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Electrochromic switching of electrodeposited ZnO+Zn₅(OH)₈Cl₂ filmsE. Rayón^{a*}, J. Cembrero^a, B. Mari^b

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Abstract

This study reports the effect of optical switching of electrodeposited ZnO+Zn₅(OH)₈Cl₂ films on a gold electrode in a bath of 0.05M Zn(NO₃)₂ + 0.1M KCl. The coating turns black when cathodic polarization is applied yet when the current is removed the electrode immediately returns to a white colour. This optical effect is reversible and can be switched through various cycles.

Keywords: Electrodeposition, optical materials and properties, solar energy materials, crystal growth, electrochromic materials, ZnO, Zn₅(OH)₈Cl₂

1.- Introduction

The colour change effect or degree of transparency of a material which can be controlled via an external energy source has been used for over 30 years. The materials used to make optical switchers can be classified as follows: liquid crystals [1,2], electrochromic materials [3-5], thermochromic materials [6,7] and that rare earths and

alloys that react with hydrogen to form transparent metal-hydrides semiconductors [8-11].

Electrochromic materials display electrochromism – a reversible change in a material's optical properties – when the material is oxidised/reduced electronically. Typically these materials can go from a whitish transparent state to a coloured or completely transparent state. This effect is common in certain oxides, such as WO_3 , MoO_3 , V_2O_5 , Nb_2O_5 , $\text{Ir}(\text{OH})$ and NiO_xH_y as well as in some electrically conductive polymers such as polyaniline [12]. In industrial processes the most widely used oxide is WO_3 , the electrochromism effect of which is governed by its reversible reaction:



When M^+ is a proton of H^+ or ions of Li^+ , Na^+ or K^+ , $0 < x < 1$. Thus, when a thin semitransparent film of WO_3 incorporates electrons (is reduced), its optical properties change.

Nevertheless, the ZnO semiconductor with a band gap of 3.4 eV is of increasing interest in applications such as photovoltaic cells, sensors and photonic devices [13-20]. Films of ZnO can be produced by electrodeposition at temperatures over the 60°C to 80°C [21-27], being a cheap and easy technique. In this work is found the effect of optical switching observed in ZnO films electrodeposited in a bath of 0.05M $\text{Zn}(\text{NO}_3)_2$ + 0.1M KCl when the layer is polarised using alternating polarisation cycles. The reversible optical switching effect is shown by the first time using photographs taken along the switching process.

2.- Material and methods

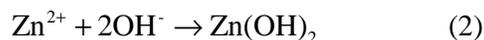
A piece of borosilicate glass was coated with a 5 μ m thick gold film using an e-beam evaporation system in a Pfeiffer Classic 500 high vacuum chamber. In order to enhance adhesion between the glass and the metal layer, a 30nm CrO_x film had previously been deposited using an e-beam evaporator in an oxidising atmosphere. A 3x2 cm area was immersed in electrolyte, while the non-immersed part was kept dry and used to electrically connect the electrode. The electrodeposition was performed in a temperature-controlled electrochemical cell and a Princeton Eg&G 732A potentiostat/galvanostat was used to polarise and record the electrochemical curves. A 0.05M Zn(NO₃)₂ + 0.1M KCl (*pH*=4.7) aqueous solution at 70°C was used as the electrolyte. A bar of Pt was used as a counter electrode and an Ag/AgCl 3M electrode was configured as the reference electrode.

The morphological characterisation of the deposited structure was performed using a JEOL JSM 6300 scanning electron microscope. The crystalline and composition structure of the coating were studied by an X-ray diffractometer (Rigaku ULTIMA IV) with CuK α radiation and 0.5° incidence glazing angle. The calorimetric tests were performed by peeling off the deposited layer in a TA Instruments thermogravimetric analyser (TGA Q50) and using a TA Instruments differential scanning calorimeter (DSC Q100) in an N₂ atmosphere.

3.- Results and discussion

The gold electrode immersed in 0.05M Zn(NO₃)₂ + 0.1M KCl was cathodically polarised at 1.2V for 60 seconds. Figure 1 shows the images obtained when the electrode was immersed (sequence 1 fig.1) and when the electrodeposition process was

completed. The mirror surface of the gold gradually acquired a whitish appearance which is due to ZnO deposition. A reduction reaction occurs on the surface of the electrode when the hydroxyl group starts to form according to the reaction:



This hydroxide which is already adhered to the electrode surface is transformed into its corresponding oxide using energy, normally thermal, following the process:



After electrodeposition, the coated electrode was cathodically polarised using a range of 1.2 to 1.8 volts at 50mVs^{-1} . Sequence 2 in Figure 1 shows the optical transition when the electrode was polarised at 1.3 V, 1.5V and 1.8V, respectively. When the electrode reached 1.3V, it gradually began to darken until it reached a state of absorption and turned black at 1.8V. Beyond this level of current, bubbles were observed, probably due to the formation of hydrogen. In the intermediate state, at around 1.3V, a greenish colour was observed although it was not well recorded by the camera. The switching was also quicker at the edges of the sample. This is due to the fact that in this area there was a greater concentration of electrochemical current, and therefore the redox reactions occurred more swiftly.

When the electrode stopped polarising (open circuit configuration), it spontaneously returned to its initial colour in just a few seconds, as sequence 3 in Figure 1 shows. This therefore showed that firstly, the effect was reversible, and secondly, that the black colour was an unstable minimum energy state which was forced by the polarisation applied. Optical switching was observed during ten cycles when the polarisation speed

was 50mVs^{-1} and up to 50 cycles when the speed was reduced to 10mVs^{-1} . After this number, the coating began to peel off around the edge of the sample where the current was higher and thus the processes were quicker, as sequence 4 in Figure 1 shows. The failure of the film in this situation may be due to a lack of adhesion to the substrate as a result of the expected change in the coating's volume during switching, or to undesired reactions which end up destroying the layer. The degradation effects could be avoided replacing the electrolyte by another less aggressive one once the layer has been deposited.

F.Wang et. al [27] and Gao-Ren et. al [28] demonstrate that other compounds and hydroxides impurities ($\text{Zn}_5(\text{OH})_8\text{Cl}_2$, $\text{Zn}(\text{OH})_2$ or $[\text{Zn}(\text{OH})_2]^{2-}$) are expected in the lattice of the crystals when nitrate salts are used as the oxygen precursor in the deposition reaction. In fact, the X-ray diffraction peaks obtained on the deposited coating (Figure 2), corresponding to a mixture of ZnO (JCPDS 36-1451) and Simonkolleite compound, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (JCPDS 07-0155). Nevertheless, the peaks of Simonkolleite in the annealed sample drop and the diffraction spectra match with those expected for pure ZnO.

The Figure 3 shows that at temperatures of 165°C , 176°C and 228°C , endothermic reactions take place, while the thermogravimetric curve reveals a material's significant weight loss. These results are agreeing with the known reversible Simonkolleite \rightarrow ZnO decomposition stages under a heat treatment [29]. This decomposition starts with loss of a single mole of the lattice water. Further dehydration at $165\sim 210^\circ\text{C}$ produces a mixture of ZnO and an intermediate $\text{Zn}(\text{OH})\text{Cl}$. At $210\sim 300^\circ\text{C}$, the intermediate $\text{Zn}(\text{OH})\text{Cl}$ decomposes to ZnO and ZnCl_2 . At higher temperatures, occurs a volatilization of the ZnCl_2 , leaving a final residue of zinc oxide.

The SEM image of Figure 4a shows the as deposited coating (before being electro-switched) and Figure 4b shows the layer structure after being heat treated in the same TGA test up to 400°C. The crystals developed nano-pores across their surface due to the volatilization of ZnCl and hydroxides which resulted of a leakage of gases.

4.- Conclusions

This paper reports the electrochromic effect on coatings electrodeposited in a gold electrode by cathodic polarisation in a $\text{Zn}(\text{ZnO}_2)_3 + 0.1\text{M KCl}$ bath. The DRX spectra and SEM images show layered crystals composed by a mixture of ZnO and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. The degradation observed after several cycles of switching could be avoided by optimising the system's conditions and configuration, for example, by replacing the electrolyte by another less aggressive one once the layer has been deposited.

Acknowledgements

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Figure captions:

Figure 1. Gold electrode immersed in 0.05M $Zn(NO_3)_2$ + 0.1M KCl (*a*), and an electrodeposited coating (*b*). Cathodic polarisation sequence at 1.3V (*c*), 1.5V (*d*) and 1.8V (*e*). Polarisation sequence in an open circuit, after 5s (*f*) and after 15s (*g*). Tenth polarisation sequence at the previously tested levels of potentials (*h*→*j*).

Figure 2. DRX scans of the as electrodeposited coating in 0.05M $Zn(NO_3)_2$ + 0.1M KCl and after annealing.

Figure 3. DSC and TGA curves of the coating obtained by electrodeposition at 0.05M $Zn(NO_3)_2$ + 0.1M KCl.

Figure 4. SEM images of the electrodeposited coating via the cathodic polarisation in a bath of 0.05M $Zn(NO_3)_2$ + 0.1M KCl (*a*). The same coating after a subsequent annealing at 400°C (*b*).

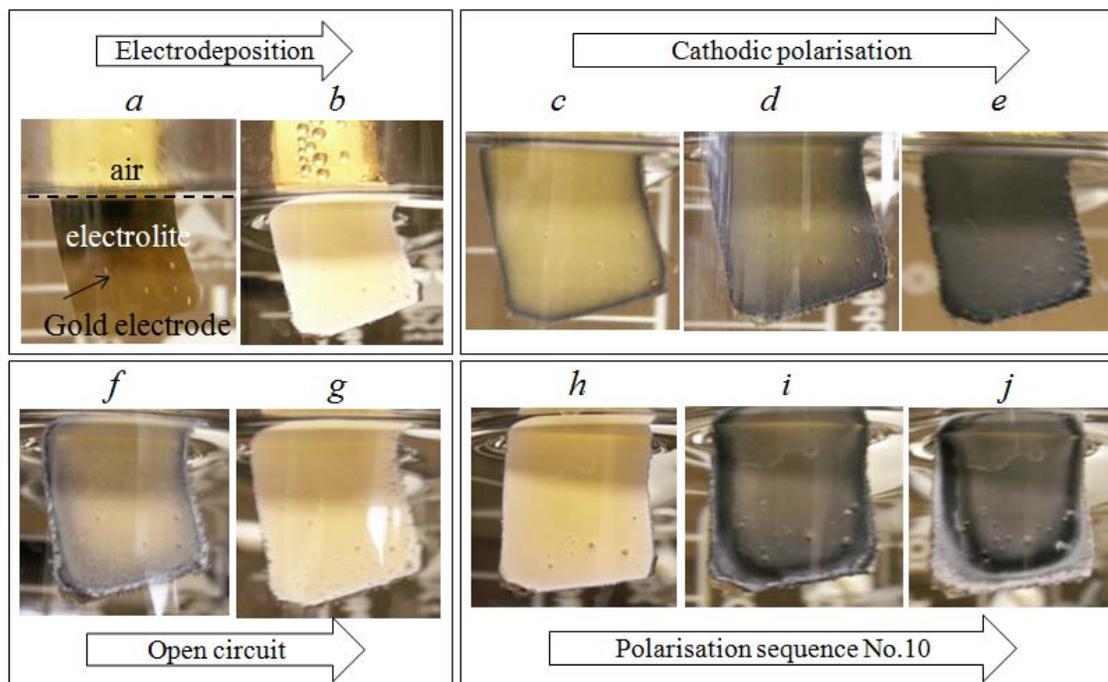
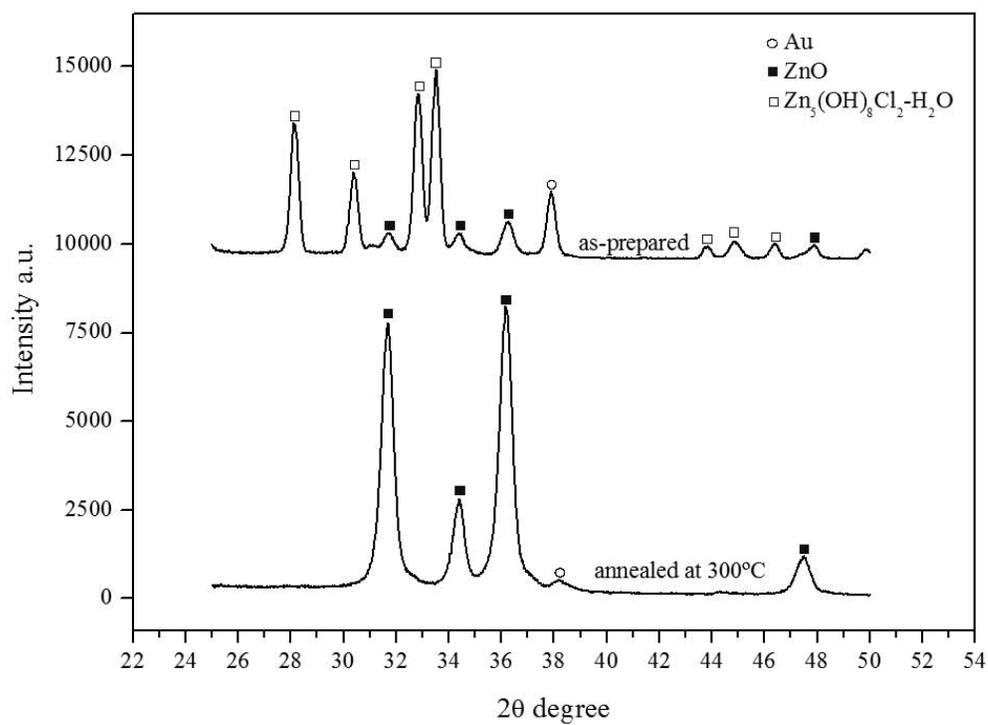
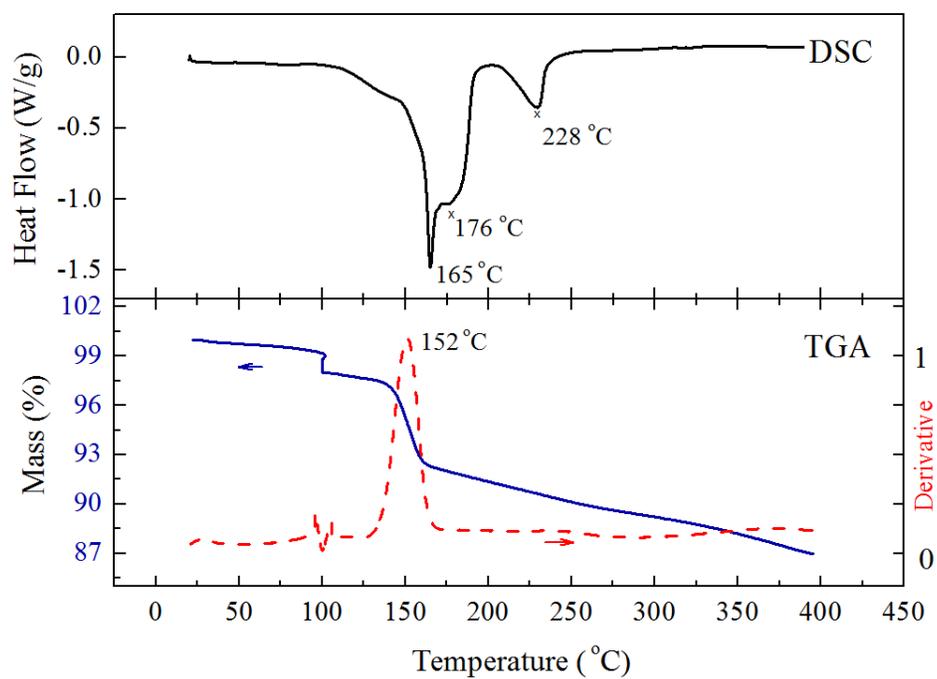


Figure 1

**Figure 2**

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**Figure 3**

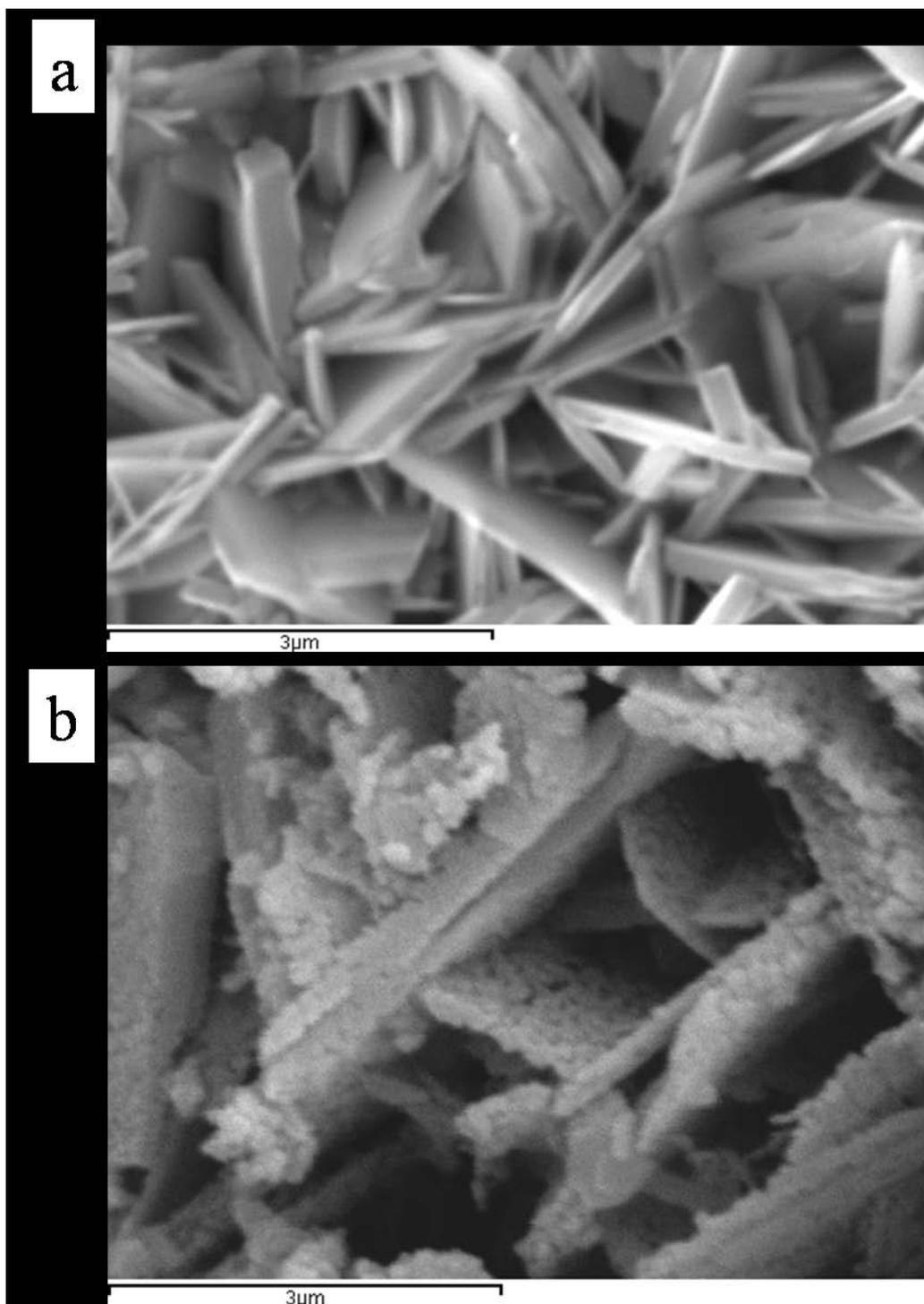


Figure 4

Highlights

- An electrochromic effect is observed in electrodeposited $\text{ZnO}+\text{Zn}_5(\text{OH})_8\text{Cl}_2$ films.
- By means of cathodic polarizations, a white $\text{ZnO}+\text{Zn}_5(\text{OH})_8\text{Cl}_2$ coating submerged in $0.05\text{M Zn}(\text{NO}_3)_2 + 0.1\text{M ZnCl}_2$ shows an optical transition to a 'black state'.
- The electrochromic effect is fully reversible and can be used in optical switchers.

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