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Surface modification of titanium nitride film by a picosecond Nd:YAG laser

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Abstract
The interaction of a picosecond Nd:YAG laser (wavelength 532 nm, pulse duration 40 ps) with a polycrystalline titanium nitride (TiN) film was studied. The TiN thin film was deposited by physical vapour deposition on a silicon substrate. The titanium nitride/silicon system was modified with an energy fluence from 0.2 to 5.9 J cm^{-2}. Multi-pulse irradiation was performed in air by a focused laser beam. Surface modifications were analysed after 1–100 successive laser pulses. Depending on the laser pulse energy and pulse count, the following phenomena were observed: (i) increased surface roughness, (ii) titanium nitride film cracking, (iii) silicon substrate modification, (iv) film exfoliation and (v) laser-induced periodical surface structures on nano- (NPSS) and micro-dimensions (MPSS).

Keywords: laser-induced surface modification, titanium nitride film, micro and nano periodical structure, picoseconds laser pulse

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Titanium nitride (TiN), being a titanium based ceramic, possesses extraordinary characteristics such as high hardness, high melting point, thermochemical stability, etc [1, 2]. Owing to these specific properties, TiN thin films have found applications in microelectronics, gas-sensor technology, material protection, medicine, etc. Conventional structuring of this material is extremely difficult because of its hardness and brittleness, and the use of a laser is a possible solution. Thermal effects are expressed in cases of thin film modifications by nanosecond laser pulses [3]. There are several advantages in material processing with pulses shorter than those, including negligible collateral thermal damage and high precision processing. Short laser-pulse modification of solids has been largely used in the past decade, especially in nano-technology applications [4–6]. Experimental data on the interaction of picosecond laser pulses with thin films are scarce in the literature [7, 8], in contrast to femtosecond and nanosecond pulse interactions [4, 9–14].

The present paper deals with the effects of a Nd:YAG laser system, 40 ps pulse at a wavelength of 532 nm, on a TiN thin film/silicon sample. Special attention was paid to the morphological surface modifications of this sample.

2. Experiment

The TiN thin film (2.63 μm thickness) was deposited on a crystalline silicon (111) substrate by physical vapour deposition. The silicon wafers (0.5 mm thick) were polished before deposition in order to obtain good adhesion and low surface roughness of the film. The deposition process was carried out using CemeCon CC800/7 equipment. The deposition method included sputtering with four unbalanced magnetrons. Three stages were integrated into the procedure:

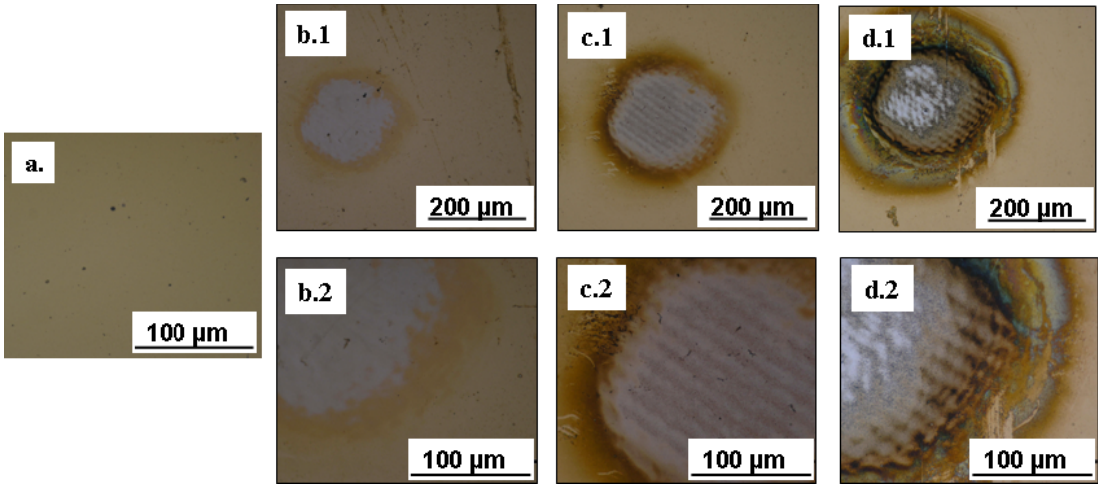

Figure 1. Picosecond Nd:YAG laser induced surface modification of a TiN film/silicon sample with constant laser fluence ($F = 0.2$ J cm^{-2}) and successive laser pulses. (a) TiN before laser irradiation; (b)–(d) TiN after modification with $N = 1, 5, 50$ laser pulses, respectively (OM).

heating by infra-heaters, ion cleaning and deposition of the film [15].

The laser used in the experiment is an active–passive mode-locked Nd:YAG system, model SYL P2 produced by Quanta System, Solbiate, Italy. It is made up of a laser oscillator, an amplifier, and a nonlinear crystal (KD*P) for second harmonic conversion. The oscillator is based on a self-filtering unstable resonator cavity [16]. Sample irradiation was performed in air by focused laser beams (TEM_{00} mode) at perpendicular incidence. Surface modification was induced by linearly polarized laser pulses (p-polarization) at a wavelength of 532 nm, pulse duration $\tau = 40$ ps, and pulse repetition rate 2 Hz. The maximum pulse energy used was 20 mJ, and the laser beam intensity (I) was up to 10^{12} W cm^{-2}.

Several analytical techniques were used to characterize the samples. The phase composition and crystalline structure of the TiN film and substrate were verified by x-ray diffraction (Cu Kα radiation). The surface morphology of the samples was monitored by optical microscopy (OM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The SEM was coupled to an energy dispersive analyser (EDAX) to determine the sample/target surface composition. A profilometer was used to characterize topological changes in the irradiated area. In addition, an optical image analyser (OIA) was used to measure the modified area dimensions, for comparison with information obtained using different microscopes.

3. Results and discussion

Both XRD and SEM/EDAX analyses of the deposited TiN confirmed that the film had a stochiometric composition of [Ti]/[N] $\approx$ 1. This composition led to the appearance of a characteristic golden-yellow colour. The XRD analysis has shown that TiN has a polycrystalline structure with small grains and preferential orientation (111). Cauliflower-like features (100–200 nm lateral dimensions) which consisted of smaller grains (10–20 nm lateral dimensions) were observed by SEM on the TiN surface. That is actually a surface picture of a columnar growth thin film. The surface roughness of the film was quantified by AFM. The *average* and *root mean square roughness* were ~4.5 and ~6 nm, respectively (analysed area 10×10 μm^2). This implies that the surface roughness of the TiN was at a low level before laser irradiation.

Irradiation of the TiN/silicon target was done with successive laser pulses. The pulse count N varied from 1 to 100. For one set of pulses ($N = 1$, 2, 5, 10, 50, and 100), the pulse energy or the laser pulse fluence (F) remained constant, with values of $F = 0.2$, 1.3, and 5.9 J cm^{-2}.

Generally, the physical processes involved in the laser–material interaction are complex. They depend on the laser wavelength, pulse duration, number of total successive pulses, material properties, etc. The morphological changes of the TiN/silicon sample can be described as: (i) increased surface roughness (with increasing pulse count), (ii) the appearance of periodical surface structures (PSS) at micro and nano levels, (iii) micro-cracking of the TiN thin film, and (iv) partial or total exfoliation of the TiN film from the silicon substrate.

An initial inspection of the laser induced surface modification areas was carried out by OM, figures 1(a)–(d). One laser pulse of $F = 0.2$ J cm^{-2} (figure 1(b)) was sufficient to produce visible surface changes. The same fluence, even after 100 successive pulses, did not result in film exfoliation, i.e. removal of the TiN film from the silicon substrate. Micro-level periodical structures (MPSS) can be observed in figures 1(b)–(d). Microscope analyses showed similar ripple spacing of about 15 μm for all N applied.

MPSS were also noticed at other pulse counts and fluence combinations: $N = 1-50$ and $F = 1.3$ J cm^{-2}, $N = 1-10$ and 5.9 J cm^{-2}. We have also observed MPSS in other experiments, using 532 nm on silicon (bulk), W–Ti thin film/silicon, and (TiAlN)/TiN multi-layer/steel. The experimental conditions in these cases were the same. The cross-section of the beam had some periodical intensity modulation that may have contributed to the formation of the MPSS structures, but the periodicity of this modulation does not exactly match the periodicity of the MPSS parallel structures. More research may make this relationship clearer.

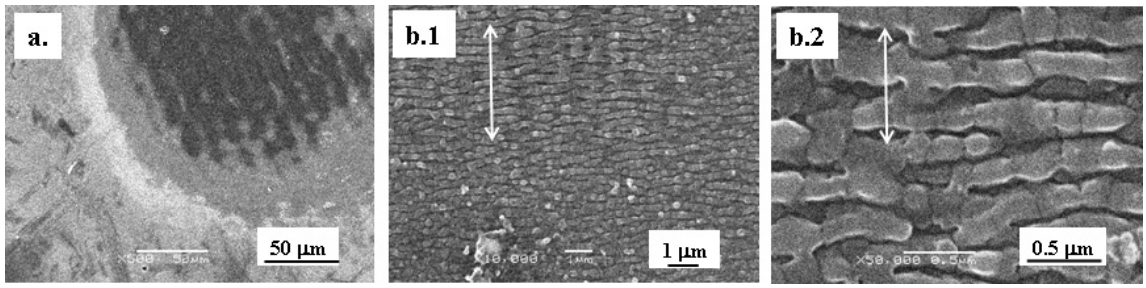

Figure 2. Induced surface modification of TiN film/silicon with a Nd:YAG laser, after $N = 100$ laser pulses, $F = 0.2$ J cm^{-2}. (a) Part of the irradiated area; (b.1) and (b.2) centre of the same area with different SEM magnifications. The arrows in b.1 and b.2 indicate the beam polarization.

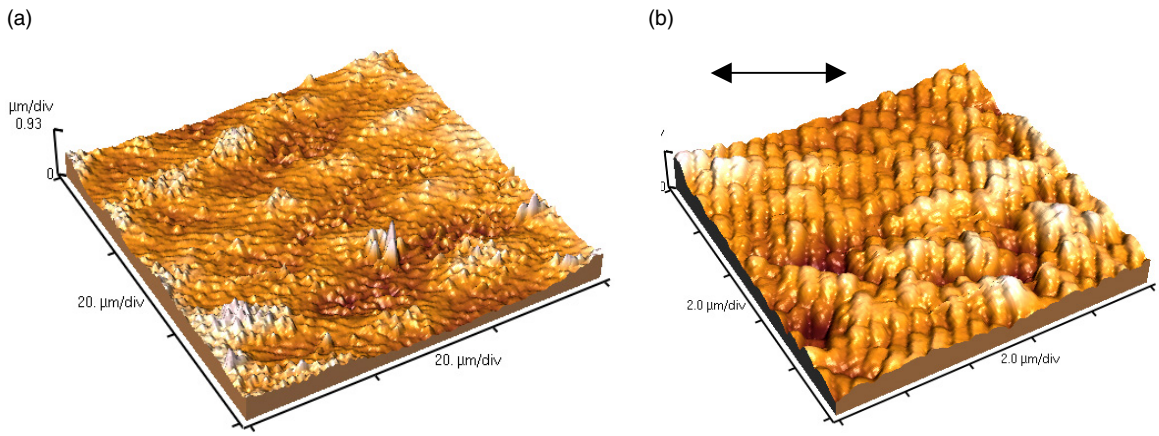

Figure 3. Laser-induced periodical surface structures on TiN/silicon after 100 laser pulses with a constant $F = 0.2$ J cm^{-2}, AFM analysis, 3D view: (a) MPSS (20 μm/div) and (b) NPSS (2 μm/div) formed in the centre of the irradiated area (part of (a), higher magnification, the arrow indicates beam polarization).

Detailed surface characterization of the TiN/silicon sample, after irradiation with the same $F = 0.2$ J cm^{-2}, was done using SEM and AFM, figures 2 and 3. These analyses revealed nano-level periodical structures, NPSS, (figures 2(b) and 3(b)). Clearly expressed NPSS appeared after 100 pulses, figure 3. The lateral dimensions of the NPSS are less than 300 nm. It should be pointed out that the increasing count of the laser pulses from 1 to 100, at a constant fluence of 0.2 J cm^{-2}, resulted in more pronounced modifications of the TiN film. The surface roughness noticeably changed in this case. The *average* and *root mean square roughness* were ∼7.1 and ∼61 nm (analysed area of 60 × 60 μm^2), respectively. In the case of the same fluence, the EDX analysis after irradiation showed that the TiN film remained on the silicon substrate, but the stochiometric ratio of Ti:N changed, and oxygen was also found. Although the effect depended on the number of pulses, the Ti:N ratio tended to change in favour of Ti.

The results of the irradiation of the TiN film/silicon sample with a higher fluence of 1.3 and 5.9 J cm^{-2} are presented in figures 4 and 5. After irradiation of the sample with one laser pulse, the integrity of the TiN film was maintained, but topography analysis showed the presence of cracked areas. SEM analyses, figures 4(b.2) and (c.2), showed that the film cracking was more pronounced with higher fluences. The reason for the appearance of cracks could be the difference in the thermo-physical properties of the TiN and silicon, and the changes during the very fast heating and cooling caused by the laser pulses.

Increasing the laser pulse count to 100, figure 5, resulted in drastic changes in the sample. The features induced can be defined as: (i) complete ablation/exfoliation of the TiN film from the silicon substrate in the central part of the irradiated area, (ii) creation of an amorphous state of the silicon substrate in the same area, (iii) appearance of non-exfoliated TiN film in the near and further periphery, and (iv) disappearance of periodic structures in the central zone, but formation of such in a narrow region at the periphery.

The formation of periodic structures, depending on laser fluence, on TiN film/silicon is known in the case of femtosecond laser pulses [17, 18]. It was found that the lateral dimensions of the NPSS structures observed depend on the laser fluence applied. The morphological appearance of NPSS varied with fluence, which indicated a variety of mechanisms involved in their formation. Agreement with this assumption can be found in our experiment. Various morphological features were registered: NPSS with varying spacing, nano-dimensional droplets, nano-dimensional holes and micro-dimensional droplets, figure 5(b).

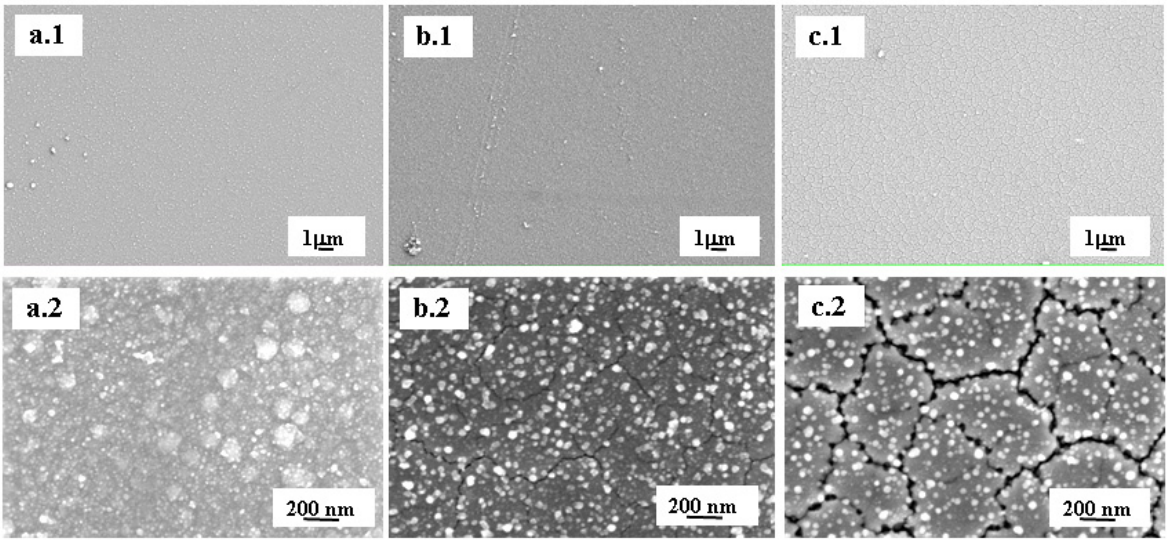

Figure 4. SEM microscopy analysis of ((a.1) and (a.2)) TiN thin film before irradiation, with different magnifications; ((b.1) and (b.2)) central part of the irradiated area with one laser pulse at $F = 1.3$ J cm^{-2}, different magnifications; ((c.1) and (c.2)) central part of the irradiated area with one laser pulse at $F = 5.9$ J cm^{-2}, different magnifications.

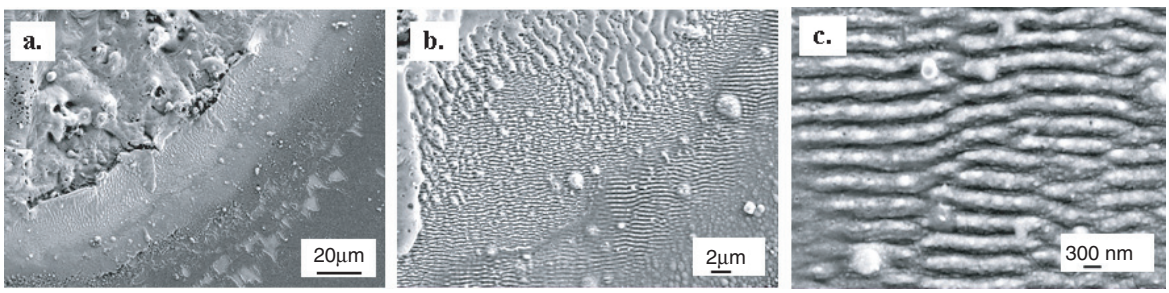

Figure 5. Surface modification of TiN/silicon by the Nd:YAG laser with 100 laser pulses ($F = 5.9$ J cm^{-2}). (a) Laser induced exfoliation of TiN from the silicon substrate; (b) near and further periphery of the non-exfoliated TiN thin film; (c) NPSS are formed in a narrow region at the periphery (SEM analysis).

Complete ablation/exfoliation of TiN from the silicon substrate was observed in the central part of the irradiated area for higher fluences in some cases. After successive irradiation with 100 pulses at a fluence $F = 1.3$ J cm^{-2} exfoliation occurred over almost the entire irradiated area; partial exfoliation of the TiN film was registered at $N = 50$. Successive pulses of $N = 50$ and 100 in the case of $F = 5.9$ J cm^{-2} caused complete film exfoliation from the silicon substrate (figure 5(a)). The same fluence produced partial exfoliation at $N = 5$ and 10.

The physical processes involved in the interaction of picosecond Nd:YAG laser pulses with TiN film/silicon are very complex. They depend on laser intensity, wavelength, pulse duration, cumulative photon energy, thin film properties, etc. For pulses of low intensity it is known that, for pulses longer than 10 ps (40 ps in our experiment), a focused laser beam in one approximation can be considered as a surface thermal source (electron and lattice temperatures equalize). In this simplified picture, in the absence of phase transitions, fast heating and cooling are present and thermal effects cannot be neglected. The heat-affected zone (HAZ), roughly the maximum of the radiation absorption length (L_{opt}), and the thermal diffusivity length (L_{th}) are important parameters for precise laser surface modification [3]. For titanium nitride, $L_{\text{opt}} \approx 30$ nm (wavelength 532 nm [6]) and thermal diffusivity length $L_{\text{th}} \approx 16$ nm. The estimated NPSS depth in the case of $N = 1$ pulse was about 7 nm. This is generally in agreement with the above calculated radiation absorption length. Increasing the number of pulses caused higher depth modulation of NPSS. This small thickness of the HAZ, after one low fluence pulse action, means that a 2.6 μm thick TiN film was surface modified but not the silicon substrate. With higher pulse fluences and a larger pulse count, a series of effects such as melting, vaporization, dissociation, ionization of evaporated material, plasma appearance, etc can be generated. The consequences are film cracking, ablation/exfoliation of the film, and substrate modification.

4. Conclusion

A qualitative/quantitative study of morphological changes on a titanium nitride film deposited on silicon, induced by a picosecond Nd:YAG laser, is presented. It is shown that

the laser induced structural changes in the titanium nitride film, as well as on the substrate. A laser fluence equal to and higher than 0.2 J cm^{-2} was found to be sufficient for surface modifications of the sample. Lower fluence, as a rule, leads to the formation of periodical surface structures on micro- and nano-levels. Higher fluences lead to complete ablation/exfoliation of the TiN film from the silicon substrate, in the central part of the irradiated area, and a change in the silicon substrate.

With the laser parameters used in the experiment, periodical structures were created on the titanium nitride film. These structures have rarely been reported so far.

Generally, the interaction of the picosecond Nd:YAG laser with TiN film/silicon is complex. The pulse duration of the Nd:YAG laser was of the order of 40 ps, meaning that thermal effects were present. Depending on the laser pulse intensity, a series of effects such as melting, vaporization, dissociation, ionization of the evaporated material, etc can be created during the interaction.

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