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Influence of the rf power and oxygen content on structural, electrical, and optical properties of V$_2$O$_5$ thin films prepared via reactive radio frequency sputtering

S Tipawan Khlayboonme$^{1, *}$ and Amorn Thedsakhulwong$^{2}$

$^1$ Surface Analysis and Plasma Applications Laboratory, Department of Physics, School of Science, King Mongkut’s Institute of Technology Ladkrabang, Bangkok 10520, Thailand
$^2$ Department of Physics, Faculty of Science, Ubon Ratchathani University, Varinchamrap, Ubon Ratchathani 34190, Thailand

* Author to whom any correspondence should be addressed.

E-mail: s.tipawan.kh@kmitl.ac.th and amorn.t@ubu.ac.th

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Abstract

Herein, V$_2$O$_5$ thin films were deposited through O$_2$-reactive radio frequency (RF) magnetron sputtering using a metallic vanadium arget without external heating on a glass substrate. The influence of the RF power and O$_2$ content on phase formation was investigated, and the percentage of the phase volume was related to the electrical and optical properties of the films. These films were composed of a mixture of α- and β-phases of V$_2$O$_5$, and the coexistence of monoclinic ($\beta$M) and tetragonal ($\beta$T) symmetries of the β-phase structure was observed. The phase of the film deposited at 100 W RF power with 10% O$_2$ was $\beta$T. Increasing the RF power to 150 W led to the development of the $\beta$M phase in the film. At 200 W, the obtained film was a mixture of $\beta$M- and α- V$_2$O$_5$ phases, and the film produced with an O$_2$ content of more than 10% was a mixture of three phases: $\beta$T-, $\beta$M-, and α- V$_2$O$_5$. Further increase in the O$_2$ content decreased the $\beta$M-phase volume but increased the $\beta$T-phase volume. The electrical resistivity and optical properties depended on the phase volume. Furthermore, the relationship between the phase volume and film properties is presented.

1. Introduction

Vanadium pentoxide thin films are intelligent materials that exhibit significant color changes through electro-, photo-, and thermochromic processes [1–3]. The chromism of V$_2$O$_5$ films has attracted considerable research interest as promising materials for applications in optical devices [4] and smart chromic sensors [5]. V$_2$O$_5$ has several crystal phases, such as α, β, and γ, and exhibits phase transitions between them [6, 7]. It has a layered structure with two adjacent layers stacked together via weak van der Waals interactions that contribute to the gliding displacement of V$_2$O$_5$ layers and lead to phase transitions [8], which in turn can induce the formation of films with different phase volumes of a phase mixture. The volume and characteristics of the phases formed in the film structure are important for the performance of devices containing these materials.

V$_2$O$_5$ thin films can be coated onto substrates by several chemical and physical techniques [9]. For chemical techniques, altering the annealing temperature and incorporation of dopants in the host lattice are two commonly used strategies to enhance the chromic behavior of V$_2$O$_5$ films. Etemadi et al [10] synthesized films by the sol-gel method and reported an enhancement in the electrochromic behavior of the tetragonal $\beta$-V$_2$O$_5$ by Co-doping. Darrodi et al [11] prepared V$_2$O$_5$ films from spray pyrolysis and showed that the increase in the nozzle to substrate distance induced formation of the tetragonal $\beta$-V$_2$O$_5$ phase. The metastable $\beta$-V$_2$O$_5$ phase can be prepared using physical techniques, especially sputtering; however, it is formed by post-annealing at high temperatures [12, 13]. The $\beta$-V$_2$O$_5$ structure composed of monoclinic ($\beta$M) and tetragonal ($\beta$T) symmetries was first reported by Asadov et al [14], who proposed that the films deposited by direct current (DC) magnetron sputtering with a V$_2$O$_5$ target exhibited phase transitions between $\beta$M and $\beta$T symmetries after post-annealing at
temperatures $> 500 \, ^\circ C$. This structure responds intensely to temperature-sensitive crystallization processes because of its layered structure and this phase is built of VO$_6$ octahedra linked in layers through shared common edges and corners, and the series of layers interact via weak van der Waals interactions of the vanadium-oxygen bond $[8]$. $\beta$-V$_2$O$_5$ with a mixture of $\beta$M and $\beta$T symmetries has attracted interest owing to the layered crystal structure with the metastable phase, which enables facile tuning of the physical characteristics via the growth condition, yielding suitable film materials for practical applications.

The thermo- and photo-chromic devices based on V$_2$O$_5$ thin films can be operated under environmental stimuli without an additional control system $[4, 5]$. This is an advantage for application in non-contact temperature sensors. Consequently, in this study, RF magnetron sputtering technique was selected for depositing V$_2$O$_5$ films because it provides uniformity of the grown thin films. Evidently, various parameters, such as types of substrates, heat treatment process, and deposition parameters of the growth process strongly influence the film structure leading to differing symmetries of the phases formed. However, this study mainly focuses on the influence of RF power and O$_2$ content on the phase volume of each phase formed in the film structure. During the last five years, some studies have reported the influence of O$_2$ content and temperature on the properties of the RF-sputtered V$_2$O$_5$ thin films. Rakshit et al $[15]$ studied the effect of oxygen content on the electrical properties and the temperature for insulator-to-metal transition. Panagopoulos et al $[16]$ reported the effect of oxygen content and substrate temperature on the optical and electrochemical properties of the grown films. Acosta et al $[17]$ reported the influence of oxygen content on the physical properties. The obtained films were $\beta$-phase films that exhibit electrochemical behavior.

In this study, V$_2$O$_5$ film was deposited on a glass substrate that enhances the formation of $\beta$-V$_2$O$_5$ with the coexistence of $\beta$M- and $\beta$T-symmetries $[18]$. The deposition was performed through RF magnetron sputtering using an O$_2$-reactive gas technique. Phase formation could be controlled by altering the RF power and O$_2$ content under growth conditions. A detailed investigation of the phase volume formed in the film structure, which is related to the electrical and optical properties, was examined. To the best of the authors’ knowledge, this study is the first to investigate the relation between the phase volume and electrical and optical properties for mixed phases of $\beta$M-, $\beta$T-, and $\alpha$-symmetries in the V$_2$O$_5$ structure, a topic scarcely reported in the literature. This relation is directly responsible for the generation and control of chromism of the V$_2$O$_5$ for thermochromic applications in temperature-sensing fields.

2. Method

2.1. Sputtering system
A custom-built RF magnetron sputtering system was used for depositing V$_2$O$_5$ thin films. Figure 1 shows the schematic of the system and magnetic field line configuration for magnetron sputtering. The Ar and O$_2$ gases were fed separately through a gas inlet over the target surface. The magnetic fields were evaluated numerically in two dimensions using finite-element modeling. The magnetic field configuration used is known as unbalanced type II $[19]$, in which some field lines are directed toward the substrate surface. The null point was positioned 60 mm above the magnet and on the plasma discharge center axis. A metallic vanadium target with diameter and thickness of 76.2 and 6.35 mm, respectively (99.95% purity; Kurt J. Lesker, USA), was used as the magnetron cathode. An RF power generator (OEM-650, ENI RF Generator, RF Global solutions Ltd, UK) with an auto-matching box was connected to the target.

2.2. Thin film preparation
V$_2$O$_5$ thin films were coated on glass substrates with a thickness of approximately 1 mm (Marienfeld, Germany). No additional heating was supplied to the substrates; however, the substrate temperature increased to 80 $^\circ C$ during deposition owing to plasma emission. The distance between the target and substrate was 75 mm. The sputtering chamber was evacuated to a pressure of $< 3.4 \times 10^{-6}$ mbar. To eliminate contamination and maintain the homogeneity of the composition, the target was pre-sputtered for 10 min with an RF power of 150 W and a shutter covering the target. Film deposition was performed for 1 h under a mixed Ar/O$_2$ gas flow, during the deposition the chamber pressure was $4.0 \times 10^{-3}$ mbar. The variation in the O$_2$ content, with a constant total mass flow rate of 25 sccm, did not substantially affect the pressure in the chamber, which may be due to the high pumping speed (700 l s$^{-1}$) of the Diffstak diffusion pump. The as-deposited films were annealed in a furnace under an ambient atmosphere. The annealing temperature was increased at a constant rate of 2 $^\circ C$ min$^{-1}$ from a temperature of 30-300 $^\circ C$ and maintained for 1 h. The cooling rate was also set to 2 $^\circ C$ min$^{-1}$. Temperature and time were controlled using an OMROM E5AN PID controller.
2.3. Thin film characterization

Scanning electron microscopy (SEM; JSM-7800F, JEOL, USA) was performed at an accelerating voltage of 5 kV to determine the film thickness. The chemical bonds in the films were studied via Raman spectroscopy (NT-MDT NTEGRA, spectrometer, NT-MDT spectrum instruments, Russia) using an Ar-ion laser ($\lambda = 514.5$ nm). The crystal structures of the films were analyzed using x-ray diffraction (XRD; SmartLab x-ray diffractometer, Rigaku, Japan) in $\theta$–$2\theta$ scanning modes, with Cu Kα radiation ($\lambda = 1.54056$ Å). Electrical resistivity was measured using a colinear four-point probe head (SP4- Colinear four-point probe, Signatone, USA). Current-voltage measurements were conducted using a current source (220 Programmable Current Source, Keithley, USA) and a digital multimeter (34401A, Agilent, USA). Chemical bonding was investigated through Fourier transform infrared (FTIR) spectroscopy (IR Prestige-21 FTIR, spectrometer, Shimadzu, Japan). Ultraviolet-visible (UV–Vis) transmission spectra were obtained using a setup consisting of a light source (DH-2000-BAL, Ocean Optics, USA) and a fiber optic spectrometer (USB4000, Ocean Optics, USA).

3. Results and discussion

3.1. Film thickness

Figure 2 shows the dependence of the film thickness on the RF power and O$_2$ content. Two sets of V$_2$O$_5$ thin films were deposited: SET 1—the films were deposited at an O$_2$ content of 10% for three RF power values; SET 2—the films were deposited at an RF power of 200 W with various O$_2$ contents. The film thickness increased with increasing RF power but decreased with increasing O$_2$ content. The number of energetic Ar$^+$ ions increase with the RF power, resulting in the sputtering of a large number of V atoms from the target. As O$_2$ content increased to 15%, the target surface poisoning and decrease in the number of Ar$^+$ ions decreased resulted in a significant decrease in the film thickness. The number of V atoms sputtered from the target is determined not only by the Ar$^+$ ion energy but also by the ion flux incident on the target and oxidation of the target surface. The variation in
the film thickness with two process parameters indicates that the mechanism underlying the development of the crystal structure are under the influence of plasma characteristics.

### 3.2. Structure and phase evaluation

Figure 3 shows the XRD patterns of the two sets of films. The variations in the RF power and O₂ content resulted in significant structural changes. Considering the samples from SET 1, the film deposited at 100 W RF power exhibited a broad peak at 12.60°, corresponding to the (200)-oriented diffraction of the tetragonal β-V₂O₅ phase (JCPDS card No. 45–1074). When the RF power was increased to 150 W, the film exhibited a new predominant peak at 12.14° and a few low-intensity peaks, whereas the peak at 12.60° disappeared. The increase in the RF power from 100 to 150 W led to the shifting of the XRD peak from 12.60° to 12.14°. The shift of the XRD peak to a lower angle indicates lattice distortion due to compressive stress, which is frequently observed in sputtering processes, especially at low substrate temperatures. Compressive stress is caused by the bombardment of sputtered species with high energy [20]. However, the XRD pattern of the film at 150 W matches well with JCPDS card No. 26–1165 for monoclinic β-V₂O₅ (β_m-V₂O₅). In addition, the experimental crystallographic pattern obtained from the film at 10% O₂ and 150 W RF power is in good agreement with those of results reported by Asadov et al [14].

A further increase in the RF power from 150 to 200 W resulted in a more prominent XRD pattern and the appearance of three new peaks. These new peaks are characteristic of the α-orthorhombic (αo) phase. The intensity of the XRD peaks for β_m-V₂O₅ increased significantly with increasing RF power from 150 to 200 W, and the centers of the peaks did not shift, indicating that a greater number of crystallites grown in the structure. The XRD pattern of the film at 10% O₂ and 200 W RF power matches with the three XRD card files, as shown in figure 3. This film was composed of a mixture of β and α phases.

![Figure 2. Film thickness t under (a) three RF power values at 10% O₂ (SET 1) and (b) various O₂ contents with an RF power of 200 W (SET 2).](image-url)
As the O₂ content increased above 10%, a new peak at 12.80° appeared and was dominant at 40% O₂. The peak at 12.80° belongs to the (200) -orientated diffraction of the tetragonal β-V₂O₅ (βт-V₂O₅) (JCPDS card No. 45–1074) as reported in [9, 21]. The peak at 12.80° shifted from the peak at 12.60° (at 100 W RF and 10% O₂). This shift is due to the reduction in compressive stress, resulting from a decrease in the energy of the sputtered V atoms. The increased O₂ level to 40% induced an increase in the βт-V₂O₅ phase volume but a decrease in the βм-V₂O₅ volume. The O₂ content also affected the formation of α-V₂O₅. The (200) -oriented α-V₂O₅ content decreased and then disappeared at O₂ levels of 30% and 40%. As reported by Singh et al [22], for the α-V₂O₅ phase, surface density of oxygen in the (h00) plane is higher than that in the (001) plane. This indicates that the increase in the O₂ level did not promote the incorporation of oxygen into the structure of α-V₂O₅ phase.

As the three phases coexisted in the films, the percentage of the crystalline content (phase volume) for each phase was determined by calculating the area of the Gaussian-fitted XRD peaks [23]. The percentage of each phase was calculated as follows:

$$\% Volume \ of \ phase_x = \frac{\sum A_x}{\sum A_x + \sum A_y + \sum A_z}$$  \hspace{1cm} (1)

where $A_x$, $A_y$, and $A_z$ are the peak areas of the βм, βт, and αφ phases, respectively. The results are shown in figure 4 for SET 1 and figure 5 for SET 2. The formation rate of the βт phase was reduced by increasing the RF power but increased with increasing O₂ content. The βм-phase content was inversely proportional to the βт-phase content, which indicates that the β phase can transition between βм and βт.

Figure 3. XRD patterns of V₂O₅ films as functions of the RF power and O₂ content. Three relevant JCPDS card patterns are shown for reference: No. 41–1426 (orthorhombic α-V₂O₅), No. 26–1165 (monoclinic β-V₂O₅), and No. 45–1074 (tetragonal β-V₂O₅).
The crystallite size $D$ along the preferred orientations for the $(200)$-$\beta\mathrm{M}$, $(200)$-$\beta\mathrm{F}$, and $(001)$-$\alpha\mathrm{O}$ phases was calculated using the integral breadth method \[24\] as $D = \frac{(0.9\lambda)}{(L\cos\theta)}$, where $\lambda$ is the x-ray wavelength (1.54056 Å); $\theta$ is the Bragg diffraction peak (in radians), and $L$ (integral breadth) is the total area under the peak divided by the peak height (in radians). The average crystallite sizes are shown in graphs (2) of figure 4 for SET 1.
and figure 5 for SET 2. The increase in the crystallite size with increasing power can be explained by the agglomeration of crystallites. A high power enhances the surface diffusion of the ejected V atoms, resulting in the merging of small crystals and the formation of several orientations and a new phase.

By contrast, an increase in the O2 content reduced the average size. This reduction was due to a stark decrease in the crystallite size of the $\alpha$ phase at high levels of the O2 content. The crystallite sizes of the $\alpha$ phase were 21.5, 27.0, 23.0, and 17.3 nm for 10%, 15%, 30%, and 40% O2, respectively. Further increase in O2 above 15% did not lead to notable changes in the crystallite size of $\beta_M$- and $\beta_T$- phases. For example, for the $\beta_M$ phase, the crystallite sizes were 34.0, 27.8, 29.0, and 27.9 nm for 10%, 15%, 30%, and 40% O2, respectively. However, higher O2 contents increased the formation rate of $\beta_T$ phase, as shown in graphs (1) of figure 5. The higher O2 content causes further oxidation of the target surface. Consequently, the energy of the ejected V atoms reduced, and several orientations disappeared due to a decrease in surface diffusion of atoms. According to the XRD measurements, it can be assumed that the phase volume for the three symmetries can be tuned via two process parameters: RF power and O2 content.

### 3.3. Atomic and chemical bonding

Figure 6 shows the Raman spectra of the all the films (SET 1 and 2). The film synthesized using 100 W and 10% O2 exhibited uncharacteristic Raman spectrum, indicating a low concentration of chemical components. As the power increased to 150 W, the film exhibited a Raman signal. A clear signal was observed for the film produced at 200 W. The intensities of all the Raman peaks decreased with increasing O2 content.

The Raman active modes of the $\alpha$- and $\beta$-V$_2$O$_5$ structures at the $\Gamma$-point are given by $\Gamma_{\text{\textit{\alpha}}-\text{phase}} = 7A_g + 7B_g + 3B_{1g} + 4B_{2g}$ and $\Gamma_{\text{\textit{\beta}}-\text{phase}} = 14A_g + 7B_g$, respectively [6]. The Raman spectral signals of the $\alpha$-V$_2$O$_5$ structure were notably stronger than those of the $\beta$-V$_2$O$_5$ structure [18, 25]. The nine signals located at 145, 197, 284, 304, 404, 484, 528, 820, and 998 cm$^{-1}$ were attributed to the Raman peaks of the $\alpha$-V$_2$O$_5$ phase with a preferential (001) orientation. The Raman signal for the $\beta$-V$_2$O$_5$ was absent. However, the 484 cm$^{-1}$ peak is due to the bending vibration of the V-O-V bridges and is related to the layered structure of $\beta$-V$_2$O$_5$. The more pronounced peak at 484 cm$^{-1}$ compared to the peak at 528 cm$^{-1}$ is attributed to the formation of the layered structure of the $\beta$ phase [25]. Therefore, the higher intensity ratio of the peaks at 484 and 528 cm$^{-1}$ for the film with a high O2 content as compared with the film with a low O2 content indicates that higher O2 content enhances $\beta$-V$_2$O$_5$ structure formation. The more evident $\beta_T$-V$_2$O$_5$ structure compared to the $\alpha\text{\textit{\alpha}}$-V$_2$O$_5$ structure weakened the Raman signal intensity from the $\alpha\text{\textit{\alpha}}$-V$_2$O$_5$ structure, owing to interference from the Raman characteristics of the $\beta$ phase.

Figure 7 shows the dependence of the FTIR spectra of the films on RF power and O2 content (SET 1 and 2). Generally, three major IR bands at 1022, 827, and 617 cm$^{-1}$ correspond to the stretching and bending vibrations of V–O bonds in crystalline $\alpha$-V$_2$O$_5$ [26]; however, characteristic peaks were observed at 1052, 971, 854, and 757 cm$^{-1}$ for the obtained films. The difference in the observed FTIR signature is because the films contained a
mixture of phases with $\beta\tau$, $\beta\mu$, and $\alpha\cdot$-crystal symmetries. The peak at 1052 cm$^{-1}$ indicated that the films were composed of inequivalent V = O groups. The reduction in intensity of the peak and broadening indicate that the layered structure of V$_2$O$_5$ was profoundly altered because of the difference in the bond lengths of the films. The band at 971 cm$^{-1}$ is assigned to the presence of the V$_4^{+}$ state in the $\alpha\cdot$-V$_2$O$_5$ structure [20, 27], which contributes to the electrical conductivity [9]. Usually, the band at 971 cm$^{-1}$ is related to the electrical conduction behavior of the films. The lowering of intensity of the band at 971 cm$^{-1}$ indicates a higher electrical resistivity of the film.

Raman and FTIR spectra confirm that the RF power and O$_2$ content affected the V-O chemical bonding and oxidation state of vanadium in the V$_2$O$_5$ films.

3.4. Electrical properties
The electrical resistivity was measured using the four-point probe method and determined using the relation $\rho = (\pi/\ln 2) \times (V/I) \times t$, where $V$ is the measured voltage; $I$ is the applied current, and $t$ is the film thickness. The electrical resistivities of the films are presented in graphs (2) of figure 4 for SET 1 and of figure 5 for SET 2. The increase in electrical resistivity corresponds to a reduction in the intensity of the FTIR peak at 971 cm$^{-1}$, confirming that the electronic band structure of the films was affected by the RF power and O$_2$ content. Figures 4 and 5 also shows that the value of resistivity increased with increasing $\beta\tau$-phase volume. The V$_2$O$_5$ films obtained in the present study contained a mixture of phases with $\beta\mu$, $\beta\tau$, and $\alpha\cdot$-crystal symmetries; therefore, three electronic band structures coexist in the films, resulting in a dependence of the electrical resistivity on the volume of each phase contained in the film structure.

3.5. Optical properties
Figure 8 shows photographs of all films from the two sets. The increase in the RF power resulted in a color change from light to dark yellow, in contrast to the O$_2$ content. The change in color is associated with the oxidation of vanadium from V$^{4+}$ to V$^{5+}$ (green to yellow). The mixture of V$^{4+}$ and V$^{5+}$ resulted in a dark yellow color. The change in the color of the films corresponds to a decrease in intensity of the 971 cm$^{-1}$ peak in the FTIR spectra. The decrease in the 971 cm$^{-1}$—peak intensity implies a decrease in the number of V$^{4+}$, resulting in a bright yellow shift.

Figure 9(a) shows the optical absorbance spectra of all the films. The optical absorbance spectra were determined from UV–vis transmittance spectra measurements using the formula $A = \log (1/T)$ [28], where $T$ is the transmittance and is given by $\alpha t > 1$, where $\alpha$ is the absorption coefficient, and $t$ is the film thickness. Considering the absorbance spectra of all films, the film deposited at 200 W RF power and 10% O$_2$ showed the highest absorption edge, while the film deposited at 100 W RF power and 10% O$_2$ showed the lowest. The higher absorption edge is a result of the decreased band gap with improved thin film conducting behavior [29]. These results correspond to the 971 cm$^{-1}$ peak from FTIR spectra and electrical resistivity measurements using the four-point probe.
The absorption coefficient is also related to the energy band gap $E_g$, which follows Tauc’s law
\[ \alpha h\nu = B(h\nu - E_g)^n \]
where $B$ is a constant; $h\nu$ is the photon energy, and $n$ is the power factor of the transition mode. $n$ is $1/2$, $2/3$, and $3$ for direct-allowed, direct-forbidden, and indirect-forbidden transitions, respectively. The value of $E_g$ is evaluated by plotting $(\alpha h\nu)^{1/n}$ against photon energy and extrapolating the linear region to the energy axis at $(\alpha h\nu)^{1/n} = 0$. Figures 9(b)–(d) show the plot of $(\alpha h\nu)^{1/n}$ versus $h\nu$ when $n$ is $1/2$, $2/3$, and $3$ and the intersection on the $h\nu$ axis.

The $E_g$ values for the direct-allowed transition ($n = 1/2$) as functions of RF power and O$_2$ content are shown in figure 10 and the $E_g$ values for the direct- ($n = 2/3$) and indirect-forbidden ($n = 3$) transitions are listed in figures 9(c) and (d), respectively. The $E_g$ values for three transition modes agree well with those of results reported in [31] and suggests that the electronic transition for the mixture of $\alpha$- and $\beta$-$V_2O_5$ phase can undergo direct-allowed, direct-forbidden, and indirect-forbidden transition modes.

The $E_g$ value for the film deposited at 100 W RF power was different from those in previous reports [31]. This difference is mainly due to the different crystal structures formed in the films. The $E_g$ values for the direct-allowed transition ($n = 1/2$) are shown in figure 10. It starkly decreased with increasing RF power but gradually increased with increasing O$_2$ content.
Considering the films from SET 1, the \( E_g \) value of 2.93 eV was obtained for the film at 100 W containing only the \( \beta_T \) phase and 2.54 eV for the film at 150 W containing only the \( \beta_M \) phase in the film structure. The incorporation of the \( \alpha \) phase in the film structure led to a lower \( E_g \) (2.34 eV) for the film at 200 W. Considering the films from SET 2, the increase in the O\(_2\) content resulted in an increase in the \( \beta_T \)-phase content but a decrease in the \( \beta_M \)-phase content, resulting in the slight increase in \( E_g \) with the O\(_2\) content. The V\(_2\)O\(_5\) films obtained in the present study contained a mixture of phases from \( \beta_T \)-, \( \beta_M \)-, and \( \alpha \)-crystal symmetries; therefore, three electronic band structures coexisted in the films. According to the Vegard’s law \([32]\), as \( E_g \) is the highest for the \( \beta_T \) phase. Therefore, a higher \( \beta_T \)-phase content incorporated in film structure results in an increase in the \( E_g \) value.

The optical band gap of a semiconductor is affected by two main factors: quantum confinement and electronic band structure. Quantum confinement is associated with the film thickness and crystallite size. According to the results, the optical band gap increased with decreasing film thickness (figure 2) and crystallite size (graphs (2) of figures 4 and 5). This seems to be the quantum confinement effect. However, the quantum confinement effect is of significant importance when the crystallite size is smaller than the Bohr radius, which is 4.52 nm for V\(_2\)O\(_5\) \([33]\). According to the XRD measurements, the crystallite sizes in the films were >14 nm, which is outside the quantum confinement regime. The dependence of the optical band energy on the crystal size and film thickness can be neglected. Therefore, the band gap variation of the V\(_2\)O\(_5\) films can be attributed to the electronic band structure effect that is associated with phase formation in the film structure. The film structure with a mixture of the three phases contributed to the strong deviation from the VO\(_6\) octahedra, which enhances the optical band gap \([34]\). Moreover, the variation in the optical band gap did not follow the Burstein-Moss effect \([35]\).

Figure 10 also presents the Urbach energy, \( E_U \). Localized and delocalized states formed and extended into the band gap of the V\(_2\)O\(_5\) thin films, and the lattice disorder is related to the \( E_U \). Urbach’s law states that the absorption coefficient near the band edges is exponentially dependent on the photon energy \( h\nu \), as given by the equation: \( \alpha = \alpha_0 \exp(h\nu/E_U) \), where \( \alpha_0 \) is a constant. The increase in \( E_U \) is related to the formation of deep-extended states in the band structure and lattice disorder. Considering the films from SET 1, the value of \( E_U \) for
the film at 200 W RF (444 meV) is higher than that for the films at 100, 150 W RF (212 and 224 meV). The films consisting of a single phase with a lower plane orientation has a low value of $E_{\Gamma}$. Considering the films from SET 2, the value of Eu decreased with increasing O$_2$ content. These two growth parameters not only influenced the electronic band structure of valence and conduction bands but also the electronic structure band of the deep-extended states of V$_2$O$_5$ formed by V 3d split-off [35]. The wider of the deep-extended states is caused by the lattice disorder due to the several plane orientations and phases formed in film structure. The $E_{\Gamma}$ values correspond to the $E_g$ values of the direct and indirect forbidden transition modes [36, 37]. Both $E_{\Gamma}$ and $E_g$ values for the forbidden transition modes are directly related to the lattice disorder and broadening of the deep states formed in the band gap.

4. Conclusion

V$_2$O$_5$ thin films comprising a mixture of phases with $\alpha$O, $\beta$M, and $\beta$T symmetries were prepared through Ar/O$_2$ reactive RF magnetron sputtering with post-annealing at 300 $^\circ$C. These films were coated onto glass substrates, which contributed to the formation of the $\beta$ phase. The effects of the RF power and O$_2$ content on phase formation were investigated and related to the electrical and optical properties. An increase in the RF power promoted the $\beta$M- and $\alpha$O-phase formation, whereas a high O$_2$ content promoted $\beta$T-phase formation. XRD analysis indicated the occurrence of a transition between the $\beta$T and $\beta$M phases. Upon increasing the RF power, the $\beta$T-phase structure changed, and $\beta$M-phase structure was formed. The opposite was observed with an increase in the O$_2$ content. The volume of each phase can be controlled by varying the RF power and O$_2$ content. An increase in the $\beta$T-phase content resulted in the widening of the optical band gap and an increase in the electrical resistivity. Therefore, tuning the percentage of the phase volume formed in the films is essential for the high film performance.

The mechanism underlying the formation of the different phases is directly related to two factors: the plasma properties associated with the plasma sheath thickness developed in the target surface and the designed configuration of the system, as shown in figures (a) and (b). These two factors facilitate the formation of certain energetic plasma species at the growth surface, resulting in a transition between the $\beta$ phases. An in-depth understanding of the phase formation in V$_2$O$_5$ thin films will help efficiently control and ultimately improve the performance of various optoelectronic devices. The correlation between the plasma sheath thickness and phase volume for the $\beta$-V$_2$O$_5$ has not been studied before and is an intended topic of future research by the author.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

ORCID iDs

S Tipawan Khlayboonme https://orcid.org/0000-0002-8075-5715
Amorn Thedsakhulwong https://orcid.org/0000-0002-2240-3877

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