

Pulsed laser oxidation and nitridation of metal surfaces immersed in liquid media

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Nitridation and oxidation of titanium and iron immersed in liquid N_2 , NH_3 , or H_2O are achieved by pulsed excimer laser treatment. Rutherford backscattering spectrometry reveals that significant quantities of nitrogen and oxygen can be incorporated in the metal matrices over a depth scale of several thousand angstroms. X-ray diffraction gives evidence for compound formation and scanning electron microscopy for large stress in the surface layer. The process is viewed as chemical reactive solute incorporation in the metal surface layer in its laser induced liquid state, followed by compound formation.

Thin films of compounds such as nitrides, oxides, carbides, and oxynitrides find applications in diversified fields such as semiconductor technology, mechanical industry, optical component technology, and magnetic device industry. Recent technological advances in these application areas have made it necessary to explore newer methods of synthesizing compound films, which could offer (i) efficient processing and high throughput possibilities, (ii) region selectivity in both the area and depth scales, and (iii) the possibility of obtaining metastable phases with new and exotic physical properties. These demanding requirements appear to be effectively met if lasers are employed for processing of materials. The early phase of research in laser processing was primarily concentrated upon developing an understanding of the physical mechanisms (especially in the case of pulsed lasers) and exploring utilization for annealing and epitaxial regrowth of semiconductors.¹ Recently, however, a considerable emphasis is being laid on the use of lasers for deposition,² etching,³ doping,^{4,5} and related applications. In the case of laser induced deposition, in most situations, the laser is used to induce gas phase chemical reactions and subsequent deposition of reaction products on a closely stationed substrate by a diffusion limited transport mechanism.⁶⁻⁹

In this letter we present the first results on the synthesis of metastable compound films via pulsed excimer laser induced chemical and mass transport processes at liquid-solid interfaces. In this method the sample is made to participate in the process both physically, via melting and resolidification involving onset and quenching of diffusive mechanisms, and chemically, via reactions between molecules or laser generated radicals of the liquid and the atoms in the metal surface. This situation is distinctly different from the case of laser deposition wherein the substrate is used as a site for the generation of a hot spot responsible for driving reactions in the ambient itself. In the present case, the specific systems which have been investigated for laser induced interface reactions are titanium and iron in pure liquid N_2 , NH_3 , and H_2O ambients.

The experiments reported here were performed by using a pulsed XeCl excimer laser ($\lambda = 308$ nm, pulse width ~ 25 ns) capable of giving a maximum energy per pulse of ~ 500 mJ. Energy densities up to ~ 3 J/cm² could be obtained within an acceptable degree of homogeneity by suitable beam guiding and focusing to a spot size of a few mm². While processing the samples in liquid ambients, the depth of liquid covering the sample surface was maintained at ~ 1.5 mm. Pure liquid ammonia was obtained by condensing ammonia vapor on a height limiting sample pool which was held at a temperature of ~ -60 °C during the experiment. Care was taken to flush the sample enclosure with pure dry nitrogen gas while cooling the sample stage, to avoid condensation of water vapor on the sample surface. Subsequently, the ammonia vapor was introduced via a jet directed towards the sample surface. The flow rate of dry nitrogen was gradually reduced to a certain minimum necessary during laser processing to sweep away the vapors of ammonia, which can absorb the UV radiation of the laser beam. The energy density of the laser pulse, spot to spot overlap per scan, and the number of scans were varied to study the influence of these parameters on the experimental results. Sample surfaces were chemically etched for cleaning prior to laser treatment. The laser spot was scanned over the sample surface to obtain an effective modified area of 5×5 mm². Rutherford backscattering spectrometry¹⁰ (RBS) was carried out near the spot center over an area of ~ 1 mm². The RBS studies were carried out by employing a 2-MeV He⁺ beam using a detection setup having a depth resolution of ~ 100 Å. To extract information on composition profiles from experimental spectra, model RBS spectra were computer simulated using a recent version of the RUMP program.¹¹ To detect the formation of compounds, the polycrystalline samples were analyzed using x-ray diffraction.¹² This was done using a powder diffractometer with a CuK α anode and a monochromator. The surface morphology of the samples after laser treatment was studied with a scanning electron microscope (SEM). In this letter we choose to present representative cases which bring out the main features of our observations.

Figure 1(a) shows a Rutherford backscattering spectrum for polycrystalline titanium foils pulsed laser treated in liquid ammonia at a temperature of -60 °C. A reference

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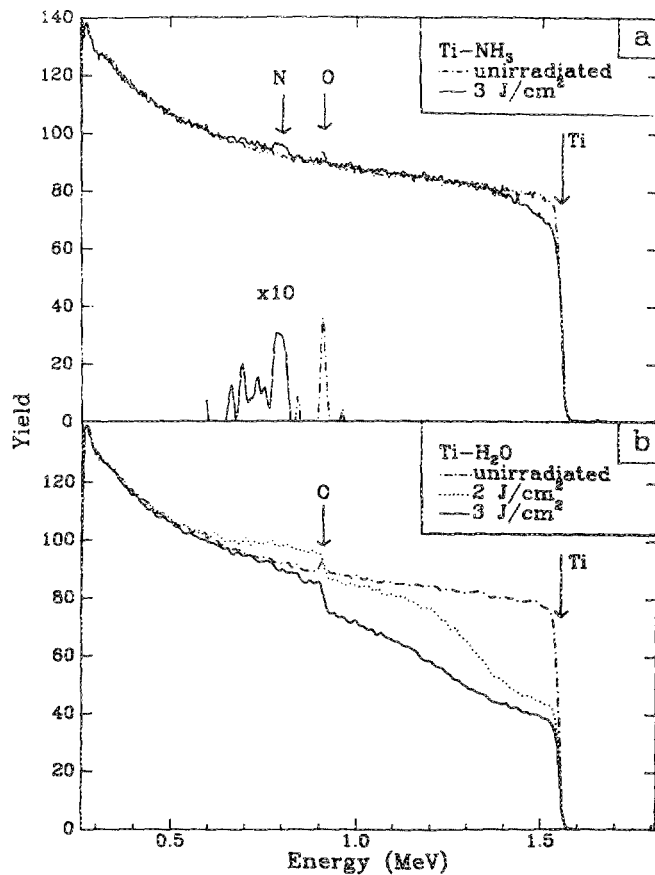


FIG. 1. RBS spectra of Ti irradiated in (a) liquid NH_3 and (b) H_2O .

spectrum of untreated Ti is also shown. The spectrum shows a significant depletion of Ti signal near the surface and a small nitrogen peak. This peak obtained after appropriate subtraction of the background Ti signal is shown enlarged in the figure, together with the native oxygen peak of the untreated sample. Simulation of the spectra revealed a reasonable agreement between the depletion of Ti signal and the area of the N peak. It was found that about 2000 Å of Ti has reacted. The N surface concentration after a single laser pulse is as high as 40 at. %. For laser treatment of Ti in liquid nitrogen ambient (results not shown here) it was also found that nitrogen could be incorporated over such depth scales with similar nitrogen concentration profiles. RBS spectra for Ti samples irradiated in water ambient at room temperature are shown in Fig. 1(b) for two cases of laser energy density. Both spectra show a large depletion of Ti signal near the surface and a large oxygen contribution. The surface oxygen concentration was found to be about 70 at. %. The total reacted Ti thickness was 3000 Å for 2 J/cm² laser energy and more than 5000 Å for 3 J/cm². It should be noticed that the oxygen profiles can be tuned rather effectively by controlling the laser energy density and scan overlap density.

Similar experiments have been done for Fe. After pulsed laser treatment of Fe in liquid ammonia no nitrogen incorporation could be detected by RBS. Liquid air (liquid nitrogen and liquid oxygen) ambient was used to incorporate these elements in Fe. In Fig. 2(a) the corresponding RBS spectra

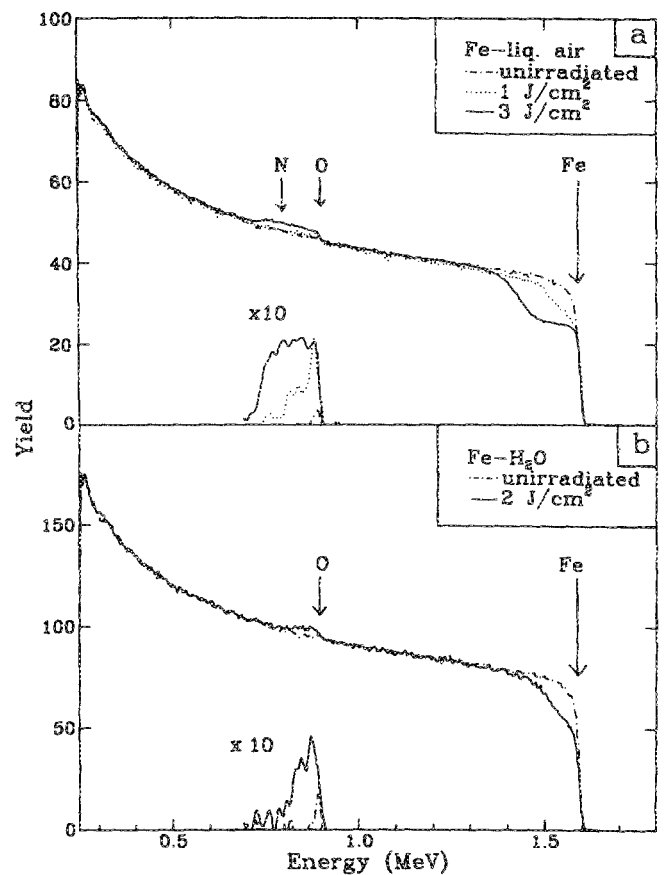


FIG. 2. RBS spectra of Fe irradiated in (a) liquid air and (b) H_2O .

are shown for two cases of different energy density. Large amounts of oxygen have been incorporated. For the cases shown, the reacted Fe thickness was 700 Å and 1000 Å, respectively. Surface oxygen concentration was about 50 at. %. For the case of 1 J/cm² no detectable amount of nitrogen was found, for 3 J/cm² O and N signals could not be resolved from each other. Irradiation of Fe in water ambient also clearly resulted in oxygen incorporation. Results are shown in Fig. 2(b).

After N and O incorporation was shown by RBS, x-ray diffraction was employed to study whether compounds had formed in the surface layers. Results of our preliminary study are given here. Figure 3(a) shows an x-ray diffraction spectrum for a Ti sample six times irradiated in liquid ammonia ambient. Large peaks in addition to the Ti peaks show that the compound TiN has formed. The spectrum in Fig. 3(b) is measured on a Ti sample irradiated in water. Peaks corresponding to TiO can be identified.

SEM analysis of the irradiated samples¹³ shows a relatively flat surface. Apparently pronounced surface texture of the polycrystalline foils present prior to laser treatment has disappeared due to melting. In addition, a large number of cracks and holes are found. These structures are expected to originate from the thermal stresses in the surface region during the melting and solidification process, and the large impurity concentration which strongly influences the surface structure. The morphology and density of these structures are found to be strongly dependent on the ambient used and

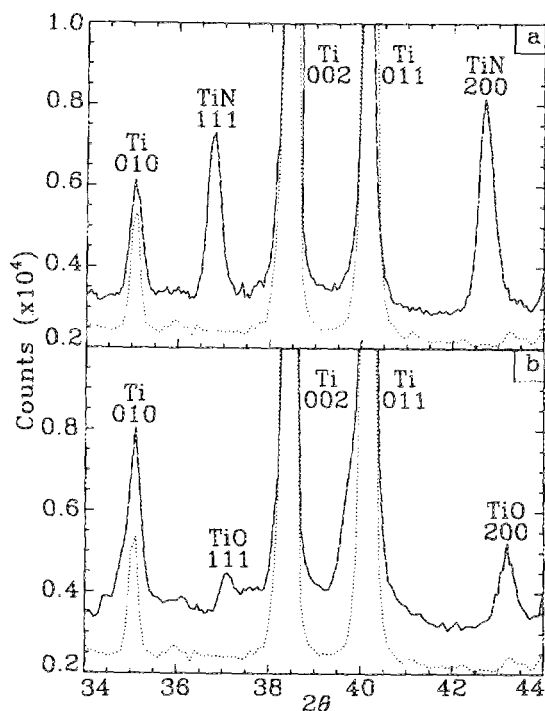


FIG. 3. X-ray diffraction spectra (solid curve) of (a) Ti irradiated in liquid NH₃ and (b) Ti irradiated in H₂O. Reference spectra for untreated Ti are also shown (dotted curve).

the number of laser scans employed.

The laser pulse has an effect on both the metal surface, which it melts, and the liquid on top of it, in which molecule fragments and radicals are produced by photodissociation or the high temperature present. These reactive species are incorporated in the metal melt and distribute by fast diffusion to deeper regions. By heat exchange from the metal to the liquid on top of it, the liquid is superheated and forms a high-temperature, high-pressure vapor, which expands only slowly compared to the duration of laser pulse and melt (~100 ns). Because of this high density vapor, there is sufficient supply of oxygen/nitrogen to keep the incorporation and diffusion mechanism going. It should be noted that by laser irradiation of metals in 1 atm gas ambient, as opposed to liquid ambient, we did not succeed in incorporating detectable amounts of oxygen or nitrogen.

Now we can speculate on factors which determine if compounds can be formed for a specific combination of a solid and a liquid. Probably the relation between the photon energy and the bond strength of the molecules of the liquid influences the formation of N or O radicals. Indeed we found that with 4.03 eV photons, nitridation of the metals was more efficient using NH₃ (N-H bond strength 3.3 eV) than using N₂ (N-N bond strength 9.9 eV). The solubilities and

diffusivities are also expected to play a role; e.g., Ti can be nitrided more efficiently than Fe, N having a higher solubility in Ti than in Fe. In addition, the high-temperature stability of the compound to be formed may be of importance. This might be an alternative explanation for the different behavior of Ti and Fe in our experiments.

Using this method, the thickness and composition of the compounds formed can be varied by choosing suitable laser parameters. The thickness is determined by the melt depth and therefore by the laser energy density. The amount of incorporated atoms and therefore the composition is determined by pulse overlap and number of laser pulses. The quenching character of the pulsed laser treatment, which might even be enhanced by heat transfer to the liquid medium, permits the formation of metastable compounds.

In conclusion, large amounts of oxygen and nitrogen can be incorporated in surface layers of iron and titanium by excimer laser irradiation of the metals immersed in liquid N₂, NH₃, or H₂O. The concentration profiles extend to a depth of several thousand angstroms. Stable nitrides and oxides such as TiN and TiO can be formed. The surface structure after laser processing, as shown by SEM, is rather smooth due to melting, but the stress in the surface layer seems to be released by the formation of micron size cracks.

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