Processing of Metallic Thin Films Using Nd:YAG Laser Pulses

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1. Introduction

Nd:YAG lasers are possibly the more widely used lasers either for basic research or for industrial and technological applications (Dubey, A. K. & Yadava, V. 2008). These lasers are also excellent pump sources for laser development, for instance Ti:sapphire ultrashort pulse lasers are based on CW Nd:YAG pumping. In particular, Nd-YAG lasers have been applied to study laser-induced oxidation in metals as titanium and chromium; semiconductors as silicon (Aygun, G. et al., 2006). (Perez del Pino, A. et al., 2004) demonstrated that the rutile phase of TiO_2 is obtained by laser oxidation in air of titanium films. Nd:YAG laser pulses have been used to laser-induce a phase transformation from W_3O thin films to WO_3 (Evans R., et al., 2007); laser ablation for micromachining of bulk metals as copper, bronze and aluminum has also been done using Nd:YAG nanosecond pulses (Maisterrena-Epstein R., et al., 2007); laser-induced oxidation and novel LIPSS formation in titanium thin films deposited on silicon substrates was demonstrated by using a single laser beam from a frequency doubled Nd:YAG nanosecond pulsed laser (Camacho-Lopez S., et al., 2008). Some works about pulsed laser oxidation have been reported (Dong, Q. et al., 2002). (Pereira, A. et al. 2004) have investigated the laser treatment in steel irradiating at various wavelengths by using different laser sources. In Table 1, we cited some works on the oxidation induced by pulsed laser irradiation in various metals. Recently, we have published results on fs-laser

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oxidation in molybdenum thin films (Cano-Lara, M. et al., 2011). (Herman et al., 2006) have studied ablation of molybdenum thin films with short and ultrashort laser pulses. This work is the first study with Nd:YAG to investigate pulsed laser oxidation in molybdenum thin films.

Material	Research group	Starting material	Laser line
Titanium	(Pérez del Pino et al. 2002)	(Lavissee, L. et al. 2002)	(Camacho-López, S. et al 2008)
	Titanium targets $\lambda=1064$ nm	Titanium targets $\lambda=1064$ nm	Titanium thin films $\lambda=532$ nm
Chromium	(Dong, Q. et al. 2002)	Chromium films $\lambda=1064$ nm	
Steel	(Pereira, A. et al. 2004)	Steel target 1064 nm 532 nm	
Molybdenum	Our work	Molybdenum Thin Films $\lambda=532$ nm	

Table 1. Some works on Nd-YAG pulsed laser oxidation.

Some advantages of laser-induced metallic oxides are:

1. Oxidation can be performed in air, so that a controlled atmosphere is not necessary.
2. The time that it takes to achieve a given stoichiometry and crystalline phase is very rapid as compared to conventional thermal treatment.
3. A high spatial resolution patterning of metallic oxides is only possible by this method. Sizes are determined by the optical diffraction limit, therefore single "pixels" made of metallic oxide in the order of the laser light wavelength are possible.
4. In some cases, the laser-induced oxidation process is accompanied by laser-induced periodic surface structures (LIPSS) formation.

Titanium dioxide is an important material due to its wide range of applications. Titanium dioxide is a biocompatible material; in its thin film form, TiO_2 has applications as an antireflective coating, or anticorrosive coating. Additionally, titanium dioxide has applications as gas sensor material, in photocatalysis, among others (Linsebigler A. M. et al., 1995). It is well known that TiO_2 exist as a crystalline material in three phases: anatase, rutile and brookite (Beattie, I. R., Gilson, T. R. 1969).

Molybdenum oxides are attractive materials due to its potential technological applications. MoO_3 possesses photo-, electro- and gasochromic properties (Livage, J. & Ganguli, D. 2001). For instance, this material can be used in gas sensors, catalysis, smart windows, lithium microbatteries (Dieterle, M. 2001). MoO_2 has potential applications as a cathode material in the area of microbatteries; field emission, and also catalysis (Jun, Z. et al. 2003; Wang F. & Lu B. 2009; Mikhailova, D. et al. 2011).

The micro-Raman technique is very useful to obtain information about the composition and structure of the material into the laser irradiated zone. Spatially studies can be carried out

since the laser beam can be Focalized down on the sample to 2 μm diameter (Witke, K. et al. 1998). For instance, we have obtained spatially resolved information about what kind of material is formed when a molybdenum thin film was irradiated with fs-laser pulses (Cano-Lara, M. et al., 2011).

In this chapter we present and discuss a series of experimental results on short (nanoseconds) and ultrashort (picoseconds) pulsed Nd:YAG laser processing of metallic thin films. Our selection of materials consisted of molybdenum (Mo) and titanium (Ti) thin films deposited on glass substrates and silicon wafers by the DC-magnetron sputtering technique. We studied the ablation features on the selected materials; once the ablation threshold fluence was determined, we carried out laser processing experiments setting our delivered fluence to a value well below ablation threshold. Under such a scenario we studied the following phenomena: laser-induced periodic surface structures (LIPSS) formation, and laser-induced oxidation on the metallic films. Our results show that it is possible to laser-induce MoO_2 and TiO_2 inside the irradiated zone; we also found that for certain laser irradiation conditions it is possible to obtain LIPSS formation driven by the polarization of the recording beam. The characterization of the laser irradiated metallic thin films consisted mainly on Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and micro-Raman Spectroscopy.

2. Materials and methods

2.1 Deposition of titanium and molybdenum thin films

Titanium and molybdenum thin films were deposited using disks of titanium and molybdenum (99.9%, Lesker), respectively. Ar gas was used to sputter the targets by means of the DC-magnetron sputtering technique. Glass slides and silicon wafers were used as substrates. In Table 2, one can see the deposition parameters used to obtain each material.

Deposition parameters	Titanium/silicon	Titanium/glass	Molybdenum/glass
Discharge Power	30 W	100 W	150 W
Pressure	1×10^{-3} mBar	1.4×10^{-3} mBar	1.4×10^{-3} mBar
Target-substrate separation	7 cm	7 cm	7 cm
Deposition time	40 min	16 min	10 min
Substrate	Silicon wafer(100)	Glass slide	Glass slide
Substrate temperature	room	room	room

Table 2. Deposition parameters for titanium and molybdenum thin films.

2.2 Laser processing of the metal thin films

The experiments were performed using a typical laser processing set up (see Figure 1) which consist of a computer controlled x-y-z translation stage, where the sample is conveniently hold; the laser beam from either a nanosecond (ns) or a picosecond (ps), frequency doubled, pulsed Nd:YAG laser was used to irradiate the samples at normal incidence; the laser beam can be either focused or non-focused onto the sample. The laser irradiation was carried out at 10 Hz repetition rate, using a single beam, taking care of using a per pulse laser fluence below the ablation threshold for the selected metallic films.

The delivered fluence is controlled by means of an attenuator made of a half-wave plate and a polarizer. An extra half-wave plate, or a quarter-wave plate, is used to change from linear

polarization to linear polarization with another orientation, or from linear to circular polarization. The as-deposited metallic thin films were exposed to a series of thousands of pulses.

Fig. 1. LIPSS and laser-induced oxidation experimental set up.

Irradiation parameters	Titanium/silicon	Titanium/glass	Molybdenum/glass
Laser Fluence (per pulse)	0.24 J/cm ²	0.08 J/cm ²	0.08 J/cm ²
Wavelength	532 nm	532 nm	532 nm
Repetition frequency	10 Hz	10 Hz	10 Hz
Pulse number	4000	4000 8000 12000	6000 12000 18000 10000 (0.16 J/cm ²)
Atmosphere	air	air	air
Substrate temperature	room	room	room

Table 3. Irradiation parameters for the ns laser exposures

Irradiation parameters	Titanium/glass	Molybdenum/glass
Laser Fluence (per pulse)	0.24 J/cm ²	0.24 J/cm ²
Wavelength	532 nm	532 nm
Repetition frequency	10 Hz	10 Hz
Pulse number	2000, 4000, 6000 8000, 10000	2000, 4000, 6000 8000, 10000
Atmosphere	air	air
Substrate temperature	room	room

Table 4. Irradiation parameters for the ps laser exposures

The pair of frequency doubled Nd:YAG lasers: a Continuum, minilite II, 9 ns pulse duration; and a Ekspla, 30 ps pulse duration, were used to irradiate the metallic thin film samples in atmospheric air. The laser irradiation parameters we used in the experiments are presented in Tables 3 and 4.

2.3 Characterization of the as-deposited Titanium and Molybdenum thin films and the laser exposed sites

The as-deposited molybdenum and titanium thin films were characterized by X-Ray Diffraction (Bruker D8 Advance with Linxeye detector) with the Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) and a Scanning Electron Microscope (SEM). The SEM analysis was performed with a JEOL JSM-6510LV microscope in the high vacuum mode. The samples were characterized without any conductive coating with secondary electrons; the acceleration voltage was 20 kV. The AFM analysis was done using a Veeco CP-II in contact mode with a silicon nitride tip. The scanned size is 5x5 microns. The modified material which turns into metallic oxides during the irradiation process was characterized by microRaman spectroscopy. A micro-Raman system, LabRaman HR-800 of Jobin-Yvon-Horiba, was used to run and capture the micro-Raman spectra. The 632.8 nm line of a He-Ne laser was utilized to excite the material and the laser power at the sample was 5 mW. An Olympus BX-41 optical microscope was used to focus down the laser beam on the sample and to collect the scattered light. This was done using a 100X microscope objective lens. All the spectra are the result of 10 acquisitions of 60 s.

3. Experimental results

3.1 X-Ray Diffraction of the as deposited thin films

Figure 2 shows the XRD patterns for the sputtered deposited titanium and molybdenum thin films. The titanium XRD pattern (Figure 2a) contains peaks corresponding to the (002), (101), (102) and (103) reflection planes, that according to the literature correspond to the α -Ti phase. The diffraction peaks in the case of the molybdenum thin film (Figure 2b) correspond to the (110) and (220) reflection planes. This indicates that the molybdenum thin films grew preferentially acquiring the cubic phase.

Fig. 2. XRD patterns of the as deposited thin films: (a) titanium and (b) molybdenum.

3.2 LIPSS formation characterized by AFM

3.2.1 Titanium / Silicon and ns pulses laser irradiation

A 320 nm thick Ti thin film deposited on silicon (100) was irradiated using a frequency doubled Nd:YAG laser, with pulses of 9 ns duration at 10 Hz repetition rate, and a per pulse laser fluence of 0.24 J/cm^2 . The delivered fluence is well below the ablation threshold, which according to (Vorobyev, A. Y. & C. Guo, C. 2007) is in the order of 0.8 J/cm^2 . Figure 3 clearly shows the formation of laser-induced periodic surface structures (LIPSS), such an effect takes place as a result of applying thousands of pulses. In this particular case, we are showing the formation of LIPSS for an exposure of 4000 pulses. Figure 3a, shows an AFM image from a non-irradiated zone in the as-deposited thin film, a homogeneously smooth surface can be identified, it is constituted by a compact layer of nanosized grains. Figures 3b-d show the results of the laser exposures on the Ti film; when either a linear or a circular polarized beam is used the film surface experiences significant changes. In Figures 3b-c, a linear polarized beam was used, notice that in those cases grating-like structures are formed, whose orientation follows the laser polarization direction (indicated with a blue arrow and a **E** which stands for the light electric field); we must observe that the grating-like structures are covered with quasi-periodically distributed craters. If we switch from a given laser linear polarization to the orthogonal linear polarization orientation the grating-like structure follows the polarization orientation. An interesting and expected result is shown in Figure 3d, where it is noticed that when circular polarization is used there is no LIPSS formation at all, however, a series of craters of a few hundred nanometers diameter are formed. Those craters are of the same nature than the ones formed on the grating-like structures under linear polarization exposures; as discussed in (S. Camacho-Lopez et al., 2008) those craters could be formed due to enhanced field effects, which would produce ablation at specific sites with sizes below the wavelength scale. Notice too that the initial nanosized grains that constitute the thin film seem to preserve well under circularly polarized light exposures.

In Figure 3e, we have a cross profile from one of the grating-like structures that result from the linear polarization exposures. It can be easily seen how the grooves periodicity is in the order of the laser wavelength (532nm); this fact is already well known in the LIPSS literature. However, we must note in this case that while in the great majority of the LIPSS reports in metals, the LIPSS formation comes from using laser fluences above the melting and even ablation thresholds (Sipe, J. E. et al., 1983; Young, J. F., et al., 1983); in our case the LIPSS features are not the result of melting or ablation, but the result of laser-induced oxidation of the Ti film. S. Camacho-Lopez et al., reported, back in 2008 for the very first time, LIPSS made of a metallic oxide. An interesting feature is that while in most of the reported work the LIPSS orientation is perpendicular to the laser polarization orientation, in the present case the LIPSS form consistently oriented parallel to the laser beam polarization.

On the optical side effects resulting of the LIPSS formation, we must mention that an angular selective reflectance was obtained when the processed sample is illuminated obliquely under white light and the sample is rotated around the normal to its surface (Camacho-Lopez S., et al., 2008). If the angle of incidence of the white light beam is varied a whole selection of colors is obtained by diffraction off the grating-like structures.

Fig. 3. AFM micrographs for a) an as deposited titanium film deposited in silicon and b-c) laser exposed spots to linear polarization and d) circular polarization; e) is a cross profile of the grating-like structures formed for linear polarization.

3.2.2 Molybdenum / glass and ps pulses laser irradiation

For the case of molybdenum, a thin film deposited on glass was laser irradiated with a frequency doubled Nd:YAG ps pulsed laser using the parameters already mentioned above (Table 4). LIPSS formation is easily obtained, as it is shown in Figure 4, for a number of pulses as low as 2000. The LIPSS formation in this case is oriented perpendicular to the laser beam linear polarization (Figure 4a). Notice that craters as those showed in Figure 3 are not formed in this case. Another characteristic to notice here is the fact that the LIPSS periodicity is in the order of twice the laser wavelength (Figure 4b). It is important to point out that a sort of cone shaped structures can be identified to cover the main LIPSS formation; a 3-D AFM profile of such cone shaped structures is presented in Figure 4c, for the case of a spot that has been irradiated with 2000 ps laser pulses.

Fig. 4. AFM micrographs for a molybdenum thin film laser exposed to 2000 ps laser pulses. a) 2-D image of the LIPSS; b) cross profile that shows the LIPSS periodicity; c) 3-D micrograph of the cone shaped structures that cover the main LIPSS.

3.3 LIPSS formation characterized by SEM

3.3.1 Titanium / glass for ns and ps pulses laser irradiation

The as-deposited (on glass substrates) metallic thin films, for both selected metals (Ti and Mo), show smooth and homogeneous surfaces, this is seen for titanium in Figure 5a, and molybdenum in Figure 6a. In the specific case of the as-deposited titanium, the film shows very compact nanosized grain structure; while in the case of the as-deposited molybdenum, a nano-porous structure dominates the film surface texture.

The titanium thin film (500 nm thick) was irradiated using 9 ns laser pulses (see Table 3) and a per pulse fluence of 0.08 J/cm^2 , at a repetition rate of 10 Hz; from Figure 5b we can observe that after 4000 pulses the surface of the metallic thin film, suffers almost no change in its morphology and texture. A few cracks developed but the nanosized grain layer still dominates the titanium film. We must mention though that no matter the lack of LIPSS formation, there is a definitely laser-induced oxidation effect on the Ti thin film, this is shown in the following section dedicated to micro-Raman characterization.

Fig. 5. SEM titanium: a) as-deposited Ti thin film; laser irradiated with b) 4000 ns pulses, c) 2000 ps pulses.

When the titanium thin film (500 nm thick) was irradiated using a 30 ps pulse duration at 10 Hz repetition rate and a per pulse delivered fluence of 0.24 J/cm^2 , and the number of pulses was set to 2000, the film is significantly modified. Figure 5c shows a typical SEM micrograph

of the irradiated spot, where we can see LIPSS formation in a similar manner as we observed in the case of the titanium on silicon substrate irradiated with ns laser pulses. It must be noticed though that the LIPSS features in the ps laser irradiation case present some differences as compared to the ns laser irradiation results; we can see for instance that the oriented structures formed in a denser pattern, notice too that the craters formed in the case of ns laser pulses do not appear in the ps laser pulses case. A very relevant feature, however, is that the orientation of the formed LIPSS on the ps laser pulses case is orthogonal to the laser beam polarization. As expected, the grating-like structures periodicity is in the order of the laser wavelength, which is consistent to the known facts of the LIPSS formation phenomenon. The deep and dark areas in the micrograph most likely correspond to an inhomogeneous intensity distribution across the laser beam and therefore across the laser exposed area. Another feature we must notice is that the grating-like structures in this case are composed by rectangular platelets which actually flake off the sample.

3.3.2 Molybdenum / glass for ns and ps pulses laser irradiation

Figure 6 shows the as-deposited on glass substrate molybdenum thin film (Figure 6a); the ns pulses laser irradiated sample (Figure 6b) and the ps pulses laser irradiated sample (Figure 6c-d).

Fig. 6. SEM molybdenum: a) as-deposited thin film; laser irradiated with b) 18000 ns pulses, c) 2000 ps pulses, notice the sharp border between the laser affected and the non-affected zones, d) LIPSS zoom in.

As it occurred in the case of titanium, the ns pulses laser irradiation did not affected the molybdenum surface texture at all (Figure 6b) for up to 18000 pulses of a per pulse fluence of 0.08 J/cm^2 , however, as it is shown in the following section dedicated to micro-Raman characterization, a laser-induced oxidation effect takes place as a result of the laser exposure.

For the ps pulses laser irradiation of the molybdenum thin film, as previously mentioned in the AFM section, the orientation of the formed LIPSS is perpendicular to the laser beam polarization. An interesting feature to be noted is a tendency to bifurcation across the grooves formed (Figure 6c-d). There are a few reports of LIPSS formed under femtosecond laser irradiation in metals, where the bifurcation effect is presented although it has not been explained yet. Notice too that craters as those showed in Figure 3 are not formed in this case; this is consistent with the results obtained on titanium deposited on glass when irradiated with the ps laser pulses.

3.4 Pulsed laser-induced oxidation characterized by micro-Raman spectroscopy

The micro-Raman spectra for the titanium thin film irradiated with ns is showed in Figure 7. Raman spectra are displayed between 200 to 800 cm^{-1} . The spectra 7(a-c) correspond to irradiated zones with 4000, 8000 and 12000 pulses at 0.08 J/cm^2 .

Fig. 7. micro-Raman spectra of a titanium film irradiated at : a) 4000, b) 8000 and c) 12000 ns pulses.

The micro-Raman spectra for the titanium thin film irradiated with ps are showed in figure 8. Raman spectra are displayed between 200 to 800 cm^{-1} . The spectra 8(a-d) correspond to irradiated zones with 2000, 4000, 6000 and 8000 pulses at 0.24 J/cm^2 . It can be observed the presence of bands mainly at 442 and 610 cm^{-1} .

Figure 9 shows a set of micro-Raman spectra for the molybdenum thin film irradiated with ns laser pulses. The Raman spectra are displayed between 200 to 1000 cm^{-1} . For comparison

purposes, the micro-Raman spectrum 9(a) of m-MoO₂ powder was included (Camacho-López M. A. et al.,). The spectra 9(b-d) correspond to irradiated zones with 6000, 12000 and 18000 pulses at 0.08 J/cm². The spectrum 9(e) corresponds to an irradiated zone with 10000 pulses at 0.16 J/cm². In all cases, micro-Raman spectra are constituted by peaks in the range 200-800 cm⁻¹.

Fig. 8. Raman spectra of the titanium thin film irradiated with ps laser pulses: a) 2000, b) 4000, c) 6000, d) 8000 pulses

Fig. 9. Micro-Raman spectra of: a) m-MoO₂ powder; molybdenum thin film irradiated with ns pulses b) 6000, c) 12000 and d) 18000 pulses at 0.08 J/cm², e) 10000 pulses at 0.16 J/cm².

Fig. 10. Raman spectra of molybdenum irradiated with: a) 2000, b) 4000, c) 6000, d) 8000, e) 10000 ps laser pulses.

The micro-Raman spectra for the molybdenum thin film irradiated with ps are showed in Figure 10. As before, the micro-Raman spectra are displayed in the range 200 to 1000 cm^{-1} . Five zones of the thin film were irradiated with 2000, 4000, 6000, 8000 and 10000 ps laser pulses. Each spectrum in Figure 10 corresponds to each irradiated zone.

4. Discussion

4.1 LIPSS formation

The LIPSS phenomenon has been well studied in bulk metals for laser fluences above ablation threshold, but there are no reports of this effect on metallic thin films when irradiated at laser fluences well below ablation threshold. On top of that, there are no reports at all of such LIPSS formed during the laser-induced growth of metallic oxides. In the present work, we have shown different features that can be achieved on the LIPSS formation depending on pulse duration. We selected two metals as titanium and molybdenum to show some of the main characteristic transformations, that occur when those metals in their thin film form are laser irradiated with a frequency doubled Nd:YAG laser in two distinct pulse duration regimes. For the case of titanium and ns laser pulses, it was easy to obtain LIPSS formation for samples deposited on a Silicon substrate; on the contrary it was not possible to obtain LIPSS formation when the titanium is deposited on a glass substrate, although we did get laser-induced oxidation. We did not try molybdenum deposited on Silicon. As for molybdenum deposited on glass it was neither possible to form LIPSS under ns laser irradiation, but laser-induced oxidation is still possible. Remarkably, the situation changes significantly when the titanium and molybdenum thin films deposited on glass substrates are laser irradiated with a frequency doubled Nd:YAG ps laser. For both cases, we obtained LIPSS formation with very distinct features; while titanium forms

compact and dense LIPSS with periodicity in the order of the wavelength, molybdenum forms LIPSS covered by cone shaped structures of a few hundred nanometers size. The periodicity of the LIPSS in the case of molybdenum is twice the laser wavelength, which is somehow unexpected.

4.2 Pulsed laser-induced oxidation

4.2.1 Titanium oxide induced by pulsed laser irradiation

From the literature it is well known that the Raman spectrum for the titanium rutile phase, in the range 200 to 800 cm^{-1} , is constituted by three bands located at 236, 444, 609 cm^{-1} (Porto et al., 1967; Beattie I. R., Gilson T. R. 1967; Escobar-Alarcón et al., 1999). There is good agreement between the Raman peak positions obtained for de irradiated zones with ns and ps pulses (Figures 7 and 8) and those reported in the literature for the rutile phase. This indicates that the irradiated material suffered an oxidation passing from Ti to TiO_2 in its rutile phase. This transformation was obtained by (Pérez del Pino et al., 2002) irradiating titanium targets by using the fundamental line (1064 nm) of a Nd:YAG laser. Additionally to the rutile phase, they found another phases like $\beta\text{-Ti}_2\text{O}_3$ and TiO into the irradiated zones. Analyzing our spectra for the ns pulses, we can observe two bands at 445 and 335 cm^{-1} that could be assigned to Ti_2O_3 . Therefore, the Raman results indicate that a mixture of TiO_2 and Ti_2O_3 is present in the irradiated zones. It is worth noting that in the case of ps pulses, the Raman spectra do not present the bands corresponding to the Ti_2O_3 phase. In this case only the rutile phase of TiO_2 is obtained in the irradiated zones.

4.2.2 Molybdenum oxide induced by pulsed laser irradiation

From the literature, only a little amount of work on the Raman features for the m-MoO₂ can be found. For instance (R. Srivastava, R. & Chase L. L. 1972) reported the Raman spectrum for a single crystal of MoO₂. (Spevack, P. A.; McIntyre, N. S. 1992, 1993) published the Raman spectrum of MoO₂ for a powder and for thin films too. (M. Dieterle, 2001) reported some molybdenum oxide Raman spectra, in particular for MoO₂. (A. Blume 2004) has extensively studied the Raman spectra of a variety of MoO_x ($2 \leq x \leq 3$). Recently, (Camacho-López et al., 2011) studied the transformation of m-MoO₂ to MoO₃ by micro-Raman spectroscopy. The following Table presents the Raman frequencies obtained for the m-MoO₂ phase by several research groups. Analyzing the Raman frequencies from the literature (Table 5), some differences are observed. More detailed Raman studies on MoO₂ are necessary to determine the spectral changes related to substoichiometry.

Table 6 presents the Raman frequencies obtained for the molybdenum thin films irradiated with ns and ps pulses. Comparing the frequencies obtained in the spectra 9(b-d) and 10(c-e) with those reported in the literature for the m-MoO₂ phase, we can point out that the position of the majority of the Raman peaks (for instance spectrum 9e) have a reasonable agreement with the characteristic Raman spectrum for the m-MoO₂ phase. However, the peaks of the spectra 9(b-d) and 10(c-e) are wider than those for the spectrum 9(a). In particular, the FWHM for the peak (744 cm^{-1}) was indicated in Table 6. This result indicates that the crystallinity of the material in the irradiated zone is not optimized for a laser fluence of 0.08 J/cm². When the laser fluence is increased (0.16 J/cm²), the peak position shifts towards higher frequencies and the FWHM decreases as it is observed in the spectrum 9(e). As a reference value, the FWHM of the peak centered at 744 cm^{-1} , for a crystalline MoO₂

powder (Table 6) and the 1D nanorods (Latha, K. et al. 2007) is 20 cm^{-1} . For a laser fluence of 0.08 J/cm^2 the FWHM is 150 cm^{-1} , while for 0.16 J/cm^2 the FWHM is 50 cm^{-1} . This indicates that crystallinity can be improved with the increase in the laser fluence. The shift in the position of the Raman peaks could be related to substoichiometric molybdenum oxide induced in the irradiated zone of the thin film. It must be noted that 6000 pulses are sufficient in the two cases (ns and ps) to induce the molybdenum oxide. Optically, the molybdenum thin film did not suffered any changes.

Single crystal MoO ₂ (R. Srivastava et al. 1972)	m-MoO ₂ (Spevack, P. A. &McIntyre, N. S. 1992)	Powder m-MoO ₂ (Camacho-lópez, M. A. et al. 2011)	m-MoO ₂ (Blume, A. 2004)	Commercial Powder MoO ₂ (Latha, K. et al. 2007)
	203	203		229
		208	208	
	228	229	232	226.3
	345	346		346.2
		350	353	
	363	365	370	360.2
			448	
	461	459	463	458.2
		469	473	
505	495	496	501	494.1
	571	569	572	567.2
595	589	588	590	584.4
760	744	744	748	738.5

Table 5. Raman frequencies for m-MoO₂ reported in the literature.

m-MoO ₂ (spectrum 9a)	Our work Nanosecond pulses Spectrum 9e	Our work Nanosecond pulses Spectra 9(b-d)	Our work Picosecond pulses Spectra 10(c- e)
203			
208	211	218	216
229	232	228	234
	251	248	
346	349		
350			
365	362		366
459	461	457	
469			
496	496	495	500
569	570	565	571
588			
		678	
744 (20 cm^{-1})	742 (50 cm^{-1})	737 (150 cm^{-1})	742
	780	778	

Table 6. Raman frequencies obtained in our work

5. Conclusions

We have demonstrated that it is possible to create laser-induced periodic surface structures (LIPSS) on metallic (titanium and molybdenum) thin films, by irradiating the thin film with either a nanosecond or a picosecond, frequency doubled, Nd:YAG pulsed laser. We found that in the nanosecond regime the LIPSS formation seems to be influenced by the substrate type (silicon or glass); although the delivered laser fluence could also be a factor. A very interesting fact is that in the case of the irradiation with nanosecond laser pulses on titanium / silicon, the LIPSS orientation forms parallel to the laser beam polarization; while in the case of the irradiation with picosecond laser pulses on titanium / glass, the LIPSS orientation switches to perpendicular to the laser beam polarization. The last also holds for the irradiation with picosecond laser pulses on molybdenum / glass. We also demonstrated that it is feasible to obtain TiO_2 in its rutile phase and MoO_2 in its monoclinic phase, by using low repetition rate Nd:YAG pulsed lasers in the short pulse regime (nanoseconds) and the ultrashort pulse regime (picoseconds). The laser-induced metallic oxides TiO_2 and MoO_2 synthesize in very specific crystalline phases which depend on the laser irradiation parameters.

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