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EFFECT OF SPUTTERING POWER ON OPTICAL PROPERTIES OF NICKEL OXIDE ELECTROCHROMIC THIN FILMS

The preparation and characterization of nickel oxide (NiO) thin film for electrochromic smart window applications are studied. The NiO thin film was prepared by the DC magnetron sputtering from a pure nickel target. The sputtering power was varies in the interval 50–200 W. The crystallinity and physical morphology of NiO films are characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM), respectively. The XRD result revealed that polycrystalline NiO thin films with preferred growth directions along (111) and (200) planes are obtained. Moreover, the electrochromic property of NiO thin films was investigated with a UV-Visible spectrophotometer. The colored state of the electrochromic cell was obtained by the ion insertion at the 1-V external applied bias in 0.1 M KOH. The reversibility between the colored and bleached states is confirmed by the optical transmittance. The result shows the optical contrast as high as 28.68.

Keywords: electrochromic, nickel oxide, DC magnetron sputtering.

1. Introduction

Glass is one of the most popular building materials. The transparency of glass opens up the vision between the inside of a building and the outside world. This is aesthetically desirable, but not energetically favorable, as the solar heat directly passed through the buildings. The control over the transmittance of visible sunlight and solar heat into a building is of importance for the energy consumption. Electrochromic coatings (EC) are switchable thin-film coatings applied to glass or plastic that reversibly change the optical transmission with a small applied voltage [1]. It can control the daylight and solar heat passing through buildings. A conventional EC window consists of an EC layer, an electrolyte layer, and an ion storage counter electrode sandwiched between two transparent conducting layers [2, 3].

Nickel oxide shows a great promise as an active electrochromic material due to the high coloration efficiency (CE), good cyclic reversibility, and low cost [4, 5]. Thin film of NiO is widely used as the counter electrode layers in EC devices [4, 6, 7]. Various techniques have been used to deposit NiO thin films [6, 8, 9], but the sputtering technique is the most widely investigated, because the large-scale deposition sets

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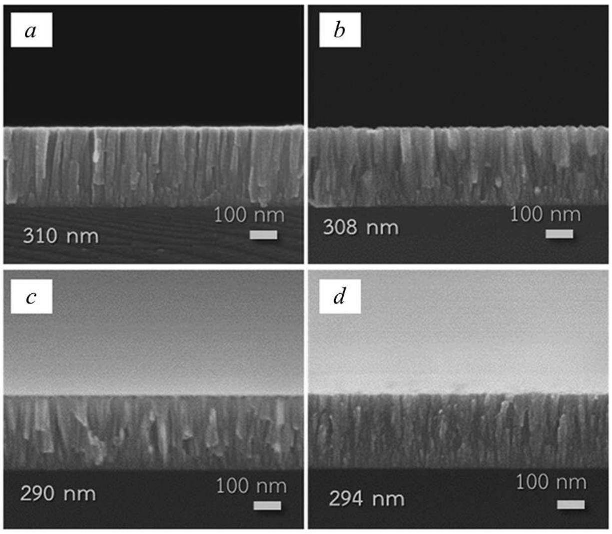

Fig. 1. FE-SEM cross-section images of NiO thin films deposited on ITO glass at various DC power: 50 W (*a*), 100 W (*b*), 150 W (*c*), and 200 W (*d*) with roughly 300 nm thickness

are available, and high-quality films are obtained [4, 7, 10].

In this research, NiO thin films were deposited by the DC magnetron sputtering technique. The influence of the sputtering power on optical properties is investigated. The reversibility between colored and bleached state was confirmed by the optical transmittance. Moreover, the crystallinity and physical morphology of the NiO films were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM), respectively.

2. Experimental Details

In this research, NiO films were formed using the reactive direct-current magnetron sputtering on glass substrates coated with an indium tin oxide (ITO) commercial sheet resistance of 11.5 Ω/□. First, the ITO glasses were ultrasonically cleaned in ethanol and deionized water for 20 min in sequence. The pure Ni (99.99 %) was used as a sputtered target. The base pressure of a sputtering chamber was 5×10^{-6} mbar. Ar and O_2 gases were introduced into the sputtering chamber through two mass flow controllers. The flow rates of Ar and O_2 gases were fixed at 30 and 10 sccm, respectively. Then the effect of the sputtering power was studied. The power of a DC source was varied in the interval 50–200 W.

Deposition rate of NiO films deposited at different DC powers for 30 min

DC power (W)	Deposition rate (nm/min)
50	2.78
100	19.85
150	33.40
200	52.66

The morphology and crystal structure of thin films were investigated by a field emission scanning electron microscope (FE-SEM, HITASHI/SU8030) and the grazing-incidence X-ray diffraction (GIXRD, Rigaku TTRAX III), respectively. The optical characteristics of thin films were investigated using a UV-Visible spectrophotometer (Agilent Technologies, Agilent Cary 7000) in the wavelength range 300–2000 nm. The colored and bleached states of the electrochromic cell were investigated by the ion insertion at the 1-V external applied bias in 0.1 M KOH.

3. Results and Discussion

First, the thin films were deposited at different DC powers in the interval 50–200 W for 30 min. The calculated deposition rate of NiO films are shown in Table. The deposition rates were 2.78, 19.85, 33.40, and 52.66 nm/min for powers of 50, 100, 150, and 200 W, respectively. The result shows that the deposition rate of thin films increases with the DC power due to the higher kinetic energy of generated sputtered particles as the DC power is increased [11].

The influence of the DC power on the morphology of the structure of NiO films was revealed by field emission scanning electron microscopy (FE-SEM). Figure 1 shows the morphological feature of as-deposited NiO thin films with roughly 300 nm thickness deposited at different DC powers in the interval 50–200 W. The cross-section SEM images of all NiO thin films show a homogeneously column-like film. The column orientation was perpendicular to the surface of the substrate. The cross-sectional image shows that the thin films presented a compact columnar structure as showed in Fig., 1, *a–d*.

Figure 2 shows top-view FE-SEM images for NiO thin films deposited on Si glass at different DC powers. The average grain sizes of NiO were 21.2 ± 2.5, 27.3 ± 4.2, 30.1 ± 3.8, and 25.2 ± 6.5 nm for the DC power of 50, 100, 150, and 200 W, respectively. It is

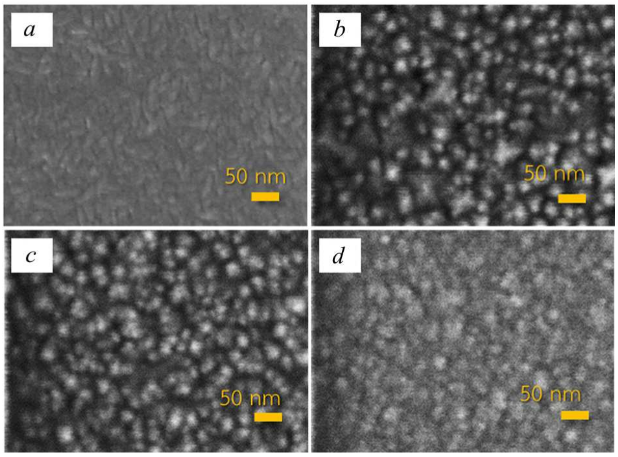

Fig. 2. Top-view FE-SEM images of NiO thin films deposited on ITO glass at different DC powers: 50 W (*a*), 100 W (*b*), 150 W (*c*), and 200 W (*d*), with roughly 300 nm thickness

notable that the grain size of NiO tends to increase, as the sputtering power increases to 150 W, and the grain size of NiO decreases for higher sputtering powers. The excessive supply of the sputtering power at 200 W limits the growth of crystalline grains due to the very high deposition rate [12], as shown in Table.

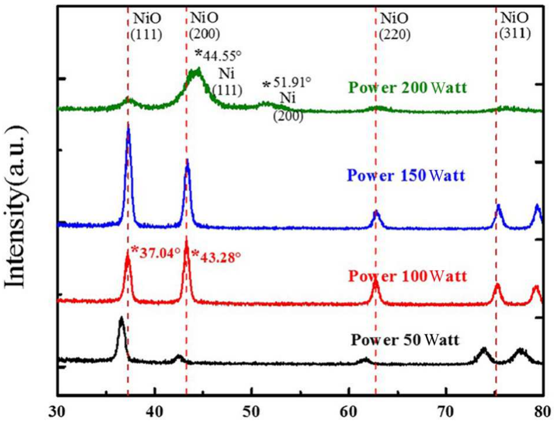

Fig. 3. XRD patterns of as-deposited NiO thin films as a function of the DC power

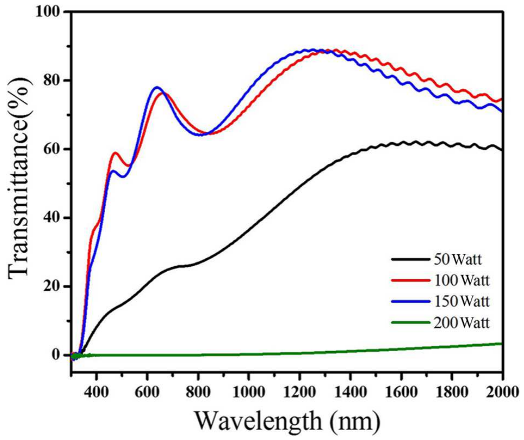

Fig. 4. Transmittance spectra of the NiO thin films deposited at different DC powers

The XRD patterns of as-deposited NiO thin films as a function of the DC power are shown in Fig. 3. The result indicates that the film deposited at a DC power of 50 W shows a suboxide of Ni. The well-defined polycrystalline structure of NiO was not obtained. According to the XRD results, it was found that the XRD peaks become gradually sharper, as the DC power increases from 50 to 150 W, indicating a larger particle size and the better crystallinity of the deposited films. The energy of the sputtered atom arriving at the substrate increases with the sputtering power to 150 W and facilitates a further crystallization [13]. The XRD pattern revealed that NiO films deposited at DC powers of 100 and 150 W exhibit the polycrystallinity with a standard face-centered cubic structure which matching well with the JCPDS card No. 47-1049 of NiO [7]. The polycrystalline films show a well-defined peaks at $2\theta = 37.04°$, $43.28°$, $62.81°$, and $75.47°$ which corresponded to the reflection of (111), (200), (220), and (311) planes, respectively. The thin films deposited at DC powers of 100 and 150 W show a preferred (200) and (111) orientations, respectively. Any reflection peaks from the impurities in XRD spectra could not be observed. However, the peak intensity extremely decreases with increasing the DC power to 200 W. The structures gradually transfer from metal oxide to metallic mode. The XRD pattern show the peaks at $2\theta = 44.55°$ and $51.91°$ which correspond to the reflection of (111) and (200) planes of Ni [14]. This result may be due to the excessive amount of Ni atoms ejected from the target at a high DC power. There is no sufficient amount of oxygen to react with the flux of sputtered metal species to form stoichiometric oxides.

Figure 4 shows the transmittance spectra of the NiO films. The result indicates that the transmittance tends to increase with the DC power in the range of 50–150 W. The transmittances at the wavelength of 550 nm (which is most sensitive to the eye) are approximately 25, 76, and 78% for DC powers of

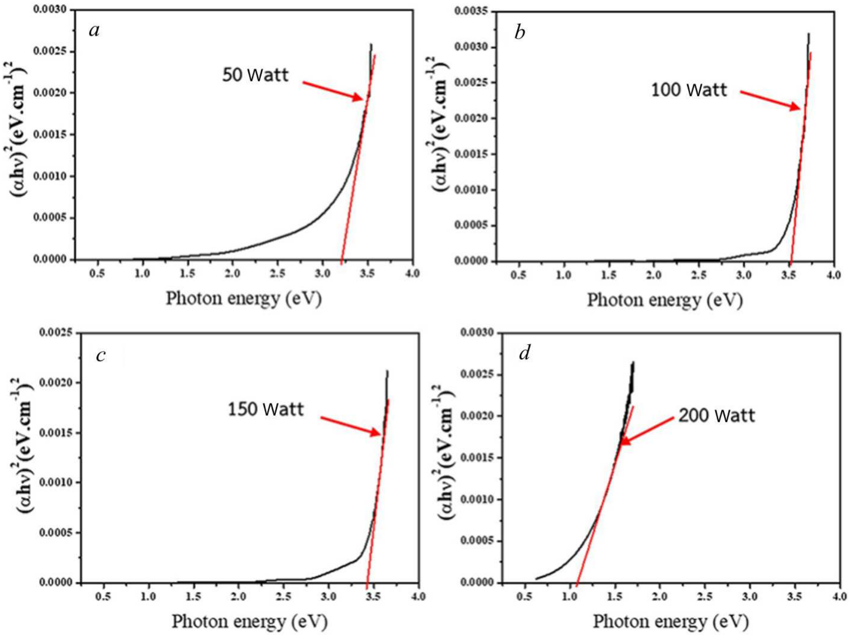

Fig. 5. $(\alpha h\nu)^2$ vs the photon energy for NiO films deposited at different DC powers: 50 W (a), 100 W (b), 150 W, and 200 W (c)

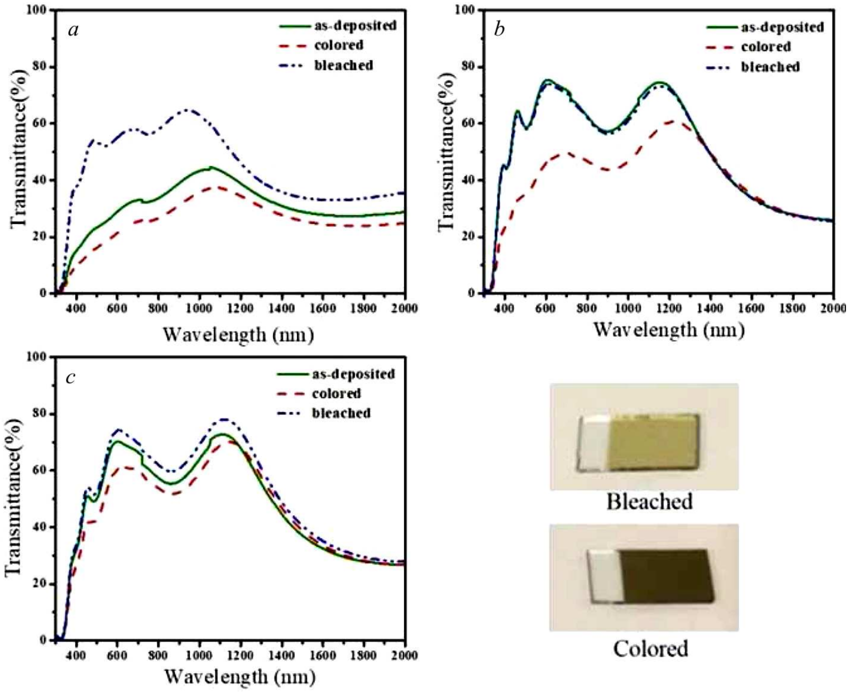

Fig. 6. Optical transmittance spectra of NiO films deposited at different DC powers: 50 W (a), 100 W (b), and 150 W (c), in the as-deposited, bleached, and colored states. The inset shows photographs of the materials in the bleached and colored states

50, 100, and 150 W, respectively. The NiO film deposited with the 200-W DC power was found to be opaque in the UV to NIR region. This result is caused by the presence of Ni metal, which corresponds to the XRD results. From the transmittance spectra, it is found that the electrochromic films with good visible transparency were obtained using DC powers of 100 and 150 W.

Figure 5 shows the plot of $(\alpha h\nu)^2$ with the photon energy in the wavelength range 300–2000 nm at room temperature. The extrapolation of the straight line into the higher energy region gives the value of the direct band gap of the *p*-type Ni. We have assumed that the NiO films are characterized by a direct band gap, as stated for the bulk NiO material. If the DC power is increased from 50 to 100 W, then the band gap width (E_g) increases from 3.2 eV to 3.5 eV. For the film deposited at a DC power of 150 W, the band gap width slightly decreased to 3.4 eV. When the DC power increases to 200 W, the band gap width extremely decreases to 1.1 eV. This result is caused by the presence of Ni metal, which corresponds to the XRD results. The highest band gap width equal to 3.5 eV is obtained for the film deposited at the 100-W DC power.

In-situ spectroelectrochemical experiments were used to evaluate the electrochromic properties of electrodeposited nickel oxide on the ITO substrate. In Fig. 6, the measured transmittance in the UV-VIS-NIR (300–2000 nm) range of a nickel oxide film in KOH electrolytes is presented. The measurements have been done both in the bleached and colored states after the application of –1.0 V for 30 s and +1.0 V for 30 s, respectively. The inset in this figure shows representative photographs of the materials in the bleached and colored states. The color of nickel oxide switches from light brown (bleached) to dark brown (colored) at potentials which are governed by the Ni(II) to Ni(III) redox process [5, 7]. From Fig. 6, it os seen that the change in the transmittance (ΔT) between the colored (red line) and bleached states (blue lines) are 31.01, 28.68, 15.89, and 0% at the wavelength of 550 nm (which is most sensitive to the eye) for the films deposited at DC powers of 50, 100, 150, and 200 W, respectively. The nickel oxide film deposited at a DC power of 50 W has a highest optical contrast between the bleached and colored state. However, the optical transmittance in the bleached state could not returned to that of the as-deposited state. The nickel oxide film deposited at a DC power of 100 W has a relatively high optical contrast between the bleached and colored state. Moreover, it is seen that the optical transmittance in the bleached state is very close to the as-deposited state. As the DC power increases from 100 W to 150 W, the sample tends to have lower optical transmittance. Therefore, the electrochromic films with good electrochromic properties were obtained by using a DC power of 100 W. The cause is that the 100-W DC power sample has smaller microcrystallite sizes as indicated by the XRD results. The boundary and surface of NiO microcrystallites are key factors in determining the electrochromism. In the research of Yoshimura *et al.* [15], they reported that the boundary acts as an active site in the electrochromic reaction. As microcrystallite sizes are small, many active sites which are related to the coloration are formed. For the sample deposited at a DC power of 200 W, the optical transmittance is absent due to the NiO films were transform to metal nickel, as is shown by the XRD results.

4. Conclusions

In this work, NiO thin films were deposited on glass by using the DC magnetron sputtering technique. The optical properties of NiO films at different DC powers are analyzed. The results reveal that the deposition rate of NiO films increases with the DC power. According to the XRD and SEM results, the high-purity polycrystalline NiO is obtained under the deposition with DC powers in the range of 50–150 W. The films deposited with DC powers of 100 and 150 W exhibit more than 75% of transmittance in the visible light region. The highest band gap width $E_g = 3.5$ eV is obtained for the film deposited at the 100-W DC power. The nickel oxide film deposited at a DC power of 100 W has a relatively high optical contrast between the bleached and colored states with a ΔT of 28.68%. Moreover, the optical transmittance in the bleached state was very close to the as-deposited state. These results all supported the use of NiO as electrochromic coatings applied in glazing units for buildings and automobiles.

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ЗАЛЕЖНІСТЬ ОПТИЧНИХ ВЛАСТИВОСТЕЙ ТОНКИХ ЕЛЕКТРОХРОМНИХ ПЛІВОК ОКСИДУ НІКЕЛЮ ВІД ПОТУЖНОСТІ НАПИЛЕННЯ

Резюме

Досліджено процес виготовлення і параметри тонких плівок NiO для застосування в електрохромних смарт-вікнах. Плівки зроблені методом магнетронного напилення з постійним струмом із використанням мішені з чистого нікелю. Потужність напилення змінювалась у межах 50–200 Вт. Кристалічна структура та морфологія плівок NiO визначені методами дифракції рентгенівських променів (ДРП) і сканувальної електронної мікроскопії (СЕМ), відповідно. Результати ДРП показують кращий ріст полікристалічних плівок в площинах (111) і (200). Крім того, електрохромні властивості тонких плівок NiO вивчались за допомогою спектрофотометра ультрафіолетового та видимого діапазону. Забарвлений стан електрохромної комірки отримано введенням іонів з концентрацією 0,1 М KOH при зміщенні 1 В. Оборотність переходів між забарвленим і безбарвним станами підтверджено за допомогою коефіцієнта пропускання. Знайдено, що величина оптичного контрасту досягає 28,68.