OXIDATION AND NITRIDATION BY PULSED LASER IRRADIATION OF SOLIDS IMMERSED IN LIQUIDS

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ABSTRACT

Nitridation and oxidation of titanium is achieved by pulsed laser irradiation of Ti immersed in liquid ammonia or water. Rutherford Backscattering Spectrometry shows that large amounts of nitrogen and oxygen can be incorporated in the metal surface to a depth of several 1000 Å. X-ray diffraction shows evidence of compound formation. Scanning Electron Microscopy reveals that initial surface texture is smoothed, and that stress induced cracks and holes may appear. Irradiation of Fe and Si immersed in various liquids shows that modification depends on which combination of solid and liquid is used. Influence of processing parameters such as laser-energy density and number of laser pulses on compound formation has been investigated. The process is viewed as a reactive solute incorporation in the laser melted surface layer, followed by compound formation.

1. INTRODUCTION

Thin films of compounds such as nitrides and oxides find applications in diversified fields such as semiconductor technology, mechanical industry, optical component technology and magnetic device industry. Both continuous and pulsed lasers are widely employed for processing of these, often new, materials. The early phase of research in laser processing was primarily focussed on developing an understanding of the physical mechanisms 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[2,3], etching[4], doping[5,6] and related applications. In the case of laser induced deposition, the laser is mostly used to induce gas phase chemical reactions and subsequent deposition of reaction products on a closely stationed substrate, by a diffusion limited transport mechanism[7-10].

In this paper we explore a new and simple method of compound formation using a pulsed laser to irradiate the surface of a solid which is immersed in a liquid. Two main features set this method[11] apart from more conventional laser treatments[2-7]: Firstly, the liquid above the surface supplies a large amount of reactive species in the immediate vicinity of the metal surface, making this method especially effective for compound formation. Secondly, the treated surface is actually melted by the laser pulses, rather than used for hot-spot generation. In this way, use is made of both enhanced diffusivity and solubility of species in molten metals and of the quenching character typical of pulsed laser melting and solidification. This paper concerns the influence of laser-energy density and the number of laser pulses on compound formation of Ti which is immersed in water or ammonia. Other combinations of solid and liquid will be discussed briefly.

2 EXPERIMENTAL

In the experiments reported here a pulsed XeCl excimer laser (λ = 308 nm, FWHM = 25 ns) was used. By focusing the beam to a spot of several mm^2, energy densities up to $\sim$ 3 J/cm^2 could be obtained on the sample's surface. Using two mirrors mounted on rotational axes, this spot could be scanned over the sample surface. In this way an area of $\sim$ 5 x 5 mm^2 could be treated with reasonable degree of homogeneity. Prior to laser treatment, samples were chemically etched. The thickness of the liquid layer covering the sample was kept at $\sim$ 1,5 mm.

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Treatment of Ti immersed in water was done using only an open beaker which contained both the sample and the liquid. Experiments involving liquid ammonia were performed by cooling the sample to -60°C and condensing ammonia vapour on the metal surface. Excess vapour was swept away with clean dry N_2 gas which filled an air-tight container in which the sample was held. Total pressure in the system was 1 atm. Laser energy density, spot to spot overlap and number of scans were varied as experimental parameters. The number of scans was varied on Ti samples covered with liquid ammonia. We used either one scan of laser pulses of 3 J/cm^2 or 7 scans of laser pulses of about 2.5 J/cm^2 energy density. Influence of laser-energy density was investigated on Ti immersed in water. These samples were irradiated with one scan of laser pulses with an energy density of either 2 or 3 J/cm^2.

Composition of the samples after treatment was measured using Rutherford Backscattering Spectrometry [12] (RBS). Beam energy was 2 MeV and spot size $\sim$ 1 mm^2. RBS spectra were simulated using a recent version of RUMP program [13,14]. Compound formation was established using Debye-Scherrer X-ray diffractometry [15] (XRD). The diffractometer was equipped with a Cu K_α anode, a monochromator and a step-motor driven counter. Surface morphology of the samples was studied with a Scanning Electron Microscope (SEM).


3   RESULTS AND DISCUSSION

3.1   INCORPORATION OF N AND O

The influence of the number of laser scans on N and O incorporation is shown in Fig 1a. This figure shows RBS spectra of Ti which has been irradiated with a pulsed laser while this sample was embedded in liquid ammonia. A reference spectrum of untreated Ti is also shown (dotted curve). One sample was scanned once with an energy density of 3 J/cm^2 (solid curve). The spectrum shows an enhanced yield near the channel for N in the surface and a depletion of Ti signal near the channel for Ti at the surface. Simulation of this spectrum revealed a reasonable agreement between depletion of Ti-signal and contents of the N peak. It was found that N was incorporated over a depth of about 2000 Å. After 1 scan the N surface concentration is already as high as 40 at.%. Another sample was scanned 7 times with an energy density of 2.5 J/cm^2 (dashed curve). Although the change of Ti-signal is considerably larger and extends to lower backscatter energies, the contents of the N peak are only slightly increased compared to the spectrum described above. Therefore, changes in Ti signal in the latter spectrum are partly due to surface texture. This will be shown below, upon examination of SEM-pictures of these samples.

Influence of laser-energy density is shown in Fig. 1b. This figure shows RBS spectra of Ti samples irradiated while immersed in water for two different laser energy densities. Both
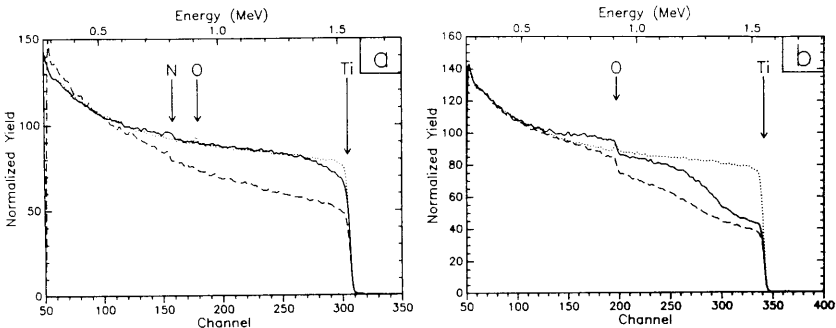
Fig.1 a) RBS spectra of Ti which has been pulsed laser irradiated in liquid ammonia. Solid curve: 1 scan of 3 J/cm^2. Dashed curve: 7 scans of 2.5 J/cm^2. A reference spectrum of untreated Ti is also shown (dotted curve). b) RBS spectra of Ti which has been pulsed laser irradiated in water with one scan of 2 J/cm^2 (solid curve) and 3 J/cm^2 (dashed curve). A reference spectrum of untreated Ti is also shown (dotted curve).
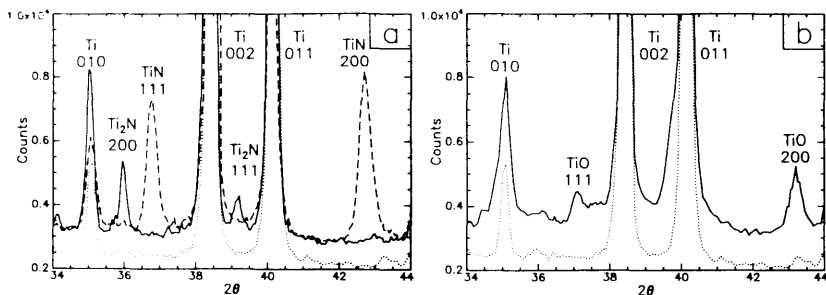
Fig.2 a) XRD spectra of Ti which has been pulsed laser irradiated in liquid ammonia. Solid curve: 1 scan of 3 J/cm². Dashed curve: 7 scans of 2.5 J/cm². A reference spectrum of untreated Ti is also shown (dotted curve). b) XRD spectra of Ti which has been pulsed laser irradiated in water with one scan of 3 J/cm² (solid curve). A reference spectrum of untreated Ti is also shown (dotted curve).

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 at 2 J/cm² and more than 5000 Å at 3 J/cm². Thus it can be noticed that the oxygen profiles can be tuned rather effectively by controlling the laser energy density.

3.2 COMPOUND FORMATION

The influence of the number of laser scans on compound formation of Ti which has been irradiated in liquid ammonia is shown in Fig. 2a. This figure shows XRD-spectra of Ti which has been irradiated in liquid ammonia and for reference a spectrum of pure Ti (dotted curve). The solid curve shows the spectrum of Ti which was scanned only once, at a laser energy density of 3 J/cm². At first, no detectable amount of TiN or Ti_2N was found on this sample by XRD, although RBS results show significant N incorporation. Therefore, this sample was thermally annealed at 600°C for 60 minutes. The spectrum which is shown was taken after this anneal. Clear peaks show that Ti_2N has formed. No other samples were treated thermally. The dashed curve was measured on Ti which was scanned 7 times with a laser energy density of ~ 2.5 J/cm². Large peaks in addition to the Ti peaks can be identified as corresponding to TiN. Apparently one laser scan suffices to incorporate a large amount of N in the sample, as was shown in the RBS results, but some more scans are necessary in order to form an amount of nitride that is detectable with standard XRD.

The spectrum in Fig. 2b was measured from Ti irradiated in water (one scan of 3 J/cm²). Peaks corresponding to TiO can be identified showing that one scan of single pulses on Ti immersed in water suffices to form titanium oxide.

3.3 SURFACE MORPHOLOGY

SEM pictures are shown in Fig. 3 a-d. Fig. 3a was taken on untreated Ti and shows sharply edged hills of several μm size. Fig. 3b shows Ti which, while covered with liquid ammonia, has been irradiated with one scan of laser pulses of 3 J/cm². The treatment resulted in N incorporation and formation of Ti_2N, as was shown by RBS and XRD. Sharp features of the Ti-surface have disappeared, indicating that melting of the surface has occurred. Some cracks appear which are expected to originate from thermal stresses which probably occur in the surface region during the rapid melting and solidification process, and due to the large impurity concentration which strongly influences the surface structure.

Fig. 3c shows a SEM picture of Ti which was irradiated 7 times with laser pulses of 2,5 J/cm², while covered with liquid ammonia, resulting in TiN-formation. Compared to Fig. 3b, some more cracks have appeared, and in addition submicron sized holes can be seen. These
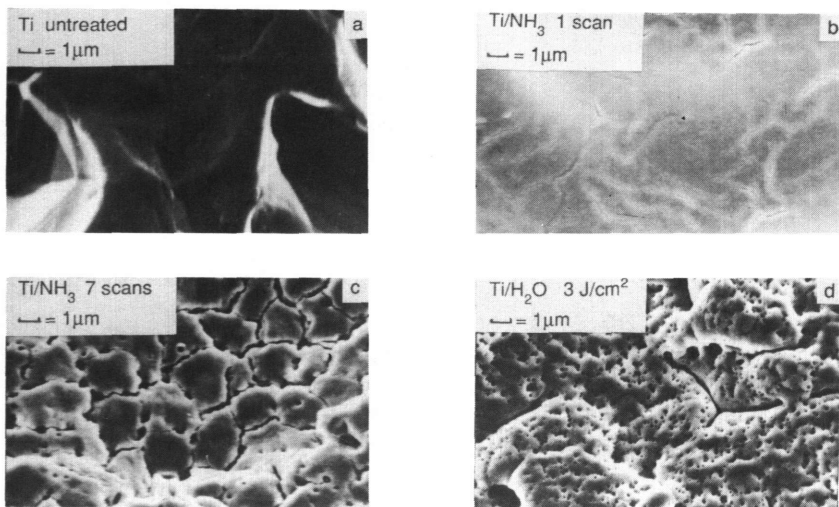
Fig.3 SEM-pictures of a) untreated Ti, b) Ti, which was covered with ammonia and irradiated with one scan of 3 J/cm^2 laser pulses, c) Ti, which was covered with ammonia and irradiated with 7 scans of 2.5 J/cm^2 and d) Ti, which was immersed in water and irradiated with one scan of 3 J/cm^2 laser pulses.

features probably account for the large depletion of Ti-signal in the RBS spectrum of this sample.

Fig. 3d shows Ti which was treated in water, resulting in TiO formation. The surface is dominated by a large number of holes and cracks of which the edges have been rounded.

Speculating on the origin of the holes that can be seen in Fig. 3b,c,d it should be noticed that the number of holes on the samples shown in Fig 3b and c is increased with the number of laser pulses, but that the amount of impurities which are incorporated in the Ti is roughly the same, as was shown by RBS. Therefore, the number of holes is not a simple function of the amount of incorporated atoms. However, it may be suggested that formation of TiN or TiO from Ti and NH_3 or H_2O is accompanied by H production. This might escape as H_2 gas which can account for gas bubbles in the rapidly solidifying liquid. Possibly O_2 and N_2 gasses are formed (and escape) as well.

3.4 OTHER SUBSTRATES AND LIQUIDS

Experiments involving other combinations of solids, e.g. Fe and Si, and liquids such as water, liquid nitrogen, ammonia, benzene and ethanol were performed. It was found that O could be incorporated efficiently into Fe by irradiating Fe immersed in water. Incorporation of N in Fe was found to be less efficient. For example when Fe was irradiated immersed in liquid air, it was found that O but no detectable amount of N was incorporated in Fe. This may be due to the fact that FeN is not a thermally stable compound. It is also suggested that the different dissociation energies of N_2 (9.9 eV) and O_2 (5.2 eV) are of influence.

On Si, incorporation of N,O or C was only found when the Si-liquid interface was irradiated with laser energy densities high enough to damage the Si surface. Below this damage threshold no detectable incorporation occurred. This is probably caused by a protective layer formed by the native oxide which covers the Si surface. This oxide layer has a much higher melt-temperature than Si and thus acts as a barrier for mass-transport from the liquid on top[16].

3.5 MECHANISM

It is tempting to offer some suggestions for the mechanisms responsible for the observed effects: The laser pulse has an effect on both the metal surface, which it melts, and the liquid on top, in which molecule fragments and radicals can be produced by photodissociation or the high temperatures present. These reactive species are incorporated in the liquified metal, and are distributed by fast diffusion to deeper regions. By heat exchange from the metal, the liquid on top is superheated and forms a high-temperature, high-pressure vapour, which probably expands only slowly compared to the duration of laser pulse and melt ($\sim$ 100 ns). This high density vapour is thought to supply sufficient oxygen/nitrogen to keep the incorporation and diffusion mechanism going. It should be noted that by laser irradiation of metals in 1 atm. air or ammonia-vapour ambient, we did not observe incorporation of detectable amounts of oxygen or nitrogen.

Now we can speculate on factors which determine if compounds can be formed for a specific combination of solid and 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. For example, the N-N bond strength of 9.9 eV in N_2 is large compared to the N-H bond strength of 3.3 eV in NH_3. Indeed we found that nitridation of the metals was more efficient using NH_3 than using N_2. The solubilities and diffusivities of O and N in the metals in their liquid state are also expected to play a role. E.g., it was found that Ti can be nitrided more efficiently than Fe, and indeed N has a higher solubility in Ti than in Fe. In addition, the reactivity of the metal and the liquid and the high temperature stability of the compound to be formed may be important.

4   CONCLUSIONS

Large amounts of nitrogen and oxygen can be incorporated in surface layers of titanium, iron and silicon by excimer laser irradiation of the metal immersed in liquid NH_3 or H_2O. The concentration profiles extend to a depth of several 1000 Å. 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. On the other hand, submicron sized holes may appear and the stress in the surface layer seems to be released by the formation of μm size cracks. Applicability of this method is probably governed by solubility and diffusivity of the liquid in the molten substrate and by the reactivity of the liquid/solid combination used. 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 composition is dependent on 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.

ACKNOWLEDGMENTS

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