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Electrical conductivity of tungsten doped vanadium dioxide obtained by the sol–gel technique

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Thin films of tungsten-doped and pure vanadium dioxide with a metal–insulator transition are prepared by a sol–gel method. The films are characterized by X-ray diffraction, and electrical conductivity is measured in a temperature range from 50 to 380 K. It is shown that the conductivity of the films varies with temperature as $\sigma \sim \exp(aT - b/T)$. The experimental results are discussed from the viewpoint of the small polaron hopping conduction theory taking into account the influence of thermal lattice vibrations onto the resonance integral. The values of the activation energy and polaron radius are found. It is shown that doping with tungsten affects severely onto the electrical properties of vanadium dioxide.

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1. Introduction

Pure stoichiometric vanadium dioxide exhibits a metal–insulator transition (MIT) at the critical temperature $T_c = 340$ K [1–5]. On cooling below T_c, the electrical conductivity of VO_2 decreases abruptly by 5 orders of magnitude and goes down further with decreasing temperature.

Notwithstanding the fact that VO_2 has been studied intensively over several decades, the electrical conductivity of the semiconducting phase of this compound is still not clearly understood. At present, no solid experimental data on VO_2 conductivity are available, which makes a theory of VO_2 electrical properties difficult to develop [4].

The sol–gel technique is currently regarded as one of the most promising LPD (liquid phase deposition) processes, particularly, for obtaining thin vanadium dioxide films [5–8], among others. Like all LPD techniques for depositing films and coatings, the sol–gel technique is noted for its simplicity and cheapness and requires no sophisticated process equipment, which is of crucial importance in mass production. This technique makes it possible to deposit thin-film coatings onto large-area and complex-shape substrates at low temperatures, as well as to carry out doping relatively easy, for instance, by introducing impurities at the sol preparation stage. This is important from both technical (doping permits T_c to be shifted) [3,5–7,9,10] and scientific viewpoint, since doping of VO_2 with tungsten up to 14 at.% results in its metallization [11], which allows one to study the properties of a VO_2 metallic phase in the low-temperature region. It should be noted that, according to recent data [12], metallization occurs at a somewhat lower concentration of W (9.5 at.%).

Among different alternative routes for the V_2O_5 sol preparation (such as, e.g., the hydrolysis of alkoxides [8,13]), the melt quenching-based technique is the most economical and effective method to prepare uniform, stable mixed oxide sols with various doping levels from which homogeneous films can be deposited [13]. In addition, vanadium dioxide samples, obtained by annealing of these films, demonstrate the sharpest conductivity change at the MIT [8].

In [14] the electrical conductivity of the switching channel of vanadium dioxide thin-film sandwich structures has been studied over a wide temperature range (15–300 K). It is shown that the electrical resistance of the channel varies with temperature as $\exp(-aT + b/T)$ in the high-temperature region (above 70 K). The experimental results are discussed from the viewpoint of the small polaron hopping conduction theory that takes into account the influence of thermal lattice vibrations on the resonance integral. The same is also true for VO_2 single crystals, as was previously shown in [4].

We are reporting here on a study of the effect of W doping on the semiconducting properties below the transition temperature, as well as on the metal–insulator phase transition parameters in vanadium dioxide.

2. Sample preparation and experimental procedures

Thin films of vanadium dioxide were prepared by a modified sol–gel method [5]. To prepare gel, analytical-grade V_2O_5 powder was melted in an alundum crucible mounted in a muffle furnace, and the melt was heated for 1 h at a temperature of 900 °C (the melting point of vanadium pentoxide is 680 °C). Next, the melt was poured into distilled water at room temperature and stirred. Once unreacted particles had been removed, a homogeneous reddish-brown gel-like

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solution was obtained. Tungsten-doped gel was prepared by adding WO_3 powder directly to molten vanadium pentoxide, which had been held at $T = 900$ °C for 1 h, followed by a 5-min hold and quenching into distilled water.

Thin gel layers were deposited onto glass–ceramic substrates and dried in air. To obtain vanadium dioxide, the samples were annealed in vacuum at a residual pressure of $1.3 \cdot 10^{-3}$ Pa and $T = 500 \pm 20$ °C. As a result, vanadium pentoxide decomposed to form vanadium dioxide: $V_2O_5(s) = 2VO_2(s) + 1/2O_2(g)$ [5]. In this way, we obtained $VO_{2-\delta}$ and $V_{1-y}W_yO_{2-\delta}$ with three values of y: 0.016, 0.03, and well above the "critical" value of 0.095 reported in [12], namely, with $y = 0.12$.

The films were characterized by X-ray diffraction (XRD) using a DRON-4 diffractometer in a symmetrical reflectance (Bragg–Brentano) geometry with CuK_α radiation. The resistivity was measured in the temperature range 50 to 380 K by means of a four-probe technique in a Gifford–McMahon cycle cryorefrigerator [5,7,14].

3. Small polaron theory and the experimental results treatment technique

Here we briefly mention some essential points from our previous work [14], which will be necessary for the subsequent discussion of results. The small polaron theory which takes into account the effect of thermal lattice vibrations on the resonance integral has been developed in [15]. Experimentally, the most important result of this theory is that the hopping conduction mechanism is essentially modified as compared to the standard temperature dependence of conductivity $\sigma \sim \exp(-E_a/k_BT)$, that is, $\ln(\sigma) \sim 1/T$, with the activation energy E_a. In particular, if the mean-square thermal displacement $\langle\rho^2\rangle$ of atoms is of the order of (or greater than) the squared polaron localization radius R_p, then, at high temperatures, the temperature dependence of conductivity becomes

$$\ln(\sigma) \sim T. \tag{1}$$

Generally, the conductivity can be written as [4,14,15]:

$$\sigma = en\frac{ea^2}{4\pi^{1/2}\hbar}\frac{I^2}{E_a^{1/2}(k_BT)^{3/2}}\exp(-E_a/k_BT + k_BT/\varepsilon), \tag{2}$$

where a is the interatomic distance, e — the electron charge, I — the resonance integral, $\hbar$ and k_B — the Planck and Boltzmann constants, respectively. The constant ε is temperature-independent and proportional to the squared polaron radius. In the high-temperature region (when $2k_BT > \hbar\omega_o$, where ω_o is the frequency of an optical phonon), this constant is given by the following expression [4]:

$$\varepsilon = \frac{1}{4}M\omega^2R_p^2. \tag{3}$$

Here M is the mass of an atom and ω is a characteristic phonon frequency.

The theory [15] takes into account the influence of the lattice atom thermal displacements on the small polaron inter-site hopping probability. The displacements of atoms lead to a change in the neighbor site wave functions overlap, and the latter contributes to the resonance integral I. The value of I depends on the inter-site hopping distance R as: $I \sim \exp(-R/R_p)$. The hopping mobility, in turn, is proportional to I^2.

In the works [4,14,16–18], it has been shown that many transition metal compounds exhibiting the MIT obey the law (1), and the values of R_p have been calculated from Eq. (3). The materials tested were: VO_2 [4,14], $CuIr_2S_4$ ($T_c = 220$ K) [16], V_2O_3 ($T_c = 150$ K) [17], and V_4O_7 ($T_c = 240$ K) [18].

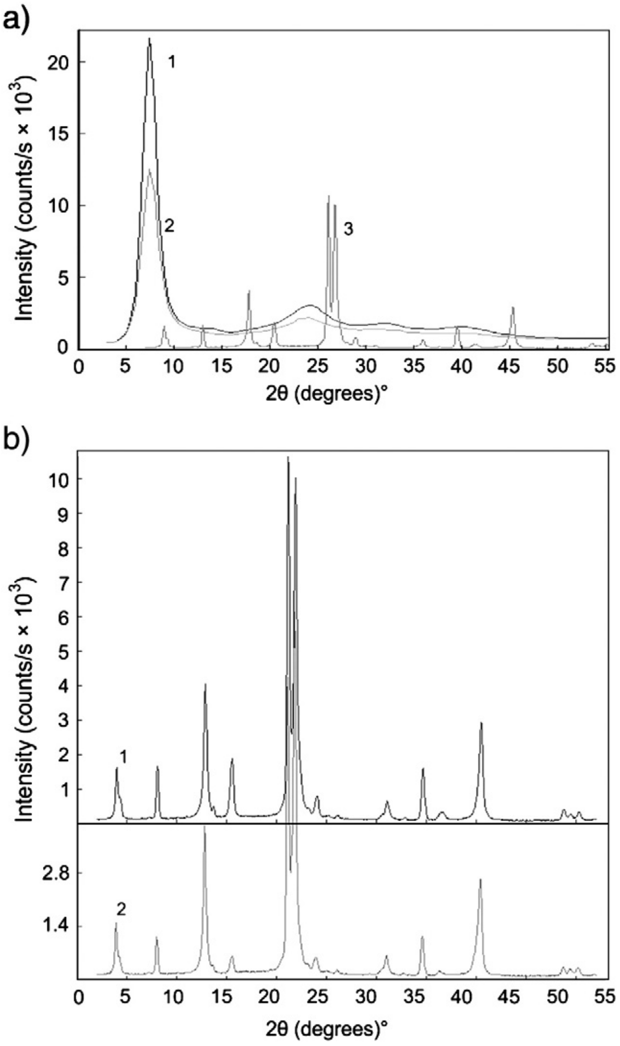

Fig. 1. (a) XRD patterns for: 1 — pure $V_2O_5 \cdot nH_2O$; 2 — $V_{2-y}W_yO_{5\pm\delta} \cdot nH_2O$, where $y = 0.12$; 3 — $V_2O_5 \cdot nH_2O$ on a glass–ceramic substrate after vacuum annealing. (b) XRD patterns for vacuum annealed films: 1 — $V_2O_5 \cdot nH_2O$; 2 — $V_{1-y}W_yO_{2-\delta}$, where $y = 0.12$.

Note that Eq. (2) can be rewritten as:

$$\ln\left(\sigma T^{3/2}\right) \cdot T = CT - \frac{E_a}{k_B} + \frac{k_B}{\varepsilon}T^2, \tag{4}$$

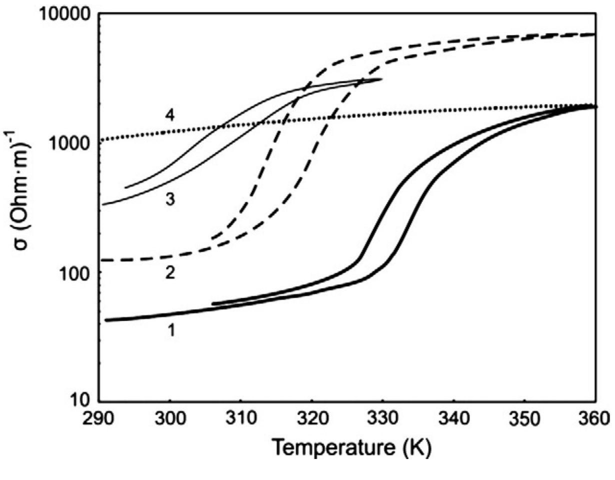

Fig. 2. Conductivity as a function of temperature for the samples of $V_{1-y}W_yO_2$ with $y = 0$ (1), 0.016 (2), 0.03 (3) and 0.12 (4).

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