

LA-UR 92-3406

CONF-92111

LA-UR--92-3406

DE93 003726

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

Revised

DEC 01 1992

TITLE EXCIMER LASER SURFACE MODIFICATION: PROCESS AND PROPERTIES

AUTHOR(S) T. R. Jervis DIR-ESD
 M. Nastasi MST-7
 J-P. Hirvonen Technical Research Centre of Finland

SUBMITTED TO Proceedings of the Materials Research Society, Pittsburgh, PA

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos Los Alamos National Laboratory
 Los Alamos, New Mexico 87545

MASTER

FORM NO. 816-104
 5/78

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Se

EXCIMER LASER SURFACE MODIFICATION: PROCESS AND PROPERTIES

T. R. JERVIS*, M. NASTASI**, AND J-P. HIRVONEN***

*Center for Materials Science, Los Alamos National Laboratory, Los Alamos, NM 87545

**Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545

***Metallurgy Laboratory, Technical Research Institute of Finland, SF-02150 Espoo, Finland.

ABSTRACT

Surface modification can improve materials for structural, tribological, and corrosion applications. Excimer laser light has been shown to provide a rapid means of modifying surfaces through heat treating, surface zone refining, and mixing. Laser pulses at modest power levels can easily melt the surfaces of many materials. Mixing within the molten layer or with the gas ambient may occur, if thermodynamically allowed, followed by rapid solidification. The high temperatures allow the system to overcome kinetic barriers found in some ion mixing experiments. Alternatively, surface zone refinement may result from repeated melting-solidification cycles.

Ultraviolet laser light couples energy efficiently to the surface of metallic and ceramic materials. The nature of the modification that follows depends on the properties of the surface and substrate materials. Alloying from both gas and predeposited layer sources has been observed in metals, semiconductors, and ceramics as has surface enrichment of Cr by zone refinement of stainless steel. Rapid solidification after melting often results in the formation of nonequilibrium phases, including amorphous materials. Improved surface properties, including tribology and corrosion resistance, are observed in these materials.

INTRODUCTION

The properties of material surfaces have been modified by coatings, rf heat treatment, and the use of directed-beam technologies including ion-, laser-, and electron-beam processes. In the case of thermally activated processes, each of these techniques has associated with it characteristic depths of treatment and associated cooling rates. Deeper penetration generally is associated with slower cooling rates because of limitations of heat transfer in the material. In this paper we will discuss the use of excimer laser light to drive thermally activated processes in surfaces of both metals and ceramics in order to alter the surface properties of the materials. Typical treatment depths are of the order of 100 nm. This depth scale is comparable to that obtained in ion-beam processing, for which there is a substantial literature and history of application.

Excimer lasers are characterized by relatively short pulse lengths ($\sim 25 \times 10^{-9}$ s), and wavelengths in the ultra-violet (UV). Common wavelengths are 193, 248, 308 or 351 nm corresponding to ArF, KrF, XeCl, or XeF laser gases. These laser wavelengths are quite efficient, with electrical conversion efficiencies comparable to those of CO₂ lasers which are widely used for cutting, heat treating, and cladding applications [1, 2, 3, 4].

The major advantage of excimer lasers for many applications lies in the strong coupling between light at these wavelengths and many materials. This coupling enhances the overall efficiency of the process. For processing with 5-10 pulses per position at 1.0 J-cm^{-2} , typical values for the experiments described here, a laboratory scale

laser with an output of 15 W (average) can treat material at approximately $1.5 \text{ cm}^2\text{-s}^{-1}$. Industrial excimer lasers with average outputs of 150 W exist and can process material at rates of approximately $15 \text{ cm}^2\text{-s}^{-1}$. These rates are extremely attractive from an industrial point of view. Finally, many processes can be carried out in air or in a shield-gas environment, eliminating the need for vacuum systems typical of ion- or electron-beam systems.

Excimer Laser Materials Interactions

Figure 1 shows the reflectance spectrum for Al, Fe, and SiC⁵. At 248 nm, the wavelength used for most of the experiments to be described below, the reflectance of many metals is similar to that of Fe. Although Al represents the worst case, the Al₂O₃ inevitably found on the surface is a good absorber so the coupling is better than it appears from the figure. The energy per photon of excimer laser radiation is high ($\sim 5 \text{ eV}$ for 248 nm), and the energy is absorbed in electron excitations that are thermalized very rapidly ($\sim 10^{-12} \text{ s}$) so that the effect of laser radiation on the surface is essentially purely thermal below the threshold for ablation. The absorption depth in most materials is of the order of 5-20 nm. This combination of properties means that much of the incident laser energy is deposited in a volume very close to the surface.

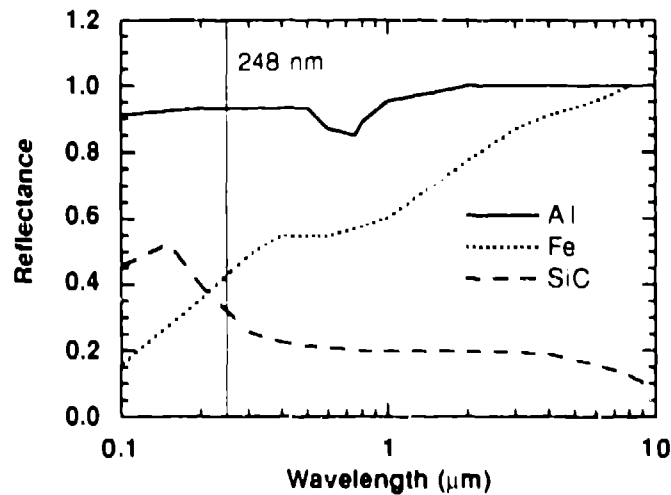


Figure 1. Reflectance vs wavelength for Al, Fe, and SiC. KrF excimer wavelength of 248 nm is indicated.

In reality, the reflectance of metal surfaces is somewhat lower than this ideal due to oxides, as mentioned above. Further, the reflectance is a dynamic variable and for most metals decreases with increasing temperature. Therefore, as the laser light interacts with the surface, heating it, the reflectance decreases, increasing the efficiency of the coupling. However, although the effect is not linear, the facts that the reflectance in the UV is not too large to begin with and the pulse length is short reduce the opportunity for thermal runaway.

The dynamics of the laser-surface interaction can be understood at a number of levels. The simplest level uses the thermal diffusivity, κ , and the pulse length t_0 to estimate the depth of material initially affected by the laser pulse. This thermal depth,

$$z_{th} = 2 \sqrt{t_0 \kappa} \quad (1)$$

defines the depth of penetration of the heat pulse during the time of the laser pulse. For metals and many ceramic materials, this depth is of the order of 100 nm. When z_{th} is much larger than the absorption depth, as it is for UV laser processing, von Allmen has shown that the details of the absorption process do not affect the temperature distribution below the absorption depth and the process can be thought of as a simple heat pulse initially affecting the surface to the thermal depth and then being conducted into the bulk of the material⁶. At this level it is a simple matter to calculate the incident fluence required to heat or melt the volume of depth z_{th} and area illuminated by the laser pulse.

At laser pulse energies of the order of a joule, spot sizes for surface processing are of the order of a square centimeter. Thus it is legitimate to ignore edge effects and think of the problem as one-dimensional heat flow from a surface source. There is also radiation from the hot surface but radiation and convection at the free liquid surface are negligible on the time scales involved here. The time history of the temperature of the melted surface layer of metals can be calculated directly from the fundamental optical and thermal constants of the material. If we assume that the laser pulse has a square temporal profile, so that the incident power is either a constant P_0 or zero, the temperature, T , of the material at any depth z and time t is given analytically by⁷.

$$T(z,t) = (1 - R) \frac{2P_0 \sqrt{\kappa t}}{K} \operatorname{ierfc} \left(\frac{z}{2\sqrt{\kappa t}} \right) \quad (2)$$

for $t \leq t_0$

and

$$T(z,t) = (1 - R) \frac{2P_0 \sqrt{\kappa}}{K} \left(\sqrt{t} \operatorname{ierfc} \left(\frac{z}{2\sqrt{\kappa t}} \right) - \sqrt{t - t_0} \operatorname{ierfc} \left(\frac{z}{2\sqrt{\kappa(t - t_0)}} \right) \right) \quad (3)$$

for $t > t_0$

where R = reflectivity, κ = thermal diffusivity, K = thermal conductivity, and t_0 = pulse length

Melting can be accommodated by a heat of fusion term in $T(t)$ and appropriate conditional statements. This calculation still ignores many significant aspects of the solidification process, such as the temperature dependence of many of the variables. This model uses no adjustable parameters and the room temperature values of all material properties and illustrates the essential features of the process. At low fluences, the material simply heats up rapidly and begins to cool when the pulse terminates. At higher fluences, the surface of the material melts, and the melt front propagates inward until the energy of the pulse is dissipated in the melting process and by conduction into the bulk of the material. The melt front then stops and a resolidification front moves back toward the free surface. It is important to understand that melt depths are of the order of a few hundred nanometers, so "bulk" of the material means only a few tenths of millimeters.

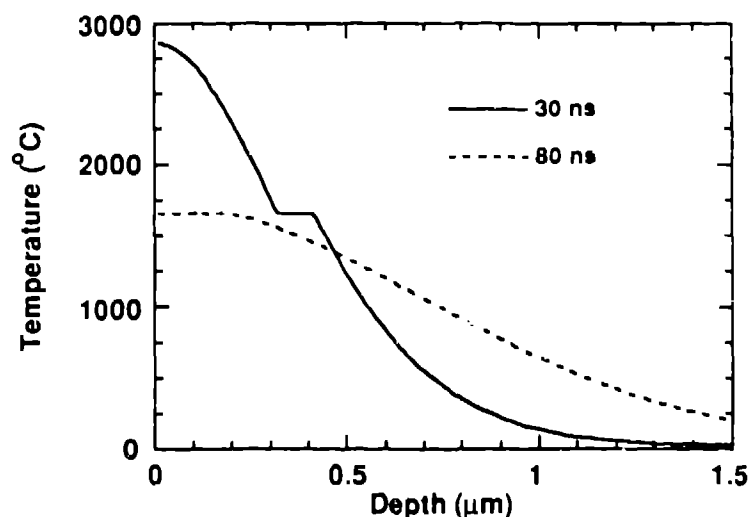


Figure 2. Temperature profile calculated for excimer laser melting of Ti-6Al-4V at $1.0 \text{ J}\cdot\text{cm}^{-2}$ at 30 ns (peak temperature) and 80 ns.

Figure 2 shows the temperature profile calculated from equation 3 for an incident fluence of $1.0 \text{ J}\cdot\text{cm}^{-2}$ on Ti-6Al-4V at 30 ns and 80 ns. These times correspond approximately to the peak temperature and freezing point, respectively. This calculation results in a melt depth of the order of $0.4\text{--}0.5 \mu\text{m}$ with the surface returning to within 5 C of room temperature within 0.02 sec and a cooling rate after solidification in excess of $10^9 \text{ K}\cdot\text{s}^{-1}$. At this fluence, the surface layer is molten for a period of approximately 50 ns . During this time, diffusion in the liquid state can occur on a distance scale of the order of 10 nm . Because the surface returns to room temperature rapidly, repetition rates of the order of 10 Hz can be used without cumulative effects and the process is essentially a serial one. Therefore multiple pulse processing can increase the diffusion distance substantially.

More detailed models of the excimer laser-surface interaction exist that include many of the aspects ignored in this calculation^{8, 9}. However, the model described above contains all the essential features of the process and we have found it useful in predicting the effect of excimer laser processing on a number of materials^{10, 11}.

The greatly enhanced diffusion rates which result from melting suggest many possible applications of the melting-resolidification process. Mixing, diffusional phase transformations, and zone refinement are all possible using excimer laser processing. As discussed above, one of the features of excimer laser processing, a direct result of the short pulse duration and shallow thermal depth, is the serial nature of the process. Even at repetition rates as high as 100 Hz , pulses can be considered to be independent events and the diffusion effects observed for a single pulse can be multiplied simply by increasing the number of pulses. This is illustrated in figure 3 which shows the distribution of implanted ^{13}C before and after processing with 5 and 10 pulses of laser radiation at $1 \text{ J}\cdot\text{cm}^{-2}$ at a repetition rate of 1 Hz ¹². A fit to the as-processed profiles yields diffusion lengths $2\sqrt{\tau D}$ of 41 nm and 51 nm respectively. For $\tau = nt$, where n is the number of pulses and t the melt duration calculated from the model described above (50 ns), diffusion lengths per melt period of 36 and 32 nm are obtained. These figures imply a

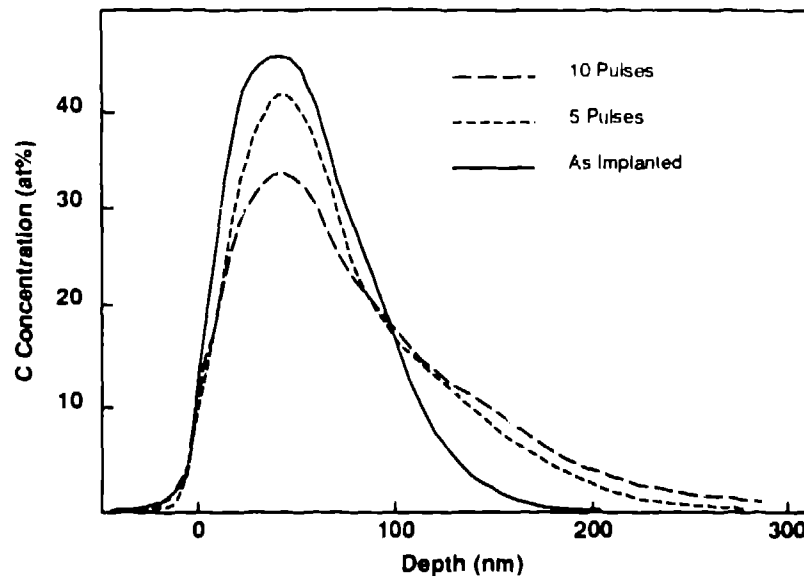


Figure 3. Concentration of ^{13}C as implanted and after laser processing with 5 and 10 pulses at $1.0 \text{ J}\cdot\text{cm}^{-2}$.

diffusion coefficient of $5 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$, in good agreement with the published value for C in Fe^{13} at 1550 C of $6\text{-}7 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$. This result also emphasizes that diffusion occurred in the liquid state, as the solid state diffusion of C in Fe is orders of magnitude slower than this value.

The ability to obtain uniform illumination of the sample during laser processing is essential to the success of the process in application. Although excimer laser beams are physically large (typically $2 \text{ cm} \times 3 \text{ cm}$ or larger), the intensity profiles are not uniform, so some means of homogenizing the intensity of the beam is necessary to obtain uniform processing. We have used a device using two arrays of cylindrical lenses at right angles to decompose and refocus the beam with a high degree of uniformity ($> 95\%$). Other methods involving prisms or reflectors can also be devised. The large size of the beam makes this problem somewhat less complex. In addition, if multiple pulse processing is involved, overlapping of the pulses in one or two dimensions serves to increase the overall uniformity of the process.

We have found that for polished metal surfaces with an average surface roughness of 50 nm , the surface roughness after multiple pulse laser processing with the homogenized beam is of the order of 70 nm . This is apparent as a slight haze on the otherwise mirror smooth surface, a result of slight imperfections in that cause locally nonuniform absorption. For most applications, this is a sufficiently smooth finish and no further processing is necessary. As described below, laser surface processing can actually be used to planarize otherwise optically rough surfaces.

APPLICATIONS

Because of the short time at temperature, transformations available to short-pulse laser processing below the melt threshold are limited to those of the diffusionless (martensite) type. These have been demonstrated in Ti alloys¹¹ but other application, for example to surface hardening of steels, has not.

The rapid solidification associated with quenching following short-pulse laser

processing often leads to metastable microstructures. This results from the inability of the atoms in the melt to readjust configurationally to their equilibrium positions in the time available prior to solidification^{14, 15}. This can result in the "freezing in" of high temperature phases, the formation of amorphous or glassy metal alloys, and local supersaturation of alloys, as well as the formation of fine grained microstructures in surface modified materials. These are features which are dependent on the short pulse duration and small z_{th} , features which are shared by other short pulse laser processing. The cooling rate is directly proportional to the temperature difference between the molten layer and the substrate. Thus, cooling or heating the substrate can result in increased or decreased cooling rates, respectively. A wide range of microstructures is therefore accessible using pulsed laser surface melting^{16,17}.

For example, Fröhlingsdorf and Stritzker used excimer lasers to probe the amorphization and crystallization of pure Ga films at low temperatures¹⁸. Amorphous Ga resulted from laser melting and resolidification of amorphous, α phase, and metastable β phase materials. Excimer laser surface melting has been used to examine the effects of rapid solidification on pre-alloyed Fe-B¹⁹ and Ni-Ti²⁰ alloys. We have observed formation of amorphous phase materials in several systems, including Fe-Ti²¹, Fe-C¹², and Ti-B²².

Surface Mixing

The earliest attempts at laser surface processing were mixing or laser surface alloying experiments. The technology was subsequently developed both for semiconductor processing²³ and, using IR lasers, for a number of applications using gas, powder, plated, or foil schemes to introduce alloying elements⁴. In IR laser mixing, substantial convection occurs in the melt pool, which complicates analysis of the mixing. In the excimer laser case, there is no convection because of the short melt duration and small z_{th} . However, many similar processes are possible although the length scales possible are much shorter than in the IR case. A number of papers have discussed the possibilities and limitations of mixing in pulsed laser processing situations^{24, 25}. The essential conclusions being that mixing will occur where allowed by thermodynamic considerations.

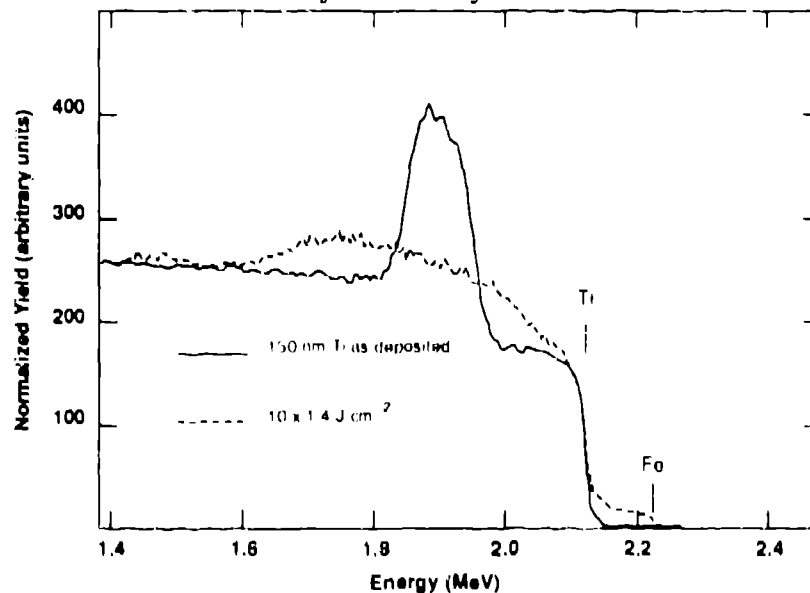


Figure 4. Rutherford backscattering spectrum showing laser mixing of 50 nm layer of Ti on AISI 304 stainless steel.

In Figure 5, we show the Rutherford Backscattering (RBS) spectrum showing excimer laser mixing of a single evaporated 150 nm layer of Ti on AISI 304 stainless steel. In the as deposited film there is no Fe on the surface and the Ti peak, superimposed on the Fe in the substrate is well delineated. After processing with 10 pulses of excimer radiation at 1.4 J-cm^{-2} , the Ti peak broadens, reflecting both the diffusion of Ti into the substrate and the diffusion of Fe into the surface layer. The broadening, as well as the amount of Fe at the surface, increases with the number of pulses, representing increased mixing. The microstructure of the surface film was found to be amorphous, reflecting the rapid solidification.

As has been observed²⁶ for steel surfaces implanted with Ti and C, an amorphous surface alloy was formed by laser mixing and this surface alloy shows improved friction and reduced wear behavior²⁷. We have also observed improved tribological properties for the oxide film resulting from excimer laser processing of AISI 304 stainless steel²⁸.

It is also possible to mix metals into ceramic substrates. Figure 5 shows the RBS spectrum of a single 100 nm layer of Ti on polycrystalline Si_3N_4 . In this case the Ti peak is well separated from the Si substrate edge and the effect of the mixing on the Ti layer and the substrate is quite clear. The Ti layer broadens and Si appears in the surface layer. X-ray diffraction of the surface before and after processing shows that the Ti reflections disappear and TiN reflections consistent with very small grain size appear²⁹. These results are generally consistent with those expected for these systems³⁰. Similar results have been found in the mixing of Ni on SiC and Si_3N_4 ³¹ and Ti on SiC¹⁰. These surfaces show improved fracture toughness³², reduced friction, and improved wear properties³³.

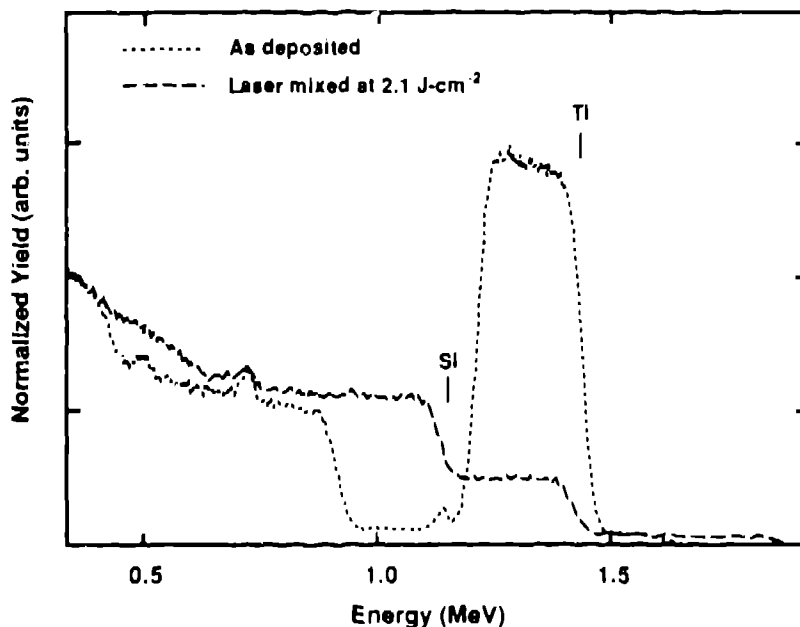


Figure 5. Rutherford backscattering spectrum showing laser mixing of 150 nm layer of Ti on a Si_3N_4 substrate. Tilt angle of sample is 60° .

Predictions of miscibility in metal-ceramic systems can be used to guide experiments in this area^{28, 34}. For example, mixing of Zr and Ti on Al_2O_3 should be difficult because of the limited solubility of these metals in Al_2O_3 . Indeed, we observed melting and beading up of the metallization in these systems when laser processed. However, although Cr has a high solubility in Al_2O_3 , attempts at laser

mixing in this system have been unsuccessful³⁵ Excimer laser surface processing has been used to improve the adhesion of Cu films to Al₂O₃ substrates^{36, 37}.

The results of laser mixing of a 100 nm layer of Si evaporated onto Nb are shown in Figure 6. As in the previous examples, Nb diffuses into the Si surface layer and the Si peak, here superimposed on the Nb signal broadens as the Si diffuses into the substrate. Reconstruction of this spectrum indicates that a 200 nm thick surface layer of NbSi₂ with a graded interface is formed after 5 pulses at 1.7 J·cm⁻². Mixing of Si on Nb with ion beams was not successful. Nb surfaces mixed with Si demonstrated substantially changed oxidation characteristics³⁸.

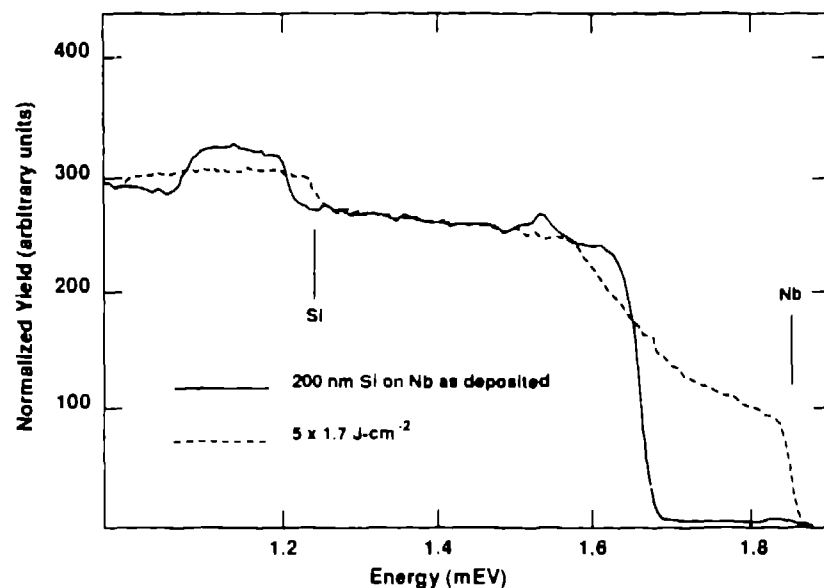


Figure 6. Rutherford backscattering spectrum showing laser mixing of 200 nm layer of Si on a Nb substrate. Reconstruction of this spectrum is consistent with a 200 nm layer of NbSi₂ with a graded interface to the Nb.

Excimer laser mixing has also been demonstrated from gas and liquid ambients. We have demonstrated formation of metastable TiO particulates in Ti alloys processed in air³⁹ and the incorporation of N into the surface when processed in a pure N₂ atmosphere⁴⁰. Carburization of Ti by processing in methane⁴¹ has also been demonstrated with formation of TiC verified by ESCA. These techniques result in the formation of what is effectively a metal matrix composite of the base metal and precipitate particles. Nitrides of Be and several transition metals have been formed by excimer laser processing in liquid N₂^{42, 43}. However, scanning electron microscope images of the surface reveal them to be rather porous, a result of boiling at the liquid-solid interface during processing. Combining gas and evaporated layer source mixing, simultaneous nitridation and silicide formation has been accomplished by processing Ti layers on Si in a N₂ atmosphere⁴⁴.

The evolution of the microstructure of laser mixed surfaces is complex, but is understandable in the context of the melt duration and solidification rates involved. This is perhaps best illustrated by consideration of laser mixed Fe-Ti-C multilayer structures⁴⁵. With these sub-micron layers, the average composition of the composite layer (FeTi_{0.8}C_{1.1}) is determined initially by the relative thicknesses of the constituent layers and phase formation is less influenced by diffusional gradients. Laser processing with a single pulse at 1.1 J·cm⁻² results in an amorphous structure with small TiC precipitates. When treated with a single

pulse at $1.7 \text{ J}\cdot\text{cm}^{-2}$, no amorphous diffraction pattern is seen but patterns consistent with small grained TiC and Fe₃C are evident. Treatment with ten pulses results in development of larger α -Fe grains.

Low fluence, single-pulse processing results in less than complete mixing of the multilayers, formation of the amorphous phase expected for this Fe/Ti ratio⁴⁶, and formation of small scale TiC precipitates, reflecting the strong driving force for TiC formation. A longer melt duration (higher fluence processing) allows the formation of more complex compounds, specifically Fe₃C. Development of fully stable structures is still inhibited by composition and rapid solidification. Finally, with multiple pulse processing, more Fe diffuses out into the surface layer from the substrate and there is sufficient time and Fe concentration for larger α -Fe crystallites to grow. Direct ion-beam mixing of Fe-Ti-C multilayers has not been successful, indicating a kinetic barrier of some kind to the ion-beam mixing process⁴⁷ which is overcome at the temperatures involved in laser processing. Rapid solidification of Ti and C implanted Fe by laser and e-beam techniques produced microstructures consistent with these results⁴⁸.

This discussion demonstrates that by judicious choice of surface layers, excimer laser mixing can selectively tailor not only the composition of the surface, but also the microstructure. The examples demonstrate the applicability of the process to a number of systems.

Surface Segregation

In the examples discussed above, mixing occurred among constituents of the surface driven by thermodynamic forces. In some cases this resulted in metastable structures. Differences between solid and liquid solubilities of particular constituents of materials can be exploited to change the surface composition of those materials. In particular, if the solubility of a constituent is higher in the liquid state than in the solid state, a moving melt front will tend to drive a concentration gradient ahead of itself. This zone refinement phenomenon can be used to change the surface concentration of materials and perhaps even to create new materials.

In AISI 304 stainless steel, the concentration of Cr exceeds the equilibrium solid solubility limit for that material. Thus, repeated melt-resolidification cycles will increase the surface Cr concentration. Figure 6 shows the ratio of Cr to Fe peak amplitudes determined by Auger electron spectroscopy⁴⁹ in the oxide films of AISI 304 stainless steel laser surface melted at $1.0 \text{ J}\cdot\text{cm}^{-2}$. In addition to increasing the Cr content, the surface oxide becomes somewhat thicker. Treatment at higher fluence ($> 1.5 \text{ J}\cdot\text{cm}^{-2}$) ablates the surface oxide and the increase in Cr is less pronounced.

The effect of the increased Cr content in the surface oxide is to stabilize that oxide, increasing the resistance of the material to corrosion. A substantial change in pitting behavior was also observed.

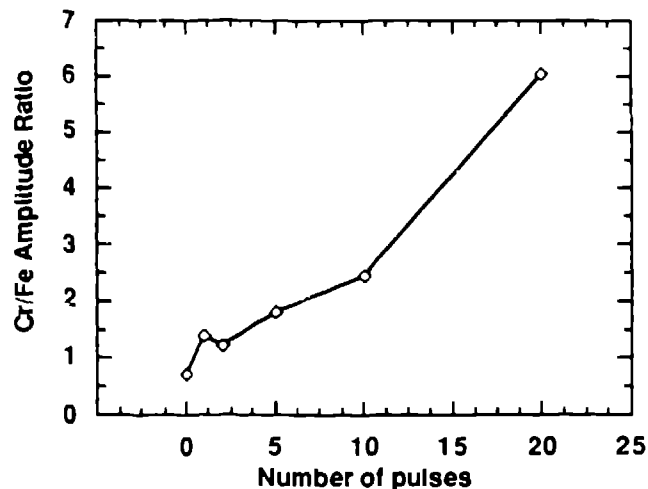


Figure 3. Cr to Fe peak amplitude ratio measured in the oxide film of AISI 304 stainless steel laser treated at 1.0 J-cm^{-2} .

A more dramatic use of this same technique is the use of excimer laser melting and resolidification to drive C atoms implanted into Cu back to the surface at high temperature and pressure to form diamond films in the surface⁵⁰. These results remain somewhat controversial as they have not been duplicated. Nevertheless, the possibility exists to concentrate constituents at the surface of a material by effectively zone refining the near-surface region. Excimer lasers have also been used to improve nucleation and adhesion of chemical vapor deposited diamond films⁵¹.

Other Processing Applications

Short absorption and thermal depths also enable the use of lasers to melt and reflow thin metal films in semiconductor devices in order to planarize the surface. The low viscosity of molten metals allows rapid filling of trenches and vias for interconnects and for further processing on the planarized surface. This has been demonstrated in Au⁵², Al⁵³ and most recently Cu^{54, 55}.

Processing at higher fluences ($> \sim 3 \text{ J-cm}^{-2}$) alters the surface morphology of most metals due to ablation as well as shock and plasma effects. Excimer laser processing at high fluences in a number of gaseous and cryogenic liquid ambients has a substantial effect on surface topography of Al, Ni, Ti, and Zn surfaces⁵⁶. These changes in surface morphology were used to try to alter the strength of wire bonds to a number of excimer processed Cu, Ni, Au, and Ag alloys, including excimer laser mixed Cr on Cu⁵⁷. Changes in the surface state following excimer laser surface processing were shown to increase the coupling between Cu surfaces and CO₂ radiation, enabling the efficient cutting and drilling of this otherwise highly reflecting material^{58, 59}.

CONCLUSIONS

Many bulk properties of materials such as fracture strength and toughness are limited by their surface properties, and many surface properties of interest such as tribology and corrosion resistance are dependent on the microstructure and local

chemistry of the surface. The ability to tailor the surface using excimer laser processing, microstructurally by controlled rapid solidification and chemically by alloying, has broad application. Virtually any metal, including refractories, can be melted by single excimer laser pulses enabling the formation of novel alloys. Microstructural control of the resultant layers through rapid solidification increases the breadth of application. Mixing of metals and alloys and even dissimilar materials such as metals and ceramics is not only possible, but relatively straightforward. The basic science of the technology is clear, what is needed is more intense development of the technology for specific applications.

ACKNOWLEDGMENTS

We would like to thank the personnel of the Los Alamos Ion Beam Materials Laboratory for technical assistance. This research was supported by the United States Department of Energy under contract W-7405-ENG-36 by the Los Alamos Center for Materials Science through D. Parkin.

REFERENCES

1. *Laser Materials Processing*, M. Bass, Ed. (North Holland, Amsterdam, (1983).
2. *Laser Surface Treatment of Metals*, C. W., Draper and P. Mazzoldi, Eds, Martinus Nijhoff, Dordrecht, 1986).
3. *Laser Treatment of Metals*, B. L. Mordike, Ed, (Informationsgesellschaft, Oberursel, (1987).
4. P. A. Molian in *Surface Modification Technologies*, T. S. Sudarshan, Ed, Marcel Dekker (New York 1989) p. 421.
5. *Handbook of Laser Science and Technology Vol 4 Part 2*, (CRC Press, Boca Raton, FL, 1986).
6. M. von Allmen, *Laser Beam Interactions with Materials*, (Springer Verlag, Berlin, 1987).
7. V. G. Gregson, in *Laser Materials Processing*, M. Bass, Ed. (North Holland, Amsterdam, 1983), p 201.
8. R. K. Singh & J. Viatella, *J. of Metals*, 3/1992, p 20.
9. S. Unamuno, M. Toulemonde, and P. Siffert, in *Laser Processing and Diagnostics*, D. Bäurle, Springer (1984) p 35.
10. T. R. Jervis, J-P. Hirvonen, M. Nastasi, and M. R. Cohen, *Mat. Res. Soc. Symp. Proc.* **157** 395 (1990).
11. T. R. Jervis, T. G. Zocco, and J. H. Steele, Jr., *Mater. Res. Soc. Symp Proc.* **201** 535 (1991).
12. J-P. Hirvonen, T. R. Jervis, and T. G. Zocco, *Mat. Res. Soc. Symp. Proc.* **157** 431 (1990).
13. J. G. Fujimoto and E. P. Ippen in *Laser Optics of Condensed Matter*, J. L. Birman, H. Z. Cummins, and A. A. Kaplyanskii, eds. Plenum, New York, 1988) p. 11.
14. F. Spaepen, *Hume Rothery Symposium on Undercooled Alloy Phases*, E. W. Collings & C. C. Koch, Eds, (TMS-AIME 1986).
15. D. Turnbull, *Met. Trans.* **12A** 695 (1981).
16. D. M. Follstaedt and S. T. Picraux, in *Surface Alloying by Ion, Electron, and Laser Beams*, (ASM, Metals Park, OH, 1987) p. 175.
17. P. S. Peercy, in *Laser Surface Treatment of Metals*, C. W., Draper and P. Mazzoldi, Eds, Martinus Nijhoff, Dordrecht, 1986) p. 57.
18. J. Fröhlingsdorf and B. Stritzker in *Laser Treatment of Metals*, B. L. Mordike, Ed, (Informationsgesellschaft, Oberursel, 1987) p.63.
19. J. W. McCamy, A. J. Pedraza, and D. H. Lowndes, *Mat. Res. Soc. Symp. Proc.*

- 74 203 (1987).
20. A. J. Pedraza, M. J. Godbole, E. A. Kenik, D. F. Pedraza and D. H. Lowndes Mat. Res. Soc. Symp. Proc. **74** 185 (1987).
 21. T. R. Jervis, M. Nastasi, T. G. Zocco, and J. A. Martin, Appl. Phys. Lett. **53** 75 (1988).
 22. T. R. Jervis, M. Nastasi, J-P. Hirvonen, & T. G. Zocco, American Institute of Physics Conf. Proc. **231** 652 (1991).
 23. C. W. White, J. Narayan, and R. T. Young, Science **204** 461 (1979).
 24. C. W. Draper and J. M. Poate, Int. Metal Rev. **30** 85 (1985).
 25. M. Von Allmen in *Glassy Metals II*, H. Beck and H-J. Güntherodt, eds (Springer, Berlin, 1983) p. 261.
 26. D. M. Follstaedt, J. A. Knapp, L. E. Pope, F. G. Yost, and S. T. Picraux, Appl. Phys. Lett. **45** 529 (1984).
 27. T. R. Jervis, J-P. Hirvonen, and M. Nastasi, J. Mater. Res. **3** 1104 (1988).
 28. T. R. Jervis & J-P. Hirvonen, Wear **150** 259 (1991).
 29. T. R. Jervis, M. Nastasi, & K. M. Hubbard, Appl. Phys. Lett. **60** 912 (1992).
 30. I. L. Singer & J. H. Wandass, in: *Structure-Property Relationships in Surface-Modified Ceramics*, C. J. McHargue, R. Kossowsky, and W. O. Hofer, (Kluwer Academic Publishers, Dordrecht, 1989) p 199.
 31. R. K. Singh, K Jagannadham, & J. Narayan, J. Mater. Res. **3** 1119 (1988).
 32. J. Narayan, D. Fathy, O. W. Holland, B. R. Appleton, R. F. Davis, & P. F. Becher, J. Appl. Phys. **56** 1577 (1984).
 33. T. R. Jervis, J-P. Hirvonen, & M. Nastasi, J. Mat. Res. **6** 146 (1991).
 34. C. J. McHargue, in *Structure-Property Relationships in Surface-Modified Ceramics*, C. J. McHargue, R. Kossowsky, and W. O. Hofer, Eds. (Kluwer Academic Publishers, Dordrecht, 1989) p 117.
 35. M. Nastasi and T. R. Jervis, unpublished results.
 36. A. J. Pedraza, M. J. Godbole, E. A. Kenik, D. H. Lowndes, and J. R. Thompson, Jr, J. Vac. Sci. Technol. **A6** 1763 (1988).
 37. M. J. Godbole, A. J. Pedraza, D. H. Lowndes, and E. A. Kenik, J. Mater. Res. **4** 1202 (1989).
 38. P. D. Stupik, T. R. Jervis, M. Nastasi, M. M. Donovan, and A. R. Barron, Mat. Res. Soc. Symp. Proc. **170** 155 (1990).
 39. T. R. Jervis, K. M. Hubbard, & T. G. Zocco, Mater. Res. Soc. Symp Proc. **236** 397 (1992).
 40. L. A. Foster, J. R. Tesmer, T. R. Jervis, and M. Nastasi, In Press, Nucl. Inst. Meth. **B** (1993).
 41. C. Boulmer-Leborgne, J. Hermann, B. Dubreuil, P. Brault, J. L. DeGiorgi, A. Luches, M. Martino, A. Perrone, I. N. Mihailescu, I. Ursu, G. Blondiaux, J. L. Debrun, H. Estrade, and B. Rousseau, Appl. Surf. Sci. **54** 349 (1992).
 42. S-W. Chan, D. Dijkkamp, X. D. Wu, T. Venkatesan, and C. C. Chang, Mat. Res. Soc. Symp. Proc. **74** 287 (1987).
 43. D. Dijkkamp, X. D. Wu, S-W. Chan, and T. Venkatesan, Mat. Res. Soc. Symp. Proc. **74** 303 (1987).
 44. E. D'Anna, G. Leggieri, A. Luches, M. Martino, A. Perrone, P. Menzucchi, I. N. Mihailescu, Appl. Surf. Sci. **54** 353 (1992).
 45. M. Nastasi, J-P. Hirvonen, T. G. Zocco, and T. R. Jervis, J. Mater. Res. **5** 1207 (1990).
 46. J-P. Hirvonen, M. Nastasi, J. R. Phillips, and J. W. Mayer, J. Vac. Sci. Technol. **A4** 2997 (1986).
 47. M. Nasatasi and J. W. Mayer, Mat. Sci. Reports **6** 1 (1991).
 48. D. M. Follstaedt, J. A. Knapp, and P. S. Peercy, J. of Non-Cryst. Solids **61 & 62** 451 (1984).

49. D. R. Baer, D. J. Frydrych, and T. R. Jervis, in *Environmental Degradation of Ion and Laser Beam Treated Surfaces*, G. S. Was and K. Grabowski, Eds. (The Metallurgical Society, Warrendale, PA 1989).
50. J. Narayan, V. P. Godbole, and C. W. White, *Science* **252** 416 (1991).
51. J. Narayan, V. P. Godbole, G. Matera, and R. K. Singh, *J. Appl. Phys.* **71** 966 (1992).
52. D. B. Tuckerman and R. L. Schmidt, *Proceedings of the 2nd International IEEE VLSI Multilevel Interconnection Conference*, Santa Clara, CA (IEEE, New York, 1985) p. 24.
53. R. Mukai, N. Sasaki, and M. Nakano, *Mat. Res. Soc. Symp. Proc.* **74** 229 (1987).
54. R. J. Baseman, T-S. Kuan, M. O. Aboelfotoh, J. C. Andreshak, F. A. Turene, R. A. Previti-Kelly, and J. G. Ryan, *Mat. Res. Soc. Symp. Proc.* 236 361 (1992).
55. S-Q. Want, E. Ong, *J. Vac. Sci. Technol.* **B10** 160 (1992).
56. J. P. Partridge, J. Pellegrino, C. Murphy, and P. R. Strutt, *Mat. Res. Soc. Symp. Proc.* **74** 173 (1987).
57. H. W. Bergmann, E. Schubert, K. J. Schmatzko, and J. Dembowski, *Thin Sol. Films* **174** 33 (1989).
58. G. Kinsman and W. W. Duley, *Appl. Phys. Lett* **54** 7 (1989).
59. G. Kinsman and W. W. Duley, *Appl. Phys. Lett* **56** 996 (1990).