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A simple solution method to prepare VO2:Co^{2+} precursors for thin film deposition by solution-processing method

Un método simple de solución para preparar películas delgadas de VO2:Co^{2+} para la deposición mediante el método de procesamiento en solución

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ABSTRACT

Solution-processing is a low-cost solution method to prepare a variety of organic or inorganic thin films. For metal oxide compounds, a solution-processing solution of an organometallic compound is frequently used as a precursor to be spin coated, followed by a thermal annealing to form metal oxide. In this work, vanadium oxide powders are obtained from a simple acid-base reaction, and then they are dispersed in isopropyl alcohol to form a solution for spin-coating. Different amount of cobalt salt are also added together with VO_x into isopropyl alcohol to form VO_x:Co^{2+} solutions. After thermal annealing at 200 °C, continuous transparent thin films are obtained. Optical, structural, morphological and chemical binding energies of those films are analyzed. It is found that amorphous VO_2:Co^{2+} compound is formed in those films with V:Co atomic ratios between 6.6:1 and 1.6:1. Optical absorption onsets of those films are around 2.3 eV. An interesting interconnected porous morphology is observed when the atomic ratio of V:Co is around 4.9:1. It is concluded that porous amorphous cobalt doped vanadium oxide thin films can be obtained from a spin-coating process at low annealing temperature from a simple solution without any complex agent.

Keywords: *cobalt doped vanadium oxide, spin-coated thin films, porous morphology, solution processing without ligands.*

RESUMEN

El procesamiento de soluciones es un método de bajo costo para preparar una variedad de películas delgadas orgánicas o inorgánicas. Para compuestos de óxidos metálicos, un procesamiento de solución de un compuesto organometálico se usa con frecuencia como solución precursora para ser recubierta por rotación, seguida de un tratamiento térmico para formar el óxido metálico. En este trabajo se obtienen polvos de óxido de vanadio a partir de una simple reacción ácido-base, y luego se dispersan en alcohol isopropílico para formar una solución para spin-coating. También se agregan diferentes cantidades de sal de cobalto junto con VOx en alcohol isopropílico para formar soluciones de VO_x:Co^{2+}. Después del tratamiento térmico a 200 °C, se obtienen películas delgadas transparentes. Se analizan las propiedades ópticas, estructurales, morfológicas y químicas. Se encontró que el compuesto VO_2:Co^{2+} es amorfo y se obtiene con una relación atómica V:Co variada de 6.6:1-1.6:1. El material presenta una absorción óptica alrededor de 2.3 eV. Se observa una interesante morfología porosa interconectada cuando la relación atómica de V:Co es ~4.9:1. Se concluye que se pueden obtener películas delgadas amorfas porosas de VO_2:Co^{2+} a partir del spin-coating a una baja temperatura de tratamiento utilizando una solución simple sin agente complejante.

Palabras clave: *oxido de vanadio dopado con cobalto, películas delgadas mediante recubrimiento centrifugo, morfología porosa, procesamiento de la solución sin complejantes.*

INTRODUCTION

Vanadium oxides (VO_x) and VO_x doped with different metal oxides are interesting semiconductor materials because of their abundance in the Earth's crust, as well as its multi-oxidation states and various crystalline structures (Silversmit *et al.*, 2004, 2006). As a semiconductor material, VO_x shows a band gap ~2.6-3.5 eV that makes it a good semiconductor material for diverse electronic application. In the literature, VO_x thin films have been deposited with different methods for diverse potential applications employing techniques such as: magnetron sputtering and spin-coating for thermochromic applications (Ho *et al.*, 2019; Zhan *et al.*, 2020; Yuan *et al.*, 2021); pulsed laser deposition for cathodes in Lithium and sodium-ion batteries (Petnikota *et al.*, 2018); sprayed solution for NO_2 gas sensing (Khatibani, Abbasi and Rozati, 2016; Mane and Moholkar, 2017); solution-processing method for smart windows applications (Peng *et al.*, 2018; Wang *et al.*, 2020; Shen *et al.*, 2021).

On the other hand, modifications of optical or structural properties of semiconductor thin films are necessary to improve application of these materials. Which by adding a different type of metal ions into a VO_x host matrix, known as a doping process, is one of the most effective ways to modify vanadium oxide structure, leading to different electrochemi-

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cal, catalytic, and magnetic properties (Lu *et al.*, 2019; Sharma *et al.*, 2021; Geng *et al.*, 2022). Metal doped vanadium oxide thin films have been obtained with different deposition techniques: Y-doped VO_x thin films by DC reactive magnetron sputtering for electrical modulation applications (Zhou *et al.*, 2020); Cs-doped VO_x thin films deposited by spun-cast as a hole extraction layer in perovskite solar cells (Yao *et al.*, 2018); Fe-doped VO_x by sol-gel spin-coated for electrochromic device applications (Bae, Koo and Ahn, 2019); In-doped VO_x thin films obtained by spray pyrolysis coating system for optical transparency modulation (Tabatabai Yazdi, Pilevar Shahri and Shafei, 2021); Co-doped VO_x thin films by microwave irradiation process for battery-type supercapacitor applications (Liu *et al.*, 2020), among others (Ji *et al.*, 2018; Li *et al.*, 2019; Xu *et al.*, 2019).

Solution-processing spin-coating is an economical method to obtain homogeneous pure or doped VO_x thin films. Compared to other chemical solution deposition methods, this method has the advantage that it enables the deposition of metal oxide thin films without seed layer on substrates such as glass, fluorine doped tin oxide (FTO), indium doped tin oxide (ITO) or coated polyethylene (PET) for transparent or flexible electronics applications (Hajzeri *et al.*, 2012). In particular, metal ion doping in VO_x thin films could be an in-situ process in a spin-coating method by adding the metal source into the vanadium precursor solution. However, expensive organometallic compounds are usually employed to prepare metal precursor solutions. In this work, we propose a simple method to prepare vanadium oxide and cobalt doped vanadium oxide solutions, without the use of organometallic compound or any complex agent that would result in a slow metal cation release, and an increased time and temperature deposition. Chemical photoelectron analysis of vanadium oxide samples, with or without cobalt doping, confirms the formation of a vanadium oxide VO_2 compound in the film samples. Cobalt oxide CoO also prevails in VO_2:Co^{2+} samples, with some neighboring atoms arranged in a short-range order. Porous surface of VO_2:Co^{2+} thin films can be obtained, giving an optical absorption onset at 2.3 eV.

EXPERIMENTAL PROCEDURE

Synthesis of VO_x powders and solution

Precursor solutions for VO_x powders were prepared by using 0.1 M solution of vanadium (IV) oxide sulfate hydrate ($VOSO_4 \cdot xH_2O$) and 1 M solution of sodium hydroxide (NaOH), as previously suggested [25]. These two precursor solutions were mixed, resulting in a blue color solution with a pH ~2 tested with a MColorHast™. After that, the blue solution was heated at 80 °C for 3 h to obtain VO_x precipitates. These precipitates were dispersed in methanol to dissolve possible impurities and then centrifuged. After centrifugation, VO_x precipitates were dried at 80 °C for 2 h to obtain VO_x powders.

To prepare a VO_x sol-gel solution, VO_x powders were dispersed in isopropyl alcohol under ultrasonic vibration at room temperature for 10 min. Then, the mixture solution was filtered with a cotton filter to remove the undispersed precipitates and obtain a transparent solution for thin film deposition by spin-coating. Pure VO_x films were called samples S_1.

Preparation of VO_x:Co solutions

To obtain cobalt doped VO_x precursor solutions, dried VO_x powders and $CoCl_2 \cdot 6H_2O$ salt were dispersed/dissolved in isopropyl alcohol. Then, the solutions were subjected to ultrasonic vibration at room temperature for 10 min. Finally, the solutions were filtered with a cotton filter to remove the undispersed precipitates and obtain transparent VO_x:Co solutions for thin film deposition by spin-coating. Four VO_x:Co solutions were prepared with $VO_x/CoCl_2 \cdot 6H_2O$ weight ratios of 0.7/0.3, 0.5/0.5, 0.3/0.7 and 0.1/0.9, called samples S_2, S_3, S_4 and S_5, respectively.

VO_x and VO_x:Co thin film deposition

The five precursor solutions, VO_x and VO_x/Co, were used to form thin films by spin-coating. Microscope glass slides from VE-P10 Velab™, to be used as substrates for vanadium oxide solutions, were washed with Alconox® detergent, rinsed with distilled water and air-dried. The clean substrates were placed in the Chemat Thecnology Spin-Coated KW-4A, 50 µL of the VO_x or VO_x:Co solutions were deposited at 2500 rpm for 2 min on the glass substrates. The obtained coatings were thermally annealed in air at 200 °C for 1 h and became solid thin films.

Thin films characterizations

X-ray photoelectron spectroscopy (XPS) was used to assess the chemical composition of the films. The tool employed was PHI 5000 Versa Probe II, with a monochromatic Al Kα (1486.6 eV) X-ray source with a 0.1 eV step size and a constant pass energy of 23.50 eV. The scale of binding energies was corrected by calibrating the main C 1*s* peak at a binding energy of 284.8 eV. Atomic compositions of VO_x/Co films were estimated from the XPS results. Crystalline structures of VO_x/Co films were probed with X-ray diffraction (XRD) employing a Rigaku DMAX-2200 diffractometer equipped with a Cu Kα (λ = 1.54 Å) X-ray source. A Jeol JSM-7800F field emission scanning electron microscope (FE-SEM) was used to evaluate the surface morphology of the films. The surface morphology of each film sample was analyzed by atomic force microscopy (AFM) with a Veeco Dimension Icon, Bruker instrument. Optical transmittance spectra of VO_x/Co films were measured with a Perkin Elmer Lambda 20 UV–visible spectrometer. Thicknesses of VO_x and VO_x:Co thin films were measured with an Ambios Technology XP 200 profilometer.

RESULTS AND DISCUSSION

Profilometry and main characteristics

The first assessment of the possible formation of continuous VO_x and VO_x:Co thin films from the above mentioned precursor solutions is film thickness measurement by profilometry. Table 1 lists the five types of VO_x:Co thin films with their respective thickness. In the Alpha-Step profiles of all film samples, large grains of 100 to 400 nm of height were obser-

ved and were embedded in continuous solid coatings with thickness from 133 to 246 nm.

Table 1. Thickness, band gap and V:Co atomic ratio of VO_x:Co film samples.
Tabla 1. Grosor, brecha de banda y proporción atómica V:Co de muestras VO_x:Co.

Sample name	Weight ratio ($VOSO_4 \cdot xH_2O$ / $CoCl_2 \cdot 6H_2O$)	Thickness (nm)	Atomic ratio of V:Co
S_1	1/0	152 ± 44	1:0
S_2	0.7/0.3	133 ± 39	6.6:1
S_3	0.5/0.5	123 ± 19	4.9:1
S_4	0.3/0.7	133 ± 26	2.9:1
S_5	0.1/0.9	246 ± 11	1.6:1

Optical properties

Optical transmittance spectra of VO_x:Co thin films can be appreciated in Figure 1a with transmittance percentage of 65 - 75 % in the 800 -1350 nm wavelength (λ) range. The main influence of Co^{2+} inclusion is observed in UV-A to blue region, at 325 - 500 nm, as reported elsewhere (Hajzeri *et al.*, 2012; Martínez-Gil *et al.*, 2020). Furthermore, samples with larger Co^{2+} concentration, such as S_4 and S_5, show lower transmittance at the visible region (400 - 700 nm). Optical absorption coefficient spectrum of each film sample, α(λ) (Figure 1b), is calculated from the simplified Beer-Lambert equation: $\alpha = -\frac{1}{d}\ln(T)$, where d is film thickness and $T(\lambda)$ the transmittance spectrum. The optical absorption onset (or band gap E_g) value is estimated by intersection of two straight fitting lines. The E_g values of pure vanadium oxide and vanadium with different amounts of Co^{2+}, are around 2.3 eV, which is very close to that previously reported for V_2O_5 [27]. It is also observed that the absorption coefficients of all the cobalt doped vanadium oxide thin films (from S_2 to S_5) are higher compared to the pure vanadium oxide sample (S_1), keeping the same forms of the spectra. Higher absorption region (> 3.8 eV) in these samples should be related to the glass substrate absorption.

X-ray diffraction

X-ray diffraction pattern of VO_x film sample (S_1) is presented in Figure 2, which appears to correspond to an amorphous material due to the broad signal around 22°, plus a monoclinic phase of $HNaV_6O_{16}\bullet 4H_2O$ with the plane orientation (100) at around 2θ ~ 8° (JCPDS# 49-0996 (Channu *et al.*, 2011)). This crystalline compound could be a residual from $VOSO_4 \cdot xH_2O$ + NaOH, reaction and was not be eliminated during the 200 °C annealing or the thin film processing. Interestingly, after Co^{2+} addition, the reflection peak around 2θ ~ 8° gradually reduces. The higher the concentration of Co^{2+}, the smaller the intensity of that peak, until its complete elimination in the sample with the highest concentration of Co^{2+} (sample, S_5). S_5 shows the diffraction pattern typical of an amorphous film, hence it is a predominantly amorphous material. Since no diffraction peaks of CoO_x or $VCoO_x$ compounds appear in the five VO_x:Co^{2+} samples, it seems that low temperature annealing leads to amorphous materials, as indicated in (Hu *et al.*, 2017; Martínez-Gil *et al.*, 2020).

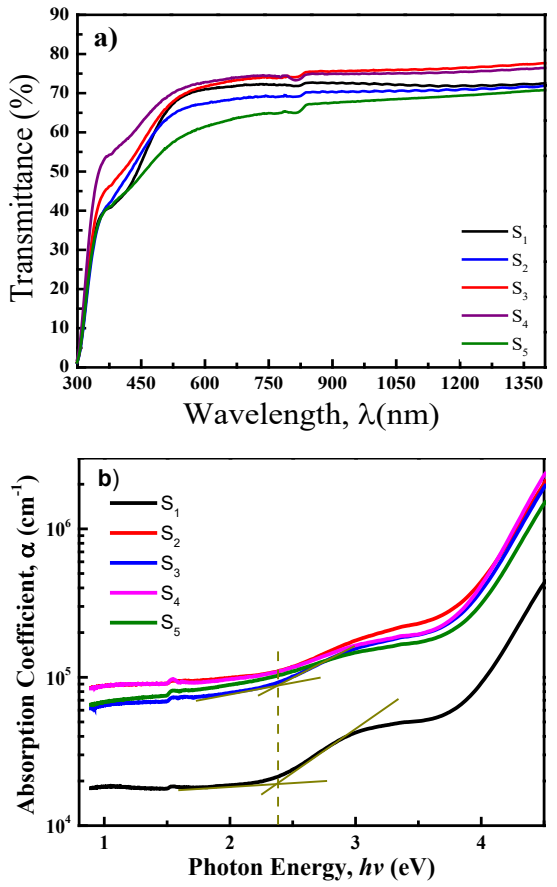

Figure 1. (a) Transmittance and (b) optical absorption coefficient spectra of vanadium oxide (S_1) and cobalt doped vanadium oxide (S_2 to S_5) thin films.
Figura 1. Espectros de transmitancia (a) y coeficiente de absorción óptica (b) para películas delgadas de óxido de vanadio (S_1) y óxido de vanadio dopado (S_2 to S_5).

Thin films surface morphology

Figure 3 shows AFM three dimensional surface topography images in scales of 2 m x 2 μm of (a) S_1, (b) S_2, (c) S_3, (d) S_4 and (e) S_5 VO_x:Co^{2+} film samples. The root-mean-square roughness of the same samples is plotted in Figure 3f. The surface topography of pure VO_x film (S_1) presents lumps and the lowest roughness. As the cobalt ions are incorporated into VO_x host, variations in shape and roughness are observed in AFM images. Notable changes are observed in samples S_3 and S_4 that exhibit a ring like morphology and increased roughness (8 - 9 nm) in comparison with S_1 and S_2 (4 - 5 nm) samples. sample S_5 that contains the highest cobalt concentration loses the ring pattern in its surface morphology and shows the highest roughness (~23 nm) among the five samples. Similar results are reported elsewhere, suggesting that the inclusion of Co^{2+} in VO_x host by solution methods modifies the superficial morphology of cobalt doped vanadium oxide thin films (Fuentes-Ríos *et al.*, 2021). Such porous morphology encourages potential use of VO_x:Co^{2+} thin films as a cathode material for lithium battery applications (Wang *et al.*, 2011).

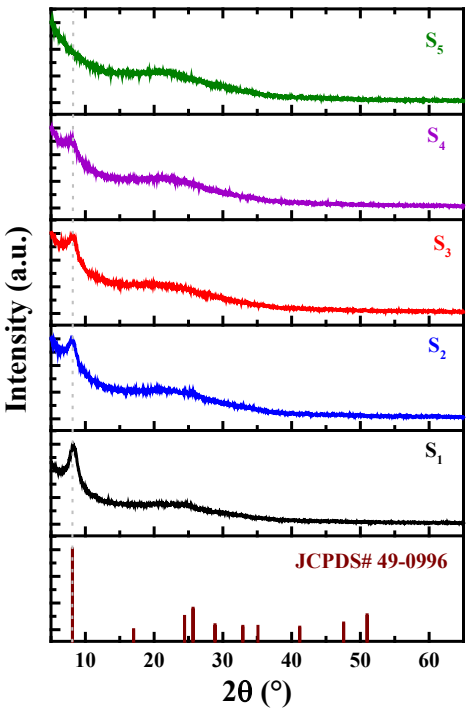

Figure 2. X-ray diffractions patterns of vanadium oxide with different Co^{2+} concentrations.
Figura 2. Patrones de difracción de rayos X de óxido de vanadio con diferentes concentraciones de Co^{+2}.

To complement the AFM results, SEM micrographs of S_1, S_3 and S_5 samples were analyzed and are shown in Figure 4. Without cobalt addition, vanadium oxide sample S_1 shows a granular ground with shallow leaves. The S_3 sample (VO_x:Cobalt salt = 50:50), presents an interconnected rings or porous arrangement, very similar to the AFM image of the same sample (Fig. 3c). The pore size distribution histogram of this film sample is in Figure 4d. It shows that the pore size varies from 100 to 300 nm, and those with ~150 nm predominates. By chemical element mapping in the SEM image of sample S_3, vanadium and cobalt elements have been detected to have a homogeneous distribution inside the pores. Finally, the sample with the highest concentration of cobalt, S_5, shows an irregular porous granular pattern at the surface, and under such pattern a continuous film is observed.

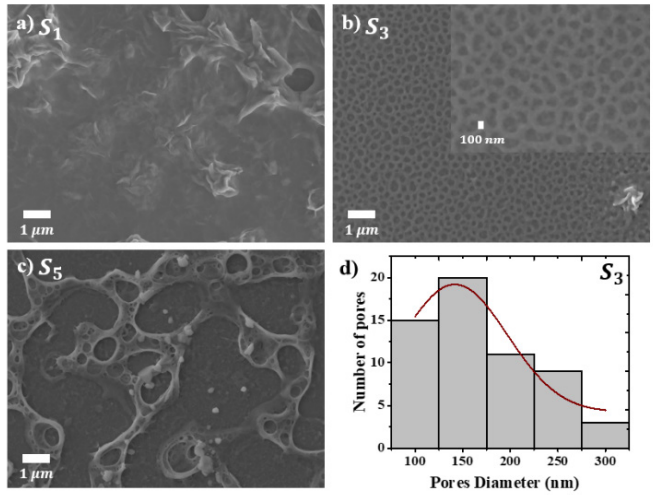

Figure 4. SEM micrographs with different magnifications of a) S_1, b) S_3, c) S_5 and d) histogram of S_3 pores.
Figura 4. micrografías de microscopia electrónica de barrido con diferentes magnificaciones de las muestras a) S1, b) S3, c) S5 y d) histograma de los poros de la muestra S3.

Chemical composition

To assess the chemical state of the VO_x:Co^{2+} film samples, an accurate peak-fitting analysis of their X-ray photoelectron spectra (XPS) (A. Herera-Gomez, no date) was carried on.

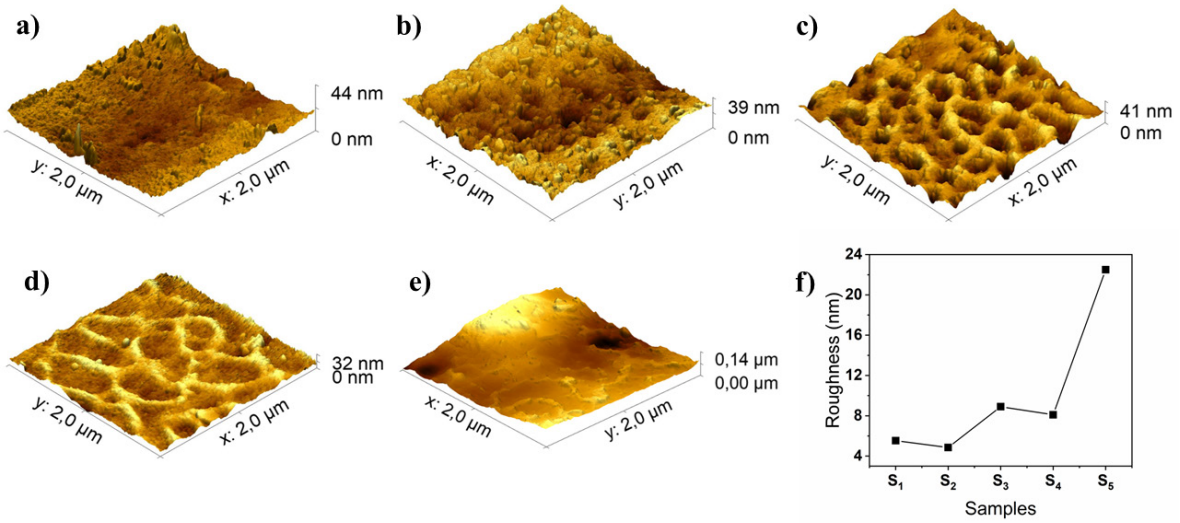

Figure 3. Three-dimensional AFM surface morphology images of (a) S_1, (b) S_2, (c) S_3, (d) S_4, (e) S_5 samples. (f) Roughness values of the same samples.
Figura 3. Imágenes tridimensionales por AFM de la morfología superficial de las muestras (a) S_1, (b) S_2, (c) S_3, (d) S_4 y (e) S_5. (f) Valores de aspereza de las mismas muestras.

Figure 5 shows the photoelectron spectra of the five samples corresponding to the (a) Co 2*p* and (b) O 1*s* and V 2*p* core-levels. From the Co 2*p* spectra (Figure 5a) we observe that the experimental data are congruent to that of the Co^{2+} chemical state, showing the main peak centered at 780.80 eV, but at the same time, three satellite peaks at higher binding energies that are characteristics of the Co^{2+} state (Yang *et al.*, 2010; Biesinger *et al.*, 2011; Martínez-Gil *et al.*, 2020). It is important to mention that the relative intensities of those satellite peaks suggest that there are neighboring atoms arranged in a short-range order, possibly having distortions that deviate from the octahedral Co^{2+} symmetry. That is, the intensities of the satellite peaks are proportional to the molecular defects or amorphous state of the material, which correlates to the amorphous XRD results for all samples.

The V 2*p* and the O 1*s* spectra share the same binding energy range (Figure 5b), where we can observe the sole presence of a vanadium oxide. Due to the large spread of the reported binding energy values of this compound, to assess the present films we have employed the method proposed by Hryha *et al*. (Hryha, Rutqvist and Nyborg, 2012), where instead of using only the energy position of the V $2p_{3/2}$ for chemical state determination, we have taken into account the difference in the binding energy between the O 1*s* and the V $2p_{3/2}$ core levels (Δ= BE(O1*s*) – BE(V$2p_{3/2}$)). The results show that for all samples the energy separation is around 13.50 eV, which suggests that the oxide obtained with our chemical process is VO_2 (Hryha, Rutqvist and Nyborg, 2012). Here it is interesting to note that the energy position of the V $2p_{3/2}$ in our samples is at 516.50 eV, which is almost the average value of those reported for VO_2 (515.95 eV) and V_2O_5 (517.20 eV), however, due to also the large spread in binding energy calibrations in the literature, we discard the possibility of the V_2O_5 compound.

From peak intensities directly derived from the photoelectron spectra, chemical compositions of our VO_2:Co^{2+} film samples have been determined. We have corrected the peak intensities with the appropriate physical parameters accounting for the photoemission signal attenuation due to scattering (Cabrera-German, Gomez-Sosa and Herrera-Gomez, 2016). The results expressed in terms of atomic percentage for each of the observed chemical species are presented in Figure 6a. Here, we observe that as the Co^{2+}concentration in the precursor solution increases, the amount of Co^{2+} in the

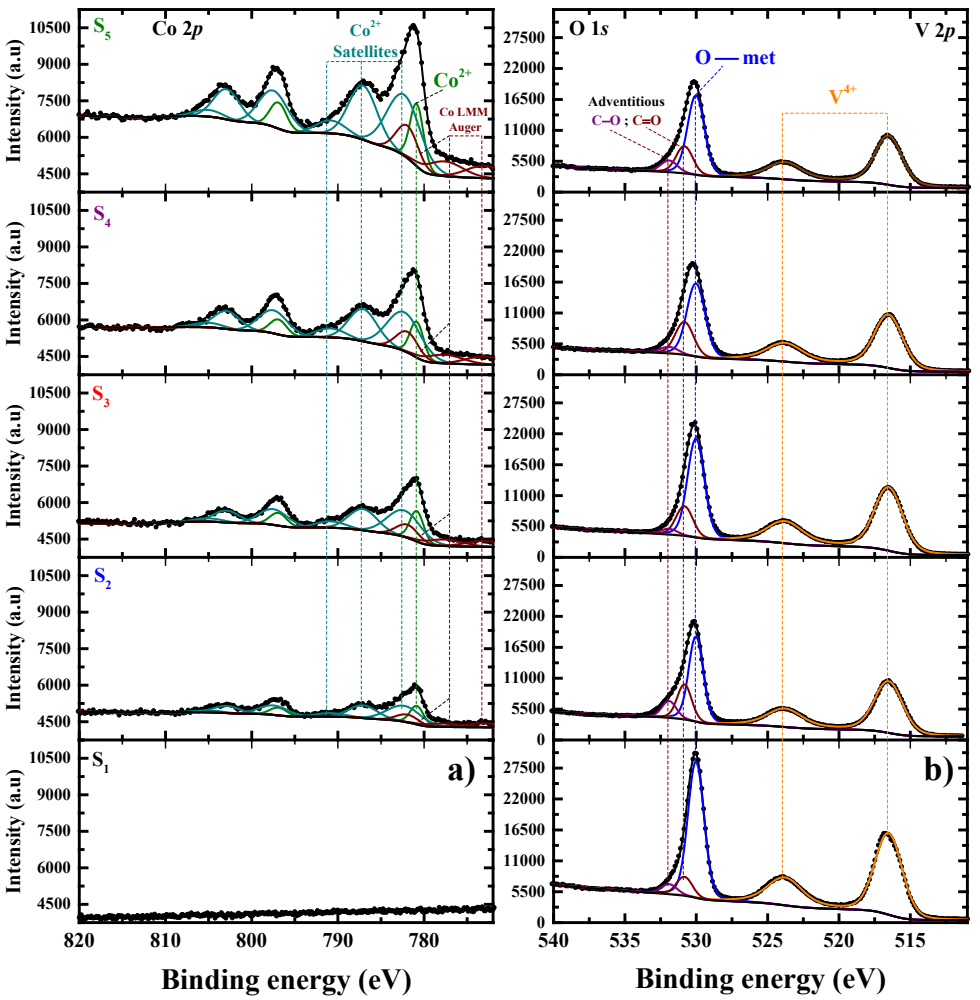

Figure 5. X-ray photoelectron spectra of VO_x:Co^{2+} films with different concentrations of Co^{2+}.
Figura 5. Espectro de rayos X de películas de VO_x:Co^{2+} con diferentes concentraciones de Co^{2+}.

deposited films also increases, from 0 to 16.55 at %. On the other hand, the V^{4+} atomic concentration in all five samples vary slightly, from 31 at % (sample S_1) to 27 at % (sample S_5), which suggests that the VO_x yield is high in all the probed samples. We can also observe that the percentage of oxygen atoms bonded to metals is coherent to the chemical species: VO_2 and CoO, reaching 69 at % for sample S_1 and decreasing up to 56.4 at % for sample S_5 as the Co^{2+} in the films is the largest. The atomic ratio of vanadium versus cobalt (V:Co) in each sample is listed in Table 1, changing from 6.6:1 (S_2), 4.9:1 (S_3), 2.9:1 (S_4) to 1.6:1 (S_5).

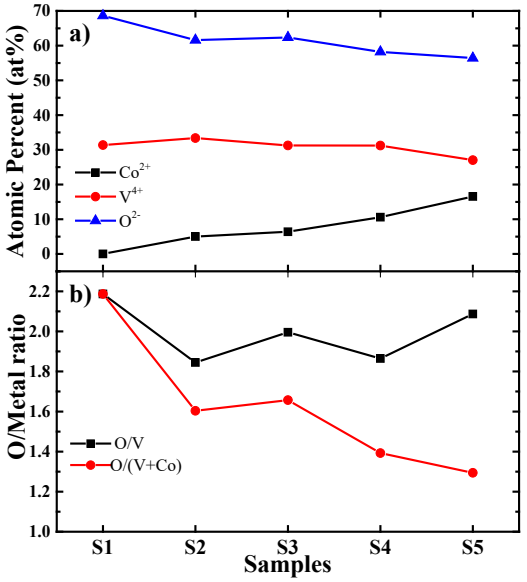

Figure 6. XPS chemical composition assessment: (a) atomic percentage (at%) of elements O, V and Co, and (b) O/V and O/(V+Co) atomic ratios of VO_x:Co^{2+} thin films.

Figura 6. Evaluación de la composición química por XPS: (a) porcentaje atómico (at%) de los elementos O, V y Co, y (b) proporciones atómicas O/V y O/(V+Co) de las películas delgadas de VO_x:Co^{2+}.

For a better assessment of metal oxide compositions in the film samples, the ratio between oxygen and metal concentrations is plotted in Figure 6b. Here, the O/V atomic ratio lies around the expected stoichiometry of VO_2 for all the samples, which further confirms our previous analysis. Yet, if we determine the atomic ratio of oxygen to the sum of the two metallic species, O/(V+Co), we observe that such ratio decreases with increasing concentration of Co^{2+} in the reaction solution, a trend that follows the expected stoichiometry of the CoO compound.

CONCLUSIONS

We demonstrate that amorphous thin films of cobalt doped vanadium dioxide can be prepared from spin-coating with a simple solution method without using any ligand or surfactant. Optical band gaps of those films are of ~2.3 eV, with higher absorption coefficients for cobalt doped samples. From detailed quantitative photoelectron analysis, we conclude that there is only one oxidation state of vanadium in all the film samples, V^{4+}, giving predominantly VO_2 products. The formation of cobalt oxide is also confirmed by XPS, showing a Co^{2+} oxidation state corresponding to possibly disordered oxygen atoms in an octahedral, correlates to the amorphous nature of the films. Furthermore, the surface morphology of the VO_2:Co^{2+} thin films is largely influenced by the cobalt concentration, giving interconnected circle pore network when the V:Co atomic ratio is around 4.9:1. The wide band gap properties with porous surface structure make these semiconductor thin films promising for cathode material in lithium battery applications.

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