

Electrochromic properties of sputtered Ni oxide thin films in neutral KCl electrolytes

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Abstract

Thin films of Ni oxide, which is a promising anodic electrochromic material, were deposited by reactive RF sputtering at 40, 60, and 100 watts, and their electrochemical and electrochromic properties were examined using neutral KCl electrolytes. Higher charge capacity and higher optical modulation were obtained for a Ni oxide film deposited at low sputtering power and low deposition rate. Electrochromic coloration efficiencies of approximately 30 cm²/C were obtained for all the Ni oxide films in KCl regardless of RF power value.

Electrochromic (EC) materials can change their optical properties (darken and lighten) by application of a small reversible dc voltage. Operation of inorganic EC devices is dependent upon a reversible electrochemical double injection of ionic/electronic species into the host lattice of multivalent transition metal oxide materials.^{1,2} Such EC devices are being developed in applications for “smart” energy efficient windows, anti-glare automobile rearview mirror, and sunroofs.³⁻⁵ A typical EC device consists of a thin film of EC material, an ion storage layer, and an ion-conducting layer sandwiched between two transparent conducting oxide layers. Aqueous solutions, nonaqueous solutions, and solid state electrolytes have been used for ion conduction.² Most of the aqueous solutions are typically acid or alkaline solutions. From a viewpoint of general safety, when an EC device is damaged resulting in electrolyte leaks, a neutral non-corrosive electrolyte is very desirable. However, reports on the EC properties in neutral electrolytes are very scarce. Recently, Lee *et al.*⁶ reported electrochemical and EC properties of NiO / Ta₂O₅ nano-composites in neutral KCl aqueous solutions. In this paper, Ni oxide thin films, which are promising anodic EC materials, were deposited by reactive sputtering and their electrochemical and EC behavior were studied using neutral KCl electrolyte solutions.

Ni oxide thin films were concurrently deposited on F doped SnO₂ (FTO) coated glass substrates for electrochemical and EC characterizations and on glass substrates for structural analyses. A Ni target was sputtered in an Ar/O₂ atmosphere using a radio-frequency (RF) magnetron sputtering system to deposit Ni oxide films (with thicknesses

of about 400nm), as reported in a previous paper.⁷ RF sputtering power was varied as a parameter from 40 to 100 W. The oxygen/argon flow ratio and substrate-target distance were 1:9 and 5 cm, respectively. Total sputtering gas pressure was maintained at 1.5 Pa with no intentional substrate heating. Crystal structure was characterized by X-ray diffraction (XRD) using Cu K α radiation. Cyclic voltammetry (CV) and in-situ optical measurements were carried out in a 1 M KCl aqueous solution using Ag/AgCl (approximately -35 mV relative to a Saturated Calomel reference Electrode, SCE) and Pt as reference and counter electrode, respectively. *In situ* optical modulation was measured with a laser diode at 670 nm wavelength, and transmittance spectra after bleaching and coloring were measured by a spectrophotometer.

The effects of RF power (40, 60, and 100 watts) on the structure of the Ni oxide thin films deposited on a glass substrate were studied by XRD. As can be seen from Figure 1, crystalline diffraction peaks due to cubic NiO were obtained for samples deposited at 60 and 100 W. The preferential crystal orientation changed from (111) to (220) by decreasing the RF power, and the diffraction peak width increased with decreasing RF power. Crystal grain size of the Ni oxide films deposited at 60 and 100 W were estimated to be 10 and 30-40 nm, respectively, using Scherrer's formula.⁸ The XRD peak intensity becomes very weak for the film deposited at 40 W, indicating nanocrystals with grain sizes of a few nanometers. These results indicate that the crystal grain size of NiO decreases with decreasing RF power. At higher RF powers, substrate temperature is elevated and most likely enhances crystal grain growth of NiO.

Corresponding to the increase of the RF power from 40 to 100 W, the deposition rate increased from 1.8 to 9.2 nm/min.

The electrochemical properties of these Ni oxide films have been studied by CV analysis in a 1 M KCl electrolyte at a voltage scan rate of 10mV/s and a scan range of 0-1.0 V. Upon initial cycling, current density increases, and became stable after 10 or 20 cycles similar to the result reported in previous papers.^{9,10} CV curves of the Ni oxide films corresponding to the 10th cycle are shown in Figure 2. The CV curves are pseudo-capacitive similar to those reported by Lee *et al.*⁶ for NiO / Ta₂O₅ nano-composites in KCl. Two broad reversible peaks, located around 0.6 V on oxidation and 0.5-0.55 V on reduction, are observed. These broad peaks are believed to be caused by the valence change process involved in Ni²⁺/Ni³⁺ transition, which shows the pseudo-capacitive behavior. A higher current density has been obtained for the Ni oxide film deposited at lower RF power. The total charge densities during cycling were 3.2, 5.7 and 8.5 mC/cm² for the Ni oxide films deposited at 100, 60 and 40W, respectively. Charge capacity increased as the crystal grain size of NiO decreases (resulting in increases active surface area of the NiO crystal) with decreasing sputtering power. In addition, the anodic and cathodic capacities are nearly the same.

Figure 3 shows transmittance spectra of an FTO coated glass substrate and a Ni oxide film (after bleaching and coloring) deposited on the substrate at a RF power of 40W. The film was colored by applying a constant voltage of 1 V (vs an Ag/AgCl reference electrode) for 5 min. The bleached state transmittance spectrum was measured after bleaching at 0 V vs. Ag/AgCl for 5 min. The bleached film exhibited a light yellow tint due to a maximum transmittance at about 570 nm and the colored film appeared dark

brown. The colored and bleached transmittance spectra are very similar to those of Ni oxide films reported by Jiang *et al.*⁹ and Estrada *et al.*¹¹ which are obtained using alkaline electrolytes. Figure 4 shows the optical density (OD) of the Ni oxide films (deposited at 40, 60, and 100 RF watts) measured *in situ* at a wave length of 670 nm as a function of charge density (Q). In order to avoid effects of irreversible side reactions, (such as gas evolution), the optical density was measured during the negative scan (bleaching) with a constant current density of 20 $\mu\text{A}/\text{cm}$.¹² The optical density increases almost linearly with increasing charge density, and coloration efficiencies (defined as $\Delta(\text{OD})/\Delta\text{Q}$), were found to be approximately 30 cm^2/C for all of the films. However, the film deposited at a RF power of 40W exhibits the greatest optical modulation due to its high charge capacity. The coloration efficiencies obtained in the KCl electrolytes are comparable to those reported for sputtered Ni oxide thin films in KOH and NaOH alkaline electrolytes (31-36 cm^2/C at wavelengths of 550-633 nm).¹³⁻¹⁶ The coloration mechanism using KCl electrolytes is not clearly understood. Valence changes of Ni ions between Ni^{2+} (bleached) and Ni^{3+} (colored) may be the reason for the color change as is the case with alkaline electrolyte.¹⁷⁻¹⁹ In this respect, the colored and bleached transmittance spectra and coloration efficiencies obtained in KCl electrolytes are similar to those obtained with alkaline electrolytes.

In summary, Ni oxide thin films were deposited by reactive sputtering (using 40, 60, 100 watts of RF power), and their electrochemical and electrochromic properties were studied in aqueous neutral KCl electrolytes. With decreasing RF power and deposition rate, the crystal grain size of NiO is decreased. All CV curves were pseudo-capacitive in

nature, and greater charge capacity and higher optical modulation were obtained for the Ni oxide film composed of nano-crystals (deposited at 40 watts). All NiO films exhibited a coloration efficiency of approximately $30 \text{ cm}^2/\text{C}$, which is comparable to that reported for sputtered Ni oxide films in alkaline electrolyte.

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Figure caption

Fig. 1. X-ray diffraction patterns of Ni oxide films deposited on glass substrates as a function of RF sputtering power (40, 60, 100 watts).

Fig. 2. Cyclic voltammograms measured in 1 M KCl for Ni oxide thin films with thicknesses of about 400 nm deposited with different RF powers (40, 60, 100 watts). Voltage scan rate was 10 mV/sec.

Fig. 3. Transmittance spectra in the bleached and colored state for a sputtered Ni oxide film deposited with 40 watts of RF power.

Fig. 4. Optical density of Ni oxide thin films with thicknesses of about 400 nm (deposited at 40, 60, and 100 watts) as a function of transferred charge density during bleaching. Optical density was measured *in situ* in 1M KCl at a wavelength of 670 nm and current density was kept constant at 20 $\mu\text{A}/\text{cm}^2$.

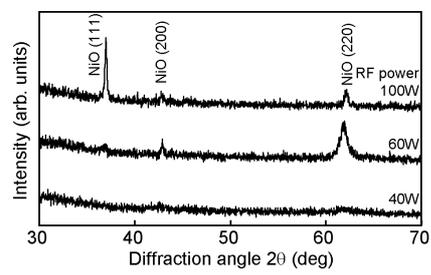


Fig. 1

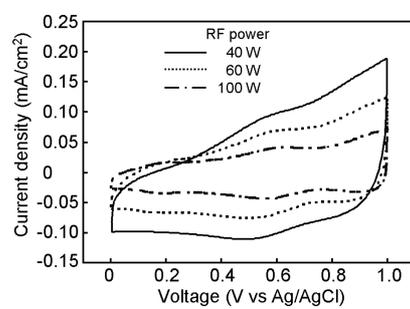


Fig. 2

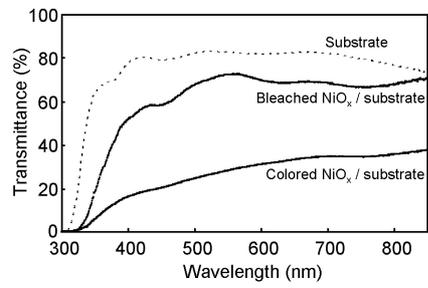


Fig. 3

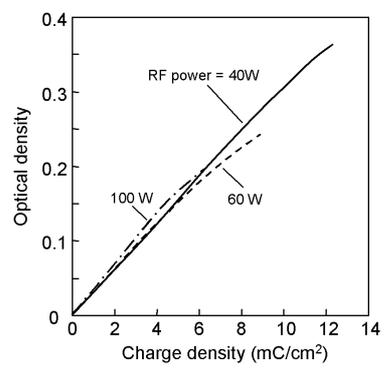


Fig. 4