

## As-Sputtered Electrochromic Films of Nickel Oxide

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### Abstract

Electrochromic nickel oxide films were deposited by rf magnetron sputtering of a Ni target in gas mixtures of Ar and O<sub>2</sub>. When electrochemically cycled in 0.1 N KOH solution, large reversible changes in visible absorption were obtained within the first 10 bleach/color cycles. Films which showed the greatest changes in optical properties and charge capacity were produced within a narrow range of oxygen flow rates. The coloration efficiency was found to be insensitive to the sputtering conditions and stoichiometry, with a value of  $34 \pm 4 \text{ cm}^2 \text{ C}^{-1}$  at 550 nm. This indicates that microstructure and charge capacity determine the absorption coefficient. The reaction rate was found to depend on the concentration of OH<sup>-</sup> in the electrolyte, supporting the growing evidence that OH<sup>-</sup> is the electrochromically active species.

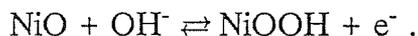
## Introduction

A large reversible change in optical transmittance can be produced in nickel oxide thin films by electrochemical reaction.<sup>1-4</sup> Such electrochromic nickel oxide films have been produced by electrodeposition,<sup>3-5</sup> by vacuum evaporation,<sup>5</sup> by reactive magnetron sputtering,<sup>6-8</sup> and by diode sputtering from an oxide target.<sup>9</sup> Although electrodeposited nickel oxide films bleach and color immediately after deposition, sputtered films have required a postdeposition treatment or extended electrochemical cycling to achieve the same change in optical absorption. Any postdeposition treatment complicates the production of multilayer electrochromic devices.

The electrochromic reaction is still in question. The most widely accepted view is that extraction of  $H^+$  causes anodic coloration by the reaction



There is increasing evidence, however, that insertion of  $OH^-$  causes or controls the coloration by a reaction of the type



Resolution of this fundamental issue is of great practical importance. For example, knowledge of the ion species that causes coloration is required to select ion conductors and other device components.

In this paper, we report on electrochromic nickel oxide films prepared by sputtering, and show that the electrochromic properties can be greatly improved by careful control over the oxygen stoichiometry of the film. We determine the coloration efficiency and find that it is the same for all  $NiO_x$  films. Also, we contribute to the evidence that  $OH^-$  ions are the active electrochromic species.

## Experimental Methods

The NiO<sub>x</sub> films were made by rf planar magnetron sputtering from a Ni target in gas mixtures of Ar and O<sub>2</sub> at a fixed total pressure and varying gas composition. The sputtering parameters are summarized in Table 1. Nickel has a high magnetic permeability, so the uneroded Ni target weakens the plasma confinement field of the magnetron. As the erosion ring forms, however, the plasma is concentrated above the narrowly etched groove. This causes a rapid decrease in discharge voltage and increase in deposition rate toward the end of the target lifetime. Films reported on in this paper were made near the middle of the target lifetime and were deposited sequentially to minimize these target erosion effects.

The films were sputtered upwards onto unheated substrates. The substrates were uncoated glass and glass coated with In<sub>2</sub>O<sub>3</sub>:Sn (ITO) with a sheet resistance of 10 Ω/□. Film thickness was determined by measuring step heights with a stylus profilometer. DC resistivity at room temperature was measured by the four-point technique on the films on plain glass. The NiO<sub>x</sub> films on ITO were bleached (reduced) and colored (oxidized) in the electrochemical cell configuration ITO|NiO|0.1 N KOH|Pt, with a Pt wire reference electrode. Optical transmittance was measured in a double-beam spectrophotometer over the visible spectrum from 300-800 nm where most of the variation occurs. In some cases the entire solar spectrum from 300-2500 nm was recorded.

## Results and Discussion

The gas composition during sputtering has a strong effect on the depositing film. Figs. 1 and 2 show the deposition rate and resistivity for films made at various O<sub>2</sub> flow rates, while holding the total pressure, rf power, substrate temperature, and substrate position constant. The films deposited at the lowest O<sub>2</sub> flows are metallic. For O<sub>2</sub>

flows above a critical value (0.5% in Figs. 1 and 2), the deposition rate and resistivity both rise sharply, and an oxide film is deposited. For even higher O<sub>2</sub> flows, the deposition rate and resistivity decrease, and the as-deposited oxide film gets slightly darker.

In this system the thickness deposition rate for the NiO<sub>x</sub> films increases as they change from metal to oxide. This contrasts with other reactive sputtering processes where the sputtering rate decreases at the transition point. The lower density of nickel oxide is not sufficient to account for the difference in deposition rates. Some further increase in deposition rate may be explained if the oxide films are more porous than the metal films. The increase in deposition rate may also be due to formation of a target surface oxide with a larger sputtering yield and/or a smaller secondary electron yield than Ni.<sup>10</sup> When a dc power supply is used, the load impedance increases during the metal to oxide transition, and this is evidence for a decrease in the secondary electron yield. A peak in the deposition rate versus total pressure is also seen for sputtering a Ni target in pure oxygen.<sup>8</sup>

X-ray diffraction reveals the oxide films to be polycrystalline with (111) and (200) peaks from cubic NiO<sub>x</sub> (JCPDS File 4-835). The average grain size, estimated from the peak widths, is approximately 10 nm, with no apparent dependence on O<sub>2</sub> flow rate (above the metal-oxide transition). The resistivity of stoichiometric crystalline NiO<sub>x</sub> is large ( $> 10^{13}$  Ω cm) while the much lower resistivity of semiconducting NiO<sub>x</sub> is attributed to impurities and lattice defects.<sup>11</sup> The peak in resistivity in Fig. 2 suggests that films deposited in flows just above the metal-oxide transition are most nearly stoichiometric and that higher O<sub>2</sub> flows produce films with excess oxygen.

The spectral transmittance of one NiO/ITO/glass sample at various stages of electrochemical treatment is shown in Fig. 3. The NiO<sub>x</sub> film was made at 3.4% O<sub>2</sub>, and was slightly gray as deposited (curve A). The film was reduced in the electro-

chemical cell at a constant  $0.5 \text{ mA cm}^{-2}$  for 20 sec, then the initial bleached transmittance (curve B1) was measured. The film was oxidized at a constant  $0.5 \text{ mA cm}^{-2}$  for 45 sec, then the initial colored transmittance (curve C1) was measured. After 9 more cycles ( $\pm 0.5 \text{ mA cm}^{-2}$  for 45 sec each), the transmittance curves B10 and C10 were measured. The sample was removed from the electrolyte, rinsed with water and dried with  $\text{N}_2$  before each transmittance measurement. Visible transmittance in the bleached state changes very little after the first cycle, but the colored state becomes progressively darker over the first 10 cycles. This behavior is similar to that of electro-deposited  $\text{NiO}_x$  films, but is different from that reported for other sputtered  $\text{NiO}_x$  films, where the fully bleached state is not reached until after prolonged electrochemical cycling.<sup>8,9</sup> Fig. 3 also illustrates that the change in optical absorption in nickel oxide is greatest in the wavelength range 300-800 nm.

To determine whether protons or hydroxyl ions are responsible for coloration and bleaching, cyclic voltammetry was performed in various concentrations of KOH. The ionic concentration was fixed at 0.1 M by addition of KCl. Peak current density in an electrochemical scan is proportional to both the concentration of the active species and the square root of the scan rate. These relationships are demonstrated in Fig. 4 for the anodic peak; similar results were obtained for the cathodic peak. The reduction in peak current with decreasing hydroxyl concentration is accompanied by a reduction in the strength of the color change in the films.

At low levels of injected charge, the change in absorbance is proportional to the charge transferred. The coloration efficiency, defined as the absorbance change per unit charge, is thus a constant over this range. Fig. 5. shows the in-situ absorbance change at constant current for five films made at 3.0%  $\text{O}_2$  flow. Collective data from  $\text{NiO}_x$  films made at various oxygen flows gives a value of  $34 \pm 4 \text{ cm}^2 \text{ C}^{-1}$  at 550 nm.

The effect of film thickness is to change the point at which the absorbance change saturates. For film thickness  $d$  up to at least 425 nm, the saturation absorbance change  $A_s$  is proportional to  $d$ , so  $2.303 A_s/d$ , the change in absorption coefficient, is independent of  $d$  and depends only on the film microstructure.

The rate of  $O_2$  flow during sputtering has a strong effect on the electrochromic properties of the films as shown in Fig. 6. For  $O_2$  flows less than 5%, the absorption coefficient in the bleached state was  $< 1 \mu\text{m}^{-1}$  at 550 nm. Some of the oxide films deposited at  $O_2$  flows less than 2.5% delaminated in the electrochemical cell and were not included in Fig. 6. Substrate curvature indicated that these films were in tensile stress. Films that were deposited at  $O_2$  flows above 6.5% had small regions ( $< 5\%$  of area in contact with electrolyte) that would not bleach or color fully. There is an optimum region of  $O_2$  partial pressure, which corresponds to 2.5 to 6.5%  $O_2$  flow in this case. Films with the greatest optical range are produced at  $O_2$  flows just above the maximum-resistivity level where they are slightly superstoichiometric.

## Conclusions

As-deposited sputtered nickel oxide films can have electrochemical coloration comparable to the best electrodeposited films. A maximum change in optical absorption occurs in films made with a slight excess of oxygen. Higher or lower levels of oxygen result in films that accept less charge transfer and that never bleach completely even after many electrochemical cycles. Nevertheless, we find that the coloration efficiency does not depend on the stoichiometry of the film. Therefore, it is primarily the defect structure that determines the effective absorption coefficient by allowing more charge transfer in the film. The concentration of  $\text{OH}^-$  in the electrolyte appears to be a factor controlling the electrochromic reaction rate.

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Table I. Deposition Parameters

Target	99.99% Ni
diameter	38 mm
thickness	1.5 mm
Target-substrate distance	40 mm
RF Power (13.56 MHz)	150 W
Working Gas	Ar + O <sub>2</sub>
Total Pressure	4 Pa
Total Gas Flow	300 sccm

### Figure Captions

Figure 1. Deposition rate of NiO<sub>x</sub> films versus composition of the sputtering gas.

Figure 2. Electrical resistivity of NiO<sub>x</sub> films versus composition of the sputtering gas.

Figure 3. Spectral transmittance of NiO/ITO/glass as deposited (curve A), after the first bleach and color half cycles (curves B1 and C1), after the 10th bleach and color half cycles (curves B10 and C10).

Figure 4. Variation of peak anodic current density with scan rate for a NiO/ITO/glass electrode at several hydroxyl ion concentrations.

Figure 5. Absorptance change of NiO<sub>x</sub> films at 550-nm wavelength under a constant current of 0.38 mA cm<sup>-2</sup>. All films were deposited at 3.0% O<sub>2</sub> flow to the indicated thickness.

Figure 6. Change in absorption coefficient at 550 nm versus composition of the sputtering gas, as calculated from saturation absorbance change and film thickness.

