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Electrochromic properties of porous NiO thin films prepared by a chemical bath deposition

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Abstract

Highly porous nickel oxide thin films were prepared on ITO glass by a simple chemical bath deposition (CBD) method in combination with a following heat-treatment process. XRD analysis revealed that the as-deposited precursor film contained β-$Ni(OH)_2$ and γ-NiOOH, and they changed to cubic polycrystalline NiO after annealing. The FTIR results showed presence of free hydroxyl ion and water in the NiO thin films. The electrochromic properties of NiO thin films were investigated in an aqueous alkaline electrolyte (1 M KOH) by means of transmittance, cyclic voltammetry (CV) and chronoamperometry (CA) measurements. The NiO thin film annealed at 300 °C exhibited a noticeable electrochromism and good memory effect. The coloration efficiency was calculated to be 42 $cm^2 C^{-1}$ at 550 nm, with a variation of transmittance up to 82%. The porous NiO thin films also showed good reaction kinetics with fast switching speed, and the coloration and bleaching time were 8 and 10 s, respectively.

Keywords: NiO; Porous film; Electrochromic properties; Chemical bath deposition

1. Introduction

Electrochromic materials are able to change the optical properties persistently and reversibly by an external voltage [1]. They have attracted much attention in recent years because of their low power consumption, high coloration efficiency (CE), and memory effect under open circuit condition [2,3]. Among these materials, NiO is an attractive material due to its high electrochromic efficiency, large dynamic range, good cyclic reversibility, and low material cost [4,5]. A variety of methods have been used to prepare electrochromic NiO films, such as vacuum evaporation [6], sputtering [7,8], chemical vapor deposition [9], electro-deposition process [10], pulsed laser deposition [11], spray pyrolysis [12], sol–gel process [13], and chemical bath deposition (CBD) [14,15], etc.

CBD of oxide films was first realized by Nagayama et al. [16] who used the technique to prepare SiO_2 films on silicon wafers. The method involves immersion of a substrate in an aqueous solution containing a precursor species. Then the desired oxide/hydroxide precipitates preferentially on the substrate surface, producing a conformal film. CBD is an advantageous technique due to its low cost, low temperature and also convenient for large-area deposition. However, there are only a few reports on the optical properties of NiO thin films prepared by CBD [17–19]. Ristova et al. [19] investigated the electrochromic properties of CBD NiO thin films. But the NiO thin films exhibited a CE with 24 $cm^2 C^{-1}$, which was lower than the value reported by Maruyama et al. [9].

The electro-deposition NiO films prepared by Wu et al. [20] showed a highly porous structure and exhibited high transmittance variation up to 80% at 550 nm. The porous structure is believed to be helpful to the enhancement of electrochromic performance. In this present work, NiO thin films with huge porosity were prepared by a CBD method. The electrochromic and electrochemical properties of porous NiO thin films were investigated.

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2. Experimental

Solution for CBD was obtained by mixing 80 ml of 1 M nickel sulfate, 60 ml of 0.25 M potassium persulfate, and 20 ml of aqueous ammonia (25–28%) in a 250 ml pyrex beaker at room temperature. Clean ITO glass substrates with $2.5 \times 2.5\,cm^2$ in sizes, masked with polyimide tape to prevent deposition on the nonconductive sides, were used in this work. The ITO samples, placed vertically in the freshly resulting solution, were kept at 20 °C for 20 min to deposit the precursor film. Then they were washed with deionized water. After removing the tape masks, the coated samples were dried at 75 °C and then were annealed at different temperatures (300, 350, and 400 °C) in air for 1.5 h. The thickness of the annealed films was approximately 480 nm, determined with an alpha-step 200 profilometry.

The powder from the as-deposited precursor film was analyzed by thermogravimetry (TG) and differential thermal analysis (DTA) under N_2 atmosphere at a heating rate of $10\,°C\,min^{-1}$ in a temperature range of 25–575 °C. The morphology and microstructure of the as-deposited and annealed films were characterized by a field emission scanning electron microscopy (FESEM, Hitachi S-4700), X-ray diffraction (XRD, Philips PC-APD with Cu Kα radiation), and Fourier transform infrared (FTIR) measurements (Perkin Elmer System 2000 FTIR interferometer).

The transmission spectra of NiO thin films in the fully colored and fully bleached states were measured over the range from 200 to 900 nm with a SHIMADZU UV-240 spectrophotometer. Each spectrum was recorded ex situ (after the samples taken out of the three-compartment system, instantly rinsed and wiped off from the remaining persistent water). The cyclic voltammetry (CV) and chronoamperometry (CA) measurements were carried out in a three-compartment system containing 1 M KOH as electrolyte, Hg/HgO as reference electrode and a Pt foil as counter-electrode. CV measurements of NiO films were performed using a CHI660B electrochemical workshop with a scanning rate of $10\,mV\,s^{-1}$ between 0 and 0.77 V at room temperature (25 ± 1 °C).

3. Results and discussion

Hydroxide precursor thin film was prepared using CBD. The chemical reactions may occur as follows [15]:

$$[Ni(H_2O)_{6-x}(NH_3)_x]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + (6-x)\,H_2O + xNH_3, \quad (1)$$

$$2Ni(OH)_2 + S_2O_8{}^{2-} \rightarrow 2NiOOH + 2SO_4{}^{2-} + 2H^+. \quad (2)$$

The as-deposited precursor films were uniform in appearance and exhibited gray in color. After annealing, the films were nearly transparent and found to be strongly adhered to the ITO substrate. The SEM images of the as-deposited precursor and annealed films are shown in Fig. 1. The as-deposited precursor film has a porous structure (Fig. 1a). After annealing treatment at temperatures in the range of 300−400 °C, the morphologies of the films have hardly any change (Figs. 1b–d). It is observed that the annealed films have porous structure, which is similar to that reported by Wu et al. [20].

The XRD patterns of powders from the as-deposited precursor and annealed films on ITO substrate are presented in Fig. 2. All the peaks of pattern a in Fig. 2

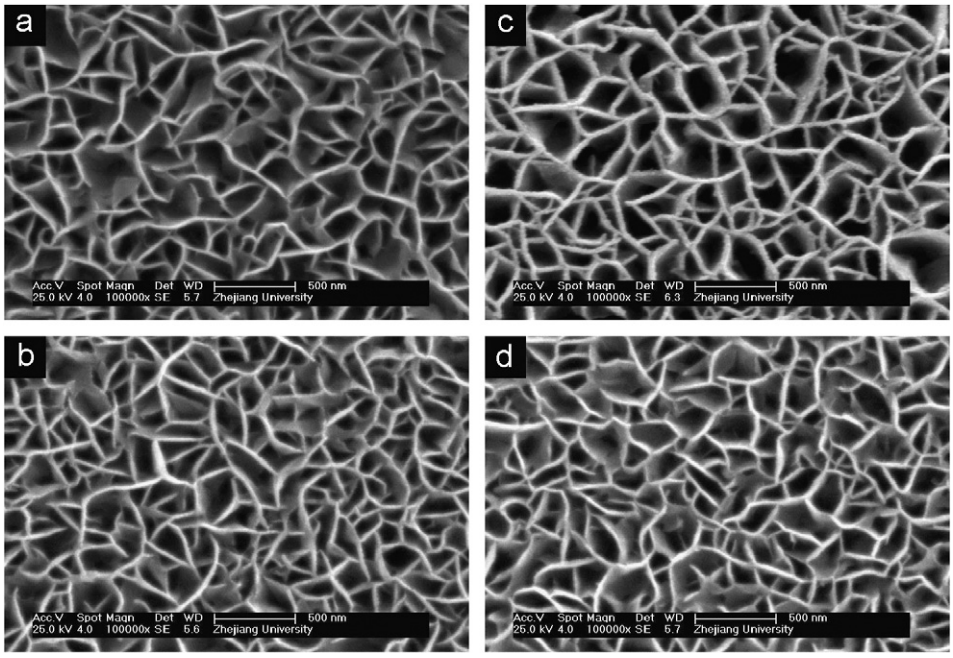

Fig. 1. SEM micrographs of (a) as-deposited precursor film and the films annealed at (b) 300 °C, (c) 350 °C, and (d) 400 °C.