

Fabrication of transition temperature controlled W-doped VO₂ nano particles by aqueous solution

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Non-doped and W doped VO₂ powders with nanometer size were synthesized using vanadium oxyisopropoxide and/or tungsten sources with H₂O₂, subsequently by drying and heat-treatment the resulting powder at 400°C for 4 h in H₂/Ar atmosphere. Tungsten pentaoxide and tungsten chloride were used as tungsten sources. The primary particle sizes of the resulting non-doped VO₂ and W doped VO₂ powder were sub-tens nm. The transition temperature of the non-doped VO₂ was 67.5°C, and that of W doped VO₂ using tungsten pentaoxide and tungsten chloride precursor solutions were 40.4 and 31.2°C, respectively.

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1. Introduction

Vanadium dioxide VO₂ exhibits a crystallographic transition from a low-temperature monoclinic phase to a high-temperature tetragonal phase at 68°C, resulting in drastic changes in its optical and electrical properties.¹⁾⁻³⁾ The transition temperature of VO₂ is near a room temperature, and the transition temperature can be controlled by doping the other metals.^{2),4)-7)} Therefore, VO₂ film can be applied to a thermochromic window and a switching material.^{4),6)-8)} On the other hand, there are several works focused on applications as VO₂ fine particles; a composite involving VO₂ powders in polymeric matrices,⁹⁾ and coating nano-size VO₂ powders on glass substrate.¹⁰⁾

The aim of this work is fabrication of non-doped and W doped VO₂ nanocrystalline powder, with controlling the transition temperature of the resulting VO₂ powder. In this investigation, the nanometer size VO₂ particles was fabricated using vanadium alkoxide/H₂O₂ aqueous, and tungsten doped VO₂ nanoparticles were also synthesized by same aqueous method using tungsten alkoxide and tungsten chloride precursor sources. Furthermore, transition temperatures of the specimens by DSC, and the effect of tungsten sources on the tungsten doping efficiency for the VO₂ particles were evaluated.

2. Experimental procedure

Vanadium oxyisopropoxide [VO(O-i-Pr)₃], tungsten pentaethoxide [W(OC₂H₅)₅] and tungsten chloride (WCl₆) were used as starting materials. These were dissolved into 35% H₂O₂ with the molar ratio of (V + W)/H₂O₂ = 1/50 in nitrogen atmosphere. Where, the W/V atomic ratio was 0 or 1.8 atomic % (hereinafter, at. %). The precursor solution was stirred at 30°C for 12 h in

order to undergo polymerization, and the solution was dried at 80°C for 3 h. This resulting powder was heat-treated at 300°C for 3 h in H₂/N₂ atmosphere, subsequently heated at 500°C for 3 h in nitrogen atmosphere (resulting powder calls the precursor powder "A" in this paper). Finally, the obtained precursor powder was heat-treated at 400°C for 0 to 4 h in H₂/Ar atmosphere with the H₂/Ar mixing ratio of 1/9.

The structure of the resulting powder was characterized by XRD using D8 Advance (Bruker AXS) with Cu-Kα at room temperature. Microstructure of the resulting powder was observed by TEM using JEM2100F (JEOL), and the specimens were supported by a copper grid. Differential scanning calorimetry (DSC) were performed for the resulting VO₂ and W doped VO₂ powder using EXSTAR600 (SII Nano Technology Inc.) with a rising temperature of 10°C/min between 10 to 90°C.

3. Results and discussion

The vanadium oxide precursor powder "A" without tungsten doping was synthesized by above mentioned method at 400°C for 0 to 4 h in H₂/Ar atmosphere. **Figure 1** shows the XRD pattern for the resulting VO_x powder heat-treatment of the precursor powder "A" for 0 to 4 h. The as-prepared specimen ("A") was V₃O₇ and V₂O₅ phases, and VO₂ phase was not observed. All peaks of the as-prepared specimen "A" were assigned as the V₃O₇ and V₂O₅ phases. For the sample after heat-treated for 2 h, the XRD pattern showed two vanadium oxide phases, one was the V₆O₁₃ as a main phase and the other was VO₂ as a secondary phase. For the sample after heat-treated 4 h, the XRD pattern confirmed the monoclinic VO₂ as a main phase, and V₂O₃, V₆O₁₃ as secondary phases. It assumed that the more heat-treatment time caused producing the more reduction phase of vanadium oxide (VO, V₂O₃, etc.). Therefore, the optimal heat-treatment condition assumed at 400°C for 4 h in H₂/Ar, and the other specimens were synthesized under this heat-treatment condition.

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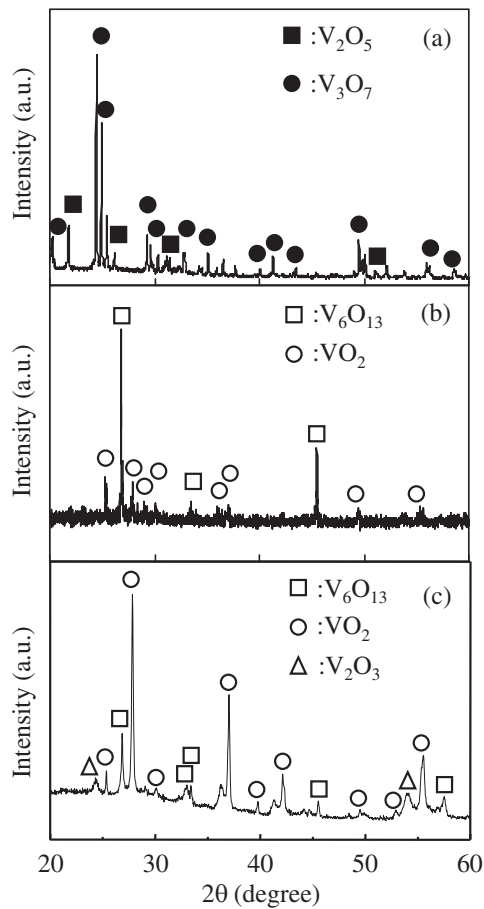


Fig. 1. The XRD patterns for the vanadium oxide powders of (a) as prepared (the powder "A"), (b) heat-treated of "A" for 2 h in H_2/Ar atmosphere and (c) heat-treated of "A" for 4 h in H_2/Ar atmosphere.

Using tungsten pentaethoxide [$W(OC_2H_5)_5$] and tungsten chloride (WCl_6) as starting agents with the 1.8 at. % to vanadium, tungsten-doped VO_x powder was fabricated by the above mentioned heat-treatment condition. **Figure 2** illustrates the XRD patterns for the resulting powders. The XRD patterns of both of the samples were assigned VO_2 as a main phase and V_6O_{13} as a secondary phase, and were not assigned the other phases including tungsten oxide phases.

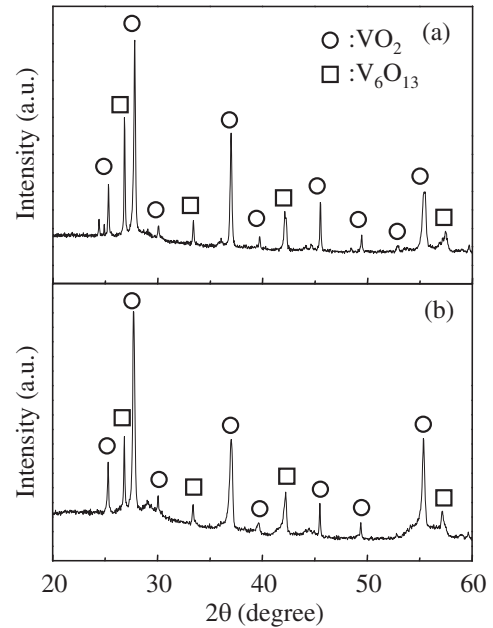


Fig. 2. The XRD patterns for the tungsten doped vanadium oxide powders using the precursor of (a) tungsten pentaethoxide and (b) using tungsten chloride.

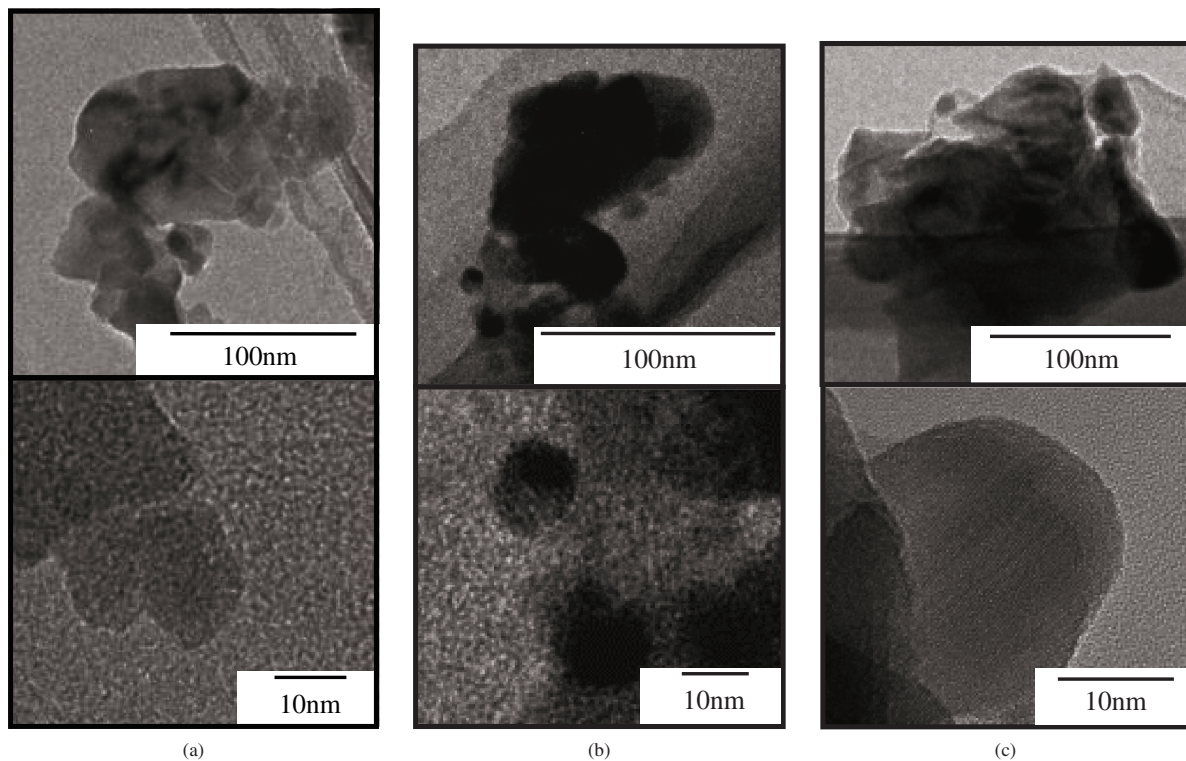


Fig. 3. TEM bright field images of (a) the VO_2 powder, (b) the W-doped VO_2 powder, using a tungsten pentaethoxide precursor, and (c) the W-doped VO_2 powder, using a tungsten chloride precursor.

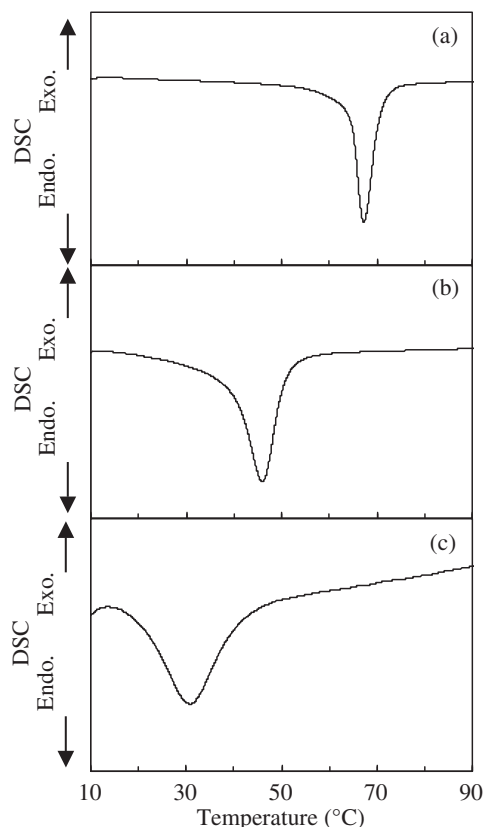


Fig. 4. DSC curves of (a) the VO₂ powder, (b) the W-doped VO₂ powder, using tungsten pentaethoxide precursor, and (c) the W-doped VO₂ powder, using tungsten chloride precursor.

In order to evaluate the particle size and the microstructure of the resulting non-doped and tungsten doped VO₂ powder, TEM observation was carried out for the specimens. **Figure 3** depicts the TEM bright field images for the resulting powders. The primary particle form of the non-doped and doped powders was sphere like shape, and aggregation of the primary particles were observed. The primary particle size of the non-doped VO₂ powder was about 15–20 nm [Fig. 3(a)]. The primary particle size of the W-doped VO₂ powder using a tungsten pentaethoxide precursor was about 10–20 nm [Fig. 3(b)]. The primary particle size of the W-doped VO₂ powder using a tungsten chloride precursor was about 30–40 nm [Fig. 3(c)], and the size was slightly larger than the non-doped or W doped VO₂ using a tungsten pentaethoxide precursor. From the TEM observation, it proved that non-doped or W doped VO₂ particles with nanometer size were obtained by this fabrication method.

To measure the transition temperature of the resulting specimens, a DSC measurement was carried out for the specimens. **Figure 4** presents the DSC curves for the VO₂ and 1.8 at. % W doped VO₂ powders. For the non-doped VO₂ powder, the endothermic peak was observed at 67.5°C. Hence the transition temperature of the non-doped VO₂ was 67.5°C, and the transition temperature of that was close to the reported values.^{1–3)}

The endothermic peak of the W-doped VO₂ powder using the tungsten pentaethoxide precursor was observed at 40.4°C, and that of the tungsten chloride precursor was observed at 31.2°C. Both

powders showed decreasing the transition temperature in comparison with the non-doped VO₂. In previous, a transition temperature of VO₂ decreases 23°C with 1 at. % tungsten solid solution in VO₂.⁴⁾ In this investigation, 1.8 at. % W was doped into VO₂, therefore; the transition temperature of the W doped specimen should be observed at 17.1°C. On the other hand, the transition temperature of the W-doped VO₂ powder using the tungsten pentaethoxide precursor was 40.4°C, and that of the tungsten chloride precursor was 31.2°C. For the both of the samples, the transition temperatures were higher than the calculated value from the reported value.⁴⁾ The transition temperature of the powder using the tungsten chloride as a starting precursor was much lower than that using the tungsten pentaethoxide. When the tungsten pentaethoxide was used as a starting material, to carry out hydrolysis of the VO₂ precursor, the tungsten pentaethoxide was also hydrolyzed by adding water. Thereby, tungsten source left for the out of the VO₂ precursor particle, and the transition temperature of the resulting VO₂ particle did not decreased. On the other hand, the tungsten chloride was used as a starting material, tungsten source was not hydrolyzed by adding water. Therefore, for this fabrication method, tungsten doping efficiency in resulting VO₂ powder was much higher using the tungsten chloride as precursor than the tungsten pentaethoxide.

4. Conclusion

Non-doped and W doped VO₂ nano-powders were successfully fabricated by aqueous method using H₂O₂, here, tungsten sources were tungsten pentaethoxide and tungsten chloride. For the final heat-treatment condition of 400°C for 4 h in H₂/Ar atmosphere, Non-doped and W doped VO₂ powders were obtained with the primary particle size of sub-tens nm. The transition temperature of the W-doped VO₂ powder using the tungsten pentaethoxide precursor was 40.4°C, and that of the tungsten chloride precursor was 31.2°C. Therefore, tungsten doping efficiency in VO₂ was much higher using the tungsten chloride as precursor than the tungsten pentaethoxide for this fabrication method.

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