Enhanced Visible Transmittance of Thermochromic VO\textsubscript{2} Thin Films by SiO\textsubscript{2} Passivation Layer and Their Optical Characterization

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Abstract: This paper presents the preparation of high-quality vanadium dioxide (VO\textsubscript{2}) thermochromic thin films with enhanced visible transmittance ($T_{\text{vis}}$) via radio frequency (RF) sputtering and plasma enhanced chemical vapor deposition (PECVD). VO\textsubscript{2} thin films with high $T_{\text{vis}}$ and excellent optical switching efficiency ($E_{\text{os}}$) were successfully prepared by employing SiO\textsubscript{2} as a passivation layer. After SiO\textsubscript{2} deposition, the roughness of the films was decreased 2-fold and a denser structure was formed. These morphological changes corresponded to the results of optical characterization including the haze, reflectance and absorption spectra. In spite of SiO\textsubscript{2} coating, the phase transition temperature ($T_c$) of the prepared films was not affected. Compared with pristine VO\textsubscript{2}, the total layer thickness after SiO\textsubscript{2} coating was 160 nm, which is an increase of 80 nm. Despite the thickness change, the VO\textsubscript{2} thin films showed a higher $T_{\text{vis}}$ value ($\lambda$ 650 nm, 58%) compared with the pristine samples ($\lambda$ 650 nm, 43%). This enhancement of $T_{\text{vis}}$ while maintaining high $E_{\text{os}}$ is meaningful for VO\textsubscript{2}-based smart window applications.

Keywords: VO\textsubscript{2}; thermochromic; SiO\textsubscript{2} passivation

1. Introduction

For improved design and practicality, the exterior of many buildings has been changed into full-window constructions in recent years \cite{1}. However, such window architecture systems lead to more cooling and heating energy loss in the summer and winter seasons. One of the best ways to solve this problem is vanadium dioxide (VO\textsubscript{2}) based thermochromic smart windows. VO\textsubscript{2} is a well-known material that undergoes a fully reversible metal-insulator phase transition (MIT) at 68 °C accompanied by structural changes from a monoclinic (semiconductor with high IR transparency) to a rutile (metallic form with IR reflection) phase \cite{2,3}. These unique properties make VO\textsubscript{2} a promising material for application in energy saving smart windows with solar heat control \cite{4-8}. However, for practical applications, several challenges must be improved: the transition temperature ($T_c$) is too high to apply on real field; the weak optical contrast in the IR region; the luminous transmittance ($T_{\text{lum}}$) is less than ~40% for films; the unfavorable color (yellow/brown). Up to now, there have been many efforts to improve the above issues \cite{9,10}. More than anything, low visible transmittance ($T_{\text{vis}}$) is the most critical drawback of VO\textsubscript{2} for applications in glazing systems. The low $T_{\text{vis}}$ originates from strong innerband and interband absorption in the short-wavelength range for both the metallic and semiconductive states \cite{11,12}. To enhance the $T_{\text{vis}}$, band gap adjustment by doping has been attempted. Zhou et al. reported on the preparation of Mg-doped VO\textsubscript{2} nanoparticles via hydrothermal synthesis \cite{13}. By controlling the Mg doping contents, they demonstrated the absorption edge of VO\textsubscript{2}.
particles with a blue-shift from 490 to 440 nm at a Mg content of 3.8 at %, representing a widened optical band gap from 2.0 eV for pure VO$_2$ to 2.4 eV with 3.8 at % doping. Similar research was reported by Chen et al., who fabricated Ti-doped VO$_2$ nanoparticles with successful improvement of $T_{\text{vis}}$ by up to 53% via a hydrothermal process [14]. Zhou et al. reported another approach to improve the $T_{\text{vis}}$ of VO$_2$ thin films by designing VO$_2$ thin films with a periodic porous structure [15]. These periodic porous thermochromic VO$_2$ thin films were fabricated via a colloidal lithography approach and exhibited a high $T_{\text{vis}}$ (81% maximum). However, in spite of the significant enhancement of the $T_{\text{vis}}$, the optical switching efficiency ($E_{\text{os}}$) of previously reported VO$_2$ thin films is still lower than that of traditional low-emission glass. Moreover, it is difficult to control the stoichiometry of a vanadium-oxygen system using the colloidal lithography approach because organic residues from the colloid might influence the valence of VO$_2$ as well as the phase transformation during the annealing process. VO$_2$-based multi-layered structures such as VO$_2$/ZrO$_2$ double layers [16] and TiO$_2$/VO$_2$/TiO$_2$ triple layers [17] are the most effective solutions to the above problems. These antireflective layers including ZrO$_2$ and TiO$_2$ can protect VO$_2$ from oxidation and provide new functions such as photocatalysis in addition to improving the visible transmittance. However, to date, the reported results on applying an anti-reflective layer have been based on more complex procedures or solution processes for which additional annealing is essential. Thus, the reported VO$_2$ thin films contain low $E_{\text{os}}$ originating from inconsistent stoichiometry due to additional annealing or other procedures [18,19].

In this work, high-quality VO$_2$ thermochromic thin films with significantly enhanced $T_{\text{vis}}$ were prepared by applying a SiO$_2$ layer using plasma enhanced chemical vapor deposition (PECVD). This SiO$_2$ layer deposited by the PECVD method has advantages such as the lack of additional post-annealing processes. Thus, damages from oxidation or reduction, which can influence the crystallinity of VO$_2$, do not occur during SiO$_2$ deposition. In addition, high uniformity and reproducibility underscore the attractiveness of PECVD. This paper also explains how the improvement of $T_{\text{vis}}$ was identified through optical analysis.

2. Materials and Methods

2.1. SiO$_2$/VO$_2$ Thin Film Preparation

VO$_2$ thin films were prepared by RF magnetron sputtering with VO$_2$ ceramic targets (Taewon Scientific, Seoul, Korea, 99.9%, 2 inch). Before deposition, the Eagle XG glass (Corning, New York, NY, USA, 2.5 × 2.5 cm$^2$) used as a substrate was cleaned ultrasonically with hydrochloric acid (1 M) and Ethanol, then was subsequently dried with N$_2$. The vacuum chamber was evacuated to $1.2 \times 10^{-5}$ Torr, and Ar gas was introduced with 150 sccm. The RF power, working pressure, and distance of the target to the substrate were maintained at 180 W, 46 mTorr and 40 mm, respectively. The deposition time for all samples was fixed at 15 min. The prepared VO$_2$ thin films were crystallized via post-annealing under vacuum conditions (10 mTorr) at a temperature of 575 °C for 4 h with a heating rate of 30 °C/min. The SiO$_2$ layer was deposited by PECVD onto the as prepared VO$_2$ thin films under a working pressure of 200 mTorr. Hexamethydisilazane (HMDSN) was used as a precursor and a thickness of 80 nm was achieved for the SiO$_2$. More detail procedure and conditions of PECVD is described elsewhere [20].

2.2. Characterizations

The surface morphologies of the films were determined using FE-SEM (JEOL, JSM-7100 F, Tokyo, Japan) and AFM (PARK system, XE-100, Suwon, Korea). Crystallization information for the films was determined using X-ray diffraction (XRD) (Bruker D8 Advance system, Billerica, MA, USA) with Cu Kα radiation (λ = 1.5416 Å). Diffraction patterns were collected for 2θ values between 10° and 80° with a 2° glancing angle, and scanned at a rate of 5°/min. The phases present were identified by comparing the peak intensities and their corresponding 2θ values to various vanadium oxide standards using the software PCPDFWIN ver. 2.1 (JCPDS-ICDD, Philadelphia, PA, USA). Raman spectra were collected with a confocal Raman microscope (Witec, ALPHNA 300 M, Ulm, Germany) based on the 532 nm CO$_2$
laser. The optical and thermochromic properties of the films were measured at the temperature range between 20 to 100 °C by using a UV-vis-NIR spectrometer (SHIMADZU, UV-3600, Kyoto, Japan) equipped with handmade heating units including a PID temperature controller. For all samples, the integral visible transmittance ($T_{\text{lum}}$, 390–830 nm) and solar transmittance ($T_{\text{sol}}$, 280–2500 nm) was obtained based on the earlier publication [21].

3. Results and Discussion

Figure 1 shows the SEM and AFM images of surface morphologies for the pristine VO$_2$ and SiO$_2$/VO$_2$ thin films. For the pristine VO$_2$, the mean grain size and film thickness were around 150 nm and 80 nm, respectively. Moreover, the clearly formed grain boundary was attributed to the surface roughness value of 11.87 nm. On the other hand, changes in the surface morphology of the films with denser and smoother grain boundaries, including those with 160 nm of total thickness, were observed after SiO$_2$ coating. In addition, an average roughness value of 4.91 nm was obtained, which is a 2-fold decrease compared to pristine VO$_2$. The obtained results suggest that the empty space between the grain boundary of pristine VO$_2$ was filled with SiO$_2$ during the PECVD process.

![SEM and AFM images of VO$_2$ and SiO$_2$/VO$_2$ thin films.](image)

Figure 1. SEM and AFM images of VO$_2$ (a–c) and SiO$_2$/VO$_2$ (d–f) thin films. The average roughness of the samples was (c): 11.87 nm and (f): 4.91 nm.

Figure 2 shows the XRD data and Raman spectra for each sample. The XRD pattern showed weak signal intensities for the crystallite, resulting from the short-range ordered nanocrystallinity and thinness of the films. The broad shoulder within 15°–40° is due to the contribution of the amorphous SiO$_2$ substrate [22]. A peak at 27.8° that can be ascribed to the (011) plane of monoclinic VO$_2$ (JCPDS no. 82-0661) was observed in the pristine VO$_2$ thin films. For the SiO$_2$/VO$_2$ thin films however, decreased peak intensity was observed, originating from disruption of the thickly covered SiO$_2$ film. Most importantly, no clear diffraction peaks for other vanadium oxides were observed. Raman models corresponding to VO$_2$ (M) appeared in each sample with peaks centered at 135, 192, 225, 263, 308, 338, 392, 440, 499, and 617 cm$^{-1}$ [23]. The change in Raman shifts for the films was within the measurement accuracy (±2 cm$^{-1}$). For pristine VO$_2$ thin film, peaks from other types of vanadium oxides were not observed. Moreover, the peaks around 195 cm$^{-1}$ and 225 cm$^{-1}$ corresponded to A$_{g}$ symmetry vibrational modes, which disappeared in VO$_2$ (R) [24,25]. These two vibrational modes play a decisive role in the structural transition of VO$_2$. Thus, the appearance of strong peaks suggests high optical switching characteristics. After SiO$_2$ coating, however, a broad peak around 480 cm$^{-1}$ attributed to amorphous SiO$_2$ was observed with a moderate signal to noise ratio while the initial
peaks corresponding to VO₂ (M) remained. In other words, SiO₂ coating via PECVD does not affect the crystallinity of VO₂ thin films. The corresponding evidence is shown in Figure 3b,c. The hysteresis loop at 2000 nm was obtained from the optical transmittance of each sample as a function of temperature, and a plot of d(Tr)/d(T)&T was obtained from one peak with a well-defined maximum. Each of the d(Tr)/d(T)&T curves were analyzed with a Gaussian function using the single peak fitting module in Origin pro 8.0 software (Originlab, Washington, DC, USA). Distinguishable changes in Tc and hysteresis width, which are closely related to the crystallographic orientation [26], were not observed except for a slight decrease in transmittance.

**Figure 2.** X-ray diffraction (XRD) (a) and Raman spectra (b) of VO₂ and SiO₂/VO₂ thin films.

**Figure 3.** Transmittance spectra (a); hysteresis loops at 2000 nm (b) as well as corresponding d(Tr)/d(T)&T curve (c) for pristine VO₂ and SiO₂/VO₂ thin films. The inset images in (a) correspond respectively to photographs of the pristine VO₂ film (left) and VO₂/SiO₂ film (right). In (a), solid line measured at 25 °C, dashed line at 100 °C.
The optical analysis results for each sample are shown in Figure 3a. Transmittance results demonstrate the thermochromic properties of each sample measured at 20 °C (solid line) and 100 °C (dashed line). The E$_{\text{os}}$ of the SiO$_2$/VO$_2$ films was 51.7%, which is slightly lower compared with pristine VO$_2$ thin films (57.1%), but the difference is not significant. The SiO$_2$/VO$_2$ thin films showed a significantly enhanced T$_{\text{vis}}$ value ($\lambda_{650\,\text{nm}}$, 58%) compared with the pristine samples ($\lambda_{650\,\text{nm}}$, 43%).

In addition, the optical band gap graph (Figure 4d) shows the absorption edge toward the blue region and a decrease in absorbance after SiO$_2$ coating. Though the SiO$_2$/VO$_2$ film is thicker, it exhibited higher T$_{\text{vis}}$ than the pristine VO$_2$. This enhancement of T$_{\text{vis}}$ can be attributed to two factors. Furthermore, these optical results can be defined by average T$_{\text{lum}}$($T_{\text{lum},\,20\,^\circ\text{C}} + T_{\text{lum},\,100\,^\circ\text{C}}$)/2 and $\Delta T_{\text{sol}}$($T_{\text{sol},\,20\,^\circ\text{C}} - T_{\text{sol},\,100\,^\circ\text{C}}$). The average T$_{\text{lum}}$ of pristine and SiO$_2$/VO$_2$ films are 37.6% and 47.7%, respectively, and $\Delta T_{\text{sol}}$ are 8.06 and 7.62. One is the difference in reflectance between pristine VO$_2$ and SiO$_2$/VO$_2$ thin films in the visible region as shown in Figure 3a. The inset images in Figure 3a clearly show a contrast change after SiO$_2$ coating. Therefore, the reflectance for the SiO$_2$/VO$_2$ thin films was decreased from 8% to 4% compared to the pristine VO$_2$ thin films. However, the change in the reflectance is not enough to confirm the enhancement of T$_{\text{vis}}$ for SiO$_2$/VO$_2$ thin films.

Figure 4 shows the haze for each sample in the visible region. For the SiO$_2$/VO$_2$ thin films, a slight decrease in haze over 500 nm was observed but other considerable changes did not appear. For this reason, more evidence is needed to validate the transmittance results.

Figure 4c shows the absorbance data for each sample measured in the visible region. The data confirms the change in the absorption edge toward the blue region and a decrease in absorbance after SiO$_2$ coating. The relative optical band gap for each sample is shown in Figure 4d, and the results correspond to the results for reflectance and absorbance. The absorption coefficient $\alpha$ was estimated using the transmittance data for the two films [27].
\[ \alpha = \frac{1}{\Delta d} \ln \left( \frac{T_1}{T_2} \right) \]  

(1)

where \( \Delta d \) is the thickness of pristine VO\(_2\) or SiO\(_2\)/VO\(_2\), \( T_1 \) is the transmittance of the substrate (Eagle glass) and \( T_2 \) is the transmittance of each sample. The optical band gap was determined with the following formula [28].

\[ (\alpha h \nu)^{1/2} = (E - E_g) \]  

(2)

linear extrapolation of \((\alpha h \nu)^{1/2}\) vs. \( h \nu \) near the band gap provided \( E_g \) as the intercept at the \( \alpha = 0 \) axis. The optical band gap for the pristine VO\(_2\) thin film increased from 1.54 to 1.74 eV after SiO\(_2\) coating. This widening of the optical band gap induces a blue shift and an enhanced visible transmittance [15]. This means that the enhancement of \( T_{\text{vis}} \) for SiO\(_2\)/VO\(_2\) corresponds to the decrease in absorbance and reflectance including the formation of denser and smoother surfaces on the films.

4. Conclusions

In this paper, high-quality VO\(_2\) thermochromic thin films with enhanced \( T_{\text{vis}} \) up to 58% were successfully prepared with the addition of a SiO\(_2\) layer. The results indicate that the enhanced \( T_{\text{vis}} \) was due to a reduction of surface roughness with a blue shift in the absorption spectra observed after SiO\(_2\) coating. In addition, the SiO\(_2\)/VO\(_2\) thin films had high \( E_{\text{os}} \) and the crystallographic orientation was maintained. This enhancement of \( T_{\text{vis}} \) while maintaining high \( E_{\text{os}} \) is meaningful for VO\(_2\)-based smart window applications.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

- PECVD: Plasma enhanced chemical vapor deposition
- \( T_{\text{vis}} \): Visible transmittance
- \( E_{\text{os}} \): Optical switching efficiency
- VO\(_2\): Vanadium dioxide
- MIT: Metal-insulator transition
- SEM: Scanning electron microscopy
- XRD: X-ray diffraction

References

1. Hee, W.J.; Alghoul, M.A.; Bakhtyar, B.; OmKalthum, E.; Shameri, M.A.; Alrubaih, M.S.; Sopian, K. The role of window glazing on daylighting and energy saving in buildings. *Renew. Sustain. Energy Rev.* 2015, 42, 323–343. [CrossRef]
2. Morin, F.J. Oxides which show a metal-to-insulator transition at the neel temperature. *Phys. Rev. Lett.* 1959, 3, 34–36. [CrossRef]
3. Qazilbash, M.M.; Brehm, M.; Andreev, G.O.; Kim, B.J.; Yun, S.J.; Balatsky, A.V.; Maple, M.B.; Keilmann, F.; Kim, H.T.; Basov, D.N. Mott transition in VO\(_2\) revealed by infrared spectroscopy and nano-imaging. *Science* 2007, 318, 1750–1753. [CrossRef] [PubMed]
4. Cao, C.; Gao, Y.; Luo, H. Pure single-crystal rutile vanadium dioxide powders: Synthesis, mechanism and phase-transformation property. *J. Phys. Chem. C* 2008, 112, 18810–18814. [CrossRef]
5. Kang, L.; Gao, Y.; Luo, H. A Novel solution process for the synthesis of VO₂ thin films with excellent thermochromic properties. ACS Appl. Mater. Interfaces 2009, 1, 2211–2218. [CrossRef] [PubMed]

6. Mlyuka, N.R.; Niklasson, G.A.; Granqvist, C.G. Thermochromic multilayer films of VO₂ and TiO₂ with enhanced transmittance. Sol. Energy Mater. Sol. Cells 2009, 93, 1685–1687. [CrossRef]

7. Vernardou, D.; Louloudakis, D.; Spanakis, E.; Katsarakis, N.; Koudoumas, E. Thermochromic amorphous VO₂ coatings grown by APCVD using a single-precursor. Sol. Energy Mater. Sol. Cells 2014, 128, 36–40. [CrossRef]

8. Drosos, C.; Vernardou, D. Perspectives of energy materials grown by APCVD. Sol. Energy Mater. Sol. Cells 2015, 140, 1–8. [CrossRef]

9. Wang, S.; Liu, M.; Kong, L.; Long, Y.; Jiang, X.; Yu, A. Recent progress in VO₂ smart coating: Strategies to improve the thermochromic properties. Prog. Mater. Sci. 2016, 81, 1–54. [CrossRef]

10. Zhou, M.; Bao, J.; Tao, M.; Zhu, R.; Lin, Y.; Xie, Y. Periodic porous thermochromic VO₂(M) films with enhanced visible transmittance. Chem. Commun. 2013, 49, 6021–6023. [CrossRef] [PubMed]

11. Xu, G.; Jin, P.; Tazawa, M.; Yoshimura, K. Optimization of antireflection coating for VO₂-based energy efficient window. Sol. Energy Mater. Sol. Cells 2004, 83, 29–37. [CrossRef] [PubMed]

12. Jin, P.; Xu, G.; Tazawa, M.; Yoshimura, K. Design, formation and characterization of a novel multifunctional window with VO₂ and TiO₂ coatings. Appl. Phys. A 2003, 77, 455–459.

13. Kusano, E.; Theil, J.A. Effects of microstructure and nonstoichiometry on electrical properties of vanadium dioxide films. J. Vac. Sci. Technol. A 1989, 7, 1314–1317. [CrossRef]

14. Griffiths, C.H.; Eastwood, H.K. Influence of stoichiometry on the metal-semiconductor transition in vanadium dioxide. J. Appl. Phys. 1974, 45, 2201–2206. [CrossRef]

15. Din, S.B.; Lee, J.S.; Choi, Y.S.; Choi, I.S.; Han, J.G. High-rate deposition and mechanical properties of SiOₓ film at low temperature by plasma enhanced chemical vapor deposition with the dual frequencies ultra high frequency and high frequency. Thin Sol. Films 2011, 519, 6334–6338. [CrossRef]

16. Wang, N.; Liu, S.; Zeng, X.T.; Magdassi, S.; Long, Y. Mg/W-codoped vanadium dioxide thin films with enhanced visible transmittance and low phase transition temperature. J. Mater. Chem. A 2015, 3, 6771–6777. [CrossRef]

17. Li, J.; Dho, J. Anomalous optical switching and thermal hysteresis behaviors of VO₂ films on glass substrate. Appl. Phys. Lett. 2011, 99, 231909. [CrossRef]

18. Petrov, G.I.; Yakovlev, V.V.; Squier, J. Raman microscopy analysis of phase transformation mechanisms in vanadium dioxide. Appl. Phys. Lett. 2002, 81, 1023–1025. [CrossRef]

19. Donev, E.U.; Lopez, R.; Feldman, L.C.; Haglund, R.F. Confocal raman microscopy across the metal-insulator transition of single vanadium dioxide nanoparticles. Nano Lett. 2009, 9, 702–106. [CrossRef] [PubMed]

20. Vernardou, D.; Louloudakis, D.; Spanakis, E.; Katsarakis, N.; Koudoumas, E. Functional Properties of APCVD VO₂ Layers. Int. J. Thin Films Sci. Technol. 2015, 4, 187–191.

21. Du, J.; Gao, Y.; Luo, H.; Kang, L.; Zhang, Z.; Chen, Z.; Cao, C. Significant changes in phase-transition hysteresis for Ti-doped VO₂ films prepared by polymer-assisted deposition. Sol. Energy Mater. Sol. Cells 2010, 95, 469–475. [CrossRef]
27. Kim, E.; Jiang, Z.; No, K. Measurement and calculation of optical band gap of chromium aluminum oxide films. Jpn. J. Appl. Phys. 2000, 39, 4820–4825. [CrossRef]

28. Jiang, M.; Li, Y.; Li, S.; Zhou, H.; Cao, X.; Bao, S.; Gao, Y.; Luo, H.; Jin, P. Room temperature optical constants and band gap evolution of phase pure M1-VO$_2$ thin films deposited at different oxygen partial pressures by reactive magnetron sputtering. J. Nanomater. 2014, 2014, 183954. [CrossRef]

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