Lithium-Based Electrochromic Mirrors

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LITHIUM-BASED ELECTROCHROMIC MIRRORS

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ABSTRACT

Antimony, antimony-copper, and antimony-silver thin films were prepared by DC magnetron sputtering on glass substrates. Their reflectance and transmittance in the visible range were measured before and after electrochemical lithiation. The mixed metal films exhibited larger changes in reflectance and small shifts in the optical absorption edge compared with pure antimony films. Electrochromic cycling speed and stability of the Sb-Li system were improved by the addition of copper and silver.

INTRODUCTION

Electrochromic devices that exhibit large dynamic ranges for reflectance in the visible and infrared regimes can now be made using a variety of materials. Devices incorporating these films can be used to improve energy efficiency in buildings and vehicles by controlling the flow of heat not only through windows and skylights, but also through opaque roof and wall panels. Mirror-to-window switching by means of reversible deposition and dissolution of reflective metals has been demonstrated in several different configurations (1-4). Metal-insulator transitions that accompany a wide variety of chemical reactions can also be effected electrochemically. Metal hydride switchable mirrors are based on rare earths and their alloys (5) or on mixtures of magnesium and transition metals (6), and can also be operated gasochromically. Electrochemical oxidation and reduction of copper and its oxides produces a system with reflective, transparent, and highly absorbing states (7). Another class of switchable mirrors utilizes the interconversion of metallic and semiconducting phases via lithiation and delithiation of host materials in a non-aqueous electrolyte (8).

The first examples of the last type were thin films of antimony or bismuth. Reflectance modulation due to lithiation is very high in the visible range and substantial in the near IR, while transmittance modulation is high at all wavelengths above the absorption edge (Fig. 1). The most transparent state corresponds to Li₃Sb. Similar performance was achieved with Bi films. Li₃Sb is yellow-green and Li₃Bi is yellow in transmitted light. The latter exhibits a narrow range of excess lithium stoichiometry which is accompanied by strong electrochromism, with colors ranging from yellow to deep red (8). Because the potentials required for lithiation are outside the stability limits
of transparent oxide conductors, it is necessary to deposit the films on uncoated glass and rely upon electron conduction through the active film. Although the conductivity is relatively low in the transparent (semiconducting) state, very high lithium mobility (9) in these phases allows reversible switching to occur. This limitation, and the large volume changes that are necessary to accommodate so much lithium, create a significant impediment to fast switching. The stresses created at the interface between the current collector and the active film also contribute to resistance and poor cycling stability. It is clear, however, from both the electrochemical behavior and the optical properties that the mechanism for performance degradation is physical disconnection of particles rather than consumption of active material in side reactions.

Adding other metals could improve performance in a number of ways. The metals may be incorporated in the lithiated phase in place of lithium, as Li$_2$MSb, for example, where M = Cu or Ag (10-12). This would reduce the amount of lithium required for switching and the corresponding volume expansion (11). Even if the metals do not participate in the reaction, they may increase the electronic conductivity of the film in the semiconducting state and/or provide a network of conduction paths to regions far from the current collector. Further, the presence of the added metal as an alloy, as a substituent in lithiated phases or as a separate phase may alter the optical properties of the films in both mirror and transparent states.

**EXPERIMENTAL**

Pure Sb, Cu-Sb, and Ag-Sb films were deposited on 25 mm x 37 mm glass substrates by DC magnetron sputtering from separate 2” diameter targets at 26° off normal, target to substrate distance: 90 mm. Film thicknesses (Table I) were measured by stylus profilometry (Dektak). Electrochemical cycling was carried out in a 50 mL fused silica cuvette containing 1 M LiClO$_4$ in propylene carbonate, using lithium foil counter and reference electrodes. Photopic transmittance was monitored *in situ* using a filtered silicon detector (International Light, Inc.) with output coupled to a computerized potentiostat/galvanostat (Arbin, Inc.). Visible spectra were recorded using a fiber optic spectrometer (Ocean Optics, Inc.).

**Table I. Film Deposition Conditions and Thicknesses**

<table>
<thead>
<tr>
<th>% Cu</th>
<th>% Ag</th>
<th>Sb Power (W)</th>
<th>Cu/Ag Power (W)</th>
<th>Deposition Time (s)</th>
<th>Thickness (nm)</th>
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</table>
RESULTS AND DISCUSSION

The visible reflectance of the mixed metal films was somewhat lower than that of pure Sb (Fig. 2), especially for Cu addition. The photopic transmittance of films after deposition was below 2% at all visible wavelengths. An area of about 5 cm² of each film was immersed in the electrolyte and loaded with lithium at a constant current of 10 µA/cm². Potential profiles for lithiation to maximum transmittance and the beginning of lithium extraction in Cu-substituted films are shown in Figure 3(a). Addition of 20% Cu had little effect on the capacity for lithium and only a slight lowering of the extraction potential from 1.07 to 1.03 V. 33% Cu, however, reduced the amount of lithium required for conversion to the maximum transmitting state by more than half, although a lower potential limit was required to achieve full lithiation via a multi-step reaction process. Lithium extraction also took place in several steps, with the bulk occurring at about 1.05 V. Despite the dramatic effect on the electrochemical behavior, the optical switching of the 33% Cu film was similar to that of pure Sb (Fig 4), except that two steps are discernable here as well. During the first, corresponding to the sloping plateau above 0.8 V, there was a gradual increase in transmittance with little change in the shape of the spectrum, with an absorption edge about 100 nm higher and transmittance about two-thirds that of the fully-lithiated Sb. During the lower potential insertion, the increase in transmittance was accompanied by a shift of the absorption edge to shorter wavelengths by more than 50 nm, and development of a region of very high transmittance around 600 nm. Increasing the Cu content to 50% substantially reduced the transmission in the lithiated state (Fig. 5).

12% Ag substitution produced a slightly increased lithiation potential and a small reduction in capacity, while the lithium extraction overpotential was almost completely eliminated (Fig. 3(b)). The effect on the transmittance spectrum (Fig. 5) was similar to that for Cu substitution, shifting the absorption edge to longer wavelengths while increasing the maximum transmittance. At 25% Ag, multi-step lithiation was evident, while lithium extraction (not shown) proceeded in an apparently single-step reaction. Again, the lithium capacity was largely unaffected. For 50% Ag, two distinct steps appeared for both lithiation and delithiation, a much lower potential limit was required for complete switching, the capacity decreased by 25%.

The effect of metal addition on extraction overpotential and galvanostatic (10 µA/cm²) cycling stability is shown in Figure 6 for a 33% Cu film. A pure Sb film loses capacity and optical dynamic range over a few cycles. The difference in potentials for lithiation and delithiation increase as the film becomes less connected, the effect on the extraction potential being much greater due to the lower conductivity of the lithiated phase and the volume contraction taking place during delithiation. Addition of copper significantly reduced and stabilized the extraction potential and thereby slowed the deterioration in optical switching. The degradation mechanism, however appears to be the same in both films.

Given sufficient activation energy, the intermetallics Cu₂Sb and Ag₃Sb could be expected to form in co-sputtered Cu-Sb and Ag-Sb films, respectively (13). In the absence of substrate heating, which was not employed here, alloying of the metals was not, however, assured. Incorporation of the metal substituent into phases formed during
lithiation may also occur. In heavily substituted films, multi-stage lithiation and delithiation was apparent for both Cu and Ag. The electrochemical and optical behaviors of the mixed metal films were consistent with the formation of phases that include the substituents at least during the final stages of lithiation.

CONCLUSIONS

Addition of copper or silver in varying amounts to antimony electrochromic mirror films produced significant changes in their electrochemical and optical properties. These effects were consistent with participation of the added metals in the lithiation reactions and included shifts in the potentials for delithiation even for small levels of substitution. The transmittance spectra of substituted films after lithiation exhibited sharper absorption edges, shifted to longer wavelengths relative to pure antimony films. Smaller effects were observed in the reflectance spectra and these attributable to the changes in absorption. As expected Cu and Ag addition improved the cycling stability of Sb films, most likely by increasing their electronic conductivity in the lithiated states. A reduction in volume changes due to lowered lithium capacity may also contribute to the cyclability. Further improvements may be achieved through use of a transparent conducting layer that is stable at low potentials, better adhesion and wetting of the substrate through pretreatment or additional layer depositions, use of solid electrolytes to reduce the mobility and coarsening of the active particles.

ACKNOWLEDGEMENT

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REFERENCES

Fig. 1. Visible-NIR reflectance and transmittance spectra of a pure Sb film before and after lithiation.
Fig. 2. Reflectance spectra of a) Sb-Cu and b) Sb-Ag thin films.
Fig. 3. Galvanostatic lithiation of a) Sb-Cu and b) Sb-Ag thin films (10 μA/cm²).
Fig. 4. Visible-NIR transmittance spectra of a) Sb and b) Sb-33% Cu films during lithiation.
Fig. 5. Visible-NIR transmittance spectra at maximum transparency of lithiated 25 nm Sb, Sb-Cu, and Sb-Ag films.
Fig. 6. Potential profiles and photopic transmittance of a) Sb and b) Sb-33%Cu films during galvanostatic lithiation and delithiation.