

LASER APPLICATIONS AND OTHER TOPICS IN QUANTUM ELECTRONICS

PACS number 42.55.Lt; 42.62.–b
DOI 10.1070/QE2003v033n12ABEH002561

Formation of microscopic coloured oxide dots on the titanium foil surface irradiated by a laser

S.B. Alekseev, V.M. Orlovskii, V.F. Tarasenko, A.N. Tkachev,
M.A. Shulepov, A.V. Fedenev, S.I. Yakovlenko

Abstract. **Experiments are performed on the formation of coloured dots of a submillimetre size on the titanium foil surface irradiated by pulsed IR lasers. It is shown that the parameters of laser pulses can be selected so that the dots produced on the titanium foil surface will change their colour from yellow to blue with increasing exposure time. The threshold laser power densities required for the formation of contrast coloured dots on the titanium foil surface irradiated by laser pulses with low repetition rates are estimated as $\sim 1.5 \times 10^3$ J cm^{-2} for a 1.73-μm Xe laser and $\sim 2.3 \times 10^3$ J cm^{-2} for a 10.6-μm CO_2 laser.**

Keywords: *interaction of radiation with matter, oxides, thin films.*

1. Introduction

Titanium oxide coatings are of interest for a number of applications, for example, as optical and decorative coatings, the components of catalysts, medical implants, and gas sensors. One of the methods for producing coatings is the laser processing of the metal titanium surface in a reactive atmosphere [1, 2].

It was demonstrated in Ref. [1] that stable coloured films could be produced in the colour range from yellow to blue on the titanium plate surface in air scanned by radiation from a repetitively pulsed laser. The authors [1] showed that the films consisted of titanium oxides and their colour was determined by the percent content of TiO, Ti_2O, TiO_2, and Ti_2O_3.

The advantage of preparing oxide films by heating the surface by laser radiation is a high localisation of laser processing allowing the production of films of the required thickness without the damage of the surrounding surface. This makes it possible to record information optically with a high spatial density [3]. Of interest for applications is the production of raster colour images on a titanium foil or a film by scanning the foil surface by a laser beam with a programmed variation in the power density in the focal spot. However, the data reported in the literature do not give information on the minimal size of titanium films produced by laser radiation, the optimal regimes of their production, and on the influence of nitrogen contained in air on the formation of these films.

The aim of this paper is to study the process of formation of coloured submillimetre dots on the titanium foil surface irradiated by pulsed or repetitively pulsed lasers in a medium of reactive gases.

S.B. Alekseev, V.M. Orlovskii, V.F. Tarasenko, M.A. Shulepov, A.V. Fedenev Institute of High-Current Electronics, Siberian Branch, Russian Academy of Sciences, prosp. Akademicheskii 4, 644055 Tomsk, Russia; e-mail: vft@loi.hcei.tsc.ru;
A.N. Tkachev, S.I. Yakovlenko A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia

Received 19 June 2002; revision received 19 March 2003
Kvantovaya Elektronika **33** (12) 1101 – 1106 (2003)
Translated by M.N. Sapozhnikov

2. Experimental

We irradiated titanium foils by a CO_2 laser or a Xe laser. When the Ar – Xe mixture was used, the 1.73-μm, 400-ns pulses with the output energy of 5 – 7 J were obtained in the laser with the gas volume of 30 L pumped by a high-power radial-converging electron beam. The laser beam diameter was 20 cm (setup no. 1) [4, 5]. The output energy density of focused laser radiation in the focal spot of diameter 5 mm achieved 20 – 25 J cm^{-2}.

The CO_2 laser excited by a discharge with the electron-beam preionisation emitted $\sim 3 - 5$ J pulses of duration from 100 ns to 15 μs and a pulse repetition rate of $f \lesssim 50$ Hz (setup no. 2) [6]. The active $72 \times 3 \times 2.4$-cm volume was confined by a copper electrode and a steel grid protecting the output foil window of an electron accelerator. The electron accelerator generated a 4-ns, 6-kA, 150-keV electron beam. A capacitor bank with a total capacitance of 0.2 μF was placed directly in the gas volume and was charged to 10 – 12 kV. The laser resonator consisted of a plane mirror with an aluminium coating and a plane–parallel KRS-5 plate used as the output window.

When the Ar : Xe = 100 : 1 mixture (1 atm) was used in this setup, lasing occurred predominantly at 1.73 μm. The laser emitted 320-ns, 10 – 15-mJ pulses with the average power of 70 and 300 mW at pulse repetition rates $f = 10$ and 25 Hz, respectively.

The electric-discharge CO_2 laser with spark-discharge preionisation emitted 300-ns, 0.6 – 0.8 J pulses with a pulse repetition rate no more than 5 Hz (setup no. 3) [7].

The laser energy and average power were measured with an IMO-2H calorimeter and a PE-25 (OPHIR Opt.) pyroelectric power meter calibrated in the optical range of measurements with an accuracy of 5 %. We studied titanium foils of thickness 8, 13, and 50 μm, which were preliminary purified in benzene and alcohol solutions in an ultrasonic bath. Laser radiation was focused by a BaF_2 lens with a

focal distance of 123 mm. The irradiated surface was investigated with a 100× MBS-10 and a 1500× MMP-4 optical microscopes.

3. Experimental results

All the samples exhibited a variation in the colour of the titanium foil surface when the exposure time or the pulse repetition rate was changed. Figure 1 shows the photographs of the titanium foil surface for different laser processing regimes on the setup no. 2 (the Xe laser was used). When the laser energy density was low ($q \sim 0.6 \times 10^3$ J cm^{-2}), the foil surface was melted. As the laser energy density increased (up to $q = 2.1 \times 10^3$ J cm^{-2} at $f = 25$ Hz or to $q = 1.5 \times 10^3$ J cm^{-2} at $f = 10$ Hz), the surface of the 13-μm thick titanium foil became yellow (Figs 1a, e). The further increase in the energy density up to $q = 4.3 \times 10^3$ J cm^{-2} at $f = 25$ Hz or to $q = 1.8 \times 10^3$ J cm^{-2} at $f = 10$ Hz resulted in a change in the colour of the spot centre from yellow to red and blue (Figs 1b, f). Finally, for $q = 6.4 \times 10^3$ J cm^{-2}, the entire surface of the spot turned blue (Fig. 1c). The main experimental results are summarised in Table 1, where the compositions of oxide films determined in Ref. [1] are also presented. Note that the coloured spot on the film reproduced the cross section of the laser beam in the focal plane and had a distinct boundary, suggesting that the process of film formation had the threshold over the surface temperature.

When a 50-μm thick titanium foil was irradiated by 400-ns single pulses from the Xe laser (setup no. 1) producing the energy density of 20 J cm^{-2} on the foil, the entire surface of the crater uniformly melted without changes in colour.

The irradiation of titanium foils by 15-μs, 6-J pulses from the CO_2 laser (setup no. 2) also produced melting and partial evaporation of the foil surface facing the laser; however, this was accompanied by the formation of a coloured film on the opposite side of the foil.

To elucidate the influence of the air nitrogen on the formation of coloured films, we irradiated the titanium foil surface by the CO_2 laser (setup no. 3) in the atmosphere of reactive gases: air, pure nitrogen (1 atm), and the mixture of argon with 20 % of oxygen. The laser pulse repetition rate was 3 Hz. The irradiation energy was varied by changing the exposure time. Changes produced by laser radiation in the titanium foil surfaces in the three reactive media were different. After the irradiation by the CO_2 laser in air, as in the case of Xe laser, a coloured film appeared on the titanium foil surface.

This process had the energy density threshold. The minimal laser energy density at which the coloured film appeared was 2.3×10^3 J cm^{-2} by neglecting reflection (the exposure time was 5 s). The linear size of the coloured film in the case of short exposure (5 s) was smaller than the diameter of the laser spot, approaching it with increasing

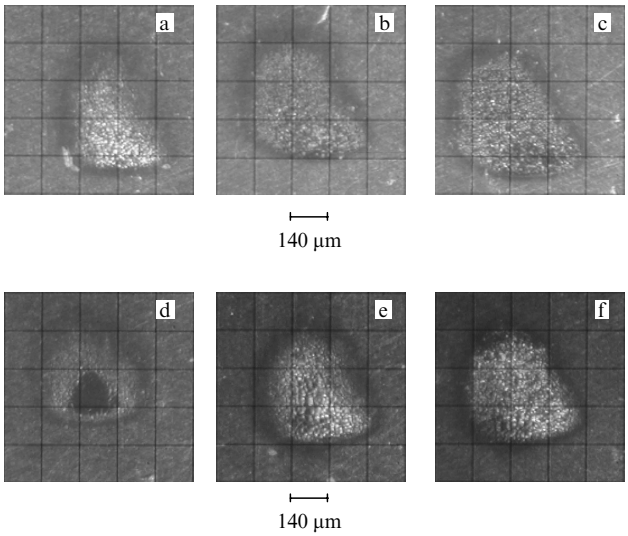

Figure 1. Microphotographs of the 13-μm thick titanium foil surface irradiated by the Ar–Xe laser with an average power of 250 mW and a pulse repetition rate of 25 Hz (a, b, c) and an average power of 70 mW and a pulse repetition rate of 10 Hz (d, e, f). The exposure time is 10 (a, d), 20 (b, e), and 30 s (c, f).

Table 1. Colours of oxide films produced on the titanium foil at different laser radiation energies and different irradiation regimes (Xe laser, setup no. 2). The film compositions are taken from Ref. [1].

Surface modification	Pulse repetition rate/Hz	Processing time/s	Total laser irradiation energy/J cm^{-2}	Composition of the surface film	Notes
Melting	10	10	$\sim 0.6 \times 10^3$	Distribution of the orientation of crystallites typical of powders	Surface cracks upon irradiation at low average powers
Melting	1	10	$\sim 0.06 \times 10^3$	–	–
Yellow colour	10	20	1.5×10^3	Possible, titanium nitride	
Reddish–yellow colour	25	10	2.1×10^3	a-Ti_2O_3 + TiO_2 (rutile)	–
Appearance of blue colour traces	10	30	1.8×10^3	a-Ti_2O_3 + TiO_2 (rutile)	At the spot centre against the yellow background
Appearance of blue colour	25	20	4.3×10^3	a-Ti_2O_3 + TiO_2 (rutile)	At the spot centre against the yellow background
Blue colour	25	30	6.4×10^3	c-Ti_2O_3 + TiO_2 (rutile)	Uniformly coloured spot

exposure time to 15–20 s. On the contrary, the film irradiated in pure nitrogen for 5–10 s clarified (due to the purification of its surface from impurities) and melted at edges. As the exposure time was increased up to 15–20 s, a dark film was formed at the central part of the focal spot (where the laser power density was maximal). The area of the dark film was substantially smaller than that of the film produced under similar irradiation conditions in air and oxygen, and it did not increase with the exposure time.

The energy density threshold and the area of films produced in the argon–oxygen mixture were in fact coincident with those observed in air; however, the distribution of darkening over the focal spot was different. The central part of the oxide film was brighter and the film had a dark border. Figure 2 shows the microphotographs of the titanium foil surface obtained in different reactive media after exposure to laser radiation for 15 s.

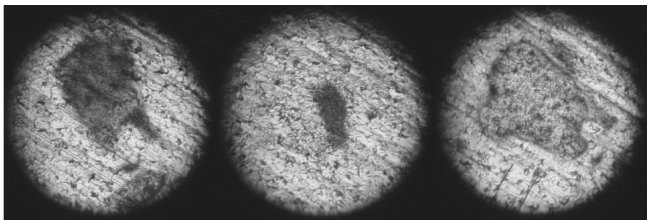

Figure 2. Microphotographs of the titanium foil surface irradiated for 15 s by the CO_2 laser (the pulse energy 0.7 J, pulse duration 300 ns, pulse repetition rate 3 Hz, energy density on the target 10^3 J cm^{-2}) in air (a), nitrogen ($p = 1$ atm) (b), and argon with 20 % of oxygen ($p = 1$ atm) (c).

To describe the dependence of the coloured film area and the intensity of its darkening on exposure to laser radiation, we introduce a new parameter – the dependence of the effective contrast ξ on the specific total laser energy density E. The latter was calculated by multiplying the relative contrast of the spot (the difference between the background and minimal brightness of the spot) by its area. Figure 3 shows the dependences $\xi(E)$ for the titanium foil processed in air and nitrogen. During irradiation in air, $\xi(E)$ increases linearly due to an increase both in the relative film contrast and area. During irradiation in nitrogen, the relative contrast of the film increases, but the spot area remains almost the same (see Fig. 2).

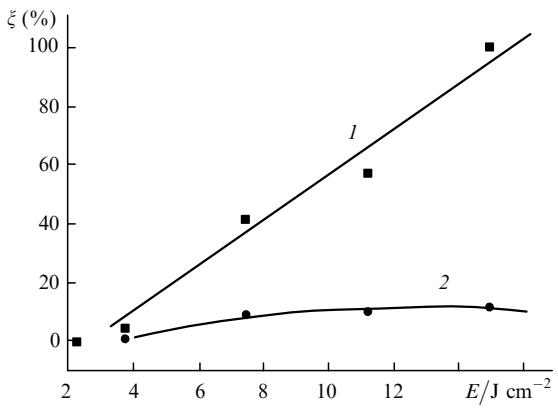

Figure 3. Dependences of the effective contrast ξ of a coloured dot on the surface of the 50-μm thick titanium foil on the specific total laser energy density E of the CO_2 laser (setup no. 3) in air (*1*) and nitrogen (*2*).

For comparison, we studied the influence of UV laser radiation on the 50-μm thick titanium foil in air. We used a 222-nm 'Photon' KrCl electric-discharge exciplex laser emitting 20-ns, 35-mJ pulses. The laser radiation was focused by a quartz lens into a spot of area $\sim 2 \times 10^{-2}$ cm^2. In some experiments, the output energy was reduced to 3 mJ with the help of an aperture. The laser operated either in the single-pulse regime or with a pulse repetition rate of 1 Hz. In both cases, laser irradiation produced a silvery crater with a melted bottom on the film surface. After irradiation by several pulses (more than five pulses), yellow–orange and blue fringes appeared around the crater. The melted surface of the crater had a wavy structure, which was most distinct after irradiation by 10–50 pulses. The coloured fringes around the crater are probably caused by the deposition of oxides (nitrides) of titanium evaporated by laser radiation from the crater and reacted with the air oxygen and nitrogen. Note that these coloured fringes reproduced in shape the regions illuminated by UV laser radiation with a large divergence.

4. One-dimensional model of nonstationary heating by laser radiation

Consider the one-dimensional nonstationary problem of the heat conduction of titanium taking into account two phase transitions: melting and evaporation. The condition of applicability of the one-dimensional approximation is

$$d \gg (4a\tau)^{1/2},$$

where d is the laser spot diameter on the irradiated surface; a is the temperature conductivity of a material ($a = 0.08$ cm^2 s^{-1} for titanium under our conditions); and τ is the laser pulse duration. Therefore, the penetration depth of the thermal flux during exposure to laser radiation should be substantially smaller than the diameter of the irradiated region.

The initial heat conduction equation has the form

$$c_p(T)\rho(T)\frac{\partial}{\partial t}T(t,x) = -\frac{\partial}{\partial x}j(t,x),\ j(t,x) = -k(T)\frac{\partial}{\partial x}T(t,x).$$

Here, $c_p(T)$ is the specific heat taking phase transitions into account; $k(T)$ is the heat conductivity; and $\rho(T)$ is the substance density.

We represent the dependence of the specific heat on temperature and parameters of phase transitions in our calculations in the form

$$c_p(T) = c_0(T) + \Delta c(T, T_\mathrm{m}, \Delta T_\mathrm{m}, \Delta H_\mathrm{m})$$

$$+ \Delta c(T, T_\mathrm{b}, \Delta T_\mathrm{b}, \Delta H_\mathrm{b}).$$

Here, $c_0(T)$ is the function describing the temperature dependence of the specific heat in the absence of phase

transitions and $\Delta c(T,T_0,\Delta T_0,\Delta H)=(\Delta H_0/\pi^{1/2}\Delta T_0)\times\exp\{-[(T-T_0)/\Delta T_0]^2\}$ is the function describing the jump of the specific heat at the phase transition point; T_m is the melting temperature; T_b is the boiling temperature; ΔH_m is the melting energy; and ΔH_b is the boiling energy. The value of ΔT_0 characterises the width of the phase-transition region. It is chosen small enough not to affect the results of calculations and at the same time large enough to avoid rigid requirements to the difference scheme.

The boundary conditions correspond to the power supply j_0 from one end of a layer (for $x=0$): $-(k\partial T/\partial x)_{x=0}=j_0(t)$. The initial conditions correspond to the constant temperature $T(t,x)_{t=0}=T_0$.

The numerical solution was obtained using the explicit difference scheme of the first order in time and of the second order over the coordinate. The coordinate network was uniform, fluxes were calculated at the boundary points of cells, while temperatures were calculated at the centres of cells. The accuracy of calculations was controlled by the fulfilment of the energy conservation law and was no worse than 0.1 %.

We performed calculations for experiments on irradiation of a titanium foil by an IR xenon laser (Figs 4, 5). The laser pulse duration was 300 ns, the melting temperature T_b was 1608 °C, and the vaporisation temperature T_m was 4260 °C. It follows from calculations that a part of the target material should evaporate during one laser pulse, which reduces the foil thickness and results in its breaking during irradiation in the repetitively pulsed regime.

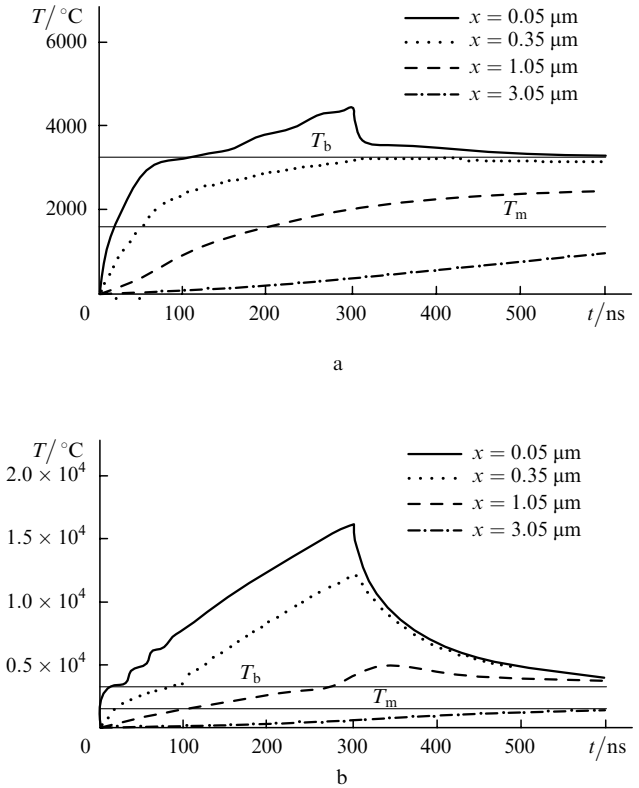

Figure 4. Time dependences of the film temperature for different distances x from the irradiated surface for the absorbed laser power densities equal to 10^7 (a) and 3×10^7 W cm^{-2} (b).

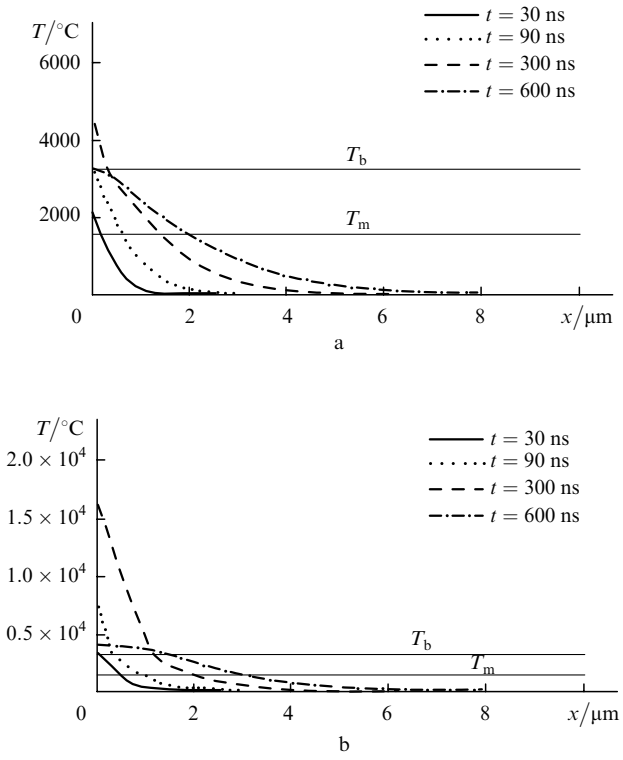

Figure 5. Dependences of the temperature on the distance x from the irradiated surface for different instants t for the absorbed laser power densities equal to 10^7 (a) and 3×10^7 W cm^{-2} (b).

The estimates of the influence of thermal radiation showed that even during the action of a laser pulse, when the surface temperature is highest, the main energy losses are caused by the heat transfer rather than thermal radiation. Therefore, we neglected the latter in the calculations. Our estimates also showed that at low pulse repetition rates, which were used in our experiments, the surface temperature had time to decrease almost down to its initial value by the onset of the next pulse.

5. Discussion of results

Our experiments have shown that coloured microscopic dots can be produced on the titanium foil surface exposed to repetitively pulsed IR laser radiation.

Our study of the interaction of laser radiation with the titanium foil in different reactive media has led to the following conclusions: coloured films are produced most efficiently in a gas containing oxygen, the threshold irradiation energy for obtaining titanium nitrides being substantially higher. We have failed to analyse the composition of the dots because of their small size. Therefore, we will use for comparison the results of analysis of film compositions obtained in papers [1, 2].

As was shown in Ref. [1], upon repetitively pulsed laser irradiation of the titanium plate surface, its colour can change from bright yellow to red and dark blue, depending on the total exposure energy. The titanium surface was oxidised in air at the atmospheric pressure upon irradiation by 300-ns, 1.9-mJ pulses from a repetitively pulsed Nd : YAG laser. The pulse repetition rate was 30 kHz and the average output power was 60 W. Several samples were irradiated by a different numbers of laser pulses per

unit area. The experiments were performed at laser energy densities from 54 to 294 J cm^{-2}. X-ray diffractometry showed that the titanium surface oxidation was absent in the case of small exposures; however, the orientation of crystallites became as that for powders. X-ray diffraction patterns obtained at large accumulated doses demonstrate the formation of the Ti_2O and TiO crystal phases among oxides, whose content monotonically increases with the irradiation dose. Other phases, such as TiO_2 in rutile or anatase crystal structures or Ti_2O_3 phase, were detected by the method of Raman spectroscopy. A low level of Raman signals and the absence of these phases in most diffraction patterns show that their content is substantially lower than that of the Ti_2O and TiO phases. Note that the dependence of the intensity of Raman lines on the laser energy was nonmonotonic. A comparison of the results of a complicated combined analysis with the colour distribution observed in the experiments showed that there exists a correlation between the colour distribution and variations in the sample composition.

In the general case, titanium oxide (nitride) is formed in the reaction

$$\mathrm{Ti} + \mathrm{O_2(N_2)} = \mathrm{TiO(TiN)} + \mathrm{O(N)} + \Delta E,$$

where ΔE is the energy released (absorbed) in the reaction. The dissociation energy of the TiO molecule is 6.9 eV, therefore, the energy $\Delta E = 1.8$ eV will be released in the reaction (the dissociation energy of the O_2 molecule is 5.12 eV). This means that the reaction is exothermic. On the contrary, the bond energy of the TiN molecule is 4.9 eV, and another 4.9 eV should be spent to dissociate the nitrogen molecule in order to form TiN, so that the reaction of TiN formation is endothermic. This probably explains a lower rate of formation of the titanium nitride film upon irradiation in air and higher laser energy density thresholds upon irradiation in pure nitrogen.

The process of oxide film formation in our experiments had the energy density threshold or, eventually, the surface temperature threshold. The blue spot had a distinct boundary, confirming the existence of the threshold temperature.

According to the theory, an oxide film is formed on the titanium surface in the following way [8]. When titanium is heated in the oxygen-containing atmosphere, scaling occurs inside the oxide–metal interface, and oxidation is caused by oxygen diffusion through an oxide layer. During heating in air at temperature $\sim 840\,^{\circ}$C and above, the oxidation rate drastically increases. This explained by the fact that nitrogen enters the rutile lattice (the O^{3-} ion is replaced by two N^{2-} ions), resulting in the appearance of a lattice defect and an increase in the elementary-unit volume, which favours oxygen diffusion inside the scale and increases the oxidation rate. For the same reasons, titanium oxidises in pure oxygen at temperature above 1100 °C slower than in air.

In the case of repetitively pulsed irradiation of the foil surface, the surface is melted during the first pulse and is purified from impurities and contamination. During the next pulses, the surface temperature during the pulse exceeds the melting and boiling temperatures of titanium. After the pulse, the foil is cooled mainly due to the heat sink in the material volume. The temperature required for efficient oxidation exists much longer than the laser pulse duration. The oxide film formed in this process has the melting temperature that is much greater than that of titanium (2020 °C for TiO) and therefore is destroyed to a lesser extent by the subsequent laser pulses. Thus, in the case of the CO_2 laser (setup no. 3), the laser radiation energy is distributed over the beam cross section nonuniformly, and the oxide film area increases during the exposure due to an increase in its thickness at the periphery of the laser spot, where the laser energy density is lower.

By comparing the results that we obtained for thin films with results [1] obtained for 1-mm thick plates, we can make the following conclusions. The modification of titanium is determined by the surface temperature and depends on the rates of heat supply and heat dissipation in a sample. The specific irradiation energies at which the titanium foil surface was modified in our experiments were several orders of magnitude higher than the corresponding energies in [1]. This can be explained as follows. In the case of a high pulse repetition rate used in experiments [1] ($f = 40$ kHz), the surface temperature increases from pulse to pulse and, although a thick plate provides a faster heat sink than a thin foil, the plate is heated more efficiently. Another factor is that the reflection of laser radiation by the metal surface decreases with temperature and decreasing wavelength. In addition, the laser pulse energy in our experiments was 3–5 times higher than that used in Ref. [1], which caused strong absorption of laser radiation in the cloud of a laser plasma and the evaporated material of the target.

6. Conclusions

Our experiments have shown that microscopic dots produced on the titanium foil surface by laser radiation can change their colour during the exposure from yellow to blue depending on the parameters of laser pulses. The threshold laser energy densities required for the formation of a contrast coloured dot upon irradiation by laser pulses with low pulse repetition rates are estimated as $\sim 1.5 \times 10^3$ J cm^{-2} for the 1.73-μm Xe laser and $\sim 2.3 \times 10^3$ J cm^{-2} for the 10.6-μm CO_2 laser. To obtain a coloured oxide film on a thin titanium foil for a single laser pulse, a longer pulse is needed to provide the foil surface heating up to the required temperature and the temperature maintenance for a time sufficient for the proceeding of the corresponding chemical reactions. The determination of the optimal parameters of the laser pulse requires additional experiments.

Acknowledgements. This work was supported by the ISTC (Project No. 1206).

References

1. Perez del Pino A., Serra P., Morenza J.L. *Appl. Surface Science*, **197–198**, 887 (2002).
2. Jimenez Perez J.L., Sakanaka P.H., Algatti M.A., Mendoza-Avarez J.G., Cruz Orea A. *Superficies y Vacio*, **9**, 286 (1999).
3. Agranovsky M.L., Korol'kov V.P., Rubenchik A.M. *J. Appl. Phys.*, **70**, 5224 (1991).
4. Abdullin E.N., Efremov A.M., Koval'chuk B.M., Orlovskii V.M., Panchenko A.N., Ryzhev V.V., Sosnin E.A., Tarasenko V.F., Turchanovskii I.Yu. *Kvantovaya Elektron.*, **24**, 781 (1997) [*Quantum Electron.*, **27**, 761 (1997)].
5. Abdullin E.N., Bugaev S.P., Efremov A.M., Zorin V.B., Koval'chuk B.M., Kremnev V.V., Loginov S.V., Mesyats G.A., Tolkachev V.S., Shchanin P.M. *Prib. Tekhn. Eksp.*, (5), 138 (1993).

6. Tarasenko V.F., Baksht E.H., Fedenev A.V., Orlovskii V.M., Panchenko A.N., Skakun V.S., Sosnin E. *Proc. SPIE Int. Soc. Opt. Eng.*, **3343**, 715 (1998).
7. Verkhovskii V.S., Lomaev M.I., Panchenko A.N., Tarasenko V.F. *Kvantovaya Elektron.*, **22**, 9 (1995) [*Quantum Electron.*, **25**, 5 (1995)].
8. Eremenko V.N. *Titan i ego splavy* (Titanium and Its Alloys) (Kiev: Izd. Akad. Nauk USSR, 1960).