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Citation: *Appl. Phys. Lett.* **81**, 3930 (2002); doi: 10.1063/1.1522478

View online: <http://dx.doi.org/10.1063/1.1522478>

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All-solid-state electrochromic device composed of WO_3 and $\text{Ni}(\text{OH})_2$ with a Ta_2O_5 protective layer

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(Received 24 July 2002; accepted 26 September 2002)

An all-solid-state electrochromic device composed of WO_3 and $\text{Ni}(\text{OH})_2$ with a Ta_2O_5 protective layer was prepared by rf magnetron sputtering and lamination with a proton-conducting solid polymer electrolyte. This device had good durability, high transmittance modulation (18%–74%) and coloration efficiency (about $84 \text{ cm}^2 \text{ C}^{-1}$), and good response times (8.5 and 18 s, respectively, during the bleaching and coloring processes). This indicates that Ta_2O_5 layers are electrochemically stable and can be used as protective layer for $\text{Ni}(\text{OH})_2$ as well as WO_3 . © 2002 American Institute of Physics. [DOI: 10.1063/1.1522478]

Electrochromism (EC) is defined as a phenomenon in which a change in color (light transmittance) takes place in the presence of an applied voltage.^{1–3} Because of their low power consumption (<2 V), high coloration efficiency, and memory effects under open circuit conditions, EC devices have many potential applications in smart windows, mirrors, displays, and optical switching devices.^{1–3} An EC device generally consists of a transparent electrically conducting layer, electrochromic cathodic and anodic coloring materials, and an ion conducting electrolyte. Such devices are currently prepared using proton-conducting solid polymer electrolytes (H^+ –SPE) for practical use, because of the advantages of this process, which involves seal development during manufacture and the inhibition of bubble formation.^{1,4} WO_3 and Ni hydroxide are currently in widespread use as, respectively, cathodic and anodic coloring materials.^{1,2,5–9} However, EC devices incorporating WO_3 and $\text{Ni}(\text{OH})_2$ may have problems related to their limited durability due to chemical incompatibility between the electrochromic layers and the adjoining electrolyte.^{10,11} WO_3 is stable in a moderately acidic electrolyte but rapidly dissolves in a basic electrolyte. On the other hand, the $\text{Ni}(\text{OH})_2$ is stable in a basic electrolyte but unstable in an acidic electrolyte. Recently, a solution to this problem was attempted by depositing a compact WO_3 protective layer on top of the Ni hydroxide.^{10,12} However, the WO_3 also has a tendency to slowly dissolve in an acidic electrolyte because hydrated WO_3 , the soluble form, is formed during the bleaching/coloring processes in the acidic electrolyte,^{1,13} which may lead to the degradation in the performance of an EC device.

Ta_2O_5 was used to protect the WO_3 in an EC system comprised of indium tin oxide (ITO)/W oxide/ H^+ –SPE/Ir oxide/ITO,^{1,2} in which Ir oxide, the electrochromic anodic coloring material, is stable in an acidic electrolyte but has a much lower coloration efficiency (CE) of about $17 \text{ cm}^2 \text{ C}^{-1}$

than that (about $37 \text{ cm}^2 \text{ C}^{-1}$) of Ni hydroxide,¹ thus limiting the practical use of the Ir oxide in EC devices. Ta_2O_5 may represent another possible protective layer on top of the $\text{Ni}(\text{OH})_2$.

In this letter, an all-solid-state, proton-based EC device with a Ta_2O_5 protective layer on top of the $\text{Ni}(\text{OH})_2$ layer was fabricated and its performance compared with a similar EC device but without a Ta_2O_5 protective layer on top of the $\text{Ni}(\text{OH})_2$. The EC device composed of spin-on-glass (SOG) (a kind of thermally decomposed SiO_2)-coated glass/ITO/ $\text{Ni}(\text{OH})_2$ / Ta_2O_5 / H^+ –SPE/ Ta_2O_5 / WO_3 /ITO/SOG-coated glass provided good durability, a high CE, and an acceptable response speed, due to the protective property of the Ta_2O_5 between the $\text{Ni}(\text{OH})_2$ and the acidic polymer electrolyte.

Two types of all-solid-state EC devices comprised of SOG-coated glass/ITO/ $\text{Ni}(\text{OH})_2$ / H^+ –SPE/ Ta_2O_5 / WO_3 /ITO/SOG-coated glass and SOG-coated glass/ITO/ $\text{Ni}(\text{OH})_2$ / Ta_2O_5 / H^+ –SPE/ Ta_2O_5 / WO_3 /ITO/SOG-coated glass were fabricated, shown as (a) EC1 and (b) EC2 in Fig. 1. First, NiO and WO_3 films were deposited on the substrates of ITO coated SOG-coated glass. NiO and W metal were used as target materials. The working pressures were 5×10^{-3} Torr and 2×10^{-2} Torr, respectively, for the NiO and WO_3 sputtering and the sputtering was performed under Ar: O_2 ratio of 1:1 and only O_2 , respectively. The NiO and WO_3 films were sputter-deposited at rf powers of 60 and 100 W, respectively, for 90 min at RT, the detailed deposition procedures for which have been reported elsewhere.^{8,9,14} Ta_2O_5 protective films were then deposited on the NiO/ITO/SOG-coated glass and WO_3 /ITO/SOG-coated glass using a rf magnetron sputtering system. Ta_2O_5 was used as the target material. The base pressure was below 5×10^{-6} Torr, the working pressure was 5×10^{-3} Torr, and the sputtering was performed under only O_2 at 40 sccm. Prior to sputtering, a presputtering process was performed for 20 min in order to remove contaminants from the target. Sputtering was then conducted at a rf power of 60 W for 10 min at RT.

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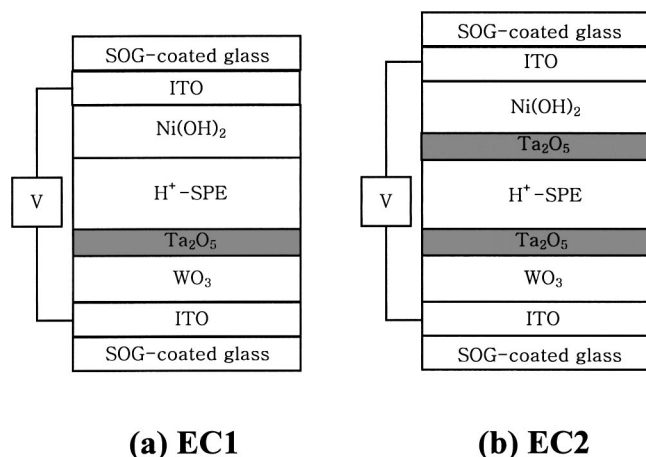


FIG. 1. Schematic diagrams of all-solid-state EC devices (a) without and (b) with a Ta_2O_5 protective layer on top of the $\text{Ni}(\text{OH})_2$.

$\text{Ni}(\text{OH})_2/\text{ITO}/\text{SOG-coated glass}$ and $\text{Ta}_2\text{O}_5/\text{Ni}(\text{OH})_2/\text{ITO}/\text{SOG-coated glass}$ was prepared by the potential cycling of the sputter-deposited $\text{NiO}/\text{ITO}/\text{SOG-coated glass}$ and $\text{Ta}_2\text{O}_5/\text{NiO}/\text{ITO}/\text{SOG-coated glass}$, respectively, in a 1 M NaOH electrolyte.^{8,9,15} The thicknesses of the sputter-deposited Ta_2O_5 , NiO , and WO_3 layers were about 60, 300, and 200 nm, respectively, as determined by cross-sectional scanning electron microscopy (SEM). The crystallographic microstructures of all the deposited films were amorphous, as evidenced by x-ray diffraction data. Finally, all-solid-state EC1 and EC2 devices in Fig. 1 were fabricated by laminating the sulfonated styrene-(ethylene-butylene)-styrene triblock copolymer used as the H^+ -SPE, which was described elsewhere.¹⁶

Both EC1 and EC2 devices were tested after storage in atmosphere for 2 days to estimate their durability. EC properties such as the CE and response time were evaluated by switching a pulse potential wave between -1.7 and 1 V (versus anodic coloring material) with a duration time of 30 s, referred to as switched pulse potential cycling. The transmittance (633 nm) was simultaneously measured *in situ* during potential cycling, as described elsewhere.^{8,14,15}

The EC properties of $\text{Ta}_2\text{O}_5/\text{Ni}(\text{OH})_2/\text{ITO}/\text{SOG-coated glass}$ and $\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}/\text{SOG-coated glass}$ were first investigated by electrochemical cell tests, for comparison to those of an all-solid-state EC device. The $\text{Ta}_2\text{O}_5/\text{Ni}(\text{OH})_2/\text{ITO}/\text{SOG-coated glass}$ and $\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}/\text{SOG-coated glass}$ were used as working electrodes in typical three-electrode electrochemical cell, where Pt wire and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively.^{8,9,14,15} Figure 2 shows *in situ* transmittance curves obtained during the switched pulse potential cycling tests for the electrochemical cells of (a) $\text{Ta}_2\text{O}_5/\text{Ni}(\text{OH})_2/\text{ITO}/\text{SOG-coated glass}$ and (b) $\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}/\text{SOG-coated glass}$. The electrochemical cell of $\text{Ta}_2\text{O}_5/\text{Ni}(\text{OH})_2/\text{ITO}/\text{SOG-coated glass}$ were potential cycled under a switched pulse potential of between -0.9 and 0.6 V (versus Ag/AgCl) with a duration time of 30 s in a 1 M NaOH electrolyte and the $\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}/\text{SOG-coated glass}$ electrochemical cell was tested under a switched pulse potential of between -0.4 and 1.8 V (versus Ag/AgCl) with a duration time of 30 s in 0.5 M H_2SO_4 . In order to evaluate the CE values of the electrochromic layers, the transmittance

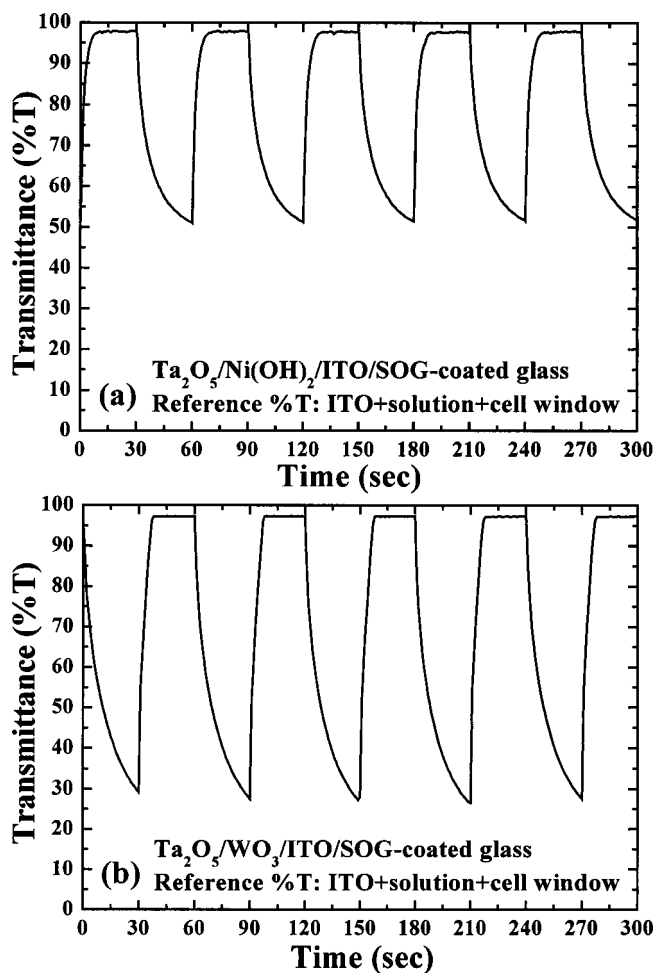


FIG. 2. *In situ* transmittance curves obtained during switched pulse potential cycling tests of (a) $\text{Ta}_2\text{O}_5/\text{Ni}(\text{OH})_2/\text{ITO}/\text{SOG-coated glass}$ and (b) $\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}/\text{SOG-coated glass}$ electrochemical cells.

of the ITO/glass with the electrolyte and the cell window was assumed to be the reference %T (or 100% transmittance). The electrochemical cells of $\text{Ta}_2\text{O}_5/\text{Ni}(\text{OH})_2/\text{ITO}/\text{SOG-coated glass}$ and $\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}/\text{SOG-coated glass}$ had CE values of about 37 and $45 \text{ cm}^2 \text{ C}^{-1}$, respectively, in which CE is defined as $\log(T_{\text{bleached}}/T_{\text{colored}})/Q$ where T_{bleached} and T_{colored} are the transmittances of the bleached and colored states, and Q is charge per unit area used during the coloring process. The response times during the bleaching/coloring processes were also quantitatively calculated from the normalized first transmittance curves of the switched pulse potential cycling.^{8,9,14,15} The EC response time was calculated on the level of a 90% transmittance change. The response times during the bleaching and coloring processes were about 5 and 17 s, respectively, for the $\text{Ta}_2\text{O}_5/\text{Ni}(\text{OH})_2/\text{ITO}/\text{SOG-coated glass}$ electrochemical cell and about 6 and 18 s, respectively, for the $\text{Ta}_2\text{O}_5/\text{WO}_3/\text{ITO}/\text{SOG-coated glass}$ electrochemical cell. The coloring response time was, on the whole, slower than the bleaching response time, because the conductivities of the bleached-state forms, $\text{Ni}(\text{OH})_2$ and WO_3 , are lower than those of the colored-state forms, NiOOH and HWO_3 .^{8,14}

Figure 3 shows *in situ* transmittance curves obtained during the switched pulse potential cycling performed after storage for 2 days for the all-solid-state EC devices. For the

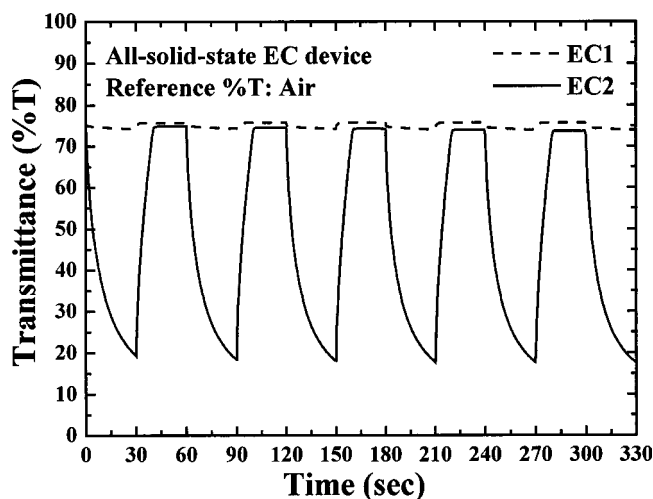


FIG. 3. *In situ* transmittance curves obtained during switched pulse potential cycling tests conducted after storage for 2 days for all-solid-state EC devices composed of (solid line) SOG-coated glass/ITO/Ni(OH)₂/Ta₂O₅/H⁺-SPE/Ta₂O₅/WO₃/ITO/SOG-coated glass and (dotted line) SOG-coated glass/ITO/Ni(OH)₂/H⁺-SPE/Ta₂O₅/WO₃/ITO/SOG-coated glass.

practical application of the EC device, air served as the basis for the reference %T. The transmittance change during the bleaching/coloring processes was barely measurable in the case of EC1 device, because the precharged Ni(OH)₂, operating as a proton source, dissolved and, as a result, barely provided the *Q* required for transmittance modulation, which agrees well with the result reported by Azens' group.¹⁰ On the other hand, the EC2 device showed good transmittance modulation (18%–74%) and durability, indicating that Ta₂O₅ functions well as a protective layer against the dissolution of the Ni(OH)₂.¹⁷ The CE value of the EC2 device was about 84 cm² C⁻¹, which generally agrees with the sum of CE values of the electrochemical cells shown in Fig. 2. This indicates that the *Q* was used entirely for the EC active reaction and not for the side reaction which may result in the degradation of the EC property. Thus, the Ta₂O₅ protective layer is electrochemically stable in an EC2 device, which has good agreement with data of potential-pH diagram.¹⁷ The response times during the bleaching and coloring processes of the EC2 device were about 8.5 and 18 s, respectively. The bleaching response time of the EC2 device is longer than those of the electrochemical cells described in Fig. 2, indicating the existence of other, as yet unknown, rate-limiting factors. The coloring response time of the EC2 device is similar to those of the electrochemical cells shown in Fig. 2, indicating that Ta₂O₅ protective layer in itself was not the rate-limiting factor for the EC2 device. Instead, the relatively lower ion conductivity of the H⁺-SPE compared to that of the aqueous electrolyte or poor interfacial property between the Ta₂O₅ and the H⁺-SPE may act as rate-limiting factors. Detailed studies of this are currently underway.

In summary, an all-solid-state EC device composed

of WO₃ and Ni(OH)₂ with Ta₂O₅ protective layer, SOG-coated glass/ITO/Ni(OH)₂/Ta₂O₅/H⁺-SPE/Ta₂O₅/WO₃/ITO/SOG-coated glass, was prepared by rf magnetron sputtering and lamination, the EC properties of which were estimated from a comparison with the electrochemical cells of Ta₂O₅/Ni(OH)₂/ITO/SOG-coated glass and Ta₂O₅/WO₃/ITO/SOG-coated glass, respectively, and an all-solid-state EC device without the Ta₂O₅ protective layer on top of Ni(OH)₂. The EC device without the Ta₂O₅ protective layer on top of Ni(OH)₂ scarcely showed any transmittance modulation, due to dissolution of the Ni(OH)₂. On the other hand, the EC device with the Ta₂O₅ protective layer on top of Ni(OH)₂ had a good durability, high transmittance modulation (18%–74%) and a CE value (about 84 cm² C⁻¹), and a good response speed of 8.5 and 18 s, respectively, during the bleaching and coloring processes. Therefore, we conclude that the Ta₂O₅ layer is electrochemically stable and can be used as a viable protective layer on top of the Ni(OH)₂ as well as WO₃. Although more detailed studies of the Ta₂O₅ protective layer are required, we expect that it will be useful as a durable smart EC window with a high CE and a good response time.

This work was supported by Grant No. 2000-30700-003-1 from the Basic Research Program of the Korea Science and Engineering Foundation and the Brain Korea 21 Project.

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