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Tuning the transmittance and the electrochromic behavior of $Co_xSi_yO_z$ thin films prepared by magnetron sputtering at glancing angle

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ABSTRACT

This work reports the synthesis and the characterization of amorphous $Co_xSi_yO_z$ thin films prepared by magnetron sputtering from a single cathode. Porous layers with outstanding electrochromic properties are obtained at room temperature in one step by performing the deposition at a glancing angle configuration. The electrochromic behavior of these layers in a basic aqueous medium was dependent on the Co/Si ratio in the films and in all cases was characterized by a fast response, a high coloration efficiency and a complete reversibility after several hundred cycles. A characteristic feature of these electrochromic layers is that, for a similar thickness, the range of transmittance modulation can be tuned by changing the Co/Si ratio in the films and, specifically for films with a high concentration of silicon, to change their aspect from an almost transparent to a full colored state.

1. Introduction

During the last years, electrochromic coatings have evolved into practical solutions for indoors energetic control, displays, and other esthetical applications [1,2]. The most popular system for fenestration and house lighting control consists of tungsten oxide as an active electrochromic layer tunable from a deep blue to a transparent state and a nickel oxide layer as contra-electrode [3]. For other applications, particularly when an ample coloration palette is sought, other oxides [4,5] and, more recently, organic compounds [6,7] have been studied very actively. Cobalt oxide systems intended for electrochromic applications have been investigated for more than two decades. Other applications of cobalt oxide films such as supercapacitors and oxygen active electrodes have been also reported [8–10]. When CoO_x is used as electrochromic layer, color transformation implies a transition from a pale yellow–brownish aspect to a dark brown–gray color in the most oxidized state [11–13]. This color transformation has been accounted for by the redox processes which can be represented schematically as $CoO_x + OH^- \rightarrow CoO_xOH + e^-$ [1,14,15]. These processes imply the oxidation of cobalt cations and the incorporation of OH^- groups within the structure of the oxide. Therefore, electrochromic devices based on cobalt oxide consist of an active CoO_x layer, typically depicting a spinel-type structure, another thin film electrode and a basic electrolyte with a relatively high concentration of OH^- anions that are incorporated in the film during the oxidation cycle. For an optimal performance of the device it is required a fast incorporation of OH^- groups within the film and their reversible release to the electrolyte during the oxidation and reduction cycles. Consequently, optimizing the electrochromic behavior implies to increase the OH^- incorporation capacity and to maximize the diffusion rate of such anions within the film structure. Therefore, a high porosity is a requisite to effectively achieve these functions, a feature that has fostered the development of a large variety of CoO_x nanostructured and highly porous layers [16–18].

Cobalt oxide electrochromic thin films have been prepared by sol–gel, electrochemical cobalt deposition and other wet chemical methods [19–22]. Magnetron sputtering (MS), widely utilized for the processing of tungsten oxide electrochromic films [1,2,23], has been also intended for the synthesis of electrochromic CoO_x layers [11,24,25]. This technique presents obvious advantages such as its one-step process character, the absence of undesirable byproducts, its scalability and the possibility to proceed at temperatures compatible with polymeric substrates. By contrast, a typical limitation of MS for the fabrication of CoO_x and other electroactive films is the generally high compactness of the deposited layers which may hinder an efficient diffusion of OH^- anions and therefore slow down the response rate of the devices. A way of

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circumvent this limitation is to grow the films in a glancing angle deposition (GLAD) configuration where the substrate forms a glancing angle with respect to the normal to the MS target. GLAD thin films, prepared by either thermal evaporation or MS are characterized by a columnar microstructure with a high porosity consisting of micro and mesopores, these latter extending from the surface of the film up to the interface with the substrate [26,27]. In recent papers dealing with the fabrication of $W_xSi_yO_z$ and WO_x electrochromic thin films by MS-GLAD [28,29], we have demonstrated that this configuration is quite favorable for the diffusion of species from the electrolytic medium. To our knowledge, this technique has not been previously used for the preparation of mixed cobalt–silicon oxide electrochromic films.

In the first part of the present work we report the normal geometry preparation of $Co_xSi_yO_z$ colored thin films by MS deposition from a single cathode and their characterization by a large variety of techniques. This part complements a recent paper where we have discussed the preparation of different $M_xSi_yO_z$ (M:Cu, Ni, Fe, Co, W and Mo) thin films intended for optical and esthetical applications [30]. In the second part, we focus on the fabrication of electrochromic $Co_xSi_yO_z$ thin films by MS-GLAD and the analysis of their electrochromic behavior. The obtained results have shown that these films, even if amorphous, comply with the high porosity requirements needed for an efficient electrochromic response. Besides, the possibility of changing the Co/Si ratio in the films has revealed a useful tool to tune their optical properties (e.g., extinction coefficient, $\boldsymbol{k}$ and refractive index, $\boldsymbol{n}$) and the possibility of changing the limits of the transmittance modulation without affecting significantly their electrochromic performance.

2. Experimental

2.1. Thin film preparation

$Co_xSi_yO_z$ thin films have been prepared by reactive pulsed DC MS using a silicon target of 50 mm diameter on which a series of cobalt strips (Goodfellow 99.95%) have been arranged axially [30]. The width of the strips was 1.5 mm. Samples were prepared with 1, 3 and 6 strips along the target diameter for the series deposited in normal geometry, and with 2, 4, 6 and 8 strips for the series prepared at glancing angles.

The magnetron was operated with a power of 100 W and a pulsed voltage of 250–400 V at a frequency of 80 kHz. The base pressure of the system was 3.0×10^{-6} mbar. The pressure during deposition was fixed at 5.0×10^{-3} mbar. The process gas consisted of O_2/Ar mixtures with mass flow ratios Φ_{O_2}/Φ_{Ar} of 0.05, 0.1, 1.0, and 2.5. The distance between substrate and target was 10 cm. Thin film growth was carried out either at normal geometry, whereby the substrates are parallel to the target, or at a glancing angle geometry with an angle of 80° between the target and substrate normal. The films were deposited on either silicon, soda lime glass, quartz, or ITO substrates.

The samples will be named in the text with the following notation: CoN-Φ_{O_2}/Φ_{Ar}, where N is the number of cobalt strips wrapped on the target. Thus, for example, Co6–0.1 corresponds to a sample prepared with six cobalt strips wrapped to the Si target and $\Phi_{O_2}/\Phi_{Ar}=0.1$. The thin films prepared at GLAD are designated according to the notation CoN-Φ_{O_2}/Φ_{Ar} GLAD.

2.2. Thin film characterization

Rutherford backscattering spectrometry (RBS) spectra were obtained in a tandem accelerator (CNA, Sevilla, Spain) with a beam of alpha particles with energy of 1.5 MeV, 1.7 nA of intensity and ~1 mm diameter. The accumulated dose was 1.5 μC in all cases.

FT-IR spectra were recorded in transmission mode in a Nicolet 510 spectrometer for samples deposited on polished un-doped silicon wafers.

X-ray photoelectron spectroscopy (XPS) was used to assess the chemical characteristics of the species at the surface of the samples. XPS spectra were recorded in an ESCALAB 210 spectrometer working in the constant pass energy mode at a value of 20 eV. The binding energy (BE) scale of the spectra was referenced to the C 1s peak of the spurious carbon contaminating the surface of the samples at a value of 284.5 eV.

UV–vis transmission and reflection spectra were recorded in a Varian Cary100 apparatus. From these curves, refractive index and extinction coefficient functions of the deposited films were derived by simulating the spectra with a Cauchy formalism [31] to describe the wavelength dispersion of the refractive index and extinction coefficient of the films.

The microstructure of the films deposited on Si(100) wafers (cross sectional and planar views) was characterized by scanning electron microscopy (SEM) using a Hitachi S4800 field emission microscope.

2.3. Electrochromic tests

Electrochemical measurements were performed at room temperature in a three-electrode cell equipped with quartz windows. The $Co_xSi_yO_z$ thin films deposited on ITO substrates were used as working electrodes. All potentials were measured against and are referred to an Ag/AgCl/KCl (saturated) reference electrode, whereas a Pt foil was used as a counter electrode. Electrochemical measurements were performed with a computer-controlled Autolab PGSTAT30 potentiostat, while UV–vis transmittance spectra were recorded on an Ocean Optics high-resolution spectrophotometer. In all experiments, the electrolyte was a N_2 purged 0.1 M NaOH (Merck p.a.) solution in ultrapure water (Millipore Direct-Q system, > 18 MΩ cm). This electrolyte provided the best reproducibility and reversibility of the electrochromic cycles.

3. Results and discussion

3.1. $Co_xSi_yO_z$ thin films prepared in a normal configuration

The atomic Co/Si ratio of the different examined samples, determined from their RBS spectra increased with the number of strips wrapped to the Si target. The percentages of the two elements and the Co/(Co+Si) ratio in the examined samples are reported in Table 1, showing a large variation between a value of 0.20 for sample Co1–0.1 and 0.91 for sample Co6–0.1 (the estimated maximum uncertainty for these calculations is of 5%). These values are similar to those obtained by quantification of XPS spectra, thus confirming that cobalt and silicon atoms distribute homogeneously through the whole thickness of the samples and that surface segregation of one component can be discarded. Moreover, these data clearly confirm that it is possible to get a precise control of the composition of the $Co_xSi_yO_z$ films by using mixed Si–Co targets. Although we have controlled this ratio by

Table 1
Composition (XPS) and refractive index of the studied $Co_xSi_yO_z$ samples.

Sample	Si (at%)	Co (at%)	Co/(Co+Si)	n(@550 nm)
Co1–0.1	19	5	0.20	1.51
Co3–0.1	11	16	0.59	1.76
Co3–0.05	8	17	0.68	1.95
Co6–0.1	3	29	0.91	2.35