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# Synthesis and thermal stability of W-doped VO<sub>2</sub> nanocrystals

# F.Y. Kong, M. Li, S.S. Pan, Y.X. Zhang, G.H. Li\*

Key Laboratory of Materials Physic, Anhui Key Laboratory of Nanomaterial and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, PR China

#### ARTICLE INFO

Article history: Received 27 January 2011 Received in revised form 15 June 2011 Accepted 24 June 2011 Available online 2 July 2011

Keywords: A. Oxides B. Chemical synthesis D. Crystal structure

# ABSTRACT

Pure and W-doped vanadium dioxide nanocrystals have been synthesized by using  $V_2O_5$  and oxalic acid as precursors via a thermolysis method. The  $VO_2$  nanocrystals have a nearly spherical morphology with size ranging from 50 to 100 nm. The metal-insulator transition (MIT) temperature of the nanocrystals decreases with increasing W-doping content. The successive heat-induced fatigue character of the MIT in W-doped  $VO_2$  nanocrystals was investigated by DSC analysis together with structural study, and a high stability upon heating-cooling cycles was found with respect to MIT temperature, peak temperature and latent heat of the phase transition.

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# 1. Introduction

The metal-insulator transition (MIT) in VO<sub>2</sub> takes place at about 68 °C [1], accompanying a structural transition from hightemperature rutile VO<sub>2</sub> (R) to low-temperature monoclinic VO<sub>2</sub> (M). It displays an about 10<sup>5</sup> decrease in resistivity and a large change in transparency in the infrared region as VO<sub>2</sub> (M) converts to VO<sub>2</sub> (R). These characteristics makes VO<sub>2</sub> a promising material for a wide variety of technological applications, such as field effect transistor-like or uncooled microbolometers [2,3], holographic storage systems [4–6], optical switching devices [7,8], sensors [9,10] and smart windows [11,12].

Much efforts have been devoted to refining growth techniques [13], to enhancing the optical transmittance by doping [14] or developing multilayer structure with  $TiO_2$  or  $SiO_2$  [15,16], to developing a better understanding of the size effects in the structural phase transition [17] and to controlling the MIT temperature. The MIT temperature can be well modified by strain control or elements incorporating in VO<sub>2</sub>, such as W, Mo and Cr.

Because of suitable for coating the substrate surface with a large dimension and/or complex morphology, the  $VO_2$  nanopowder has attracted much attention recent years. Different synthetic techniques have been developed, such as hydrothermal method, liquidphase hydrolysis method, and the evaporative decomposition of solutions technique [18–21], and among them the thermolysis method is a most promise technique that can be easily integrated

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into commercial production lines with a short cycle period and simple operation. The thermal stability of the  $VO_2$  nanopowder is an important issue that should address clearly for practical applications. Nevertheless, only few reports focus on the thermal stability of  $VO_2$  [22].

In this paper, we report the synthesis of pure and W-doped VO<sub>2</sub> nanocrystals by a thermolysis method and study of the thermal stability of the nanocrystals by DSC analysis. It was found that the transition quality of the VO<sub>2</sub> powder is much stable without degradation up to successive 100 heating–cooling cycles.

# 2. Experimental

# 2.1. Sample synthesis

In a typical synthesis procedure, oxalic acid  $(C_2H_2O_4 \cdot 2H_2O)$ (3.56 g) was first resolved into 100 mL ion-exchange water with constant stirring. Then 2.0 g of V<sub>2</sub>O<sub>5</sub> powder was added to the solution to make a yellow suspension at a temperature of about 60 °C. The solution turned green and then blue with final pH value between 2 and 3, indicating the reduction of V<sup>5+</sup> to V<sup>4+</sup>. Finally, the solution was dried at 75 °C for 2 days to obtain the precursor powders. The obtained powders were heated in a horizontal vacuum tube furnace at 550 °C for 1 h under a flow air gas of about 15 sccm. VO<sub>2</sub> nanopowders were then obtained through the thermolysis. The W-doped VO<sub>2</sub> powders were prepared in the same way. Ammonium tungstate was added into the blue solution and stirred before drying in the oven. The samples with different W-doping were defined as V0 (un-doped), V1 (0.5 at%), V2 (1.5 at%) and V3 (2.5 at%).

<sup>\*</sup> Corresponding author. Tel.: +86 551 5591437; fax: +86 551 5591434. *E-mail address*: ghli@issp.ac.cn (G.H. Li).

#### 2.2. Sample characterization

The valence state and the chemical composition of the samples were studied by X-ray photoelectron spectroscopy (XPS; Perkin-Elmer PHI-5600ci). The microstructure was determined by X-ray diffraction (XRD; Philips X'Pert Pro MPD and Cu K $\alpha$  radiation at 1.540 56 Å, at temperature of about 26 °C), and transmission electron microscope (TEM; JEOL Model 2010). Thermal gravimetric analysis (TGA) was carried out with a Perkin-Elmer Pyris 1 Thermal Gravimetric Analyzer with a heating rate of 10 °C/min in a flowing nitrogen atmosphere. The phase transition behavior and the thermal stability were analyzed by differential scanning calorimetry (Netzsch DSC-204) at a constant heating rate of 10 °C/min from 0 to 100 °C.

#### 3. Results and discussion

#### 3.1. Morphology, structure and component analysis

The reaction of  $V_2O_5$  powder with  $H_2C_2O_4$  solution can be expressed by following eqation [23]:

$$V_2O_5 + 3H_2C_2O_2 \rightarrow VOC_2H_4 + 3H_2O + 2CO_2 \tag{1}$$

in which the obtained precursor powders is vanadyl oxalate after dry. To understand the decomposition process of the vanadyl oxalate powders, the thermal gravimetric analysis (TGA) was conducted in flowing N<sub>2</sub> atmosphere, as shown in Fig. 1. From the TGA curve, one can see there are four weight losses in temperature range of 50–700 °C: ~5.92% form 50 °C to 131 °C, which is related to the elimination of adsorption water [24], ~7.96% from 131 °C to 221 °C, related to the procedure of dehydration, ~38.16% from 221 °C to 329 °C and ~2.95% form 329 °C to 499 °C, related respectively to the decomposition and oxidation of the precursor, which is a complex decomposition procedure, including the oxidation of carbon and hydrogen. No further weight loss was observed at temperature higher than 500 °C, indicating that the precursor vanadyl oxalate powders have completely thermal decomposed, and thus the 550 °C was selected as thermal treatment temperature to prepare VO<sub>2</sub> samples.

Fig. 2 shows the XRD patterns of the as-prepared VO<sub>2</sub> samples with and without W-doping after thermal treatment at 550 °C. From Fig. 2(a), one can see that for the samples VO, V1 and V2, all peaks can be indexed to M-phase VO<sub>2</sub> (JCPDS Card No. 44-0252, monoclinic,  $P_{21}/C$  14), and no other vanadium oxides, such as V<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, were observed. No peaks for ammonium tungstate were observed, suggesting the formation of a VO<sub>2</sub>–WO<sub>3</sub> solid solution. While for sample V3 shown in Fig. 2(b), all the diffraction peaks can



Fig. 1. Typical TGA and DTG curves of the precursor powders.

be indexed to R-phase VO<sub>2</sub> (JCPDS Card No. 44-0253, P42/mnm). The difference of XRD peak position between M- and R-phase is very small, to prove the formation of the R-phase, the enlargement of the three strongest diffraction peaks for samples V0 and V3 were shown in Fig. 2(c)–(e). From these figures one can clearly see that the diffraction peaks positions for sample V3 (curve 2) either slightly shift to left (Fig. 2(c) and (e)) or right (Fig. 2(d)) as comparison with sample V0 (curve 1), and match well with R-phase. This result shows that the R-phase VO<sub>2</sub> with room temperature phase transition temperature can be obtained using present synthesis method.

Fig. 3 shows SEM and TEM images of sample V1. One can see that VO<sub>2</sub> nanopowders have a nearly spherical morphology with size ranging from 50 to 100 nm. The corresponding SAED pattern shown in Fig. 3(b) clearly indicates that VO<sub>2</sub> nanopowders have a monoclinic structure. The HRTEM image shown in Fig. 3(c) proves that the VO<sub>2</sub> (M) nanopowder is a single crystalline. The fringe spacing of 0.25, 0.22 and 0.45 nm match well with the (2 0 0), (0 2 0) and (2 1 0) interplanar spacing of VO<sub>2</sub> (M) nanocrystals, with is in according well with the XRD spectra ( $2\theta \approx 37^{\circ}$ , 39.8°, 42.2°). SEM observations indicate that the as-prepared VO<sub>2</sub> (M) nanocrystals have a spherical shape with partially agglomeration, see Fig. 3(d), in which the primary grain size is in the range of 50–100 nm and is good agreement with TEM result.

The chemical state and composition of the W-doped  $VO_2$  nanocrystals was investigated by XPS analysis. The XPS spectra



**Fig. 2.** XRD patterns of sample: (a) V0 (curve (1)), V1 (curve (2)), V2 (curve (3)) and that from JCPDS Card No. 44-0253, (b) V3 and that from JCPDS Card No. 44-0252; (c)–(e) part enlargement of the XRD peaks for samples V0 (curve (1)) and V3 (curve (2)).



Fig. 3. (a) TEM image and (b) corresponding SAED pattern; (c) HRTEM images of a single nanocrystal and (d) SEM image for sample V2.

were calibrated by the  $C_{1s}$  peak (284.6 eV) from adventitious hydrocarbon contamination on the sample surface. Only four elements C, V, W and O can be observed in the wide energy range survey spectrum. The high-resolution analyses of the  $O_{1s}$  and  $V_{2p3/2}$ peaks, as well as their deconvolution analysis based on Gaussian function are shown in Fig. 4(a). One can see that the main fitting peak of  $V_{2p3/2}$  is centered at 516.46 eV, which is consistent with binding energy of V<sup>4+</sup> ion [19], the small peak at binding energy of 514.53 eV corresponds to  $V^{3+}$  ions, indicating there is some  $V_2O_3$  phase in the sample, which is consistent with the deconvolution of the V<sub>3p</sub> peak shown below. The O<sub>1s</sub> peak can be separated into two components relating to a peak with a binding energy of 530.57 eV, and an unknown peak with a binding energy of 528.17 eV. Deconvolution of the  $V_{3p}$  peak indicates that the V ions present in  $V^{4+}$  and  $V^{3+}$  with a binding energy of 41.30 and 38.14 eV, respectively, as shown in Fig. 4(b). Quantitative calculation indicate that the main existence chemical state is  $V^{4+}$ , and there is only 6.5% in the form of  $V^{3+}$ , which indicating the dominant existing form of V ions is V<sup>4+</sup>. It should be noted that this assignment has a measure of uncertainty because of the overlap between the W peaks and the  $V_{2p3/2}$ . The present of the V<sup>3+</sup> is helpful to the reduction of the MIT transition temperature due to the disruption of the  $V^{4+}-V^{4+}$  unit in  $VO_2(M)$  by formation of  $V^{3+}$ and causing a destabilization of the monoclinic phase of  $VO_2$  [25,26]. From the deconvolution of the  $W_{4f}$  peak (Fig. 4(b)), one can see that the W is present as  $W^{6+}$ , with  $W_{4f5/2}$  and  $W_{4f7/2}$  binding energies of 34.46 and 36.30 eV, respectively. This result indicates that the W is VI value state after incorporating into the VO<sub>2</sub> lattice. The XPS analyses also show the existence of both  $V^{4+}$  and  $V^{3+}$  in pure VO<sub>2</sub> nanocrystals.

The preparation of  $VO_2$  by the decomposition of the vanadyl oxalate is a controlled oxidation process, and the reaction can be described as:

$$2VOC_2O_4 + O_2 = 2VO_2 + 4CO_2 \tag{2}$$

The controlling of the flow rate of air in the thermal treatment is essential in obtaining  $VO_2$  phase. It was found that  $V_2O_3$  phase will



Fig. 4. High resolution scans of XPS peaks of (a)  $V_{2p}$  and  $O_{1s},(b)$  V3p and W4f and the corresponding Gassian fittings.



Fig. 5. DSC curves and phase transition temperature of  $VO_2$  with W-doping content of (1) 0 at%, (2) 0.5 at%, (3) 1.5 at% and (4) 2.5 at%.

be formed without air flow, equaling to thermal treatment in vacuum, and different amounts of  $V_6O_{13}$  phase will be coexisted with  $VO_2$  if the air flow rate is higher than 20 sccm. The  $V_2O_5$  and  $VO_2$  phase mixture will be obtained when the air flow rate is higher than 200 sccm. The pure  $V_2O_5$  phase can be obtained only when the thermal treatment is performed in air atmosphere, as reported by Pan and colleague using the same vanadium precursor [23].

# 3.2. Thermal stability of phase transition

The phase transition behaviors of the VO<sub>2</sub> nanocrystals with and without W-doping were characterized by DSC analysis, as show in Fig. 5. In the heating cycle, a clear endothermic peak can be seen in each of the DSC curves, which is attributed to the monoclinic/rutile structural phase transition. Three parameters can be obtained in a typical DSC curve: the onset transformation temperature ( $T_{onset}$ ), peak temperature ( $T_p$ ) and latent heat of phase transformation ( $\Delta H$ ). In this study the  $T_{onset}$  was defined as the transition temperatures ( $T_c$ ). The phase transition temperature of the undoped VO<sub>2</sub> nanocrystals is about 67 °C, which is close to the reported value [21]. While for sample V3, the phase transition temperature is at about 24.2 °C, close to room temperature. This result is fully consistent with the XRD results, in which when doped with 2.5 at% W, the VO<sub>2</sub> nanocrystals become rutile phase at



Fig. 6. DSC curves of VO<sub>2</sub> at cycle of (1) 1st, (2) 35th, (3) 75th and (4) 100th.



**Fig. 7.** (a) Latent heat of phase transformation,  $\Delta H$ ; (b) peak temperature,  $T_{\rm p}$  and onset phase transition temperature,  $T_{\rm c}$ , as a function of thermal cycle.

room temperature, whereas others are monoclinic phase. One also can see from Fig. 4 that the decrease in phase transition temperature almost linear with increasing W content. The result indicated that the reduction of phase transition temperature of VO<sub>2</sub> nanocrystals is about 16.5 °C per W at%, which is slightly lower than the reported value (19 °C per 1 at%) by Troy D. Manning et al. using a APCVD method [26]. Our results indicate that the phase transition temperature of VO<sub>2</sub> nanocrystals can be adjusted easily by W-doping, and demonstrate promising application in future smart windows.

The thermal stability of sample V3 was investigated by DSC analysis with successive thermally induced MIT. As shown in Fig. 6, all the DSC curves with different cycling numbers show evident endothermic peaks and the peaks almost have the same shape. The cycling number dependence of the latent heat of phase transition ( $\Delta H$ ) obtained from the area of the endothermic peak in DSC data are shown in Fig. 7(a), the  $\Delta H$  has almost a constant value of about  $6.3 \pm 0.2$  J/g and no attenuation was detected, indicating the phase transition from high-temperature rutile VO<sub>2</sub> (R) to low-temperature monoclinic phases VO<sub>2</sub> (M) is stable. In addition, the phase transition temperatures of the onset temperature  $(T_c)$  and peak temperature  $(T_p)$  also have a constant value at different heating-cooling cycles, as shown in Fig. 7(b). The  $T_{\rm c}$  and  $T_{\rm p}$  are about 23.9  $\pm$  0.3 and 39.4  $\pm$  0.2 °C, respectively. From the analysis, one can clearly seen that there is no degradation in the phase transition parameters, implying that the stoichiometry of VO<sub>2</sub> nanocrystals do not degraded under multiple thermally induced transition, and the transition quality is well maintained within successive 100 cycles and the phase transition is completely reversible. Since the phase transition temperature varies with different W contents, the doped W in the nanocrystals is proved to be of excellent stability, and this high stability is considered due to both the size effect and the existence of  $V^{3+}$  in the VO<sub>2</sub> (M) nanocrystals [26]. Accordingly, the W-doped VO<sub>2</sub> nanocrystals synthesized by the thermolysis method have excellent thermal stability, which is very important and beneficial for the technological application of VO<sub>2</sub> nanocrystals as smart windows.

#### 4. Conclusion

Rutile and monoclinic  $VO_2$  nanocrystals were synthesized by the thermolysis method with ammonium tungstate as a substitutional dopant. The dopant is in the  $W^{6+}$  form, and there is a small amount of  $V^{3+}$  in the  $VO_2$  nanocrystals. A significant correlation between phase transition temperature and W dopant was confirmed. The room temperature stable rutile VO<sub>2</sub> was obtained with 2.5 at% W doping with onset phase transition temperature of 24.2 °C. It was found the transition character of VO<sub>2</sub> nanocrystals is very stable upon 100 heating–cooling cycles in the temperature range of 0–100 °C, and this excellent thermal stability is beneficial for applications as thermochromic material.

# Acknowledgements

This work was financially supported by the National Basic Research Program of China (2009CB939903), and innovation project of the Chinese Academy of Sciences (KJCX2-YW-H2O).

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