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Studies on electrochromic properties of nickel oxide thin films prepared by reactive sputtering

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Abstract

The non-stoichiometric nickel oxide (NiO_x, $x > 1$) films deposited on a conducting substrate by RF magnetron sputtering have been investigated for electrochromism in alkaline solution. It was found that both Ni^{3+} and Ni^{2+} existed in NiO_x films. The intercalation and deintercalation of H^+ ions causes the bleaching and coloring of NiO_x films. The atomic ratio of Ni and O in the NiO_x films is 0.7:1 (as-deposited); 0.51:1 (bleached); 0.45:1 (colored). The maximal optical density change was found to be 0.78 at a spectral of 326 nm. With the increase of temperature of heat treatment, the electrochromic properties of NiO_x films were weakened.

Keywords: Nickel oxide; Sputtering; Electrochromic properties; Optical properties

1. Introduction

Electrochromism (EC), defined as a reversible and persistent optical transformation induced by electrochemical processes [1,2], captured the interest of researchers for its technological applications, such as high contrast non-emissive information displays, smart windows, reflectance-adjustable car rearview mirrors, gas sensors and device for thermal control because of its low power consumption, high coloration efficiency and open-circuit memory [3,4]. Electrochromic materials could be divided into two types: cathodic EC materials, which colored under charge insertion, and anodic EC materials, which are colored under charge extraction [4].

Nickel oxide is an outstanding anodically coloring electrochromic material due to a large span in optical density between fully bleached and fully colored states and low materials cost. It is also considered to be a model semiconductor with p-type conductivity because of its wide band-gap energy range from 3.6 to 4.0 eV [5]. Additionally, NiO_x thin films play important roles as a complementary counter layer against tungsten oxide layer for enhancing the coloration efficiency and contrast ratio [6]. There are several methods to prepare nickel oxide films, which include sputtering [3], spray pyrolysis [7], chemical vapor deposition [8], electroless [9] and sol–gel deposition [10]. Among these methods, reactive sputtering is the most widely used one and NiO_x films with good electric and optical properties have been obtained [11–14]. However, there have been not so many studies about the mechanism of electrochromic nickel oxide film by redox cycles.

In this study, the electrochromic properties of non-stoichiometric NiO_x ($x > 1$) films prepared by radio-frequency magnetron sputtering were investigated. The variation of structure, composition, optical transmittance, cyclic voltammetry and optical density change (ΔOD) were measured for investigating the mechanism of electrochromism. Band theory was also used to explain the electrochemical mechanism of nickel oxide film.

2. Experimental

2.1. Preparation of the NiO_x thin films

Nickel oxide films were deposited on the SnO_2 coated transparent glass (sheet resistance 15 Ω/□, the average transmittance 80%, thickness of SnO_2 film 500–600 nm) by a radio-frequency (RF, 13.56 MHz) magnetron sputtering system from a pure (99.99%) nickel target in an $O_2 + Ar$ gas mixture with varied gas flow ratios. The RF power was 60 W and the sputtering voltage was kept at 2 kV. The distance between the target and the substrate was approximately 40–45 mm. The chamber was evacuated to a pressure below 5×10^{-4} Pa before deposition. During sputtering, the working pressure was set at 1.3–5.6 Pa. The

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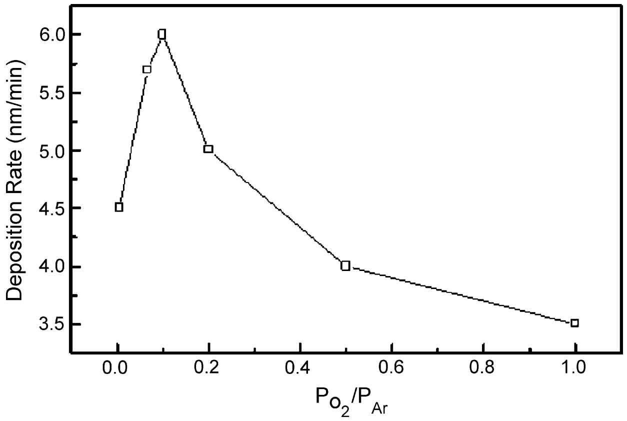

Fig. 1. Deposition rate for NiO_x films made by sputtering at the oxygen partial pressure (sputtering pressure 1.1 Pa).

substrate was not heated. Prior to each deposition, the target was cleaned with pure argon gas for 5 min in order to remove the surface oxide layer.

2.2. Characterization

The crystal structure of the nickel oxide films was investigated by a D/Max-2400 X-ray diffractometer using monochromatic high-intensity Cu Kα radiation ($\lambda = 0.15406$ nm) with a grazing incidence of angle 1°. The chemical states of O and Ni for the as-deposited, colored and bleached NiO_x films were determined with a PHI5702 XPS/AES USA X-ray photoelectron spectroscopy system. The transmittance of the prepared films was measured with a DLM2000 UV–vis spectrophotometer.

Deposition rate was obtained from sputter time and ensuing film thickness recorded by a surface profilometry across a step made in the film. The deposition rate of nickel oxide films were varied due to different ratio of the oxygen partial pressure to argon partial pressure (Fig. 1) and sputtering pressure (Fig. 2).

Electrochemical measurements were made by a three-electrode system with Ag/AgCl as the reference electrode, Pt as the counter electrode, and the NiO_x films as the working electrode. Cyclic voltammetry was carried out in a 1 M KOH electrolyte at a scan rate of 20 mV/s. The electrochemical current was obtained with a BAS 100B comprehensive electrochemical analyzer.

3. Results and discussion

3.1. Structural properties

X-ray diffraction patterns of the NiO_x films before and after annealed at 400 °C are showed in Fig. 3. The ratio of the oxygen partial pressure to argon partial pressure was 1:8. The two main diffraction peaks of NiO thin film have been presented at $2\theta = 37.7°$ (1 1 1), 42.7° (2 0 0) (JCPDS 78-0423) [15]. X-ray analysis indicates that heat treatment does not cause any structural change. But there is an intensification of NiO (2 0 0) diffraction peak at $2\theta = 42.7°$, which clearly shows the increase of inert ideal-stoichiometric NiO and decrease of active non-stoichiometric NiO_x.

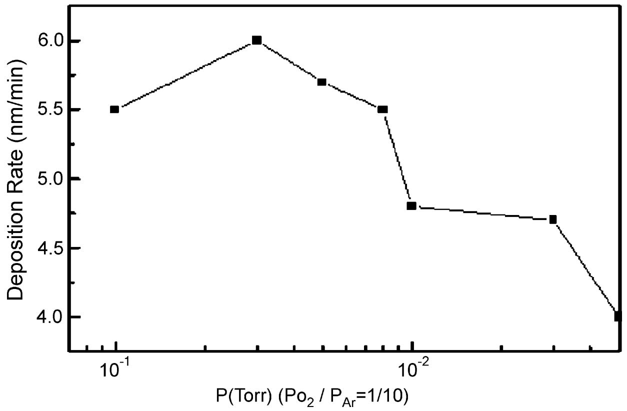

Fig. 2. Deposition rate for NiO_x films made by sputtering at the sputtering pressure.

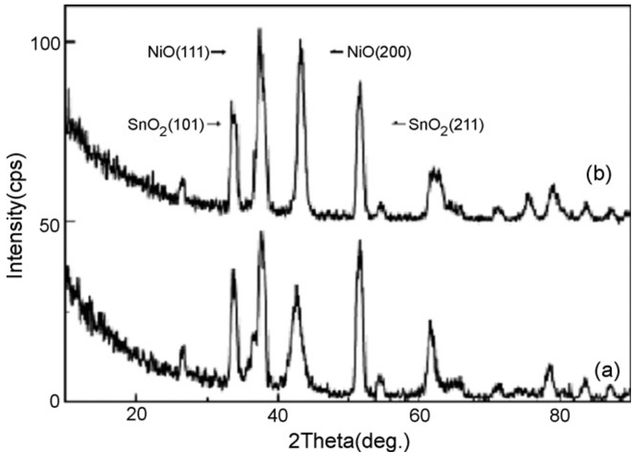

Fig. 3. XRD patterns of NiO_x films: (a) before and (b) after annealing at 400 °C for 150 min.

XRD also provides data about crystallite size. The peak broadening is caused by the finite size of the crystallites, about 0.1 μm [16]. Crystallite size can be determined by an analysis of peak shapes for several diffraction orders, since the crystallite size affects the peak width [17]. Crystallite size can also be estimated from the peak width using the Debye-Scherrer Eq. (1) [16]:

$$D = \frac{0.9\lambda}{B \cos \theta} \tag{1}$$

In this formula, B denotes the width at half maximum. To obtain this value, the diffraction peaks were fitted to a Gaussian function. The crystallite size at different annealing temperature was shown at Fig. 4 when the above formula is used.

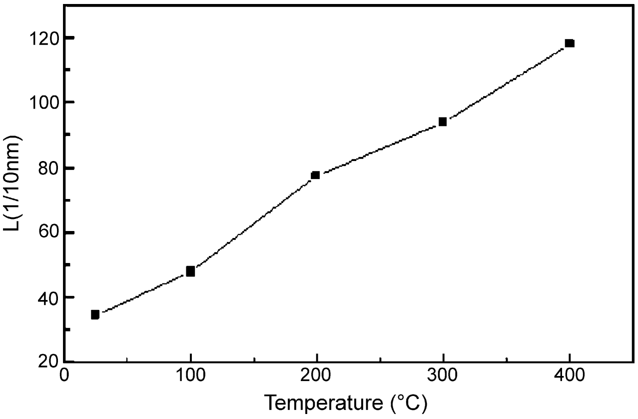

Fig. 4. The relations between the crystallize size and different annealing temperature.