The effect of solution concentration on the physical and electrochemical properties of vanadium oxide films deposited by spray pyrolysis

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Abstract: Vanadium oxide thin films were prepared on glass substrates by using the spray pyrolysis technique. The effect of solution concentration (0.1 M, 0.2 M and 0.3 M) on the nanostructural, electrical, optical, and electrochromic properties of deposited films were investigated using X-ray diffraction, scanning electron microscopy, UV–vis spectroscopy, and cyclic volta-metrics. The X-ray diffraction shows that only the sample at 0.1 M has a single β-V_2O_5 phase and the others have mixed phases of vanadium oxide. The lowest sheet resistance was obtained for the samples prepared at 0.3 M solution. It was also found that the optical transparency of the samples changes from 70% to 35% and the optical band gap of the samples was in the range of 2.20 to 2.41 eV, depending on the morality of solution. The cycle voltammogram shows that the sample prepared at 0.3 M has one-step electerochoromic but the other samples have two-step electerochoromic. The results show a correlation between the cycle voltammogram and the physical properties of the films.

Key words: vanadium oxide; thin films; optical properties; cycle voltammogram
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1. Introduction

The transition metal oxides have many potential applications due to their unique physical, chemical, electronic, optical, magnetic, and thermal properties. This has attracted the attention of scientists and engineers for decades. Among the transition metal oxides, vanadium oxides offer many convenient physical effects which can be used for different microelectronic device applications[1].

As a result of its different valence states, vanadium can form a variety of oxides including VO, V_2O_3, VO_2, and V_2O_5. In addition to these simple oxides, there are many other closely related structures where vanadium atoms have different valences (+2, +3, +4 and +5). In particular, mixed valence materials of V (+4)/V (+5) show a particularly rich crystal chemistry[2]. Especially, V_2O_5, as a wide band gap (2.80 eV)[3] and n-type semiconductor material, is widely investigated because of its interesting applications such as in electrochromic devices (ECDs), cathodic electrodes for lithium batteries, and gas sensors[4–8].

Electrochromic (EC) phenomena can be observed for a range of transition metal oxides and exhibit a reversible color change or a general change in the optical properties during electrochemical oxidation or reduction processes[9].

Vanadium pentoxide thin films have been prepared using various techniques including: pulsed laser deposition (PLD)[10], electron beam evaporation[11], sputtering[12, 13], sol–gel process[14] and spray pyrolysis[15]. Among these methods, spray pyrolysis is a rather simple and low cost technique which has the ability of coating large areas.

In this paper, the electrochromic behavior of spray pyrolysis V_2O_5 thin films under different solution molarities is investigated. The evolution of the optical, electrical and structural characteristics of these films are studied. The electrochemical behavior, which is investigated by cyclic voltammetry, is also reported. It has been shown that the deposition technique greatly affects the electrical and optical properties of vanadium oxide thin films[16].

2. Experimental method

2.1. Film deposition

Vanadium oxide thin films were deposited on glass substrates using spray pyrolysis technique and for the electrochromic measurements of films, they were deposited on florin-tin oxide (FTO) coated glass substrates. First, a certain amount of vanadium chloride (VCl_3, $2H_2O$) was dissolved in distilled water to make the initial (precursor) solution. All samples were deposited under a fixed nozzle-to-substrate distance (d) = 35 cm and compressed air (P_{air}) = 3 atm as the carrier gas. Samples were prepared with different solution morality to contain 0.1 M, 0.2 M and 0.3 M, at constant substrate temperature (T_{sub} = 450 ℃) and solution spray rate (R = 5 mL/min).

2.2. Characterization

Structural characterization of the films was carried out using X-ray diffraction (XRD) (D8 Advance Bruker system) with Cu Kα (λ = 0.15406 nm) in 2θ = 10°–70° in continuous scan mode with a step width of 0.06. The average crystallite size (D) of the samples was estimated using Scherrer's formula[17]:

$$D = \frac{k\lambda}{\delta w \cos\theta}, \quad (1)$$

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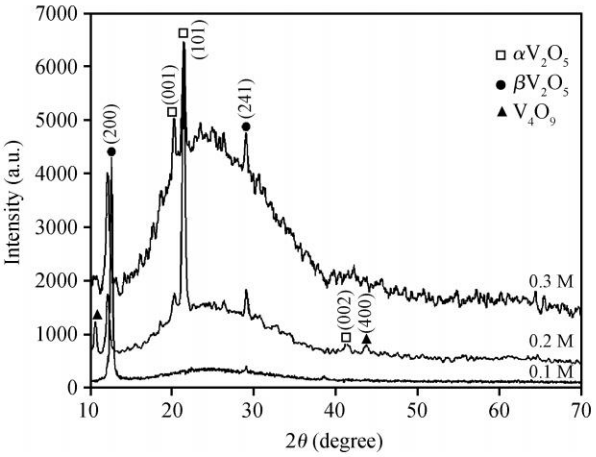

Fig. 1. XRD patterns of vanadium oxide films deposited at different solution concentrations.

where δw is the full width at half maximum (FWHM) of the corresponding XRD peak, k is a constant (~ 0.9), and θ is the Bragg angle. Sample morphology of the films was studied by SEM (VEGA TESCAN system).

The sheet resistance (R_s) of the films was measured using the two-point probe method with Al electrodes made by thermal evaporation in vacuum in an Edwards E-306A coating system. Optical measurements were carried out in the range of 300–1100 nm using a Unico 4802 spectrophotometer system. The direct band gap (E_g) of the prepared films was obtained from the extrapolation of the linear part of the $(\alpha h\nu)^2$ curve versus photon energy ($h\nu$), using the following equation[18]:

$$(\alpha h\nu)^2 = A(h\nu - E_g), \tag{2}$$

where α and E_g are the absorption coefficient and the energy band gap, respectively and A is a constant.

The electrochoromic measurements were performed with a standard three electrodes. A Pt as counter electrode and an Ag/AgCl reference electrode, at voltages between -0.4 and $+1.2$ V with the scan rate of 50 mV/s, were used. The electrolyte was 1 M LiCl in distilled water solution.

3. Results and discussions

3.1. Structural properties

The XRD patterns of the vanadium oxide films prepared at various mol concentrations (0.1, 0.2 and 0.3 M) are shown in Fig. 1. As can be seen, the sample made at 0.1 M solution has a tetragonal β V_2O_5 structure by orientation along [200]. By increasing the mol concentration from 0.1 to 0.2 M, the relative intensity of the peak [200] corresponding to β V_2O_5 phase has decreased at the expense of the appearance of orthorhombic α V_2O_5 and tetragonal V_4O_9 phases. By increasing the mol concentration from 0.2 to 0.3 M, the relative intensity of the [101] peak, corresponding to α V_2O_5 phase, has decreased, but α V_2O_5 [001], [200] and [241] peaks of β V_2O_5 have increased. It should be noted that the minor V_4O_9 phase seen in the 0.2 M sample has almost disappeared in the 0.3 M sample. It can be seen that the samples tend to be a mixed structure of different vanadium oxides phases, as the solution concentration increases. A similar behavior, i.e., multi-phase samples as a result of increasing the substrate temperature, has been reported[19]. The average crystallite size grows from 24.47 to 29.19 nm by increasing the solution concentration from 0.1 M to 0.2 M and then decreases to 25.66 nm by increasing the solution concentration to 0.3 M. Figure 2 shows SEM images of the vanadium oxide samples. As shown in Figs. 2(a) and 2(b) the sample prepared at 0.1 M solution concentration has a nano belt shaped structure. Similar morphologies have also been reported for films of this compound prepared by other methods[20]. By increasing the solution concentration from 0.1 to 0.2 M, a nano-sized platelet formed and by increasing the solution concentration to 0.3 M, nano disks are obtained (Figs. 2(c) and 2(d)).

Table 1. The electrical measurement results (thickness determination error is $\sim \pm 5\%$).

Sample	R_s (kΩ/□)	t (nm)
0.1 M	940	110
0.2 M	176	123
0.3 M	101	168

3.2. Electrical property

The results of the electrical measurements of the films prepared at different solution molarities and the thickness of the films, which were determined from the transmission data using Puma software[21], are summarized in Table 1.

The electrical measurements show that the sheet resistance of the films decreases with increasing solution concentration. This is because of an increase in the thickness of the films and also improvement of the stoichiometry and thus an increase in the carrier concentration, as seen in Table 1 and X-ray diffraction patterns.

3.3. Optical properties

Transmittance was measured at room temperature to investigate the optical properties of the prepared vanadium oxide films. Figure 3 shows the transmittance spectra of the samples decreasing from 70% to 35% by increasing the solution concentration, related to the increase of film thickness[22]. The value of the band gap of the samples was obtained as depicted in Fig. 4. As Figure 4 shows, the value of the band gap decreases from 2.41 to 2.20 eV by increasing the solution concentration from 0.1 to 0.2 M and then it increases from 2.20 to 2.35 eV by increasing the concentration from 0.2 to 0.3 M. This behavior is related to the grain size growth[23].

3.4. Electrochemical property

The CV of the 5th cycle of vanadium oxide films prepared with three layers at different solution concentrations in the potential windows between -0.4 and $+1.2$ V are shown in Fig. 5. Two anodic peaks at $\sim +0.02$ V and $\sim +0.31$ V and two cathodic peaks at ~ -0.024 V and ~ -0.263 V are shown for the film prepared at 0.1 M solution concentration, which can be due to the V^{+4} and V^{+5} ions for the oxidation peaks and V^{+4} and V^{+3} for the reduction peaks respectively. The as-deposited sample at 0.1 M is yellow in color. The film prepared at 0.2 M has two oxidation peaks at $\sim +0.048$ V and $\sim +0.64$

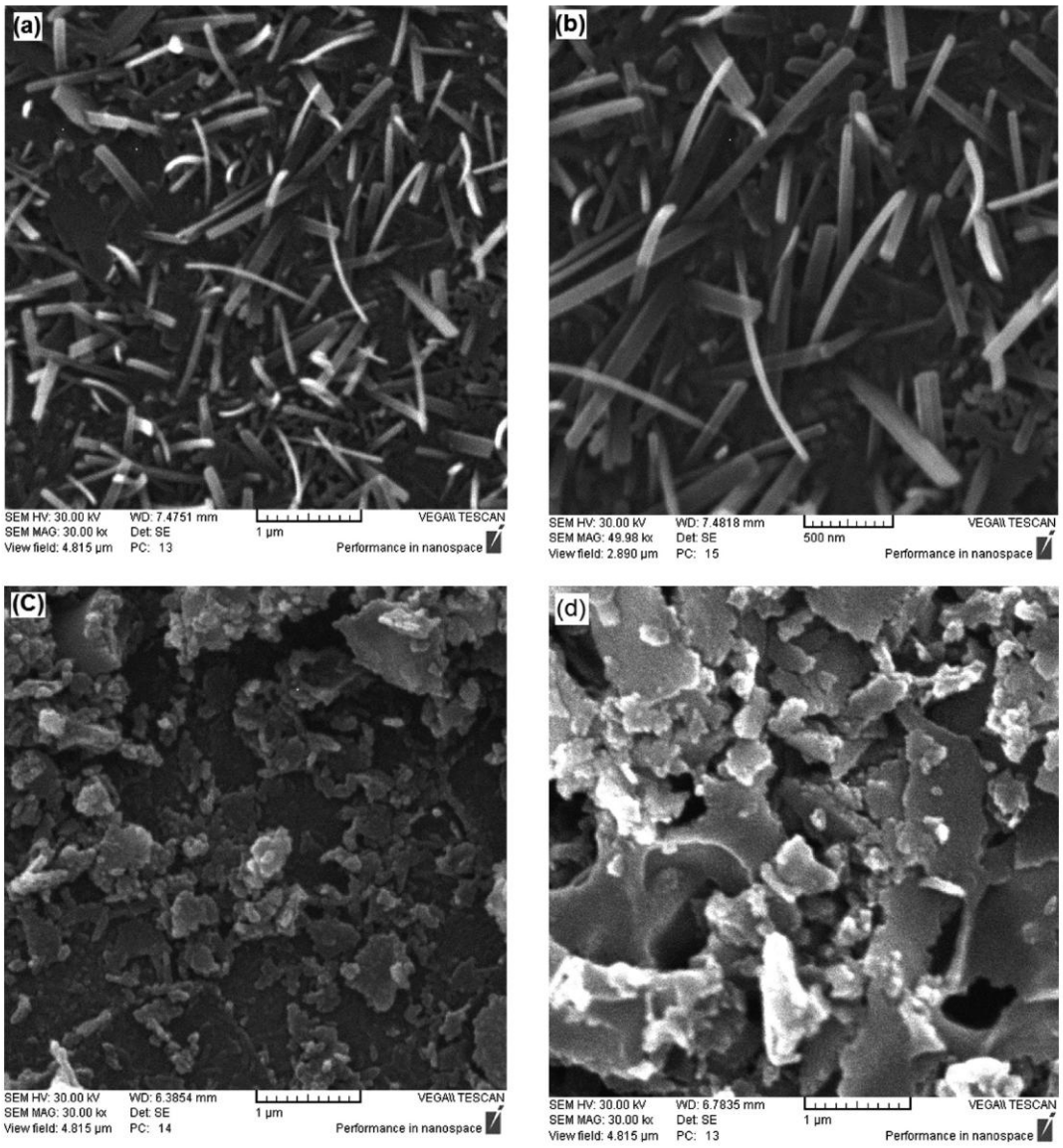

Fig. 2. SEM images of vanadium oxide films: (a), (b) deposited at 0.1 M V-concentration, (c) deposited at 0.2 M V-concentration and (d) deposited at 0.3 M V-concentration.

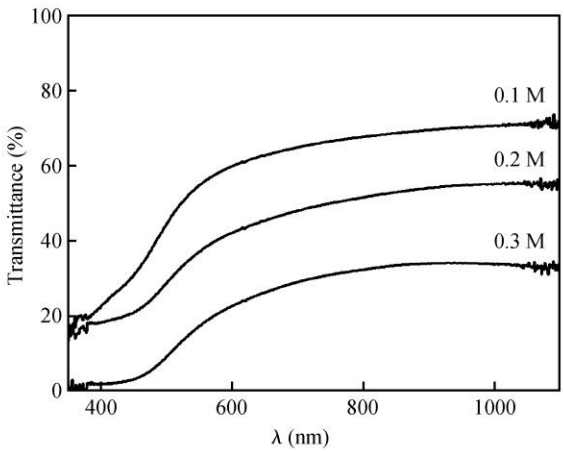

Fig. 3. The transmittance spectra of the samples deposited at different solution concentrations.

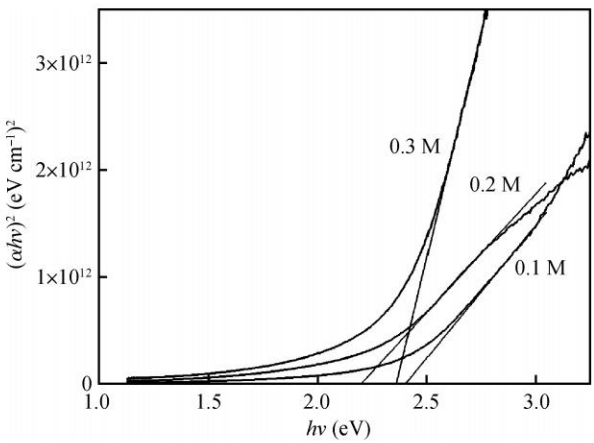

Fig. 4. Plots of $(\alpha h\nu)^2$ versus $h\nu$ (photon energy) for deposited films with various solution concentrations.

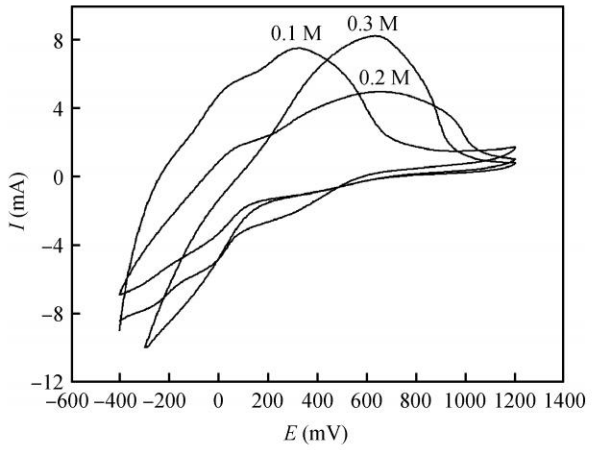

Fig. 5. Cyclic voltammogram of vanadium oxide thin films deposited at different solution concentrations. The scan rate is recorded at 50 mV/s.

V and two reduction peaks at ~ -0.031 V and ~ -0.274 V. The color of the film is greenish yellow. When sweeping the potential downward and upward, the CV curves for 0.1 M and 0.2 M samples show two-step electrochromism, i.e. from yellow (V^{+5}) to blue (V^{+4}) and then green (V^{+3}), respectively. This behavior has also been reported by the others[24]. The film prepared at 0.3 M solution concentration is a little different: while the as deposited film is yellow, the CV pattern shows an oxidation peak around $\sim +0.653$ V and a reduction peak at ~ -0.058 V. This sample has one-step electrochromism, i.e. yellow to blue because of the reduction process occurrence which results in V^{+4} ions, in consistence with the vanadium pour baix diagram. As can be seen, the different nanostructure films of vanadium oxide with significantly different morphologies (Figs. 2(a)–2(d)) have different CV shapes. This is reasonable since the morphology or the total surface area of the nanostructure materials may affect the reaction rate on the electrochromic experiment. This relation between the morphology of the film and the electrochromic properties has also been observed for vanadium oxide films prepared by using the thermal evaporation method[20]. The CVs obtained for the sample with 0.3 M solution concentration exhibit a more intense characteristic anodic peak. On the other hand, as mentioned above, the 0.3 M film has lower resistance. The conductivity of the film can be associated with oxygen vacancies and the presence of oxygen vacancies enables easy access for lithium ion intercalation and diffusion[25].

4. Conclusion

In this work, we report the effect of solution concentration on the physical properties of vanadium oxide thin films prepared by spray pyrolysis method. Our results revealed that the physical properties of the films depend strongly on the solution concentration.

(a) XRD patterns show that the structure of the deposited film in 0.1 M solution concentration has a β-V_2O_5 single phase but by increasing the solution concentration mixed phases of α-V_2O_5, β-V_2O_5 and V_4O_9 appear.

(b) The electrical measurements showed that the sheet resistance of the prepared films decreases with increasing the solution concentration. This can be related to the growth of the grain size and also the improvement of the stoichiometry of the samples.

(c) The transparency of the film decreases from 70% to 35% with increasing the solution concentration. The energy band gap decreases from 2.41 to 2.20 eV for the samples prepared at 0.1 M and 0.2 M, respectively and then increases from 2.20 to 2.35 eV by increasing solution concentration from 0.2 M to 0.3 M, related to the grain size growth.

(d) The CVs obtained for the samples with 0.1 M and 0.2 M solution concentration are two-step electrochromic (yellow, blue and green) and the sample prepared at 0.3 M solution concentration is one-step electrochromic (yellow and blue). The morphology of the vanadium oxide layers can affect the electrochromic properties of the samples. The sample with 0.3 M solution concentration shows a more intense characteristic anodic peak. This is due to the lower resistance. Finally, we can conclude that the conductivity of the samples enables easy access for lithium ion intercalation and diffusion.

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