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ELECTROCHROMIC COPPER(I) OXIDE THIN FILM AS A CANDIDATE FOR SMART WINDOW

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Abstract: Electrochromic materials are able to reversibly change their colour when placed in a different electronic state. Such materials have a broad range of commercial applications. The most desired application are smart windows - windows with electrochromic thin film coatings that allow them to darken and lighten upon the application of a very small electric voltage and are the next significant advance in window technology for energy efficiency and comfort enhancement.Semiconducting copper(I) oxide, Cu_2O, films were prepared by electrodeposition method onto transparent conductive glass substrates. Those films revealed significant difference in transmittance in their coloured and bleached state, with an average relative modulation of about 53%, so they could be a candidatefor windowcoatings to control the inlet of sun light and heat.
Keywords: electrochromism, copper(I) oxide, electrodeposition, smart window

INTRODUCTION

Optically active (chromic) materials, such as thermochromic, photochromic and halochromic materials, change their colour reversibly when they are placed in a different environment (temperature, exposure to electromagnetic radiation, pH of the solution, respectively). One of the most useful form of chromism is electrochromism, discovered in 1969 by S. K. Deb. Electrochromic materialsare able to reversibly change their colour when voltage is applied across it. Electrochromic materials possess different colour in their reduced (when absorbing an electrons) and oxidized (electrons are ejected) state. They can be divided into two classes, depend on the potential where the colouration process occurs: cathodically and anodically colouring materials. Catodically colouring substances possess a reduced coloured state, i.e. they colour at the negative potential, while anodically colouring materials are those with an oxidized, coloured state, i.e. they colour when a positive potential is applied. Electrochromism is well known in numerous inorganic and organic substances [1]. Almost all of the interesting materials are oxides that are employed in the form of thin film. Electrochromism in different materials is strongly related to the method of preparation, i.e. it is affected by structure, stoichiometry, binding condition, and water content in the film.

The principle of monitoring the changes in color of selected materials by controlling their electrochemical reactions and its technological implications were first recognized in the early seventies and the route for their utilization for the fabrication of electrochemically driven optical displays was opened. There are many uses of materials whose optical properties can be varied reversibly and persistently by a low-voltage signal. The four main applications of electrochromic devices are:

- information display,
- electrochromic smart windows,
- variable emittance surface (infrared reflecting/absorbing surface, i.e., the thermal emittance is low/high) and
- mirror with variable specular reflectance.

Electrochromic (EC) smart windows are architectural or automotive windows with coatings that allow them to darken and lighten upon the application of a very small electric voltage, windows with variable transmittance so that a desired amount of visible light and/or solar energy is introduced. This application seems to be the most mature one. We all want the houses we live in and the buildings we work in more energy efficient, to the point where air conditioning isn't necessary. We can insulate the walls and the roof of a building easily, but windows are a problem area. We need

them to allow light into a building, so we can't insulate them with typical non-transparent insulation materials. Sunlight streaming through a window can really heat up a room. In thewinter we tend to welcome that extra warmth. But in thesummer, that heat increases cooling costs. Early studies at Berkeley Lab suggested EC smart windows could reduce a commercial building's annual energy use 15 to 25 percent [2]. According to computer simulations of building performance in the National Renewable Energy Laboratory of U.S. Department of Energy, the electrochromic windows [3]:

» reduce electricity consumption for cooling by up to 49 percent;
» lower peak electrical power demand by up to 16 percent; and
» decrease lighting costs by up to 51 percent.

As of today EC windows are still in an early stage of technological development. Only a few manufacturers offer commercial products. The technology is still expensive. The cost can be reduced using cheaperelectrochromic materials and by refining the manufacturing process. Today's thin film deposition equipment is the same one that's used to make flat panel displays and thin film solar panels and is much better than that used a few decades ago, when the electrochromic window concept emerged.

Electrochromiccopper(I) oxide thin filmsare appropriate for use in electrochromic smart windows because of the abundance of starting material and its cost. Copper(I)oxide (Cu_2O) thinfilms have been subject of numerous studies as a candidate for solar cell application. It has been recently found that these oxide thin films exhibit cathode electrochromism [4-8], i.e. they are transparent for visible light in their oxidized state, and almost black when switched to their reduced state.

Copper(I) oxide thin films could be made by different techniques: sputtering, chemical bath deposition, electro-deposition, sol-gel-like dip technique, thermal oxidation, anodic oxidation, etc.

The subject of this research were the electrochromic thin cuprous oxide films prepared by a electrodeposition method described by other authors [9], onto a fluorine doped tin oxide (SnO_2:F or FTO) pre-coated glass substrates.

EXPERIMENTAL DETAILS

A conductive and transparent fluorine doped tin oxide electrode was produced onto microscopic glass slides (25x75x1 mm) using the spray pyrolysis method [6]. The FTO deposition on glass requires previous degreasing of the glass slides in a mixture of chromic and sulphuric acid for 24 hours. The substrates were then rinsed with distilled water and wiped off with a cotton wool. The spraying of 300 ml 0.05 M aqueous solution $SnCl_2 \cdot 2H_2O$ was performed with a commercial BOSH paint sprayer. The fluorine doping was done by adding NH_4F to the solution, until neutrality was achieved. The spraying intervals were adjusted to about 1 s with pauses of about 5-6 s between. The spraying lasted about 20-30 min, until all the spraying solution was depleted. The substrate temperature was maintained constant at 400°C. Such prepared FTO was about 2 μm thick, 80% transparency for the visible light, with sheet resistance 18-38 Ω/sq [7].

The prepared FTO substrates were subjected to the electro deposition method of Cu_2O films. Besides the convenience of this method for obtaining thin films of copper(I) oxide on the transparent conductive glass, which is one of the conditions for examining the electro-chromic properties of thin films, the method of electrochemical deposition was selected because of its efficiency. The thickness and quality of the deposited film can be controlled during the electro-deposition. Deposition was performed with classical electrolysis, which makes this method simpler and more economical. The electrolysis container was placed in a large bowl with water (water bath) with a thermostat. The water bath provided a constant temperature for the electrolyte solution during electrolysis. The temperature of the electrolyte was an important requirement for the deposition of high-quality films. During the electrolysis, the temperature was maintained at 60°C. A copper clad for printed circuit board, with a thickness of 50μm, with dimensions 25x75 mm was used as the anode. The electrolysis solution was prepared from 64 g/l (0.4 M), anhydrous copper sulfate, $CuSO_4$, 242 g/l (2.7 M) lactic acid $C_3H_6O_3$, and about 125 g/l (or 3.1 M) sodium hydroxide, NaOH. The voltage between the cathode and the anode during operation was maintained in the range of 0.5 to 0.6 V, with a current density of 0.8 to 1 mA/cm^2.

Cleanliness of the surface of the anode and the cathode was very important for the quality of film formed as well as its adhesion to the substrate. Therefore, the anode was first cleaned mechanically and then chemically. Then the plate was cleaned with liquid detergent, washed with distilled water and dried. Prior to immersion in the electrolytic solution, the plates were cleaned with alcohol. Transparent conductive glass was used as the cathode. The process of cleaning it was the same as in other methods for deposition of thin films of copper(I) oxide, using chromosulfuric acid.

The thickness of the films obtained by this method, determined by gravimetric method, was about 200 nm.

The composition and crystal structure of the films were studied by X-ray diffraction (XRD) by Cu K_α radiation at wavelength $1.54 \cdot 10^{-10}$ m, with a Siemens D-500 diffractometer.

In order to examine the electrochemical behaviour of the electrodeposited Cu_2O films, an Electrochromic Test Device (ECTD) was designed (Fig. 1). It consisted of a transparent glass cuvette with a 0.1 M $LiClO_4$ aqueous solution electrolyte in which two electrodes were immersed. The working electrode represented the copper (I) oxide thin film onto FTO coated glass, whereas the counter electrode was FTO coated glass.

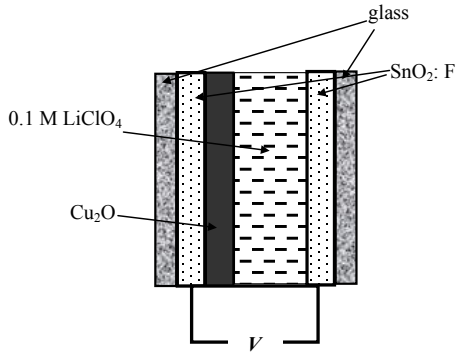

Figure 1. The cross-section of the so-designed ECTD

Devices are designed in such a way that they shuttle ions back and forth into the electrochromic layer with applied potential. When a voltage is applied between transparent electrical conductors ions are moved uniformly into and out of the electrochromic film. The charge-balancing counterflow of electrons through the external circuit then leads to a variation of the electron density in the electrochromic film and thereby a modulation of their optical properties, which remain stable for a long period of time.

The optical properties of the Cu_2O films were studied with a Varian CARY 50 Scan UV-Visible spectrophotometer, in the wavelength range from 300 to 800 nm. The visible transmission spectra were taken in-situ (the Cu_2O film incorporated as a working electrode into the ECTD) for the following film states: as prepared, coloured and bleached. The blank probe data were taken as the working electrode from the ECTD was replaced with FTO/glass electrode, so that the transmission spectrum could be normalized to 100%. The coloration and the bleaching of the cuprous oxide thin films were performed by application of a voltage - 1 V and + 1 V respectively.

RESULTS AND DISCUSSION

The films prepared by the electrodeposition method revealed cathode electrochromism, i.e. they showed coloration at a negative voltage, and bleaching at positive. The XRD pattern of the as deposited film onto the FTO substrate is presented in Fig. 2. The two most distinct detected peaks were found to originate from the SnO_2 substrate. The other four detectible wide peaks at $2.978 \cdot 10^{-10}$ m, $2.427 \cdot 10^{-10}$ m, $2.12 \cdot 10^{-10}$ m and $1.486 \cdot 10^{-10}$ m were crystalline Cu_2O [10]. The conversion from D values to 2Θ values for those four peaks is given in Table I. Hence, the XRD analysis showed that the composition of the as deposited films was Cu_2O.

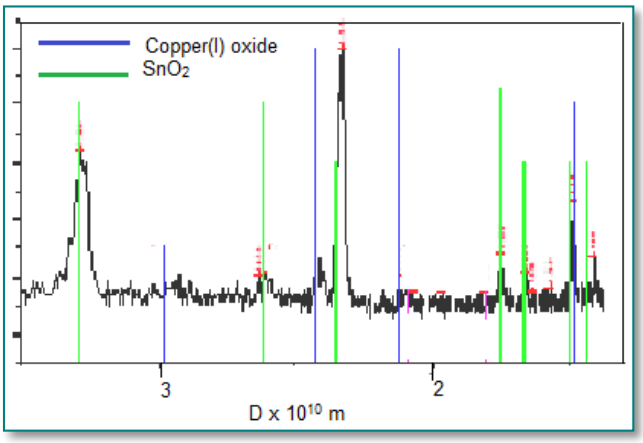

Figure 2. XRD spectrum of the 200 nm thin Cu_2O film.

Table 1. Cu_2O peak identification and D speacing to 2Θ conversion

Peak (JCPDS, 34-1354)	Dx10^{10} m	2Θ
1.	2.978	29.97
2.	2.427	37.00
3.	2.12	42.59
4.	1.486	62.42

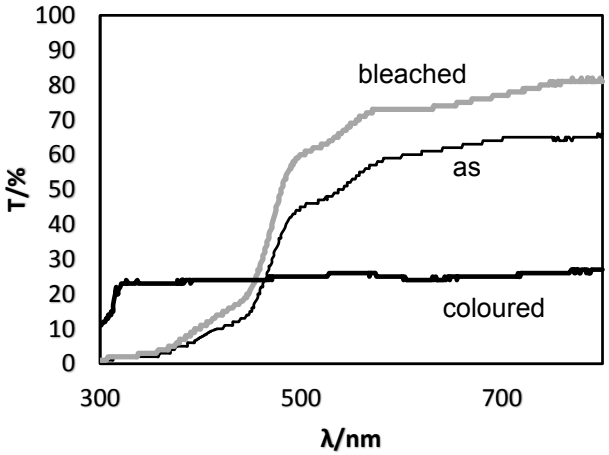

Figure 3. Transmittance spectra of the Cu_2O film.

The optical change is obvious on the visible transmittance spectra presented on Fig. 3 for: as prepared film, film in colored and film in bleached state taken in-situ: spectra were taken within the ECTD and then subtracted with a blank probe. A significant difference in the transmittance between the colored and bleached film is obvious throughout the whole spectral range. The relative

change in transmittance of film in bleached and colored state is around 53%:

$$\text{Modulation} \approx \frac{\sum T_{bleached} - \sum T_{coloured}}{\sum T_{bleached}} x\,100\,\% = \frac{51-24}{51} x\,100\,\% = 53\,\%$$

CONCLUSION

The fundamental property of an electrically activated chromogenic material is that it exhibits a large change in its optical properties upon a change in either electrical field or injected or ejected charge. The change in optical properties can be in the form of absorbance, reflectance or scattering. This optical change results in a transformation from a highly transmitting state to a partly reflecting or absorbing state. This change can be either totally or partly over the visible and solar spectrum. Typically it is over some portion of the spectra. Electrochromism can be used for the control and modification of incident daylight, solar energy and glare. Prepared EC thin copper(I) oxide films revealed about 53% modulation in transmittance in their bleached and coloured state. Because of this, EC window system coated with copper(I) oxide thin films could save energy. By controlling for daylight and glare it also provides occupants a more pleasant work environment, with year-round access to views and comfortable visibility of computer screens and work surfaces.

Note

This paper is based on the paper presented at The 12th International Conference on Accomplishments in Electrical and Mechanical Engineering and Information Technology – DEMI 2015, organized by the University of Banja Luka, Faculty of Mechanical Engineering and Faculty of Electrical Engineering, in Banja Luka, BOSNIA & HERZEGOVINA (29th – 30th of May, 2015), referred here as [11].

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