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Monochromatic double coloring effect on V2O5 thin films deposited by electron beam

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ABSTRACT

Electrochromic material is a thin film technology that has a close relationship with environmental sustainability since they can control the light and heat that enter and leave a building. Vanadium oxide films are electrochemically active for lithium and electron co-intercalation, presenting low optical variation in the low energy visible light, which is suitable for application as a passive electrode in the electrochromic devices. The spectral double coloration of vanadium oxide thin film has been investigated but the monochromatic, in particular, for high photons energy, remains poorly explored. To understand the optical behavior of the vanadium oxide films, in high photons energy (E > 2.0 eV), films were opto-electrochemically investigated. The films were electron beam deposited and modified by heat treatment in an inert atmosphere. All samples show crystallographic orientation in a [110] direction, and the charge capacity showed to be dependent on the film conditioning. The charge capacity of the as-grown film is about 6 mC while for the film heat-treated at 100 ºC it is five times higher. The vanadium oxide films showed reversible Li^+ intercalation, presenting a double spectral and monochromatic coloration. It was concluded that for low energy photons the small polaron model fully explains the phenomenon of double monochromatic coloration, and, for high-energy, the monochromatic double coloration is due to the crystallographic phase transition.

Keywords: Double coloration, vanadium oxide, ionic intercalation, thin films.

1. INTRODUCTION

Electrochromism is an optical absorption phenomenon associated with electron-ion co-intercalation in the, respectively, electronic and crystallographic materials structure mainly metal oxides [1, 2]. Among the electrochromic oxides, vanadium oxide (VO_x) is the only one to present two optical absorption processes, which depend on the incident light wavelength [3–5]. For low-energy photons, in the infrared and red regions (1.1 eV to 2.1 eV) the absorption increases with the electron-ion co-intercalation. In the other hand, it decreases to high-energy photons in the blue and ultraviolet regions (2.1 eV to 3.5 eV). Conversely, when electrons and ions are deintercalated from the ionic host the absorption decreases to low energy photons and increases to those of high energies, these processes are known as the phenomenon of the double coloration [2, 3, 6].

The double coloration phenomena in vanadium oxides films are extensively studied due to technologically useful properties in coloration optoelectronic devices, optical switches, temperature and gas sensors and energy efficient smart windows [7–10]. However, the literature does not make sufficiently clear the consequences of this phenomenon, when dealing with the optical spectrum variation, during the absorption of photons with a single wavelength concomitant to the electron-ion co-intercalation in the electronic and crystallographic material structure. The variation of the transmittance spectrum for photons with a single wavelength was named as double monochromatic coloration. Talledo e Granqvist describes the phenomenon of the double spectral coloration for V_2O_5 thin films, but only for the region of low energies, red and infrared region [11]. In the other hand, Wu et al. dealt with how this intercalation affects the phenomenon of dual spectral coloration at high energies [12].

The double monochromatic coloration phenomenon of vanadium oxide thin films deposited by vacuum electron beam was investigated exploring the optical absorption of the films excited by visible light photons of the electromagnetic spectrum. For this, was used the known models on the optical absorption for this kind of material, the model of small polaron and the rigid band for low and high energies, respectively.

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2. MATERIALS E METHODS

The vanadium oxide films were evaporated under high vacuum by electron beam bombardment in a Balzers (EB327F) brand system. The substrates used were glass plates coated with electrically conductive and optically transparent, indium tin oxide (ITO) film. The starting material used for evaporation was a 0.7 g of V_2O_5 pelletized and hydraulic pressed (MaTecK, 99.9%). The parameters of the electron beam were: beam position 3.5 L, frequency 4, current at filament 45 A, beam acceleration voltage 5 kV, emission control current 5.8 mA, longitudinal amplitude 1 and latitudinal amplitude 1.5, beam focus control 0.55. The pressure during the deposition was 1.5 x 10^{-5} mbar. The film's thickness was 1,300 Å.

The films without any modification were nominated as grown (AG). Part of them was heat treated in an electric furnace (Maitec model FT - 1200 with controller FE - 50RP - Flyever) at 100, 200 and 300 ºC in argon atmosphere (Ar) under atmospheric pressure. The heat treatment had as objective to restructure the crystallographic structure of the films without, however, changing their stoichiometry. Heating was performed at a rate of 3 °C/min, remaining for 10 hours at each of these temperatures and cooled at the same rate.

The crystalline phases identification in the films was done by X-ray diffractometry in a PANanalytical diffractometer, X'Pert Pro, with CuKα radiation. The diffractograms were collected by the grazing incidence technique. The scanning range 2θ from 10 to 70º, with an incidence angle of 2º, with an angular pitch of 0.04º and counting time of 3 s per point. The voltage and current used were 40 kV and 50 mA, respectively.

The opto-electrochemical measurements were performed with a three-electrode electrochemical cell, with the V_2O_5 film as a working electrode and metallic lithium wires as a counter electrode and reference electrode. The electrolyte used was a solution of lithium perchlorate ($LiClO_4$) dissolved in propylene carbonate (PC) at a concentration of 1.0 mol L^{-1}. Optical measurements of the electrochromic effect in the range of 350 to 1000 nm were performed using an optical fiber spectrophotometer (Ocean Optics). The maximum of transmittance was calibrated from the cell without the film and substrate. Spectroelectrochemical was done taking each spectrum in different percent's of states of charge by cyclic voltammetry (CV). Before spectroelectrochemical tests, the charge capacity was previously measured to provide the total of ions and electrons that can be driven by each film. The CV was done in the 2.00 to 3.60 V versus $Li|Li^+$ range, and at 5.00 mV/s.

3. RESULTS AND DISCUSSIONS

The analysis of the diffractograms, Fig. 1, show some peaks corresponding to the ITO film and the orthorhombic phase of V_2O_5, characterized by the (110) peak evidencing that the films have a preferred orientation at [110] direction, that is perpendicular to the substrate surface and the (110) Miller plane [13–16].

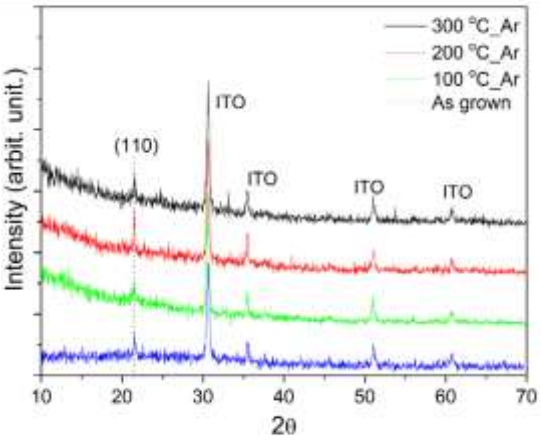


Figure 1: Diffractogram of the vanadium oxide thin films studied.

The UV-vis transmittance spectra of the films before and after lithium ions intercalation are shown in Fig. 2A. The changes in the transmittance spectra are due to the lithium ions intercalation into the crystallographic sample structure and electrons in the electronic one by cyclic voltammetry, Fig. 2B. In Fig. 2A is shown a common point of convergence in a specific photon wavelength. These isosbestic points are separating the region where the vanadium oxide films change from anodic coloring to cathodic coloring [17]. The isosbestic point reinforces the coexistence of these two processes [18, 19]. The wavelength position of the isosbestic point is shifted as the treatment temperature of the samples is increased. In the lithium intercalation into the V_2O_5 film process (electrochemical reduction reaction), two optical absorption phenomena are concomitantly present. While in the high energy photons (at the left of the isosbestic point) films become bleached, in the low energy photons (at the right of the isosbestic point), the films become colored. It is known as a spectral double coloration effect [20]. These results agree with those presented by Cogan et al [21].

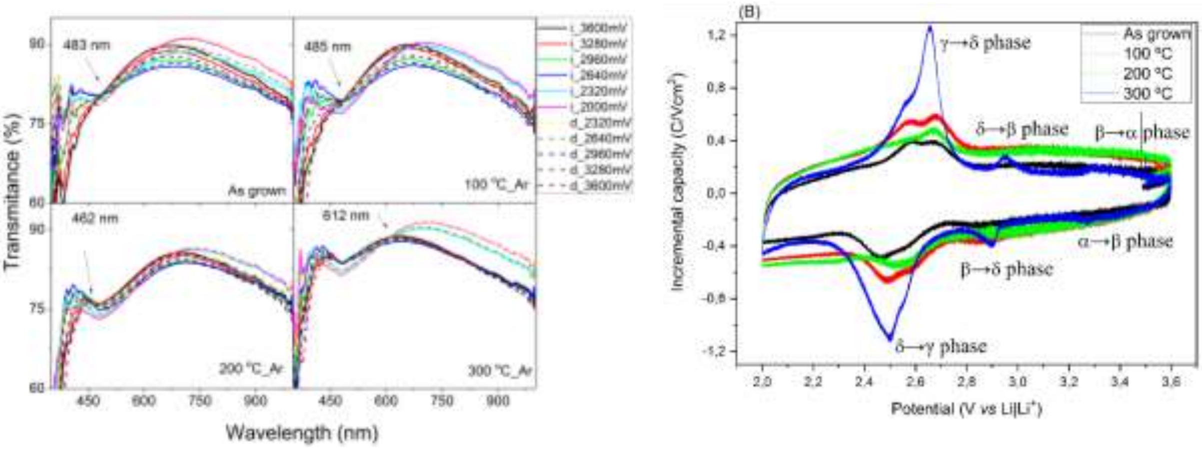


Figure 2: (A) Transmittance as a function of wavelength. The arrows indicate the isosbestic point. In the legend the letter **(i)** corresponds to the intercalation process and **(d)** the deintercalation; (B) cyclic voltammetry for AG and 100, 200 and 300 ºC heat treated films.

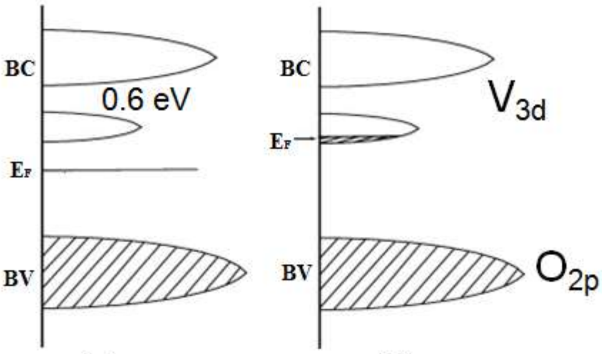
The oxi-reduction reaction is represented by the following equation, where x is the number of electrons and lithium ions that participate in the reaction.

$$V_2^{+5}O_5^{-2} + xe^- + xLi^+ \underset{oxidation}{\overset{reduction}{\rightleftarrows}} Li_x^+[V_{2-x}^{+5}V_x^{+4}]O_5^{-2} \tag{1}$$

The absorption in low energy photons, studied by Talledo and Granqvist, is usually explained by the formation of small polarons optical absorption center, that is due to the electron hopping between the reduced (V^{4+}) and oxidated (V^{5+}) vanadium ion pair in the material [7,11,22]. The small polaron optical absorption is described schematically following equation 2, where j and k are neighbors in the oxide network and hν is the energy of the absorbed photon [23].

$$V_j^{+4} + V_k^{+5} + h\nu \rightarrow V_j^{+5} + V_k^{+4} \tag{2}$$

At the high energy, photons absorption can be explained by the interband electronic excitation in the film band structure, Fig. 3 [5, 23, 12, 24]. In the V_2O_5 its vanadium 3d orbital is divided, and the energy difference between the lower and upper band is about 0.60 eV. The lowest conduction band energies are related to the V_{3dxy} and V_{3dyz} orbitals, with gap energy of about 2.00 eV [25]. The Fermi energy level (EF) is located in the middle of the region of the optical absorption gap in the non-intercalated V_2O_5, and in the intercalated film, the EF assumes the value of the last electron occupancy [12, 26].



(a) **(b)**

Figure 3: Banding structure scheme for (a) non-intercalated V_2O_5 and (b) intercalated [Adapted from Wu et al. [12]].

In Fig. 4 is shown the optical transmittance at two different wavelengths during the electrochemical reduction process. It is clear that the charge capacity of the films depends on heat treatment conditioning.

As can be seen in Fig. 4, the electrochromic variation of the V_2O_5 film exhibits in addition to the double spectral coloration a double monochromatic coloration. To analyze in detail this behavior, photons of two specific energies, each one from the high (400.0 nm) and low (632.8 nm) energy, was taken to investigate its transmittance, that varies in a "V" form for both photon energies. It can be understood as a saturation of the absorption phenomena related to intercalation of about more than one lithium by V_2O_5 molecule in the film, $x > 1$ in equation 1.

For low photon energy (632.8 nm), when only V^{5+} is present in the film $x = 0$ in equation 1 and the chemical formula is $V_2^{5+}O_5^{2-}$ and the film is transparent. As the reduction process occurs, the film begins to be opaque due to the V^{4+} concentration growth. At 50% of V^{5+} and V^{4+} concentration, the maximum of small polaron absorption center is achieved ($Li_1^{1+}V_1^{5+}V_1^{4+}O_5^{2-}$), and the film transmittance reaches its minimum. From there and continuing in the reduction process, the concentration of V^{4+} become higher than V^{5+}, and the film comes to be transparent again ($Li_2^{1+}V_2^{4+}O_5^{2-}$).

For high photon energy (400.0 nm) the initial transmittance is low and was expected to rise during ions and electrons intercalation in the vanadium electronic band, described by the band model [27, 28]. Possibly during the intercalation of lithium ions in the crystallographic structure of V_2O_5, the ions first lodge at sites located in the vanadyl oxygen forming a structure of triangular prismatic sites. These structures characterize a crystallographic phase that occurs when $x \leq 1$. When the change to the next crystallographic phase occurs, $x > 1$, the structure of the material starts to present tetrahedral sites [29, 30], where the lithium ions probably intersect at sites located between two oxygens of the crystal lattice. The electron-ion co-intercalation has a local effect in the electronic structure of the O_{2p} and V_{3d} orbitals. Particularly, when the lithium ions intercalate at the sites located in the vanadyl oxygen, the electronic structure varies strongly causing a high electrochromic variation [20, 31], as observed in Fig. 4. The colors used are those used in Fig. 2A for the different electrochemical potentials in which the transmittance spectra were obtained.

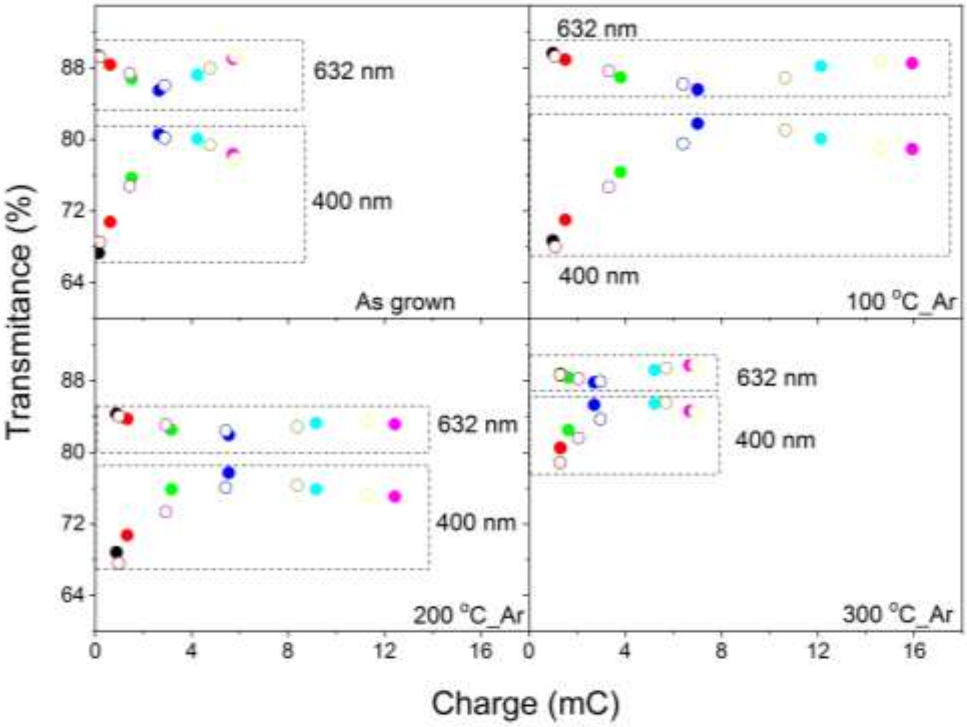


Figure 4: Transmittance as a function of a state of charge, showing distinct regions of optical absorption for blue light (400 nm) and red light (632 nm). The fill colored points correspond to the intercalation process and bleached points the deintercalation.

4. CONCLUSIONS

The monochromatic double coloration phenomenon of vanadium oxide thin film was investigated in two different ranges of energies in the visible of the electromagnetic spectra. It has been verified that for low energy photons ($E \leq 2,0$ eV) the small polaron model explains the double coloration phenomenon, and for high energy photons ($E > 2,0$ eV) the rigid band model can describe the double coloration, but it has to take in account that the absorption is affected by crystallographic phase transitions. This behavior makes the material suitable for application in electrochromic devices as high energy photons modulation or as a passive electrode for low energy photons.

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