Applied Surface Science 257 (2011) 2647–2656

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Nanoporous nickel oxide thin films and its improved electrochromic performance: Effect of thickness

D.S. Dalavi[a], M.J. Suryavanshi[a], D.S. Patil[a], S.S. Mali[a], A.V. Moholkar[b], S.S. Kalagi[a], S.A. Vanalkar[a], S.R. Kang[b], J.H. Kim[b], P.S. Patil[a,*]

[a] Thin Films Materials Laboratory, Department of Physics, Shivaji University, Kolhapur-416004, Maharashtra, India
[b] Department of Materials Science and Engineering, Chonnam National University, South Korea

ARTICLE INFO

Article history:
Received 20 July 2010
Received in revised form
30 September 2010
Accepted 8 October 2010
Available online 16 October 2010

Keywords:
NiO thin films
Chemical bath deposition (CBD)
Scanning electron microscopy
Electrochromic properties
CV
CA

ABSTRACT

Electrochromic properties of chemically bath deposited nanoporous NiO thin films were investigated as a function of film thickness using Ni sulphate precursor, aqueous ammonia and potassium persulphate as complexing and oxidizing agents respectively. The films were characterized for their structural, morphological, optical and electrochromic properties using X-ray diffraction, scanning electron microscopy, FT-IR spectroscopy, cyclic voltammetry, chronoamperometry and optical transmittance studies. X-ray diffraction patterns show that the films are polycrystalline, consisting of NiO cubic phase. Infrared spectroscopy results show the presence of free hydroxyl ion and water in NiO thin films. SEM micrographs revealed nanoporous nature composed of interconnected nanoporous network, forming well defined 3D nano envelopes. The optical band gap energy was found to be decreased from 3.22 to 2.80 eV with increasing film thickness. The electrochromic properties of all the films were investigated in aqueous (KOH) and non aqueous ($LiClO_4$-PC) electrolyte by means of cyclic voltammetry (CV), chronocoulometry (CC) and optical studies. The transmittance modulations or optical density differences during the coloring/bleaching process were found to be increased with the film thickness. This increment in optical differences led to an increase in coloration efficiency (CE) to about 95 cm^2/C, which is two times more than that observed in KOH and response time of 2.9 s for bleaching (reduction) and 3.5 s for coloration (oxidation) observed for the film deposited at 60 min with excellent electrochemical stability up to 3000 c/b cycles in $LiClO_4$-PC electrolyte.

1. Introduction

Electrochromism is a phenomenon which involves persistent and reversible change of color in electrochromic (EC) material by simultaneous injection of electrons and small ions (H^+, Li^+, Na^+, etc.) [1]. EC devices can be used for transmittance modulation, reflectance, thermal emittance, and scattering, thus opening new avenues for applications in optical technology, including smart windows for energy efficient building [1,2]. NiO/hydroxide films have attracted special attention due to their good dynamic range, cyclic reversibility, durability, gray coloration and low material cost useful for smart window technology. NiO exhibits anodic electrochromism due to intercalation/deintercalation of ions into it. NiO thin films have been widely investigated due to their potential applications in large scale optical switching glazing, electronic information display [3], transparent organic light emitting diode (TOLED) [4], tandem dye-sensitized solar cells [5], lithium ion batteries [6] and supercapacitors [7].

EC properties of NiO thin films were investigated by different techniques [8–12] but due to compact nature their CE is rather limited. In order to override this limitation several novel ways have been adapted to nanoporous films. Remarkable improvements have been reported for nanostructured [13,14], nanoporous NiO thin film [15,16] and combination of NiO with conducting polymers such as: poly (3,4 ethylenedioxythiophene) (PEDOT), polyaniline (PANI) and polypyrrole (PPy) [17–20].

The designation of a material as nanoporous is of particular significance when it has a model or tailor-made pore structure. The term porous structure defines the structure with cavities or channels that are deeper than they are wider. Nanoporous network provides specific surface area and can facilitate the contact between electrolyte and oxide surface with open space between individual pores which allows the easier diffusion of ions among them. A representative elementary volume may be found if the pore structure is relatively homogeneous above a certain length scale and one of the simplest ways to further improve the EC

* Corresponding author at: Thin Films Materials Laboratory, Department of Physics, Shivaji University, Kolhapur-416004, Maharashtra, India.
Tel.: +91 231 2609230; fax: +91 231 2691533.
E-mail addresses: patilps_2000@yahoo.com, psp_phy@unishivaji.ac.in (P.S. Patil).

0169-4332/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2010.10.037

performance and augment CE is to increase the volume of active mass deposited without perturbing nanoporous network. An interesting and facile methodology for augmenting the overall performance of nanoporous NiO thin films has been reported by Xia et al. [15]. This is the promising way which can be exploited further and has a potential of scaling-up if the CE is appreciably enhanced without compromising response time. In order to enhance CE, the optical modulation must be high with less charge intercalation or deintercalation and it can be attenuated only if the pore structure with deeper channel (film thickness) at an adequate length scale. Thickness of the thin film plays an important role in determining the film properties unlike a bulk material and almost all film properties are thickness-dependent.

EC properties of NiO films have been investigated in electrolytes based on KOH [21], NaOH, Na_2SO_4 [22], H_2SO_4 [23], $H_2SO_4 + K_2SO_4$ [24], $H_2SO_4 + Na_2SO_4$ [25], K_2CO_3 [26] and $LiClO_4$-PC [27–31]. Green et al. reported that although optical modulation of NiO thin films in $LiClO_4$-PC electrolyte was low its CE was found to be two times more than that observed in KOH electrolyte [32]. Lin et al. reported the CE of 63.8 cm^2/C at 550 nm in a 1 M $LiClO_4$-PC electrolyte for NiV_xO_y thin film [33]. Sonavane et al. [18,20] reported high CE of 85 cm^2/C and 358 cm^2/C for NiO/PANI and NiO/PPy with cyclic stability up to 10,000th cycle in non aqueous 1 M $LiClO_4$-PC electrolyte. The insertion extraction kinetic of Li^+ ions in NiO thin films is faster than that of OH^- ions due to its small size than that of latter [34]. This motivated us to study the variations of electrochromic properties of NiO thin films in non aqueous electrolyte, i.e. $LiClO_4$-PC. $LiClO_4$-PC electrolyte is also beneficial in rocking chair type EC devices employing WO_3 as cathodically and NiO anodically coloring materials. The use of only one electrolyte to simultaneously color and bleach WO_3 and NiO simplifies complications in device fabrication.

Hence, looking at the recent state of art of the electrochromism for NiO films, one can conclude that there is a lot of scope for the improvement of EC performance by monitoring the pore structure with deeper channels of desired thickness, and the choice of suitable electrolyte.

2. Experimental

NiO thin films have been deposited using CBD as reported elsewhere [15]. We have used the similar methodology to obtain relatively thicker films. A precursor solution was prepared by using 80 ml of 1 M $NiSO_4 \cdot 6H_2O$, 60 ml of 0.25 M $K_2S_2O_8$, and 20 ml of aqueous ammonia (25–28%) in 250 ml beaker. Indium doped tin oxide (ITO) (Kintec Corp. Ltd, Hong Kong) coated transparent conducting glass was used as substrate with sheet resistance of 25–30 Ω/cm^2. Prior to deposition, ITOs were cleaned with ultrasonic vibrations in acetone and de-ionized water respectively. Finally the ITO samples were placed vertically in the freshly prepared quiescent solution at room temperature and extracted with/after a time interval of 10, 20, 30, 40, 50 and 60 min and are abbreviated as Ni_{10}, Ni_{20}, Ni_{30}, Ni_{40}, Ni_{50} and Ni_{60}, respectively. The deposited films were washed with deionized water in order to remove loosely bounded particles and further annealed at 300 °C in air for 90 min. The structural properties of the films were studied from X-ray diffractometer (Philips, PW 3710, Almelo, Holland) operated at 25 kV, 20 mA with Cr Kα radiation (λ = 1.54 Å). The infrared (IR) spectrum of powder collected from all NiO samples were recorded using Perkin-Elmer IR spectrophotometer (model-100) in the spectral range 400–4000 cm^{-1}. The pellets were prepared by mixing KBr with NiO powder collected by scratching film from glass substrates, in the ratio of 300:1 and then pressing the powder between two pieces of polished steel. The surface morphology of the films was examined by scanning electron microscopy (SEM) (Model JEOL-JSM-6360, Japan), operated at 20 kV. The optical transmittance was measured using a UV–vis spectrophotometer (Systronics, model 119, Bangalore, India) in the wavelength range of 350–1000 nm.

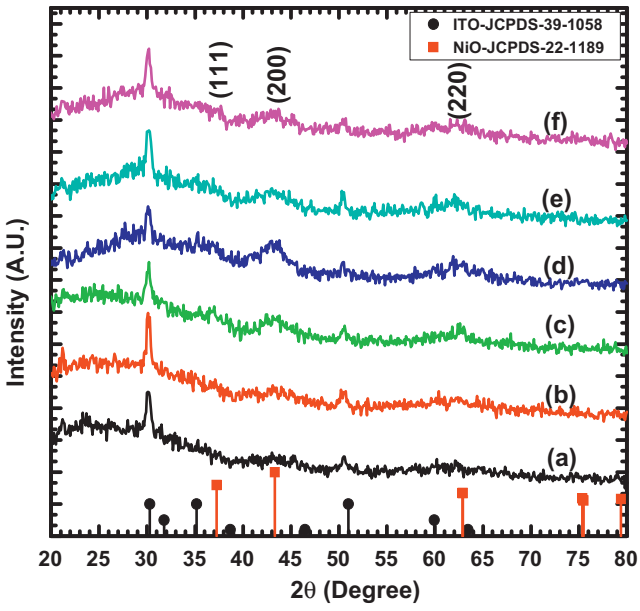

Fig. 1. XRD pattern of NiO samples: (a) Ni_{10}, (b) Ni_{20}, (c) Ni_{30}, (d) Ni_{40}, (e) Ni_{50}, and (f) Ni_{60}, annealed at 300 °C.

All the films were electrochemically cycled in two different electrolytes 0.5 M $LiClO_4$-PC and 0.5 M KOH at a scan rate of 50 mV/s in a conventional three-electrode arrangement comprising NiO thin film as a working electrode, graphite as the counter electrode and saturated calomel electrode (SCE) serving as the reference electrode using electrochemical quartz crystal (EQCM) measurements (model-CHI-400A) made by CH Instrument, USA. The response time of the films was measured by means of in situ transmittance system using a laser source at 630 nm and photodiode as a square-wave voltage (+1.4 V and −0.8 V).

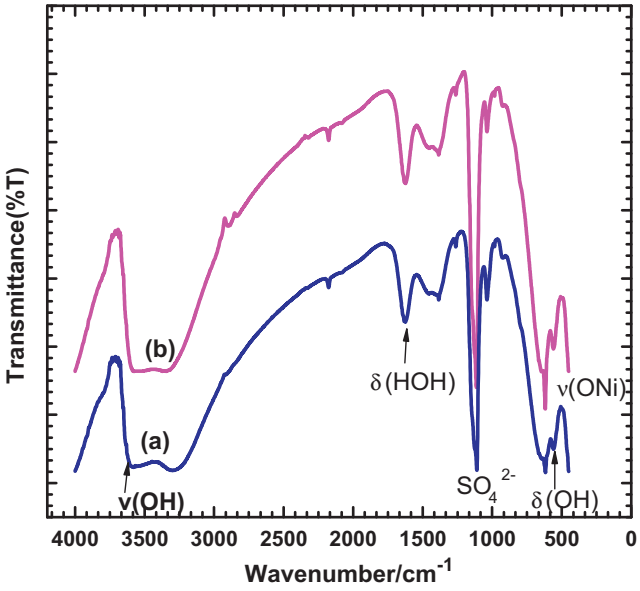

Fig. 2. FT-IR spectra of NiO films (a) as deposited and (b) annealed at 300 °C.