

Some properties of electrochromic low vacuum evaporated copper(I) oxide thin films

Ratka Neshkovska¹, Mimoza Ristova² and Julijana Velevska²

Abstract – Electrochromic copper(I) oxide thin films were deposited onto conductive glass substrates using low vacuum evaporation method. An electrochromic test device with aqueous solution as an electrolyte was constructed. The transmittance spectra of the films in their three different states: as-prepared, coloured and bleached in the visible part of spectrum were recorded and the data were used to estimate of the energy band gap.

Keywords – Copper(I) oxide, Thin films, Electrochromism, Energy band gap.

I. INTRODUCTION

Copper oxides are available in two stable forms, copper(I) oxide (or cuprous oxide) Cu_2O and copper(II) oxide, CuO (or cupric oxide). These two oxides have two different colours, crystal structures and physical properties.

Copper(I) oxide, Cu_2O , is a semiconductor with a p-type conductivity due to copper vacancies [1-3]. The presence of Cu^{2+} ions in some places in the lattice instead Cu^+ ions leads to Cu^+ vacancies, resulting in a p-type conductivity [1-3]. By using multiple methods, Cu_2O films with n-type conductivity can be produced. One way is by dipping the copper foil in a solution of HCl with a pH of 3 at 40°C [1-3], or by potentiostatic electrodeposition.

The optical properties of copper(I) oxide depend on the methods and parameters of deposition. The density of copper (I) oxide ranges from 5.88 to 6.06g/cm^3 . The melting temperature of this oxide is 1235°C , the boiling point is 1800°C , the molar mass is 143.09g/mol . Its crystal structure is cubic, with a lattice constant of $4.27 \cdot 10^{-10}\text{m}$. The unit cell of this oxide is shown in Fig. 1. The unit cell consists of four copper atoms and two oxygen atoms. The coordinates of the copper and oxygen atoms are as follows [1-3]:

Cu: $1/4\ 1/4\ 1/4$; $3/4\ 3/4\ 1/4$; $3/4\ 1/4\ 3/4$; $1/4\ 3/4\ 3/4$

O: $0\ 0\ 0$; $1/2\ 1/2\ 1/2$.

In this structure each copper atom only has two close oxygen neighbors, while each oxygen atom is surrounded (directly connected) with four copper atoms. The Cu-O

distance is $1.85 \cdot 10^{-10}\text{m}$. Oxygen atoms are at a greater mutual distance ($3.69 \cdot 10^{-10}\text{m}$) and copper atoms Cu-Cu are at a smaller distance of $3.01 \cdot 10^{-10}\text{m}$. On the other hand, each oxygen atom has six valence electrons, and each copper atom has one valence electron. Thus, any molecule of Cu_2O has eight valence electrons which are necessary in the formation of four homeopolar (covalent) bonds between each oxygen atom and the four surrounding copper atoms. The structure can be envisioned as two inter-penetrating cubic lattices: one face-centered with the lattice points occupied by Cu atoms and the other one body-centered with the lattice points occupied by O atoms. Each O atom is tetrahedrally coordinated by four Cu atoms, while each Cu atom is centered between two O atoms.

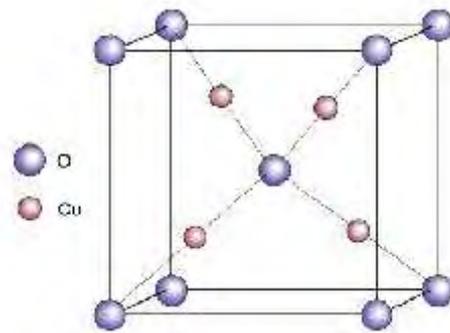


Fig. 1. One unit cell of the crystal structure of Cu_2O .

The energy band gap of Cu_2O is in the range from 1.9eV to 2.40eV [4]. The difference in the energy band gap is due to the different methods of preparation of films and the substances used. The lowest value of 1.9eV was measured in films deposited by the method of electrochemical deposition, and the highest value for the energy band gap was found in chemically deposited films. The acceptor type energy level is situated 0.4eV above the edge of the valence band of a Cu_2O single crystal prepared by oxidation of copper in air at a temperature of 1000°C . Two donor type trapping levels at 1.3eV - 1.34eV and 1.03eV - 1.1eV below the conduction band edge have also been identified [1-3]. The resistivity of copper(I) oxide strongly depends on the heating process of the oxide after its deposition and ranges from several tens of Ωcm to $10^{14}\Omega\text{cm}$. The resistivity of the films obtained by the method of electrochemical deposition is in the range of $10^9 - 10^{12}\Omega\text{cm}$, while of the single crystal of copper(I) oxide ranges from $10^2 - 10^4\Omega\text{cm}$. This high specific resistance of

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the film is due to the effect of compensation between the donor's and the acceptor's levels [4] and can be lowered by doping and heating the film.

The methods for deposition of copper(I) oxide often result in combined deposition of copper(II) oxide, CuO, which is also a semiconductor. Cu₂O is transparent with a yellowish color and copper(II) oxide is black in color. The energy bandgap of CuO is in the range of 1.35eV to 1.7eV. Therefore Cu₂O absorbs under 630nm and CuO absorbs strongly in the entire visible spectrum. The absorption coefficient of Cu₂O at 510nm is of the order 10⁴ cm⁻¹ [1-3].

Copper(I) oxide is one of the oldest semiconductor which attracted the attention of physicists. Its photoconductivity was first observed by Pfund in 1916 and since then has been subject to numerous studies. Interest in copper(I) oxide as semiconductor started with the discovery of Cu₂O rectifiers by Grondhal in 1920 [1]. Properties of Cu₂O and its characterization were widely investigated in the period from 1930 to 1940. After 1940 the interest in copper(I) oxide decreased, when the interest shifted to selenium, germanium, silicon and other materials. The interest in Cu₂O returned in the 1970s when researchers started working in the field of photovoltaic conversion in semiconductors. The material was studied as a possible low cost material for solar cells. Cu₂O remains an attractive alternative to silicon and other semiconductors producing cheaper solar cells. The main advantage of Cu₂O is its non-toxic nature, abundance of copper as a starting material for the preparation of copper oxide and cheap and easy procedures for obtaining this oxide. The energy band gap of this oxide is acceptable and suitable for manufacturing photovoltaic cells. Also, the theoretical value of the coefficient of efficiency of such cells (13 to 20%) is a great motivation for exploring this material. Beside this application for solar energy conversion, copper-oxide-based materials have found applications in other various areas including heterogeneous catalysis, gas sensing and superconducting. They have been studied for photoelectrochemical hydrogen production from solar-driven water splitting [5] and for the development of a novel electrochemical sensor based on electrodeposition of copper oxide nanoparticles onto a carbon nanoparticle film modified electrode for the analysis of the anti-HIV drug transport [6].

It has been recently found that Cu₂O thin films exhibit cathode electrochromism [7-11, 13]. The electrochromic materials reversibly and persistently change their optical properties and colour upon application of an external electrical field [7]. Cu₂O thin films are transparent to visible light in their oxidized state and almost black in their reduced state.

Several methods for obtaining thin copper(I) oxide films have been developed, i.e. thermal oxidation, electrodeposition, sputtering, anodic and chemical oxidation, chemical oxidation, chemical deposition, sol gel technique, laser ablation, etc.

In this work electrochromic Cu₂O thin films were prepared by low vacuum deposition method onto glass substrates precoated with fluorine-doped tin oxide (FTO) film.

II. EXPERIMENTAL

A. Deposition of the conductive layer

Because the purity of the substrates is essential for getting uniform colouring and bleaching of the films, standard microscopic glass slides were cleaned with immersion in a mixture of chromic and sulfuric acid and rinsed with distilled water. The conductive FTO coating was deposited onto glass substrates kept at 400^o C with the spray pyrolysis technique, performed with a BOSH sprayer, spraying a 0.05 M aqueous solution of SnCl₂·2H₂O and crystals of NH₄F, with a pH of about 7 [12]. The FTO prepared with this method was about 2μm thick, with an 80% transparency for the visible light, and with sheet resistance of 18 – 38Ω/sq .

B. Deposition of Cu₂O thin films by low vacuum deposition method

The prepared FTO substrates were subjected to the low vacuum evaporation method for deposition of Cu₂O thin films [13].

The melting temperatures of Cu, CuO and Cu₂O are 1083^o C, 1326^o C and 1235^o C respectively. The temperature difference between elemental and oxides melting points makes the evaporation technique attractive for depositing of copper oxide thin films. Stable copper oxides can be deposited over a source temperature region of 1090–1350^o C. In general, the oxidation rate and the evaporation rate of the source material define the deposition rate of the product grown on the substrate surface. Copper oxide thin films were deposited on glass substrates pre coated with FTO by the low vacuum evaporation technique, using granulated (0.3mm) copper with 99.8 % purity as a starting material. Deposition was performed in a Balzers Automatic BA 510 apparatus. The distance between the source (copper) and the substrates was about 50cm. The evaporation pressure was 0.67 Pa. During evaporation the transparency of the substrates changed by 50 %. The deposition lasted several minutes, until all of the starting material from the tungsten boat was evaporated. If the vacuum in the chamber is very high, pure copper will be deposited on the glass substrates. In our case the vacuum was not so high, so evaporated copper reacted with the gasses in the chamber. As a result of that reaction cuprous oxide thin films were obtained on the substrates. Some films were deposited onto conducting glasses and some were deposited onto glasses without conductive oxide film onto them.

The deposited films were yellowish in appearance. The film thickness, measured by weight different method was about 130nm [13].

The films deposited onto glass without a transparent conducting layer were characterized by X-ray diffractometer [13].

The constructed electrochromic test devices (ECTD) consisted of a glass substrate/FTO/Cu₂O film as a working

electrode, a 0.1 M NaOH aqueous solution as an electrolyte and an FTO/glass substrate as a counter electrode.

The visible transmission spectra were recorded for the three film states: as-deposited, coloured and bleached, using a Varian CARY 50 Scan UV-Visible spectrophotometer in the wavelength range from 330 to 850nm . Prior to the recording of the spectrum, the transmission spectrum for the glass/FTO substrate (blank probe) was recorded and it was normalized to 100 % transmission. The data were used to calculate absorption coefficient spectrum and the optical band gap for the films in their coloured and bleached state.

III. RESULTS AND DISCUSSION

The prepared Cu₂O films revealed cathode electrochromism. They were coloured at a negative potential of -4V and were bleached at a positive potential of +4V .

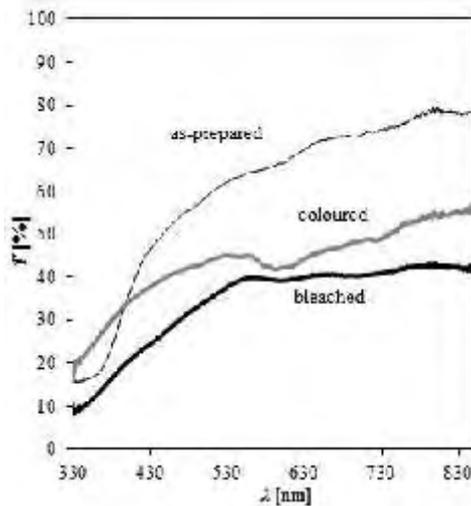


Fig. 2. Visible transmittance spectra of low vacuum evaporated thin Cu₂O films in: as-prepared, coloured at -4V and bleached at +4V states.

The transmission spectra of the films in as-prepared, coloured and bleached state are presented in Fig. 2. The difference in the transmittance in the three states of the films is obvious.

The transmittance data were used to evaluate the absorption coefficient $r(h\epsilon)$ and the band gap E_g for films in coloured and bleached state. The absorption coefficient $r(h\epsilon)$ for a given film with thickness d is related with the photon's energy $h\epsilon$ and the optical band gap E_g :

$$(rh\epsilon)^{2/n} = A(h\epsilon - E_g) \quad (1)$$

where A is a constant, and n is a number which depends on the type of transition. The absorption coefficient was evaluated from:

$$r = \frac{1}{d} \ln \frac{100}{T(\%)}, \quad (2)$$

where T are transmittance data values. Calculated values of the coefficient r versus wavelength of incident radiation are presented on Fig. 3 and Fig. 4.

The value of n and the type of transition were estimated from the graphical presentation of $(rh\epsilon)^{2/n}$ versus photon energy (Fig. 5 and Fig. 6). Linear dependence of $(rh\epsilon)^{2/n}$ versus $h\epsilon$ is obtained for $n = 1$, which corresponds to direct band to band electron transition mechanism.

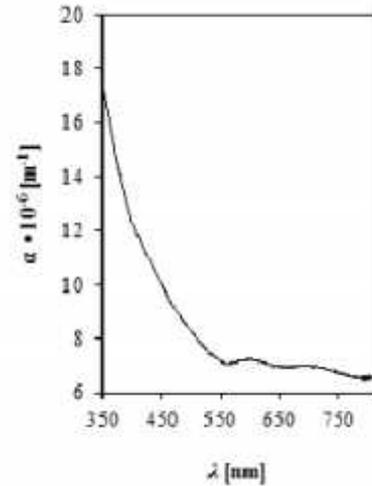


Fig. 3. Absorption coefficient in visible part of spectrum for low vacuum evaporated thin Cu₂O films in coloured state.

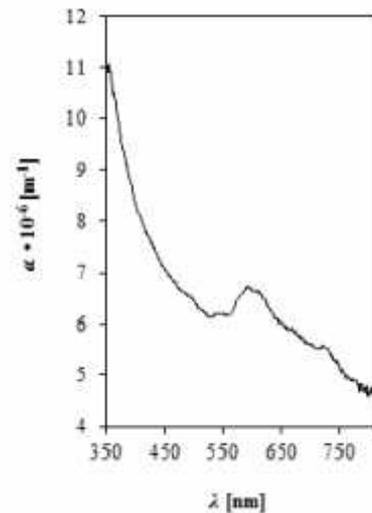


Fig. 4. Absorption coefficient in visible part of spectrum for low vacuum evaporated thin Cu₂O films in bleached state.

The band gap energy was evaluated from the graphs in Fig. 5 and Fig. 6, as interception of the linear part with the photon energy axis. The evaluated band gap values for the prepared film by method of low vacuum evaporation in coloured state

are 2.83eV and 2.77eV and 0.8eV in bleached state. They are given in Table I. The band gap for the as-prepared films was evaluated elsewhere [13]. The obtained values are higher than reported values for films obtained with other methods of preparation [1-4].

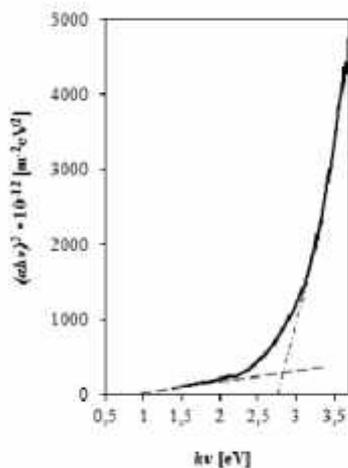


Fig. 5. $(\alpha h\nu)^2$ versus photon energy in visible part of spectrum for low vacuum evaporated thin Cu_2O films in coloured state. Intercepts of the dashed lines corresponds to the direct band.

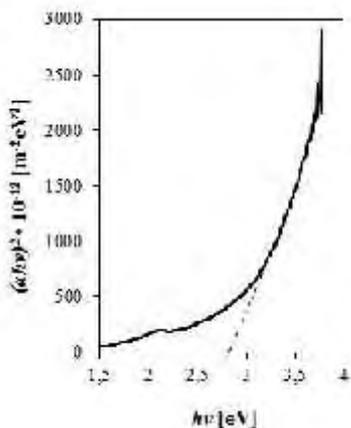


Fig. 6. $(\alpha h\nu)^2$ versus photon energy in visible part of spectrum for low vacuum evaporated thin Cu_2O films in bleached state. Intercepts of the dashed lines corresponds to the direct band gaps.

IV. CONCLUSION

In this paper a method of low vacuum evaporation for depositing of Cu_2O thin films onto conductive and transparent FTO pre-coated glass substrate is given. The deposited films exhibited cathode electrochromism. The difference in the transmittance of films in the visible region in their coloured and bleached state is obvious. The evaluated values of the band gap in the coloured and bleached states of films are different and are higher than those presented in literature. This investigation of energy band gap shift may help mechanism of electrochromism to be understood in future. The thin films

prepared by the presented method could be applied in solar cells or other devices.

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