JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 3, March 2010, p. 496 - 499

Laser control of the properties of nanostructures on Ta and Ni under their ablation in liquids

E. V. BARMINA[a], M. BARBEROGLOU[b,c], V. ZORBA[a,b], A. V. SIMAKIN[a], E. STRATAKIS[b,d], C. FOTAKIS[b,c], G. A. SHAFEEV[a*]

[a]*Wave Research Center of A.M. Prokhorov General Physics Institute of the Russian Academy of Sciences, 38, Vavilov street, 119991, Moscow, Russian Federation*

[b]*Institute of Electronic Structure and Laser, Foundation for Research & Technology—Hellas, (IESL-FORTH), P.O. Box 1527, Heraklion 711 10, Greece.*

[c]*Physics Department, University of Crete, Heraklion 714 09, Greece.*

[d]*Materials Science and Technology Department, University of Crete, Heraklion 710 03, Greece*

The process of nanostructures (NS) formation on bulk Ta and Ni immersed into liquids is experimentally investigated under its exposure to short laser pulses. Three types of lasers sources have been used, a Nd:YAG laser with pulse duration of 350 ps, an excimer laser at wavelength of 248 nm and pulse duration of 5 ps, and a Ti:sapphire laser with pulse duration of 180 fs. The morphology of NS on Ta and Ni is characterized with either a nanoprofilometer or a Field Emission Scanning Electron Microscope. Average lateral size of nanostructures decreases with the decrease of the laser fluence. The morphology of nanostructures is investigated depending on laser parameters, such as laser pulse duration and laser fluence. Average lateral size of NS varies in the range 40-250 nm for Tantalum and 30-300 nm for Nickel. Possible applications of generated NS are discussed.

(Received June 20, 2009; accepted November 30, 2009)

Keywords: Laser, Nanostructures, Tantalum, Nickel

1. Introduction

The interaction of laser radiation with solids is accompanied by various instabilities, which may lead to the formation of surface textures. These are as a rule divided into large- and small-scale textures. The large-scale textures result from the capillary motion of the melt produced by laser irradiation of the target. Under ordinary conditions, their characteristic length scale is tens of μm. The length scale of the finer surface textures is of the same order as the laser wavelength, and they originate from the interference of the incident laser radiation and the surface electro-magnetic wave (SEW) generated on the surface of conducting solid. The resulting interference pattern is stationary because the waves are in phase, and the corresponding surface morphology is determined by a variety of processes (oxidation, sublimation, and others), whose rate is temperature-dependent. Typical morphology of these structures consists in straight periodic ripples, and their period scales with the laser wavelength. Laser ablation of solids in liquids is also accompanied by surface texturing of the target, but this is due to other mechanisms because the liquid adjoining the melt on the target surface undergoes a phase transition. Sufficiently high laser fluence leads to surface melting of the target, solid at room temperature. Short pulses produce not only superheated liquid but also a transient zone of elevated pressure near the target, which may transfer the substance adjacent to the target to a supercritical state. The pressure wave interacts with the melt layer on the target surface, changing its configuration. At pulse duration below 1 ns, this viscous interaction leads to nanotexturing of the solid surface. Nanotextures were first observed on silver [1] and then on gold [2,3], after laser ablation of Ag and Au targets in some liquids. It results in formation of self-organized nanostructures (NS) that look like periodic protrusions of the surface. Similarly, the NS formation on Al has been reported [4,5]. Nanotexturing is accompanied by changes in the absorption spectrum of the target: additional bands emerge near the plasmon resonances of metal NS. At the present stage, surface nanotexturing in response to the ablation of targets with short laser pulses in liquids lacks of theoretical interpretation. To handle this complicated problem, one must jointly solve the heat equation and the Navier-Stokes equation for hydrodynamic flow when the two media that are in contact, a metal and a liquid, undergo phase transitions. Therefore, accumulation of experimental data on surface nanotexturing of various materials is of interest per se. In view of this, in the present study Ta and Ni were chosen as target materials. Another reason is that Ta possesses unique physical and chemical properties. This refractory metal, with a melting point of ~ 3000^{o} C, offers high chemical stability. Its natural oxide, Ta_2O_5, has high electric strength and passivates the metal

surface preventing its oxidation even at elevated temperatures. These advantages make tantalum an attractive material for a variety of applications, from medicine to micro-electronics. The aim of this work was to produce NS on Ta and Ni by their ablation with pico- and femtosecond laser pulses in water and to study their morphology in relation to process parameters. The possibility of fabrication of bi-metallic NS on these metals is also studied.

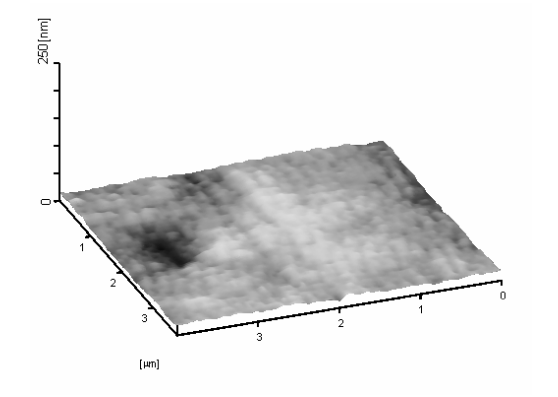
2. Experimental

As targets we used 100-μm-thick tantalum and nickel foils. Prior to irradiation, the targets were abrasively ground or polished to a rms roughness value of about 50 nm and placed on the bottom of a glass cell, which was then filled with water. To produce NS on Ta and Ni, three laser sources were used. One of them was a 1.064-μm pulsed Nd : YAG laser (pulse duration, 350 ps; repetition rate, 300 Hz). The cell was then mounted on a computer-controlled stage which ensured a constant translation velocity. Another source was a KrF laser (248 nm) with a pulse duration of 5 ps and repetition rate of 10 Hz, which was used for stationary irradiation. The third source was a Ti :sapphire laser operating at a repetition rate of 1 kHz (180-fs pulses at 800 nm). Laser exposure was performed in a stationary regim. In all cases, the laser beam was focused onto the target through a water layer several millimeters in thickness. The spot area was determined from the dimensions of the modified zone. The surface morphology of irradiated targets was examined using an NPX 2000 nano-profilometer (an analogue of Atomic Force Microscope, AFM), and that of the other targets was examined with a Field Emission Scanning Electron Microscope (FE SEM). Ni electroplating was realized on the nanotextured surface of Ta using a standard solution of electrolyte.

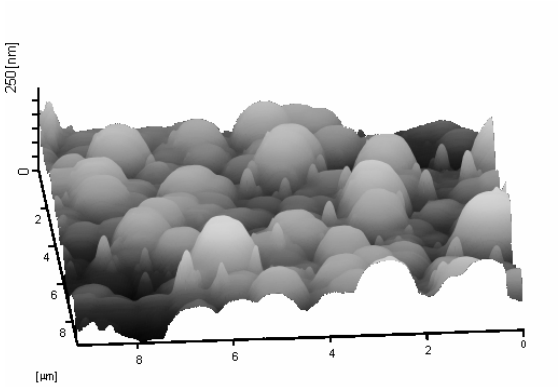
3. Results and discussion

Typical view of NS on Ta is illustrated in Fig. 1b.

The surface of the tantalum target is covered with nanohillocks 200-250 nm in height. Their lateral size depends on the laser fluence on the target. To assess this effect, we measured the average lateral size of the nanohillocks as a function of energy density (Fig. 2) [6].



a



b

Fig. 1. Initial surface of a Ta target (a) and NS (b) on it after ablation in water. AFM image of a Ta target irradiated trough a water layer at fluence of 0,31 J/cm^2, pulse duration of 350 ps, 300 pulses. Z-scale is 250 nm for both images.

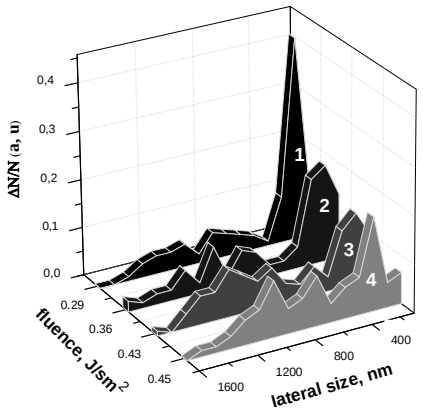


Fig. 2. Lateral size distribution of NS on the Ta surface irradiated trough a water layer at fluence of 0.29 (1), 0.36 (2), 0.43 (3), and 0.45 (4) J/cm^2.

As seen in Fig. 2, with decreasing energy density the average lateral size of the nanohillocks drops to 200-300 nm, and the percentage of hillocks of the order of 1 μm in lateral size markedly decreases (the fraction of nanostructures of the order of 200 nm is 0.43 at fluence of 0.29 J/cm^2 and 0.05 at fluence of 0.45 J/cm^2, but percentage of hillocks of the order of 1 μm in lateral size drops from 0.12 to 0.04 in this fluence range). This part of NS can be attributed to SEW interference with the laser beam, since their size is closed to the laser wavelength of 1.06 μm.

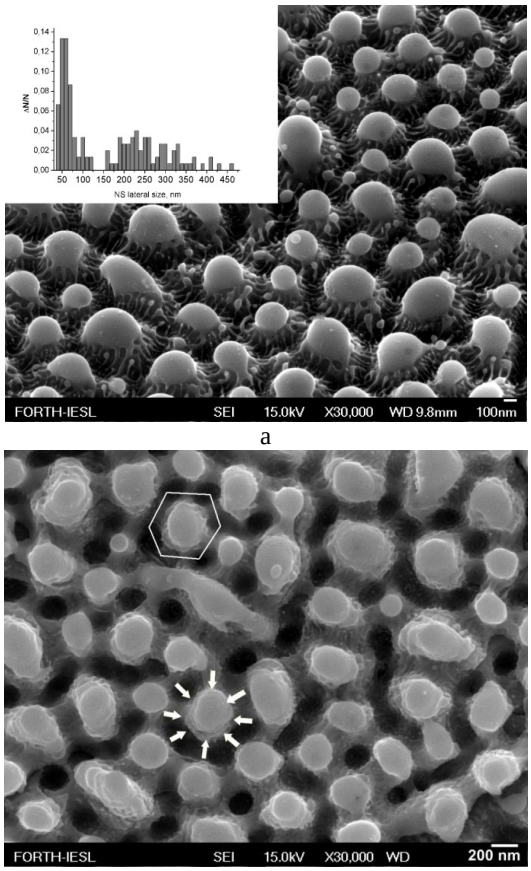


Fig. 3. FE SEM view of a Ta target subjected to exposure of 5 ps laser pulses of a KrF laser at 248 nm in water, 200 pulses. a - tilted view, b – top view. The inset shows the lateral size distribution of NS.

Fig. 3 shows the FESEM view tantalum surface after KrF laser irradiation with 5 ps pulse duration. The average lateral size of the NS is by a factor of 5 smaller that in case of 350 ps pulses. The inset shows the lateral size distribution of NS. This distribution is bimodal, like in case of 350 ps laser exposure (Fig. 2). One maximum is around 50-60 nm, while the second is around 250 nm that is close to laser wavelength of 248 nm. Note that laser ablation in water significantly increases the surface area of the target. The surface density of nano-hillocks as estimated from Fig. 3 is 10^6 cm^{-2}. Each nano-hillock is symmetrically surrounded by several pits, from four to six (in Fig. 3b the centers of six pits are connected with a hexagon). It seems likely that the hillocks appear due to repulsion of the melt from the neighboring pits as result of different pressure of the surrounding medium above these locations. This is indirectly evidenced by the presence of solidified metal jets ending with a rounded droplet (Fig. 3, a).

Finally, the dominating type of NS under ablation of Ta in water with a Ti:sapphire laser radiation at 180 fs are periodic ripples.

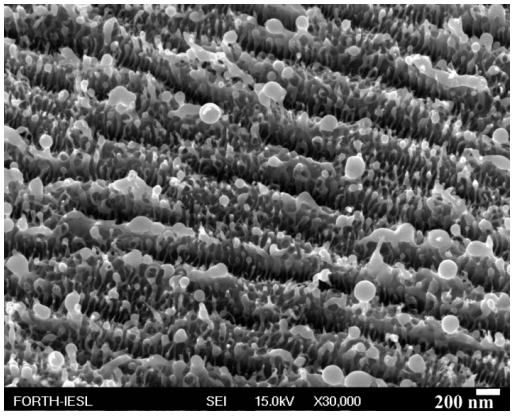


Fig. 4. FE SEM view of Ta target after ablation in water by Ti:sapphire laser, 1000 pulses.

Spherical mushroom-like NS are situated on the top of the ripples [6].

3.1 Estimation of the pressure of surrounding medium during the NS formation

The isolated spherical NS is typical for NS obtained via laser ablation in liquids, especially of long laser pulses (Fig. 5). This morphology was observed on Ag, Al, and other metals. Note that probe microscopes, e.g., AFM or STM cannot provide the real profile of such structures – they will be imaged as cones.

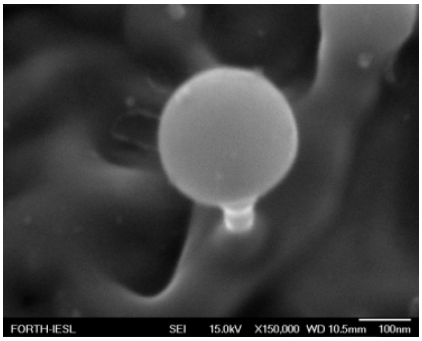


Fig. 5. Isolated NS on Ta formed under ablation of a Ta target in H_2O with the help of a 350 ps laser radiation.

The formation of NS can be interpreted as the result of the work of pressure. This work is spent to increase the interface length against the surface tension of the melt. In view of this, the elementary work *dA* needed to increase a circular interface length of *2R* by *dR* can be expressed as follows:

$$dA = \sigma 2\pi R dR ,$$

where σ stands for the coefficient of surface tension of the melt. The total work, *A*, for the generation of a spherical NS of radius *R* can be found as follows:

$$A = 2\int_0^R \sigma 2\pi R dR = 2\pi\sigma R^2$$

On the other hand, this work is performed by a force equal to $S\Delta p$, where *S* is the surface of the NS and Δp is the pressure difference. As this force acts on a distance $l=2R$ its corresponding work is:

$$A = Fl = \pi R^2 \Delta p 2R$$

Equalizing the two above expressions one finds the following estimation for the pressure difference:

$$\Delta p = \frac{\sigma}{R}$$

Substituting the parameters for NS on Ta shown above, with R = 100 nm, one obtains $\Delta p = 4\text{x}10^7$ Pa. This is the order of magnitude of the pressure difference existing above the melt surface, applied on a very short distance, of the order of NS period. It is important that the estimated value for Δp exceeds the critical pressure for H_2O. Furthermore, the temperature of the liquid layer adjacent to the melt is close to the melting temperature of the target, equal to 3000º C in case of Ta. As a result, the medium that surrounds the target (H_2O) is in its supercritical state.

Smooth surface of domes (Fig. 3) suggests that dissolution of the target material in supercritical water, if at all occurs, contributes little to nanotexturing. Indeed, if Ta were partially dissolved in supercritical water, precipitation of the dissolved material from the supersaturated aqueous solution after cooling would result in dendritic morphology and not in smooth shapes. Moreover, dissolution in pure supercritical water occurs more slowly than in aqueous solutions of salts and alkalis. The observed symmetric arrangement of the pits may be due to the development of instability at the interface between the superheated water and melt layer.

3.2 Nanotexturing of Nickel by laser ablation in liquids

Nanotexturing of Ni was carried out in the same experimental setup. Fig. 6 shows the morphology of Ni surface subjected to a femtosecond laser radiation in liquid ethanol.

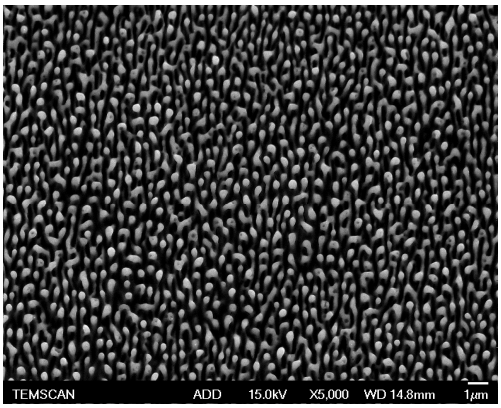
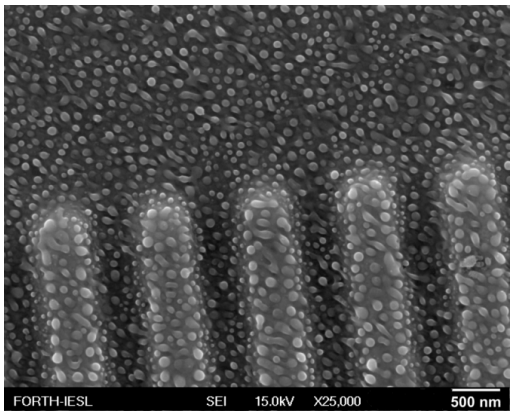
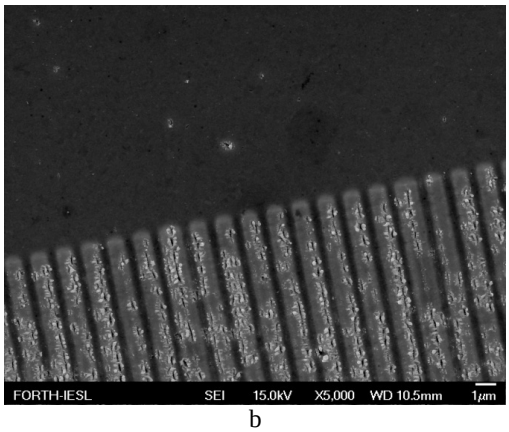


Fig. 6. NS on Ni produced by its ablation in ethanol with a femtosecond Ti:sapphire laser, wavelength of 800 nm, pulse duration of 180 fs, 1000 pulses.



a



b

Fig. 7. The influence of pre-structuring of Ni on the formation of NS via laser ablation in ethanol. The stripes on the bottom of two images were formed via electron beam lithography. a: KrF laser, pulse duration of 5 ps, 250 pulses. b – a Ti:sapphire laser, pulse duration of 180 fs. No NS are observed on the initial Ni surface.

Note that NS in Fig. 6 are nor round and have some polygonal shape. This si probably due to the competition

between ripples and typical spherical NS usually observed for ablation in liquids. Initial pre-structuring of the surface, either an artificial relief or the residual roughness facilitates the formation of NS. This was first reported for NS on Ag [1]. For Ni this is illustrated in Fig. 7. On top of stripes produced on Ni by electron beam lithography the average size of NS is higher that on the initial Ni surface (Fig. 7a).

It is believed that the results presented in the paper may find various applications. Only few laser pulses are needed to produce high-density array of NS on any metallic surface. In a sense, one may speak about laser writing of nanostructures. Fast laser nanostructuring of Ta is of interest for its use as a biocompatible medical implant. Also, nanotextured Ta surface may find applications in micro-electronics as electrodes for batteries and capacitors. Ni NS can be considered as magnetically isolated NS for potential use in data storage applications.

4. Conclusions

Thus, nanotexturing of both Ta and Ni targets has been successfully realized via ablation in liquids with short laser pulses. Nanostructures (NS) on these metals are characterized by bimodal size distribution. One maximum is associated with the laser wavelength, while another depends on the pulse duration. Estimations of the pressure difference above the target during the laser pulse indicate that the surrounding medium is in its supercritical state. On the other hand, the dissolution of the target material in the supercritical medium has little if ever effect on the NS formation. It is ascribed to development of instability at the interface melt-vapors of the liquid. Periodic ripples are dominating surface nanostructures on both metals under their exposure to femtosecond laser radiation. Pre-structured surface facilitates the formation of NS.

Acknowledgements

The work was partially supported by Russian Foundation for Basic Research, grants ## 07-02-00757, 08-07-91950, and by Scientific School 8108.2006.2. Dr. V. Popov (Moscow State University) is thanked for supplying Ni substrates with e-beam lithography patterns.

References

[1] E. V. Zavedeev, A.V. Petrovskaya, A.V. Simakin, G. A. Shafeev, Quantum Electronics **36**(10), 978 (2006)

[2] S. Lau Truong, G. Levi, F. Bozon-Verduraz, A. V. Petrovskaya, A. V. Simakin, G. A. Shafeev, Appl.Phys. **A89** (2) 373 (2007).

[3] S. Lau Truong, G. Levi, F. Bozon-Verduraz, A. V. Petrovskaya, A. V. Simakin, G. A. Shafeev, Applied Surface Science **254**, 1236 (2007)

[4] E. Stratakis, V. Zorba, M. Barberoglou, C. Fotakis, G. A. Shafeev, Applied Surface Science **255,** 5346 (2009).

[5] E Stratakis, V Zorba, M Barberoglou, C Fotakis, G. A. Shafeev Nanotechnology **20,** 105303-7 (2009).

[6] E. V. Barmina, M. Barberoglou, V. Zorba, A. V. Simakin, E. Stratakis, C. Fotakis, G. A. Shafeev, Quantum Electronics, **39,** 89 (2009).

*Corresponding author: shafeev@kapella.gpi.ru