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Thermochromic VO_2 nanorods and other vanadium oxides nanostructures

Kinson C. Kam, Anthony K. Cheetham *

Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA

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Abstract

Thermochromic VO_2 nanorods were prepared via thermal conversion of the metastable VO_2–B phase synthesized by hydrothermal methods. We observe an increased thermochromic transition temperature to ~75–80 °C by variable-temperature infrared spectroscopy. Nano- and sub-micron structures of other vanadium oxides (V_3O_7, $(NH_4)_{0.5}V_2O_5$, and V_2O_5) were obtained simply by varying the starting materials in the hydrothermal synthesis. We also obtained nanostructures of the high temperature tetragonal rutile phase of VO_2 by thermolysis of single-source vanadium (IV) precursors.

Keywords: A. Nanostructures; A. Oxides; B. Chemical synthesis; C. Infrared spectroscopy; D. Optical properties

1. Introduction

The development of a wide range of nanomaterials has sparked tremendous interest on account of their novel physical properties and their potential applications in constructing electronic and optoelectronic devices at the nanoscale [1]. Much of the effort has been focused on nanoparticles and nanowires of semiconducting and metallic systems such as CdSe [2], GaN [3], ZnO [4], In_2O_3 [5], and metals [6]. Among such systems, thermochromic rutile-type vanadium dioxide (VO_2) is of considerable interest due to its applications in optical switching devices, smart windows, thermal sensors, and field-effect transistors. These applications are based on its ability to undergo a reversible structural distortion as a function of temperature that is accompanied by a semiconductor-to-metal transition [7]. Above the transition temperature ($T_c = 67$ °C), VO_2 is metallic and adopts the tetragonal rutile ($P4_2/mnm$) structure with chains of edge-shared VO_6 octahedral along the c-axis (the V–V distances along the chain are 2.851 Å). Below T_c, in the semiconducting monoclinic ($P2_1/c$) crystal structure, the vanadium atoms dimerized and have alternate V–V distances of 2.619 and 3.12 Å. The behavior causes large reversible changes of optical and magnetic properties, as well as a change of resistivity by several orders of magnitude.

Nanostructures of VO_2 have been prepared using various techniques. Thin films of thermochromic VO_2 have been obtained by pulsed laser deposition onto SiO_2/Si substrates [8], sol–gel deposition using vanadium alkoxides [9,10], and atmospheric pressure chemical vapor deposition with $VOCl_3$ [11]. VO_2 nanowires and nanorods have been prepared by hydrothermal methods using glycol reduction [12] or surfactants [13,14], and Liu et al. have recently

* Corresponding author. Tel.: +1 805 893 8767; fax: +1 805 893 8797.
E-mail address: cheetham@mrl.ucsb.edu (A.K. Cheetham).

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showed that VO_2 nanobelts can be synthesized hydrothermally using formic acid as the reducing and acidifying agent [15]. However, these nanowire, nanorod and nanobelt materials adopt the metastable VO_2–B structure, which does not exhibit the metal to semiconductor transition. Nanoparticles of thermochromic VO_2, on the other hand, have been prepared by pulsed laser deposition followed by thermal oxidation [16,17], and stoichiometric vanadium and oxygen ion implantation [18,19].

VO_2 nanowires of the low temperature monoclinic phase have been prepared by vapor transport method from bulk VO_2 powders in flowing argon [20], but their thermochromic behavior was not reported. Here, we describe the synthesis and thermochromic behavior of VO_2 nanorods through phase conversion of the metastable form, VO_2–B, as reported in Ref. [15]. Other methods of preparing VO_2 nanorods have also been explored in the present work. For example, thermolysis of V (IV) precursors of acetates, glycolates, and tartrates under nitrogen atmosphere yielded tetragonal VO_2 nanorods and nanoparticles. We have also synthesized nanorods of other vanadium oxides by varying the starting materials and conditions in the reaction medium.

2. Experimental

Nanorods of metastable VO_2–B were synthesized hydrothermally, as reported in Ref. 15. NH_4VO_3 (Aldrich) was used as the source of vanadium. In a typical synthesis, formic acid was added to a 10 ml aqueous solution containing 0.1 mol of vanadium, while stirring, until the pH reached ~2.5. The mixture was then sealed in a Teflon-lined autoclave and heated at 180 °C for 2 days. After cooling to room temperature, the precipitate was separated by centrifugation (3000 rpm for 15 min) and the supernatant liquid was discarded. This separation procedure was repeated twice more after additional rinsing with ethanol. The product was then dried in a vacuum oven at 60 °C for 3 h. Conversion of the metastable phase VO_2 nanorods to the thermochromic phase was performed by heating up to 700 °C at 10 °C/min in an N_2 atmosphere. Variations on this synthetic procedure in which we used alternative sources of vanadium, such as $VOSO_4$ and V_2O_5, in combination with other carboxylic acids, including acetic, oxalic and propionic acids, yielded nanostructures of other vanadium oxides.

Vanadyl acetate and vanadyl glycolate precursors were prepared as reported by Weeks et al. [21]. Vanadyl D,L-tartrate precursor was synthesized in a closed vial containing 10 ml DI-H_2O and stoichiometric amounts of vanadyl acetate and D,L-tartaric acid at 100 °C for 2 days. Blue diamond-shaped crystallites were obtained after cooling to room temperature. The product obtained was rinsed with DI-H_2O and dried in air. All precursors were subjected to thermolysis in a N_2 atmosphere between 500 and 700 °C with a gas flow-rate of 50 ml/min.

X-ray diffraction (XRD) measurements were obtained with a Philips XPERT diffractometer (Cu Kα radiation). Variable-temperature infrared spectroscopy (IR) was performed on a Nicolet Magna 850 IR spectrometer. Scanning electron microscopy (SEM) images were obtained using a FEI XL30 Sirion FEG microscope at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed with a FEI T20 microscope operating at 200 kV.

3. Results and discussion

The XRD patterns of the VO_2 nanorods are shown in Fig. 1. The pattern of the as-synthesized sample (Fig. 1a) can be indexed as the metastable VO_2–B phase [JCPDS 81-2392]. In Fig. 1b, the XRD pattern obtained after thermal treatment corresponds to the low temperature monoclinic VO_2 phase [JCPDS 44-0252]. No peaks of any other phases or impurities are observed, suggesting the conversion to thermochromic VO_2 nanorods is complete.

In Fig. 2a, we show the SEM image of the metastable VO_2–B nanorods with diameters ranging between 50 and 100 nm and with lengths extending up to several microns. After phase conversion of the VO_2 nanorods to the thermochromic phase, the overall rod-like morphology is maintained, with the majority of the nanorods having diameters between 50 and 250 nm (Fig. 2b). However, while the length of the nanorods remains nearly constant, we observe a decrease of the average aspect ratio due to agglomeration of neighboring nanorods, with their diameters increasing up to 500 nm; this is expected since grain growth of nanorods becomes more favorable with thermal treatment at high temperatures. A TEM image of the VO_2 nanorods after thermal treatment is shown in Fig. 3a. Selected area electron diffraction (SAED) patterns of individual nanorods reveal that they are single-crystalline (Fig. 3b). Careful analysis of the SAED pattern reveals that the nanorods grow along the [1 0 0] direction, as found in previous work [20].