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Investigation of mechanical bending instability in flexible low-temperature-processed electrochromic display devices

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ABSTRACT

In this study, polyethylene naphthalate (PEN) was investigated as a flexible substrate because, compared with polyethylene terephthalate, it achieves a lower root mean square roughness and transmittance, which is favorable for reducing leakage from the bottom of flexible substrates. A flexible device structure composed of tungsten oxide/indium-doped tin oxide/PEN was used in an electrochromic (EC) test. The experimental results show that the flexible EC display device achieved a high transmittance difference of >40% and color efficiency of 70.2 cm^2/C at 560 nm. The transmittance difference was degraded in the visible range after 200 cycles of continuous bending. Furthermore, compared with flat fresh devices, the WO_3 device exhibited poor retention properties in a colored state after being subjected to longer bending cycles.

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1. Introduction

The flexible electronics devices used in health care and fitness are typically composed of a gas sensor, biosensor, and wireless communications, and have been regarded as a crucial technology for wearable and portable applications in the future. Although flexible display technologies have been well developed, challenges such as reducing fabrication costs, operating at low temperatures, simplifying device structures, and operating at a low voltage remain. Electrochromic (EC) film [1–13] has attracted considerable attention because of low temperature fabrication, low power operation, and energy-saving design, which have contributed to potential applications in green building (smart windows), electric vehicle (auto-dimming glass), and wearable electronics (flexible displays). Among the various materials used in EC films, electroplated tungsten oxide (WO_3) [6–13] has demonstrated high potential because of its low cost, high optical contrast, and stability. The operations of these EC devices are based on the reaction of electrons and cations (Li^+, Na^+, K^+, H^+) between EC films and electrolytes. Although WO_3 EC display (ECD) films have been compressively investigated on solid substrates, few studies have mentioned the reliability of ECD devices on flexible substrates.

In this study, we investigated the EC characteristics of WO_3 ECD devices on a flexible substrate by performing endurance cycling tests with a fixed bending radius to evaluate the reliability of flexible WO_3 ECD devices. The self-bleaching behaviors observed in substrate bending tests can directly indicate transmittance difference and coloration efficiency. The origin of electrochromic degradation is ascribed to the generation of point defects near the center of the WO_3/ITO interface.

2. Experiments

Flexible ITO/PEN substrates were used to fabricate ECD devices. A 250-nm-thick indium-doped tin oxide (ITO) layer was deposited by sputtering it on a PEN substrate as the bottom electrode. The surface roughness (the root mean square; RMS) of the PEN substrate (RMS = approximately 9.08 nm, 5 × 5 μm) was reduced after covering the ITO electrode (RMS = approximately 1.64 nm, 5 × 5 μm). First, the ITO electrode was precleaned with acetone for 10 min. Subsequently, a 200-nm-thick WO_3 film was electroplated to create an ECD layer for the EC test. The steps for synthesizing a WO_3 solution are described as follows. A peroxotungstic acid solution was synthesized using tungsten powder (4.2 g) and a hydrogen peroxide aqueous solution (30 mL) in chilled water (0 °C–10 °C) for 24 h. Next, 30 mL of glacial acetic acid was mixed with the peroxotungstic acid solution at 55 °C for 12 h. Subsequently, the WO_3 electroplating solution was completed. Because electroplated WO_3 films crystallize easily, no additional thermal budget must be applied. To inspect colored and bleached behaviors, the electrodeposited and crystallized WO_3 film was filled with a lithium electrolyte for the EC test.

To evaluate the reliability of flexible bending, a flexible bending test was performed on a 3 × 1-cm device. Continuous mechanical cycling was applied with a large bending radius of 1 cm. Additionally, the

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crystallinity, composition, and thickness of the WO_3 EC films were characterized using an X-ray diffraction (XRD) system (D5000, Siemens) with Cu–Ka radiation in the θ–2θ Bragg configuration. The optical properties of the transmission and absorption spectra were measured using an ultraviolet/visible/near-infrared spectrophotometer.

3. Results and discussion

XRD patterns (Fig. 1) revealed that the electroplated WO_3 developed into a well-crystallized phase on the flexible ITO/PEN substrate. We found that the peak densities at the (002), (202), and (222) planes can be indexed to the monoclinic phase of WO_3. The apparent peak corresponding to the (200) plane of hexagonal WO_3 was also observed. The stoichiometric or nonstoichiometric WO_3 generated various ion valences and electrons participating in the reduction and oxidation (redox) process when positive or negative voltages were applied. The optical absorption of WO_3 film in colored and bleached states mainly originated from changes in the tungsten ion valance because of the inter-reaction with the electrolyte ions and injected electrons (Fig. 2). To evaluate the bending reliability, 1-cm-radius mechanical bending was performed on this flexible ECD device. Fig. 2(a–c) shows the optical transmittance spectra of the WO_3 EC films without bending, with 100 bending cycles, and with 200 bending cycles, respectively. The transmittance in the colored state and transmittance difference apparently degraded in the visible range after 200 cycles. Moreover, the retention time became shorter, resulting in a coordinate shift to the white light region after the films were subjected to 100–200 cycles. This indicated that the retention characteristics depended strongly on the number of bending cycles. Therefore, investigating the failure mechanism is urgent.

In general, the reversible electrochromism in WO_3 is adequately described by the model of charge transfer between W^{6+} and W^{5+} ions. The Li^+ ion was used as a conductor to reach the optical change through redox processes on the WO_3 film. Although a fast switching speed (approximately 1 ms) can be implemented in a WO_3 film [14], the response time of the redox process remained dominated by the lithium ion diffusion rate. In our previous research, we have demonstrated the role of oxygen vacancies in a solid-state metal/insulator/metal capacitor [14], and showed that oxygen vacancies may form low-valence tungsten ions and influence the retention time of the coloration state. The reversible reaction can be expressed as WO_x (colored) + $yLi^+ + ye^- \leftrightarrow Li_yWO_x$ (bleached) [12]. In this study, an over-stressed bending test was performed on a flexible stack of WO_3/ITO/PEN. As the number of bending cycles increased, point defect centers were generated at the interface between the WO_3 and ITO/PEN substrate, as expressed in the equation $V_{WOx}^{2+} + 2e^- + WO_x \rightarrow WO_x{}^*$, where V_{WOx}^{2+} represents the oxygen vacancy in WO_3 film [14]. These defective centers or vacancy complexes affect the charge transfer and valence change, particularly in the bleached state. This occurs because injected electrons trapped by positively charged vacancies can lead to a reduction of Li^+ diffusion current, which governs the redox process and holding time in the bleached state [14]. As shown in Fig. 2(b–c), the 200-cycle device required half the bleaching time of the fresh device that was not subjected to bending, which is clearly supported by our proposed mechanism.

As shown in Fig. 3(a), the colored transmittance of the WO_3 film measured at a wavelength of 560 nm degraded from 22% to 40% at a holding time of 10 min after 200 cycles. Furthermore, linear dependence was observed when the bending time was increased to 60 min. Fig. 3(b) shows that the degradation of transmittance gradually saturated after 100 bending cycles, indicating that the defect generation rate slowed after 100 bending cycles, which was observed at a wavelength of not only 560 nm but also 450 nm (not shown here). The rapid

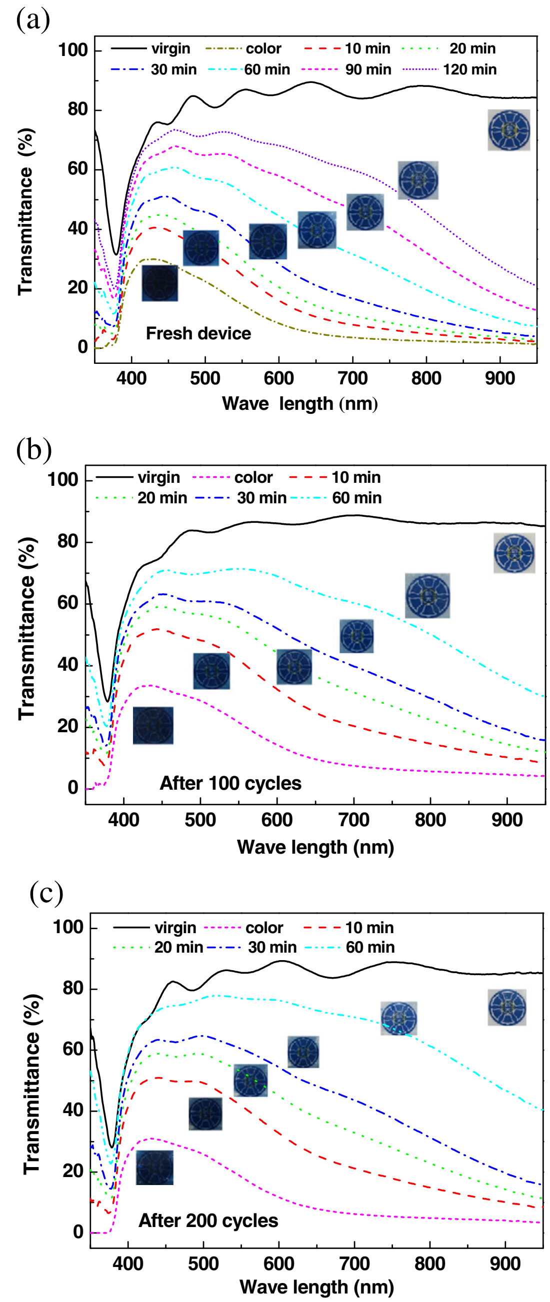

Fig. 2. Optical transmittance spectra of flexible WO_3 ECD devices (a) without and with (b) 100 and (c) 200 bending cycles.

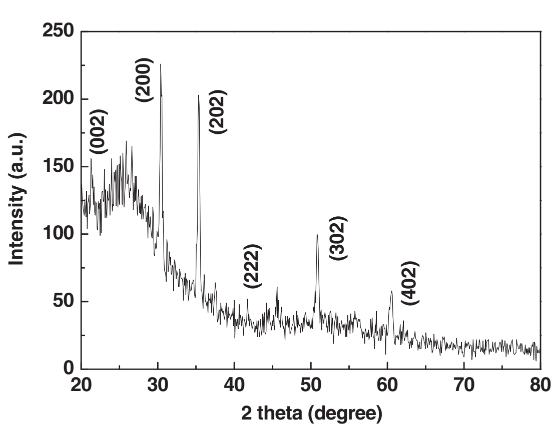

Fig. 1. XRD patterns of the electroplated WO_3 electrochromic film.

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