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RF 스퍼터링에 의해 제조된 Li-Ni-O 박막의 전기변색 특성

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RF Sputtered Lithium Nickel Oxide Films and Their Electrochromism

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요 약. RF 스퍼터링법을 써서 $Li_{2x}Ni_{1-x}O$ 박막을 제조하였으며, 그 과정에서 기판의 온도(50/230 °C)와 분위기(Ar/O_2)를 변수로써 막의 미세구조를 조절하였다. 투과전자현미경을 이용한 막 구조 분석에 의해 낮은 기판 온도와 O_2 조건에서 막의 조성입자가 작아짐을 관찰하였고, 50 °C/O_2 하에서 얻어진 $Li_{2x}Ni_{1-x}O$ 박막은 약 80 Å 크기의 입자로 이루어져 있었다. 전기화학적 조건 하에서 $Li_{2x}Ni_{1-x}O$ 박막의 변색현상을 조사한 결과, 박막의 미세구조 발달에 의해 Li^+ 이온의 가역적 수용량이 증가하고, 결과적으로 전기변색 기능이 향상됨을 알 수 있었다. 50 °C/O_2 하에서 얻어진 170 nm 두께의 $Li_{2x}Ni_{1-x}O$ 박막은 30 mC/cm^{2}의 Li^+ 이온 수용력과 함께 약 1.3의 흡광밀도(OD)를 나타내었다.

ABSTRACT. Lithium nickel oxide ($Li_{2x}Ni_{1-x}O$) thin films have been prepared by the RF sputtering of lithiated nickel oxide target, where the film microstructure was controlled by the sputtering atmosphere (Ar/O_2) and the substrate temperature (T_s=50/230 °C). From the transmission electron microscopic analysis, it is found that the most porous film with the grain size of ~80 Å could be fabricated under the sputtering atmosphere of $P(O_2)=8\times10^{-2}$ mbar with the T_s=50 °C. In the optical and electrochemical studies, the $Li_{2x}Ni_{1-x}O$ films exhibit a significant electrochromic property in association with the lithium insertion/deinsertion process. The amount of charge insertion (Q_i) and the optical density (OD) variation depend on the crystallinity of the film as well as its thickness, and for the $Li_{2x}Ni_{1-x}O$ film (170 nm thickness) prepared under O_2 atmosphere and T_s=50 °C, the OD could be increased up to ~1.3 by the charge insertion with Q_i=30 mC/cm^2.

INTRODUCTION

The electrochemical properties of lithium nickel oxide have been widely studied because of its importance as an active electrode material of electrochromic window or, rechargeable battery systems.[1-14] The fundamental electrochromism of nickel oxide involves the Ni^{2+}/Ni^{3+} redox process, and it is reported that $Li_{2x}Ni_{1-x}O$ can have a wide optical range and neutral coloration, compared to other electrochromic oxides. In case of $Li_{2x}Ni_{1-x}O$, the color changes reversibly from transparent ($Li_{2x}Ni^{2+}_{1-x}O$) to brown ($Li_{2x-y}Ni^{2+}_{1-x-y}Ni^{3+}_yO$) upon cathodic (charge injection) and anodic (charge extraction) electrochemistry, respectively. Therefore, the lithium nickel oxide material can serve as an anodic coloration material.

Recently, we have investigated the electrochromic property of the lithium intercalated nickel oxide film as a counter electrode complementary to the cathodic coloring WO_3 electrode in the electrochromic device.[7,8] From the optical and electrochromic measurement of the electrochemical cell [Li_xWO_3|$LiClO_4$-propylene carbonate (PC)|$Li_{2x-y}Ni_{1-x}O$], the optical transmittance at 550 nm could be greatly modulated from ~80% (bleached state) to ~10% (colored state) and the coloring/bleaching electrochromic behavior was found to be reversible up to 10^4 cycles. Obviously, the high performance of this cell could be attributed not only to the coloration of WO_3 but also to the simultaneous anodic function of $Li_{2x}Ni_{1-x}O$. Though $Li_{2x}Ni_{1-x}O$ itself may serve as a poor host lattice for Li^+-insertion, a good electrochromic property can result from the fast diffusion, and/or migration, of Li^+ ions along the grain boundaries. Therefore it can be expected that the Li^+ insertion property of $Li_{2x}Ni_{1-x}O$ would be improved by reducing the crystallite size of the Li-Ni-O semiconductor.

In this work, we report the influence of crystallinity or density of the RF sputtered lithium nickel oxide films on the electrochromic properties, in order to find out the most suitable conditions to produce lithium nickel oxide film with favorable electrochromism.

EXPERIMENTAL

The glass substrates of $5\times5\ cm^2$ size, coated with a transparent conducting indium tin oxide (ITO), were used. The lithium nickel oxide films were prepared by RF sputtering of home-made target under the conditions listed in *Table* 1. Transmission electron microscopy (TEM, JEOL JSM-840) was used to examine the film texture and nano-structure.

Table 1. The experimental conditions for the RF sputtering of $Li_{2x}Ni_{1-x}O$ films

Target	Atmosphere	Power	Substrate temperature
$LiNiO_2$ (ϕ=20 cm)	Ar 6×10^{-3} mbar	60 W	50 °C
	O_2 8×10^{-2} mber	120 W	50 °C 230 °C

Target to substrate distance was 10 cm.

Electrochemical experiments were performed with a computer-controlled potentiostat/galvanostat (TACUSSEL, PGS 201T) in a dry box. The Ni-based film and the Li foil were used as a working electrode and a reference electrode, respectively. Both electrodes were immersed in a 1 M $LiClO_4$/PC electrolyte. Optical propereties of the colored and bleached states were investigated using a UV-Vis-NIR spectrophotometer (Varian Cary 2415), equipped with DS15 Data Station.

RESULTS AND DISCUSSION

Electrochromism of lithium nickel oxide film can be expressed with the following process

$$\underset{\text{brown}}{Li_{2x-y}Ni^{2+}_{1-x-y}Ni^{3+}_yO} + yLi^+ + ye^- \rightleftarrows \underset{\text{transparent}}{Li_{2x}Ni^{2+}_{1-x}O}$$

where the reaction proceeds to the left or right depending on the applied voltage. Upon Li^+-insertion into $Li_{2x-y}Ni^{2+}_{1-x-y}Ni^{3+}_yO$ (brown), the film becomes to be a transparent $Li_{2x}Ni^{2+}_{1-x}O$ state, and the change of transmittance (T) can be expressed in terms of the optical density (OD) variation, which is defined here as below

$$\begin{aligned}\Delta OD &= OD_c - OD_b \\ &= Log(1/T_c) - Log(1/T_b) \\ &= Log(T_b/T_c)\end{aligned}$$

where c and b denote the colored and bleached states, respectively.

Fig. 1 illustrates the evolution of OD as a function of the inserted charge (Q_i) for the two films prepared in different operating atmospheres, Ar and O_2. Higher Q_i and thereby higher OD values occur for the film deposited in an O_2 atmosphere compared to the film obtained in Ar one, which is due to the porous texture of the film. The deposition in an O_2 atmosphere can produce more porous film than that under Ar one because the moving path of the ionized particles is relatively more intercepted by heavier O_2 gas compared to

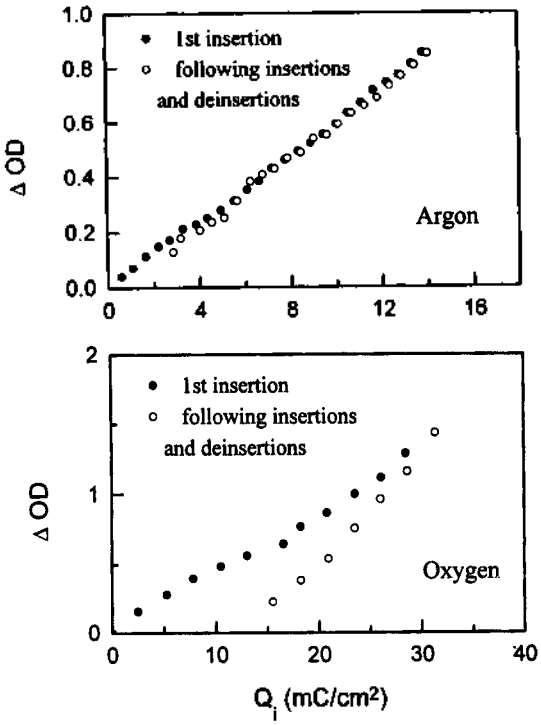

Fig. 1. Evolution of the change of the optical density (OD) as a function of charge (Q_i) of the $Li_{2x}Ni_{1-x}O$ films with the thickness of 170 nm deposited under Ar or O_2 atmosphere. Transmittance data were collected at 550 nm wavelength.

the case in the Ar atmosphere.

For both films, insertion and deinsertion processes are found to be reversible, but in case of the film deposited in O_2, there is a discrepancy of OD between the first insertion and the repeated cycles. This difference of OD profiles can be explained by the formatting process occurring at earlier insertion/deinsertion procedures. The formatting process can be regarded as the Li^+-uptake by the reactive ions or sites within the as-deposited lithium nickel oxide film. From the X-ray photoelectron spectroscopy (*Fig.* 2), it was found that the film contains considerable amount of peroxide species,[15,16] therefore we could describe the formatting process by the formation of lithium oxide at the inter-grain space in the film.

$$Li_{2x-y}Ni^{2+}{}_{1-x-y}Ni^{3+}{}_yO + 2Li^+ + 2e^- \rightleftarrows Li_{2x-y}Ni^{2+}{}_{1-x-y}Ni^{3+}{}_yO + \underline{Li_2O}$$

Li^+ ion can not be deinserted

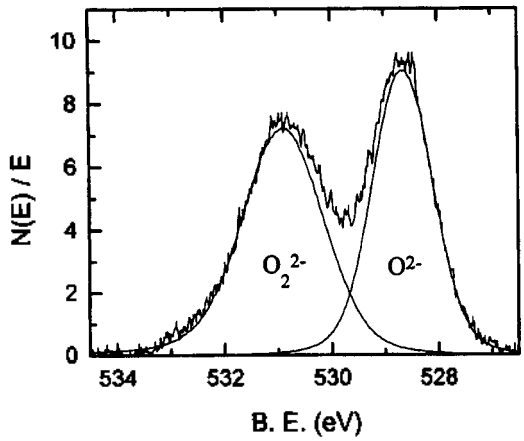

Fig. 2. O 1s XPS spectrum and its deconvolution result, showing the presence of O_2^{2-} species in the porous nanocrystalline $Li_{2x}Ni_{1-x}O$ film deposited at 50 °C under O_2 atmosphere.

The TEM study could directly show the nanocrystalline texture and porous nature of the present $Li_{2x}Ni_{1-x}O$ films. In this study, the most porous film was obtained from the deposition at 50 °C in O_2, and the corresponding TEM photograph is shown in *Fig.* 3, where the film consists of nanocrystallites with an average size of ~80 Å. Its electron diffraction pattern (*Fig.* 3) was also analyzed as summarized in *Table* 2, where it was found that the nano-crystallites are isostructural with the cubic NiO.

For the $Li_{2x}Ni_{1-x}O$ film deposition at 50 °C in an O_2 atmosphere, the sample thickness was varied by adjusting the sputtering time in order to investigate the dependence of inserted/deinserted charge on the sample thickness. *Fig.* 4 illustrates the evolution of the inserted and deinserted charges as a function of the film thickness. As is well expected, the higher Q_i is obtained for the thicker film due to the increase of total Li^+-inserion sites therein. We can also observe that the decrease rate of Q_i upon repeated cycles becomes greater with increasing the film thickness. It is not surprising phenomenon because much more O_2^{2-} adsorbent can be present at the surface or grain-boundary of thicker porous film. We observed a lack of transparency in the Li^+-inserted film when the sample is thicker than 50 nm, which can be understood

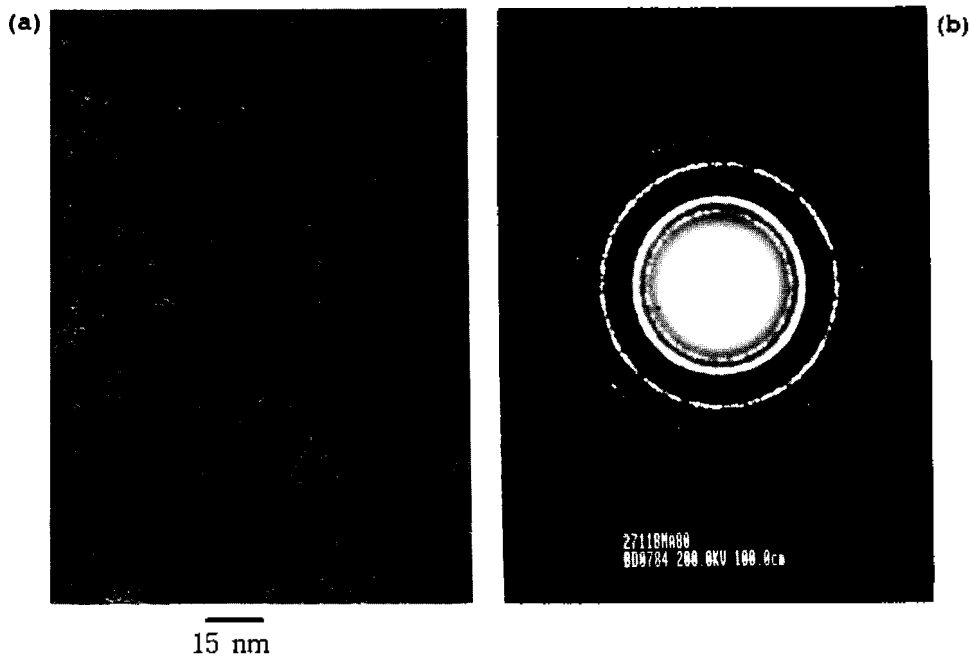

Fig. 3. Transmission electron microscopic morphology (a) and electron diffraction profile (b) of the $Li_{2x}Ni_{1-x}O$ film with the thickness of 170 nm deposited at 50 °C under O_2 atmosphere.

from the formatting effect mentioned above. We would like to say that the formatting process was not negligible, even for the film thinner than 50 nm. *Fig.* 5 shows the transmission spectra for the 40 nm thick film measured at bleached and colored states, respectively. From the both spectra, it can be found that though the film is rather thin there is a considerable electrochromic effect, and even at the bleaching potential film remains slightly brown.

When the substrate temperature is raised from 50 °C to 230 °C, Q_i decreases as shown in *Fig.* 6. An increase of the substrate temperature induces obviously the higher particle energy and surface mobility during the film deposition and thereby film

Table 2. The electron diffraction pattern analysis for the $Li_{2x}Ni_{1-x}O$ film, corresponding to *Fig.* 3

$Li_{2x}Ni_{1-x}O$ film (prepared at 50 °C in O_2)		NiO bunsenite (cubic) ASTM 4-0835	
(*hkl*)	d (Å)	d (Å)	Rel. Intensity
(*111*)	2.41~2.46	2.41	91
(*200*)	2.07~2.17	2.09	100
(*220*)	1.47~1.51	1.48	60
(*311*)	1.28	1.26	16
(*222*)	–	1.23	13
(*400*)	1.07	1.04	8

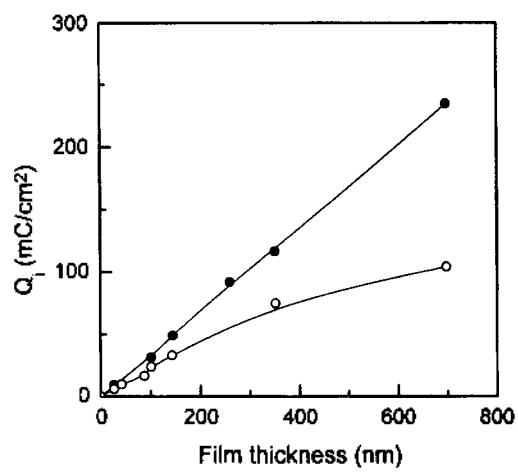

Fig. 4. Evolution of the inserted charge (Q_i) at E=2 V vs. Li as a function of the film thickness of $Li_{2x}Ni_{1-x}O$ deposited at 230 °C under O_2 atmosphere. Filled (●) and open circles (○) represent the first insertion and the following deinsertion/insertions, respectively.

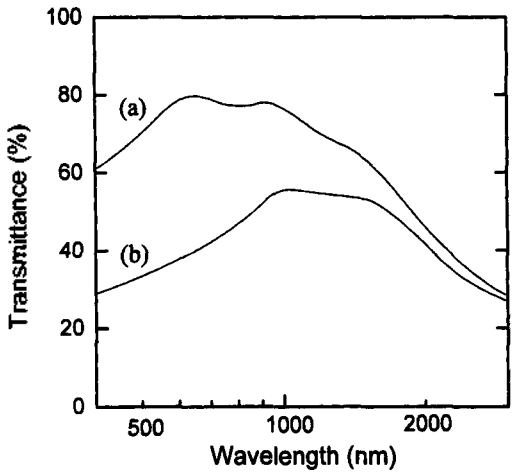

Fig. 5. UV-Vis-NIR spectra of inserted-transparent state at E=2 V vs. Li/Li^+, (a) and deinserted-colored state at E =3.5 V vs. Li/Li^+ (b) of the $Li_{2x}Ni_{1-x}O$ film with a thickness of 40 nm deposited at 50 °C under O_2 atmosphere.

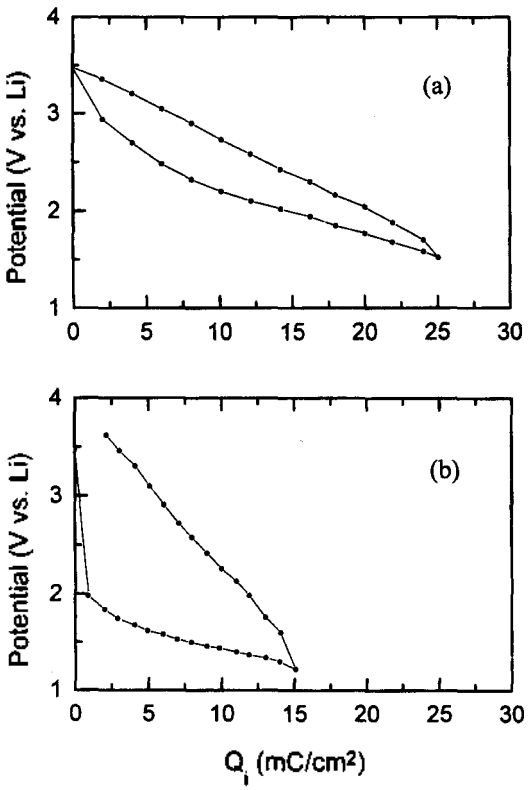

Fig. 6. Charge insertion capacity depending on the substrate temperature for the $Li_{2x}Ni_{1-x}O$ films with the thickness of 170 nm deposited at 50 °C (a) and 230 °C, (b) under O_2 atmosphere.

density. Therefore it is regarded that a lower T_s (if we compare between 50 °C and 230 °C) is favored for the better electrochromic property of sputtered $Li_{2x}Ni_{1-x}O$ film.

SUMMARY

The dependence of crystallinity (porosity and density) of the RF sputtered lithium nickel oxide film on the electrochromic properties has been studied by optical and electrochemical measurements. The electrochromic efficiency is dependent on the film preparation condition, and higher Q_i and OD values could be observed in the more porous film. The porosity of the $Li_{2x}Ni_{1-x}O$ film is enhanced by the O_2 sputtering atmosphere and at lower T_s, where the film could be fabricated with a crystallite size of ~80 Å. Such a porous and nano-textured film exhibits highly reversible electrochromic property and fast lithium ion intercalation/deintercalation after formatting process. In conclusion, we propose that the nanocrystalline $Li_{2x}Ni_{1-x}O$ film is highly promising for a practical application to the electrochromic system.

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