Effects of annealing parameters on phase, structure and thermochromic properties of VO₂ (M) derived from nanostructured VO₂(B)

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Synthesis of thermochromic VO₂ (M) was successfully done by annealing hydrothermally-prepared VO₂ (B) at different temperatures and times. Conversion of the metastable VO₂ (B) to the thermochromic VO₂ polymorph was studied using thermogravimetric analyzer (TGA) under N₂ atmosphere. Moreover, the phase and morphology of the synthesized samples were studied using X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM), respectively. Accordingly, the XRD scans of all the annealed samples exhibited the presence of monoclinic VO₂ (M), while the FE-SEM images of the samples showed the formation of nanorods and nanospheres, particularly those heated at high temperatures (650 °C and 700 °C). Meanwhile, differential scanning calorimetry (DSC) was used to measure the phase transition temperature (τ_c), hysteresis, and enthalpy of the prepared VO₂. Based on these results, all samples displayed a τ_c of about 66 °C. However, the hysteresis was high for the samples annealed at lower temperatures (550 °C and 600 °C), while the enthalpy was very low for samples heated at lower annealing time (1.5 h and 1 h). These findings showed that crystallinity and nanostructure formation affected the thermochromic properties of the samples. In particular, the sample annealed at 650 °C showed better crystallinity and improved thermochromic behavior.

Keywords: *annealing; hydrothermal synthesis; thermochromic; vanadium dioxide*

1. Introduction

Vanadium dioxide (VO₂) belongs to a special group of thermochromic materials that display phase change from metal to semiconductor at a certain critical temperature, τ_c [1]. Accordingly, this phase change is due to molecular rearrangement from monoclinic to rutile structure, which are denoted by VO₂ (M) and VO₂ (R), respectively [2]. At temperature below τ_c , there is dimerization of vanadium ions responsible for the localization of the outer-shell vanadium electrons. When the temperature rises above τ_c , a rapid increase in electrical conductivity occurs and the lattice relaxes to a rutile structure [3]. Moreover, VO₂ has many

positive attributes such as: (1) it is thermodynamically stable in both phases [4]; (2) its transition time response is ultrafast of 10 picosecond [5]; and (3) it has greater endurance towards structural deformity [6]. Interestingly, the τ_c of VO₂, which is 68 °C, is closest to room temperature compared with other thermochromic compounds [7]. Hence, extensive studies have been carried out to gain understanding about its potential applications in various areas including temperature-sensing devices, cathode materials, electrical switching devices, and smart windows [8–14].

Recently, a significant number of studies have focused on the synthesis of VO₂ in nanostructure form [15]. The main route to achieve this is by hydrothermal technique wherein unique structures are obtained from a solution that is enclosed

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in an autoclave and heated (around 160 °C to 270 °C) inside an oven for a certain duration of time [16]. Previous results show that experimental conditions in this method can affect the morphology and crystallinity of VO₂ [17]. Consequently, it has been shown that the morphology and structure of VO₂ material directly affects its thermochromic and functional properties [18–20].

The widely used V(V) precursor is vanadium pentoxide (V₂O₅) because it is less expensive and easily obtainable [21]. To reduce its oxidation state from 5+ to the preferred 4+, reduction agent, such as oxalic acid is needed. Under soft chemical conditions, the metastable state VO₂ (B) is usually formed in nanobelt or nanorod form [22, 23]. To convert it to the thermodynamically stable and thermochromic VO₂ (M/R), further heating is required in vacuum or under argon (Ar) flow [24, 25]. As a continuation of these studies, we studied the evolution of VO₂ (B) to VO₂ (M/R) using nitrogen (N₂) as annealing atmosphere. Hence, in this paper, we report on the hydrothermal synthesis of VO₂ (B) nanobelts and their conversion to the thermochromic phase of VO₂ by annealing under nitrogen atmosphere. Furthermore, we investigated the effects of annealing temperature and time on the structure, morphology and thermochromic properties of the VO₂.

2. Experimental

The experiments were carried out using vanadium pentoxide (V₂O₅) and oxalic acid (H₂C₂O₄) as vanadium source and reduction agent, respectively. These chemical reagents were of analytical grade and used without further purification. To begin the hydrothermal synthesis, 1.875 g of V₂O₅ was dissolved in 150 mL deionized water under magnetic stirring. H₂C₂O₄ with a mass of 3.4024 g was then added continuing vigorous stirring. When the solution turned blue-green, it was transferred into a 240 mL Teflon-lined steel autoclave and heated inside an electric oven at 180 °C for 72 h. When it was cooled to room temperature, the blue-black precipitate was collected. Then, it was centrifuged and washed with water and ethanol several times. Finally, the powder was dried at 60 °C

overnight. The obtained VO₂ powder was then divided into six portions. Each portion was heated in a tube furnace under nitrogen atmosphere at varying times and temperatures. Four samples were annealed for 2 h at temperatures of 550 °C, 600 °C, 650 °C and 700 °C, while two samples were heated at 650 °C with corresponding durations of 1 h and 1.5 h. Meanwhile, the heating rate for all annealing runs was kept at 10 °C/min.

Analyses on the phase and crystal structure of the prepared samples were done by X-ray diffraction (XRD) using the diffractometer of X'Pert Pro Panalytical Philips DY 1861 with CuK α radiation ($\lambda = 1.54060$ Å). Meanwhile, the surface morphology and microstructures were examined by field emission scanning electron microscope (FE-SEM, JEOL-JSM7600F). The evolution of the VO₂ polymorphic phases from B to M under nitrogen atmosphere was studied using thermogravimetric analyzer (TGA, Mettler Toledo TGA/DSC1) with a heating rate of 10 °C/min. Moreover, the phase transition temperatures as well as the hysteresis and enthalpy properties of the samples were measured using a differential scanning calorimetry (DSC, DSC822, Mettler Toledo) in the temperature range between 30 °C and 200 °C under nitrogen flow with heating and cooling rates of 10 °C/min.

3. Results and discussion

The metastable phase of VO₂ was successfully synthesized hydrothermally as evidenced in the XRD pattern in Fig. 1. The peaks can be indexed to VO₂(B) with ICSD code 98-003-1439. The FE-SEM image of the sample (inset in Fig. 1), shows the formation of belt-like shapes with a width and length of about 50 nm and 1 μ m, respectively. This result is consistent with other research findings [26, 27]. Meanwhile, the behavior of VO₂ (B), when heated under nitrogen flow is illustrated in the TGA curve in Fig. 2, where the occurrence of weight loss from 52.61 °C to 213.40 °C and from 213.40 °C to 320.47 °C can be observed. These losses, with derivative peaks at 84.15 °C and 262.35 °C, respectively, can be attributed to the removal of water and other hydroxyl groups formed during the hydrothermal process [28, 29].

Another weight loss can be seen from 320.47 °C to 665.28 °C, which indicates the transformation of VO₂ (B) to the thermodynamically stable VO₂ (R). A final change in wt.% from 665.28 °C indicates potential conversion to other V–O compounds.

Fig. 1. XRD scan of the hydrothermally synthesized VO₂ (B). Inset: FE-SEM image of the acquired particle.

Fig. 2. TGA thermogram and first derivative curve (inset) of VO₂ (B) recorded at a heating rate of 10 °C/min under N₂ atmosphere.

The effect of annealing conditions on the phase formation of VO₂ is shown in Fig. 3. It can be observed that the thermochromic phase VO₂ (M) was achieved in all experimental runs. It must be noted that the XRD scans were carried out at room temperature, which is below the critical temperature of VO₂; hence, only the presence of VO₂ (M) was detected and not the tetragonal rutile VO₂ (R). The peaks can be matched with monoclinic VO₂ of the space group P2₁/c with ICSD code 98-007-8277. However, the peaks belonging to V₆O₁₃ were detected for the samples heated at a lower annealing

time and temperature. The presence of this compound with oxidation state greater than 4+ implies possible incidence of oxidation. The sample annealed at 650 °C for 2 h did not show any non-VO₂ compound. Also, the intensities of its peaks are relatively higher with narrow peak width which indicates good crystallinity. Meanwhile, annealing at 700 °C led to a further reduction of oxidation state from 4+ to 3+ as seen in the presence of V₂O₃. This result agrees with the TGA finding where a possible change in structure occurred at 665 °C. The average crystallite size, *D*, of the samples was calculated using Scherrer equation [30]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where *k* is shape factor (~0.9), λ is the X-ray radiation wavelength ($\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$), β is the half maximum peak width, and θ is the diffraction angle. Accordingly, for samples annealed at varying duration of 1 h, 1.5 h, and 2 h, the calculated values of *D* were 81.60 nm, 81.57 nm, and 61.80 nm, respectively. Meanwhile, for samples annealed at differing temperatures of 550 °C, 600 °C, 650 °C, and 700 °C, the values of *D* were 81.56 nm, 61.71 nm, 61.80 nm, and 61.81 nm, respectively. This shows that increasing heating time and temperature decreased the crystallite size of the acquired particles.

In addition, the annealing time and temperature affected the morphology and structure of the samples. As shown in the FE-SEM images in Fig. 4, the sample transformed from nanobelt VO₂ (B) (inset of Fig. 1) to nanorod and nanosphere VO₂ (M) (Fig. 4c and Fig. 4d). In particular, the samples annealed at lower times and temperatures mostly have irregular shapes with dimensions in micrometers (Fig. 4a, Fig. 4b, Fig. 4e and Fig. 4f), which could be caused by a clamping of the nanobelts during heating as shown in other works [31]. Meanwhile, the samples annealed at 650 °C and 700 °C show mostly rod, oblate and spherical structures (Fig. 4c and Fig. 4d). The measured dimensions of the rods are as low as 170 nm × 230 nm × 0.83 μm, while the diameters of the spheres and oblates range from 48 nm to micrometers.

Fig. 3. XRD scans of the samples annealed at different times (a) and temperatures (b).

Another important factor that validates the synthesis of VO_2 (M) is its thermochromic property. This can be seen in the DSC curves of the annealed samples in Fig. 5, where sharp endothermic and exothermic peaks can be observed during the heating and cooling processes, respectively. The values of the phase transition temperatures, τ_c , were measured by determining the onset temperature (τ_{on}) in the DSC curve. Accordingly, all samples exhibited a τ_c of about 66 °C, which is lower compared to the value for bulk VO_2 (68 °C). However, significant differences in hysteresis (the difference of τ_c in the heating and cooling directions) and enthalpy (the strength of phase change) can be observed. Table 1 summarizes the τ_c values including hysteresis, enthalpy as well as the crystallite size from the XRD scans. Specifically, a high crystallite size resulted in either higher hysteresis or lower enthalpy. As can be observed in Table 1, the hysteresis decreased from 3.23 to 0.15 when the annealing temperature was increased from 550 °C to 650 °C. Meanwhile,

Fig. 4. FE-SEM images of the samples annealed for 2 h at varying temperatures: (a) 550 °C, (b) 600 °C, (c) 650 °C, and (d) 700 °C; as well as samples heated at 650 °C at different times: (e) 1 h, and (f) 1.5 h.

there was a considerable difference in the enthalpy of the samples when the annealing time was increased. In particular, the samples annealed in 1 h and 1.5 h had very low enthalpy compared to the enthalpy of bulk VO_2 (37.38 J/g to 51.85 J/g) [32], which indicates poor phase change strength. Similar to other research findings [33], these low enthalpies may have resulted from poor crystallinity, presence of non- VO_2 compounds, and formation of micron-sized structures. Additionally, the sample annealed at 650 °C for 2 h exhibited the least hysteresis (0.15) and a high enthalpy (40.33 J/g).

4. Conclusions

Effective synthesis of nanostructured VO_2 (B) was done using hydrothermal method under soft-chemical condition. Conversion of this metastable phase to the thermodynamically stable

Table 1. Crystallite size, τ_c , hysteresis, and enthalpy of the samples.

Annealing time [h]	Crystallite size [nm]	Phase transition temp. [°C]			Hysteresis		Enthalpy, H [J/g]		
		τ_{heat}	τ_{cool}	$^{*}\tau_c$	$ \tau_{\text{heat}} - \tau_{\text{cool}} $	$-H_{\text{heat}}$	H_{cool}	$^{**}H_{\text{ave}}$	
1	81.60	66.47	65.4	65.94	1.07	1.20	1.80	1.50	
1.5	81.57	65.08	66.65	65.87	1.57	22	21.70	21.85	
2	61.80	66.31	66.46	66.39	0.15	39.56	41.10	40.33	
Annealing temp. [°C]									
550	81.56	63.40	66.63	65.02	3.23	39.35	39.79	39.57	
600	61.71	66.78	64.75	65.77	2.03	35.75	35.42	35.59	
650	61.80	66.31	66.46	66.39	0.15	39.56	41.10	40.33	
700	61.81	65.63	67.10	66.37	1.47	33.13	29.73	31.43	

$$^{*}\tau_c = (\tau_{\text{heat}} + \tau_{\text{cool}})/2; ^{**}H_{\text{ave}} = (|H_{\text{heat}}| + H_{\text{cool}})/2$$

Fig. 5. DSC curves of the annealed samples at varying temperature (a) and time (b).

phase, VO₂ (M/R), was carried out via annealing under N₂ atmosphere. TGA analysis showed that the evolution of VO₂ (B) to VO₂ (R) began at a temperature of 320 °C. Based on the XRD scans, all heat-treated samples exhibited the monoclinic

VO₂ (M). However, the presence of V₆O₁₃ was detected for samples annealed at lower times (1 h and 1.5 h) and temperatures (550 °C and 600 °C). Furthermore, the sample annealed at 700 °C exhibited further reduction of oxidation state as shown by the presence of V₂O₃. Also, it was found that the nanobelt VO₂ (B) was converted to VO₂ (M) nanorods and nanospheres at annealing temperatures of 650 °C and 700 °C. Results of the DSC measurements showed that all samples had a τ_c of about 66 °C. It was further shown that hysteresis decreased as annealing temperature was increased. In particular, the sample annealed at 550 °C displayed the highest hysteresis at 3.23. Meanwhile, the enthalpy of the samples significantly decreased at a lower annealing time. This low enthalpy may be caused by poor crystallinity, the presence of non-VO₂ compound as well as micron-sized particles formation. All things considered, the sample annealed at 650 °C for 2 h showed the best crystallinity, which resulted in improved thermochromic properties.

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