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Direct synthesis of titanium nitride on Ti sample surface by laser-plasma

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In this work titanium nitride synthesis is carried out by direct laser irradiation onto Ti sample surface in presence of ambient N_2. The experimental procedure is performed in a chamber allowing plasma study by emission spectroscopy. Two pulsed laser types are used, a TEA-CO_2 (10.6μm) and a XeCl excimer (308nm) in order to compare the laser-material coupling influence on the layer synthesis process depending on the laser wavelength. In both cases the TiN synthesis is evidenced. The plasma created by laser interaction with the Ti target in N_2 ambient gas is studied to understand the TiN synthesis mechanism.

1. INTRODUCTION

TiN film synthesis on Ti targets has been achieved directly on the metal surface by laser irradiadion in ambient N_2. The compound synthesis on the target surface induced by laser-plasma depends on the material characteristics as weel as on the laser wavelength and power density. In this work, the experiment is successively performed with a Transverse Excited Atmospheric (TEA) CO_2 laser (λ=10.6μm) and a XeCl excimer laser (λ=308nm). In both cases, TiN synthesis is obtained. The plasma created by the laser-material interaction has different composition and behaviour depending on the large difference between the laser wavelength values. The spectroscopy plasma study helps the understanding of the TiN layer synthesis mechanism on the Ti sample surface.

The synthesised films are analysed : surfaces are controlled by scanning electron microscopy and roughness measurements, chemical composition is investigated (50Å depth) by X-ray photoelectron spectroscopy (XPS), and by nuclear analysis (bulk), Rutherford Back-Scattering (RBS) with α particles and Back-Scattering (BS) with protons. Thus the best procedure to obtain the TiN layers can be evidenced.

2. EXPERIMENTAL-SET-UP

The experiments are respectively performed with a TEA-CO_2 (Gen-Tec DD-250-A Head) laser source emitting at 10.6μm wavelength and an excimer laser source XeCl

(Questek 2520Vβ) emitting at λ=308nm. Both lasers are pulsed working. The CO_2 laser pulse presents a 200ns width peak followed by a 4μs tail, 70% of the energy is in the peak. The XeCl laser pulse is a 20ns width rectangular shape.

The Ti targets are placed in a chamber containing N_2 gas with a pressure varying from 100Torr to 760Torr. The best N_2 pressure condition to obtain the thickest TiN films is 760Torr with the CO_2 laser, whereas a 380Torr to 760Torr N_2 pressure yields to similar characteristics for TiN films synthesised with the XeCl laser. The laser beam is focused perpendicularly to the Ti target (10mm x 10mm x 1mm). The targets are placed over the focal point to obtain the largest treated zone with the necessary laser power density to obtain the nitride. Thus these treated zone area is ≈1mm^2 with the CO_2 laser and ≈6mm^2 with the XeCl laser. The laser power density for TiN synthesis lies in the respective ranges [30MW/cm^2 - 70MW/cm^2] for the CO_2 laser and [40MW/cm^2 - 100MW/cm^2] with the XeCl laser. The targets are step by step displaced after irradiation of a surface spot to nitride all the sample area. The following scheme presents the set-up.

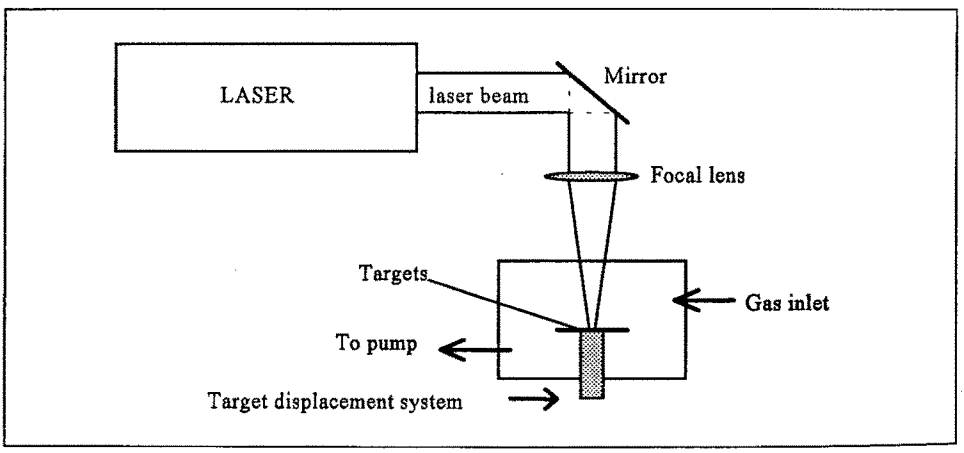

Figure 1.
Experimental set-up : the laser is either a CO_2 or a XeCl laser ; optical lens material is adapted to each laser wavelength (ZnSe for λ=10.6μm and quartz for λ=308nm).

3. PLASMA STUDY

3.1. Laser-material interaction and plasma formation

The plasma formation requires the vaporisation of the material as a first step. When the laser radiation is absorbed at the surface, the light energy is transformed into heat and the surface temperature increases. The target surface state is responsible for the lowering of the theoretical breakdown threshold as the surface defects and impurities have a vaporisation and ionisation threshold lower than the sample bulk [1]. The quantity of vaporised mass depends on the laser wavelength and on the laser energy absorbed by the target. It is clear that short laser wavelengths favour the ablation process [2] [3]. The CO_2 laser power density threshold for titanium target vaporisation has been experimentally determined to be 50MW/cm^2. With the XeCl laser, the titanium vaporisation has been observed for power densities over 25MW/cm^2.

The vapour is primarily ionised and electrons gain energy in the laser field through inverse Bremsstrahlung absorption. In Ref. [4], it is shown that the electron

temperature is larger for the CO_2 laser (λ=10.6μm) than for excimer laser (λ=308nm), because inverse Bremsstrahlung process heating the electrons is more efficient for IR. Indeed the laser radiation absorption coefficient varies in λ^{-2}.

Electrons will lose energy by collisions with neutral particles and will be lost by attachment. Lateral expansion of the vapour out of the laser beam and diffusion of electrons out of the breakdown volume are also a source of losses. The frequencies characteristic of these electron loss processes are generally negligible compared to the energy loss frequency if the ambient gas pressure is larger than 100Torr. When the laser irradiance is high enough, primary electrons, in spite of the energy loss processes, will gain an energy larger than the ionisation energy. These electrons will generate new electrons by impact ionisation of vapour atoms leading to cascade growth. The condition for initiating the electron avalanche is that the rate of electron energy increase exceeds the rate of energy loss [5]. The threshold intensity to produce a gas breakdown is deduced from this criterion, the threshold is 3 orders of magnitude larger for λ=308nm than for λ=10.6μm.

Only 20MW/cm^2 laser power density is necessary to obtain the nitrogen plasma with the CO_2 laser whereas more than twice is needed to vaporise the target. The IR laser beam interacts with the target, the primary electrons are produced from the vaporisation of the surface defects, then the gas plasma breakdown occurs and ionisation avalanche holds. The surface defect vaporisation stops as the plasma becomes denser, the laser beam is completely absorbed in the plasma and does not reach anymore the target surface ; the nitrogen plasma is self-sustained. Laser absorption waves have been observed in this plasma [6]. Pressure pulses produce stress waves in the target material which can lead to deformation or fracture.

With the XeCl laser, the power density necessary to obtain the gas breakdown is not reached and the plasma is dominated by Ti vaporisation. The laser photons are more energetic and directly interact with the solid. The material is ejected from the target and ionised. The plasma formation is due to the emission of primary electrons during the first ns of the laser-target interaction, then followed by electron-Ti atom collisions at the sample surface as soon as the vaporisation process begins yielding to vapour ionisation (during the laser pulse). The ambient gas is also excited and ionised but the emission lines can only be recorded at low N_2 pressure (≤0.1Torr).

3.2. Experimental observation

3.2.1. CO_2 laser irradiation

With the IR laser beam, a nitrogen plasma is created on the irradiated surface. As soon as the plasma is ignited, nitrogen reacts with titanium. No Ti line can be recorded by emission spectroscopy, excepted if the nitrogen pressure is decreased [7]. Whatever the experimental conditions, no N_2 line is observed whereas N^+ and N^{++} lines are always present. N_2 seems to be completely dissociated in the first ns of the interaction. Fig.2 shows a typical result of emission line kinetics. The first part of the plasma is an ionisation phase, during the laser pulse peak (≅200ns), followed by a recombination phase : when the laser power is too weak to sustain the gas ionisation, the plasma recombination starts. The electron density Ne has been determined by Stark broadening on (868nm) N and (399.5nm) N^+ lines. At 1μs time it equals to $\approx 2.10^{18}$cm^{-3} then decreases to $\approx 10^{16}$cm^{-3} after 9μs. It is a function of the gas pressure as electrons in the plasma are furnished by the gas ionisation. It depends on the laser power density too [8]. In order to restrain the plasma recoil action on the target, due to the laser absorption

wave development, Ne has to be limited. The higher N concentration in the synthesised layer being obtained for at least 760 Torr N_2 pressure in the chamber, Ne can only be controlled by the laser power.

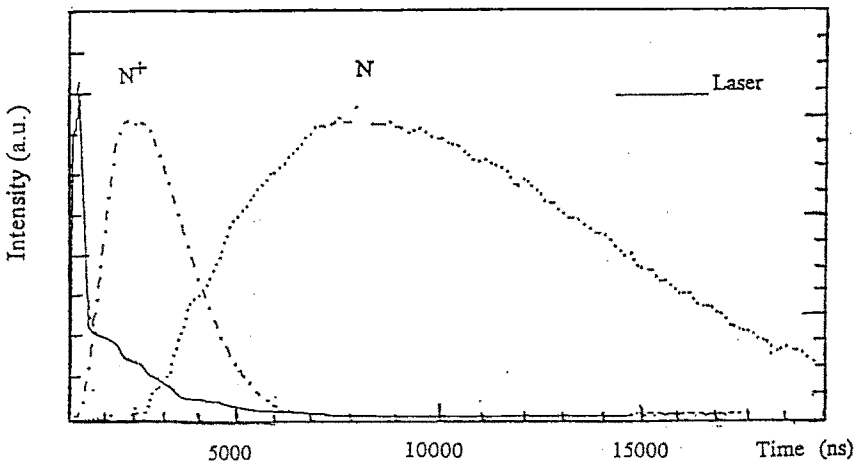

Figure 2
Plasma kinetics [(868nm) N and (399.5nm) N^+ lines] CO_2 laser (40MW/cm^2), 760Torr N_2.

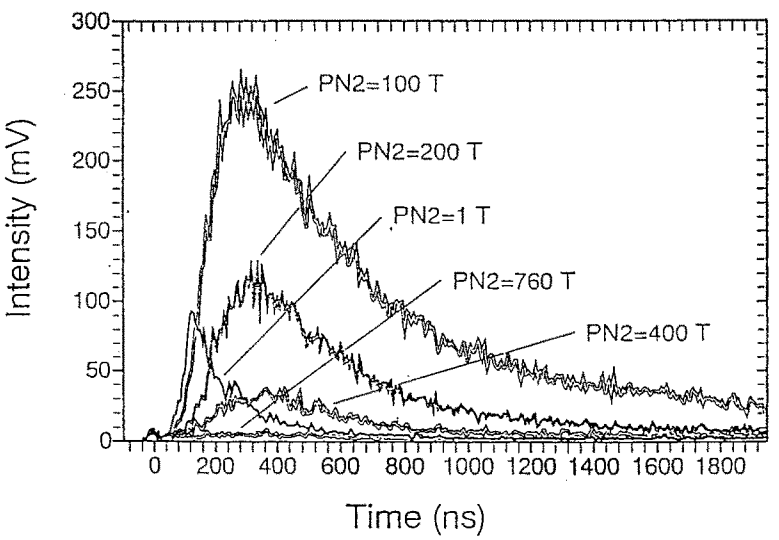

Figure 3
(399.9nm) Ti line kinetics for various N_2 gas pressure. XeCl laser, 60MW/cm^2

3.2.2. XeCl laser irradiation

The plasma formation seems to be limited to Ti vapour as no atomic or molecular nitrogen lines have been observed in the investiged gas pressure range. But N and N^+ spectral lines have been recorded in decreasing the gas pressure at 0.1Torr. Indeed the

gas pressure increase yields to a reduced plasma volume favouring the light reabsorption phenomenon. The N line intensities being weak in comparison with Ti lines, they are only observed when the pressure is ≤0.1Torr, then for higher pressures they are masked by the high intensity continuum. Fig.3 presents this confining effect with a Ti line kinetics recorded at 1mm from the surface for different N_2 pressures. It can be seen that the plasma time duration increases from 1Torr gas pressure to 100Torr (2μs), then equals ≈ 500ns at 400Torr. Simultaneously the kinetics intensities increase in the [1-100Torr] pressure range, then decrease for larger pressures and cannot be recorded at 760Torr.

Ne has been determined at 0.1Torr N_2 gas by Ti line Stark broadening [5, 6] and decreases from 2.10^{18} to $10^{16}cm^{-3}$ versus time. The electrons are produced by vapour ionisation, Ne varies with the plasma volume resulting in different ionisation conditions. Thus it is difficult to obtain a real variation of Ne with the experimental conditions. Nevertheless these results give an order of magnitude of Ne. The total kinetics signal of the plasma has been recorded and it appears that there is a ionisation phase with the Ti^{++} line emission beginning during the laser pulse duration, then the Ti^{+} and Ti lines are observed, this is the recombination phase (≈2μs).

4. CHEMICAL ANALYSIS

Both laser treatments yield to TiN synthesis : with the CO_2 laser the compound is yellow, the sample roughness is ≈±2μ and cracks and pores appear ; with the XeCl, the nitride is grey with a lower roughness (±1μ), less cracks and no pore.

4.1 XPS Results - (50Å depth investigation)

XPS measurements have been performed in a XPS VG ESCALAB UHV chamber (10^{-8}Pa) with a non momochromatised Mg Kα X-ray source (1253.6eV). In the Ti spectrum region, there are 2 doublets ($Ti2p_{1/2}$ and $Ti2p_{3/2}$) relative to the Ti-O bounds in TiO_2 (458.5-464.4eV) and to the metallic bounds (454.3-460.4eV). The doublet with main peak ($Ti2p_{3/2}$) located at 455eV stands for TiN (maybe no-stoichiometric) and the peaks relative to TiOxNy with various (x, y) are located between Ti-O and Ti-N bond peaks.

4.1.1 CO_2 laser irradiation

Fig.4 shows the evolution of the XPS spectrum with the number of laser pulses. There is a number (800) for which TiN and TiOxNy quantity is maximum, for a larger number this quantity falls. It appears that nitriding operation is a function of the plasma time duration. When this irradiation time is exceeded, destruction of synthesised TiN and TiOxNy species occurs. This seems to be due to the plasma recoil action on the surface. Thus the plasma time duration must be limited. The number of pulses necessary to obtain the TiN layer is weaker when the power is increased since the plasma ignition time is shorter. Working at high laser power densities leads to a faster nitriding treatment.

4.1.2 XeCl laser irradiation

Fig.5 shows the XPS result for Ti targets submitted to XeCl laser irradiation for various numbers of pulses. The 3 species, TiN, TiOxNy and TiO_2 are present. For 200 pulses, the TiN and TiOxNy peak intensities of the spectrum are the largest in comparison with TiO_2 peaks. For 400 pulses, the TiOxNy peak intensities diminish, for 1000 the TiN peak intensities decrease too. For larger numbers of pulses (2000), both TiN and TiOxNy peak intensity decrease. Nevertheless, further nuclear analysis show that the layer reaches its optimum thickness and N concentration for 2000 pulses. Different laser power densities have been used for experiment [40-100 W/cm^2], and the XPS spectra show that the same species are synthesised in each case. It appears that the largest nitride peak intensity is obtained for a weaker number of laser pulses when the

laser power density is increased (as checked with the CO_2 laser treatment). Moreover, it seems that the XeCl laser treatment leads to a reduced formation of oxinitride in comparison with the nitride.

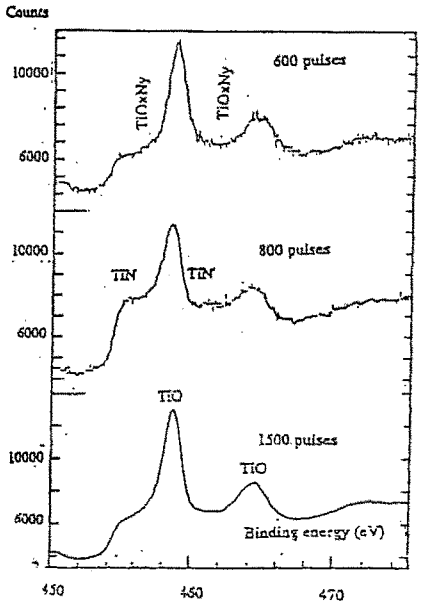

Figure 4.
XPS spectra in the Ti2p region for different numbers of pulses CO_2 laser irradiation, 45MW/cm^2

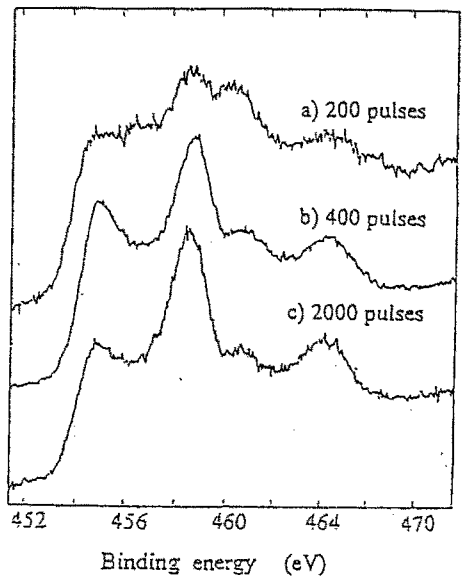

Figure 5.
XPS spectra in the Ti2p region for different numbers of pulses XeCl laser irradiation, 60MW/cm^2

4.2. Nuclear analysis results - (several μ depth investigation)

4.2.1 CO_2 laser irradiation

The samples obtained with the CO_2 laser irradiation at 45MW/cm^2, 760Torr N_2 for different numbers of laser pulses, have been analysed by (RBS) method with 1.3Mev α particles. The N concentration profile in the synthesised layer is deduced from the rump program fit of the experimental signals and is a decreasing exponential function of the layer depth from the surface. Moreover these analysis show that N amount in the layer increases with the number of pulses from 100-200 to 600-800, then saturates for larger numbers. In addition to XPS results, it can be deduced that the plasma created on the surface yields the N diffusion into the bulk, this process is limited to a ≈3μm thickness layer, for larger plasma times the surface is damaged and the layer thickness does not grow anymore. (BS) analysis have been also performed on these targets irradiated with 2MeV protons. Fig.6 presents a typical result for targets submitted to 600 and 800 laser pulses. The nitrogen peak increases with the pulse number. The presence of an oxigen peak must be noted, it intensity increases too with the laser peak number.

4.2.2 XeCl laser irradiation

With XeCl laser, the TiN film thickness (≈2-3μm) is maximum for 2000 to 1000 pulses depending on the laser power density in the [40-100MW/cm^2] range. The layer

thickness increases with the laser power and with the number of pulses to a saturation value.

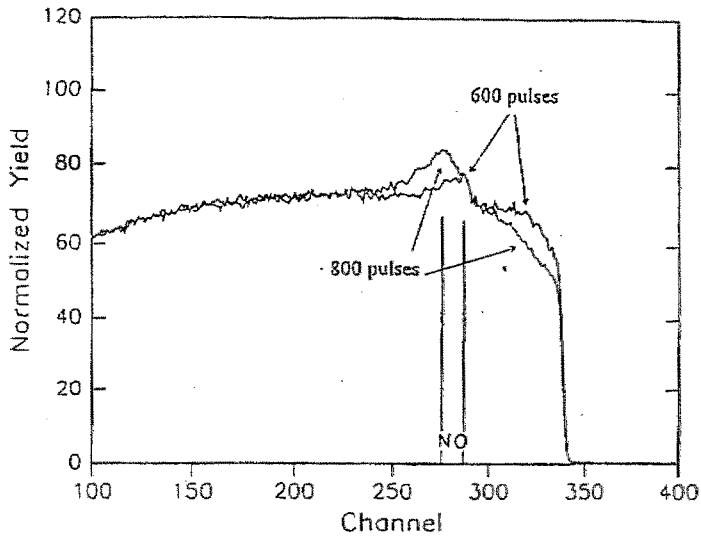

Figure 6.
BS spectra for TiN films for 600 and 800 pulses, CO_2 laser irradiation, 45MW/cm^2

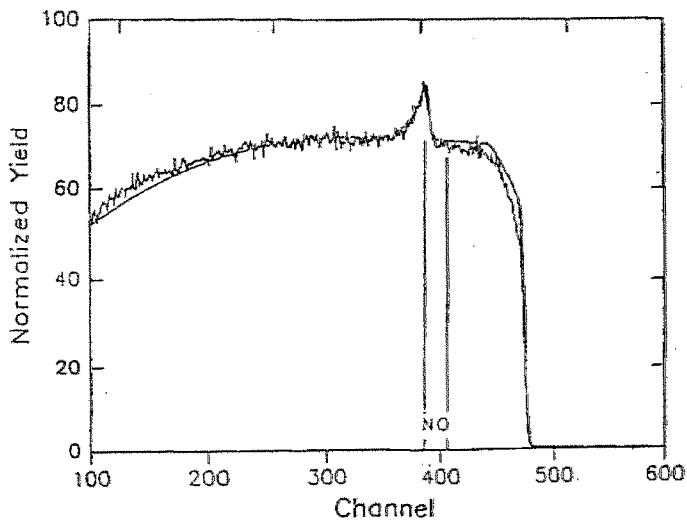

Figure 7.
BS spectrum for TiN films1000 pulses XeCl laser, 760Torr N_2, 60MW/cm^2

In BS spectra no oxide peak is observed as seen in Fig.7. In this experiment, the layer thickness reaches a maximum value for 2000 pulses and rump fit shows that the titanium nitride becomes stoichiometric at the top of the layer for this number of pulses. Then the stoichiometry holds when the number of pulses is increased but surface cracks are more numerous. Varying the experimental parameters, it appears that the larger is the laser power and the smaller is the number of pulses necessary to obtain stoichiometric nitride. Nevertheless, when the experiments are achieved with various N_2 pressures from 760Torr to 50Torr, the BS analysis results show that the layer contains more and more oxigen when the gas pressure is diminished.

5. CONCLUSION

TiN film synthesis on Ti targets has been achieved directly by laser treatment. The layer is 2-3μm thick, but its composition and crystal phase depend on the laser wavelength used for nitriding operation. Synthesised layer surfaces (100Å thickness) exhibit a large oxigen contamination due to TiO_2 native oxide on the metal sample. The N concentration decreasing with the layer depth, there is no adherence problem.

With CO_2 laser irradiation the main parameter to control the TiN synthesis is the time duration N_2 plasma interacting with the target. The best result for film synthesis is obtained for at least 760Torr N_2. The synthesised layer is composed of no-stoichiometric TiN and TiOxNy. The plasma develops laser sustained detonation waves leading to a plasma recoil action on the target surface that yields to the nitrogen diffusion in the titanium lattice but also to the TiN layer damage : the roughness is really important (as large as the layer thickness) and the surface shows many pores and cracks. The laser power density must be limited to avoid these damages.

With XeCl laser irradiation, no N_2 plasma is observed but Ti vapour plasma. The synthesised TiN film is stoichiometric for 2000 to 1000 pulses depending respectively on the laser power density in the [40-100 MW/cm^2] range. No TiOxNy appears excepted in the surface contamination layer if the gas pressure is at least equal to 760Torr. The target surface aspect looks better than those obtained with the CO_2 laser as the roughness is weaker and no pore appears.

The laser-plasma nitriding treatment time duration is shorter for a larger laser power density, furthermore the laser power has not to be limited with the XeCl laser since the plasma does not lead to damage surface. This last argument as the TiN layer quality make the excimer laser to be the best candidate for this nitriding process.

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