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Title: **ADVANCES IN EXCIMER LASER PROCESSING OF MATERIALS**

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# ADVANCES IN EXCIMER LASER PROCESSING OF MATERIALS

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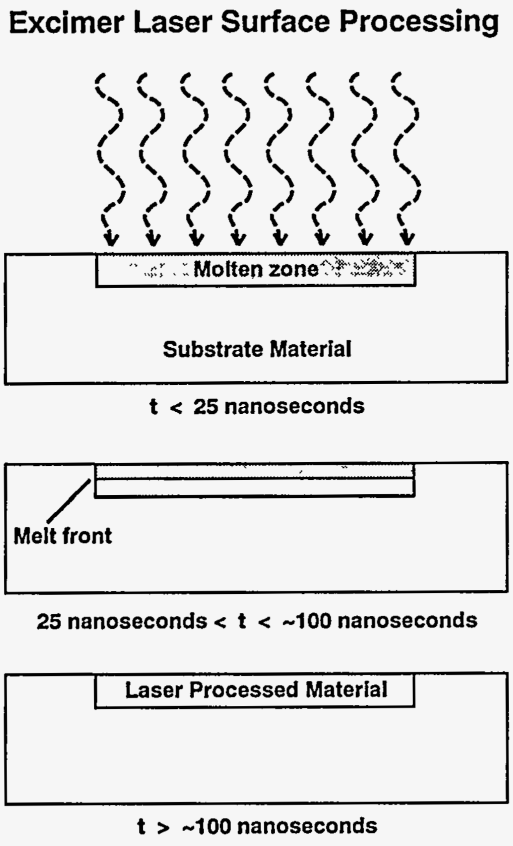
The use of pulsed excimer lasers to surface processing of materials hinges on an understanding of the nature of the interaction between the laser energy and the material. One of the advantages of excimer laser processing is the relative uniformity of that interaction across diverse materials. The short wavelength, (200–400 nm depending on the laser gas) and the short pulse length (~ 30 ns) mean that for most materials, the energy is absorbed in a region of the surface that is shallow (~10 nm) relative to the thermal diffusion length (~100 nm) in the material. These conditions mean that the details of the absorption process do not affect the temperature distribution below the surface[1] and the thermal effect is that of an instantaneous heat pulse incident on the surface. The large size of a typical excimer beam spot for fluences in the 1–3 $J\text{-}cm^{-2}$ range ensures that the heat flow is essentially one dimensional. The net effect of an incident excimer laser pulse is to rapidly heat the surface of the material with cooling occurring at a rate determined by the 1-D heat flow to the back of the sample. The process is also highly efficient, due to the low reflectivity of most materials in the ultra-violet. Typical cooling rates for surface-melted materials are of the order of $10^9$ $K\text{-}s^{-1}$ with a typical melt–solidification–cooling cycle back to ambient temperature taking less than $10^{-3}$ s. The short duration of the liquid state and the thin melt layer eliminates any chance for convection. These aspects of the laser-materials interaction mean that surface effects, whether thermal transformation or melting and resolidification are dependent entirely to the incident fluence and the thermal properties of the material.



The application of this understanding of the laser materials interaction to surface modification must also recognize the existence of thermodynamic driving forces and kinetic limitations in light of the short duration of a single pulse event. Single pulse processing can result in amorphizing[2], recrystallization[3], or martensitic transformations[4]. For modifications that require substantial migration of individual species, either mixing or segregation, multiple pulse processing may be necessary. For typical liquid state parameters, diffusion lengths of the order of 50 nm per pulse can be obtained and net effects can be related directly to the number of incident pulses[5]. Metastable microstructures often result from rapid solidification from the melt[6].

For species that have higher solubility in the liquid than in the solid phase, segregation by "zone refinement" from multiple passes by a solidification front to the surface results in surface enrichment of those species[7]. Mixing of alloying elements can occur when there is an appropriate driving force[8]. The most straightforward case is for mixing at a solid-solid interface that is melted by the laser energy, but the use of a gas or liquid atmosphere can lead to alloying directly from the fluid phase[9, 10]. Additions that alter the chemical or mechanical properties of the surface region can be incorporated with a graded interface that is not prone to delamination. The high temperatures reached during laser processing facilitate mixing in some systems that cannot be mixed with ion beams due to kinetic constraints[11]. The short duration of individual pulse events means that multiple pulse processing, even at rates at high as 100 Hz, can be thought of as a series of independent events, allowing for very rapid processing.

The most obvious applications for surface processing occur where the bulk properties of a component are not commensurate with the needed surface properties. Excimer laser processing has been shown to increase the resistance to pitting of AISI 304 SS due to an increase in the surface Cr concentration and the formation of a thicker layer of the stable Cr oxide. Enhancement of Cr results from zone refinement. Mixing of Si layers into Nb surfaces has also provided increased corrosion resistance in Nb through formation of stable surface compounds[12]. In an inverse process, $WSi_2$ was formed by mixing of W layers on Si substrates[13].

Improvements in surface mechanical properties have been observed in a number of metal[14, 15, 16] and ceramic alloys[17, 18]. In tribological applications, improvements are related to changes in the surface hardness, finer-grained or amorphous microstructure, and the formation of high-lubricity transfer films on the surface. Fundamental changes in the wear mechanism have typically been observed. Excimer laser surface processing has also been used to increase the bulk fracture strength of ceramic materials, which often fail due to surface defects[19., 20].

In the microelectronics industry, apart from micromachining or material removal applications, for which excimers are indeed well suited, the same features of the laser-materials interaction that are use to modify the mechanical or electrochemical properties of a surface can be used to advantage. Single-shot recrystallization of large areas of amorphous Si to poly-Si for production of active-matrix liquid crystal display has been demonstrated, as has multiple-pulse annealing[21]. Exploiting the low viscosity of liquid metals, laser melting and resolidification has been demonstrated for planarization of Al[22] and other metal layers.

The fundamentals of excimer laser surface modification have largely been established. As in many "boutique materials" developments, process optimization is required for particular applications. Further advances, such as those demonstrated in microelectronics, await these application-specific developments.

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