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LETTER TO THE EDITOR

Effect of Laser Irradiation on the Properties of Transition Metal Oxides

F. A. Chudnovskii,*[,1] A. L. Pergament,† D. A. Schaefer,‡ and G. B. Stefanovich†

*A. F. Ioffe Physical–Technical Institute, Academy of Sciences of Russia, 194021 St. Petersburg, Russia; †Department of Solid State Physics, Petrozavodsk State University, 185640 Petrozavodsk, Russia; and ‡Towson State University, Physics Department, Towson, Maryland 21204

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It has been shown that laser irradiation can significantly modify the physical properties of transition metal oxides. A correlation between threshold energies of the laser modification and enthalpy of formation of TiO_2, To_2O_5, Nb_2O_5, and V_2O_5 has been established. Selective chemical etching of the laser-treated films was also observed. The possibility of application of the anodic vanadium oxide films as an effective optical medium for the recording of holography information has been demonstrated. © 1995 Academic Press, Inc.

Compounds (particularly oxides) of transition metals, containing atoms with unfilled *d*-shells, exhibit a number of distinct valence states. That is why they are generally subject to various chemical and structural transformations, via thermal or electrochemical treatment, electron and ion bombardment, laser irradiation, etc. In this work we report on effects of laser irradiation on properties of thin film oxides of V, Ti, Ta, and Nb.

Oxides films were obtained by electrochemical anodic oxidation in acetone- and phosphoric acid-based electrolytes, using procedures described in (1). Anodizing procedures were selected so that the thicknesses of all films were nearly the same, about 200 nm. As-prepared films were of nearly the same thickness. Such films were amorphous or, as in the case of titanium oxides, amorphour-crystalline. As a rule, they crystallize so that the metal is in (nearly) the highest valence states i.e., TiO_2, Ta_2O_5, Nb_2O_5 for Ti, Ta, and Nb, and mainly V_2O_5 for anodic films deposited on vanadium. A YAG : Nb^{3+} laser (λ = 1.06 μm, pulse duration 15 ns) was used to irradiate the oxide films. The energy of radiation E was varied from zero to 100 mJ/cm^2. Beyond a critical value of $E = E_0$, we encountered visible changes of the optical properties

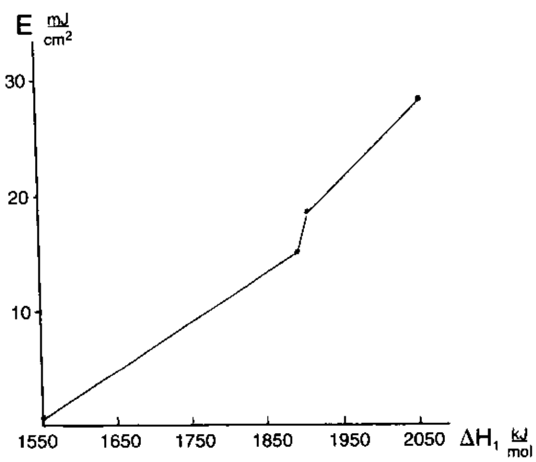

FIG. 1. Threshold energy of laser modification as a function of enthalpy of forming for different oxides. Data on ΔH from Ref. [2] were used.

in the films. The threshold energies E_0 vary considerably for different oxides: ~0.8, 15, 18, and 28 mJ/cm for oxide films of V, Ti, Nb, and Ta, respectively, which correlates with the enthalpies of formation ΔH of the corresponding oxides (Fig. 1). This ΔH characterizes the energy of chemical bonds of the oxide and, consequently, is also associated with the activation energies of the various phases and with their structural transformations. Thus, Fig. 1 suggests that laser radiation will induce some phase and/or structural changes in the transition metal oxides. X-ray measurements of vanadium oxide showed laser treatment to crystallize an initially amorphous film. Additionally, electrical switching in laser-treated films of vanadium oxide was observed after irradiation within a narrow range close to E_0. This effect differs from the usual switching in anodic vanadium oxide (1) by the absence of the previously encountered electroforming process. The switch-

[1] To whom correspondence should be addressed.

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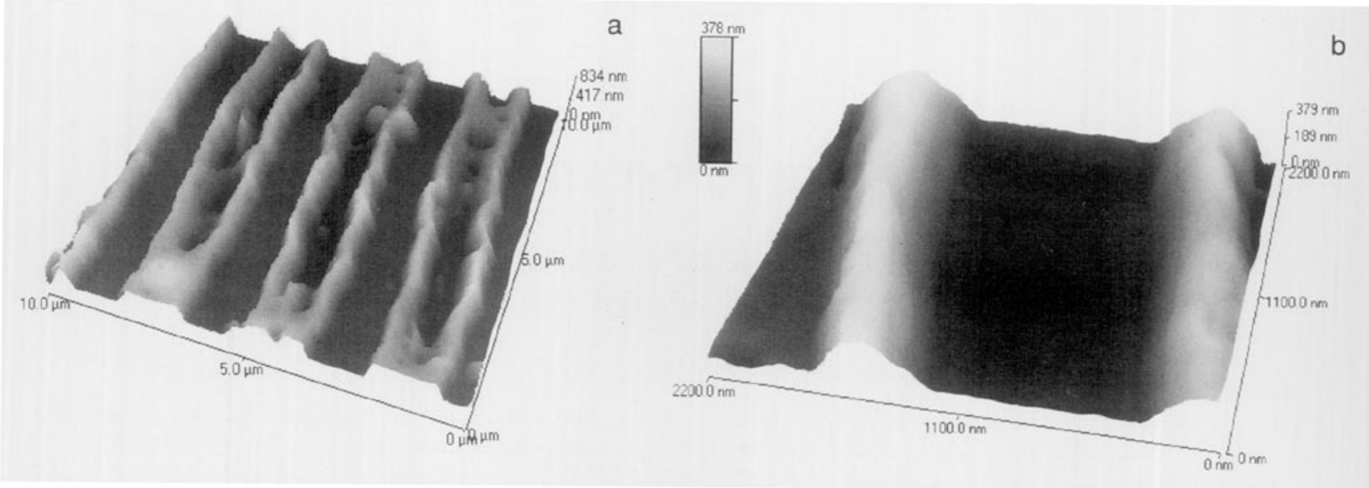

FIG. 2. Atomic force microscope image of the holographic grating with following parameters: (a) X, Y scan range, 10 μm × 10 μm; Z range, 677 nm; scan rate, 20 μm/sec; (b) X, Y scan range, 2.2 μm × 2.2 μm; Z range, 378 nm; scan rate, 8 μm/sec.

ing mechanism is linked to the metal-insulator transition near 67°C in vanadium dioxide. Therefore, the present results indicate that in some cases crystalline VO_2 is formed; i.e., there is a change of composition of the film, apart from crystallization.

Selective chemical etching of the laser-treated films was also observed. The etching of vandium oxide was carried out in 5% aqueous solution of nitric acid; that of Nb and Ta oxides was carried out in concentrated HF. The rate of dissolution of the laser-treated (crystallized) oxide film is significantly less than that of the initial anodic amorphous oxide.

The laser modification of the optical properties described above led us to consider transition metal oxides as candidate materials for various applications in optics and optoelectronics, e.g., as a medium for optical information recording. Vanadium oxide seems to be especially well suited because it requires the least energy for laser modification. An experiment which demonstrates the feasibility of hologram recording was carried out with a standard laser holographic system. Diffraction gratings were recorded on films of V and Ti oxides. The recording possibilities are made possible by crystallization of the film material in locations where the two incident laser beams exhibit constructive interference. The diffraction efficiency of the grating (determined as the intensity of incident light relative to the first diffraction maximum) on vanadium oxide is near 3%. The efficiency can be increased up to 5–10% by chemical etching of the as-prepared grating. Thus, a grating with periodic variation in optical constants or thickness can be formed.

An atomic force microscope was used to image the amorphous regions and the irradiated regions of the vanadium oxide surface. The amorphous region was found to be granular, with a mean roughness of ~8 nm. Grating regions exhibited a well defined, parallel structure (see Fig. 2a). The period for one of the samples was found to be ~1 μm (see Fig. 2b).

Thus, in this study it has been shown that laser irradiation can significantly modify the physical properties of transition metal oxides. A correlation has also been established between threshold energies of the laser modification and thermodynamic characteristics of oxides. Last, the possibility of application of the anodic vanadium oxide films as an effective medium for the holography recording has been demonstrated.

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