

Thermochromic tungsten doped $\text{VO}_2\text{-SiO}_2$ nano-particle synthesized by chemical solution deposition technique

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Tungsten doped VO_2 coated SiO_2 nano-particles with mono-dispersion were fabricated by the chemical solution deposition method. The resultant W-doped VO_2 coated SiO_2 particle size was about 40 nm. The transition temperature of non-doped VO_2 coated SiO_2 particles was 68°C, and the transition temperature of 1.1 atomic% tungsten doped VO_2 coated SiO_2 particles was 52°C.

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1. Introduction

Vanadium dioxide (VO_2) is well known to undergo a reversible thermally induced metal-semiconductor transition around 68°C,¹⁾ resulting in great changes on its optical and electrical properties.²⁾⁻⁴⁾ The transition temperature is close to room temperature; therefore, VO_2 has a potential application of a smart window.²⁾⁻¹⁰⁾ The transition temperature T_t of VO_2 can be decreased close to room temperature by means of doping with other ions, such as tungsten.^{7),8),11)}

Previously, Suzuki et al. reported fabrication of size controlled SiO_2 nano-particles with mono-dispersion.¹²⁾ Using this mono-dispersed SiO_2 nano-particle, the authors fabricated VO_2 coated SiO_2 ($\text{VO}_2\text{-SiO}_2$) nano-powder with mono-dispersion,^{13),14)} and the transition temperature of the resulting $\text{VO}_2\text{-SiO}_2$ particles was confirmed as 68°C. The aim of this investigation is the fabrication of $\text{VO}_2\text{-SiO}_2$ mono-dispersed nano-particles with controlling the transition temperature by tungsten doping.

2. Experimental procedure

A suspension of mono-dispersed SiO_2 nano particles was prepared with tetra ethyl ortho silicate (TEOS) as a starting material, and the particle size of SiO_2 was controlled to 50 nm by changing TEOS and NH_3 concentration. The details of the synthesizing method were described in the previous report.¹²⁾

Subsequently, the $\text{VO}_2\text{-SiO}_2$ nano-particle was synthesized by coating the vanadium precursor specimen onto the above mentioned SiO_2 nano particle using vanadium isopropoxide solution. The details of a preparation procedure for the $\text{VO}_2\text{-SiO}_2$ hybrid nano-particle was described in the previous reports.^{13),14)} In order to dope tungsten to VO_2 , the procedure was carried out as described below.

Tungsten precursor solution was prepared by dissolving tung-

sten chloride into 2-methoxyethanol, followed by the partial hydrolysis with a controlled chemical modification method under the condition of RA = 2 (acetic acid to alkoxide ratio) and RW = 1 (water to alkoxide ratio). This tungsten precursor solution was mixed with the vanadium precursor solution, which was prepared by dissolving vanadium alkoxide into a mixed solvent of isopropanol and 2-methoxyethanol to form V-O-W bonding. Here, W/V mixing ratio was 0.92%. Then, this molecular-designed precursor solution was mixed and reacted with the mono-dispersed SiO_2 nano-particle to form the $\text{VO}_x\text{-SiO}_2$ hybrid sol. The resulting precursor tungsten doped $\text{VO}_x\text{-SiO}_2$ nano-particles were suction-filtrated and annealed at 200°C for 30 min. The resultant $\text{VO}_x\text{-SiO}_2$ particle was annealed at 600–700°C for 1 h in N_2 atmosphere. **Figure 1** depicts a sequence of the fabrication procedure. In this article, the authors described “ VO_x ”, since the vanadium valence x of the precursor specimens or unidentified specimens could not be known.

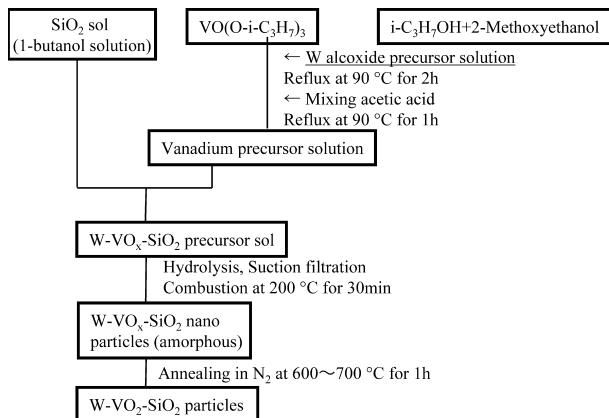


Fig. 1. Fabrication procedure of tungsten doped $\text{VO}_2\text{-SiO}_2$ nano-particles.

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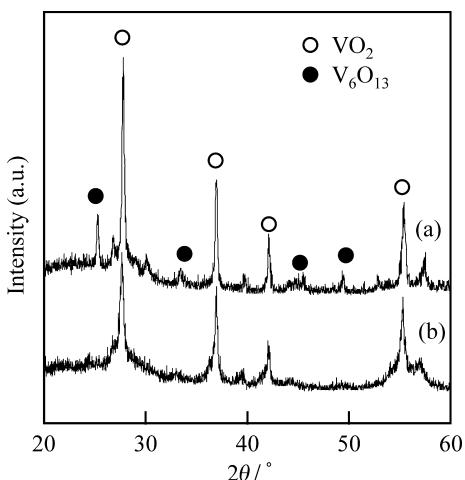


Fig. 2. XRD pattern for the resultant specimens of (a) non-doped and (b) 1.1% tungsten doped $\text{VO}_2\text{-SiO}_2$ particles.

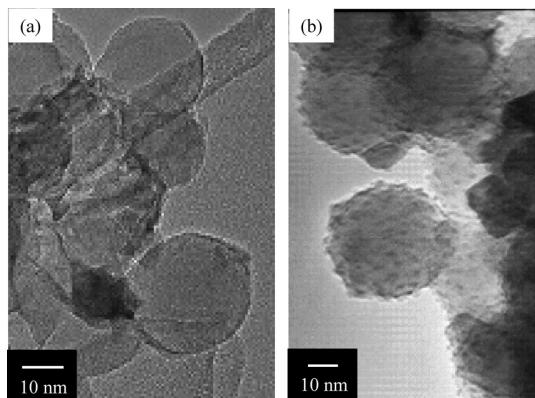


Fig. 3. TEM image of (a) the non-doped $\text{VO}_2\text{-SiO}_2$ particles and (b) 1.1% tungsten doped $\text{VO}_2\text{-SiO}_2$ particles.

The W/V elemental ratio of the resultant W-VO_x coated SiO_2 particle was evaluated by inductively coupled plasma (ICP) analysis (Spectro, Flame Modula-S), then the specimens were solved in hydrochloric acid. The crystal structure of the W-VO_x coated SiO_2 particle was characterized by X-ray diffraction (XRD) using Rigaku RINT 2200 with $\text{Cu K}\alpha$ radiation. Differential scanning calorimetry (DSC) was performed for the resulting powder using Rigaku thermoplus2 TG8120 with a rising temperature of $10^\circ\text{C}/\text{min}$.

3. Results and discussion

In order to confirm the tungsten quantity in the VO_2 , ICP measurement was carried out for the resultant specimens. When the W/V atomic mixed ratio was 0.92% in the precursor solution, the doped tungsten ratio to vanadium was 1.1% for the resultant W doped $\text{VO}_x\text{-SiO}_2$ particle. Hereinafter, in this investigation, the authors call these specimens 1.1% W doped $\text{VO}_x\text{-SiO}_2$ particle.

Tungsten non-doped and 1.1% W doped $\text{VO}_x\text{-SiO}_2$ particle were fabricated by the above mentioned technique, and the crystalline structure of the resultant $\text{VO}_x\text{-SiO}_2$ particle was confirmed by XRD measurement. Figure 2 shows the XRD patterns for the resulting specimens. The diffraction peaks of all the samples were assigned to a monoclinic VO_2 phase (JCPDS 33-1440) as the main phase, and the broad peak was attributed to an amorphous SiO_2 particle. For the non-doped specimen, V_6O_{13} phase was observed as a secondary phase.

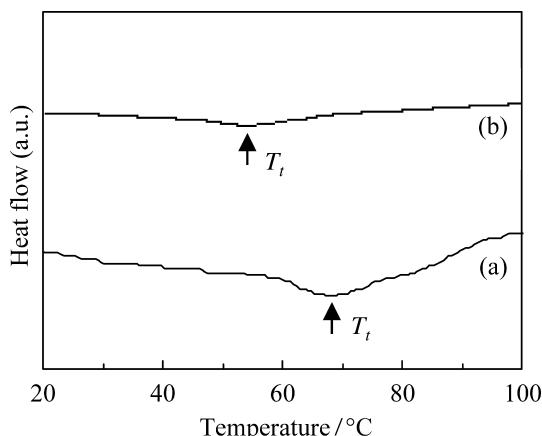


Fig. 4. DSC curves of (a) the non-doped and (b) the 1.1% tungsten doped $\text{VO}_2\text{-SiO}_2$ particles.

In order to confirm the particle size, TEM observation was carried out for the specimen. Figure 3 shows the bright field TEM image of the non-doped $\text{VO}_2\text{-SiO}_2$ and W doped $\text{VO}_2\text{-SiO}_2$ particles. The particle sizes of both of the resulting particles were 40 nm. The target size of the precursor SiO_2 particle was 50 nm, thus it was expected that the particle size of the resulting $\text{VO}_2\text{-SiO}_2$ particle was slightly smaller than the target size of 50 nm.

Vanadium dioxide VO_2 undergoes a metal-semiconductor transition at a critical transition temperature (T_t) of 68°C .¹⁾ In order to evaluate the transition temperature of the resultant tungsten doped or non doped $\text{VO}_2\text{-SiO}_2$ powder, DSC measurement was performed for the sample with a raising temperature of $10^\circ\text{C}/\text{min}$, as shown in Figure 4. An endothermic peak corresponds to the T_t of $\text{VO}_2\text{-SiO}_2$ or W doped $\text{VO}_2\text{-SiO}_2$ specimens. From the figure, the T_t of the tungsten non-doped and 1.1% W doped VO_2 coated SiO_2 particles were 68 and 52°C , respectively. The T_t of the non-doped specimen was very close to the reported value.¹⁾ On the other hand, the T_t of the 1.1% W doped specimen was 52°C , a decrease of 16°C . From this result, tungsten was solid-soluted to the coated VO_2 layer. In the previous reports, T_t of VO_2 decreased 20°C with 1 atomic% W doping.⁸⁾ The decreasing degree of T_t of the specimen fabricated by this method was slightly smaller than that of the previous study.⁸⁾ Hence, for the specimen in this study, it assumed that a part of tungsten segregated on the grain boundary or the particle surface.

4. Conclusion

The tungsten doped $\text{VO}_2\text{-SiO}_2$ powder was fabricated by the chemical solution deposition method. Using the tungsten and vanadium mixed precursor solution; W- VO_2 layer coated SiO_2 nano-particles can be obtained. The transition temperature T_t of the resulting 1.1% W doped $\text{VO}_2\text{-SiO}_2$ particles was 52°C , therefore; the T_t controlled $\text{VO}_2\text{-SiO}_2$ particles can be fabricated by this CSD method.

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