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Optical, structural and electrochromic properties of nickel oxide films produced by sol–gel technique

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Abstract

Nickel oxide films have been deposited from nickel acetate precursor using a sol–gel dip coating method, onto glass and conducting fluorine doped tin oxide (FTO) glass substrate. The direct energy gap (E_{gd}) values for the 2–10 layered films are in the range of 3.62 eV–3.72 eV. X-ray diffraction (XRD) analysis reveals that films consisting of 2–6 layers are amorphous, while films consisting of 8–10 layers are poly-crystalline with cubic grains of around 12 nm–20 nm and preferential growth along the (1 1 1) and (2 0 0) planes. Fourier Transform Infrared (FTIR) spectrum confirms the formation of Ni–O. Electrochromic properties of the nickel oxide coatings were studied using cyclic voltammetric (CV) technique. The 8 layered NiO films exhibit the anodic/cathodic diffusion coefficient of 16.7/5.73×10^{-13} cm^2/s and the change in optical transmission is $\Delta T_{630nm} = 53\%$ with a photopic contrast ratio of 2.87.

Keywords: Thin films; Sol–gel; Electrochromics; NiO

1. Introduction

Electrochromic (EC) devices find applications in automobiles, sunroof of buildings, display devices, light regulation and architectural glazing (Niklasson and Granqvist, 2007; Nah et al., 2008; Granqvist, 1995). Electrochromism is defined as a reversible change in the optical properties of materials under an applied electric field (Granqvist, 1995). The colour change in the materials, usually in the form of a thin film, is due to injection/extraction of electrons and ions. Among various oxide films for electrochromic applications, NiO is an interesting material due to change of colour from transparent to deep brown at a positive potential and its ability to be reversibly bleached when the potential is reversed. Together with tungsten trioxide thin film as a counter electrode, it forms a grey coloured device in the coloured state (Bouessay et al., 2005). NiO is a p-type semiconductor with a wide band gap (3.6–4 eV) (Sato et al., 1993). At room temperature the stoichiometric NiO is an insulator with resistivity of the order of 10^{13} Ω cm (Cerc Korosec and Bukovec, 2004). Nickel cation vacancies and interstitial oxygen in NiO crystallites results in the non-stoichiometric NiO_x. Electrochromism in nickel oxide films is complicated. The generally accepted mechanism for electrochromism is that that the transition from a coloured to the bleached state is associated with the $NiOOH/Ni(OH)_2$ two phase system. Nickel oxide films can be prepared by number of deposition techniques such as chemical deposition, spraying, sputtering, pulsed laser deposition, vacuum deposition and sol–gel technique (Bouessay et al., 2005; Chen et al., 2006; Kamal et al., 2004; Magana et al., 2006; Sasi et al., 2003; He et al., 2006). Among these techniques the sol–gel process is low-cost and can be used to

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prepare large area films, it is easy to add different material components using the sol–gel technique and it has a low thermal budget in layer or device production.

In the present work nickel oxide films of different thickness were coated on glass substrate and FTO coated glass substrate by sol–gel dip coating technique. The effect of thickness on their structural, morphological, optical and electrochromic properties has been studied.

2. Experimental details

Nickel oxide films were prepared by sol–gel dip coating method. A homemade pulse generator and a stepper were used for withdrawal of the substrate from the sol–gel. Analytical reagent grade $Ni(Ac)_2{\cdot}4H_2O$ (3.7329 g) was dissolved in 100 ml of 2-methoxyethanol and 0.1 ml of conc. HCl was added to the solution. The solution was stirred at 60° C for an hour and then aged for 24 h at room temperature to obtain the sol–gel. The FTO film was coated onto a glass substrate using spray pyrolysis method (Purushothaman et al., 2007). The FTO exhibited a sheet resistance of 6 Ω/□. The nickel oxide films were coated on an FTO substrate at a withdrawal speed of 15 cm/min. Films of different thickness were prepared by varying the number of layers of nickel oxide. After each coating the films were dried in air for 5 min and oxidised in an atmosphere of air at 350 °C for 5 min. Finally all the films were annealed for 1 h at 400 °C. X-ray diffraction pattern of the films were recorded using Cu Kα radiation (1.540560 A°). The FTIR spectra have been recorded using JASCO 460PLUS spectrophotometer. Transmission spectra of the films were recorded in the range of 190–1100 nm using a Perkin–Elmer Lambda-35 UV–VIS spectrometer. The FESEM images were recorded using JEOL JSM 6701F instrument. The thickness of the films is calculated by weight gain method. The films were subjected to electrochemical ion insertion/extraction in a three electrode cell with Pt as the counter electrode, Ag/AgCl as the reference electrode and 0.1 M KOH as the electrolyte. Cyclic-voltammetry (CV) curves are generated using a CHI 643B electrochemical analyser (TEXAS, USA) at a scan speed of 25 mV/s.

3. Result and discussion

3.1. Optical properties

The dip coated 2–10 layered NiO films exhibit transmission greater than 60% from 500 nm to1000 nm (shown in Fig. 1). Interference patterns were observed for 8 and 10 layered films are due to the thin film nature of the films. The relationship between maxima and wavelength is $m\lambda = 2nd$, where m is an integer, n is refractive index, d is film thickness and λ is wavelength. The transmission T is given by

$$T_\lambda = T_{0\lambda}\exp(-\alpha_\lambda t) \quad (1)$$

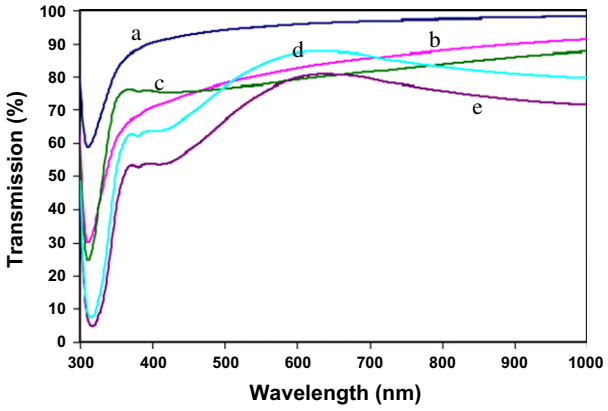

Fig. 1. Transmittance spectra for (a) 2, (b) 4, (c) 6, (d) 8 and (e) 10 layered NiO coatings on glass substrate.

where α is the absorption coefficient, t is the thickness of the film. The relation between absorption coefficient and photon energy is given by the relation

$$\alpha h\nu = A(h\nu - E_g)^m \quad (2)$$

where A is constant and m depends on the nature of the electronic transition. The value of m is ½ for direct transition and $m = 2$ for an indirect transition. The detailed calculation of direct and indirect energy gap values and also the phonon energy values have been discussed by Kamal et al. (2004). The values of these parameters for 2–10 layered NiO films are presented in Table 1. The 2 and 4 layers NiO films show only a direct transition and 6–10 layers films exhibit both direct and indirect transitions (Figs. 2.1a and 2.2a). Figs. 2.1b and 2.2b show the direct and indirect energy gap calculation for 8 layers NiO film. The average value of the direct energy gap (E_{gd}) is 3.65 ± 0.01 eV and indirect energy gap (E_{gind}) is 3.33 ± 0.01 eV. The observed average phonon energy (20 meV) in the present work are low as compared to the phonon energy of 80 meV as reported by Kamal et al. (2004) for the NiO films prepared via spray pyrolysis. They reported the direct energy gap to be 3.88 eV and the indirect energy gap to be of 3.62 eV. Desai et al. (2006) in their work on NiO films prepared via spray pyrolysis, reported an energy gap of 3.61 eV. The results obtained in the present work are in good agreement with the results of Kamal et al. (2004) and Desai et al. (2006).

Table 1
The change in thickness, direct energy gap, indirect energy gap and phonon energy for 2–10 layers of NiO.

No. of coatings	Thickness (nm)	Direct energy gap (E_{gd}) (±0.01) eV	Indirect energy gap (E_{gind}) (±0.01) eV	Phonon energy (E_p) meV
2	150	3.62	–	–
4	232	3.64	–	–
6	325	3.72	3.31	20
8	445	3.64	3.47	15
10	550	3.61	3.21	25