Microstructural and optical characterization of CaWO\textsubscript{4} and SrWO\textsubscript{4} thin films prepared by a chemical solution method

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Abstract

Stoichiometric CaWO\textsubscript{4} and SrWO\textsubscript{4} thin films were synthesized using a chemical solution processing, the so-called polymeric precursor method. In this soft chemical method, soluble precursors such as strontium carbonate, calcium carbonate and tungstic acid, as starting materials, were mixed in an aqueous solution. The thin films were deposited on glass substrates by means of the spinning technique. The surface morphology and crystal structure of the thin films were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Nucleation stages and surface morphology evolution of the thin films on glass substrates were studied by atomic force microscopy. The films nucleate at 300 °C, after the coalescence of small nuclei into larger grains yielding a homogeneous dense surface. XRD characterization of these films showed that the CaWO\textsubscript{4} and SrWO\textsubscript{4} phases crystallize at 400 °C from an inorganic amorphous phase. No intermediate crystalline phase was identified. The optical properties were also studied. It was found that CaWO\textsubscript{4} and SrWO\textsubscript{4} thin films have an optical band gap, $E_{\text{gap}} = 5.27$ and 5.78 eV, respectively, of a direct transition nature. The excellent microstructural quality and chemical homogeneity confirmed that this soft solution processing provides an inexpensive and environmentally friendly route for the preparation of CaWO\textsubscript{4} and SrWO\textsubscript{4} thin films.

Keywords: CaWO\textsubscript{4}; SrWO\textsubscript{4}; Scheelite-type structure; Chemical solution method; Thin films

1. Introduction

In recent years, crystal structures based on the scheelite-type have attracted much interest because of their approved use as scintillating medium and in electro-optic applications [1–3]. In addition, scheelite-type structure materials have been a subject of numerous investigations on the luminescent properties [4,5]. Typical oxides of scheelite-type structure are SrWO\textsubscript{4}, CaWO\textsubscript{4}, PbWO\textsubscript{4} and BaWO\textsubscript{4}. In the scheelite structure, W ions are within tetrahedral O–ion cages and are isolated from each other, while Ca, Ba, Sr and Pb ions are surrounded by eight oxygen ions [6].

A variety of preparation techniques have been proposed to produce these materials, including solid-state reaction, hydrothermal, sputtering and the sol–gel processes [7–10]. However, new routes for obtaining solutions for thin film deposition and crystal growth remain an interesting subject. The use of the chemical process for thin film production allows the accurate control of the chemical composition. Nowadays, new solution deposition methods, based on wet chemistry, have been used for the preparation of oxide thin films. In this regard, chemical processing using solutions, including soft solution processing, has been attracting increased interest. The soft solution processing can be defined as environmentally friendly, using aqueous solutions [11]. Together with a few techniques of soft solution processing, the polymeric precursor method [12–15] can be included, because of the liquid nature of the constituents and the relatively low processing temperatures used. This technique is a very promising alternative for better three-dimensional, molecular-scale control of nanostructured materials and for being environmentally friendly. The basic idea behind the polymeric precursor methods is to reduce individualities of
different metal ions, which can be achieved by encircling stable metal complexes with growing polymer networks. Immobilization of metal-complexes in such rigid organic polymeric networks can reduce the segregation of particular metals, thus ensuring the compositional homogeneity at a molecular scale. This is of vital importance for the synthesis of multicomponent oxides with complicated compositions, since the chemical homogeneity with respect to distribution of cations throughout the entire gel system often determines the compositional homogeneity of the final complex mixed oxides.

Considering that this method has been successful in preparing some oxide thin films, this work reports on the preparation and characterization of CaWO₄ and SrWO₄ thin films based on a soft solution processing, the so-called polymeric precursor method.

2. Experimental procedure

The flow chart for the SrWO₄ and CaWO₄ thin films synthesis used in this study is outlined in Fig. 1. Tungsten citrate was formed by dissolution of tungstic acid (H₂WO₄) (Vetec—purity 99.98%) in an aqueous solution of citric acid under constant agitation to homogenize the tungsten citrate solution. After homogenization of the solution, SrCO₃ (Aldrich—purity 99.99%) or CaCO₃ (Aldrich—purity 99.99%) salt was slowly added. The complex was well stirred for several hours at 70–80 °C to produce a clear, homogenous solution. After homogenization of the solution containing Sr or Ca cations, ethylene glycol was added to promote the citrate polymerization by the polyesterification reaction. With continued heating at 80–90 °C, the solution became more viscous, albeit devoid of any visible phase separation. The molar ratio between the cations strontium or calcium and tungsten was 1:1, the citric acid/ethylene glycol ratio was fixed as 60:40 (mass ratio). The viscosity of the deposition solution was adjusted to 15 mPa/s by controlling the water content. The polymeric precursor solution was spin-coated on substrates by a spinner operating at 7000 rev/min for 40 s using a commercial spinner (spin-coater KW-4B, Chemat Technology). The polymeric precursor solution was deposited onto the glass substrates via a syringe filter to

Fig. 1. Flow chart illustrating the procedure for the preparation of CaWO₄ and SrWO₄ solutions and thin film production.

deposition of the precursor solution onto the substrates by spin-coating

Heat-treatment in the furnace

SrWO₄ or CaWO₄ thin films

Formation of the polymeric precursor solution (SrWO₄ or CaWO₄) (80-90°C)

Ethylene glycol

Viscosity adjusted with H₂O

Deposition of the precursor solution onto the substrates by spin-coating

Heat-treatment in the furnace

SrWO₄ or CaWO₄ thin films

Tungsten citrate

60-80°C

Strontium carbonate or Calcium carbonate

Strontium or calcium tungsten citrate in water

Fig. 2. X-Ray diffraction patterns of CaWO₄ thin films annealed at different temperatures: (a) 200 °C, (b) 300 °C, (c) 350 °C, and (d) 400 °C.
avoid particulate contamination. Corning 8800 glass was chosen as substrates. After spinning onto the substrates, the films were kept in ambient air at 150 °C on a hot plate for 20 min to remove residual solvents. After the preannealing, the films were annealed between 200 and 400 °C for 4 h in air.

The film thickness was controlled by adjusting the number of coatings and each layer was pyrolyzed at 200 °C and crystallized before the next layer was coated. These coating/drying operations were repeated until the desired thickness was obtained.

X-ray diffraction (XRD) patterns were obtained using a Cu Kα radiation source to determine the structure evolution of the thin films. The thickness of the coated films was measured by a cross-section analysis using scanning electron microscopy (SEM). The optical transmittance of the crystalline thin films was measured in the wavelength range from 200 to 800 nm, using a Cary 5G (Australia) spectrophotometer. Atomic force microscopy (AFM) was used to obtain a 3D image reconstruction of the sample’s surface. These images allow for an accurate analysis of the sample’s surface and the quantification of highly relevant parameters such as roughness and grain size. A Digital Instruments Multi-Mode Nanoscope IIIa was used. AFM imaging was carried out in the contact mode, using a triangular-shaped 200-μm-long cantilever with a spring constant of 0.06 N/m. The scanning rate used ranged from 1 to 2 Hz and the applied force from 10 to 50 nN, depending on the sample/tip interactions.

3. Results and discussion

Figs. 2 and 3 show the X-ray patterns of the SrWO₄ and CaWO₄ thin films deposited onto glass substrates after calcination at several temperatures. A diffuse X-ray diffraction (XRD) pattern is observed at 200, 300 and 350 °C, indicating the formation of an inorganic amorphous phase after the pyrolysis process for the SrWO₄ thin films. As for temperatures above 350 °C, the crystallization of SrWO₄ phase is observed at 400 °C. No intermediate phase was noticed, what suggests a direct crystallization from the amorphous phase to a crystalline phase of the scheelite-type structure. All the peaks are ascribed to a tetragonal structure having a = 5.405 Å and c = 11.922 Å lattice parameters. These figures are close to the bulk material values (a = 5.416 Å and c = 11.951 Å).

On the other hand, XRD patterns for CaWO₄ thin films show the formation of an inorganic amorphous phase at 200 and 300 °C. However, the crystallization of the CaWO₄ scheelite phase starts at 350 °C and crystalline structure patterns were identified in the thin films heat-treated at 400 °C. Again, no intermediate phase was observed, which suggests a direct crystallization from the amorphous phase. The 400 °C diffractogram reveals well-defined peaks showing a good degree of crystallinity. All the peaks are ascribed to a tetragonal structure. A further analysis of the XRD data indicate lattice parameters of a = 5.234 Å and c = 11.356 Å.

Fig. 3. X-Ray diffraction patterns of SrWO₄ thin films annealed at different temperatures: (a) 200 °C, (b) 300 °C, (c) 350 °C, and (d) 400 °C.

Fig. 4. SEM micrograph of CaWO₄ thin films heat-treated at 400 °C/4 h in air. Transversal section.
These values are also close to the bulk material ($a = 5.242$ Å and $c = 11.373$ Å).

Fig. 4 shows the transversal cross-section micrographs of the CaWO$_4$ thin film on glass substrate by SEM. Both, SrWO$_4$ and CaWO$_4$ thin films have thickness of about 80 nm, measured by transversal cross-section by SEM.

In addition, a more detailed observation made by atomic force microscopy (AFM) revealed a difference in the surface morphology of the films prepared at different temperatures. This AFM analysis showed a considerable variation in the surface morphology between the samples annealed at the range from 200 to 400 °C. Table 1 shows the evolution of sample roughness measured by AFM analysis. It is evident from the AFM analysis that the sample heat-treated at 200 °C showed a homogeneous surface morphology with very low roughness (see Table 1). There was no evidence of a granular structure (see Figs. 5 and 6). When the sample was annealed at 300 and 350 °C, the increased roughness suggests that the material’s structure became increasingly ordered. In addition, the AFM analysis revealed that the samples heat-treated at 300 and 350 °C displayed a homogeneous nucleation with a nuclei size distribution approximately within the 25–30 nm range, at the initial growing stage (see Figs. 5 and 6). Moreover, a large amount of the nuclei is homogeneously distributed in the thin films deposited at 350 °C. On the other hand, the surface morphology changes dramatically at 400 °C. At this stage of growth, the coalescence of nuclei occurs, with the formation of a granular structure that results in a significant increase of the rms roughness. This result is in agreement with the XRD analysis. In addition, Cho et al. [16] showed that the CaWO$_4$ thin films grown by an electrochemical method consisted of grains with various sizes with a heterogeneous surface.

Fig. 7 shows the optical transmission spectra of the crystalline thin films recorded in the 200–800 nm wavelength range on amorphous silica substrates. Such type of substrate was chosen once it is transparent in that spectrum region. The thicknesses for the SrWO$_4$ and CaWO$_4$ thin films were about 160 and 110 nm, respectively. The films shown good transparence and their transmittance decreases to zero near 260 nm. The optical band gap energy, $E_{\text{gap}}$, for the crystalline thin films was determined from the sharply falling transmission region. According to Tauc and Menth’s

<table>
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<tr>
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<th>CaWO$_4$</th>
<th>SrWO$_4$</th>
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<tr>
<td></td>
<td>200 °C</td>
<td>300 °C</td>
</tr>
<tr>
<td>Rms (nm)</td>
<td>0.188</td>
<td>1.329</td>
</tr>
<tr>
<td>A.G.S. (nm)</td>
<td>–</td>
<td>25</td>
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A.G.S. = average grain size; Rms = roughness.
law [17], the absorption coefficient has the following energy dependence,

$$\alpha = \frac{A (h\nu - E_{gap})^m}{h\nu}$$

where $A$ is a proportionality constant, $m$ is another constant, which is different for the different types of transitions ($m = 1/2, 2, 3/2$ or $3$ for allowed direct, allowed indirect, forbidden direct and forbidden indirect electronic transitions, respectively), $h\nu$ is the photon energy, and $E_{gap}$ is the Tauc optical band gap.

So the straight line plot between $(zhv)^{1/m}$ and $h\nu$ would yield the value of the Tauc optical band gap ($E_{gap}$). The plots of $(zhv)^2$ vs. and $h\nu$ for crystalline thin films are displayed in Fig. 7. The direct transition band gaps of the crystalline thin films were $5.27$ and $5.78$ eV for the CaWO$_4$ and SrWO$_4$ thin films, respectively, corresponding to a direct allowed transition between valence and conduction bands. In the high energy region of the absorption edge, $(zhv)^2$ varied linearly with $h\nu$. In the low energy region of the edge, the absorption spectrum deviated from the straight line plot. This straight line behavior in the high energy region was
taken as prime evidence for the direct band gap. The optical band gap was therefore determined by extrapolating the linear portion of the plot relating, \((\alpha h)^2\) vs. \(h\) to \((\alpha h)^2 = 0\) (see Fig. 7). The optical band gap of the crystalline CaWO\(_4\) thin film is close to that of a CaWO\(_4\) thin film determined by Saito et al. [18], which was of 5.4 eV.

**4. Conclusions**

We have successfully demonstrated the growth of CaWO\(_4\) and SrWO\(_4\) thin films with scheelite-type structure by a soft chemical route, called polymeric precursor method. Polycrystalline, homogeneous, dense, and crack-free thin films were successfully prepared on glass substrates using a spin-coating technique. The XRD results showed that no intermediate phase was detected and a single CaWO\(_4\) or SrWO\(_4\) phase was crystallized from an amorphous matrix. XRD results showed a tetragonal structure for the polycrystalline thin films, with lattice parameters of \(a = 5.234\) Å and \(c = 11.356\) Å, and \(a = 5.405\) Å and \(c = 11.922\) Å for CaWO\(_4\) and SrWO\(_4\) thin films, respectively. The crystalline thin films presented an average grain size of approximately 260 and 180 nm for CaWO\(_4\) and SrWO\(_4\), respectively. We have observed the nucleation and surface morphology evolution of thin films on glass substrates using atomic force microscopy. CaWO\(_4\) and SrWO\(_4\) thin films undergo a homogeneous nucleation in an early stage. The coalescence of isolated nuclei results in the formation of large grains. At 200 °C, the thin films showed a surface with low roughness compared with those at 400 °C. The CaWO\(_4\) and SrWO\(_4\) thin films obtained at 400 °C in this study are well crystallized with low roughness and present a dense and homogeneous microstructure. The band gap energy of the crystalline thin films was found to be 5.27 eV (CaWO\(_4\)) and 5.78 eV (SrWO\(_4\)) by the Tauc approach, using the linear fitting of the product \((\alpha h)^2\) vs. \(h\). It is believed that the good structural and microstructural qualities resulted from the soft solution processing that, besides its low energy consumption, uses aqueous solutions to create shaped, sized, and oriented materials with the desired chemical composition and crystal structure.

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**References**