

Optical Properties of a Thermo-chromic Film Fabricated with Nanoporous Monoclinic VO₂ Particles

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Abstract

Monoclinic vanadium dioxide (VO₂(M)) powder was synthesized by injecting air over a vanadium precursor powder at 190 °C for 1 h. The reversible metal-insulator phase transition was observed at 67 °C under heating conditions and at 61 °C under cooling conditions based on thermal and electrical property analysis. The VO₂(M) powder has a porous nanorod structure required to realize excellent optical performance. The VO₂(M) powder was mixed with an acrylic resin to fabricate VO₂ films on glass substrates. The films consisting of porous VO₂ particles exhibited a clear difference in optical performance as a function of the coating thickness. The glass with the thinnest coating of 33.5 nm showed a higher transmittance of the visible light (as high as 86 %) and inferior NIR switching performance (as low as 15 %). A thicker coating leads to decreased visible light transmittance and improved NIR switching performance; the glass with a coating thickness of 70 nm exhibited the best NIR switching performance of 31 %. However, the visible-light transmittance decreased and the NIR switching performance deteriorated significantly when the coating was significantly thick. This suggests that controlling the film thickness is a key factor for achieving excellent optical performance of the VO₂ film.

Keywords: Vanadium dioxide, thin film, optical transparency, thermo-chromic effect, NIR protection

I. Introduction

Vanadium dioxide (VO₂) is known to exhibit metal-insulator phase transition (MIPT) behavior involving rapid changes in its electric and optical properties at the transition temperature of 68 °C¹. VO₂ has a monoclinic structure below the transition temperature and is in an insulating state, where it exhibits properties that allow transmission of all Near-Infrared Radiation (NIR) of low energy without absorption. VO₂ has a tetragonal rutile structure above the transition temperature, and transforms into a metal state to absorb or reflect the NIR. The thermo-chromic property of VO₂ is useful for various technical applications²⁻⁴. In particular, it is a promising material for energy-saving smart windows via the transition switching function. VO₂ film may block the near-infrared (NIR) radiation accompanying the heat and prevent an increase in the room temperature in hot weather. Meanwhile, it can elevate the room temperature by allowing the NIR radiation to penetrate the coating layer in cold weather.

Various processes have been developed for the fabrication of thermo-chromic VO₂ films on glass substrates⁵⁻⁷. Guinneton *et al.* compared the optical responses of the films made either by means of RF sputtering or by nanoparticle dispersion. It was shown that efficient surface of coating layers is critical to the transmittance of mid-IR range. Manning *et al.* applied a thin film of vanadium oxide by means of chemical vapor deposition of vana-

dium tetrachloride and water. The phase deposited was dependent on the substrate temperature and the reagent mixing ratio. Kang *et al.* used the mixture of vanadium oxide precursor and poly(vinylpyrrolidone) to prepare thermo-chromic film. It was accompanied by another heat treatment at high temperature (600 °C) after spin coating.

However, these methods cannot be used for large-area fabrication. Furthermore, they involve complicated procedures and yield products with low visible-light transmittance and NIR-switching performance. A coating process using VO₂ powder was recently suggested. In this method, VO₂ is dispersed in a polymer solution for fabrication of a thin film of VO₂^{8,9}. This process has several advantages, such as convenient processing, ease of scaling up to coat large areas, and low cost.

In a previous study, optimal processing conditions were established for the synthesis of monoclinic VO₂ powder, using specific heat treatment conditions to prevent the oxidation of VO₂ to V₂O₅. A highly pure and crystalline VO₂(VO₂(M)) powder was obtained at room temperature after pyrolyzing a pure vanadium precursor powder¹⁰. The high-quality powder prepared under the described conditions shows a porous structure, which is necessary to realize excellent transmission as well as thermo-chromic properties.

In this study, high-quality VO₂(M) powder synthesized in the aforementioned process was used to prepare a VO₂-polymer solution to fabricate IR-blocking thermo-chromic thin films on glass substrates. The film was

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fabricated in a simple spin-coating process that allowed easy control over the film thickness on the glass plate. The change in the optical properties of the film was analyzed as a function of temperature and assessed according to the coating thicknesses. This was done to establish the fabrication conditions for the coating according to the intended application by analyzing the reversible thermochromic properties of the VO₂ (M) powder in the film.

II. Experimental Procedure

(1) Sample preparation

Ammonium metavanadate (NH₄VO₃ > purity 99.0 %, Daejung Chemicals & Metals Co., Ltd.) and ethylene glycol (C₂H₆O₂, Daejung Chemicals & Metals Co., Ltd.) were used as starting materials for the preparation of the vanadyl ethylene glycolate (VEG) precursor powder.

NH₄VO₃ powder (1 g) and ethylene glycol (20 ml) were mixed in a round-bottom flask and heated in an oil bath at 160 °C for 2 h with vigorous stirring. The purple-colored precipitate formed was rinsed thrice with acetone (C₃H₆O, Daejung Chemicals & Metals Co., Ltd.) and centrifuged. Then, the compound was dried in a vacuum desiccator to obtain the final product, the vanadium precursor powder. Subsequently, manual grinding was conducted for 10 min to increase the reaction surface area of the prepared vanadium precursor powder. The ground powder was then placed in an Al₂O₃ crucible and pyrolyzed under an air flux of 10 l/min at 190 °C for 1 h to obtain the VO₂ (M) powder.

The VO₂ (M) powder (0.1 g) was dispersed in 5 ml of isopropyl alcohol by means of ultrasonication. Acrylic resin (10 ml) was added into the suspension and mixed in a ball mill for 24 h. After milling, an appropriate volume of the VO₂-polymer solution was coated onto quartz glass plates by means of spin coating. The thickness of the thin films was controlled by varying the spin-coating speeds (2 500, 2 000, 1 500, 1 000, 500, and 250 rpm). Then, the spin-coated glass plates were dried in an oven for 6 h at 50 °C to obtain the thermochromic VO₂ thin films on glass plates.

(2) Characterization

The crystal structure of the VO₂ (M) powder was analyzed at variable temperatures with an X-ray diffractometer (D/max-2500, PC, Rigaku, Japan) equipped with a high-temperature attachment (SHT-1500/Rigaku, Japan). The oxidation state of vanadium was examined by means of X-ray photoelectron spectroscopy (XPS; PHI 5000 Versaprobe II, Ulvac-PHI, Japan). The microstructure of the VO₂ (M) powder was observed with field emission scanning electron microscopy (FE-SEM; JSM-2F, JEOL, Japan).

The reversible thermochromic properties of the synthesized powders were evaluated with a thermal analyzer (SDT Q600, TA instruments, USA). The measurements were carried out between 50 and 100 °C, and the heating speed was set to 1 K/min. The reversible changes in the electric properties of VO₂ (M) powder in accordance with the variable temperature were analyzed by means of an electric conductivity measurement system (RZ2001i, Ozawa Science, Japan) in the temperature range

of 25–110 °C range. The VO₂ (M) testing structure was prepared in the form of hexahedron measuring 30 × 30 × 100 mm.

The thicknesses of the VO₂ thin films coated on quartz glass plate were measured with an ellipsometer (Elli-SE UaM12, Ellipso Technology, Korea). The optical properties of the prepared VO₂ films were assessed as a function of temperature by means of a UV-Vis-NIR spectrophotometer (JASCO, V-770, Japan); the measurement temperature was controlled with a Peltier thermostated single cell holder (JASCO, ETCS-761, Japan). The wavelength range was set between 250 and 2 200 nm and the temperature before and after MIPT was set to 25 and 90 °C, respectively.

III. Results and Discussions

(1) Thermochromic properties of monoclinic VO₂ powder

Fig. 1 shows the phase analysis of the synthesized VO₂ powder. The peaks of single-phase VO₂ (M) are observed for the sample heat-treated at 190 °C for 1 h under an air flux of 10 l/min. No impurities or other crystalline peaks were observed in the XRD diffraction pattern. The pyrolysis was performed in air because oxygen is required to obtain the VO₂ (M) phase from the VEG precursor. If the precursor is overheated, VO₂ powder is oxidized to V₂O₅ by the peroxidation of the surface of the VO₂ (M) powder. Therefore, the heat treatment temperature and atmosphere were carefully controlled^{11–13}.

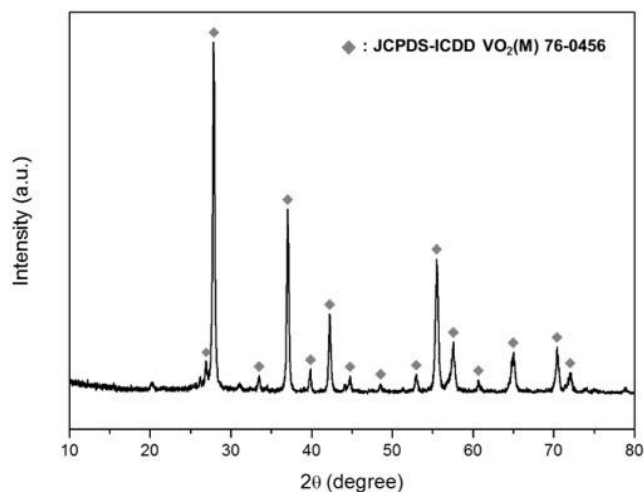


Fig. 1: XRD pattern of the synthesized VO₂ powder.

XPS was used to observe the chemical composition and binding state of the VO₂ (M) powder surface. The results are shown in Fig. 2. The peak fitting was performed with the Shirley method, and the presence of O₂, V, and C was confirmed. Fitting was performed for each element based on a C peak of 284.6 eV. The valence state of vanadium was recognized as V⁴⁺ around 515.8 eV and as V⁵⁺ around 517.2 eV in the V2p_{3/2} peak^{14,15}. The valence states of vanadium were quantitatively analyzed based on the areas of the fitted peaks. The results of the analysis indicate that the V⁴⁺ content was 50.58 % and the V⁵⁺ content was 49.42 %.

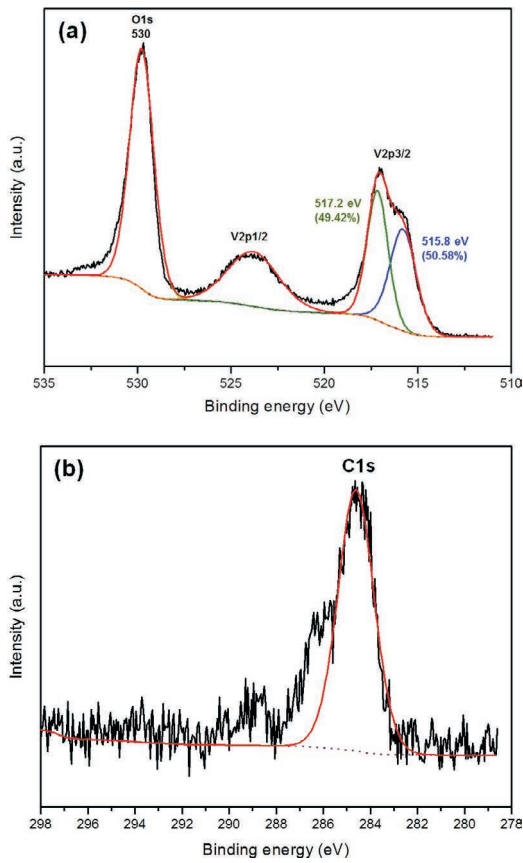


Fig. 2: High-resolution XPS profiles of (a) V2p3/2 and O1s, (b) C1s.

The MIPT phenomenon in the synthesized VO₂ (M) can be verified by the XRD patterns acquired as a function of temperature. As shown in Fig. 3(a), when the temperature increases, the monoclinic diffraction peak corresponding to the (011) plane shifts to a lower angle that corresponds to the tetragonal rutile diffraction peak of the (110) plane. Moreover, as shown in Fig. 3(b), the monoclinic diffraction peak corresponding to the (211) plane clearly changes to the tetragonal rutile diffraction peak (i.e. the peak shifts to a higher angle) corresponding to the (211) plane with an increase in the temperature.

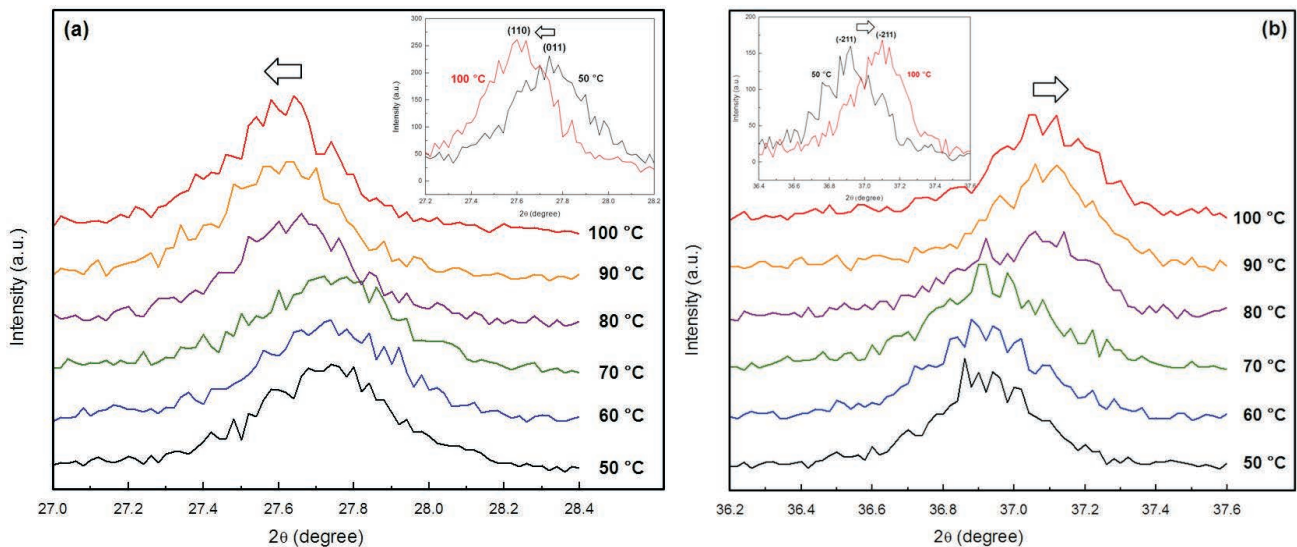


Fig. 3: XRD pattern of the prepared VO₂(M) powder as a function of temperature (inset: shift in the diffraction angle of (a) the main peak and (b) a secondary peak of VO₂ with temperature increase).

This result is consistent with that of a prior study on the MIPT phenomenon, in which corresponding changes in the diffraction peak positions were observed in the XRD pattern in respect of temperature under similar experimental conditions 11,16.

Fig. 4 shows the microstructure of the prepared VO₂ (M) powder. At low magnification, the VO₂ (M) powder (Fig. 4(a) & (b)) exists as nanorods with different thicknesses and lengths, which form a mesh-like structure with lengths in the range of several micrometers. At higher magnifications, the nanorod microstructure (Fig. 4(c)) is seen to comprise spherical nanoparticles (diameter between 20 and 50 nm) that are irregularly agglomerated and form nanorods in the range of tens to hundreds of nanometers and micrometers.

Fig. 4(d) shows the FE-TEM images of the VO₂ (M) nanoparticles. Numerous nanopores are formed due to irregularly agglomerated VO₂ (M) nanoparticles. It has been reported that these nanopores are generally smaller than 10 nm; this size enables the transmission of light, because it is within the range that does not scatter visible light 17,18. The spherical nanoparticles and nanopores observed here are known to be characteristic of VO₂ (M) particles.

DSC thermal analysis was conducted to observe the reversible MIPT phenomenon of the VO₂ (M) powder as a function of temperature change. As seen in the DSC thermogram in Fig. 5, during the heating cycle, an increase in the heat flow in the VO₂ (M) powder begins at ~67 °C, with a peak at ~83 °C. This suggests that the endothermic reaction is accompanied by the phase transition of the structure from monoclinic to the tetragonal rutile phase. The opposite phase transition begins at ~61 °C during the cooling cycle, with a peak at ~55 °C. This implies that the endothermic process is accompanied by the reversible metal-insulator phase transition from the tetragonal rutile structure to the monoclinic one. The delayed endothermic peak during the cooling process is attributed to the lower cooling rate under ambient cooling conditions.

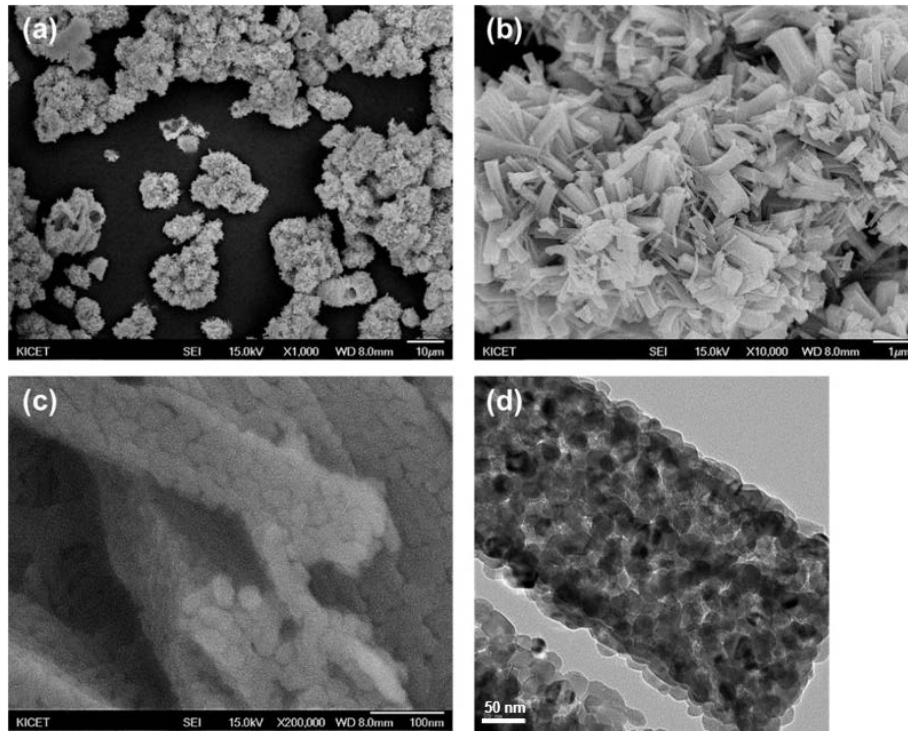


Fig. 4: (a-c) FE-SEM images and (d) an FE-TEM image of the as-prepared VO₂ (M) powder.

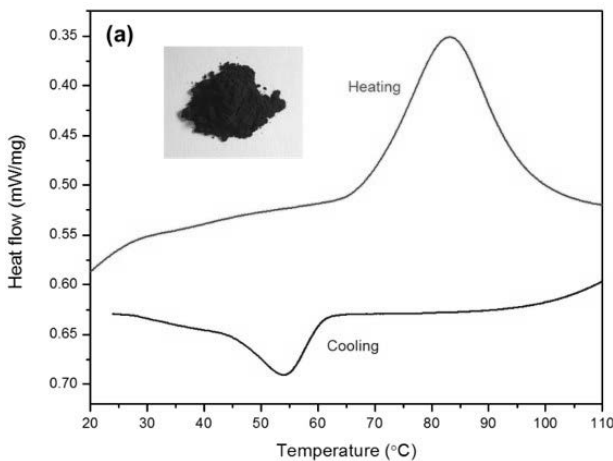


Fig. 5: DSC thermogram of the VO₂ (M) powder.

Fig. 6 shows the change in the electrical conductivity of VO₂ (M) powder as a function of temperature. The VO₂ (M) powder shows insulating properties, with the electrical conductivity being close to 0 (zero) at room temperature. However, upon heating, the conductivity starts to increase at ~67 °C. The conductivity increases significantly with increasing temperature, until the temperature of ~90 °C is reached, and then gradually stabilizes. The conductivity at the high temperature represents metallic properties. The conductivity begins to slowly decrease during the cooling cycle and reduces significantly at ~60 °C. The more gradual change during the cooling cycle than that during the heating one is probably caused by the decreased cooling rate under ambient cooling conditions. Furthermore, hysteresis of 18 °C is observed between the heating and cooling cycles. The result is consistent with the endothermic and exothermic reactions and corresponds to the phase transition observed during the DSC analy-

sis. Thus, we confirm the rapid change in the conductivity, which in the case of the VO₂ (M) powder, is accompanied by MIPT.

Acrylic binder, which is the matrix in VO₂ thin films, has a transmittance of 92–98 % and a refractive index of 1.48–1.50 n, and is a suitable material for visible light transmittance. Furthermore, the nanoporous structure of the VO₂ powder contributes to excellent visible light transmission in thick films. In actual scenarios, appropriate visible light transmittance is required for windows. However, to achieve a distinct NIR switching efficiency, films must have a certain minimum thickness.

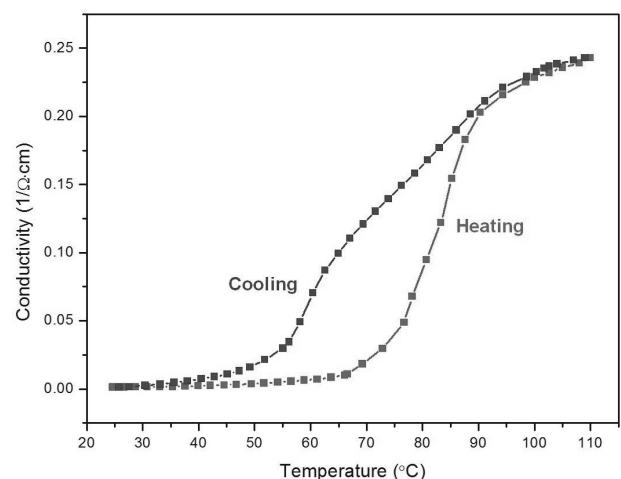


Fig. 6: Temperature-dependent conductivity of the as-prepared VO₂ (M) powder.

(2) Optical performance of the thermochromic VO₂ film

The transmittance spectrum of the thermochromic VO₂ thin film applied on a glass plate was recorded. Fig. 7 shows

the transmittance spectra of the VO₂ film on the glass plate before and after the MIPT temperature as a function of the coating thickness. Table 1 summarizes the results. The coating thickness was varied from 33.5 to 129 nm.

The transmittance of the visible light calculated by the integration of the spectrum at temperatures before and after MIPT (T_{int}^{25} , T_{int}^{90}) clearly increased as the film became thinner. The film with a thickness of 33.5 nm showed high transmittances of 86.37% and 85.40% at temperatures before and after MIPT, respectively, and the film with a thickness of 129 nm showed low transmittances of 5.84% and 7.65% at temperatures before and after MIPT, respectively. The transmittances

before and after MIPT (T_{700nm}^{25} , T_{700nm}^{90}) at 700 nm, the visible light wavelength, showed the same trend. In contrast, the switching performance before and after the MIPT temperature in the NIR region ($\Delta T_{2000nm}^{25-90}$) improved as the film thickness increased. However, if the coating was significantly thick, a low visible light (T_{int}^{25} , T_{int}^{90}) transmittance and inferior switching performance was observed in the NIR region ($\Delta T_{2000nm}^{25-90}$) at temperatures before and after MIPT. These results suggest that the exceptional visible light transmittance and NIR switching performance is lost and the film becomes a static absorber when its thickness exceeds a certain value.

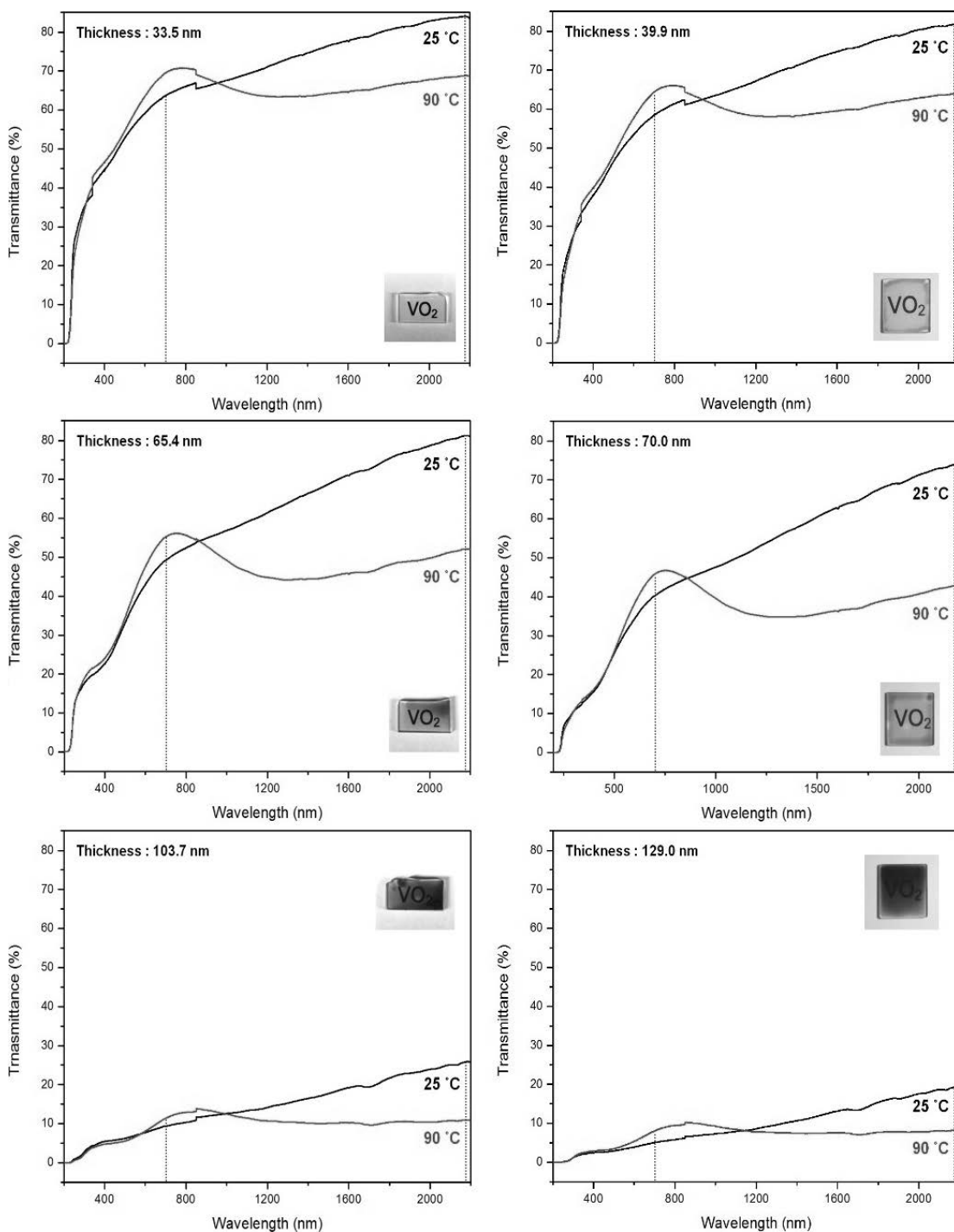


Fig. 7: Thickness-dependent transmittance spectra of VO₂ films. Dotted lines indicate the wavelengths of 700 and 2 200 nm.

Table 1: Optical performance of VO₂ thin films of various thicknesses

Film Thickness	$T_{700\text{nm}}^{25}$	$T_{700\text{nm}}^{90}$	T_{int}^{25}	T_{int}^{90}	$\Delta T_{700\text{nm}}^{25-90}$	$\Delta T_{2000\text{nm}}^{25-90}$
33.5 nm	63.62	69.49	86.37	85.40	5.87	14.86
39.9 nm	58.43	64.33	77.49	74.27	5.90	17.67
65.4 nm	49.17	55.18	59.89	60.55	6.01	28.98
70.0 nm	40.20	45.78	47.28	47.90	5.58	31.01
103.7 nm	9.36	11.34	11.52	11.38	1.98	14.93
129.0 nm	5.06	8.11	5.84	7.65	3.06	11.19

The differences in the optical properties at temperatures before and after MIPT at the visible light wavelength of 700 nm ($\Delta T_{700\text{nm}}^{25-90}$) are relatively small for all the samples, as shown in Table 1. However, the differences in the optical properties at temperatures before and after MIPT at the NIR wavelength of 2 200 nm ($\Delta T_{2200\text{nm}}^{25-90}$) are relatively large. This result shows that MIPT is accompanied by rapid changes in optical properties in the NIR region rather than in the visible regions. These characteristics are suitable for smart windows with excellent NIR switching performance. The selective control of the optical properties by varying the film thickness is a key factor in fabricating a smart window with excellent optical properties. The maximum NIR switching performance ($\Delta T_{2000\text{nm}}^{25-90}$) of the film fabricated in the study is ~31 %, which is comparable to the maximum NIR switching performance obtained in previous studies (30 %) ¹⁹. Thus, VO₂ films can be used as an energy-saving smart window material in which the optical properties can be adjusted based on the intended use.

$T_{700\text{nm}}^{25}$ and $T_{700\text{nm}}^{95}$ are the measured transmittances for the 700 nm wavelength at 25 °C and 90 °C, respectively. T_{int}^{25} and T_{int}^{90} are the calculated visible transmittances at the same temperatures based on the transmittance spectra.

IV. Conclusions

Herein, we have presented the fabrication of thermochromic VO₂ thin films via an inexpensive and facile process using high-quality VO₂ (M) powder synthesized according to processing conditions established in a prior study. First, a pure VEG precursor powder was synthesized as a precursor to the VO₂ (M) powder. Then, pure crystalline VO₂ (M) powder was obtained by pyrolyzing the VEG powder at 190 °C for 1 h at an air flux of 10 l/min.

The change in the reversible crystalline transition was verified at the transition temperature by analyzing the crystallinity of VO₂ (M) with XRD. Further, the reversible MIPT phenomenon was observed at 67 °C under heating conditions and at 61 °C under cooling conditions by means of thermal analysis. The accompanying electrical properties were also verified.

Observation of the microstructure of the prepared VO₂ (M) powder revealed the presence of nanorods with a porous structure formed by the agglomeration of 20–50-nm spherical nanoparticles. The observed porous struc-

ture is an important factor in realizing the optical properties of the material.

The VO₂ (M) powder was mixed with a polymer to fabricate VO₂ films. The optical performances of the thin films varied markedly with coating thickness. The glass with the thinnest coating of 33.5 nm showed a higher transmittance for visible light (as high as 86 %) and an inferior NIR switching performance (as low as 15 %).

The results suggest that a thicker coating leads to decreased transmittance of visible light and increased NIR switching performance; the glass with a 70-nm-thick coating showed the best NIR switching performance (31 %). However, both the visible light transmittance and NIR switching performance decreased drastically when the coating thickness increased significantly.

Acknowledgements

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