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Metal-insulator phase transition in thin films of vanadium dioxide with aluminum impurity

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The paper established that addition of aluminum impurity into vanadium dioxide with oxygen deficiency will not result in formation of insulator phase M2. Doping in this case is accompanied with reduction of temperature of R-phase transition to M1 phase and reduction in the electroconductivity jump that accompanies this phase transition. To explain the temperature dependence of insulator M1-phase electroconductivity, the hopping conductivity model was applied, taking into account the impact of thermal oscillations of atoms at the resonance integral.

Keywords: phase transition, electroconductivity, doping, polaron.

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1. Introduction

Interest in vanadium dioxide VO_2 is related, first of all, to the fact that in single crystals of this compound when cooled below temperature $T_C = 340\,\mathrm{K}$, structural phase transition takes place from tetragonal R-phase to monoclinic M1-phase [1–3]. This transition is accompanied by sharp (by 4−5 orders) reduction of electroconductivity and is characterized by metal-insulator transition (MIT). Optical parameters of vanadium dioxide also vary in a hopping manner below T_C. Phase transition is of martensite nature and is accompanied by occurrence of elastic mechanical stresses, which cause damage of macroscopic specimens. Therefore, only nanocrystals and thin films VO_2 are suitable for practical applications. For the latter it is shown that in non-equilibrium conditions the phase transition of M1 phase to R phase takes place for the time of around 100 fc [4]. Since the phase transition is of martensite nature, temperature dependences of electrical and optical parameters in the vicinities of T_C look like a hysteresis loop.

Strong effect at the temperature position of the hysteresis loop is provided by addition of non-valent cation impurities into the structure of vanadium dioxide [5–9]. Addition of such donor impurities as W^{6+} results in reduction of phase transition temperature [1,5]. On the opposite, addition of acceptor impurities, such as Cr^{3+} or Al^{3+} increases T_C [1,6]. In this case instead of insulator phase M1, where all V^{4+} ions are paired, insulator phase M2 is formed, where only half of vanadium ions is paired, whereas the other half at MIT only shifts from the center of oxygen octahedrons. It should be noted that formation of M2-phase is also observed in pure single crystals VO_2 that were exposed to uniaxial mechanical stresses [10,11]. Reduction of T_C is caused by oxygen deficiency in vanadium dioxide [1,2]. The proposed paper considers the impact of aluminum impurity at MIT in thin films of vanadium dioxide with oxygen deficiency.

2. Experiment

Vanadium dioxide polycrystalline thin films of $V_{1-x}Al_xO_2$ were synthesized by simultaneous laser sputtering from metallic V (99.9 %) and metallic Al (99.9 %) in an oxygen atmosphere at 700−900 K. To produce the films of vanadium dioxide with oxygen deficiency, the pressure of the latter in the working volume in process of synthesis was reduced compared to the standard one. The degree of doping (x) was judged from the relative evaporation time of each target. Al_2O_3 (1000) and Si(100) were used as substrates. The film thickness was 100 nm. The phase transition in the samples under study was monitored by the change in the electrical conductivity of the films measured by the standard four-probe technique. Raman scattering spectra were recorded at room temperature at micro-Raman spectrograph HORIBA JY MRS 320 with spectral resolution above $3\,\mathrm{cm}^{-1}$.

3. Results and discussion

Figure 1 presents the temperature dependences of the electric conductivity in the studied films. Compared to MIT temperature in thin films of pure stoichiometric dioxide, this temperature is lower approximately by 2 K in the studied undoped films. Such DMT temperature shift, according to [1] is compliant with the composition of $VO_{1.998}$ films. Addition of aluminum impurity causes reduction in phase transition temperature and lower jump in electroconductivty that accompanies it. These effects increase as the aluminum

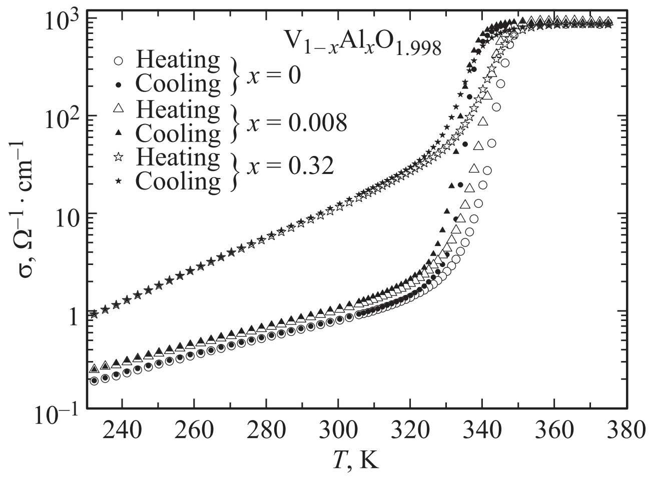

Figure 1. Temperature dependences of the electrical conductivity of $V_{1-x}Al_xO_{1.998}$ films with varying aluminum concentration.

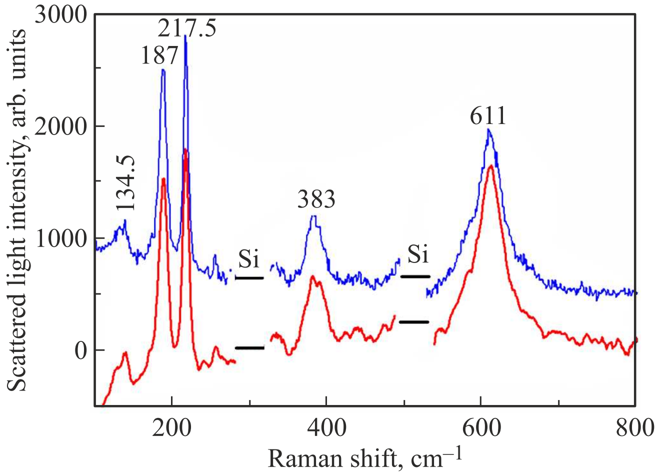

Figure 2. Raman scattering spectra of $V_{1-x}Al_xO_{1.998}$ films. Lower curve — pure vanadium dioxide ($x = 0$). Upper curve — doped vanadium dioxide ($x = 3.2$).

concentration increases in the thin film. The obtained result is radically different from what was obtained for the stoichiometric vanadium dioxide. In [12] they studied in detail the phase diagram of VO_2-Al system and showed that addition of aluminum into vanadium dioxide causes growth of MIT temperature and appearance of M2 phase instead of M1 phase.

Raman scattering spectra (Figure 2) showed that in our case only M1 phase exists at room temperature. This is indicated by the fact that spectrum lines specific for this phase (for example, line $611\,cm^{-1}$) will not shift when the aluminum impurity is introduced. In [6,12] they show that instead of this line, when M2 phase is formed, line $630\,cm^{-1}$ appears.

In case of stoichiometric vanadium dioxide, the reaction that accompanies introduction of aluminum into the crystalline structure in the Kroeger–Wink symbols may be recorded as:

$$\mathrm{Al_V^{\bullet}} + \mathrm{V_V^x} \rightleftarrows \mathrm{Al_V^x} + \mathrm{V_V^{\bullet}}$$

i.e. substitution of vanadium ion with aluminum ion in the cation sublattice causes appearance of V^{5+} ion therein ($\mathrm{V_V^{\bullet}}$ — in the Kroeger–Wink symbols).

In case of oxygen deficiency in vanadium dioxide, i.e. if oxygen vacancies are present in the structure, the most probable is the reaction

$$\mathrm{Al_V^{\bullet}} + V_{\mathrm{O}}^{\mathrm{x}} \rightleftarrows \mathrm{Al_V^x} + V_{\mathrm{O}}^{\bullet},$$

where $V_{\mathrm{O}}^{\mathrm{x}}$ — neutral oxygen vacancy.

I.e., in this case the effect of vanadium substitution with aluminum is appearance of first once-, and then twice-ionized oxygen vacancies ($V_{\mathrm{O}}^{\bullet}$ and $V_{\mathrm{O}}^{\bullet\bullet}$ — in the Kroeger–Wink symbols).

It is well-known that stresses of uniform compression increase the MIT temperature in pure vanadium dioxide [1]. In stoichiometric VO_2 with Al the compression stresses occur not only around the aluminum ions, but additionally around ions of pentavalent vanadium. In our case of thin films of vanadium dioxide with oxygen deficiency, instead of these additional compression stresses, elastic extension stresses arise, which are related to the appearance of charged oxygen vacancies. The total stress is seemingly insufficient to form M2 phase in the nonstoichiometric films. It is necessary to note that as it is shown in [13], increase of acceptor impurity concentration causes increase of oxygen vacancies concentration.

As the degree of vanadium dioxide doping with aluminum increases, the electroconductivity σ of oxide insulator phase increases, and the value of the electroconductivity jump decreases (Figure 1). The metal phase electroconductivity value at the same time does not change. Electroconductivity of metal phase of pure $VO_{1.998}$ is equal to $\sigma_{\mathrm{m}} \sim 10^3\,\Omega^{-1} \cdot cm^{-1}$, which is close to Mott's limit for the minimum metal conductivity [14], however, the nature of $\sigma(T)$ is not metal. This is apparently due to Anderson localization at defects and grain boundaries (polycrystalline films). In single crystals $\sigma_{\mathrm{m}} \sim 10^4\,\Omega^{-1} \cdot cm^{-1}$ the conductivity is of metal nature as well [2].

Figure 3, *a*, *b* accordingly shows dependences $\sigma(T)$ in the MIT region when heating and cooling thin films of pure $VO_{1.998}$ and $V_{1-x}Al_xO_{1.998}$ ($x = 0.008$, 0.032). The temperature range of MIT in doped thin films shifts slightly towards lower temperatures and broadens with increasing aluminum concentration against the background of a decreasing jump in electroconductivity $\Delta\sigma$. Broadening of the temperature region of phases coexistence can be caused by the gradual transformation of the first-order phase transition into a second-order transitiondue to diffusion of the metal-insulator phase boundary.

The results of measuring the electrical conductivity of pure and aluminum-doped $VO_{1.998}$ upon cooling to a temperature of $T = 230$ K are shown in Figure 1. You can see that the dependence of $\sigma(T)$ in the insulator phase is linear in the coordinates $\lg(\sigma)$ on T. Previously, we

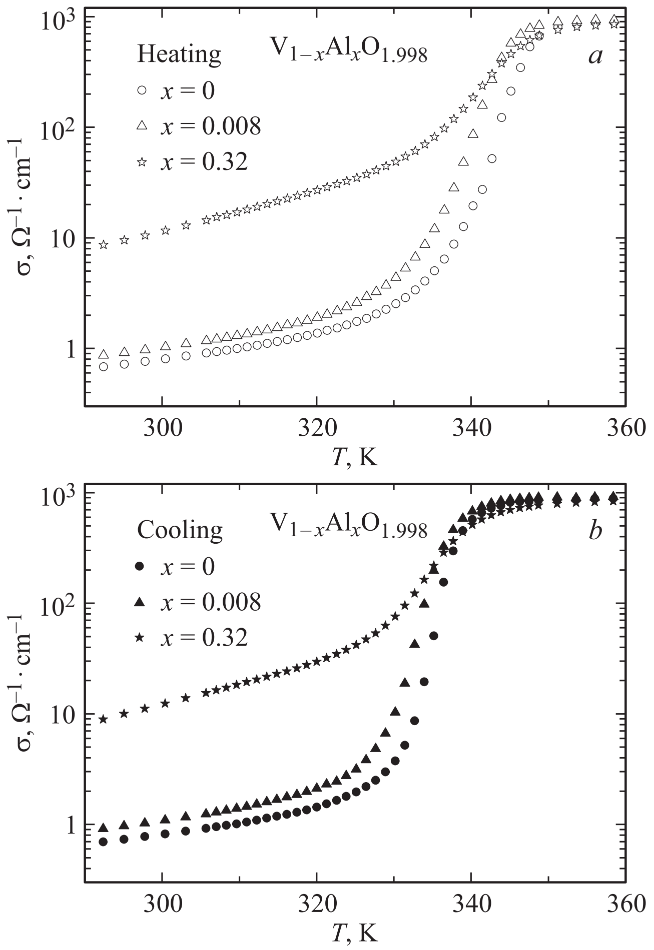

Figure 3. Temperature dependences of the electroconductivity of pure and aluminum-doped $VO_{1.998}$ in the phase transition region: (*a*) — obtained by heating; (*b*) — obtained by cooling.

studied the electrical conductivity of vanadium dioxide and showed that its conductivity is described by small-radius polaron hops, which are affected by thermal vibrations of the lattice [2]. Since the mechanism of charge transfer in the insulator phase should not change when vanadium dioxide is doped, it is appropriate to consider the electrical conductivity $V_{1-x}Al_xO_{1.998}$ within the framework of the Bryskin model [15]. This model takes into account the effect of thermal displacement of lattice atoms on the probability of interstitial jumps of small polarons. Displacements of atoms lead to changes in the overlap of the wave functions of states at neighboring nodes. This overlap defines the resonance integral (I). In the first approximation I changes with the distance (R) at which the jump occurs, as $\exp(-\alpha R)$, where α^{-1} is the effective localization radius. In turn, the hopping mobility of the charge carrier, which determines the electrical conductivity of vanadium dioxide, is proportional to I^2. For small values α^{-1}, on the order of the lattice oscillation amplitude (ρ), it can be assumed that I^2 should depend linearly on ρ. Therefore, if I^2 depends on ρ, it is permissible to replace I^2 by $\langle I^2\rangle$, where the angle brackets denote phonon averaging in terms of the renormalization of the Debye-Waller factor.

$$\langle I^2\rangle = I^2 \exp(2\alpha^2\langle\rho^2\rangle), \tag{1}$$

where $\langle\rho^2\rangle$ is the rms thermal displacement of atoms at lattice nodes. The calculation of the hopping conductivity in the model of small-radius polarons, taking into account the effect of thermal vibrations of the lattice on the resonance integral, leads to the following dependence of the electrical conductivity on temperature:

$$\sigma = en\,\frac{ea^2}{2h}\,\frac{\pi^{1/2}I^2}{E_a^{1/2}(k_BT)^{3/2}}\,\exp\{-E_a/k_BT + k_BT/\varepsilon\} \tag{2}$$

where a is lattice constant, E_a is energy required for electron hopping, n is concentration of charge carriers, e is electron charge, h is Planck's constant, ε is a quantity having the dimension of energy and taking into account the effect of thermal vibrations of the lattice on the resonant integral. In the region of high temperatures, when $2k_BT > \hbar\omega_q$ (where $\hbar = h/2\pi$, ω_q — frequency of optical phonon), ε is related to rms thermal displacement $\langle\rho^2\rangle$ with the following ratio:

$$\varepsilon = k_BT/2\alpha^2\langle\rho^2\rangle \tag{3}$$

An analysis of expression (2) shows that at low temperatures the second term under the exponent becomes negligibly small compared to the first one, while at high temperatures the second term already dominates. Therefore, in the low-temperature limit, expression (2) can be represented as

$$\ln(\sigma T^{3/2}) = A - E_a/k_BT, \tag{4}$$

where A and E_a do not depend on temperature.

On the contrary, in the high-temperature limit, expression (2) can be represented as

$$\ln(\sigma T^{3/2}) = A + k_BT/\varepsilon, \tag{5}$$

where A and ε do not depend on temperature.

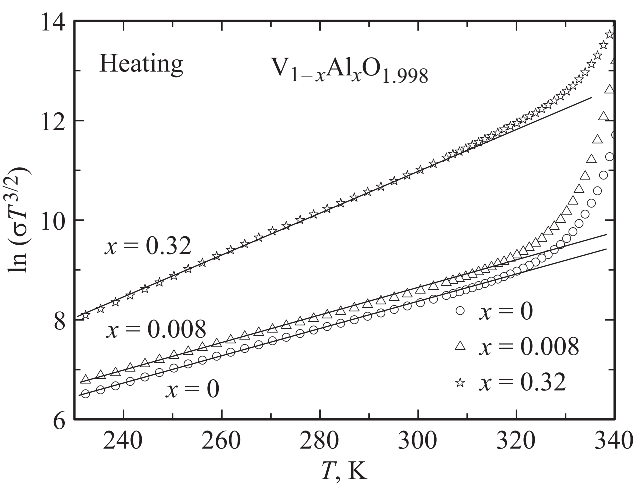

Figure 4. Dependence $\ln(\sigma T^{3/2}) = A + k_BT/\varepsilon$ of films $V_{1-x}Al{-}xO_{1.998}$ with different concentration of aluminum.

In [2] we showed that $\sigma(T)$ VO_2 at temperatures above $T \sim 240$ K can be described by the dependence (5). These are dependences for pure $VO_{1.998}$ and $V_{1-x}Al_xO_{1.998}$ ($x = 0.008$ and 0.032) shown in Figure 4. From comparison of pure $VO_{1.998}$ and doped $V_{1-x}Al_xO_{1.998}$ you can see that the inclination of the straight line equal to ε^{-1}, under weak doping ($x = 0.008$) practically does not change compared to the inclination in pure $VO_{1.998}$. At higher quantity of doping impurity ($x = 3.2$) this inclination grows. Value ε for pure $VO_{1.998}$ is equal to $\varepsilon = 3.2 \cdot 10^{-3}$ eV, and for doped specimens $V_{1-x}Al_xO_{1.998}$ ($x = 0.032$) $\varepsilon = 2.04 \cdot 10^{-3}$ eV. It follows from (1) and (3) that the value ε is proportional to the time of small polaron tunneling through the barrier between neighboring nodes. In other words, the greater the mobility of the polaron, the smaller the ε value. It follows from our data that when vanadium dioxide is doped with high quantity of aluminum, ε decreases, and this can be interpreted as a decrease in the charge carrier localization at the node.

4. Conclusion

It is shown that vanadium dioxide doping with aluminum leads to a significant change in the temperature dependence of the electroconductivity of $V_{1-x}Al_xO_{1.998}$ compared to pure $VO_{1.998}$. It has been suggested that additional diffusion of the MIT region with an increase in the degree of doping of thin films $VO_{1.998}$ may be a consequence of diffusion of the R$-$M1. phase boundary. The electroconductivity of the insulator phase $V_{1-x}Al_xO_{1.998}$ is well described by the small polaron model, which takes into account the effect of lattice atoms thermal vibrations on the resonance integral. The characteristic parameter of the model ε is determined for pure and indium-doped $VO_{1.998}$.

Conflict of interest

The authors declare no conflict of interest.

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