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Material, Electrical and Optical Analyses of Electrodeposited Electrochromatic NiO Film with Heat Treatment

Hsiang Chen[1], Chia-Hung Chen[1], Hua-Yu Shih[1], Jun Yu Lin[1] and Yih-Min Yeh[2]

[1]Department of Applied Materials and Optoelectronic Engineering, National Chi Nan University
[2]Graduate School of Opto-Mechatronics and Materials, WuFeng University,
No.1, University Rd, Puli, Nantou County, 54561 Taiwan, R.O.C.

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Abstract: *In this study, we propose two-step method of electrochemical deposition and heat treatment to fabricate electrochromic NiO films. A precursor NiO film was electro-deposited on fluorine-doped tin oxide (FTO). Then, the deposited film was crystallized with heat treatment. X-ray diffraction (XRD) was used to examine the crystalline structure and scanning electron microscope (SEM) was used to analyze the surface morphologyfor the film in different deposition and heat treatment conditions. Moreover, the cyclic voltammetry (CV) and optical performance of the film was evaluated. Based on multiple material and optical analysis, the film grown with plating solution with a pH value of 8.0 treated by heat treatment at 500ºC was the most desirable electro chromatic film. The fabricated NiO electro-chromic film shows promise for use in future device applications.*

Keywords: NiO, electrodepostion, electrochromatic device, cyclic voltammetry, heat treatment

1. INTRODUCTION

Electrochromic materials have been intensively studied owing to its applications of light modulation and heat load control over the past decades. Among those materials, transition metal oxides such as WO_3 [1], NiO [2], IrO_3 [3] have raised public attention for electrochromic device technology, such as ingenious windows capable of varying the throughput of visible light and solar energy applications. As for the electrochromatic NiO thin film, various vacuum and non vacuum fabrication methods such as sputtering [4], chemical vapor deposition (CVD) [5], chemical bath deposition (CBD) [6] have been applied to deposit the NiO film. Compared with other fabrication methods, electrochemical deposition method has also been proposed due to advantages of low cost, large area fabrication, and good adhesion to the substrate [7, 8]. In this study, we present an alternative two-step fabrication method of electrodeposition and heat treatment to grow the film [9, 10]. During the deposition process various concentrations of sulfuric acid were used to modulate the pH values of the plating solution [11]. Furthermore, the amorphous-like electrodeposited NiO film was processed with heat treatment. The well-crystallized high quality film was formed with a proper heat treatment temperature. Based on our experiment, the optimum condition was found to be with the heat treatment temperature at 500°C. To evaluate the performance of the NiO film, material, electrical, and optical measurements were applied to characterize the film [12]. Compared with recent studies [13-16], the electrodeposited NiO electrochromatic film exhibited broad wavelength range modulation between 300 nm and 700 nm, fast modulation speed, and high coloration efficiency in this study. Furthermore, since the electrodeposition preparation method has advantages of low cost, simple fabrication process, and large area fabrication possibilities, the electrodeposited NiO film shows promise for future industrial applications.

*To whom correspondence should be addressed: Email: hchen@ncnu.edu.tw
Phone: +886-49-2910960 ext. 4909 Fax: +886-49-2910413

2. EXPERIMENTAL

To fabricate the electrochromatic film, a NiO film was deposited on the fluorine-doped tin oxide (FTO) working electrode with an area of 2cm×1.5cm. The plating solution was made up by the mixture of lithium perchlorate (LiClO),and propylene carbonate (PC). The compositions of electrolyte were $NiSO_4$, $(NH_4)_2SO_4$, NH_4OH. During the deposition process, a constant voltage of 1.3V was used to deposit the NiO film for 30 minutes with power supply unit AUTOLAB potentiostat / galvanostat model PGSTAT320. Plating

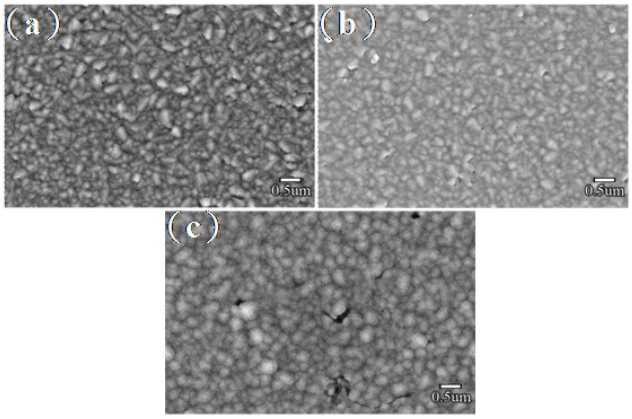

Figure 1. SEM images of surface morphology in solutions with various pH values of (a) 7.0 (b) 8.0 and (c) 8.5.

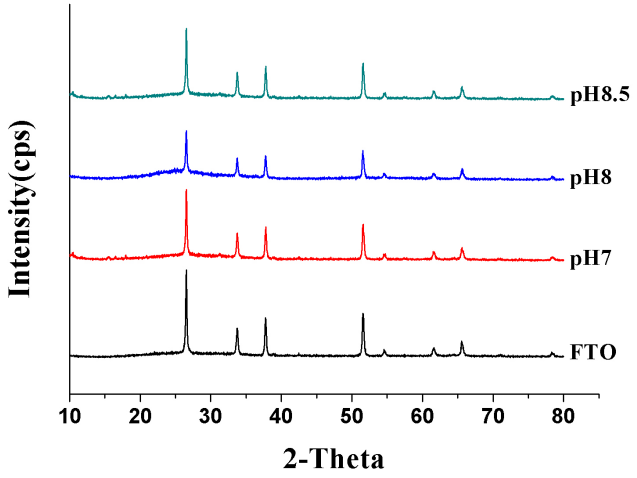

Figure 2. XRD analysis of the deposited film in solutions with various pH values.

solutions with different pH values from 7 to 8.5, which was controlled through adding different concentrations of sulfuric acid, were used to grow the NiO film. The electrolyte composition was shown in Table 1. After electro-deposition was completed, heat treatment was applied in order to crystallize the film. The heat treatment was performed in a quartz tube with temperatures from 100°C to 500°C. Eventually, the NiO thin film was inspected by using scanning electron microscope (SEM), X-ray diffraction (XRD), cyclic voltammetry (CV) and transmittance measurements to evaluate the film quality.

3. RESULTS AND DISCUSSIONS

In order to find preferable deposition conditions, the NiO precursor film was deposited in various solutions with different pH values and the precursor film was then processed in heat treatment of different temperatures. SEM and XRD analysis were applied to reveal the film quality and the growth condition. To investigate the influence of pH values on the NiO precursor film, SEM images of surface morphology of the NiO film deposited in solutions of different

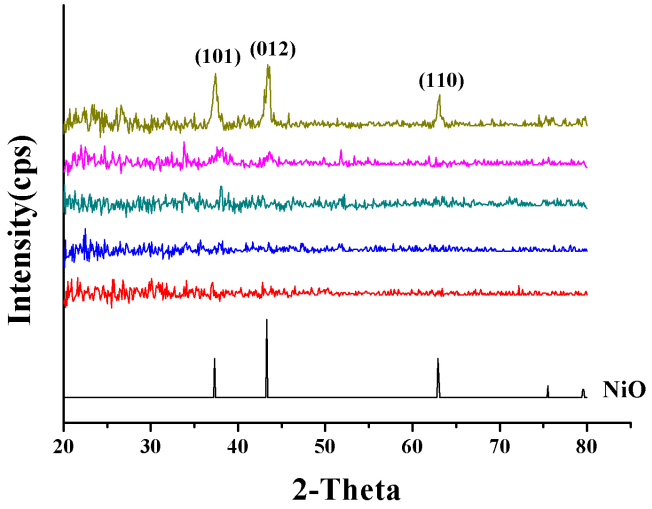

Figure 3. XRD analysis of the NiO precursor heat treated with different final temperatures.

pH values are shown in Fig.1 (a), (b), (c). Fig.1 (a) shows the elliptic, irregular polygonal surface structure of the film fabricated in the neutral solution. Since the pH value increases to 8, the elliptic, irregular polygonal surface structure started to aggregate and grow. Therefore, a more compact film was formed as shown Fig.1 (b). As shown in Fig.1 (c), when pH value continuously increases to 8.5, the NiO precursor thin film become denser and every individual grain gradually forms coaxial structure. However, some cracks came into existence. Consistent with the SEM images, the XRD analyses of the grain phase and grain structure of the thin film were performed as shown in Fig. 2. Since the NiO precursor thin film is an amorphous material due to the merely occurrence of the grain structure of the FTO plate while directly depositing the film at room temperature without any heat treatment, the FTO peaks in the XRD spectra could reveal the compactness of the film. As for the film deposited in a solution with a pH value of 7.0, the FTO peaks in the XRD spectrum were strong because the lossy growth of the NiO film. When the pH value increased to 8.0, the film became more compact and the FTO peaks became weaker. As the pH value further increased to 8.5, the FTO peaks became stronger again because of the cracks. Therefore, we chose the film deposited in a solution with a pH value of 8.0 to form the electrochromatic film. After the precursor film was deposited, heat treatment was applied to crystallize the NiO precursor film. Fig. 3 shows the XRD analysis of the NiO thin film with heat treatment at different temperatures. Apparently, as the temperature of the heat treatment increased to 400℃, the crystallization phase of the film is gradually enhanced. When the temperature of the heat treatment increased to 500℃, main grain phases (101), (012), and (110) can be clearly observed. Thus, according to the results, in order to transform the NiO precursor material to the electrochromatic NiO phase, the temperature of the heat treatment with a temperature of 500℃ was required. Since a high temperature above 500℃ might damage the substrate, a heat treatment temperature of 500℃ might be a prefera-

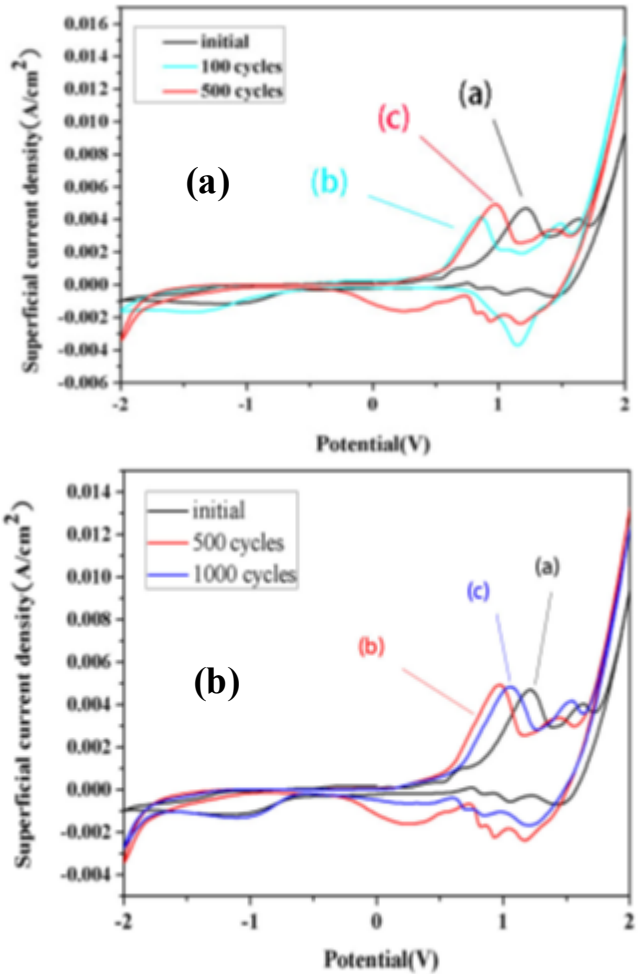

Figure 4. Cyclic voltammetric tests for the deposited film after (a) 500 cycles (b) after 1000 cycles.

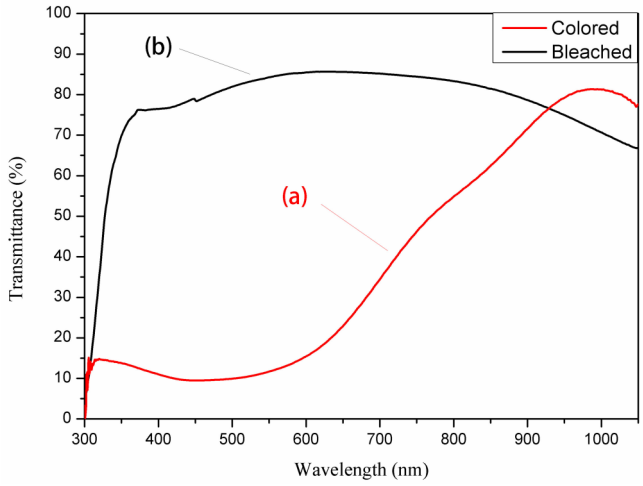

Figure 5. Transmittance from 300 nm to 1100 nm could be modulated.

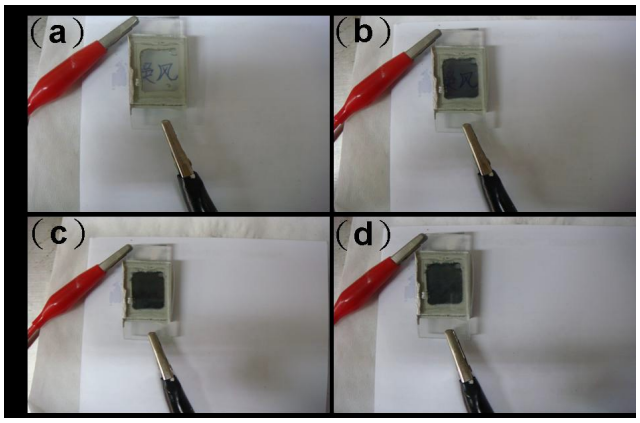

Figure 6. The electrochromic NiO film with (a) no bias and biased at (b) 1.5V (c) 2.5V (d) 3.5 V.

ble treatment condition. After the electrochromatic film was fabricated with preferable deposition and heat treat conditions. The CV characteristics and optical transmission of the film were examined. The film deposited at 1.6 V in a solution with pH value 8.0 followed by a heat treatment of 500°C was circulated for 500 cycles as shown in Fig. 4 (a) and 1000 cycles in Fig. 4(b). The electrolyte composition is the same as Table 1 (pH = 8.0). The voltage scanning speed was 10mV/s and the scanning range was from -2 V to 2 V. The superficial current density could reach 10 mA/cm^2 after circulations of 1000 cycles. The film possessed good reliability after repeated circulations. After we optimized the fabrication condition as shown in the experiments, the film exhibited excellent electrochromatic properties with the relation between transmittance and the variation of voltage of the colored NiO thin film was analyzed as shown in Fig. 5. The transmittance of the film was measured from 300 nm to 1100 nm could be modulated well. The good-quality film obtained good electrochromatic properties. As shown in Fig. 5, the \transmittance of light with wavelengths between 300 nm to 700 nm can be modulated well under bias voltages. The transmittance modulation of the film was around 84% (around 500 nm) and the coloration efficiency was 132.5 cm2/C. Coloration efficiency (η) depends on modulation in optical density (△OD) and charge density (Q) per unit area as shown in the equation below.

Table 1. Electroplating Conditions

Electroplating conditions	
$NiSO_4$	0.01M
$(NH_4)_2SO_4$	0.03M
NH_4OH	5~20cc/100ml
pH	7~8.5
deposition potential	1.3V
deposition time	30 min
temperature	Room temperature

(Transmittance change,ΔT)

$$\Delta T = T_{bleaching}\ T_{coloring}\ (\%) \quad (1)$$

Optical density change, ΔOD

$$\Delta OD = \log T_{bleaching} / T_{coloring} \quad (2)$$

The total supplied charge is equal to the integration of the current density

$$\Delta Q = \int_{t1}^{t2} * j(t)dt \quad (3)$$

$$\eta = \Delta\ OD / Q\ (cm^2/C) \quad (4)$$

As for the coloration speed, the coloration time for the NiO electrochromatic device biased at 4V is around 2s and the bleaching time for the NiO electrochromic device biased at -4V is around 4s.

4. CONCLUSION

In this research, NiO electrochromatic films were fabricated with a two-step process of electro-deposition and heat treatment. By examining the film with SEM and XRD analyses, a plating solution with a pH value of 8.0 followed by heat treatment at 500□ was the preferable condition. The CV and transmittance of the film were also studied in experiments. The fabricated NiO electrochromic film shows promise for use in future device applications.

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