



Nitrogen-doped nickel oxide thin films for enhanced electrochromic applications

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ABSTRACT

In this work, Ni oxide and nitrogen (N)-doped Ni oxide electrochromic films were fabricated with radio frequency magnetron sputtering from a ceramic Ni oxide target. Nitrogen gas was used as the precursor for N doping. The N dopant resulted in Ni oxide films with decreased lattice parameters, increased degree of crystallinity and enhanced surface roughness. The electrochromic performance of the resulting films was evaluated in a LiClO₄ electrolyte dissolved in propylene carbonate. The charge reversibility and coloration efficiency as well as the coloration and bleaching kinetics for the N-doped Ni oxide films were significantly improved relative to the undoped Ni oxide films.

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1. Introduction

Oxide semiconductors have been intensively investigated for electrochromism [1], photovoltaics [2], catalysis [3] and Li-ion batteries [4]. Detailed studies on oxide semiconductors for these applications have been conducted primarily on transition metal oxides, such as TiO₂, ZnO, NiO and WO₃ [1,5,6]. Often times the physical properties of transition metal oxides are tailored through band-gap engineering due to prerequisites imposed by their technological applications. One of the most common routes to tune the band structure of a transition metal oxide is by elemental doping [7]. For instance, nitrogen (N) doping has been found to significantly influence the band structure and optical properties of TiO₂ [8]. Controlling the band-gap in transition metal oxides is of significant importance for emerging energy applications, such as electrochromism. Electrochromism is the reversible modulation of optical properties upon the charge and discharge of ions (e.g., Li⁺) and charge-compensating electrons. Ni oxide is the most studied electrochromic counter electrode material due to its known advantages over other materials [1]. The nickel ions in Ni oxide are capable of exhibiting multiple valences due to the variation of Ni3d electrons. It has been suggested that these Ni valence states provide the basic foundation for the physical and chemical processes observed in electrochromic devices [1]. Ni oxide materials color complementarily with WO₃ materials and thus provide a visually comfortable and neutral dark state for an electrochromic device [1]. The electronic structure of

Ni oxide is a determining factor for enhancing electrochromic effects [9] and various efforts have been made to modify the electronic structure of Ni oxide materials. Recent efforts have modified the band-gap of Ni oxide by introducing cationic dopants [10]. In addition, Sun et al. reported observing promising effects on the electrochromic performance of cathodic WO₃ thin films through N-doping [11]. However, very few efforts have been targeted to experimentally dope Ni oxide with anions. Theoretical studies reported the shrinkage of the Ni oxide band gap after N-doping due to the impurity states driven by N 2p [12,13]. Thus far, N-doped Ni oxide has not been experimentally achieved via magnetron sputtering. One of the possible difficulties in depositing N-doped Ni oxide is the phase impurity nickel nitride that can be produced via the nitridation of nickel [14].

A desirable electrochromic material must maintain a stable charge/discharge reversibility, high coloration efficiency and fast coloration/bleaching switching kinetics. However, Ni oxide materials tend to have inferior coloration efficiency [1], slower switching kinetics relative to WO₃ materials [15,16] and poor charge/discharge reversibility (i.e., net decrease in charge capacity). Efforts to improve the electrochromic performance of Ni oxide have been primarily focused on cationic dopants, however we believe that anionic dopants are also suitable for optimizing the electrochromic properties of Ni oxide due to their known effects on the Ni oxide band structure [12,13]. Conversely, understanding the role of a dopant in modifying the morphology of Ni oxide is equally as important as the band structure of Ni oxide to fully impact the electrochromic properties [17]. Herein, we report the deposition of an N-doped Ni oxide thin film prepared by radio frequency (RF) magnetron sputtering from a ceramic Ni oxide target. It is shown that the N-doped Ni oxide thin film has superior performance (i.e., charge/discharge reversibility, switching

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kinetics, coloration efficiency) relative to a pure Ni oxide thin film prepared using a similar deposition protocol.

2. Experimental details

2.1. Thin film fabrication

RF magnetron sputtering was employed to deposit Ni oxide and N-doped Ni oxide thin films from an NiO ceramic target (CERAC, Inc.). The sputter depositions were performed on an Angstrom EvoVac deposition system housed in a glove box under an argon atmosphere. The target–substrate distance was 10 cm and remained constant throughout the study, and no additional heating was applied to substrate. The gas mixtures for depositing Ni oxide and N-doped Ni oxide materials are 80% Ar/20% O₂ and 80% Ar/20% N₂, respectively. The gas composition was tuned in order to obtain Ni oxide and N-doped Ni oxide thin films with similar optical modulation, thus enabling a direct comparison of charge capacity, coloration efficiency and switching kinetics between the two types of films. The base pressure and working pressure were 1.33×10^{-5} Pa and 0.4 Pa, respectively. The films were deposited on F-doped SnO₂ and witness glass substrates. The F-doped SnO₂ substrates were purchased from Hartford Glass CO, Inc. (TEC 15, 1.5 in. × 0.82 in. × 2.3 mm). The substrates were cleaned successively with soapy water, acetone, isopropanol and deionized water, and dried under flowing N₂.

2.2. Material characterization

Scanning Electron Microscopy (SEM) was performed on a JEOL JSM-7000F Field Emission Scanning Electron Microscope with an EDAX Genesis Energy Dispersive Spectrometer. Crystal structure of the resulting films was characterized on a Philips X-ray diffractometer Model PW1729 operated at 45 kV and 40 mA using CuK_α radiation using theta–2theta scan, where the X-ray diffraction (XRD) patterns were acquired from the thin films deposited on glass witness substrates. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis HSi Ultra X-ray Photoelectron Spectrometer using an Al K_α X-ray source operated at 14 kV and 10 mA.

2.3. Thin film performance evaluation

Methods for the performance evaluation have been reported previously [18,19]. Briefly, the electrochromic performance was measured in a liquid electrolyte half-cell where the electrolyte was 1 M lithium perchlorate (LiClO₄) dissolved in propylene carbonate. Cyclic voltammetry (CV) was carried out using a BioLogic VMP3 multichannel potentiostat with a scan rate of 20 mV/s and a voltage range of 1.7–4.2 V vs. Li/Li⁺. Switching kinetics (*i.e.*, coloration, bleaching) was measured under a chronoamperometry (CA) cycling between 1.7 and 4.2 V vs. Li/Li⁺, where the potential was held for 5 min at each potential step. The switching speed is defined as the time required to achieve ~90% of total transmittance change within a potential step. *In-situ* transmittance was measured using a diode laser with a wavelength of 670 nm. All measurements were carried out under an Ar atmosphere in a glove box.

3. Results and discussion

The SEM images of the as-prepared thin films are shown in Fig. 1, where the thickness is *ca.* 200 nm for both films. A significant morphological difference is observed between these two films; namely, the N-doped Ni oxide film has a higher proportion of surface irregularities leading to an increase in surface roughness (area). These surface irregularities may provide additional sites for Li intercalation/deintercalation, which has the potential to accelerate the switching kinetics. Fig. 2 displays the XRD patterns for the Ni oxide and N-doped Ni oxide thin films. The diffraction patterns are consistent

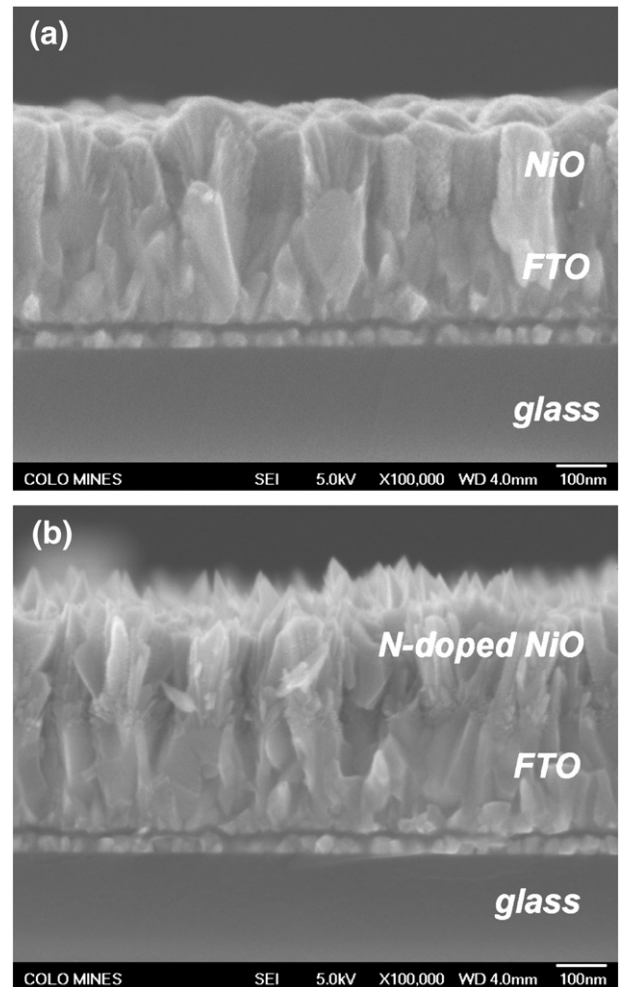


Fig. 1. Cross-sectional SEM images for (a) Ni oxide and (b) N-doped Ni oxide thin films.

with the standard face-centered cubic NiO structure (JCPDS 65-2901) [3]. The NiO <111> orientation is preferred and indicated by the height ratio between NiO (111) and NiO (200). Based on the full width at half maximum and diffraction angle for the NiO (111) it is clear that N-doping leads to an increase in the degree of crystallinity and

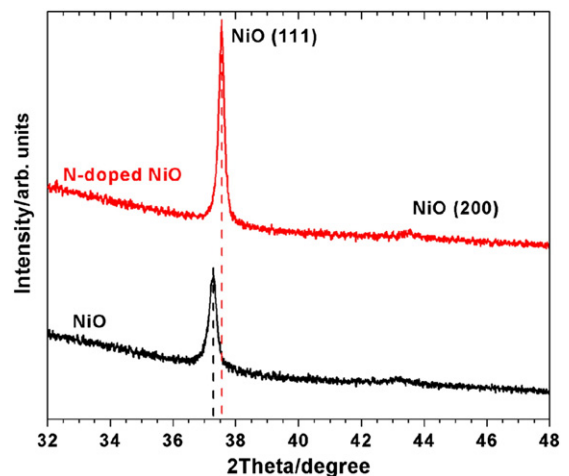


Fig. 2. XRD patterns for Ni oxide (black) and N-doped Ni oxide (red) thin films, where two peaks are indexed as NiO (111) and NiO (200). The XRD patterns were acquired from the as-deposited thin films on glass witness substrates.

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