FTIR spectra of electrochromic copper(I) oxide thin films prepared by different methods

Ratka Neshkovska[1], Mimoza Ristova[2] and Julijana Velevska[2]

Abstract – **Electrochromic copper(I) oxide thin films were deposited onto conductive glass substrates using chemical bath deposition method and electrochemical method. An electrochromic test device with aqueous solution as an electrolyte was constructed. The reflectance spectra of the films in their three different states: as-prepared, coloured and bleached in the infrared part of spectrum were recorded.**

Keywords – **Copper(I) oxide, Thin films, Electrochromism, FTIR spectra.**

I. Introduction

.Electrochromism is defined as a change of the optical properties of the materials when a voltage is applied across them. The optical properties should be reversible, i.e., the original state should be recoverable if the polarity of the voltage is changed [1]. The electrochromic materials change their colour, transmittance, absorbance and reflectance. Many inorganic and organic materials exhibit electrochromic properties. Electrochromic materials are incorporated in electrochromic (EC) devices, consisting of two electrodes separated with an ion conductor which can be a liquid electrolyte or a solid inorganic or organic (polymeric) material. The liquid electrolytes are convenient for research work, while solid ones are preferred for practical devices. The electrochromic material is deposited onto a conductive working electrode. Each of the films in the device can have a thickness of less than one micrometer. Electrochromic materials could reveal cathodic or anodic electrochromism, depending on the potential at which they darken. Cathodic electrochromic materials show cathodic coloration state, under the application of a negative potential and are in bleached state on a positive potential. Anodic electrochromic materials coloured at a positive potential and bleached at a negative potential. The coloration/bleaching process results from the insertion/extraction of electrons and charge balancing small ions (H^+, Li^+, Na^+ and K^+ are the best) from the electrolyte into or out of the material. Cathodic electrochromic materials possess reduced coloured and oxidized bleached state, while anodic materials are coloured in their oxidized state and bleached in their reduced state.

This phenomenon was discovered about 50 years ago and some materials are widely investigated, their electrochromic properties are improved, new materials are synthetized and EC devices are fabricated. The applications of EC materials has been extended to smart windows, displays, antiglare mirrors and active camouflages [2]. Among them, smart windows represent an important application because they can effectively save energy by regulating solar heat gain, and provide indoor comfort by reversible color changes.

Numerous inorganic and organic electrochromic materials are widely investigated to develop energy efficient windows. If an electrochromic thin film is deposited onto a conductive window, then it is possible to control the transmission or reflection properties of the window, by applying a small voltage of several volts and thus saving energy for heating or cooling of the buildings. Electrochromic materials possess open circuit memory, therefore their coloured/bleached state and optical properties remain stable for a long time, which means that electrical current needs to be applied only during the colouring or bleaching of the film.

II. Experimental

A. Deposition of the conductive layer

The conductive layers are necessary for all EC device types. In all EC devices the electrochromics thin films should be deposited on a conductive layer. If the purpose of the EC device is to modulate the incident radiation, then the conductive layer should be transparent and deposited onto a transparent substrate, such as glass substrate or plastic. The quality and cost of transparent conductors is essential for all electrically activated devices. They must have low resistivity (bellow $100\Omega/\text{sq}$), to have good conductivity for ions and electrons, to be transparent and thermally and chemically stable. The conductive fluorine-doped tin oxide, SnO_2:F (FTO) film meets these requirements. In this work FTO coating was deposited onto cleaned standard microscopic glass substrates kept at temperature of $400^0\,C$, by spraying a 0.05 M aqueous solution of $SnCl_2 \cdot 2H_2O$ and crystals of NH_4F, with a *p*H of about 7 [3], with a BOSH sprayer. The FTO prepared with this method was about $2\,\mu m$ tick, with an 80% transparency for visible light, and with sheet resistance of $18-38\,\Omega/\text{sq}$.

B. Deposition of Cu_2O thin films by chemical bath deposition method

The electrochromic Cu_2O films were deposited onto glass substrates pre-coated with FTO by successive immersion into

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two solutions, a hot one and a cold one [4]. The hot solution was 2 M NaOH at $60-80^0$ C. The cold solution contained a colourless complex mix of 1 M $CuSO_4$ and 1 M $Na_2S_2O_3$. The number of immersions determines the thickness of the films, with each immersion yielding 0.1μm in the film thickness. This procedure lasted until the desired thickness of the film (200 nm) was obtained.

C. Deposition of Cu_2O thin films by electrochemical deposition method

Electrodeposition is a simple and low cost method for deposition of oxides at low temperatures. Such deposited films have high quality. In our case the deposition was performed using a two electrode classical system [5]. A copper clad for printed circuit board, with a thickness of $50\,\mu m$ with the same dimensions as a classical microscopic glass was used as an anode, while the glass substrate coated with FTO was a cathode. The electrolyte was prepared from 0.4 M anhydrous copper sulfate $CuSO_4$, 2.7 M lactic acid $C_3H_6O_3$ and 3.1 M sodium hydroxide NaOH. The temperature of the electrolyte was maintained at 60^0 C, the voltage between the electrodes was in the 0.5 to 0.6 V range, with a current density of 0.8 to 1 mA/cm^2.

D. Recording of the FTIR spectra

All spectroscopic techniques can be used to identify and study chemicals. Infrared (IR) spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. A common laboratory instrument that uses infrared light is Fourier transform infrared spectrometer (FTIR). FTIR is an interferometer for IR light. The incoming IR light beam is divided into two separate beams in a beam splitter where half of the beam is reflected to a fixed mirror and half is transmitted through a splitter and is directed to a movable mirror. After the reflection from the mirrors, the two light beams are directed to the beam splitter and pass through the sample. The detector records the transmittance or reflectance as a function of wavelength λ, or wavenumber $1/\lambda$.

The reflectance FTIR spectra for the films prepared by two different techniques, chemical bath deposition and electrochemical deposition were taken using PERKIN ELMER System 2000 FT-IR in the wavenumber range of 400 to 4000 cm^{-1}. Spectra were taken for the films in three different states: as deposited, coloured and bleached. In order to perform colouring and bleaching of the films, an electrochromic test device (ECTD) was constructed, consising of a glas supstrate/FTO/Cu_2O film as a working electrode, a 0.1 M $NaNO_3$ aqueous solution as an electrolyte and an FTO/glass substrate as a counter electrode.

The films were coloured at negative potential of -4,5 V and bleached at a positive potential of +4 V. Prior to the recording of the spectra, the reflectance spectrum for the glass/FTO substrate was recorded.

III. Results and Discusion

The prepared Cu_2O films revealed cathode electrochromism [6-8]. They were coloured at a negative potential of -4V and were bleached at a positive potential of $+4$V. The spectra were taken ex-situ.

The reflectance FTIR spectrum for the glass/FTO is given in Fig. 1. Fig. 2 represents the reflectance FTIR spectra for the film prepared by chemical bath deposition method in its as deposited, coloured and bleached states. The same spectra for the electrochromic Cu_2O film prepared by electrodeposition method are presented in Fig. 3.

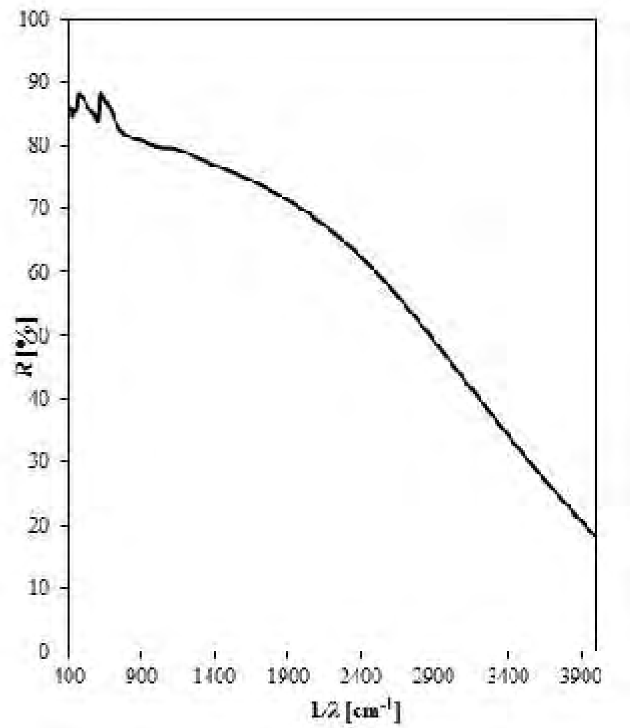

Fig. 1. FTIR reflectance spectra of glass/FTO.

From the given spectra one can notice that they do not exhibit peaks characteristic for Cu_2O, so they can't be used for chemical identification of the Cu_2O films or for the possible ion intercalation/deintercalation processes. The reason for this may be a small thickness of the films. However, they are useful for determining the reflective properties of the films in the infrared part of the spectrum. The difference in the reflection coefficients of the films prepared by two different methods in coloured and bleached states is evident for a wavenumber value over about 2400 cm^{-1}.

The electrochromic smart windows are the most desired application of the electrochromic materials. With the application of a small current or voltage the windows can dynamically darken and lighten, so daylight, solar heat gain and internal heat loss through the windows of buildings and vehicles could be easily controlled and energy could be saved. The calculations showed that 4.5% of the annual energy use in the USA could be saved with highly insulating dynamic windows applied in both the commercial and residential sector

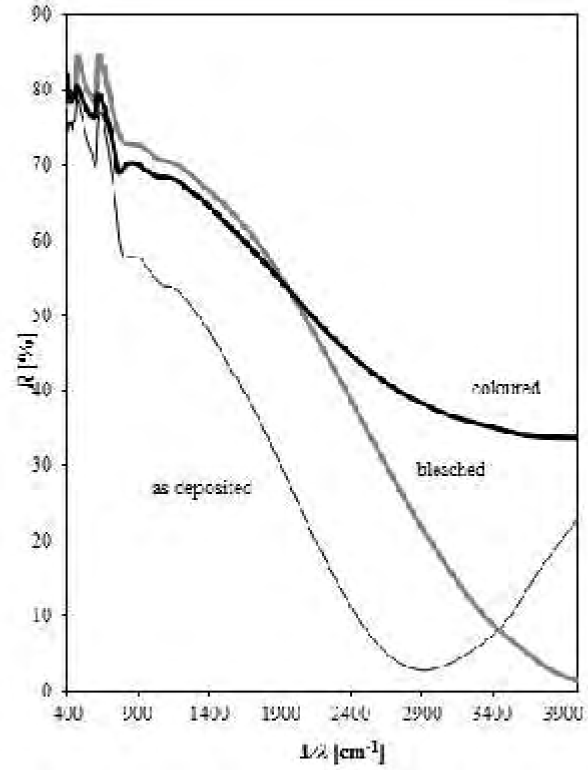

Fig. 2. FTIR reflection coefficients in the infrared part of the spectrum for the chemically deposited thin Cu_2O film in its as deposited, coloured and bleached states.

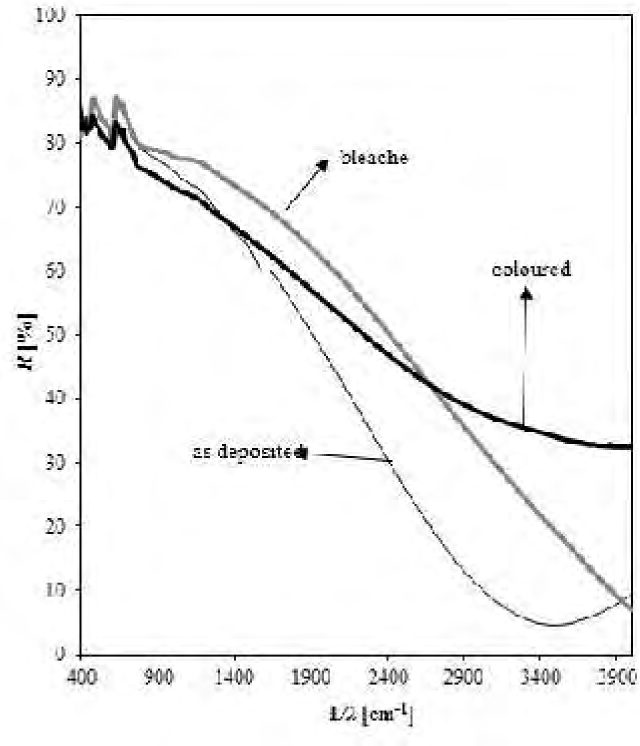

Fig. 3. FTIR reflection coefficients in the infrared part of the spectrum for the electrochemically deposited thin Cu_2O film in its as deposited, coloured and bleached states.

[9]. The colour of the electrochromic film is essential, because windows should be transparent enough to provide good illumination of the working and living area, but they should also reduce the amount of heat that enters the room (in summers) or coming out of it (in winters). From the reflectance FTIR spectra the modulation of the incident solar spectrum in the infrared part of spectrum could be calculated. The films with higher reflectance are preferred for application in smart windows.

IV. Conclusion

Cu_2O thin films were deposited onto conductive and transparent FTO pre-coated glass substrate by two different methods. The deposited films exhibited cathode electrochromism. The FTIR spectra of the films in three different states: as prepared, coloured and bleached were taken ex situ. The difference in the reflection coefficient in the infrared part of the spectrum is obvious for values of the wavenumber over 2000 – 2400 cm^{-1}. These films may find their own application in electrochromic devices, such as smart windows, as an alternative of other thin films (for example the most explored WO_3 thin films) because of their cost, simple methods of preparation, non toxic nature and abundance of the starting material.

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