The characteristics of semiconductor-to-metal transition in VO₂ of different morphology

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Abstract. Vanadium dioxide nanoparticles (NPs) of different morphologies were obtained using the hydrothermal technique. Their shape and size were studied by SEM, XRD and SSA estimation. The functional properties, structural changes and thermal behavior of samples obtained were investigated to clarify the SMPT peculiarities. It is shown that the introduction of a doping element changes a mechanism of the nanoparticles growth and so that the SMPT becomes less expressed. The detailed study of SMPT in undoped VO₂ showed the steps of the transition process. The testing of VO₂ coating on glass for «smart» windows was successfully performed.

1. Introduction

Bulk vanadium dioxide undergoes a semiconductor-to-metal phase transition (SMPT) at 340 K resulting in an abrupt change of magnetic, electrical and optical properties. Due to this fact, VO₂ becomes a perspective material for optical switchers and IR sensors [1], «smart» covers for windows [2], electrical switchers and elements of energy-independent memory [3]. What is more, vanadium dioxide has a rutile structure so that the different ions are able to intercalate easily into the lattice. Therefore, this material can be used as an electrode material for Li-ions batteries [4].

Nowadays powders of vanadium dioxide are mainly synthesized in hydrothermal route because well-crystallized nanoparticles with different morphologies can be obtained by variation of the reaction conditions [5 - 7].

It was already discussed that the dimension of the material is a determinant factor for expression of the SMPT characteristics. [8] The VO₂ thin films show weak change in a magnetic susceptibility after transition so it is needed to be verified if this tendency of size reduction influence on the SMPT will repeat for nanoparticles.

It is known that application of VO₂ depends on characteristics of the transition which in its turn is effected by VO₂ morphology. As we have shown before, the temperature of the SMPT can be lowered by doping [9]. But there is one more way to regulate morphology of the product obtained. The introduction of a chelating agent such as etidronic acid leads to change in a growth mechanism and thereby influences on particles size and shape.

So the hydrothermal synthesis of undoped and Fe and Cr-doped VO₂ particles in presence and in absence of the chelating agent are reported. The dependence of their physico-chemical and functional characteristics on oxide morphology is shown.
2. Experimental

VO$_2$ powders were synthesized from H$_2$C$_2$O$_4$ and V$_2$O$_5$. The yellow suspension in distilled water was mixed on a magnetic stirrer at a constant temperature 60°C. Over this, the solution became homogeneous and colored dark blue. On this step solutions of the doping ions and the chelating agent were added if necessary. The solution was transferred into a 500 ml teflon-lined autoclave. After hydrothermal synthesis the product was obtained as a black precipitate which was transferred to centrifuge tubes of 50 ml and washed several times with distilled water. Then the product was placed in an oven and dried at 80°C for at least 12 hours.

The morphology of powders obtained was analyzed by XRD, SEM and SSA estimation. X-ray powder diffraction was performed on the Bruker “D2 Phaser” X-ray diffractometer with CuK$_\alpha$ radiation. Particles form and size were characterized by scanning electron microscope Hitachi S3400N. Specific surface area was determined by the Brunauer-Emmett-Teller metod on a surface area analyzer Micromeritics ASAP-2020MP. The temperature dependence of conductivity was determined using an electrical impedance spectroscopy (EIS) in a cell under normal pressure, in the temperature range of -160 to 165 °C with step of 20°C. The Novocontrol Concept 40 impedance analyzer was used in the frequency range of 10 to 10$^7$ Hz. The magnetization was measured on the vibrating magnetometer Lake Shore 7410 in the auxiliary magnetic field of 15 kOe and the temperature range of -196 to 127°C. The detailed investigation of SMPT in undoped VO$_2$ was conducted by DSC and XRD at temperatures ranges 7 – 400 K. The IR transmittance of VO$_2$ coating on glass at temperature range 279 – 333 K was studied by IR spectroscopy.

3. Results and discussion

3.1. The regulation of NPs morphology by variation of synthesis conditions

The results of XRD showed that the powders obtained contain no other phase of any vanadium oxides except VO$_2$.

By analysis of SEM images it is shown that the particles shape changes from ribbons and microplates obtained before with large amounts of dopant [9] to carambola-like and sponge-like spheres with the chelating agent (Figure 1) and smooth hollow spheres with one (Figure 2). The tendency of nanoparticle formation both for Fe and Cr-doped samples is mostly the same.

![Figure 1. SEM image of Fe-doped vanadium dioxide without etidronic acid: carambola-like and sponge-like spheres morphology.](image1)

![Figure 2. SEM image of Fe-doped vanadium dioxide with etidronic acid: smooth hollow spheres morphology.](image2)
An undoped VO$_2$ synthesized without the chelating agent represents rods with 80 nm thick and 1.5 µm length (Figure 3).

![SEM image of undoped vanadium dioxide: rods morphology.](image)

Figure 3. SEM image of undoped vanadium dioxide: rods morphology.

The results of particles size calculated by SEM correspond to values of specific surface area.

3.2. The dependence of SMPT characteristics on the morphology of VO$_2$

From the magnetic and electrical properties of doped vanadium dioxide it is found that the SMPT become less expressed and the temperature of the transition decreases to 200 K with the chelating agent and 150 K without one compared to the bulk material. There is no difference appeared between samples with varied amount of doping element which means that the characteristics of SMPT depend on morphology of the sample but not the quantity of dopant. The shape of doped samples makes them perspective for Li-ion batteries, because spheres are supposed to effectively interact with a matrix substance and distribute in it more evenly.

The detailed study of SMPT in undoped VO$_2$ has shown the abrupt change in magnetic characteristics near 280 K and the crystalline structure modification near room temperature. The thermal effects of transition and decrease in IR-transmittance were observed at about 310 K. It means that the transition consists of several steps appearing on different levels of structural organization. Thereby the SMPT takes place in temperature range which is convenient for “smart” cover application. The decrease in IR transmittance of VO$_2$ coating on glass above the room temperature was shown.

All conclusions about the transition are summarized in a Table 1. The SMPT peculiarities revealed require more detailed investigation.

### Table 1. The dependence of SMPT characteristics on morphology of vanadium dioxide.

| Presence of the chelating agent | Morphology                        | Particle size, µm | $T_{SMPT}$, K | Expressiveness of SMPT | Application              |
|---------------------------------|-----------------------------------|-------------------|---------------|------------------------|--------------------------|
| Fe/Cr-doped VO$_2$              | No                                | Carambola-like and sponge-like spheres | 2–5          | 150                    | weak                     | Li-ion batteries         |
| Fe/Cr-doped VO$_2$              | Yes                               | Smooth hollow spheres | 2–5          | 200                    | weak                     | Li-ion batteries         |
| Undoped VO$_2$                  | No                                | Rods              | 0.08×1.50     | 280                    | strong                   | “Smart” covers, termosensors |
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