Fabrication of electrochromic displays by chemically vapor depositing and patterning WO_3 films on SnO_2:F covered glass substrates

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It has been suggested in the past (1, 2) that electrochromism in WO_3 films is divided in two parts: 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. The presence of electrons only in the WO_3 film causes the splitting of the conduction band in two sub-bands (the so-called Hubbard bands (1, 2)). Electronic oscillations between these two bands cause photon absorption leading to film coloration. In this work the fabrication of electrochromic displays based on chemically vapor deposited (CVD) WO_3 films is described. Their electrochrromic performance is reported and discussed when biased with DC and AC voltage, in view of the above suggestion.

For the fabrication of electrochromic devices, W films were deposited on commercially available SnO_2:F covered glass substrates. Depositions were carried out in a horizontal, radiativelly heated CVD reactor at low pressure (0.1 Torr) at 400 ^oC, from decomposition of $W(CO)_6$ vapors. After deposition the W films were patterned with AZ 5214^{TM} photoresist using various photomasks, and etched with aqueous solutions containing tetra-methyl ammonium hydroxide. The patterned W layers were oxidized to WO_3 in a horizontal furnace at temperatures varying between 550 and 650 ^oC and at various times dependent on film thickness. Electrochromic devices were formed using another SnO_2:F covered glass substrate as counter electrode and a 1M H_2SO_4 aqueous solution as ionic conductor. In Fig. 1 a photograph of such a colored display is shown.

Fig. 1. A colored electrochromic display

For the response measurements a setup shown schematically in Fig. 2 was used. For the measurements the sample was placed on the beam of a laser diode (λ=632,8 nm) and was power supplied with a pulse generator. The signals from the generator and the photo-detector were driven trough a programmable card to a personal computer for processing.

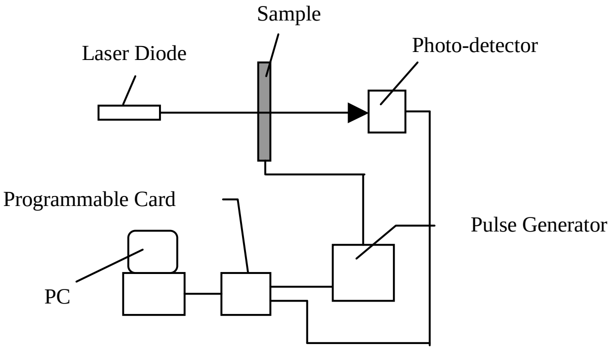

Fig. 2. Schematic of the setup used for the measurement of the response of the electrochromic devices.

It must be pointed out that the coloration of the device was faster than the bleaching. Typical coloration times to the half of the initial transmission were of the order of 0.5 sec while for the bleaching at least 10 sec were needed. This can be explained assuming that after powering the device, electrons are rapidly injected into the conduction band of the WO_3 film leading to a fast coloration. During this period, similarly to all electronic devices, the electrochromic device is out of equilibrium and the overall electric neutrality is assured by the formation of a Helmholtz (depletion) region in the electrolyte. Simultaneously, ions are injected into the film enhancing further the coloration. When the polarization is inversed, again a fast initial bleaching occurs related with the rejection of the electrons from the WO_3 film back to the SnO_2:F film. This initial fast part of bleaching is followed by the rejection of ions back to the electrolyte, which is a slower electrochemical reaction, hence the longer times needed for the complete bleaching of the device. In order to separate these two parts we polarized our electrochromic devices with square pulses with various frequencies using the setup shown in Fig. 2. Results for 0.64 Hz are shown in Fig. 3. It is observed that When the WO3 film is positively polarized starts to color and the light intensity measured by the photo-detector decreases. This decrease is not linear. During approximately one quarter of the polarization period light intensity decreases from 275 to 150 and during the next quarter from 150 to 100 units. Similarly, the bleaching occurs in two steps; an initial fast followed by a slower one. At higher frequencies coloration and bleaching seem to vary linearly with the time of polarization.

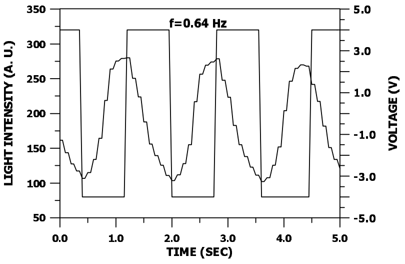

Fig. 3. Response of an electrochromic device when polarized with square pulses with frequencies of 0.64 Hz measured with the setup of Fig. 2. Light intensity refers to the signal measured by the photo-detector.

In conclusion, the electronic and ionic-related parts of electrochromism can be separated in devices based on WO_3 LPCVD films applying on the devices alternative polarizations of various frequencies. Taking advantage of this possibility one can fabricate electrochromic devices with high or slow response times.

1. A. Donnadieu, D. Davazoglou and A. Abdellaoui, Thin Solid Films 164, 333-338 (1987).
2. D. Davazoglou and A. Donnadieu, Thin Solid Films 164, 369-375 (1987).