for direct patterning with high resolution. Different optical configurations have been reported and three basic approaches exist:

1. A laser beam is focused to a small spot producing a small hole. If the substrate is moved in relation to the laser beam, lines are made—a method known as “direct write.”
2. A contact mask, in most cases made of metal, is placed directly on the substrate. The beam is scanned across the mask, resulting in the pattern being transferred onto the substrate. The advantages here are that no special optics are required and the homogeneity and stability of the laser beam is not critical. The disadvantages are loss of resolution and alignment difficulty. The latter can be overcome by producing the mask directly onto the substrate so it becomes part of the structure.
3. A projection system that optically images the mask onto the surface of the substrate is the most versatile approach. The large beam available from the excimer laser has the advantage of illuminating a greater area with a uniform fluence and intensity. First, a homogenizer is used to produce a spatially uniform beam before irradiating either a chrome pattern on optical quartz or a dielectric transmission mask. Then the patterned beam is imaged onto the substrate by a lens system that projects it one-to-one or reduces it to the size desired.

Independent of any of these three optical delivery systems, an in-depth knowledge of the interaction of laser light with the material is essential for good results.

**LASER ABLATION OF MATERIALS**

Direct patterning of organic polymers has been the subject of many investigations due to the technological importance of polymers in the electronic and optoelectronic industry where they are used as dielectrics in packaging, resist materials, waveguides, and insulators. Polyimides used in multilayer circuit boards have received even greater attention. Via hole drilling in polyimides was the first application of excimer lasers on a production line.

Investigations of direct patterning of inorganic materials used for waveguides, insulators, fibers, or conductors are increasing as researchers better understand laser interaction with materials. The actual mechanisms of excimer laser ablation continue to be controversial and are not yet fully understood. Even so, our current understanding points to similarities in ablation behavior of different materials. Four groups of materials are described below.

**Polymer Ablation**

To ablate a polymer cleanly, it is necessary to have a high absorption coefficient and nanosecond laser pulse lengths. For significant material removal, the absorbed energy has to exceed a volume energy density threshold value. Two significant characteristics are observed when a polymer is ablated with UV laser pulses.

First, the etch depth/pulse at a
certain fluence is very reproducible; second, thermal damage to the surrounding area of the substrate is minimal. The amount of material removed from the polymer surface at a given wavelength and pulse length increases with increasing fluence. With an increase in wavelength (generally resulting in lower absorption coefficient), the removal threshold increases but the etch rate/pulse increases because of the larger penetration depth.

Knowledge of the fluence threshold is important for understanding the ablation mechanism. Different methods have been used to determine the threshold. Interpretation of the threshold results is difficult if the polymer is not highly absorbing, as in the case of PMMA.

**PMMA**

In the case of polymethyl methacrylate (PMMA), several pulses may be required before the etch depth/pulse at a given fluence (193 and 248 nm) settles to a constant value. This phenomenon of "incubation" is readily seen in other weak absorbers. The transformation of the surface during the incubation pulses has been analyzed by UV and IR spectroscopy and by analyzing the blast wave produced by the products that emerge from the surface. Both of these studies indicate that PMMA, when irradiated with UV laser pulses, undergoes a chemical transformation to a more absorbing material before measurable material removal takes place. This chemical change was confirmed by dipping the sample in a solvent to remove the photodegraded material, thereby revealing a hole.

Irradiation with 248 nm on PMMA produces a pit with a melted and bubbled surface. The solid material that is ejected from the etched area coalesces into spheres around the irradiated area. A gas dynamic study shows that the material release continues for ~6 μsec, which is about 500 times the pulse length, and that this release is more likely due to a thermal process than to photochemistry. Gas dynamics results for PMMA irradiated with 193 nm also indicate that the bond breaking takes place long after the pulse is over. However, at 193 nm the etching leaves a clean pit with little or no thermal damage to the surrounding area. Another study found the product composition of the decomposed material to be significantly different when going from 248 nm to 193 nm. Considering these different results, the mechanism at 193 nm cannot easily be established.
Ablation might well start as an initial photochemical bond breaking, which then becomes enhanced by a thermal component.

**Polyimide**

In contrast to PMMA, polyimide absorbs strongly at all the excimer laser wavelengths and therefore can easily be ablated at 193 nm, 248 nm, and 308 nm. Clean etching can also be obtained at other wavelengths with nanosecond laser pulses if the polyimide has a strong absorption at that wavelength. This has been clearly demonstrated by Brannon and Braun, both of whom showed clean etching of polyimide with a pulsed CO₂ laser at 9.2 μm.

A recent study by Küper and Brannon using a quartz crystal microbalance and UV laser pulses found that the temperature at the onset of ablation is independent of wavelength. This study’s calculated temperature—850°C based on a one-dimensional heat flow equation—is in agreement with the direct measurements of Brunco et al., who concluded that the decomposition of polyimide at 248 nm was predominantly a thermal process. The only difference in ablation behavior at the various wavelengths found by Küper and Brannon was in the threshold region where irradiation with 193 nm showed a sharply defined threshold. At 248 nm, where the absorption coefficient is lower, the plot of etch depth vs. fluence in the threshold region does not show a sharply defined threshold, but rises smoothly in an exponential fashion.

The biggest problem resulting from laser processing of polyimide is redeposition of surface debris around the irradiated area. The debris has been found to consist of 100% carbon and, if present at the irradiation site, can result in cone formation by shadowing the underlying material.

Understanding the debris formation and the pattern it creates is necessary to effectively eliminate it. As can be seen in Figure 1, the pattern around the irradiated area depends very much on the fluence. A gas dynamic model, although simplified, shows that there are two kinds of particles produced by polyimide ablation in air. Light particles (atoms, molecules, etc.) emitted with high velocity escape the surface first and form a shock wave. Heavy particles, which are 100% carbon, are emitted later and are impeded by the light particles, thereby causing sideways expansion and leaving debris on the target surface beyond the irradiated area.

The model concluded that a flow of helium eliminates the debris by increasing the velocity of the light particles. This allows the heavy particles to leave the surface and be carried away in the gas stream (see Fig. 2). These results have great importance for future use of polyimide in microelectronics packaging.

**Polyurethane**

Of the many other polymers that have been investigated, polyurethane (used as an insulating coating for small magnet wires) is unique. Polyurethane’s relatively strong absorption below 260 nm makes 248 nm laser pulses very efficient in cleaning magnet wires without any surface debris. This lack of debris indicates that polyurethane is one of the few polymers that only decompose into small volatile fragments. The mechanism for decomposition is not completely clear, but the process appears to involve significant heating above 37 mJ/cm².

**Ablation of Ferroelectrics**

Lithium niobate is an important material for integrated optical devices and optical waveguides. Since it is very difficult to pattern LiNbO₃ with standard wet etch methods, excimer laser processing is seen as a possible solution.

Several groups have examined etching of lithium niobate using 193 nm or 248 nm with pulselengths of approximately 15 nsec. Because ablation with 15 nsec pulses starts during the pulse, the incident beam is attenuated via absorption or scattering by the ablated cloud of material flying out with supersonic velocity. The etch rate decreases for larger irradiated areas because more material is in the ablated plume. Beuermann et al. investigated the use of picosecond 308 nm pulses to overcome the attenuation of the incident beam. They found that the etch rate/pulse for the picosecond laser increased three times relative to a nanosecond laser at the same fluence and that the etch rate/pulse is independent of the diameter of the irradiated area. These ultrafast pulses clearly exhibit many advantages that might be useful for material processing in the future with the advancement of picosecond UV lasers.

The mechanism of nanosecond ablation favors a thermal process at 248 nm. Threshold results at 248 nm and 308 nm were found to be similar; how-
ever, an enormous difference in absorption coefficient exists. Therefore, decomposition at the longer wavelength cannot be explained by a purely thermal process.

**Ceramic Ablation**

The success of pulsed laser deposition of high temperature superconductor films in the late 1980s gave new impetus to the application of this deposition technique (see Cheung article, page 24), as well as etching, to other materials. The basic mechanisms for material removal in deposition and etching processes are the same. Studies show that, depending on fluence, the irradiation of the target causes surface heating followed by melting and evaporation.\(^2\)

Tam et al.\(^2\) found that good quality patterning of ferrites with straight edges and almost vertical sidewalls (20 μm wide features, 70 μm deep) can be obtained by projection imaging using 248 nm and 1J/cm\(^2\). The debris problem was overcome by applying a polyester film (a piece of tape) to the surface to protect the surrounding area from the ejected material.

**Ablation of Glass**

Etching of glass shows very interesting behavior.\(^18\) The fast non-Maxwellian velocity distribution of the excited species is difficult to explain by photothermal or photochemical processes at the surface. The most likely mechanism for these high velocities involves the interaction of electrons and decomposition products produced by the first part of the 20 nsec, 248 nm pulse with the latter part of the ablation pulse.

**Conclusion**

As knowledge of excimer laser interaction with materials has increased, it has become more evident that excimer laser ablation of materials involves a predominantly thermal process. Clean etching is not inherent to UV laser ablation, but is governed by the absorption coefficient of the material and the pulsewidth of the laser at a given wavelength.

Excimer laser patterning in manufacture is now well established for polymers. New applications for different materials will emerge as researchers increase their understanding of laser interactions with these materials. The direction of future research in laser processing of materials depends in part on the development and availability of short pulsed, reliable lasers at all wavelengths from ultraviolet to infrared.

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**References**

14. S. Kueper and J. Brannon, "KrF laser ablation of polyurethane," Lasers in Microelec-

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