Fabrication of WO₃-based electrochromic displays using solid or gel-like organic electrolytes

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Abstract: New all solid-state electrochromic displays were fabricated by chemically vapor depositing and patterning a tungsten oxide film on SnO₂:F covered glass substrates. Aluminum sheets were used as counter electrodes to form electrochromic displays using solid or gel-like organic electrolytes. These ionically conductive and electronically insulating electrolytes were based on poly(methyl methacrylate) (PMMA) and poly(2-hydroxyethyl methacrylate) (PHEMA) into which phospho-tungstic acid was added at various concentrations. In some devices the electrolyte was formed by addition of photoacid generator into the polymeric matrix and exposure at deep UV light. It was found that displays exhibit an intense, reversible electrochromic effect with reflectivity varying by a factor of five between the uncolored to the colored state. The coloring voltage depends strongly on the polymeric matrix, the thickness of the electrolyte and post-apply baking conditions and is of the order of 6-9V. The response time was found to be of the order of 500 ms; coloration and bleaching times were comparable.

1. Introduction
Electrochromism is defined as a reversible change in the transmittance and/or reflectance of a material caused by the application of an electrical current or potential. Its potential applications include smart windows [1] for the modulation of the incoming light and in large area displays [2]. Electrochromism is exhibited by a variety of organic [1, 3] and inorganic materials [1] in bulk and film form. Among the inorganic electrochromic films the most studied are those of WO₃ since they provide a memory effect, good contrast, high coloration efficiency and low switching voltage [4]. It has been suggested that electrochromism in WO₃ films is divided in two parts [5, 6]: a fast electronic one, during which the film is colored by electronic injection and a slower one associated with the insertion of ions in it. In this paper the fabrication of an electrochromic displays based on chemically vapor deposited (CVD) WO₃ films and novel solid or gel like electrolytes is described. Electrochromic performances are investigated and discussed when biased with DC voltages.

2. Experimental
For the fabrication of electrochromic displays, W films were chemically vapor deposited on commercially available SnO₂:F covered glass substrates by decomposing W(CO)₆ vapors at a pressure of 0.1 Torr and a temperature of 400 °C [7]. After deposition the W films were patterned with AZ 5214™ photoresist, etched using aqueous solutions containing tetra-methyl ammonium hydroxide...
(TMAH) [8] and oxidized to WO$_3$ in oxygen at 600 °C. Transparent electrochromic displays, like those shown in figure 1, were formed using another SnO$_2$:F covered glass substrate as counter electrode and solid or gel-like polymeric electrolytes formed as follows. In a polymeric solution composed either by poly-methyl methacrylate (PMMA) in methyl-iso-butyl ketone (MIBK) at concentrations of 2 or 4 % w/w or poly-hydroxy-ethyl methacrylate (PHEMA) in ethyl-lactate at a concentration of 2% w/w, phosphotungstic acid hydrate was added at concentrations varying between 1:1 to 1:8 of polymer mass. Displays using gel-like electrolytes were formed by dipping the electrochromic (EC) glass/SnO$_2$:F/WO$_3$ “sandwich” in the above solutions and then the counter electrode was pressed on the electrolyte. Solid electrolytes were applied by spinning electrolytes on the EC “sandwiches” at 2000 rpm followed by bake at 80 °C for min.

A Perkin-Elmer Lamda 40 spectrophotometer running the WinLab software was used to record the optical transmission spectra of electrochromic devices within the range 300 to 1000 nm.

3. Results and Discussion
In figure 2 typical reflection spectra are shown for WO$_3$-based EC displays using as electrolytes PMMA solutions 8% in MIBK containing acid at concentrations 1:1 (left) and 1:8 (right) of the polymer mass and Al sheets as counter electrodes. Spinning and curing as described before was used to deposit electrolytes. Displays were colored at various degrees with various voltages. For each measurement a DC voltage was applied on the display, which was remaining throughout the duration of the measurement (about 2 min). It can be observed that the reflection of the displays can be varied gradually and reversibly to the half of the initial value with a

![Figure 1. An electrochromic display in its uncolored (left), lightly (middle) and highly colored (right) state.](image1)

![Figure 2. Reflection spectra of electrochromic displays based on WO$_3$ films and using as electrolytes films applied by spinning from PMMA solutions 8% in MIBK containing acid at concentrations 1:1 (left) and 1:8 (right).](image2)
voltage of 4 V. Moreover, it seems that the degree of coloration does not depend on the concentration of acid. It must be pointed out that for displays using such electrolytes coloration and bleaching times were comparable and equal to approximately 500 ms. This is contrary to what has been observed for EC displays using liquid electrolytes and may be explained assuming that after insertion of the protons generated from the acid decomposition in the electrolyte film into the WO₃, the last remains charged. This creates an internal electric field, which superimposes to the bleaching voltage facilitating this process.

![Figure 3](image-url) Reflectance spectra of electrochromic displays based on WO₃ films using as electrolytes films of PMMA solutions in MIBK 4 % (left) and 8 % (right). The acid concentration for both displays was the same and equal to 1:4.

When the concentration of PMMA in the solution decreases the thickness of the electrolyte film also decreases. The EC displays using electrolytes containing PMMA at 4% need higher voltages to color at the same degree as displays using electrolytes containing PMMA at a concentration of 8% and similar acid concentrations as shown in figure 3. The thicknesses of the electrolyte films were 1 and 0.5 μm, respectively. Displays using electrolytes with low PMMA content are very hard to bleach. This result is somehow curious since thinner films means that higher voltages are applied on the mobile ions so the coloration and the bleaching, which are associated with the insertion and the extraction of these ions in and out of the WO₃ film respectively, should have to be facilitated. The phenomenon does not seem to be related to the lack of mobile ions in the thinner films since coloration occurs, hence it is rather related to the ionic mobility. Indeed, thinner PMMA films are easier to solidify at the curing temperature of 80 °C than thicker ones and this solidification implies a drop of mobility of ions.

![Figure 4](image-url) Reflectance spectra recorded on an EC display using gel-like electrolyte composed of PHEMA added phosphotungstic acid hydrate (1:2) 0.25 μm thick.
In figure 4 reflectance spectra taken on an EC display using as electrolyte PHEMA 2\% in ethyl-lactate containing phosphotungstic acid at a concentration 1:2, colored and bleached with various voltages are shown. It can be seen that the voltages involved are higher than those used for PMMA-based displays. The thin electrolyte film was solidified and this is a possible explanation for the high voltages needed for the coloration of this display. Another possible explanation is that protons produced by the acid, the incorporation of which into the WO$_3$ causes the coloration, are now captured by the hydroxyl ions of the PHEMA.

![Figure 4](image1.jpg)

Figure 5. Reflectance spectra recorded on an EC display using gel-like electrolyte composed PMMA 4\% added phosphotungstic acid hydrate at a concentration of 1:2.

In figure 5 reflection spectra taken at the fully colored and bleached states on a display in the beginning of its operation and after 24 hours of operation are shown. It can be seen that the curves do not entirely coincide and this is probably due to protons that remain into the WO$_3$ film after every coloration cycle. However, in agreement with results made using liquid electrolytes the long-time use renders displays faster [9].

4. Conclusions
EC devices based on WO$_3$ LPCVD films have been fabricated using lithographic and etching techniques standard in Si technology and solid and gel-like electrolytes. A clear reproducible and stable electrochromic effect was observed on all devices. Devices using gel-like electrolytes exhibited a faster coloration and bleaching and at lower voltages than those using solid electrolytes. Coloration and bleaching times were comparable due to the creation of an internal field after insertion of protons in the WO$_3$ film, which superimposes on the bleaching voltage.

5. References
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