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Metal–insulator phase transition in thin films of vanadium dioxide with zirconium impurity

© V.N. Andreev, V.A. Klimov

Ioffe Institute,
St. Petersburg, Russia
E-mail: vn.andreev.solid@mail.ioffe.ru

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It was found that doping of thin polycrystalline films of vanadium dioxide with zirconium was accompanied by a lower temperature of transition of the metallic R-phase to the insulator M_1 phase. The electrical conductivity hopping caused by the phase transition declines with the growth of zirconium concentration. To explain the temperature dependence of electroconductivity of insulator M_1-phase, a 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

In vanadium dioxide single crystals VO_2, when cooled below $T_C = 340$ K, a structural phase transition occurs from the tetragonal R-phase to the monoclinic M_1-phase [1–3]. This transition is accompanied by a drastic (by 4–5 orders) reduction of electroconductivity and is characterized by a 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. Unlike the latter, MIT in thin films VO_2 is not accompanied by their destruction. Moreover, for the thin films it is shown that in non-equilibrium conditions the transition of M_1-phase into R-phase takes place around 100 fc [4]. This allows using the thin films of VO_2 in laser power limiters [5]. 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 on the temperature position of the hysteresis loop is provided by addition of non-valent cation impurities into the structure of vanadium dioxide. Addition of such donor impurities as W^{6+} results in reduction of phase transition temperature [1,6,7]. On the opposite, addition of acceptor impurities, such as Cr^{3+} or Al^{3+} rises T_C [1,8–10]. In the latter case instead of insulator phase M_1, where all ions $V^{4+}$are paired, the insulator phase M_2 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 M_2-phase is also observed in pure single crystals of VO_2 that were exposed to uniaxial mechanical stresses [11,12]. Higher values of T_C can also be explained by a uniform compression of vanadium dioxide [1]. The effect of doping with isovalent, i. e., tetravalent cationic impurities on MIT in vanadium dioxide is significantly understudied. The proposed paper considers the impact of zirconium impurity on MIT in thin films of vanadium dioxide with oxygen deficiency.

2. Experiment

Thin films of vanadium dioxide $V_{1-x}Zr_xO_2$ were synthesized by simultaneous laser sputtering from metallic V (99.9 %) and metallic Zr (99.9 %) in an oxygen atmosphere at 700–900 K. The degree of doping was judged from the relative evaporation time of each of the targets. Al_2O_3 (0001) were used as substrates. The film thickness was 100 nm. The phase transition in the studied specimens was monitored by the change in the electrical conductivity of the films measured by the standard four-probe technique.

3. Results and discussion

The temperature dependences of the electrical conductivity of thin films of pure and zirconium-doped vanadium dioxide are shown in Figure 1. It can be seen from the Figure that as the impurity concentration rises, the temperature of MIT shifts towards low temperatures. At low concentrations of Zr (up to 2 %), the parameters of MIT change slightly. The transition temperature is shifted approximately by 3 K. As in pure VO_2, the electrical conductivity jump in doped specimens is approximately three orders of magnitude, and the hysteresis width remains equal to 8 K. The introduction of an isovalent impurity into the structure of vanadium dioxide is not accompanied by the formation of electronic defects.

Thus the introduction of Zr^{4+} doesn't lead to appearance in VO_2 structure the ions V^{3+} or V^{5+}. Lower T_C in this case is associated with the difference of ionic radii V^{4+} and Zr^{4+}.

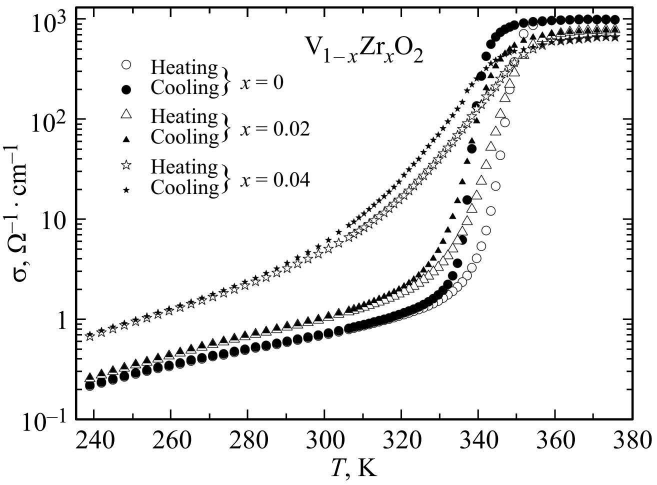

Figure 1. Temperature dependences of the electrical conductivity of thin films of $V_{1-x}Zr_xO_2$ with variation of zirconium concentration.

According to [13], the effective ionic radii V^{4+} and Zr^{4+} make 0.58 Å and 0.72 Å respectively. Thus, the introduction of zirconium impurity causes the appearance of elastic tensile stresses, which leads to a decreased T_C. With a further increase in the zirconium concentration, the MIT begins to deteriorate, which manifests itself in a significant decrease in the electrical conductivity jump and a broadening of the transition region. Apparently, this is due to the weakening of the phase transition of the first kind and its gradual transformation into a transition of the second kind due to smearing of phase boundaries.

Figure 2, *a, b* accordingly illustrates the dependencies $\sigma(T)$ in MIT region during heating and cooling for the pure VO_2 and $V_{1-x}Zr_xO_2$ ($x = 0.02$, 0.04). Electroconductivity in the metallic phase σ_m for the given specimens make $\sim 10^3 \Omega^{-1}cm^{-1}$, which is close to Mott's limit for the minimum metal conductivity [14], however, the nature of $\sigma(T)$ is not metal. This is probably due to Anderson localization caused by heterogeneities in the grain composition and defects in the grain boundaries (polycrystalline films). Note that in single crystals σ_m is of the order of $10^4\,\Omega^{-1}cm^{-1}$ and has a metallic nature [2]. The phase transition in a polycrystalline film differs from a single crystal not only in the magnitude of the jump σ, but also in the shape of the temperature dependence of the transition. When cooling single crystals, MIT proceeds as a hopping in the temperature range of about 0.1 K. This is due to the fact that the formation of martensitic domains of R-phase is carried out by an avalanche-like transition throughout the entire volume of the specimen. In this case the hysteresis width is close to 3 K. In a polycrystalline film, the martensitic transition occurs independently across each grain, and it is strongly influenced by the presence of a substrate [15,16] and elastic intergranular interaction. Therefore, the temperature range ΔT where MIT occurs is stretched approximately by 50 K, and hysteresis width makes around 8 K. It should be stressed that the phase transition in vanadium dioxide is initiated by the appearance of a covalent bond between neighboring vanadium ions located in the center of oxygen octahedra. Maximal vanadium valence makes +5. Four of these valence electrons are involved in the formation of bonds with oxygen ions. The fifth electron is highly likely to participate in the metallic conductivity of the tetragonal R-phase. The maximum valence of zirconium is +4, therefore, the replacement of vanadium ions with zirconium ions reduces the concentration of free electrons in R-phase. On the one hand, this reduces the electrical conductivity of the tetragonal phase in doped films, and on the other hand, it prevents the formation of a mature covalent bond between metal ions. As a result, the MIT region in doped thin films is additionally shifted towards low temperatures.

Based on the measured electrical conductivity of pure and zirconium-doped VO_2 when cooled to a temperature of $T = 240$ K, shown in Figure 1, it can be seen that $\lg(\sigma)$ versus T in the insulator phase is linear. Previously, we studied the electrical conductivity of vanadium dioxide and

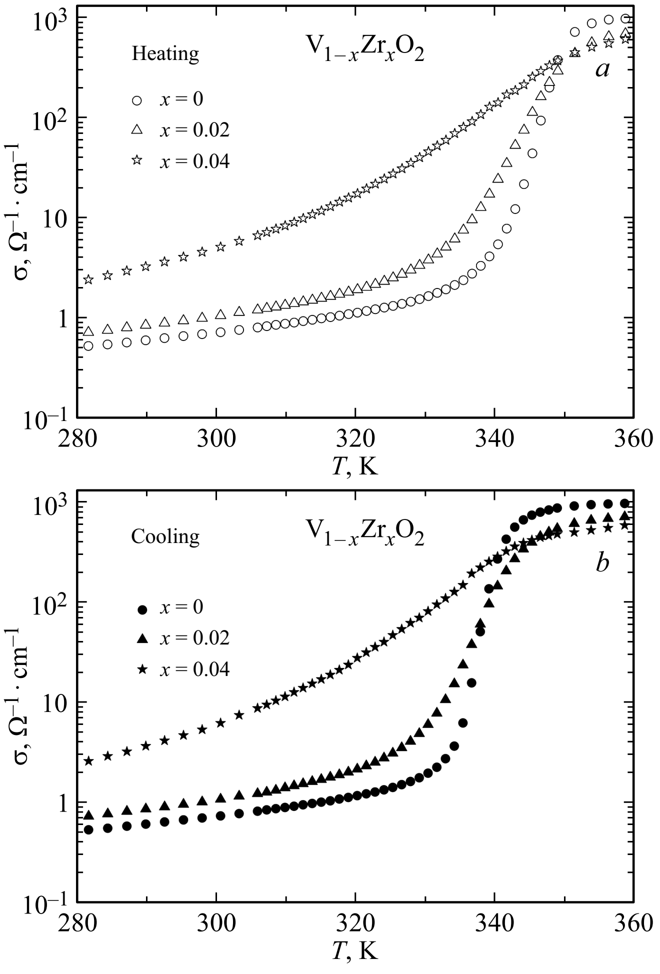

Figure 2. Temperature dependences of the electrical conductivity of thin films of pure and zirconium-doped VO_2 in the phase transition region obtained by heating (*a*) and cooling (*b*).

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 of $V_{1-x}Zr_xO_2$ within Bryskin model [17]. This model takes into account the effect of thermal displacement of lattice atoms on the probability of interstitial flips of small polarons. Atomic displacements lead to changes in the overlap of the wave functions of states at neighboring sites. This overlap defines the resonance integral I. In the first approximation I changes with the distance R at which the flip 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}, around the amplitude of the lattice vibrations ρ, it can be assumed that I^2 should depend linearly on ρ. Therefore, when 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:

$$\langle I^2\rangle = I^2\exp(2\alpha^2\langle\rho^2\rangle), \quad (1)$$

where $\langle\rho^2\rangle$ — is the rms thermal atomic displacement in the lattice sites. From the calculated hopping conductivity in the model of small-radius polarons, taking into account the effect of thermal vibrations of the lattice on the resonance integral, we may find the following dependence of the electrical conductivity on temperature:

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

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

$$\varepsilon = k_BT/2\alpha^2\langle\rho^2\rangle. \quad (3)$$

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 written as

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

where A and E_a do not depend on temperature.

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

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

where A and ε do not depend on temperature.

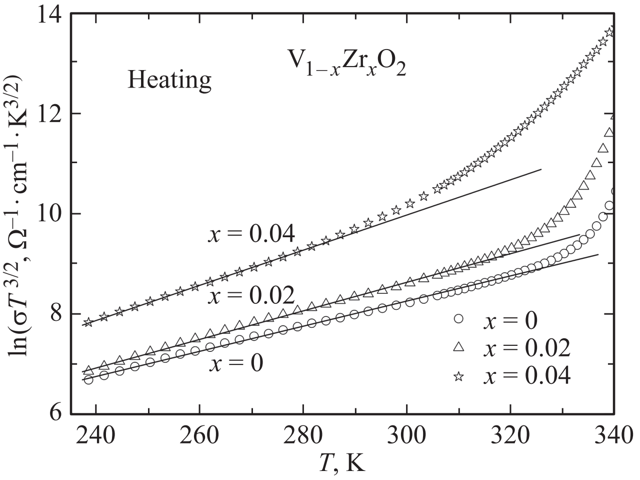

Figure 3. Dependence $\ln(\sigma T^{3/2}) = A + k_BT/\varepsilon$ of thin films of $V_{1-x}Zr_xO_2$ with different concentration of zirconium.

In [2] we showed that $\sigma(T)$ VO_2 at temperatures above $T \approx 240$ K can be described by the dependence (5). Temperature dependencies $\ln(\sigma T^{3/2})$ for the pure VO_2 and $V_{1-x}Zr_xO_2$ ($x = 0.02$, 0.04) are given in Figure 3. By comparing pure VO_2 and doped $V_{1-x}Zr_xO_2$, we may see that the slope of a straight line equal ε^{-1} in conditions of weak doping ($x = 0.02$) changes insignificantly compared to the slope in pure VO_2. With a high amount of the doping impurity ($x = 0.04$) this slope becomes more steep. For the pure VO_2 $\varepsilon = 3.43\cdot 10^{-3}$ eV, and for the doped specimens $V_{1-x}Zr_xO_2$ at $x = 0.02$ $\varepsilon = 3.02\cdot 10^{-3}$ eV, and at $x = 0.04$ $\varepsilon = 2.35\cdot 10^{-3}$ eV. The overlap of the states wave functions at neighboring sites, and, consequently, the probability of the charge carrier transition to a neighboring site, depends on the resonance integral I, which, as follows from (1) and (3), is proportional to ε. Therefore, parameter ε may be interpreted as a value proportional to the tunneling time of the small polaron through the barrier between the neighboring sites. In other words, the greater the mobility of the polaron, the smaller the value ε. It follows from our data that when vanadium dioxide is doped, ε declines with the growth of zirconium concentration, and this can be interpreted as a decrease in the charge carrier localization at the site.

4. Conclusion

It is shown that vanadium dioxide doping with zirconium leads to a significant change in the temperature dependence of the electrical conductivity of $V_{1-x}Zr_xO_2$ compared to the pure VO_2. It is suggested that additional diffusion of the MIT region with an increase in the degree of doping of thin films of VO_2 may be a consequence of diffusion of $R-M_1$ phase boundary. The electroconductivity of the insulator phase $V_{1-x}Zr_xO_2$ 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 of ε is determined for pure and zirconium-doped VO_2.

Conflict of interest

The authors report no conflict of interest.

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