
니켈금속 박막에서의 수산화 니켈 박막의 전기변색속도 개선

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Ni(OH)₂/Ni Glass 박막에서 전기변색 속도 개선에 대한 연구를 수행하였다. 이는 선글라스의 변색속도가 수 분 이상 소요되는 단점을 해결하고자 e-beam evaporator를 이용하여 니켈 금속 박막을 증착시킨 후, 전기화학적 산화-환원 반응으로 Ni(OH)₂에 대한 전기변색 특성을 연구하였다. 전기전도성을 갖는 ITO에서보다 Glass 위에서 Ni(OH)₂의 변색 속도가 오히려 빠르다. 이는 전위와 투과율을 측정함으로써 알 수 있다. XPS를 이용하여 Glass와 Ni(OH)₂ 사이의 초박막($\sim 10\text{\AA}$) Ni 금속의 존재를 확인하였고, 이 나노 박막은 전기변색 장치의 응답 속도에 영향을 미쳤다. 기존의 선글라스가 5분 정도 소요되는 반면, 니켈 나노 박막을 이용한 변색소자에서는 1~2 초 정도 소요된다. 이론적으로는 수 ms 이내이지만 전기적 저항으로 인해 초 단위의 응답속도를 보이고 있다.

Enhanced Electrochromic Switching Performance in Nickel Hydroxide Thin Film by Ultra-Thin Ni Metal

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Improved optical switching property of electrochromic nickel hydroxide/nickel/glass thin film is reported. Nickel metal film was deposited on glass by e-beam evaporation before following electrochemical redox cycling to form nickel hydroxide for electrochromic activation. Without ITO (indium tin oxide) layer as electrical conductor, this electrode showed more rapid coloration rate than nickel hydroxide film on ITO substrate in the change of the electric voltage and optical transmittance. XPS analysis confirmed the existence of ultra-thin nickel metal layer ($\sim 10\text{\AA}$) between electrochemically grown nickel hydroxide and the glass substrate. It is concluded that the remained nickel metal nano-layer attribute to the conduction layer and the enhanced response time.

I INTRODUCTION

Recently, electrochromism has been widely studied and mostly focused on the tungsten oxide,^[1,2] although the exact mechanism is not clear. Among the transition metal oxide, nickel hydroxide films have received much

interest in solid-state electrochromic application due to the high transmittance modulation.^[3] It can serve as optically passive counterelectrode against WO₃.^[4] Optical passivity is mainly caused by the ion intercalation / deintercalation process in nickel hydroxide which is slower than that for the case of WO₃.^[5] With related to the development of counterelectrode, several approaches

have been reported, using ITO,^[6] V_2O_5 ^[7,8] and LiCoO_2 .^[9] Recently, durable electrochromic coating of hydrated nickel oxide were reported grown by reactive rf magnetron sputtering of Ni followed by treatment in KOH.^[10] The practical application of solid-state electrochromic display (ECD) is mostly restricted by response time of the devices. However, the ITO electrode generally used as a transparent electrode has higher sheet resistance than metal,^[11] and may possible to cause slow response time of the electrochromic devices. To overcome the low electric conductivity of ITO, it has been reported that a coating of a thin gold layer onto the WO_3 surface decreased the response time and obtained a further enhancement of coloration and bleaching.^[12]

In this letter, we report that the optical switching performance is more enhanced in $\text{Ni}(\text{OH})_2/\text{Ni}/\text{glass}$ film than direct deposited $\text{Ni}(\text{OH})_2/\text{ITO}/\text{glass}$ one. This result is regarded as a effect of nano-layered nickel metal layer, which is remained after electrochemical oxide growth process in aqueous electrolyte solution. The nickel metal layer plays an important role for the enhancement of response time and further the conducting layer. To our knowledge, there is no report in the literature on the deposition of electrochromic films on glass directly without ITO.

II EXPERIMENTAL

Nickel metal films were prepared by e-beam evaporator onto cleaned glass substrate of $1 \times 3 \text{ cm}$, with the vacuum of the evaporation chamber maintained at $8 \times 10^{-7} \text{ torr}$. The deposited thickness of the nickel film was measured by surface profilometer about 100 \AA . Continuous potential cycling were carried out between -0.2 V and 0.7 V vs. Ag/AgCl (3.5 M KCl) reference electrode to form nickel hydroxide from the surface as described elsewhere.^[13,14] Potential cycling was performed up to 1500 cycles at 50 mV/s scan rate in 1 M KOH aqueous electrolyte solution. Ni/glass and a platinum mesh were used as working and counter electrodes. $\text{Ni}(\text{OH})_2/\text{ITO}/\text{glass}$ films also made by potential cycling in $0.1 \text{ M NiSO}_4 + 0.1 \text{ M NaAC}$ (sodium

acetate) + 0.005 M KOH known as Brigg's solution to compare the response time with $\text{Ni}(\text{OH})_2/\text{Ni}/\text{glass}$ electrode.^[15] The potential cycling were performed up to 500 cycles to identify the deposited film thickness with $\text{Ni}(\text{OH})_2/\text{Ni}$ film grown on glass substrate. The current response was measured according to applied dc bias voltage of -0.2 V and 0.7 V with a 5 sec delay in 1 M KOH .

III RESULTS AND DISCUSSION

Cyclic voltammetry of $\text{Ni}(\text{OH})_2/\text{Ni}/\text{glass}$ electrode showed typical redox curves of Ni hydroxide and gradual increases in peak current. In addition, according to the increase of the cycling, the redox peak current shifted to more anodic and cathodic directions. This reaction was physically coinciding with the growth of nickel hydroxide. Microstructural characterization was accomplished by atomic force microscopy (AFM). Fig. 1 shows some representative $10 \times 10 \text{ nm}$ surface images manifesting distinct morphology and structure. As can be seen, the as-deposited nickel on glass grows as a 2-D growth mode and show smooth surface [Fig. 1(a)]. However, after 1500 cycles in the KOH solution from -0.2 V to 0.7 V , the surface structure drastically change to roughen feature [Fig. 1(b)]. RMS roughnesses were 38.4 \AA and 350 \AA , respectively. Directly deposited $\text{Ni}(\text{OH})_2$ film on ITO substrate exhibits the random growth of many islands and measured RMS roughness was 97.9 \AA [Fig. 1(c)]. This result coincides with a creation of more porous oxide structure by electrochemical oxidation process, also observed by SEM images.

To analyze precise chemical nature of nickel hydroxide grown by evaporation and subsequent oxidizing process, X-ray photoelectron spectroscopy (XPS) technique was introduced. Fig. 2 shows a comparison of the XPS spectra profiles of the Ni $2\text{P}_{3/2}$ peak with each fitted chemical component among initially grown nickel hydroxide by electrochemical oxidation cycling, 1500 cycled electrode and 3min sputtered surface after 1500 cycling with the sputtering rate of 3 nm/min . Curve fitting of the Ni $2\text{P}_{3/2}$ XPS spectrum gives different chemical states with binding

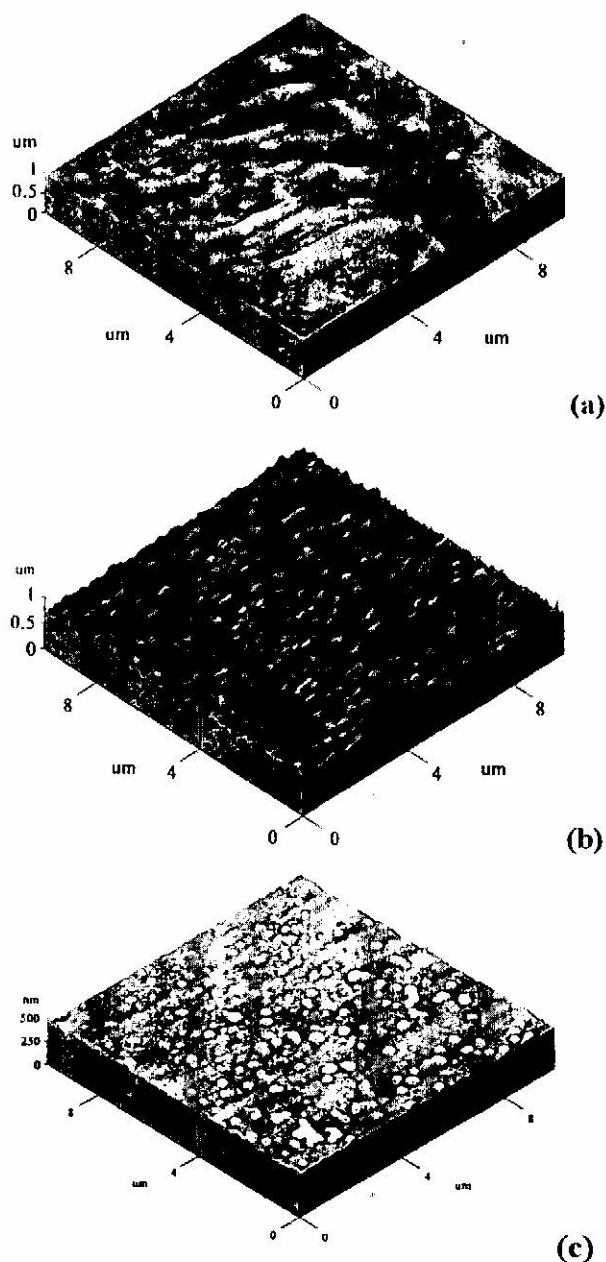


Fig. 1 10×10mm 3-D AFM images after (a) nickel deposition by e-beam evaporation on glass, (b) 1500 cycle in 1 M KOH, and (c) directly deposited Ni(OH)₂ on ITO substrate.

energies of 852.7eV, 854.3eV, 855.8eV, and 858.2eV, which on the basis of their binding energies were assigned to Ni metal, NiO, Ni(OH)₂ and NiOOH, respectively.¹⁶ Initially grown nickel hydroxide has several (hydr)oxides phase in Fig. 2(a). However, as shown in Fig. 2(b), after 1500 cycling, nickel metal peak is disappearing and Ni(OH)₂ form is observed as main compound (80.13%)

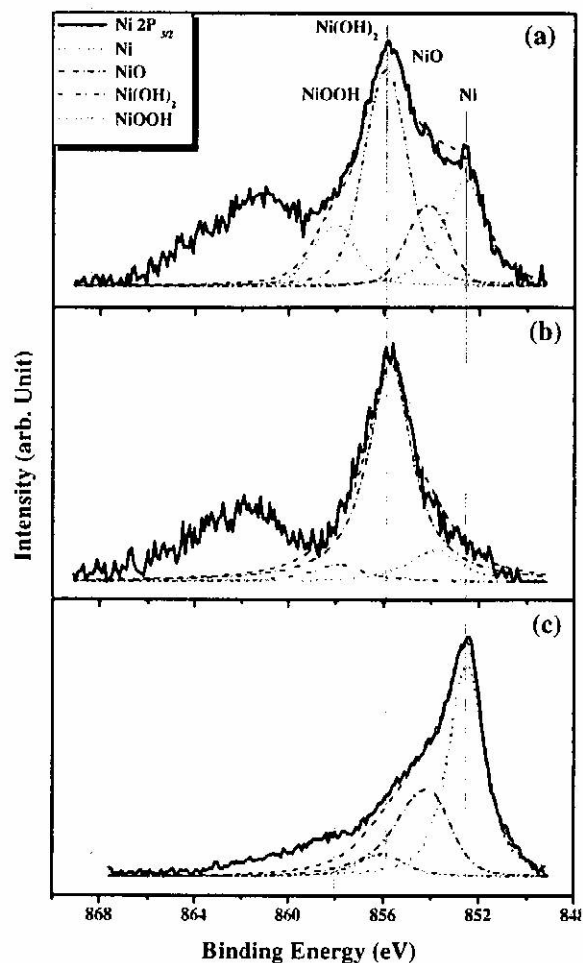


Fig. 2 XPS spectra of Ni 2P_{3/2} region for (a) initially grown nickel hydroxide by electrochemical potential cycling from -0.2V to 0.7V vs. Ag/AgCl in 1M KOH solution, (b) after 1500cycle, and (c) after 3min sputtering at a rate of 3nm/min

with small quantities of NiO(12.56%) and nickel oxyhydroxide (7.31%). This result indicates that as-deposited nickel metal is gradually converted to mostly nickel hydroxide by electrochemical oxidation process. However, Fig. 2(c) shows about 1nm thickness of nickel metal layer when the surface was sputtered out.

Fig. 3(a) compares the current response of Ni(OH)₂/Ni/glass with electrochemically grown Ni(OH)₂/ITO/glass during the switching the voltage from 0.2V (bleached) to 0.7V (colored). When the slopes of current density vs. time curves are compared between the two samples, it can

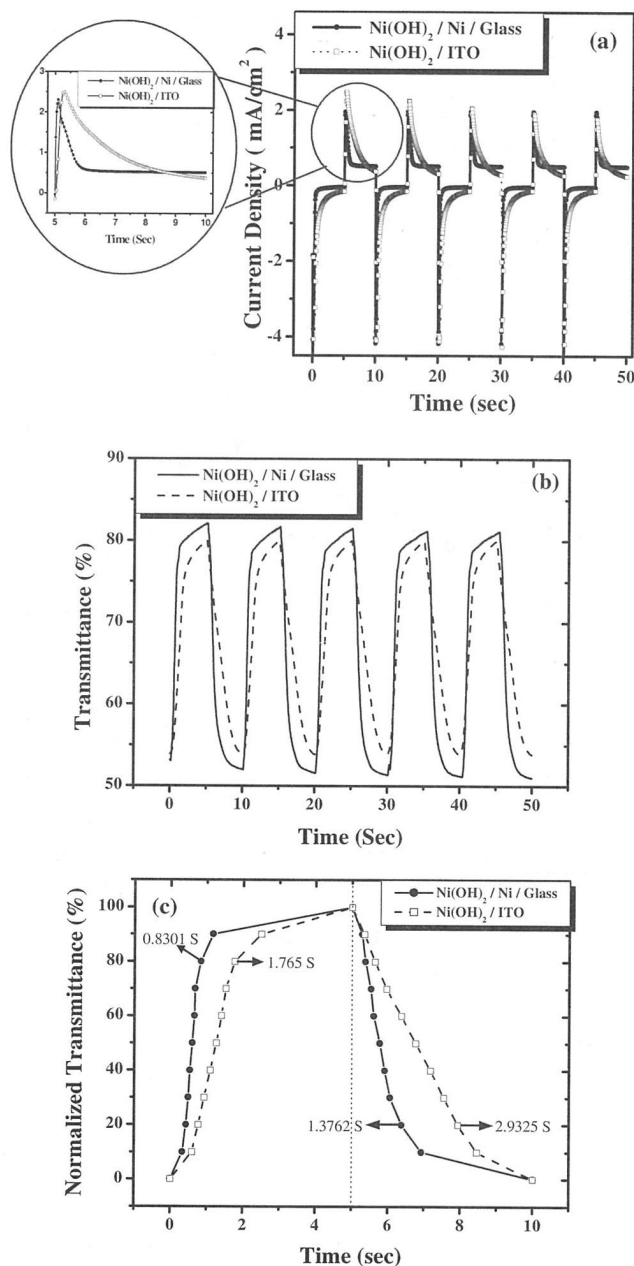


Fig 3 (a) current density vs. time for $\text{Ni(OH)}_2/\text{Ni/ITO}$ and $\text{Ni(OH)}_2/\text{ITO}$ films subjected to 5 sec potential pulses of -0.2V and 0.7V . (b) Comparison of Electrochromic transmittance(%T) modulations. Results taken initial 5cycles are shown. (c) Following change in optical transmittance at a wavelength of 500nm during the 1st coloration and bleaching sequence. Calculated transmittance values at each percentage were relatively normalized by the proportional to the difference between maximum and minimum transmittance value.

be found that the former electrode has faster switching performance than the latter case. This sharp slope feature in $\text{Ni(OH)}_2/\text{Ni/glass}$ electrode coincides with the varied transmittance according to the applied bias as shown in Fig. 3(b). Unfortunately, there are no consistent criteria for determining optical response time. In general, it is defined as the time necessary for some fraction of the color to form, such as a particular increment of optical density or the time for all or part of the charge to be injected.¹⁷ To compare the response time quantitatively, we defined the response time as a required time to vary in proportional to the transmittance values, normalized to the difference between measured maximum and minimum transmittance values, at each percentage. As shown Fig. 3(c), normalized transmittance change of the $\text{Ni(OH)}_2/\text{Ni/glass}$ is > 2 times more faster than $\text{Ni(OH)}_2/\text{ITO/glass}$ electrode in every coloring/bleaching step. For example, to change 80% of transmittance, it is required to consume 0.8s and 1.8s when they are bleached, and 1.4s and 2.9s when colored, respectively. The observed improvement of transmittance switching performance in $\text{Ni(OH)}_2/\text{Ni/glass}$ film is obviously caused by thin nickel metal layer which was not oxidized. The enhanced response time can be possibly attributed to more enhanced conductivity or improved adhesion of the nickel metal layer than those of ITO.

IV CONCLUSION

In summary, for the first time, we investigated to fabricate electrochromic $\text{Ni(OH)}_2/\text{Ni}$ film on glass substrate without ITO and compared the response time of pulse potential and optical transmittance with $\text{Ni(OH)}_2/\text{ITO}$. It is concluded that remained nickel metal nano-layer attributes to the enhanced response time. These results provide to fabricate an improved counterelectrode in the switching performance by $\text{Ni(OH)}_2/\text{Ni/glass}$ instead of $\text{Ni(OH)}_2/\text{ITO/glass}$. In addition, it opens new possibility to substitute ITO with cheap nickel as an electronic conducting layer in electrochromic devices. Further researches on these issues are in progress.

References

- [1] S.-H. Lee, H. M. Cheong, C. E. Tracy, A. Mascarenhas, J. R. Pitts, G. Jorgensen, S. K. Deb, Appl. Phys. Lett. 76, 3908 (2000).
- [2] S.-H. Lee, H. M. Cheong, J.-G. Zhang, A. Mascarenhas, D. K. Benson, S. K. Deb, Appl. Phys. Lett. 74, 242 (1999).
- [3] K. Itaya, T. Ataka, S. Tohima, J. Am. Chem. Soc. 104, 3751 (1982).
- [4] A. M. Andersson, C. G. Granqvist, J. R. Stevens, Proc. S.P.I.E. 1016, 41 (1988).
- [5] S. Passerini, B. Scosati, A. Gorenstein, J. Electrochem. Soc. 137, 3297 (1990).
- [6] B. C. H. Steele, S. J. Golden, Appl. Phys. Lett. 59, 2357 (1991).
- [7] A. Talledo and C. G. Granqvist, J. Appl. Phys. 77, 4655 (1995).
- [8] S. F. Cogan, R. D. Rauh, N. M. Nguyen, T. D. Plante, J. D. Westwood, J. Electrochem. Soc. 140, 112 (1993).
- [9] G. Wei, T. E. Haas, R. B. Goldner, Solid State Ionics 58, 115 (1992).
- [10] J. S. E. M. Svensson, C. G. Granqvist, Appl. Phys. Lett. 49, 1566 (1986).
- [11] H. Kaneko, K. Miyake, Appl. Phys. Lett. 49, 112 (1986).
- [12] A. R. Haranahalli, D.B. Dove, Appl. Phys. Lett., 36, 791 (1980).
- [13] R. S. Schreiber Guzman, J. R. Vilche, A. J. Arvia, J. Appl. Electrochem. 9, 183 (1979).
- [14] A. Seghioeur, J. Chevalet, A. Barhoun, F. Lantelme, J. Electroanal. Chem. 442, 113 (1998).
- [15] G. W. D. Briggs, E. Jones, W. F. K. Wynne-Jones, Trans. Faraday Soc. 51, 1433 (1955).
- [16] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, (Eden Prairie, MN, 1995), p. 84.
- [17] P. M. S. Monk, Roger J. Mortimer, David R. Rosseinsky, Electrochromism : Fundamentals and Application (VCH, Weinheim, 1995), p. 17.