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Effect of ethanol vapour sorption on the semiconductor-metal phase transition in powdered vanadium dioxide

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Abstract

We studied the effect of ethanol vapour on the parameters of the semiconductor-metal transition in a polycrystalline vanadium dioxide powder of the stable monoclinic phase α -VO₂. It was synthesised by reducing vanadium pentoxide with oxalic acid while heated in air. The DC electrical resistance of the samples was studied between room temperature and 100 °C in a tubular heater, in a microcompressor-generated air stream with saturated ethyl alcohol vapour. It was found that in the presence of ethanol vapour, the hysteresis loop shifted to higher temperatures by ten degrees and its cooling branch (corresponding to the transition of vanadium dioxide from the metallic phase to the semiconductor phase) became stepped.

Keywords: Vanadium dioxide, Semiconductor - metal phase transition, Ethanol vapour, Sorption

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1. Introduction

Semiconductor – metal phase transition (SMPT) in vanadium dioxide (VO₂) has been a topical area of research for more than sixty years due to the various practical applications of this effect [1]. Vanadium dioxide as a binary compound with different phase modifications is described in Table 1, their transformation scheme is shown in Figure 1. The structures of vanadium dioxide consist of [VO₆] octahedra. Depending on the synthesis conditions and kinetics, the octahedra can be distorted, connected by edges and vertices in different crystallographic directions, forming

two stable modifications (VO₂ (M₁) and VO₂ (R)) and several metastable modifications.

The stable monoclinic M₁ (P2₁/c) modification (otherwise called α-VO₂) is built from chains of distorted [VO₆] octahedra, which form a three-dimensional structure with a distance of 0.352 nm between vanadium atoms in adjacent chains and 0.265 nm inside the chain. At temperatures above 68 °C (the SMPT temperature), the distortion of the crystal structure is eliminated, when the localised V-V bonds within the chain are broken and the previously paired electrons are released. As a result, the monoclinic structure transforms

Table 1. Lattice parameters of different vanadium dioxide modifications

VO ₂ modifications	Crystal structure (space group)	Lattice parameters			
		a (Å)	a (Å)	a (Å)	β (°)
VO ₂ (M ₁)	Monoclinic (P2 ₁ /c)	5.7513	4.5259	5.3836	122.618
VO ₂ (R)	Tetragonal (P4 ₂ /mnm)	4.55	4.55	2.86	-
VO ₂ (B)	Monoclinic (C2/m)	12.03	3.69	7.68	106.6
VO ₂ (A _T)	Tetragonal (P4/ncc)	8.43	8.43	7.68	-
VO ₂ (A _H)	Tetragonal (I4/m)	8.476	8.476	3.824	-
VO ₂ (M ₂)	Monoclinic (C2/m)	9.07	5.80	4.53	91.9
VO ₂ (C)	Monoclinic (I4/mmm)	5.743	4.517	5.375	121.61

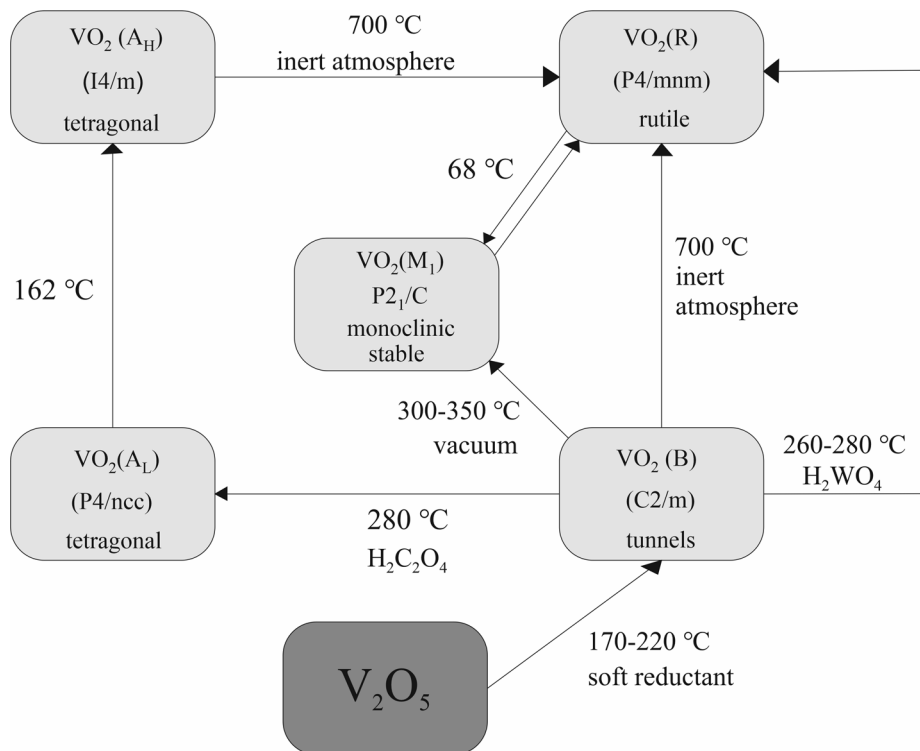


Fig. 1. Technological scheme for the transformations of vanadium dioxide phase modifications (explained in the text)

into a tetragonal (R) ($P4_2/mnm$) rutile structure. In the resulting structure, electrical conductivity, magnetic susceptibility, and light absorption increase dramatically [2]. This allows the M_1 modification to be used as a material for electrical and optical switches, IR-sensitive windows, temperature sensors, and thermochromic indicators.

VO_2 (R) is obtained by heating VO_2 (B) in an inert atmosphere [3]. The rutile (R) modification can also be obtained directly by hydrothermal method. It is similar to the synthesis of VO_2 (B), but it is performed at a higher temperature (260–280 °C) with the addition of tungstic acid (1 %) [4, 5].

Metastable monoclinic modification VO_2 (B) ($C2/m$) has a characteristic structural feature: channels (tunnels) formed by chains of distorted $[VO_6]$ octahedra. This modification is an important and promising material for lithium-ion battery cathodes because lithium cations can be reversibly introduced into the VO_2 (B) tunnel structure [6]. VO_2 (B) is obtained under hydrothermal conditions at a temperature of about 170–220 °C [4, 7] by treating V_2O_5 with a mild reducing agent. When heated in a vacuum to 300–350 °C, VO_2 (B) turns into VO_2 (M_1). At 700 °C in an inert atmosphere it transforms into the thermochromic modification VO_2 (R) [3].

Metastable VO_2 (A) has two modifications. The low-temperature form (A_L , $P4/ncc$) changes to the high-temperature (A_H , $I4/m$) when heated to 162 °C. Both phases have a similar oxygen frame structure in the $[VO_6]$ octahedron, but they have different arrangement of vanadium atoms inside the coordination polyhedron. The abrupt change in the optical properties of VO_2 (A) during the $A_L \leftrightarrow A_H$ phase transition makes it a promising material for optical switches. VO_2 (A_L) can be produced by the reduction of the VO_2 (B) modification with oxalic acid under hydrothermal conditions at 280 °C [5]. The product fraction increases considerably if the starting material is briefly exposed to a pressure of 440 MPa [8]. When VO_2 (A_H) is heated in an inert atmosphere to 700 °C, VO_2 (R) is formed [5].

The monoclinic metastable modification VO_2 (C) ($I4/mmm$) is close to the monoclinic $M1$ phase in structure and lattice energy. It has a layered structure and can be used to produce cathodes

for lithium-ion batteries. VO_2 (C) is obtained by heating $VO_2 \cdot 0.5H_2O$ semihydrate at 200 °C in a vacuum for 4 days [9].

The semiconductor-metal phase transition changes not only the electrical conductivity of vanadium dioxide, but also its optical characteristics, which is beneficial for the production of thermochromic smart glass. Glazing technologies based on the use of chromogenic materials are called “smart”. Chromogenic materials change their optical properties as a result of exposure to electric current, light radiation, changes in temperature, and other factors. Thus, there are electrochromic, photochromic, and thermochromic materials [10]. The heating of vanadium dioxide to 68 °C results in the SMPT, which significantly changes its optical characteristics [11]. The transition temperature depends on the vanadium dioxide crystal state, oxygen nonstoichiometry, and doping. The use of composite coatings based on a transparent film matrix filled with thermochromic material makes smart window technology more flexible and affordable [12, 13].

For smart glasses with chromogenic coatings, the ability to reversibly change light transmission parameters is important. When vanadium dioxide is used as a thermochromic filler, the SMPT temperature and the shape of the hysteresis loop can be regulated by surface doping of the oxide under gas adsorption conditions. A chromogenic layer on the inner surface of the glass in a standard window glass unit makes it possible to chemically sensitise the thermochromic material by introducing electron donor gases (e.g., alcohol vapour) into the air between the panes. Some results obtained in this area of research [14] refer mainly to mixed-valence vanadium oxide films.

This paper is devoted to the study of the effect of ethanol vapor on the parameters of the SMPT in single-phase powdered vanadium dioxide.

2. Experimental

Polycrystalline vanadium dioxide powder (n -type conductivity as determined by the Seebeck effect) was synthesised by reducing vanadium pentoxide with oxalic acid when heated in air to 600–700 °C according to the reaction:



X-ray phase analysis of the powder obtained by the reduction reaction showed the reflexes of vanadium dioxide of the stable α -VO₂ (VO₂ (M₁)) monoclinic phase. At 300 bar, we formed tablets with a diameter of 1 cm and a thickness of 1 mm from the powder. We applied tin foil contacts to the flat surfaces of the tablets. The change of electrical resistance of the samples at direct current was studied in the temperature range from room temperature to 100 °C. The measurements were carried out in a tubular heater in an air stream generated by a microcompressor with saturated ethyl alcohol vapour (about 5% of the volume). The heating and cooling rate was about one degree per minute.

3. Results and discussion

When the samples were heated in air, the sample resistance decreased by two orders of magnitude in the temperature range of 60–80 °C, and the hysteresis loop was slightly asymmetrical (Fig. 2a). In the presence of ethanol vapour, there were significant changes in the parameters of the phase transition. The hysteresis loop shifted to higher temperatures by about ten degrees, and the cooling branch (corresponding to the transition of vanadium dioxide from the metallic phase to the semiconductor phase) became stepped (Fig. 2b).

There is a step on the cooling branch of the hysteresis loop at 80–90 °C (Fig. 2b, branch (2)) under the action of a donor-active gas (ethanol) on the surface of vanadium dioxide. It may result from the asymmetry of the so-called elementary hysteresis loops due to elastic deformation of crystallites during the phase transition [15]. The cooling branch of the thermal hysteresis loop is not multi-step in the absence of donor-active gas on the vanadium dioxide powder surface.

We had previously observed the multi-step shape of both branches of the thermal hysteresis of the semiconductor-metal phase transition in nanocrystalline films of mixed vanadium oxide on silicon in AC conductivity measurements [16]. The steps were formed due to the influence of the size effect on the phase transition in certain groups of crystallites of nearly similar size.

We had also observed “abnormal” electronic semiconductor (VO₂) responses to the chemisorption of electron-donor gas (ethanol) for vanadium dioxide films. Study [17] suggested an energy band model of the structure of vanadium dioxide crystallites that took into account the possible inversion of the conductivity type in the surface layers. An increase up to certain limits (up to inversion) of the electron concentration in the space charge region of the VO₂ surface layer should lead to

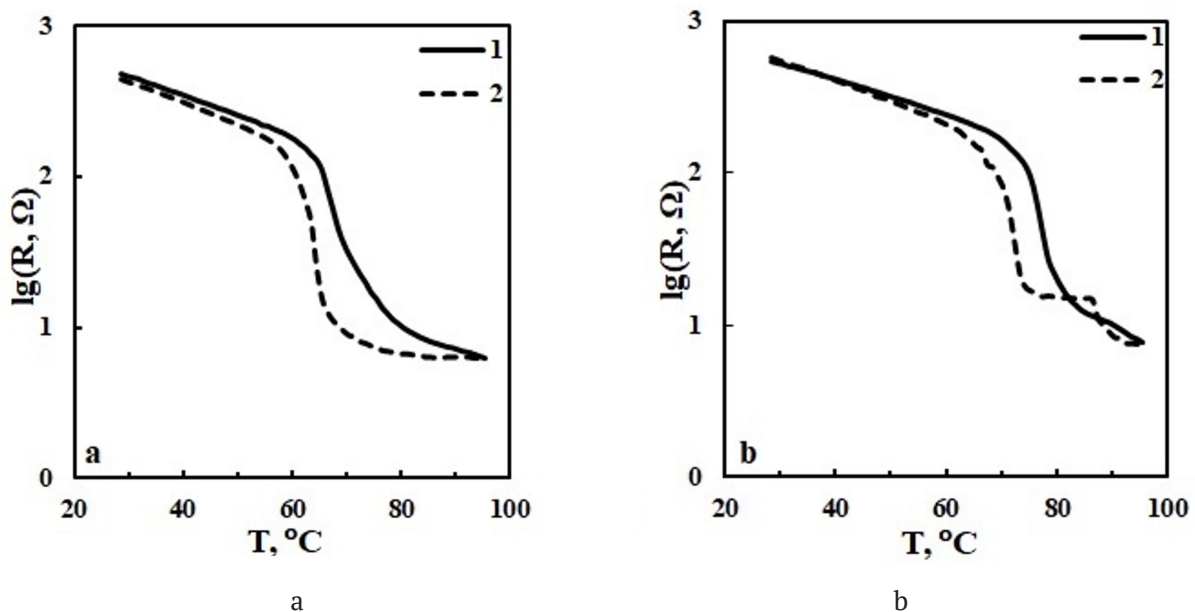


Fig. 2. Dependence of vanadium dioxide resistance on temperature in a clean air stream (a) and in an air stream with saturated ethanol vapour (b): 1 – heating branch, 2 – cooling branch

an increase in the electrical resistance of the material.

4. Conclusions

Thus, using ethanol vapour as an example, this study shows that it is possible to control the semiconductor - metal phase transition parameters in polycrystalline powdered vanadium dioxide by chemisorption of gases.

Authors contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no conflict of interest.

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