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Laser modification of the electrical properties of vanadium oxide thin films[♣]

G.B. STEFANOVICH[1*], A.L. PERGAMENT[1,2], F.A. CHUDNOVSKII[2], and D.O. KIKALOV[1]

[1]Department of Solid State Physics, Petrozavodsk State University,
185640 Petrozavodsk, Russia
[2]Applied Phase Transition Inc., 1758 Berkeley Str., Santa Monica, CA 90404, USA

The effect of laser irradiation on amorphous films of anodic vanadium oxide was studied using a YAG:Nd^{3+} laser at wavelength 1.06 μm. Irradiation was found to lower the electrical conductivity of the oxide films and modify significantly the parameters of electroforming and switching in metal/oxide/metal sandwich structures. The threshold energy for laser modification was measured to be ~0.3 mJ/cm^2. It is shown that the changes of the electrical properties are associated with structural (crystallization) and chemical (in particular, the reduction $V_2O_5 \to VO_2$) transformations and that non-thermal photo-stimulated effects play an important role in the laser modification of the vanadium oxide thin films.

Keywords: vanadium oxide, thin films, laser modification, electrical switching

1. Introduction

Laser-radiation control of processes in solids has received increasing attention in recent years. Laser-induced modification of properties of transition metal oxides is of particular interest, because transition metals usually exhibit multiple oxidation states and form a number of oxide phases. That is why oxides of transition metals can undergo various structural and chemical transformations under the action of different external perturbations; heat treatment, electron and ion bombardment, and laser irradiation. For example, vanadium forms more than 10 distinct oxide phases with different electronic properties, ranging from metallic to insulating; VO, V_2O_3, V_nO_{2n-1} series (n = 3 to 8), VO_2, V_2O_5. Several vanadium oxides undergo metal-insulator transitions at different temperatures [1,2]. Electrical switching due to metal-insulator transition has also been reported for planar thin-film VO_2-based structures [2].

Vanadium anodic oxide films, i.e., the films obtained by anodic oxidation of vanadium in an electrolyte, have been shown to consist of either almost pure VO_2 or a mixture of phases with a gradual decrease in the oxygen stoichiometry from V_2O_5 at the surface to lower oxides near the vanadium metal substrate [3,4]. The oxygen distribution in the films strongly depends on the oxidation conditions (electrolyte composition, current density, and oxidation time). In all cases, however, near the outer boundary, there exists a layer which is close to the V_2O_5 stoichiometry [4].

In Ref. 3 we have reported on laser modification of the optical properties of anodic oxide films on transition-metals (V, Ti, Ta, Nb). Vanadium oxide was found to require extremely low energy for laser modification (~1 mJ/cm^2) and the possibility to apply these films as effective media for optical information recording was demonstrated [5].

In this paper we report the results on the laser-induced modifications of the electrical properties (d.c. conductivity and voltage-current characteristics in sandwich structures, switching effect) of anodic oxide films on vanadium.

2. Experimental

Samples under study were prepared by oxidation of vanadium metal layers obtained by vacuum deposition onto glass-ceramic substrates. Anodic oxidation

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[*] e-mail: gstef@mainpgu.karelia.ru

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was carried out under voltstatic conditions in the acetone-based electrolyte containing benzoic acid and saturated aqueous solution of sodium tetraborate [3]. The thickness of the oxide films was d ≈ 100 nm. Laser irradiation was performed using a Q-switched YAG:Nd^{3+} laser operated at wavelength 1.06 µm with 15 ns pulse duration. The energy of radiation, E, was varied from zero to 10 mJ/cm^2.

The sandwich structures for the electrical transport properties measurements were fabricated on the basis of both the initial anodic oxide films and those exposed to laser radiation at different energies. Aluminium electrodes were evaporated onto the surfaces of oxide films to complete the metal-oxide-metal (MOM) structure. The spring-loaded point contacts, gilded wires, were also used in some cases. Electrical properties of these MOM structures (conductivity and V–I characteristics, parameters of electroforming and switching) were studied using previously described techniques [6].

3. Results and discussion

As-fabricated MOM structures are initially in a high resistance state. The voltage-current characteristics are non-linear, and the resistance in the ohmic (low-voltage) region, measured with the point contact, is in the range $10^7 - 10^8\ \Omega$ (Fig. 1).

When the applied voltage reaches a certain magnitude, V_f , a sharp and irreversible increase in conductivity is observed and the I(V) curve becomes S-shaped. This electroforming process results in growth of the channel, consisting of vanadium dioxide [6], through the film from one electrode to another. The S-shaped voltage-current characteristic is completely reversible. The switching mechanism in the structures based on vanadium anodic oxide has been shown to be caused by the insulator-to-metal transition in the VO_2-channel [6].

The voltage-current characteristic for the electroformed MOM structure is shown in Fig. 2. The switching parameters (threshold voltage V_{th}, off-state resistance R_{off}, and other) vary by up to an order of magnitude for different structures. Such a wide range of variation of the V_{th} and R_{off} values leads to the conclusion that resistance and threshold parameters are mainly determined by the forming process. Conditions of electroforming cannot be unified in principle, because its first stage is associated with conventional electrical breakdown of the surface V_2O_5 dielectric layer. The phenomenon of electrical breakdown is statistical in nature, and statistical character of the

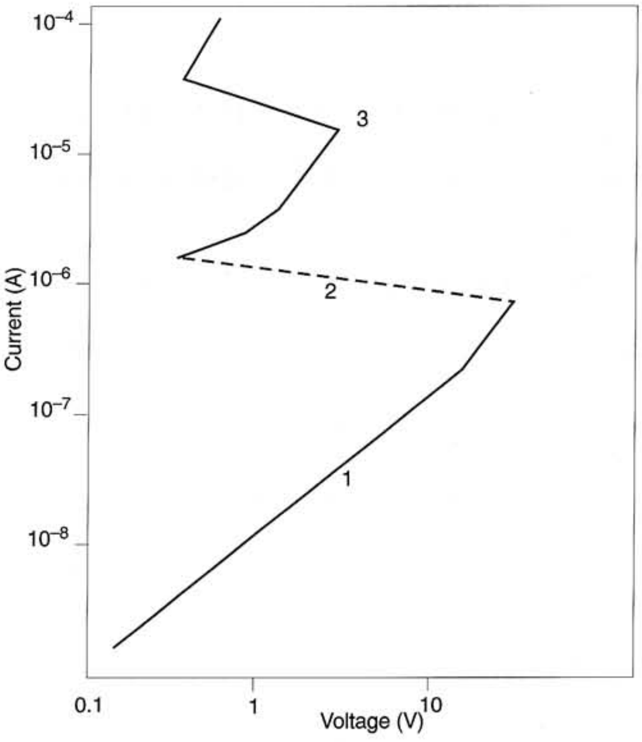

Fig. 1. Voltage-current characteristic of the initial MOM structure (1); electroforming (2); and V–I characteristic after forming (3).

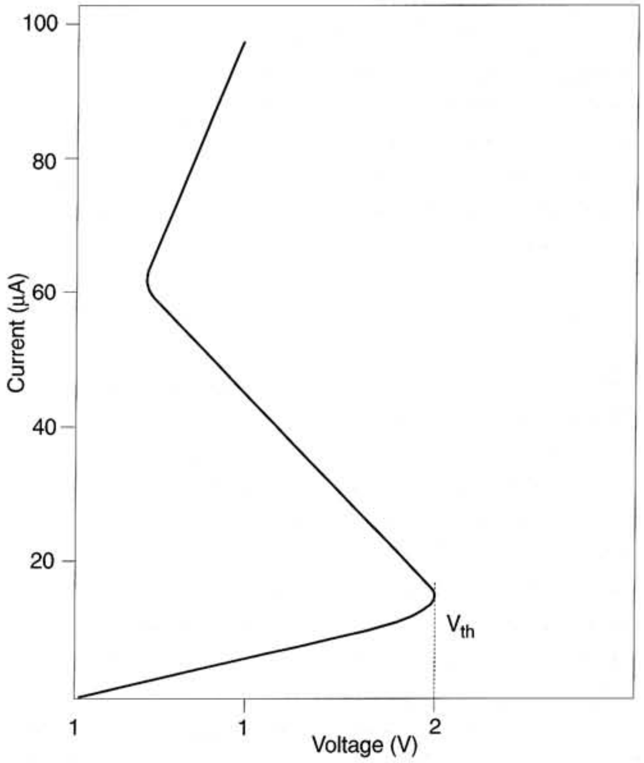

Fig. 2. S-shaped V–I characteristic of the electroformed MOM structure with anodic oxide film on vanadium (region 3 in Fig. 1).

electroforming process shows itself as a spread in the observed forming voltages. As a result, the diameter and precise phase composition of the ensuing channel (and, consequently, its effective specific conductivity) vary with position in the sample and for different samples. This accounts for the scatter in the R_{off} and threshold parameters of the electroformed devices.

Laser irradiation of the oxide films results in a change of their electrical conductivity. The beginning of the laser modification occurs at energy density of about 0.2 – 0.3 mJ/cm^2. For E = 0.6 mJ/cm^2, the resistance decreases by approximately an order of magnitude, and at higher energies it falls abruptly. The mean value of V_f also decreases with increasing radiation energy and tends to zero at $E \approx 1.5$ mJ/cm^2 (Fig. 3). It is important to note that in the case of laser treatment (or "laser forming", unlike the above described electroforming) the parameters of the MOM structures are characterized by the absence of the scatter, i.e., the V–I characteristics of all structures are almost identical.

With X-ray diffraction analysis it was determined that as-prepared oxide films were amorphous, and laser treatment resulted in the crystallization of an initially amorphous film. Analogous transformations were observed after thermal annealing of the anodic oxide films on vanadium. However, unlike conventional heat-induced crystallization, in the case of laser modification, the mechanism of the change is obviously non-thermal, what is supported by simple calculations. Maximum temperature, T_{max}, without taking into account energy losses from reflection and heat dissipation into the substrate, is given by the heat balance equation:

$$\Delta T = E/c\rho d, \qquad (1)$$

where c = 0.7 J/gK and $\rho = 3.4$ g/cm^3 are, respectively, heat capacity and density of V_2O_5 [7]. For E = 1 mJ/cm^2 and d = 100 nm, heating over room temperature is $\Delta T = 42$ K and $T_{max} \approx 60$°C. In reality, the temperature is even much less and it is evidently insufficient for thermal crystallization. Note that for other oxide phases, e.g., for VO_2 instead of V_2O_5, the calculations from equation (1) yield qualitatively the same result: T_{max} is much less than the equilibrium temperature of recrystallization.

Also, it should be emphasized that in the laser-treated samples (with E > 1.5 mJ/cm^2), the switching effect is observed without any preliminary electroforming. The voltage-current characteristics of the irradiated samples are S-shaped (similar to that presented in Fig. 2) and, as the temperature increases, the switching voltage V_{th} decreases, tending to zero at a certain temperature T_t (Fig. 4). The value of T_t was found to coincide with the critical temperature of the metal-insulator transition in VO_2, ~70°C [1,2]. This indicates that, apart from crystallization, laser irradiation results in a change of composition of the films, namely in formation of the vanadium dioxide phase. The mechanism for VO_2 formation is apparently the reduction of the surface layer consisting of higher oxides. The reduction of polycrystalline V_2O_5 to VO_2 in air has been studied also using a relaxation-oscillating ruby laser [8]. However, in that case the energy was about 10^4 mJ/cm^2 and the process therefore has been

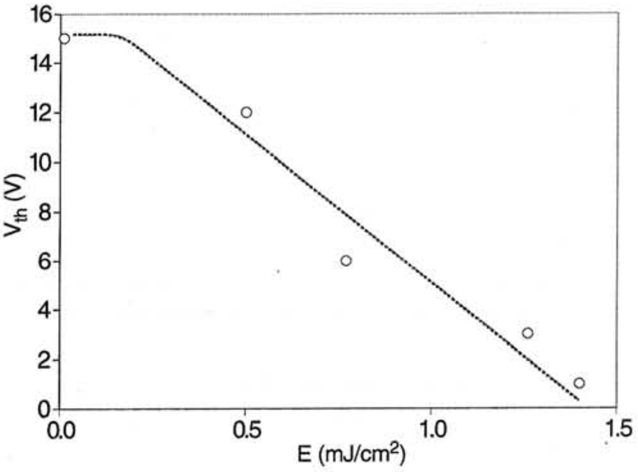

Fig. 3. Dependence of forming voltage on laser radiation energy; for the initial sample (E = 0), $V_f \approx 15$ V.

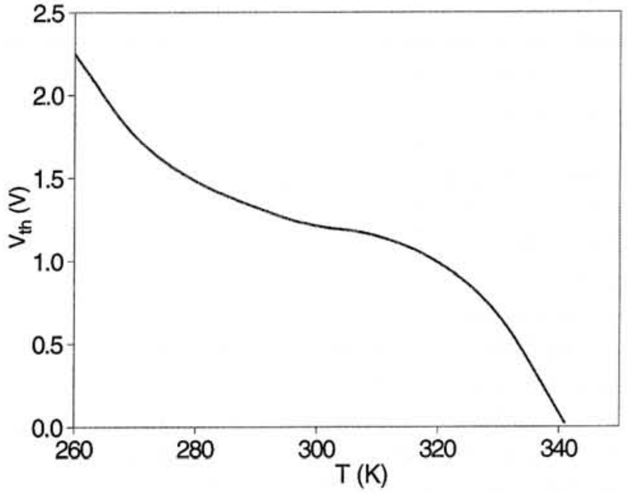

Fig. 4. Threshold voltage for the MOM structure on the basis of vanadium oxide film exposed to laser radiation with E = 1.46 mJ/cm^2.

considered to be pure thermal. Further studies seem to be required to clarify a physical mechanism of laser-induced processes of crystallization and chemical (oxidation-reduction) transformations in amorphous anodic vanadium oxide. Nevertheless, the above calculations provide firm support for the proposal that non-thermal photo-stimulated effects do play an important role in the laser modification of this material. A mechanism for laser-induced modification of vanadium oxide films appears to include a complex of processes, involving, particularly, generation of a high density electron-hole plasma. This type of recrystallization mechanism has been proposed, for example, in the interpretation of experiments on laser annealing of amorphous silicon [9].

4. Conclusions

The results presented above indicate that laser irradiation modifies significantly the electrical properties of vanadium anodic oxide. The threshold energy for laser modification has been measured to be ~0.3 mJ/cm^2. This value is consistent with the previously reported data for laser modification of the optical properties (0.8 mJ/cm^2 for vanadium anodic oxide films with d = 200 nm) [3,5]. As the radiation energy increases, the resistance and forming voltage decrease, and the latter tends to zero at $E \approx 1.5$ mJ/cm^2. For the MOM structures based on vanadium oxide films exposed to laser radiation with energies beyond this value, the switching effect occurs without preliminary electroforming. These modifications are associated with the laser-induced crystallisation accompanied by chemical transformations (in particular, formation of VO_2) in the oxide films. Amorphous vanadium oxide was found to possess high sensitivity (~1 mJ/cm$_2$) in comparison with other materials, such as, e.g., crystalline vanadium pentoxide (~10^4 mJ/cm^2 for reduction [8]) or glassy carbon (~300 mJ/cm^2 for crystallization) [10].

Finally, the switching effect with current—controlled negative resistance has obviously potential applications in electronics. The process of "laser forming" can prove to be useful in technical applications, because, unlike electroforming, it ensures the stable and reproducible parameters of the switching devices.

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