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Effect of polarised laser radiation on the oxidation of titanium films upon thermal annealing

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Abstract. The effect of laser irradiation of heated Ti films on their phase composition is studied. The exposure of Ti films to a beam of linearly polarised 1.96-eV photons during their annealing in vacuum was found to suppress the oxidation reaction.

Thermal annealing of polycrystalline thin metal films is accompanied by recrystallisation processes resulting in the transition of the film to a more equilibrium thermodynamic state [1]. However, the annealing of polycrystalline getter films in vacuum leads, as a rule, to their oxidation, which considerably hampers the use of these films for the production of microelectronics elements [2]. In recent years, photochemical processes induced in thin films by laser radiation are extensively studied [3 – 5]. This is caused by the fact that the exposure of films during their annealing to a beam of photons with a certain energy [6, 7] allows one to control the oxidation kinetics of metal films and the sequence of formation and growth of oxide phases. However, the physical aspects of structural and phase transformations taking place in this case are poorly studied.

In this paper, we study structural and phase transformations taking place in thin titanium films upon their stationary thermal treatment and simultaneous exposure to cw polarised laser radiation with photon energy 1.96 eV.

Titanium films 100 nm thick were produced by thermal deposition in vacuum (the residual pressure was $p \sim 0.3$ mPa) on a substrate, which represented a freshly cleaved NaCl single crystal, at 373 K. It is known that titanium is a good getter. Because of this, to decrease the concentration of atoms of residual gases in the films, they were deposited with a rate of the order of 100 Å s^{-1}. Before deposition, substrates were covered with a shutter. After the evaporation process (10 – 15 s after the beginning of evaporation), stabilised the shutter was opened and films of desired thickness were deposited. Preliminary evaporation of the material also favoured the improvement of vacuum and, therefore, a decrease in the concentration of impurity atoms of residual gases in the films. To separate deposited titanium films from NaCl crystals, the latter were dissolved in distilled water.

Titanium films separated from a substrate were positioned on molybdenum grids 3 mm in diameter for further study on a setup whose schematic is presented in Fig. 1.

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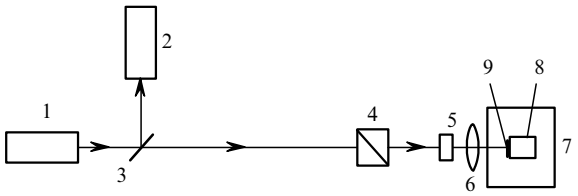

Figure 1. Schematic of the experimental setup for film treatment. (1) LGN-215 laser; (2) IMO-2 power meter; (3) semitransparent mirror; (4) Glan prism; (5) $\lambda/4$ plate; (6) focusing lens; (7) vacuum system; (8) oven for sample heating; (9) sample.

The films were thermally treated in vacuum ($p \sim 0.05$ mPa) at the temperature $T = 500$ °C during the time $\tau = 1$ and 5 s. They were exposed to radiation of an LGN-215 laser at 0.63 μm. The power of radiation focused onto a sample surface was 35 mW; the laser beam was 5 mm in diameter. The films treated in this way were studied by electron microscopy and electron diffraction techniques using a JEM-120 electron microscope. To identify electron diffraction patterns, we used the ASTM tables [8] and original papers.

Preliminarily studies showed that $T = 500$ °C and $\tau = 1$ and 5 min were of most interest from the viewpoint of studying the processes taking place in thin titanium films at a laser radiation power of 35 mW. Note that laser radiation of this power causes no increase in temperature of the sample surface being irradiated. The laser radiation power during irradiation was monitored by an IMO-2 power meter.

Irradiation was carried out before the film heating, during heating, and until the end of its complete cooling. For the purity of the experiment, we used two samples in an oven in the vacuum system. One of them was subjected only to thermal treatment, and the other was subjected to combined treatment; i.e., it was simultaneously thermally treated and exposed to cw polarised laser radiation. Parameters of thermal treatment of two samples were identical. The polarisation of laser radiation was changed by a Glan prism; circular polarisation was obtained using a $\lambda/4$ plate.

Initial films were polycrystalline and fine-graded. The average grain size was 20 – 30 nm (Fig. 2a). Our studies showed that thermal annealing of titanium films in vacuum caused their oxidation, an increase in grain size, and the appearance and growth of oxide nuclei. Electron diffraction patterns of the samples annealed at $T = 500$ °C and $\tau = 1$ min show the presence of Ti_3O_5 and Ti_2O_3 (Fig. 2b and the table). As the annealing time was increased up to 5 min, traces of Ti_3O (a solid solution of oxygen in titanium) and Ti_2O_3 (Fig. 2c and the table) appeared in electron diffraction patterns. The formation of titanium oxides is caused by the interaction of titanium with oxygen adsorbed by a film

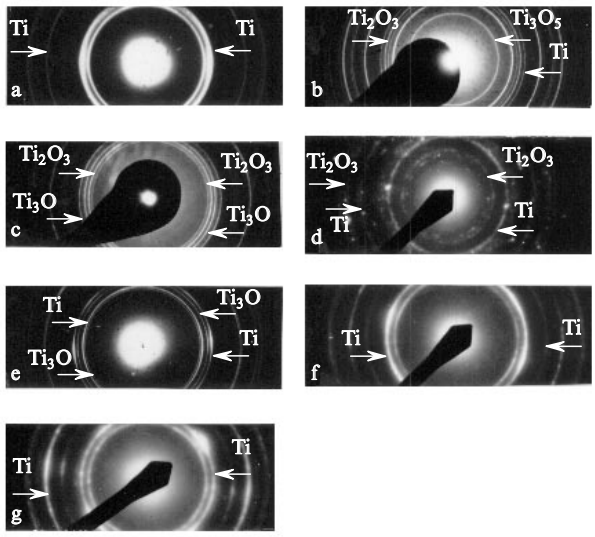

Figure 2. Electron diffraction patterns of titanium films. Initial sample (a) and samples thermally annealed at $T = 500$ °C during 1 and 5 min, respectively, without exposure to laser radiation (b, c) and upon exposure to laser radiation with circular (d, e) and linear polarisation (f, g).

Table 1. Phase composition of Ti films subjected to thermal annealing and exposure to laser radiation at 0.63 μm with different polarisations.

Interplane spacing/нм	Without laser treatment		Linear polarisation		Circular polarisation	
	1 min	5 min	1 min	5 min	1 min	5 min
0.354	Ti_3O_5	–	–	–	–	–
0.346	Ti_3O_5	–	–	–	–	–
0.271	Ti_2O_3	Ti_2O_3	–	–	Ti_2O_3	–
0.268	Ti_3O_5	–	–	–	–	–
0.257	Ti_2O_3	Ti_2O_3	–	–	Ti_2O_3	–
0.239	–	Ti_3O	–	–	–	Ti_3O
0.235	Ti	–	Ti	Ti	Ti	Ti
0.233	–	Ti_3O	–	–	–	Ti_3O
0.224	Ti	–	Ti	Ti	Ti	Ti
0.218	–	Ti_3O	–	–	–	Ti_3O
0.173	Ti	–	Ti	Ti	Ti	Ti
0.170	Ti_2O_3	Ti_2O_3	–	–	Ti_2O_3	–
0.148	–	–	Ti	Ti	Ti	Ti
0.142	–	Ti_3O	–	–	–	Ti_3O

during deposition and diffusing from the environment. The grains of oxide phases were 50 – 80 nm in size.

During deposition of getter materials, which include titanium, the residual oxygen is dissolved in the film. The dissolution process is determined by the ability of a solvent metal to ionise atoms of elements being dissolved. Cations of light elements are formed in a metal lattice when their valence electrons undergo transitions to cooperative states. During thermal annealing, oxygen atoms adsorbed by the film diffuse to the bulk of a grain and interact with titanium atoms by forming Ti_3O_5 and T_2O_3 oxides. As a result of annealing, oxygen cations are redistributed over tetrahedral pores, and an ordered solid solution of oxygen in titanium Ti_3O is formed.

Upon thermal treatment of titanium films and simultaneous exposure to circularly polarised laser radiation, there take place thermodynamic stabilisation of the film structure, migration of intergrain boundaries, recrystallisation of grains, and an increase in their size. Note that the rings observed in the electron diffraction patterns are very thin and textured. This suggests that collective recrystallisation processes occur upon thermal annealing and laser radiation, which caused an increase in the grain size. Grains, whose average size is 80 – 100 nm, are, as a rule, polygon shaped. Our studies of titanium films exposed to a circularly polarised laser beam upon stationary thermal annealing at $T = 500$ °C during 1 and 5 min showed that these films were oxidized, resulting in the formation of Ti_3O and Ti_2O_3 oxide phases (Figs 2d, 2e, and the table).

A different situation is observed in titanium films annealed under the same conditions but exposed during annealing to a linearly polarised laser beam. The corresponding electron diffraction patterns are presented in Figs 2f and 2g. The analysis of these patterns shows that they contain only the rings corresponding to titanium. Thus, upon annealing titanium film in vacuum and simultaneous exposure to a linearly polarised beam of 1.96-eV photons, oxidation processes are suppressed. This is explained by both thermal and photochemical action of radiation. At $T = 500$ °C, laser radiation initiates the oxidation suppression reaction in a film; at $T < 500$ °C, this effect is not observed.

In Ref. [9], the 'quasi-optic' theory of diffusion of light impurities in metals was developed, which shows that electromagnetic radiation, specifically polarised light, substantially affects the impurity redistribution. The exposure to polarised light leads to an anisotropic redistribution of impurities upon transition from one equilibrium state to another. It is likely that the anisotropic redistribution of oxygen over octahedral and tetrahedral pores of titanium in our case should have a substantial effect on both the oxygen diffusion and the kinetics of formation of oxide phases.

The experiments on exposure of titanium films to a beam of 1.96-eV photons showed that their phase composition substantially depends on the flux density [5, 10]. This effect was observed at sufficiently high annealing temperatures, when oxygen diffusion into titanium was rather efficient. The study of the phase composition of annealed films by the electron diffraction technique showed suppression of oxidation processes when titanium films were subjected only to linearly polarised laser radiation, whereas the films exposed to a circularly polarised laser beam in the course of thermal annealing were characterised by the formation and growth of oxide phases.

We also experimentally studied the effect of polarised laser radiation at other wavelengths on the oxidation of titanium films upon thermal annealing. In particular, we used an LG-126 ($\lambda = 1.15$ and 3.39 μm) and an LG-106M-1 ($\lambda = 0.46$ – 0.52 μm) gas lasers. In this case, no suppression of the oxidation reaction in titanium films was observed [10 – 12], and the formation and growth of titanium oxides, predominantly of Ti_3O_5 and Ti_2O_3, took place. The effect of the radiation intensity on the phase composition of titanium films was studied in [10]. The result obtained indirectly supports the statement of the quasi-optic diffusion theory concerning the anisotropic character of oxygen cation migration in the titanium matrix.

Thus, the suppression of oxidation of titanium films under thermal annealing and simultaneous exposure to a beam of photons is caused, first of all, by linearly polarised incident laser radiation.

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