Electrochromism of nanoparticulate-doped metal oxides: optical and material properties

J.P. Coleman a, *, J.J. Freeman a, P. Madhukar a, J.H. Wagenknecht b

a Monsanto Co., 800 N. Lindbergh Blvd., St. Louis, MO 63167, USA
b Cedar Hill LLC, 7510 Horseplay Lane, Cedar Hill, MO 63016, USA

Received 20 September 1998

Abstract

Nanoparticulate antimony-doped tin oxide (ATO) has been used as the electrochromic material for the production of printed, interdigitated electrochromic displays. We report here some results on elemental and ionic modifications to the ATO in an attempt to improve electrochromic switching. We have also briefly studied the effects of antimony and tin distribution in the mixed oxide by a sequential preparation method. Lastly, we show here that the optical changes observed by electrically switching these displays are caused solely by changes in absorption coefficient of the ATO and not by any change in diffuse scattering coefficient related to refractive index modulation. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Electrochromism; Doped tin oxides; Printed displays; Interdigitated; Nanoparticles

1. Introduction

We have been engaged in a development program to determine the feasibility of producing low-cost electrochromic displays, for low end applications, utilizing printing technology and interdigitated metallic electrodes, instead of the more conventional transparent electrodes [1–8]. During this work, it was discovered that nanoparticulate doped tin oxides, typically supported on inert, inorganic particles, exhibited significantly different reflectivity in the oxidized vs. reduced states. These supported doped tin oxides were compounded into inks, printed onto interdigitated conductors in the desired shapes and coated with electrolyte to yield simple, printed electrochromic (EC) devices. Fig. 1 shows one of these interdigitated displays: in (a) and (b) the lettering is polarized cathodically and anodically, respectively, at 1.5 V and in (c) the same display is shown in use in a grocery store test. In this shelf unit, two of the displays were mounted back to back in a holder with two “D” batteries and a custom chip driver to cycle the display at 0.5 Hz.

The optical properties of doped tin oxides, or conductive tin oxides (CTOs), have previously been investigated, particularly for their application as heat mirrors since CTO films are transparent to visible light but reflect infrared light [9]. It has been shown that the visible light transparency of conductive CTO films can be altered somewhat by oxidation or reduction [10], and in particular by electrochemically oxidizing and reducing such films. The resulting electrochromic device then functions in a similar way to one based on more common electrochromic materials such as tungsten oxide. However, the electrochromic color change of typical CTO films is relatively small compared to other oxides [10] and, whilst that property is particularly useful for fabricating neutral, transparent electrodes, it is not sufficient to support useful electrochromic devices.

Nanoparticles of some CTOs, particularly antimony-doped tin oxide, supported on inert inorganic particles, such as titania, silica, alumina or aluminum borate, show surprisingly large differences in reflectivity in the oxidized vs. reduced states. Reported here are the contrast ratios for tin oxide doped with a variety of metals, as well as a couple of examples of doped indium oxide. Electrochromism in varying degrees is shown to be a general feature of these nanoparticulate conductive metal oxides. Also reported here are experiments demonstrating the effects of preparation methods on the properties of supported antimony-doped tin oxides (ATOs).

The perceived contrast of reflective displays produced...
from these CTOs may be influenced by a large number of factors as indicated in Fig. 2. We have previously reported the effects of some of these factors, including the observed change in contrast ratio of printed reflective displays as a function of doping level, substrate particle type and firing temperature of the tin oxide [1,2].

During the course of this work we observed that a darkening of antimony-doped tin oxide (ATO)-based displays may be brought about in a number of ways. In addition to cathodic polarization, we observed that significant darkening could occur by the application of a solvent to the dry display, by pressure on the display with electrolyte added or by photochemical exposure. It seems likely that the darkening observed by solvent wetting is a result of a change in the index of refraction of the medium contacting the ATO. The effect of pressure on the film in the presence of aqueous electrolyte, which varies with different substrate particles, might also be the result of the same effect caused by forcing the electrolyte into contact with the ATO particles. This therefore raises a question as to whether the observed electrochromic effect is the result of a change in the environment (and index of refraction and light scattering) at the surface of the ATO particles, as ions are drawn to or expelled from the surface of the particles, or is the result of a change in molar absorptivity of the ATO. Experiments were performed to answer this question.

2. Experimental

2.1. Typical preparation of supported nanoparticulate CTOs

A typical procedure for preparation of a supported CTO follows. A solution of SnCl\(_4\)·5H\(_2\)O (Aldrich 98%, 40 g) in DI water (20 ml) is mixed with SbCl\(_5\) (Aldrich 99%, 25 g) in conc. HCl (20 ml). Alumina (Aldrich, 10 g) is stirred in 200 ml deionized water in a beaker while heating to 90°C. The mixed Sb/Sn chloride solution is added (over a period of about 45 min) from a burette with concurrent addition of 15% NaOH from another burette to keep the pH at 0.8–1.2. After the additions are complete, the pH is adjusted to 2.0, the heat is turned off and the mixture is left to stir and cool for 3 h. Solids are then filtered off and washed with about 1.5 l of water and then dried under vacuum at 60°C for 3 h in air. At the end of the firing time, the sample is removed from the hot oven and allowed to cool quickly in air.

2.2. Preparation of display samples

Inks were prepared by dispersing the appropriate conductive (electrochromic) pigment in a solution of polymer binder, e.g. a 22% solution of fluoroelastomer (Viton) in 2-butoxyethylacetate, with sufficient mixing to give a smooth dispersion. Pigment to binder ratio was typically 2.5:1. The inks were either screen printed or drawbar coated onto interdigitated electrodes that were created by printing silver ink overprinted with a white conductive ink [2]. The ink was dried at 130°C for 10 min. A coating of electrolyte (25% aqueous LiCl containing a polyacrylic acid thickener) was applied and the device was covered with adhesive PET film.

2.3. Contrast ratio measurements

Integrated wavelength contrast ratio measurements were obtained with a Nikon Microphot FXL microscope using a 10× objective in the dark field, reflectance mode as described previously [1,2].

2.4. Optical measurements

Diffuse reflectance spectra were obtained with a Hunter Ultrascan diffuse reflectance spectrometer operating with Hunter Laboratory Universal software, Version 3.0. The system was operated in either the diffuse reflectance mode with specular excluded or in the scattered total transmission mode as was appropriate. For functioning ATO displays, the display, covered with 0.01 in. PET, was mounted directly against the sample port of the reflectance sphere.

The Hunter system was set up to record the diffuse spectrum of the sample using visible light only (400–750 nm). The system was set to record in the diffuse reflectance,
specular excluded (RSEX), mode with a 1/4 in. diameter viewing port. Software spectral correction options were set to TL84 (white fluorescent bulb) illumination, 10° observation and CIE LAB international scales were used to calculate diffuse reflectance properties. The system was calibrated against the Hunter white tile reflectance standard (100% R, Hunter standard number 7684) and black light trap (0% R). The Hunter software could display the spectral data in units of either %Reflectance or Kubelka–Munk (K/S) units. A Kodak #6091 white reflectance BaSO₄ powder standard (99 + %R between 400 and 700 nm) coated with a 0.01 inch thick PET sheet was used as the “100% reflectance display”.

2.5. Index of refraction measurements

Index of refraction measurements of the particulate materials were conducted with the Nikon FXL microscope using the Becke Line Method as detailed by Allen [11] and employing a set of Cargille immersion oils with refractive indices ranging from 1.40 to 2.00.

2.6. Electrical resistivity measurements

Resistivity of powdered samples was measured on pressed samples as previously described [2].
2.7. Crystallography measurements

X-ray diffraction studies were carried out using a Scintag/Seifert PAD V automated powder diffractometer with an ORTEC HyperPure germanium crystal (energy dispersive) detector system.

3. Results and discussion

3.1. Contrast ratios of various CTOs

Previously [1,2] we reported the excellent contrast ratios observed with supported ATO and the manner in which the contrast ratio was affected by varying the Sb dopant level, firing conditions, support material and quantity of ATO on the support. It seemed reasonable that other conducting oxides might also exhibit good electrochromism if prepared in nanoparticle form. Indeed, indium–tin oxide which has little electrochromism in thin film form (hence the widespread use as transparent conductor) was found to have significant electrochromism in particle form, as we have previously described [12]. A series of mixed oxides (mostly doped tin oxides) were therefore prepared in powdered form, compounded into inks, coated onto interdigitated electrodes, coated with electrolyte and evaluated for electrochromic effect. The results of the contrast ratio measurements are displayed in Table 1.

From Table 1 it may be observed that, whilst all of these materials exhibit some degree of electrochromism, none of them provide an integrated contrast ratio close to the ATO sample. The intensity of the ATO color has been attributed, in chemical terms, to an antimony III/V charge transfer complex [13] or, in materials terms, to an accessible antimony energy state in the band gap of the mixed oxide [14]. In the new samples described here, no such states exist and what we observe is a relatively weak electrochromism based on the presence or absence of conduction band electrons. In the case of tin-doped indium oxide, as we described previously [12], there is an accompanying spectral shift resulting in a yellow to blue color change which is visually much more distinct than the integrated contrast ratio would imply.

We would expect that, with further work, it would be possible to identify other examples of nanoparticulate semiconductor materials with properties more akin to the ATO system.

The structure of antimony–tin oxides with high levels of dopant, such as we have used, have been the subject of some disagreement in the literature in terms of the homogeneous distribution of the antimony, or lack thereof. Volta and coworkers claim [15] that solid solutions of up to 40% antimony(V) in tin(IV) oxide may be formed at moderate temperatures. Berry [16] suggests for these high levels of antimony that, whilst there is no separate antimony phase measured in addition to the cassiterite structure, there is some amorphous material present. Another set of experiments was therefore aimed at elucidating the effects of modifying the antimony–tin distribution on the electrochromic properties of the materials. We compared the

Table 1
Contrast ratios of various conducting tin oxides

<table>
<thead>
<tr>
<th>Dopant</th>
<th>At.% dopant</th>
<th>Support</th>
<th>Wt.% support</th>
<th>Contrast ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$^{12}$</td>
<td>20</td>
<td>Al$_2$O$_3$</td>
<td>25</td>
<td>1.4</td>
</tr>
<tr>
<td>F</td>
<td>33</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>98</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>90</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>75</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>75</td>
<td>SiO$_2$</td>
<td>25</td>
<td>1.2</td>
</tr>
<tr>
<td>In/Sb</td>
<td>90/10 (no Sn)</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>100 (no Sn)</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In/Eu</td>
<td>90/10 (no Sb)</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>0.5</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>43</td>
<td>SiO$_2$</td>
<td>25</td>
<td>6.8</td>
</tr>
</tbody>
</table>

*Remainder Sn(IV).

Table 2
Effect of order of deposition of metal hydroxides on alumina support (75% ATO–25% alumina; Sn(57%) Sb(43%); 600°C/3 h)

<table>
<thead>
<tr>
<th>Order of deposition</th>
<th>Crystallite size (Å)</th>
<th>Resistivity ($\Omega$ cm)</th>
<th>Contrast ratio</th>
<th>Pyrochlore phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb first</td>
<td>55</td>
<td>6.1</td>
<td>2.3</td>
<td>Yes</td>
</tr>
<tr>
<td>Sn first</td>
<td>32</td>
<td>133</td>
<td>3.0</td>
<td>Yes</td>
</tr>
<tr>
<td>Simultaneous</td>
<td>50</td>
<td>11.1</td>
<td>6.8</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 3
Effect of added NaCl to ATO

<table>
<thead>
<tr>
<th>% Added NaCl</th>
<th>Resistivity ($\Omega$ cm)</th>
<th>Light state</th>
<th>Contrast ratio</th>
<th>Cassiterite crystallite size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12</td>
<td>Dark gray</td>
<td>6.8</td>
<td>50</td>
</tr>
<tr>
<td>1</td>
<td>33</td>
<td>Dark gray</td>
<td>7.0</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>290</td>
<td>Light gray</td>
<td>4.5</td>
<td>45</td>
</tr>
<tr>
<td>10</td>
<td>5680</td>
<td>Light gray</td>
<td>3.4</td>
<td>45</td>
</tr>
</tbody>
</table>
properties of a sample where the antimony and tin (43/57%) were co-precipitated onto alumina in the usual way with two other samples where the antimony and tin were precipitated sequentially in different order. Properties of the resulting powders after firing are shown in Table 2.

Several points are apparent from Table 2, the first of which is that electrochromic contrast is clearly better in the case of the “homogeneous” sample where the antimony can make the greatest electronic contribution to material properties.

The second observation is that, since all three samples are clearly different from one another, the antimony and tin have not completely interdiffused under the conditions of this experiment. Crystallite size is smallest in the case of the initially precipitated tin: this may be interpreted as the effect of an outer layer of antimony oxide in preventing agglomeration of the initially formed tin crystallites. A separate antimony pyrochlore phase is observed in this sample and it is presumably this, which is also responsible for the relatively high electrical resistance.

With antimony precipitated first, a coating of partially doped tin oxide is expected to form the outside of the material: this seems to be confirmed by the observation of the lowest electrical resistance of all three samples. Further, it also seems that some agglomeration of the exposed tin oxide is occurring since crystallite size is significantly larger in this sample. As expected for a tin oxide sample with a low level of antimony dopant, contrast ratio is low.

Our conclusion from these experiments is that a homogeneous distribution of high levels of antimony dopant is possible and is required for optimal electrochromic properties.

3.2. Effects of modifications of ATO synthesis procedure

It was postulated that by adding salts to the metal oxide precursor, before firing, it might be possible to improve electrochromic properties by facilitating the access of ions to the metal oxide by “building in” ionic pathways during firing. Thus the synthesis of ATO was modified by adding sodium chloride to the oxide before firing. The composition of the ATO not including NaCl was 43:57 atomic ratio Sb:Sn and 75 wt% ATO on 25 wt% alumina. The effects on contrast ratio of added NaCl to the oxide are presented.
in Table 3 along with dry powder resistivity and color of display samples in the oxidized or light state.

As Table 3 shows, the addition of NaCl to ATO results in lower electronic conductivity in the dry state and lighter color of the oxidized state in an operating EC device. One may speculate that NaCl collects at the grain boundaries of the ATO, resulting in lower electronic conductivity. Alternatively, the addition of salts could affect the final average oxidation state of the antimony dopant: more highly oxidized antimony would give not only a lighter color but a lower electron density leading to decreased electrical conductivity. The lighter color of the oxidized state of the material may also be the result of a modification of the light scattering properties of the ATO composite, thus increasing the reflectivity of the surface. At the higher loadings of NaCl a modest decrease in average crystallite size is observed.

Another series of experiments was performed in order to determine the effect of changing the ionic content of the ATO by varying the final pH used in the preparation of ATO deposited on alumina. The results of these experiments are shown in Table 4.

A number of trends are apparent from Table 4. As the pH of the preparation is increased from 2 to 7, sodium ions are exchanged into the ATO, ultimately resulting in the partial formation of a separate, electrically insulating ilmenite phase. With increasing sodium content, electrical resistivity increases, cassiterite crystallite size decreases, the samples become lighter in color and contrast ratio declines, as we observed with the addition of sodium chloride. Thus, unfortunately, neither of these attempts to ionically modify the ATO for improved electrochromic properties were successful.

3.3. Optical studies of ATO

As indicated above, printed ATO surfaces could be darkened by several treatments including contacting the surface of a dry coating with organic solvent such as butoxyethylacetate, pressing on a surface covered with aqueous electrolyte or by making the electrolyte covered surface cathodic. Examples of each of these effects are shown in Fig. 3 for “test square” displays based on antimony–tin oxide on an aluminum borate substrate (Mitsui Passtran 5210), for which the non-electrochemical coloring effects were the strongest. In (a) is shown the electrochemical switching (center cathodic), in (b) the effect of solvent drops (2-butoxyethyl acetate) and in (c) the effect of “writing” by pressing on the polyester film on top of the electrolyte.

Since it seems apparent that the darkening caused by the addition of solvent to the dry surface is a physical, rather than chemical, effect, as is the darkening due to pressure, it seemed possible that the darkening caused by electrical switching might also be caused by purely physical changes. One might imagine a significant index of refraction change as ions and associated solvents are moved to or from the surface of an ATO crystallite. The following experiments were performed in order to better define the actual cause of reflectivity change in electrical switching of the nanoparticle ATO devices.
The physical model which best describes the appearance of a relatively opaque layer of particulate solids is that describing the diffuse reflection of light by an “infinitely” thick\(^1\) layer of compacted particles. Two key variables in this model are: the linear absorption coefficient, \(k(l)\) and the linear scattering coefficient, \(s(l)\). Both coefficients have units of \(\text{cm}^{-1}\). The relationship between these two coefficients and the observed reflectance of diffusely scattered light, \(R(l)\), from an “infinitely” thick layer of sample is given by the Kubelka–Munk equation as discussed by Kortü m [17] (among others):

\[
f(R_{\infty}(\lambda)) = \frac{(1 - R_{\infty}(\lambda))^2}{2R_{\infty}(\lambda)} = k(\lambda)/s(\lambda).
\]

This is the simplest expression for relating the observed spectral dependence of the reflectivity of a compacted powder and its optical parameters.

The key factors affecting the linear absorption coefficient \(k(\lambda)\) (\(\text{cm}^{-1}\)) are the wavelength dependent molar extinction coefficient (mmol cross-section), \(\varepsilon(\lambda)\) (\(\text{cm}^2/\text{mmol}\)), and the molar concentration of the absorbing species \(c\) in mmol/cm\(^3\).

Thus linear absorption coefficient \(k(\lambda)\) (\(\text{cm}^{-1}\)) is defined as the product of these two variables:

\[
k = \varepsilon(\lambda)(\text{cm}^2/\text{mmol})c(\text{mmol/cm}^3)
\]

The linear scattering coefficient \(s(\lambda)\) (\(\text{cm}^{-1}\)) is much more complex. Some of the key factors given by Kortü m [17] which affect \(s(\lambda)\) (\(\text{cm}^{-1}\)), as derived from the Mie theory of light scattering, are as follows:

\[
s \propto \frac{1}{d}\text{ where } d\text{ is the diameter of the particles,}
\]

\[
s \propto (1/\lambda)^n\text{ for } d < 2\ \mu\text{m}
\]

\[
s \neq f(\lambda)\text{ if } d > 2\ \mu\text{m}
\]

\[
s \propto \text{volume packing coefficient (ratio of the powder density to the true sample density)}
\]

\[
s \propto \Delta n(\lambda)\text{ where } \Delta n(\lambda)\text{ is the difference between the index of refraction of the particle and the surrounding medium. } \Delta n(\lambda)\text{ can be quite wavelength dependent for semimetallic materials and/or materials having an absorption band in the middle of the spectrum under observation.}
\]

In general, an attempt to quantitatively compare the reflectance properties of two different ATO display devices will require some knowledge about all the parameters affecting both \(k\) and \(s\) such as molar extinction coefficients, molar concentrations (volume packing coefficients), sample thickness, particle size distributions, and indices of refraction of both the ATO and the medium surrounding the ATO. Alternatively, the effect of various parameters on the diffuse reflectance properties can be studied by holding all other parameters at fixed values in the two experiments. This is particularly important when comparing ATO supported on metal oxides of differing (and often very high) indices of refraction.

The CIE Lab values obtained from the diffuse reflectance spectra obtained on the Hunter spectrometer were selected as a valid measure of the reflectance of the display to be...
used for comparison with the microscopic measurements of the reflectance of the same display and based upon the following considerations:

1. The reflectance measurement obtained with the microscope operating in the dark field, reflectance mode represents an integrated value for visible light diffusely reflected by the display and detected by the silicon detector. The reflectance across the entire visible spectrum is weighted more towards the red/near IR by the output characteristics of the tungsten illumination and the red spectral sensitivity of the silicon detector. In this case a reflectance value of the sample is given by the ratio:

\[
\% \text{Reflectance} = 100 \frac{R}{R_0}
\]

where \(R_0\) is the reflectance of the white standard.

2. The CIE Lab \(L^*\) value measured with the Hunter instrument also represents an integrated reflectance measurement, but in this instance weighted toward the green part of the visible spectrum, and mathematically weighted to match the visual “lightness perception” response of a human observer. In this case a \(L^*\) value is given by the expression:

\[
L^* = \frac{116(Y/Y_n)^{1/3}}{Y_n}
\]

where \(Y\) is the ordered weighted tristimulus \(Y\) value of the sample and \(Y_n\) is the ordinate weighted tristimulus \(Y\) value of the standard illuminate. In this case the TL84 (white fluorescent light) illuminate was chosen based on the assumption that the displays would be viewed most times in a fluorescent light environment.

Thus the microscopically measured total \%Reflectance differs from the \(L^*\) values measured on the Hunter diffuse reflectance spectrometer both in the spectral weighting of the results and in the mathematical algorithm used to calculate reflectance ratios. The values calculated by the two different methods scale together but in a nonlinear way. Either method may be used to mathematically characterize the electrochromic display, but the values calculated by the two different methods are not interchangeable!

Three variables can have a direct effect on the \(k/s\) spectrum. (1) A change in concentration of the absorbing species (free charge carriers, Sb\(^{3+}\), etc.). (2) A change in the molar extinction coefficient through the creation of a new absorbing species. (3) A change in the index of refraction mismatch which might occur with the creation of a new absorbing species with its own new extinction coefficient. All other parameters (i.e. particle size, powder packing density, total Sb concentration, etc.) known to affect the diffuse reflectance of the display can be considered to be held constant when comparing the optical properties of a device being switched between light and dark states.

To separate the variables listed above, one must obtain independent measurements of \(k(\lambda)\) and \(s(\lambda)\). This may be accomplished by comparing the measurements of diffuse reflectance of both dark and light states of a thin, semi-transparent ATO device with transparent back electrode and black backing surface \((R_0(\lambda))\) and an infinitely thick ATO device. The \(R_\infty(\lambda)\) (and \(R_0(\lambda)\) spectra are then used to calculate \(k(\lambda)\) and \(s(\lambda)\) independently for each of the switched states using the following relationships \([17]\):

\[
k(\lambda)/s(\lambda) = (1 - R_\infty(\lambda))^2/2R_\infty(\lambda)
\]

\[
a = 1/2(1/R_\infty(\lambda) + R_\infty(\lambda))
\]

\[
b = 1/2(1/R_\infty(\lambda) - R_\infty(\lambda))
\]

\[
s(\lambda)d = (1/b)\text{ctgh}[(1 - aR_\infty(\lambda)/bR_\infty(\lambda))]
\]

A measure of \(d, R_\infty(\lambda),\) and \(R_0(\lambda)\) is sufficient to determine both \(k(\lambda)\) and \(s(\lambda)\) in both the light and dark switched states. The diffuse reflectance spectra of light and dark states of semitransparent and infinitely thick devices were recorded (Fig. 4 shows the spectra of the infinitely thick sample). The spectra were transferred to an EXCEL spread sheet for calculation of \(k(\lambda)\) and \(s(\lambda)\) for both light and dark states. These are plotted in Fig. 5. While there is much noise in the spectra, the \(s(\lambda)\) values are equivalent for the light and dark states, whereas, the \(k(\lambda)\) values increase by a factor of 4 or 5 going from light to dark states. This indicates that the color change in ATO displays is due directly and solely to a change in the linear absorption coefficient \(k(\lambda)\).

If the electrochemical alteration of the ATO was altering the index of refraction of the particles and ultimately its linear scattering coefficient, \(s\) (cm\(^{-1}\)), then a measurement of the index of refraction of the particles in the two switched states should bear this out. Such measurements have been made by Stjerna et al. \([18]\) on pure, thin transparent films of ATO where transmittance and reflectance data have been used to calculate the wavelength dependence of the index of refraction. \(\eta(\lambda)\) of SnO\(_2\) (and (Sb,Sn)O\(_2\)) at % Sb. They find that sputtered SnO\(_2\) films have an index of refraction of ca. 2.0 (vs. 2.006, 2.0972 for cassiterite) while 4 at.% Sb in SnO\(_2\) films has a highly dispersive index of refraction ranging from 2.05 in the blue to 1.85 in the deep red. (The antimony oxides have variable indices of refraction between 2.00 and 2.35 depending upon oxidation state and mineral structure.)

To date, no index of refraction measurements have been reported for powdered ATOs or ATOs supported on powdered substrates such as silica, alumina or titania. It is not possible to conduct such measurements on diffusely scattering, powdered ATO in functioning electrochromic devices of the type described here. The best that can be done is to measure the index of refraction of the powdered material separate from an assembled electrode. To this end, the index or refraction was measured on ATOs supported on silica. The supported ATO contained 75% by weight (45.7 mol%) silica shell and 25% by weight (54.3 mol%) (Sn,Sb)O\(_2\). The ATO was 43 at % in Sb. Portions of the sample were treated with SnCl\(_2\)/HCl to reduce the ATO to its dark state, and part treated with Chlorox bleach to
oxidize the material to its light state. The indices of refraction of the as prepared ATO silica shell and amorphous silica shell precursor (Dupont TLF88220) were measured by optical microscopy using Cargill index of refraction oils and the Becke line method. The index of refraction measurement results are as follows:

- Dupont silica shell (TLF 8822) = 1.42–1.43.
- ATO/\(\text{Si}_2\) (Chlorox bleached) = 1.62–1.63.
- ATO/\(\text{Si}_2\) (SnCl\(_2\) reduced) = 1.62–1.67.
- ATO/\(\text{Si}_2\) (as received) = ca. 1.65.

Within the index of refraction range recorded, there are no significant differences between the index of refraction of the oxidized and reduced silica supported ATO powders. This observation supports the previous conclusion that changes in the optical contrast of the ATO device are NOT due to changes in scattering coefficient, \(s(\lambda)\).

One final qualitative way of determining whether changes in the diffuse absorption coefficient or in the diffuse scattering coefficient dominate the change in optical contrast when the EC is switched, is to observe the device with an optical microscope using both transmission and dark field reflectance observation (equivalent to diffuse only, obliquely illuminated sample). For this experiment, the EC device must be constructed with a transparent back electrode so that the system may be viewed in transmitted as well as reflected light. Also the ATO layer must be thin enough to permit the transmission of light so that a comparison can be made between dark field reflectance and bright field transmission of an EC device undergoing switching.

This was accomplished using the same semi-transparent ATO EC device used for the reflectance measurements. The electrode was mounted in the NIKON FXS microscope and viewed with a \(10 \times\) objective in the dark field mode. Illumination was switched back and forth between reflectance and transmittance while the area of the display being viewed was switched back and forth between light and dark states by the application of \(\pm 1.5\) V DC. The results show that in the dark state, the ATO is dark in both diffuse and transmitted light, while both transmission and reflection become lighter on voltage reversal. This observation is consistent with the conclusion that the voltage switching of the EC device is changing the diffuse absorption coefficient, \(k(\lambda)\), of the ATO and voltage switching does not affect the diffuse scattering coefficient, \(s(\lambda)\).

4. Conclusions

From the work described here, we may draw the following conclusions regarding electrochromism in nanoparticulate, doped tin oxides.

Of the dopants studied, none thus far has shown an electrochromic effect comparable to antimony. This is attributed to the presence in the antimony–tin oxide band gap of energy states for antimony just below the conduction band which are populated/depopulated on electrochemical switching. Such states are absent in the other oxides.

Sequential precipitation experiments seem to support the formation of a homogeneous antimony–tin mixed oxide at high (43%) dopant levels under our conditions. Physical properties are changed significantly by sequential, rather than simultaneous, deposition of the component metals and the maximum electrochromic effect is observed in the homogeneous sample.

Attempts to ionically modify the antimony–tin oxide, either by the addition of sodium chloride before firing or by changing the pH of formation, did not significantly improve the electrochromism but did modify physical properties.

It was shown conclusively, with three different approaches, that the electrochromic effects observed in this work were caused solely by changes in the linear absorption coefficient, \(k(\lambda)\), of the composite particle and not by modification of the linear scattering coefficient \(s(\lambda)\).

References


