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Polarization-dependent single-beam laser-induced grating-like effects on titanium films

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In this paper we present results on polarization-dependent laser-induced effects on titanium (Ti) thin films. We irradiated the titanium films, in ambient air, using a nanosecond Nd:YAG laser (532 nm, 9 ns pulse duration, 10 Hz). Using a series of pulses of fluence well below the ablation threshold, it was possible to form grating-like structures, whose grooves run parallel to the linear polarization of the incident beam. No grating-like structures were obtained when circularly polarized light was used. Our results revealed the remarkable formation of tiny (100 nm and even smaller diameter) craters, which self-arrange quasi-periodically along the ridges (never on the valleys) of the grating-like structure. Optical and scanning electron microscopy were used to study the laser-induced changes on the surface of the titanium films. Micro-Raman spectroscopy was used to analyze the irradiated areas on the titanium films. The Raman analysis demonstrated that the grooves in the grating-like structure, build up from the laser-induced oxidation of titanium. This is the first time, to the best of our knowledge, that periodic surface structures are reported to be induced below the ablation threshold regime, with the grooves made of crystalline metal oxide, in this case TiO_2 in the well-known Rutile phase. The laser irradiated areas on the film acquired selective (upon recording polarization) holographic reflectance.

1. Introduction

The interaction of laser pulses with solids is capable of producing very interesting effects. An example of such is the case of the laser-induced periodic surface structures (LIPSS) on semiconductors and metals studied in great detail by Sipe et al. [1,2]. These authors have shown both theoretically and experimentally that nominally smooth solid surfaces can develop grating-like structures under intense laser irradiation. In particular, Pérez del Pino et al. [3] have studied the laser-induced effects in titanium targets. They have found that a variety of polycrystalline titanium oxide phases are formed by irradiating titanium in air using a CW-Nd:YAG laser operated at 1064 nm; they also report coloring of the titanium as a result of the laser irradiation. Zhao et al. [4] have recently reported the growth of nanospikes on subwavelength ripples on tungsten foils by using femtosecond laser pulses. Varlamova et al. [5] also report on the formation of ripples under femtosecond laser irradiation on different materials like CaF_2 and Si, their study focus on the influence of the polarization state on the ripples orientation. Pedraza et al. [6] report on the surface nanostructuring of Si, they report the growth of nanoparticles linear arrays when linear polarized beams are used; an interesting finding in their results is that when non-polarized light is used there are not linear arrays formed, however, if there is a microstructured surface then non-polorized light produces nanoparticles linear arrays in the vicinity of the microstructured region. Interestingly, in all the above cited work, the polarization state of the exciting laser beam seems to play an important role in the ripple orientation, however, the claims on how the polarization influences such an orientation is not consistent through all the reports in literature. It is worth to mention that laser-induced ripple formation has been reported in the literature for experiments ran both in air and high vacuum; and for laser irradiations below and above the ablation threshold of the

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irradiated materials, with nanosecond and femtosecond laser pulse duration; at visible, near infrared and ultraviolet wavelengths, [1,2,4–6]. Although, the studies on this topic are extensive and a wide variety of effects have been published, there are new and remarkable results to report like the one demonstrated in the present article.

In this work we present results of single-beam laser-induced grating-like features on titanium thin films. The experiments were performed in air at atmospheric pressure using fluence well below the titanium laser ablation threshold. A pulsed (9 ns) frequency doubled (532 nm) Nd:YAG laser was used to irradiate the titanium films. We will show that grating-like structures form on the films during laser irradiation and, as a matter of fact, the grooves are oriented parallel to the incident light polarization for the case of linear polarization; there were not grating-like structures formed when circularly polarized light was used, as are the cases shown in [4,5]. We will also show how, in our case, additional fine features grown within the main grating-like frame. Those additional features are composed by a quasi-periodic arrangement of small craters which form on the ridges and never on the valleys across the grating-like structure. Using Micro-Raman spectroscopy we also show that, as expected, the initially crystalline hexagonal α-Ti phase of metallic titanium film transforms during irradiation into titanium dioxide (TiO_2) in its crystalline Rutile phase.

The development of laser micro- and nano-processing of materials such as titanium is very relevant for medical and technological applications. Pure titanium and TiO_2 have proved great biomedical applications [7], and TiO_2 is also suitable for gas sensing applications [8]. As it has been shown by different authors Pérez del Pino et al. [3], Gratzke and Simon [9], Evans et al. [10], Camacho-Lopez et al. [11], Haro-Poniatowski et al. [12], Aygun et al. [13] a large variety of oxides in distinct phases can be obtained by laser irradiation of starting materials like the metals titanium, and tungsten; glass molybdenum oxide, and the semiconductor silicon. The characteristics of such a wide choice of materials can be easily tailored on demand by laser micro-processing, which can develop into a convenient and powerful technological tool for micro-fabrication of sensors and other devices.

2. Experimental

2.1. Film deposition

Titanium thin films were deposited using a pure (99.9%) titanium target that was sputtered in an Ar discharge by means of a DC magnetron operated at a pressure of 1.0×10^{-6} Bar, and at a 30 W discharge power. The substrates used in these experiments were silicon (1 0 0) wafers. The target-substrate separation was kept at 7.0 cm during deposition. The substrate was kept at room temperature during deposition. The as-deposited Ti films thickness was measured by profilometry of 320 nm corresponding to a deposition time of 40 min. The as deposited titanium films, were characterized by X-ray diffraction (diffractogram not shown here) obtaining the crystalline hexagonal α-Ti phase.

2.2. Pulsed laser irradiation of the films

In our experiments, we used frequency doubled Nd:YAG laser pulses of 9 ns time duration to irradiate the titanium thin films at a repetition rate of 10 Hz. The unfocused laser beam, at normal incidence onto the film surface, had a beam diameter of 2.4 mm. We carried out long exposures of 4000 pulses per site, where we used per pulse fluences of $\sim$0.24 J/cm^2, well below the titanium laser ablation threshold fluence; which according to Vorobyev et al. [14] is of 0.8 J/cm^2 for pure titanium. Linear, linear orthogonal and circular polarizations of the incident beam were used at different sites on the target film. The linearly polarized pump beam was rotated to the orthogonal polarization and changed to circular polarization through the use of half and quarter wave plates, respectively. The on target delivered fluence was finely controlled by a half-wave plate-polarizer pair. The irradiation of the films was carried out in ambient air. Fig. 1 shows a schematic diagram of the experimental set up.

2.3. Characterization of the irradiated regions

The irradiated spots on the titanium films were analyzed by means of optical microscopy under white light (fiber bundle)

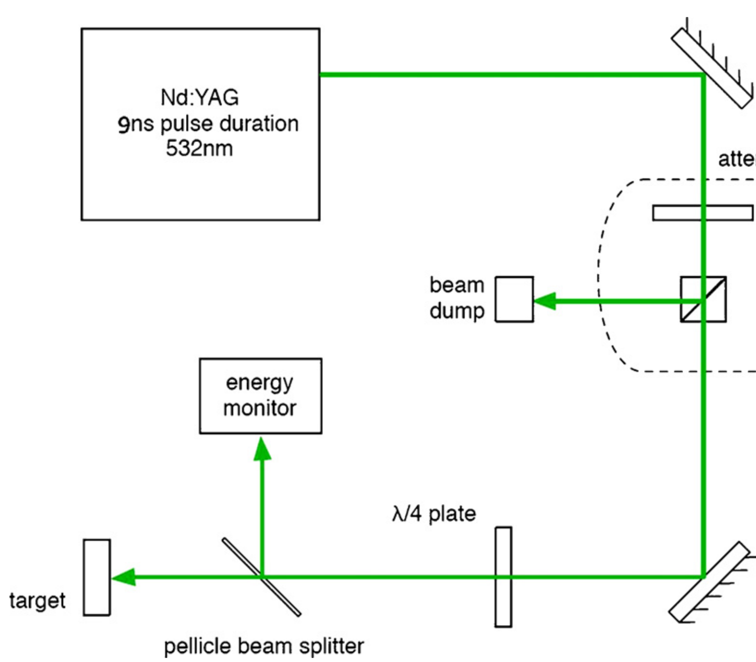

Fig. 1. Experimental set up.