

Short Communication

Preparation and Investigation of Optical Properties of Tungsten-doped VO₂

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VO₂ thin film is deposited on glass substrate by using spin-coating technique. Tungsten (W) has been doped as acidic solution to the precursor of vanadium solution. Energy gap has been investigated via absorption coefficient to explore its value with and without W doping. Reflectance spectroscopy results showed that there is a clear difference using few percentages of W doping. Optical transmissions have found for undoped and W-doped VO₂ thin film are approximately 75% and 35%, respectively. Empirical models of refractive index and optical dielectric constant are investigated.

Keywords: VO₂; Optical; Sol-gel.

1. INTRODUCTION

The saving energy system is employed via windows of low-emissivity and solar-control [1]. This is could not automatically switch between passing thermal energy and blocking [2]. While, high-technique-based windows can interact to external factors like weather situation. So, in summer, majority of visible radiations can pass through, while in winter, majority of invisible radiations can pass through [1]. This system is coated by vanadium dioxide (VO₂) that has attracted great interest

due to their rapid response to temperature changes, their capability of reducing the transition temperature to near room temperature and their ability to absorb ultraviolet radiation of the light [3].

The metal-insulator transitions (MIT) of VO₂ are discovered by Morin [4]. Vanadium oxides are classified into two groups: Magneli phases with V_nO_{2n-1} general formula (such as VO₂, V₂O₃); and Wadsley phases with V_{2n}O_{5n-2} general formula (such as V₂O₅) [5]. VO₂ is an attractive material because its transition temperature is close to room temperature. The metal-insulator transition temperature for VO₂ is at 68 °C, so the low-temperature monoclinic insulator phase (P2₁/c, a= 455 pm, b= 452 pm, c= 538 pm, β= 122.6°) crosses to high-temperature rutile metallic phase (P4₂/mnm, a= 455 pm, c= 286 pm). It is mentioned that the transition from insulator to metallic phase is an impetus of change into optical and electrical properties [6]. This transition is higher than room temperature, but VO₂ stays an appropriate choice. There are different types of doping to reduce the transition temperature to room temperature such as doping with bigger ionic radius (W⁶⁺ and Nb⁵⁺) to produce free electrons for reducing transition temperature. Contrarily, a shift to higher transition temperature when doping with smaller ionic radius (Sn⁴⁺, Gd³⁺ and Cr³⁺) [7]. The coating by VO₂ is appropriate for high-technique-based utilities [8-11], polarization convertors [12] and thermoelectric applications [13]. These have been prepared by several methods like ion beam enhanced deposition [14], atmospheric pressure chemical vapor deposition [15], solution-based deposition [16], pulsed laser deposition [17] and electron-beam deposition [18].

In the current work, VO₂ is coated on glass substrate via sol-gel method due to its effective-cost and gives punctual results. Spin-coating technique is widely utilized in thermochromics manufacturing [19]. Where the tungsten (W) is a familiar dopant to reduce VO₂ transition temperature, the main feature for studying its optical properties is by adding a tungstic acid to VO₂ precursor solution. The band gap of W-doped VO₂ has been measured and predicted to be a reference for future works. Absorption coefficient, reflection and transmission are investigated to support related researches. The refractive index and optical dielectric constant have been investigated. This work is organized as the followings: section 2 details the experimental process. The results and discussion are elaborated in section 3. Conclusions are summarized in section 4.

2. EXPERIMENTAL PROCESS

Starting materials for the preparation of solutions are vanadium pentoxide (V₂O₅, >99.5% purity, 100824 numbered Merck), acid of oxalic (H₂C₂O₄, > 99% purity, 816144 numbered Merck), ethanol of (C₂H₅OH, >99.9% purity, Merck No. 1.00983.2500), peroxide of hydrogen 30% (H₂O₂, Merck No. 1.07210.2500) and tungstic acid (H₂WO₄, >99% purity, 7783-03-1 numbered Merck CAS). These reagents are utilized without further purification. The sol-gel method is used to prepare vanadium solutions with/without doped tungsten [20]. The prepared vanadium solutions (W-free and 1 wt.% W-doped) are utilized on preheated slide glasses (corning slide glasses and 20×20×0.5 mm) by spin coater at 750 rpm for 20 sec with a ramping time, 6 sec. The glasses are purified into ultrasonic bath at 25 °C and 40 kHz via deionized water, ethanol and acetone for 10 min to eliminate inorganic and organic contaminations for obtaining a uniform material. Thenafter, the mentioned coated glasses are put into

oven at 80 °C to eliminate excess solvent. Afterthat, it heat-treats into electric furnace under nitrogen atmosphere (flow rate=16.6±1.7 sccm, 99.999% purity) at 550 °C including heating rate, 5 °C.min⁻¹ for 2 h. The reflectance spectroscopy (DRS, UV 2550 Shimadzu, Japan) is employed to estimate the band gap. And, the optical properties are analyzed using UV-Vis-NIR spectroscopy (UV-Vis-NIR, PG Instrument Ltd. T80 UV/VIS Spectrometer, UK).

3. RESULTS AND DISCUSSION

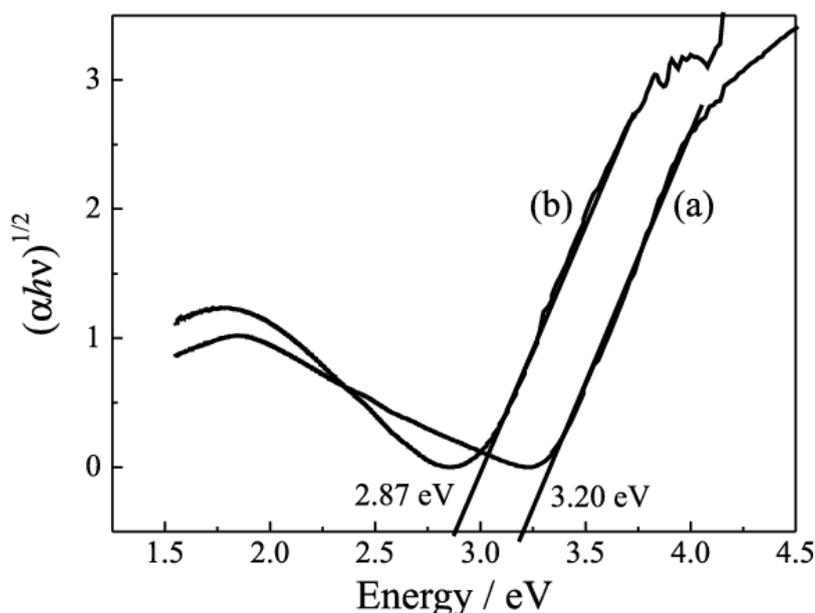


Figure 1. Calculated $(\alpha hv)^{1/2}$ versus $h\nu$ plot of (a) W-free and (b) 1 wt.% W-doped VO₂.

Band gap (with/without dopant) is calculated according to eq. (1) [20]:

$$A(h\nu - E_g) = (\alpha hv)^n \quad (1)$$

where A is constant, h is Plank constant, ν is light frequency, E_g is band gap, α is absorption coefficient which can be calculated according to Ref. [20], and n is constant which can be $1/2$, $1/3$, 2 , $2/3$ for indirect-allowed, indirect-forbidden, direct-allowed and direct-forbidden optical transition, respectively. The latter constant is set to 0.5 for VO₂ because of its indirect-allowed band transition [19]. Band gap is estimated by plotting $(\alpha hv)^{1/2}$ versus $h\nu$ and finding the intercept on the x-axis ($h\nu$) by extrapolating the plot to $(\alpha hv)^{1/2} = 0$ [20]. Figure 1a shows the calculated band gap to be 3.20 eV for W-free VO₂. It is E_g between O $2p$ and π^* bands. While, Fig. 1b illustrates E_g for 1 wt.% W-doped VO₂ to be 2.87 eV. Thus, E_g of VO₂ is reduced 0.33 eV by added 1 wt.% W.

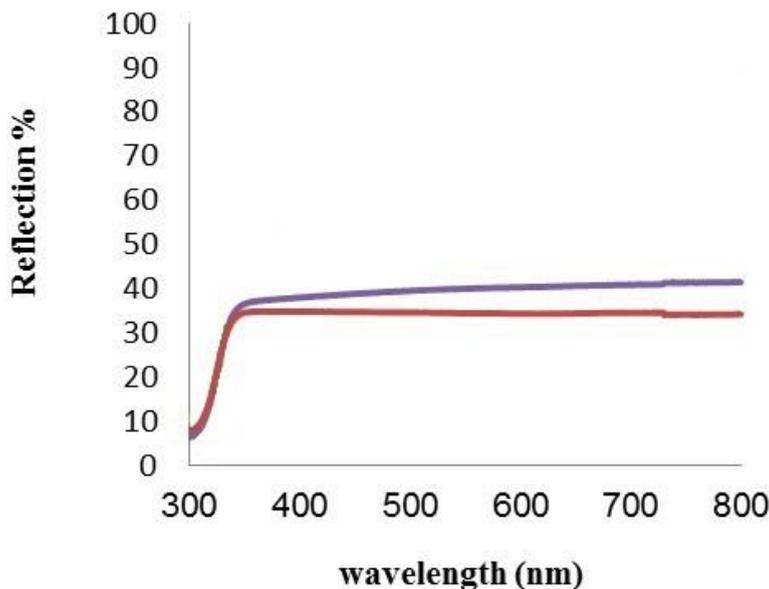


Figure 2. Reflection spectra of (a) W-free (violet color) and (b) 1 wt.% W-doped VO₂ (red color).

The index of refraction, n regards an important parameter for interactions of atomic microscopic. From view point of theory, there is more than one approach to local polarizability and density [21]. Therefore, there are available attempts to relate energy gap, E_g and index of refraction [22-27]. Anyway, the relations of n are separate of incident photon energy and temperature. The correlation between E_g and n will be revised. Ravindra et al. [27] had researched a correlation between E_g and n :

$$n = \alpha + \beta E_g \quad (4)$$

where $\beta = -0.62 \text{ eV}^{-1}$ and $\alpha = 4.048$. Refraction of light and dissipation will stimulate. Herve and Vandamme [28] have suggested another equation:

$$n = \sqrt{1 + \left(\frac{A}{E_g + B} \right)^2} \quad (5)$$

where $A = 13.6 \text{ eV}$ and $B = 3.4 \text{ eV}$. For group-IV semiconductors, Ghosh et al. [29] have published an empirical relationship based on the band structure and quantum dielectric considerations of Penn [30] and Van Vechten [31]:

$$n^2 - 1 = \frac{A}{(E_g + B)^2} \quad (6)$$

where $(E_g + B)$, $B = 0.225E_g + 2.25$ and $A = 8.2E_g + 134$ indicate to a suitable moderate energy gap. The calculated indices of refraction are presented in Table 1, as confirmed by the calculation of index of refraction, n and optical dielectric constant ϵ_∞ . Here is $\epsilon_\infty = n^2$ [32]. It is shown that the calculated index of refraction by Herve and Vandamme model [28] is appropriate for W doped VO₂ in improving the optical conversion. That is meaning high efficiency is attributed to low reflection and high absorption.

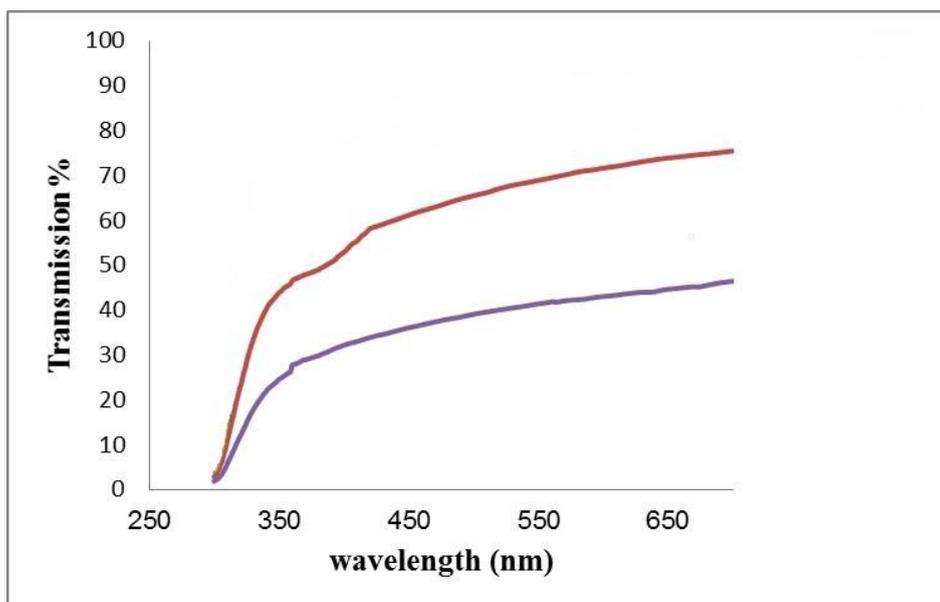
Table 1 The energy gap (E_g), refractive index (n) and optical dielectric constant (ϵ_∞) using Ravindra et al. [27], Herve and Vandamme [28] and Ghosh et al. [29] models of W doped VO₂.

W concentration	E_g (eV)	n	ϵ_∞
0%	3.20	2.064 ^a	4.26 ^a
		2.28 ^b	5.19 ^b
		2.29 ^c	5.24 ^c
1%	2.87	2.26 ^a	5.10 ^a
		2.38 ^b	5.66 ^b
		2.39 ^c	5.71 ^c

^aRef. [27]; ^bRef. [28]; ^cRef. [29].

Reflection spectra in the range, 300-800 nm for W-free and 1 wt.% W-doped are illustrated in Fig. 2. The highest reflectance is for W-free, it is attributed to the tendency towards metallic behavior of dopant percentage, E_g reduces gradually to the lowest value.

Figure 3 shows the transmission spectra of W-free and 1 wt.% W-doped VO₂. The transmission is increased for W-free from 30% to 40% from 275 nm and 675 nm, respectively. At 1 wt.% W doping, maximum transmission reaches 75%. The transmission percentage increases by increasing the wavelength from 275 nm and 675 nm. The change of transmission is attributed to phase transition (monoclinic to rutile (M→R)). Our results showed investigated ones.

**Figure 3.** Transmission spectra of (a) W-free (violet color) and (b) 1 wt.% W-doped VO₂ (red color).

The electrochemical contribution is a vital in a wide range of technological applications. The batteries are important in energy storage for devices and vehicles, and for enabling renewable energy

conversion technologies that give a relationship between electricity generation and associated chemical changes in a reaction.

4. CONCLUSIONS

VO₂ thin film was successfully deposited on glass via sol-gel method using V₂O₅ and H₂C₂O₄ as W acid dopant solution and V solution precursor. The W doping effect on E_g of VO₂ was investigated, E_g was 3.20 eV and 2.87 eV for W-free and 1 wt.% W-doped VO₂, respectively. Furthermore, the dopant role is to prevent the crystallization of V₆O₁₃. The optical results were displayed that the maximum transmission for 1 wt.% W doping and W-free was 75% and 40%, respectively. The Ravindra et al. model is convenient to W doped VO₂. It is concluded that 1 wt.% W-doped VO₂ has lowest energy gap, lowest reflectance and highest transmittance applicable for technological fields.

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