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Electrochromic behavior of NiO thin films deposited by e-beam evaporation at room temperature



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ABSTRACT

In this work we report the role of thickness on electrochromic behavior of nickel oxide (NiO) films deposited by e-beam evaporation at room temperature on ITO-coated glass. The structure and morphology of films with thicknesses between 100 and 500 nm were analyzed and then correlated with electrochemical response and transmittance modulation when immersed in 0.5 M LiClO₄-PC electrolyte. The NiO exhibits an anodic coloration, reaching for the thickest film a transmittance modulation of 66% between colored and bleached state, at 630 nm, with a color efficiency of 55 cm² C⁻¹. Very fast switch between states was obtained, where coloration and bleaching times are 3.6 s cm⁻² and 1.4 s cm⁻², respectively.

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1. Introduction

Electrochromic (EC) materials are able to change their optical properties by the application of an electric potential [1]. Their optical absorption can be reversibly modified through ionic (or proton) insertion and charge compensating electrons allowing for adjustable color modulation and making possible its application in electrochromic devices. When considering inorganic materials this phenomenon can be observed in many oxides of transition metal elements, where two different types of coloration may occur depending on whether the material darkens under ion insertion (cathodic coloration) or ion extraction (anodic coloration) [2–4]. Tungsten trioxide (WO₃), the most studied electrochromic material [5,6] presents cathodic coloration so, in order to improve the optical modulation of an electrochromic window, it is relevant to study materials that present complementary coloration (anodic coloration) [7,8]. One good candidate is nickel oxide (NiO) that is a low cost material allowing for good cyclic reversibility, high coloration efficiency and good durability [9–11]. NiO presents a brownish color on the colored state and it is highly transparent on the bleached state [12,13]. If both NiO and WO₃ are combined in the same electrochromic device it is possible to improve the transmittance modulation making them very attractive for applications on smart windows or displays to be used in automobiles,

buildings or airplanes [14–16]. These devices can even be incorporated in thermal sensitive substrates (e.g. paper) due to the low temperature deposition process required [17,18].

There are several reports on NiO thin films for electrochromic applications obtained by different physical or chemical deposition techniques. Among the physical routes known, sputtering and resistive thermal evaporation both have been often used [3,19,20]. In most of these works usually NiO requires a post-deposition annealing treatment [9,11,21,22], being known few reports on non-annealed NiO films aiming their use as electrochromic material [20,23]. In this work we report the electrochromic behavior of evaporated NiO layers without any intentional substrate heating or post-deposition treatment. Moreover, we have focused the present work on the role of the thickness of NiO films on the morphology, structure and electrochromic properties. The films were tested on a nonaqueous solution of 0.5 M LiClO₄-PC as this electrolyte is compatible with both WO₃ and NiO turning possible in future work the development of electrochromic windows with a ITO/WO₃/LiClO₄-PC electrolyte/NiO/ITO structure. Also, due to the small size of a Li⁺ containing electrolyte the insertion/extraction kinetics is faster than that of OH⁻ ions [24].

2. Experimental

NiO thin films were deposited on indium tin oxide-coated glass (ITO from Xin Yan Technology with a sheet resistance of 10 Ω/□ and a transmittance in the visible region of 85%) by e-beam

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evaporation, in a homemade system. The ITO-coated substrates were previously cleaned in ultrasonic bath for 10 min, first in acetone and then in isopropanol. Films with thicknesses ranging from 100 nm to 500 nm were deposited without intentional substrate heating using NiO commercial pellets (random pieces 3–6 mm, 99.99% purity from SCM – Super Conductor Materials). The initial chamber pressure was 7×10^{-4} Pa and the growth rate was around 6 nm/min for all films deposited. The maximum thickness of the NiO films was fixed at 500 nm to avoid excessively long deposition times.

The structural analysis of the films was done by X-ray diffraction (XRD, PANalytical, model X'Pert Pro) in Bragg–Brentano geometry with Cu K α line radiation ($\lambda=1.5406$ Å). The surface morphology was examined by Scanning Electron Microscopy (Zeiss Auriga SEM-FIB) operated with an acceleration voltage of 2 kV and aperture size of 30 μ m, using secondary electrons image. The atomic force microscopy (AFM) was performed in non-contact mode using an Asylum MFP-3D instrument. The resolution of the image was 512 lines by 512 columns and the scan size was 2×2 μ m².

The optical transmittance between 380 and 800 nm was measured using a UV–vis spectrophotometer (HR4000, Ocean Optics). For calibration, the measurements were performed considering the glass cell with ITO glass plus the electrolyte (0.5 M LiClO₄–PC) as 100%. The in situ transmittance changes and the durability of the NiO electrochromic films were measured with the same spectrophotometer combined with an electrometer (Keithley 238 High Current Source Measure Unit) at a wavelength of 630 nm, applying a voltage of -2 V and 2 V. The samples were immersed in the electrolyte contained in a glass cell, using a platinum wire as counter electrode. In order to quantify the color obtained at the colored and bleached states, colorimetric measurements were performed by analyzing the transmittance spectra on a UV–vis spectrophotometer (Perkin–Elmer) using a color analysis software, in accordance with the CIE system of colorimetry, the 1931 Yxy color space.

The electrochromic behavior was studied by cyclic voltammetry (CV) on a potentiostat (Gamry reference 600). All films were electrochemically cycled in 0.5 M LiClO₄–PC, at a scan rate of 50 mV/s, in a three-electrode arrangement, with NiO film as the working electrode, platinum wire as counter electrode and Ag/AgCl as the reference electrode.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the X-ray diffraction patterns of as-deposited films, where are visible the characteristic peaks of cubic NiO phase,

indicating the presence of a polycrystalline structure (ICSD 98-005-2868) [23]. All samples reveal one predominant peak corresponding to (200) planes meaning the films are highly textured, as also reported by Xia et al. [9]. For the thinnest samples (100 and 200 nm) only reflection related with (200) planes was detected, while for 300 and 400 nm thick samples diffraction associated to (111) crystallographic planes is also visible. For the 500 nm films, a third diffraction peak associated with (220) planes appears. The peaks intensity also increases with thickness (as expected) suggesting an improvement of the crystallinity. The grain size was estimated by the Debye–Scherrer formula, increasing from 24 nm, for the thinnest sample (100 nm), up to 31 nm, for the thickest one (500 nm). This shows that polycrystalline NiO thin films can be deposited by e-beam evaporation without any thermal treatment or substrate heating, which is an advantage when comparing with other works that report the same kind of structure but only after annealing [9,11,21,22].

SEM images of the surface of films with different thicknesses are presented in Fig. 2. A uniform granular morphology with needle shape grains was observed. As suggested by the XRD structural analysis, the grain size increases with thickness as also reported by other authors [19]. This promotes a rough surface along the grain boundaries that is more pronounced as the grain size increases, which can be beneficial for the ion insertion/extraction.

The AFM topography of the NiO films is presented in Fig. 3 confirming the increase of the roughness (root mean square roughness, R_{rms} , from 1.3 to 3.2 nm) as the NiO thickness increases, corroborating the SEM analysis.

3.2. Electrochromic and electrochemical behavior

The electrochromic behavior of NiO was investigated by measuring the transmittance variation between 380 and 800 nm for films with different thicknesses. In order to get comparable results the same active area (1 cm²) was defined for all samples. The data shown in Fig. 4 were obtained after 10 coloration/bleaching cycles in 0.5 M LiClO₄–PC, applying ± 2 V, in order to stabilize the redox reactions.

The NiO films change from dark brown, at the colored state, to neutral transparent coloration, at the bleached state. It is clear that the transmittance modulation increases with films thickness, being 29%, 38%, 51%, 53% and 66%, at 630 nm for films with 100, 200, 300, 400 and 500 nm, respectively. This is somehow expected as thin samples have less active mass [21]. The transmittance modulation tends then to remain constant with further increase of the thickness. The maximum thickness used in this work (500 nm) is not far from the reported values although the thickness where

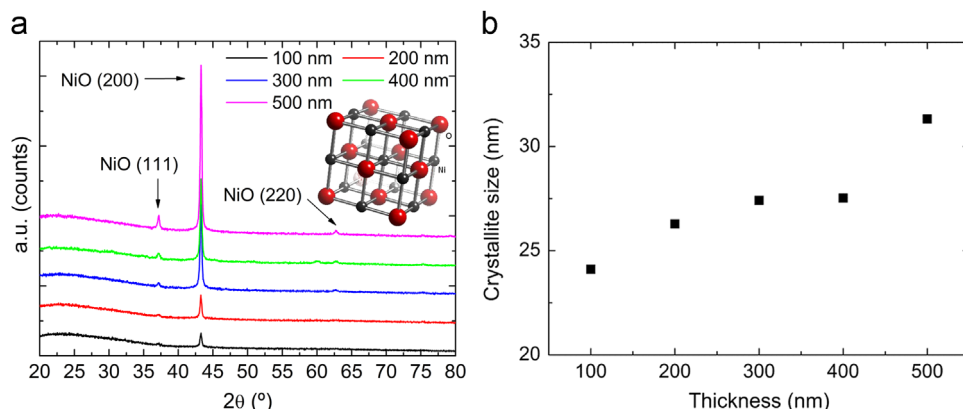


Fig. 1. (a) XRD diffractograms of the NiO films with different thicknesses deposited on glass substrates and (b) crystallite size as a function of thickness determined by Debye–Scherrer formula.

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