

1 Mist CVD of Vanadium Dioxide Thin Films with Excellent
2 Thermochromic Properties Using a Water-Based Precursor Solution
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1 Abstract

2 Mist chemical vapor deposition (mist CVD), which is capable of producing oxide films
3 over large areas at a high productivity and low cost, has been proposed as a fabrication
4 method for VO₂ thin films for smart windows. However, the thermochromic properties
5 of the VO₂ films previously prepared by mist CVD are not sufficient for application in
6 smart windows. In this study, to obtain a high-quality VO₂ film, we investigated the effects
7 of the solvent of the precursor solution on the resulting film in mist CVD. Films consisting
8 of a single phase of VO₂ were obtained when a water-based precursor solution was used.
9 In contrast, V₂O₃ films are formed when a methanol-based precursor solution is used. The
10 VO₂ film deposited from water solution exhibited high visible transmittance along with a
11 large change in the infrared transmittance with temperature change. The high quality of
12 the VO₂ film indicates that mist CVD is an effective method for the fabrication of VO₂-
13 based smart windows.

14

15 **Keywords:** Vanadium dioxide, Chemical vapor deposition, Smart window,

16 Thermo-chromic window, Mist CVD.

17

1. Introduction

Transition-metal oxides exhibit interesting electrical, optical and magnetic properties, which have attracted considerable attention as promising materials for devices used in energy fields, such as solar cell [1–5], batteries [6,7], sensors [8] and smart windows [9,10]. One of the most fascinating devices is the smart window that utilizes metal-insulator transition (MIT) of vanadium dioxide (VO_2). MIT of VO_2 occurs at about room temperature [11–18]. Both visible and infrared lights are transmitted through VO_2 below the phase transition temperature (T_c); however, above T_c , only visible light is transmitted [19,20]. Owing to this property of VO_2 , the windows coated with VO_2 block infrared light from entering when it is hot outside, while still allowing the transmission of visible light. Infrared radiation, which accounts for approximately 50% of the solar radiation energy, is the heat source that flows in buildings. Therefore, the control of the heat intake through VO_2 -based smart windows can effectively reduce the amount of energy consumed for air conditioning in a building.

VO_2 thin films can be fabricated by various methods such as the hydrothermal method [14,21,22], sol–gel method [23], pulsed laser deposition [24], sputtering [25,26], atomic layer deposition [27] and chemical vapor deposition (CVD) [28,29]. However, physical vapor deposition and conventional CVD require vacuum equipment, resulting in high process costs. Solution processes generally require a long reaction time of more than several hours for the fabrication of a VO_2 thin film, thus resulting in low productivity [14,21,22]. For practical mass production of VO_2 -based smart windows for buildings, a low-cost and highly productive fabrication process for VO_2 should be developed.

As a low-cost and highly productive deposition process, mist CVD, which is also referred to as aerosol-assisted CVD, has been proposed in previous studies [30–36]. In mist CVD, a mist of precursor solution atomized by ultrasonic vibrations is supplied to the substrate with a carrier gas, and thermal decomposition of this precursor mist results in a film formation on the substrate. Since no vacuum system is required in this process, highly productive and low-cost films can be produced. However, to date, no VO_2 thin films with sufficient performance have been obtained through mist CVD. The visible transmittance reported for VO_2 films fabricated through mist CVD is generally <40% at a wavelength of 550 nm, and the change in the infrared transmittance at a wavelength of 2500 nm below and above T_c is also as small as <30 percentage point (pp) [37–42]. For other oxide films, such as Ga_2O_3 and ZnO , high-quality films comparable to those obtained by vacuum processes are produced through mist CVD [31,36]. Therefore, it is expected that high-quality VO_2 films can also be obtained through mist CVD by exploring

1 the deposition conditions in further detail.

2 The optical properties of VO₂ are strongly affected by its stoichiometry.
3 Contaminating a VO₂ crystal with V³⁺ and V⁵⁺ deteriorates its visible transmittance and
4 infrared transmittance change [43–45]. Although films composed of a VO₂ single phase
5 were reportedly obtained through mist CVD using an ethanol solution of vanadyl
6 acetylacetonate (VO(acac)₂) as the precursor [39], further control of the stoichiometry of
7 the VO₂ film is necessary to enhance its properties.

8 In mist CVD, metal salt and the solvent of the precursor solution are the factors
9 that can significantly affect the crystal phase and physical properties of the resulting film,
10 because the latter can change the oxygen potential of the deposition atmosphere
11 [39,46,47]. A study on the oxidation of V₂O₃ to VO₂ reported that a water vapor
12 atmosphere is suitable for stabilizing vanadium in the tetravalent state [48,49]. Although
13 it was reported that mist CVD using a precursor solution composed of vanadium(III)
14 acetylacetonate (V(acac)₃) and water resulted in V₂O₃ [39], mist CVD using a
15 combination of tetravalent vanadium salt and water has not yet been investigated.

16 In this study, we perform mist CVD of vanadium oxide using a methanol solution
17 and a water solution of VO(acac)₂ to investigate the effect of the solvent on the crystal
18 phase of the resulting film. Furthermore, we demonstrate that VO₂ films with high visible
19 transmittance and a large infrared transmittance change by MIT are obtained through mist
20 CVD using a water-based precursor solution.

22 2. Experimental

23 2.1. Materials

24 The precursor solutions were prepared by dissolving bis(acetylacetonato)
25 vanadium oxide (VO(acac)₂; 98%, STREM) in distilled water or methanol at a
26 concentration of 0.010 mol/L. A quartz plate (25 mm × 25 mm; thickness = 0.7 mm) was
27 used as the substrate for mist CVD. Before use, the quartz substrate was washed
28 sequentially in acetone, distilled water and isopropanol in an ultrasonic cleaner and dried
29 by blowing air.

31 2.2. Mist CVD of VO₂

32 A custom-built hot-wall mist CVD system (Fig. 1) was used for the deposition of
33 the VO₂ films. The apparatus and deposition procedure of mist CVD in this study were

1 the same as those described in our previous report [40], except for the method of placing
2 the substrate. Herein, the substrate was placed on a holder installed at the center of the
3 tube furnace. The precursor mist was supplied to the substrate through N₂ flow for 10 min
4 and 20 min in the cases of using a methanol solution and water solution, respectively, as
5 the precursor. The durations for the film growth were determined by considering the
6 difference in the amount of mist generated from two different solvents. The flow rate of
7 the carrier gas and dilution gas was 3.0 L min⁻¹. After the mist supply was turned off, the
8 substrate was cooled to <100 °C in a furnace under N₂ gas flow.

10 2.3. Characterization of films

11 X-ray diffraction (XRD) measurements were performed with an X-ray
12 diffractometer (X'pertPRO-MPD, PANalytical) using Cu K α radiation to identify the
13 crystal phases of the obtained films. The incident angle was fixed at $\omega = 1.5^\circ$. The
14 morphology of the films was observed through field emission scanning electron
15 microscopy (SEM, JSM-6510LV, JEOL) and atomic force microscopy (AFM, Nano Navi
16 IIs Nanocute, SII Nano Technology). The cross-section of the film was observed after Au
17 sputtering using a sputter coater (SC-701, SANYUELECTRON). X-ray photoelectron
18 spectroscopy (XPS) was performed using a JPS-9030 spectrometer (JEOL) to analyze the
19 chemical states of the elements present in the obtained films. The details of the XPS
20 measurements are described in the Supplementary material. The electrical resistivity was
21 measured by a four-probe method using a source meter (2450 SourceMeter, KEITHLEY)
22 while changing the temperature of the films using a hot plate. The temperature of the film
23 was measured using a thermocouple attached to the film. The logarithmic derivatives of
24 the temperature dependence of resistivity ($d(\log R)/dT$) were extracted to evaluate the
25 phase transition temperature (T_c) and width of the hysteresis loop (ΔH). Further, T_c and
26 ΔH were defined using the temperature corresponding to the maximum of $d(\log R)/dT$ in
27 heating and cooling cycles (defined as T_{heating} and T_{cooling} , respectively) as follows.

$$28 \quad T_c = \frac{T_{\text{heating}} + T_{\text{cooling}}}{2} \dots (1)$$

$$29 \quad \Delta H = T_{\text{heating}} - T_{\text{cooling}} \dots (2)$$

30 For an obtained VO₂ films, the temperature dependence of the resistivity was also
31 measured by the van der Pauw method with a Hall effect measurement system
32 (ResiTest8300, Toyo Technica) to validate the accuracy of the measurement. The
33 difference in the values of log (R) obtained by the two methods at the same temperature
34 was typically less than 0.2. The transmittance spectra of the films were measured using a

1 UV-Vis-NIR spectrophotometer (SolidSpec-3700DUV, Shimadzu) at room temperature
 2 (~26 °C) and 100 °C using a heating stage (Mettler FP82 hotstage). The measurement
 3 error of the transmittance, which was mainly caused by baseline variation, was less than
 4 a few percent. The visible transmittance ($T_{lum}(\theta)$, 390–760 nm) and solar spectrum
 5 transmittance ($T_{sol}(\theta)$, 280–2500 nm) at a measurement temperature of θ were calculated
 6 using the following equations:
 7

$$8 \quad T_{lum}(\theta) = \frac{\int \varphi_{lum}(\lambda)T(\lambda, \theta)d\lambda}{\int \varphi_{lum}(\lambda)d\lambda} \dots (3)$$

$$9 \quad T_{sol}(\theta) = \frac{\int \varphi_{sol}(\lambda)T(\lambda, \theta)d\lambda}{\int \varphi_{sol}(\lambda)d\lambda} \dots (4)$$

10
 11 where $T(\lambda, \theta)$ is transmittance at wavelength λ and measurement temperature θ ,
 12 $\varphi_{lum}(\lambda)$ is the standard luminous efficiency function for the photopic vision of human
 13 eyes, $\varphi_{sol}(\lambda)$ is the solar irradiance spectrum for an air mass of 1.5 (corresponding to
 14 the sun standing 37° above the horizon). T_{lum} and ΔT_{sol} values of the obtained films were
 15 calculated using the following equations:

$$16 \quad T_{lum} = \frac{T_{lum}(26\text{ }^\circ\text{C}) + T_{lum}(100\text{ }^\circ\text{C})}{2} \dots (5)$$

$$17 \quad \Delta T_{sol} = T_{sol}(26\text{ }^\circ\text{C}) - T_{sol}(100\text{ }^\circ\text{C}) \dots (6)$$

20 3. Results and discussion

21 3.1. Appearance and phase of the films

22 Mist CVD was performed using a methanol or water solution of VO(acac)₂ to
 23 examine the effect of the solvent of the precursor solution on the resulting film. Fig. 2a
 24 and 2b show the appearance of the films deposited at 400–750 °C from methanol and
 25 water solutions, respectively. The colors of the samples show that the films were formed
 26 from methanol and water solutions at temperatures above 450 and 400 °C, respectively.
 27 The films deposited from methanol solution were gray or black, while the films deposited
 28 from water solution were brown, which is the color of monoclinic VO₂ reported in the
 29 literature [51,52].

30 Fig. 2c shows the XRD patterns of the samples before and after the deposition using
 31 methanol solution. After the deposition at 400 °C, the sample showed only a halo from

1 the quartz substrate, confirming the absence of film formation at 400 °C. In addition to
2 the halo from the substrate, the films deposited from methanol solution at 450–650 °C
3 showed XRD patterns corresponding to that of V₂O₃ (JCPDS 074-2037). The XRD
4 pattern of the film deposited at 750 °C did not match any reference pattern, which
5 indicates that an unidentified crystalline phase was formed at this temperature. Fig. 2d
6 shows the XRD patterns of the films deposited from water solution. The sample after the
7 deposition at 400 °C showed no diffraction peaks from the film (Fig. 2d), although the
8 formation of the film was visually confirmed (Fig. 2b), thereby suggesting that the film
9 was amorphous. The film deposited at 450 °C exhibited only a small peak at $2\theta = 11^\circ$;
10 thus, the phase of the film could not be identified. The films deposited at 550 and 650 °C
11 exhibited the XRD patterns of VO₂ (JCPDS 072-0514), in addition to a halo from the
12 substrates. Further, the films showed no additional peaks, thereby indicating that the films
13 were composed of a single phase of VO₂. The film deposited at 750 °C showed no XRD
14 peaks. However, the extension of the deposition time from 20 to 60 min resulted in the
15 formation of a film with the XRD patterns of VO₂ (Fig. S1). This indicates that the
16 deposition time of 20 min was significantly short to form a VO₂ film that is sufficiently
17 thick for producing a detectable XRD pattern. In general, when mist CVD is performed
18 at low temperatures, amorphous or unintended phases are formed because the
19 decomposition of the precursor and the crystallization of the deposited material do not
20 proceed sufficiently. At excessively high temperatures, the deposition rate tends to
21 decrease owing to the increase in the re-evaporation rate of the adsorbed precursor atoms
22 on the substrates [53–56]. The aforementioned results are consistent with these general
23 trends and indicate that the optimal temperature for the formation of VO₂ film through
24 mist CVD using a water solution was 550–650 °C. The reproducibility of the formation
25 of single-phase VO₂ films was confirmed by performing the deposition under the same
26 growth conditions several times. While VO₂ was obtained from water solution, V₂O₃ was
27 obtained from methanol solution at 550–650 °C. The vanadium precursor employed for
28 the film deposition was VO(acac)₂, which consists of V⁴⁺. The XRD results indicated that
29 the vanadium precursor was reduced to V³⁺ by methanol during the deposition process,
30 whereas the oxidation state of the precursor was unchanged during the deposition process
31 using water solution.

32

33 3.2. Composition and chemical states of films

34 XPS measurements were performed on the V₂O₃ and VO₂ films deposited at 650 °C

1 from methanol and water solutions, respectively, to analyze the chemical states of the
2 elements in the films. The survey spectra (Fig. S2a) indicate the presence of V, O and
3 contaminated C in both the films. Fig. 3a and 3c show the XPS spectra of the O1s and
4 V2p regions. The spectra were deconvoluted into several peaks assuming the presence of
5 oxygen with two different chemical states and vanadium with valence states ranging from
6 +3 to +5. As shown in Table S1, the peak positions for each chemical state resulting from
7 the deconvolution are in agreement with the reported peak positions [57–60]. The
8 deconvolution of the V2p peaks indicates the presence of V^{3+} , V^{4+} and V^{5+} in the V_2O_3
9 film and V^{4+} and V^{5+} in the VO_2 film. The presence of vanadium atoms with higher
10 oxidation numbers (V^{4+} and V^{5+} in V_2O_3 , and V^{5+} in VO_2) can be attributed to the surface
11 oxidation of the films exposed to ambient air [57,61]. No V^{3+} signal was observed in the
12 VO_2 film, which indicates that the precursor was not reduced during the deposition
13 process using water solution. This is consistent with the XRD pattern of the film (Fig. 2d).
14 It should be noted that Ar^+ etching, a well-known technique for removing the surface
15 oxidation layer, is not applicable for identifying the valence state of vanadium oxides
16 because it results in the reduction of vanadium [62].

17 In the O1s region (Fig. 3a and 3c), two peaks corresponding to O in the V–O bond
18 and O in the C–O, C=O and –OH bonds (denoted as O–C,H) were observed in both the
19 V_2O_3 and VO_2 films. In the C1s region (Fig. 3b and 3d), two peaks corresponding to C in
20 the C–C and C–O bonds were observed. The O–C, H, C–C and C–O peaks were not
21 observed after Ar^+ ion etching (Fig. S2b and S2c); thus, they were assigned to surface
22 contamination. However, another peak emerged at a binding energy slightly lower than
23 that of the C–C bond in the C1s region for the V_2O_3 film after etching (Fig. 3b). The
24 intensity of this peak remained almost unchanged even after increasing the etching time.
25 The peak position (283.6 eV) was close to that of C1s in V–C [63], and thus the detection
26 of this peak presumably indicates the presence of carbon atoms in the V_2O_3 crystal. In
27 contrast, the VO_2 film exhibited no peaks in the C1s region after Ar^+ ion etching. This
28 indicates that the VO_2 crystal deposited from water solution was not contaminated with
29 carbon, except for the surface contamination layer.

31 3.3 Morphology of films

32 Fig. 4 shows the morphology of the VO_2 films deposited at 550 and 650 °C from
33 water solution. The surface SEM images (Fig. 4a, 4b, 4e and 4f) revealed that both the
34 films were composed of densely deposited crystal grains with a diameter of several tens
35 of nanometers. The thicknesses of the films deposited at 550 and 650 °C were 56 and 49

1 nm, respectively (Fig. 4c and 4g). These are within the thickness range of 40–80 nm, where VO₂ films show a balanced combination of high visible transmittance and infrared switching efficiency [64]. The root-mean-square (RMS) roughness values of the surface of the films were determined to be 19 and 12 nm, respectively, through AFM (Fig. 4d and 4h). The film deposited at 650 °C was slightly smoother than that deposited at 550 °C.

3.4. Metal–insulator transition behavior

The temperature-dependent resistivities of the obtained films were measured to evaluate their phase transition behaviors. The resistivity of the VO₂ films deposited from water solution at 550 and 650 °C drastically decreased when heated above a certain temperature, and returned to its original value when cooled, thereby showing the typical MIT behavior (Fig. 5). In contrast, the films showing no XRD peaks of VO₂ (for instance, the film deposited at 450 °C) exhibited no MIT behavior. The resistivity of the V₂O₃ films deposited from methanol solution was nearly constant, independent of temperature, thereby confirming that no MIT occurred within the measured temperature range (Fig. S3).

The MIT characteristics of the VO₂ films, such as the magnitudes of resistivity change, phase transition temperature (T_c) and width of hysteresis loop (ΔH) determined from the resistivity–temperature curves are summarized in Table 1. T_c and ΔH values of the films were calculated from the $d(\log R)/d\theta$ curve (Fig. S4) using Equations (1) and (2), respectively. The obtained VO₂ films exhibited a resistivity change of more than two orders of magnitude. T_c and ΔH of the films were approximately 70 and 10 °C, respectively. These values are similar to those obtained by vacuum and solution processes [65,66], thus demonstrating that mist CVD is capable of producing VO₂ films with excellent phase transition properties.

Table 1 Resistivity change, transition temperature (T_c) and width of the hysteresis loop (ΔH) of the VO₂ film deposited at 550 and 650 °C using water solution.

Deposition temperature (°C)	Log($R_{30\text{ °C}}/R_{100\text{ °C}}$)	T_c (°C)	ΔH (°C)
550	2.1	63	11
650	2.4	73	13

3.5. Optical properties

Fig. 6 shows the transmittance spectra measured at 26 and 100 °C for the VO₂ film deposited at 650 °C from water solution. The near-infrared (NIR) transmittance of the VO₂ film decreased with an increase in temperature from 26 to 100 °C. The transmittance change was as large as 50 pp at a wavelength of 2500 nm. On the other hand, the visible transmittance was nearly constant or increased with the increasing temperature. The temperature-dependent salient change in the NIR transmittance is the typical MIT behavior of VO₂.

From the transmittance spectra, T_{lum} and ΔT_{sol} of the film were determined to be 48.1% and 5.2 pp, respectively. Gao et al. [13] reported that T_{lum} and ΔT_{sol} of VO₂ films are in the range of 10%–50% and 1–10 pp, respectively. The VO₂ film obtained in this study showed a high T_{lum} of 48.1% and a moderate ΔT_{sol} of 5.2 pp, as compared to the reported values.

Although T_{lum} and ΔT_{sol} are often used as performance indicators for smart windows, not all studies on VO₂ films have reported these values. In particular, the values for VO₂ films grown by mist CVD in previous studies are unavailable in most cases. Therefore, instead of T_{lum} and ΔT_{sol} , the transmittance at a wavelength of 550 nm ($T_{550 \text{ nm}}$) and the transmittance change at a wavelength of 2500 nm between the low and high temperatures ($\Delta T_{2500 \text{ nm}}$) [67–70] were used to compare the performance of the VO₂ films obtained in this study with those prepared through other processes. High $T_{550 \text{ nm}}$ and $\Delta T_{2500 \text{ nm}}$ are desirable for smart windows, as the former can save lighting, while the latter can effectively control heat flow [16].

Fig. 7 shows the values of $T_{550 \text{ nm}}$ and $\Delta T_{2500 \text{ nm}}$ for the non-doped VO₂ single-layer films prepared through various processes. $T_{550 \text{ nm}}$ and $\Delta T_{2500 \text{ nm}}$ of the VO₂ film obtained in this study were 47.8% and 57.6 pp, respectively. Compared to the values for previously reported mist-CVD-grown VO₂ films, $T_{550 \text{ nm}}$ of the film obtained in this study was nearly the highest and its $\Delta T_{2500 \text{ nm}}$ was significantly higher.

Some VO₂ films prepared by other processes have higher values of either $T_{550 \text{ nm}}$ or $\Delta T_{2500 \text{ nm}}$ than the VO₂ film obtained in this study; however, we did not find any studies reporting higher values of both the parameters. As many studies have pointed out, $T_{550 \text{ nm}}$ and $\Delta T_{2500 \text{ nm}}$ show a trade-off relationship [13], assuming the same quality of VO₂. For example, depending on the thickness of VO₂, one of these values will increase at the expense of the other. Therefore, among the reported VO₂ films, those with the data points ($T_{550 \text{ nm}}$, $\Delta T_{2500 \text{ nm}}$) located within the zone connecting the highest $\Delta T_{2500 \text{ nm}}$ and $T_{550 \text{ nm}}$ (the blue region) in Fig. 7 can be considered to be of similar high quality. The VO₂ film

1 obtained in this study was located within this zone, thereby exhibiting excellent smart
2 window properties comparable to those of high-quality VO₂ films fabricated by other
3 methods.

4 The enhancement in the quality of the mist-CVD-grown VO₂ films can be
5 attributed to the use of water as the solvent of the precursor solution; previous films were
6 formed from ethanol-based precursor solutions. According to previous studies, water
7 vapor atmosphere is suitable for stabilizing vanadium in the tetravalent state [48,49]. It is
8 known that the performance of smart windows decreases when V³⁺ and V⁵⁺ contaminate
9 VO₂ [43–45]. The excellent thermochromic properties of the VO₂ film obtained in this
10 study can be attributed to the suppression of V³⁺ and V⁵⁺ contamination during the
11 deposition by the water solution used in the mist CVD process. Note that, although V⁵⁺
12 was detected in the VO₂ film by XPS (Fig. 3a and 3c), it does not indicate the presence
13 of V⁵⁺ in the bulk of the film because XPS only detects the surface elements.
14
15

16 4. Conclusion

17 High-quality VO₂ films were fabricated through a mist CVD method, which can deposit
18 films at low cost and with high productivity. VO₂ and V₂O₃ films were obtained using
19 water-based and methanol-based precursor solutions, respectively. The obtained VO₂ film
20 showed a high visible transmittance and a large infrared transmittance change compared
21 to those of previously reported mist-CVD-grown VO₂ films. These values are similar to
22 those of high-quality VO₂ deposited by solution and vacuum processes, demonstrating
23 that mist CVD is a promising method for the fabrication of VO₂-based smart windows.
24 However, the VO₂ deposition temperature of 550–650 °C is significantly high for coating
25 on inexpensive soda-lime glass, which is commonly used for windows. In future work,
26 the deposition temperature of VO₂ is expected to be lower in mist CVD.
27

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32

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10 and Largely Enhanced Luminous Transmittance, *Langmuir.* 32 (2016) 759–764.
11 <https://doi.org/10.1021/acs.langmuir.5b04212>.
12
13

1 Figure captions

2 Fig. 1 Schematic illustration of a hot-wall mist CVD system.

3 Fig. 2 (a, b) Photographs and (c, d) XRD patterns of the substrates before and after film
4 deposition at 400–750 °C using (a, c) methanol and (b, d) water solutions of VO(acac)₂.

5

6 Fig. 3 (a,c) O1s and V2p spectra of the films deposited at 650 °C from (a) methanol and
7 (c) water solutions. (b,d) Deconvolution of C1s spectra for the films deposited at 650 °C
8 from the (b) methanol and (d) water solutions before and after Ar⁺ ion etching.

9

10 Fig. 4 Surface and cross-sectional SEM and AFM images of the VO₂ films deposited (a–
11 d) at 550 and (e–h) at 650 °C.

12

13 Fig. 5 Electric resistance of the films deposited from water solution at 550–650 °C as a
14 function of temperature.

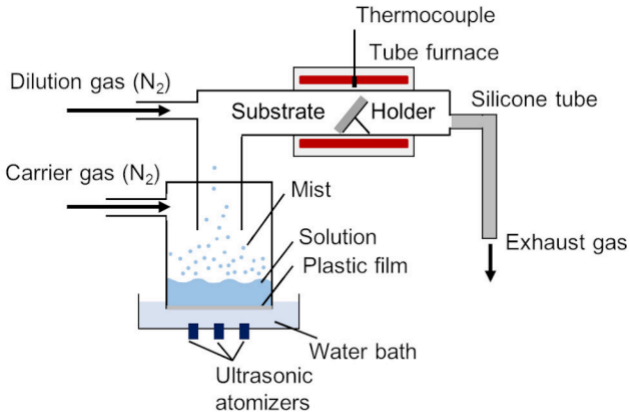
15

16 Fig. 6 Transmittance spectra measured at 26 and 100 °C for the VO₂ films deposited at
17 650 °C.

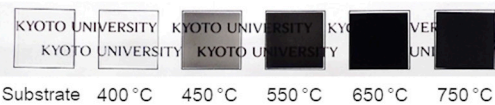
18

19 Fig. 7 Visible transmittance at a wavelength of 550 nm ($T_{550\text{ nm}}$) and infrared transmittance
20 difference at a wavelength of 2500 nm between low (26 °C) and high temperature states
21 (100 °C) ($\Delta T_{2500\text{ nm}}$) of VO₂ fabricated through vacuum processes (●) [15,16,57,61–78],
22 atmospheric pressure process (▼) [89], solution processes (◆) [64,70,90–94] and the
23 mist CVD method (★) [37–42].

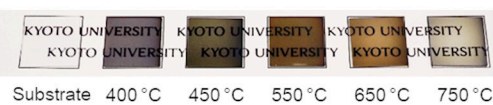
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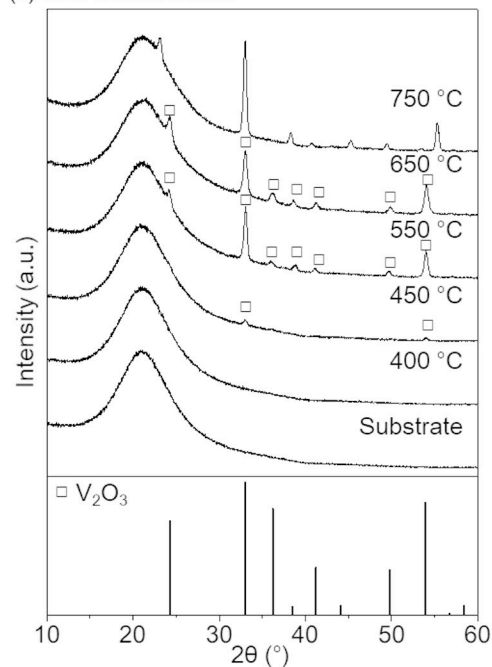
(a) Solvent: Methanol



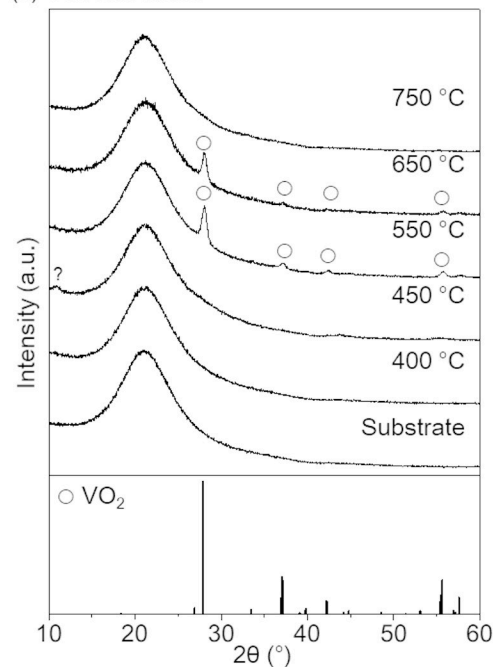
(b) Solvent : Water

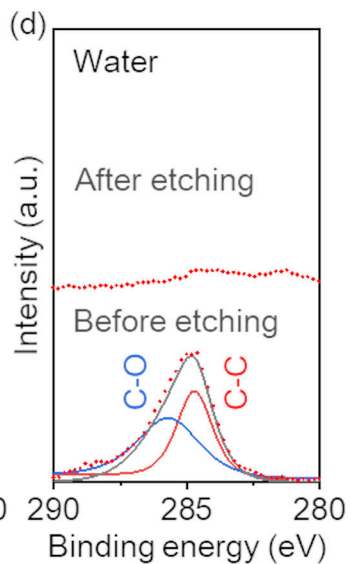
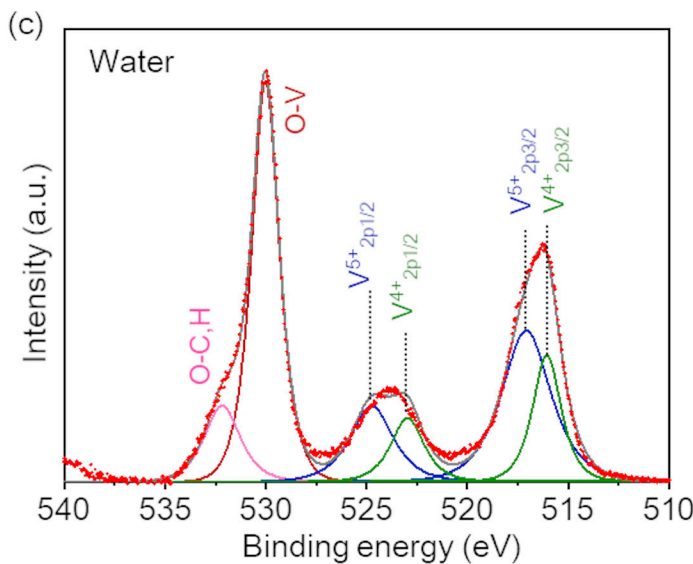
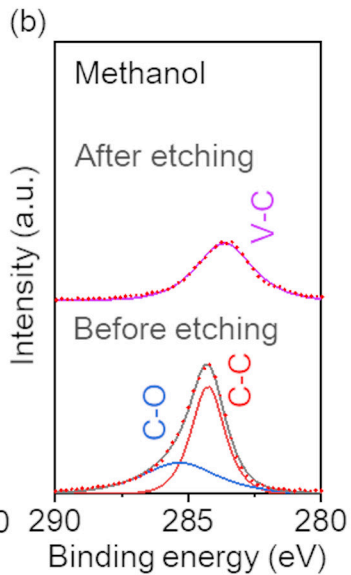
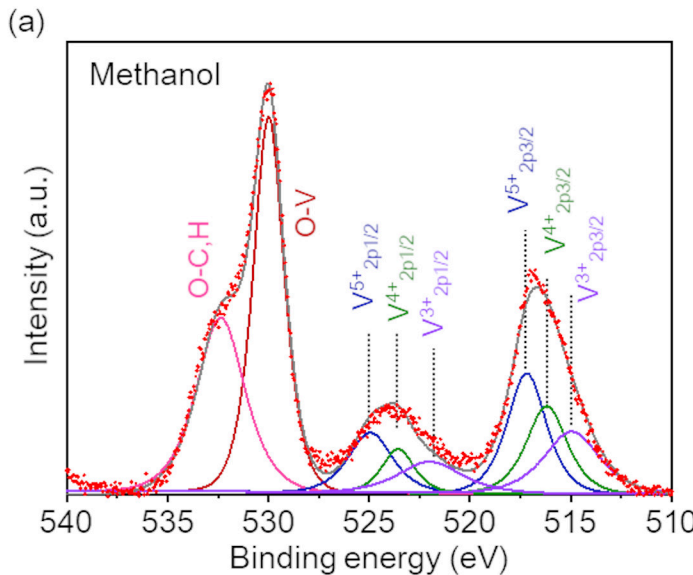


(c) Solvent: Methanol

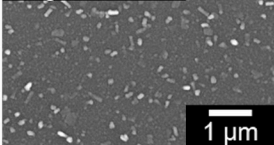


(d) Solvent: Water

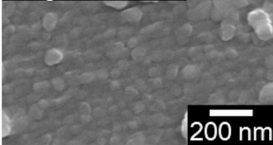




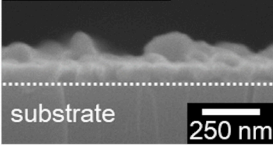
(a) 550 °C low magnification



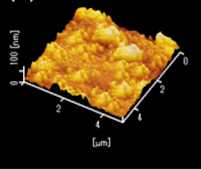
(b) 550 °C high magnification



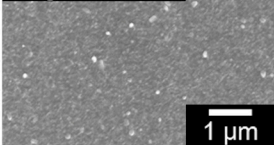
(c) 550 °C cross-section



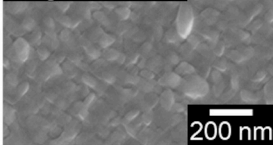
(d) 550 °C



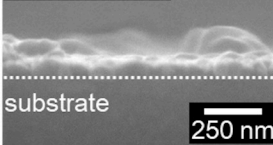
(e) 650 °C low magnification



(f) 650 °C high magnification



(g) 650 °C cross-section



(h) 650 °C

