

## Study of zinc salt concentration effect on the growth of zno nanostructured oxides obtained by direct electrodeposition

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Effect of zinc salt concentration on the growth of electrodeposited zinc oxide phases was investigated. ZnO thin films were elaborated via chronoamperometry on fluorine doped tin oxide (FTO) substrates from aqueous mixed bath of zinc nitrate and chlorate at 70°C. X ray diffraction patterns showed nanocrystalline films of hexagonal wurtzite phase with (101) preferential orientation for ZnO as grown in low concentration of Zn<sup>2+</sup> salt. High concentration of Zn<sup>2+</sup> favor the formation of Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub>O simonkolleite phase. After heat treatment at 400 °C for 1h this later decomposes to ZnO oxide which presents no preferential orientation. The route mean square RMS roughness of surfaces estimated from AFM technique shows that ZnO generated from heat treated Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub>O present more increasing roughness than ZnO deposits obtained at lower salt concentration. The photoelectrochemical answer indicated important generated photocurrents for both films which present n-type electrical conductivity.

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### 1. Introduction

Zinc oxide (ZnO) have attracted a lot of interest in recent years due to their remarkable physical and chemical properties, in optoelectronics [1, 2], solar cells [3, 4], UV photodetectors [5], photonic devices [6] and transparent conducting film [7]. ZnO has been one of the most promising semiconductor material with a well-known large direct band gap between 3.2 and 3.4 eV at room temperature [8], and high exciton binding energy (60 meV). Several techniques have been used for ZnO oxide elaboration such as pulsed laser deposition [9], magnetron sputtering [10] metal organic chemical vapour deposition (MOCVD) [11] and spray pyrolysis [12] and others (so forth).

Electrodeposition technique presents a simple non complicated and non expensive method compared to some of the above techniques. For that several authors used this technique in elaborating ZnO oxide [13-19]. Deposits can be carried out on different conductive substrates regardless to their nature glass, graphite, polymer and semiconductor. Non special requirement needed for substrates except its conductivity. Thin films of crystalline ZnO can be electrodeposited from aqueous and non aqueous solutions [17, 18]. Most of the cathodic electrodeposition was done from Zn salts and promoted by OH<sup>-</sup> generated upon reduction of the nitrate [13,15,19] other have

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used molecular oxygen and peroxide as oxygen precursor [20,21]. Most of the deposits were carried under temperature below 100°C. The proportions of the zinc salts used and the ratio between the OH<sup>-</sup> ions production (from nitrate, peroxide or oxygen) and Zn<sup>2+</sup> diffusion rates seems to be the crucial parameters determining the oxide growth.

In the present work we report the formation conditions of two distinctive ZnO deposits on indium tin oxide substrate when varying zinc salt oxide proportions. First deposits were obtained from aqueous mixed bath with lower concentration salt and lower temperature meanwhile the second deposits are generated after the simonkolleite (Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub>O) annealing at 400°C for 1h. In addition, the differences occurred in structural and morphological studies for both deposits were also reported comparatively to the simonkolleite (Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub>O) phase. Impedance spectroscopic curves and photoelectrochemical behaviour of three films are also investigated, they inform on the electrical conductivity of the deposits and their photosensitivity.

## 2. Experimental details

ZnO and zinc hydroxylchloride Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub>O were grown by electrodeposition on FTO glass. A conventional three electrodes cell was used with TCO glass (fluorine-doped SnO<sub>2</sub> coated glass) substrate as the working electrode, platinum as the counter electrode and an Ag/AgCl KCl saturated electrode as the reference electrode for electrodeposition experiments.

Electrochemical studies are carried out with Voltalab PGZ 301 made up of a potentiostat-galvanostat equipped with software Volta Master 4, controlled by a microcomputer. Analytical grade chemicals of zinc salts Zn(NO<sub>3</sub>)<sub>2</sub> and ZnCl<sub>2</sub> were purchased from Sigma Aldrich, the oxygen precursor KNO<sub>3</sub> and nitric acid HNO<sub>3</sub> are Biochem products. The electrolyte consisted of an equimolar solution of 0.005 M Zn(NO<sub>3</sub>)<sub>2</sub> and ZnCl<sub>2</sub> with 0.1 M KNO<sub>3</sub> and KCl with an initial pH adjusted to 6.5. Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub>O electrodeposition was obtained with higher concentration of Zn<sup>2+</sup> (0.01M). The bath temperature was kept at 70°C. The deposition was performed at a fixed potential of -1 V versus the Ag/AgCl electrode during one hour. After formation, the films were washed with de-ionized water. Samples of Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub>O deposits were then annealed in the air at 400°C for 1 h.

The morphology was observed by using a Digital Instrument Nanoscope III (Scanning Probe Microscope Controller) AFM in tapping mode was employed to observe the film topography and to estimate surface roughness. The crystalline structure was investigated based on the X-ray diffraction (XRD) patterns of the films were recorded with Philips X'Pert Pro Multipurpose X-ray diffractometer using CuK<sub>α</sub> radiation λ<sub>Kα</sub>= 1.5418Å°. The photoelectrochemical study is carried out in a quartz cell, the photosensitization source is an Hg lamp used to illuminate an active area of 1cm<sup>2</sup> of the sample.

## 3. Results and discussion

### 3.1. Electrochemical deposition

The mechanism of ZnO formation from nitrate ions and dissolved oxygen has been developed by some papers [21, 22]. Cathodic electrodeposition of ZnO thin films from nitrate and chlorated solution occurred according to an EC (electrochemical-chemical) mechanism. Hydroxide ions were generated by reduction of nitrate ions as shown in Eq. (1). Hydroxide ions production increased interfacial pH between electrode and solution. Zn(OH)<sub>2</sub> adsorbats are formed by chemical reaction between Zn<sup>2+</sup> and hydroxide ions as shown in Eq. (2).



ZnO was produced at the interface electrode/solution simultaneously with water formation after  $\text{Zn(OH)}_2$  is spontaneously dehydrated as presented in Eq. (3) [22]:



The overall expression of the reaction therefore is,



The nitrate reduction ions contributed to increase the interfacial pH as well as oxygen reduction. The contribution of nitrate ions in the crystallization of ZnO was already discussed by Mondal et al. [23]. The pH reached during the Eq. (1) and Eq. (2) led the ZnO to precipitate on the working electrode surface. It was noticed that nitrate reduction involved a higher pH value at an applied potential of -1 V/ Ag/AgCl with a negligible contribution of water reduction [24]. The formation of  $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$  phase can be attributed to the high concentration of  $\text{Zn}^{2+}$  in electrolyte, which gives rise to the large ionic products ( $[\text{Zn}^{2+}][\text{OH}^-]_2$  and  $[\text{Zn}^{2+}][\text{OH}^-]_x[\text{Cl}^-]_y$ ) in solution and hence the precipitation of zinc hydroxylchloride compounds ( $\text{Zn(OH)}_x\text{Cl}_y$ ) in the as-synthesized nanodeposits to Eq. (5). Peulon and co-workers [15] mentioned this steps before.



Fig. 1(a, b) shows chronoamperometric transient curves recorded during ZnO growth under constant potential at -1V with two  $\text{Zn}^{2+}$  concentrations: (a)  $5 \cdot 10^{-3}$  M, (b) 0.1 M. The shape of Fig. 1a related to ZnO deposit is typical of a three dimensional electrocrystallisation growth process as mentioned by [25]. This chronoamperogram is divided into three phases of current response. The first one under 180s corresponds to the step of double layer charging and adsorption of  $\text{NO}_3^-$  anions (causing an increase in the conductivity). In the second phase between 180s and 400s of deposition time, increase of cathodic density current is observed; it becomes narrower due to free growth of ZnO. The cathodic current increases rapidly because of the instantaneous nucleation and the three-dimensional growth of each crystal which led to the rapid increases of the active surface area [16]. In the third phase the current density reaches a plateau value and remains more or less constant. Such answer is a typical result of diffusion controlled growth.

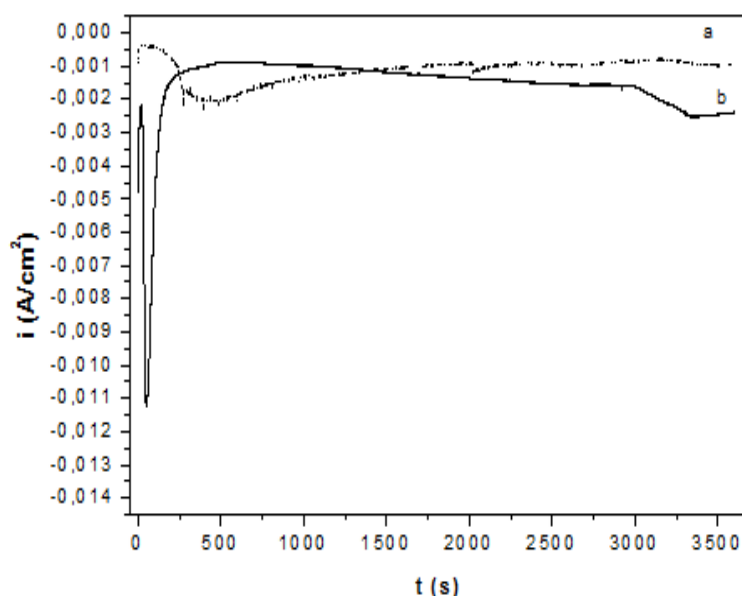


Fig. 1. Current transients during film growth on FTO at  $70^\circ\text{C}$  and  $E = -1$  V vs Ag/AgCl in various  $\text{Zn}^{2+}$  concentrations: (a) 0.005 M and (b) 0.1 M.

The illustrated curve confirms that the ZnO films are electrical conductors, because the current density collected at the electrode is kept at a significant value. It is about  $-1 \text{ mA/cm}^2$  after 1200 s of growth. *Fig. 1b* related to the growth of  $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$  phase is obtained with higher concentration of  $\text{Zn}^{2+}$  salt, the density current changes in similar manner to that observed at lower concentration. However, at the end of the plateau the current density reaches a mean value of  $2 \text{ mA/cm}^2$ . This value is higher than the one obtained at low concentration of  $\text{Zn}^{2+}$  salt.

The observed increase of  $\text{Zn}^{2+}$  in electrolyte concentration ensures a subsequent increase in the conductivity of the solution, indicating a linear increase in the mass movement up to the saturation point. However, higher concentrations of  $\text{Zn}^{2+}$  were found to decrease both the concentration of  $\text{OH}^-$  ions in the solution and the growth rate of the ZnO nanostructure [26].

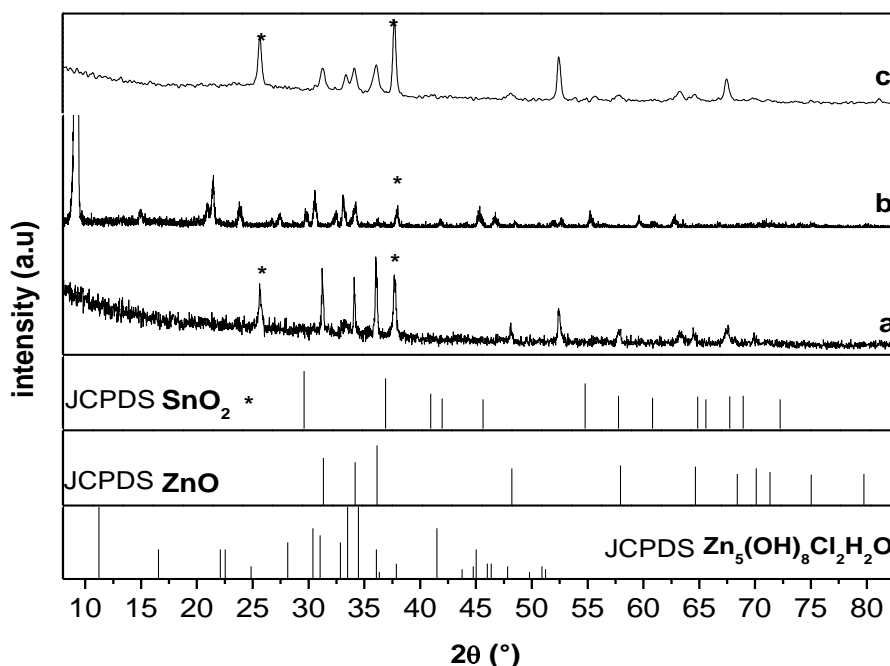
The as deposited  $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$  film was annealed in the air at  $400^\circ\text{C}$  for 1h, it finally decomposes to ZnO according to Eq. (6):



## 3.2. Structural and morphological characterizations

### 3.2.1. X ray diffraction

*Fig. 2* shows the X ray diffraction pattern of ZnO as-synthesized and  $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$  phases before and after annealing. The diffraction peaks are identified as belonging to both ZnO and  $\text{SnO}_2$  (FTO substrate). Pattern related to ZnO reveals an hexagonal wurtzite structure (JCPDS: 36-1451) shown in specter (a) *Fig. 2*. The appearance of several peaks indicates that the films are polycrystalline. It is clear that the preferred growth orientation for the nanocrystalline ZnO is the (101) direction as evidenced by the increase of the ratio between the two peaks associated to the (002) orientation ( $2\theta=34.42^\circ$ ) and the (101) orientation ( $2\theta = 36.25^\circ$ ). This orientation is completely different from that reported by Peulon et al [27], we attribute this fact to the differences in the bath composition which we used. On the other side, our films have the same preferential orientation as obtained by Izaki and Omi with the lowest applied potential [28]. It is evident that not only the mode but also the difference applying potentials influenced the preferential orientation and also the cristallinity of the deposits.



*Fig. 2.* XRD patterns for deposits grown at  $70^\circ\text{C}$  and  $E=-1\text{V}$  vs  $\text{Ag}/\text{AgCl}$  prepared from solutions with  $\text{Zn}^{2+}$  concentrations: (a) 0.005 M (as-deposited); (b) 0.1M (simonkolleitea); (c) 0.1M (annealed).

The full-width at half-maximum (FWHM) small values of the XRD pattern shows that ZnO deposits are made of small grains. Evaluating from the (101) diffraction peak using the Debye-Scherrer formula, the mean grain size of ZnO nanocrystalline is about 31 nm. *Fig. 2 (b)* confirm the formation of  $Zn_5(OH)_8Cl_2$  (JCPDS 07-0155) and no other peaks were observed. The mechanistic study carried on by Peulon et al [15] on ZnO electrodeposition shows also the existence of such phase, they inferred that the formation of these hydroxyl compounds occurs when the ionic products of the corresponding ions are higher than the solubility product. This situation arises when the  $Zn^{2+}$  concentration is greater than 0.01M (with 0.1MKCl). The present results are in good agreement with such conclusion, for the fact that obtention of  $Zn_5(OH)_8Cl_2$  phase is observed but with higher  $Zn^{2+}$  concentration and not with 0.005 M of  $Zn^{2+}$  salt.

A noteworthy result was obtained with the annealed film of  $Zn_5(OH)_8Cl_2$  at 400°C for 1-hour *Fig. 2c*: all its diffraction peaks match with the standard data of hexagonal ZnO structure (JCPDS 07-155). This indicates that the deposited material is composed of wurtzite ZnO generated from the decomposition of  $Zn_5(OH)_8Cl_2$  to ZnO as mentioned before in reaction 6. We can note the decrease in the peaks intensities and the absence of preferential orientation. This can be attributed to the fact that ZnO preparation here occurs in two steps and needs heating treatment in contrast for the first deposits. The increase of temperature here did not favour a specific orientation since we have the decomposition of  $Zn_5(OH)_8Cl_2$  and the growth of the oxide did not occur on a fresh activated surface of FTO. Furthermore, the size of grains is also decreased comparatively to the Simonkolleitea crystallites.

### 3.2.2. Force atomic microscopy

AFM technique was used to investigate surface morphology of each kind of film, we present here the two dimensional images. With lower concentration of Zn salt(0.005M), ZnO deposits display a compact homogeneous surface of dense film structure formed by agglomeration of smaller grains as seen in *Fig. 3a*. At high concentration of Zn salt, the Simonkolleitea films illustrated in *Fig. 3b* exhibit different surface morphological features than that of as-deposited ZnO films, the distribution of grains seems to be more sparse and inhomogeneous. *Fig. 3c* display the morphology of ZnO generated after Simonkolleite annealing at 400°C for 1 h. This later presents a real change in its surface developing more larger grains with absence of defects observed in the simonkolleitea surface and less smoother surface than as-deposited ZnO films, this is due to the fact that growth of ZnO crystal took place on already formed nuclei and not on initial FTO substrate. Differences occurrence from simonkolleitea surface may be attributed to the volatilization of ZnCl and hydroxides products.

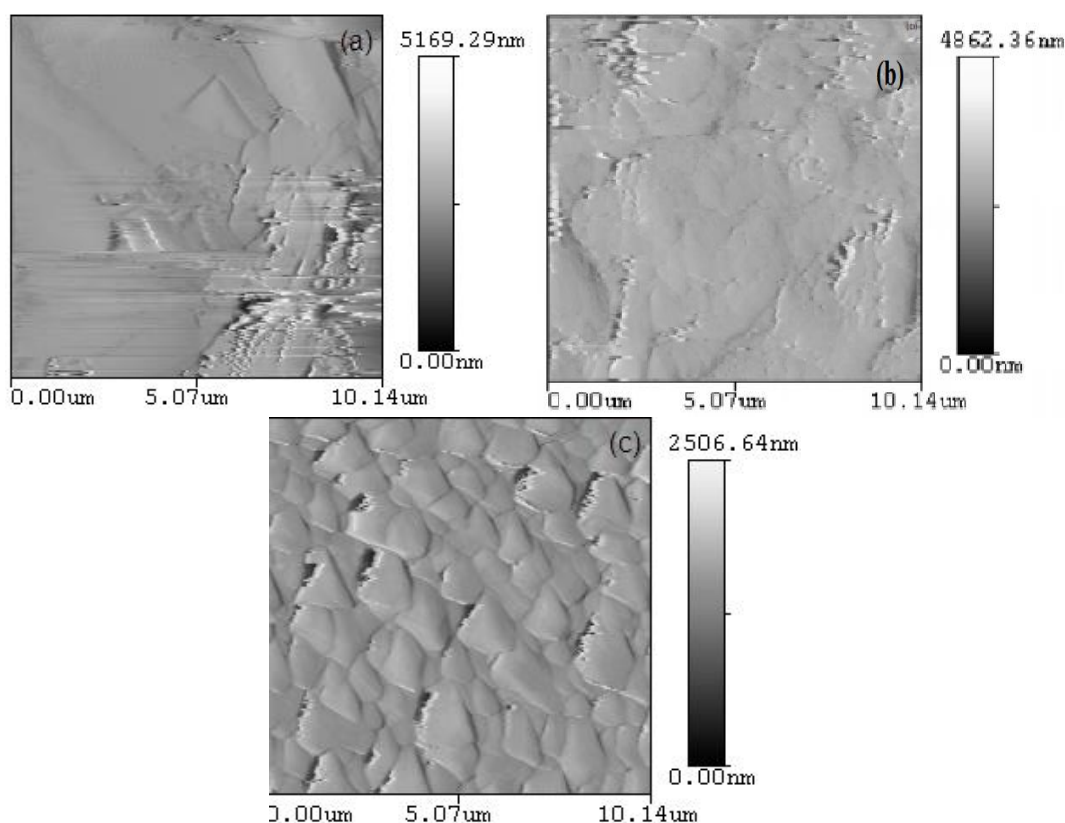


Fig. 3. AFM images of films electrodeposited at  $E = -1V$  vs  $Ag/AgCl$ : (a) in  $0.005 M$  zinc salt (as-deposited under  $70^{\circ}C$ ); (b) in  $0.1M$  zinc salt (simonkolleite); (c) annealed at  $400^{\circ}C$  for 1 hour.

The root mean square RMS roughness of surfaces shows that ZnO films obtained after annealing process present more increasing roughness ( $246.19 \text{ nm}$ ) than as-deposited ZnO films elaborated at low temperature ( $159.81 \text{ nm}$ ). Furthermore the corresponding roughness of Simonkolleite surface indicates the most important value ( $371,02 \text{ nm}$ ) showing the influence of the heat treatment and initial salt concentration on the crystallinity and deposits surface characteristics. These measurements are in agreement with the DRX results.

### 3.3. Impedance measurements

The electrochemical impedance spectroscopy (EIS) measurements were performed to verify the influence of the electrical contact behaviour between TCO and ZnO elaborated oxide and to check about the conductive behaviour of the deposits. Typical complex plane plots for these electrodes are presented in Fig. 4(a,b) which were recorded under the following conditions: the frequency ranged from  $100 \text{ kHz}$  to  $20 \text{ mHz}$  at potential of  $0.9 \text{ V}$  under dark and UV light in  $K_2SO_4$  solution.

Fig. 4(a) shows that Nyquist plots of these films are similar in the dark for the all films; the plots contain one semicircle with larger diameter due to charge transfer resistance. The main differences of the impedance curves occur in the diameter of semicircles which change from one deposit to another. For the as deposited film (ZnO at lower concentration  $0.005M$ ) the semicircular loop at low frequency is small. This small semicircle indicates a low interfacial charge transfer resistance which can be attributed to the good electrical conductivity of the oxide.

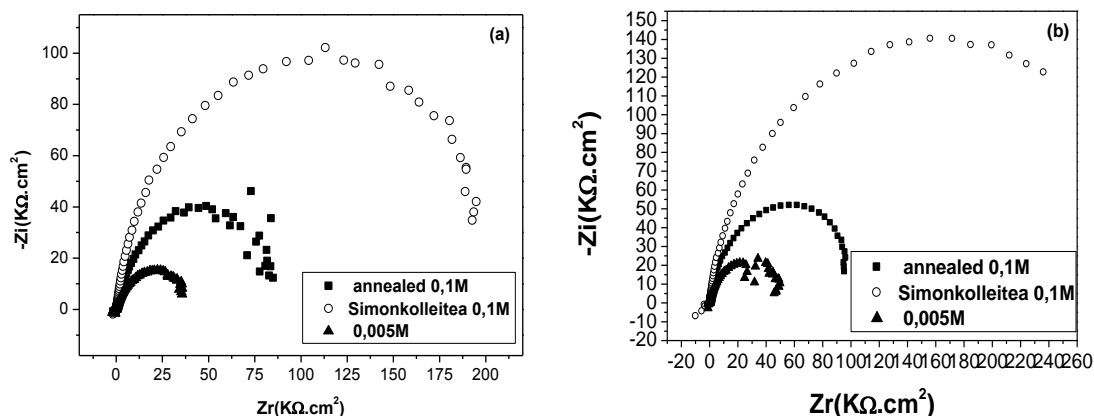


Fig. 4. Impedance spectra of the three deposits (a) under dark (b) under light, in (■) 0.005 M zinc salt (as-deposited under 70°C); (○) in 0.1M zinc salt (simonkollitea); (▲) annealed deposit at 400°C for 1 hour.

Fig. 4(a) shows that Nyquist plots of these films are similar in the dark for all films; the plots contain one semicircle with larger diameter due to charge transfer resistance. The main differences of the impedance curves occur in the diameter of semicircles which change from one deposit to another. For the as-deposited film (ZnO at lower concentration 0.005M) the semicircular loop at low frequency is small. This small semicircle indicates a low interfacial charge transfer resistance which can be attributed to the good electrical conductivity of the oxide. However, the Simonkollitea film presents larger semicircle indicating poor electrical conductivity as compared to the as-deposited ZnO films. Concerning ZnO generated from simonkollitea annealing its impedance curve shows a decrease in the diameter of the arc which remains more important than the one of the initial obtained ZnO and smaller than the one of Simonkollitea. It exhibits an intermediary conductivity. As shown in Fig. 4(b), the impedance behaviour of films under UV light is similar: Nyquist plots of three deposits show an important decrease in the diameter of the semicircle of the impedance curves in comparison to the curves under dark Fig. 4(a) denoting the increase of the conductivity of all films.

### 3.4. Photoelectrochemical behaviour

In order to have additional insights on the semi-conducting electrical behavior of our deposits we study their photosensitive answer under light and compare it to the response under dark. Fig. 5 shows the photoelectrochemical response related to the three kinds of deposits under intermittent illumination (UV lamp) in the same conditions under linear anodic polarization (0.9V/Ag/AgCl).

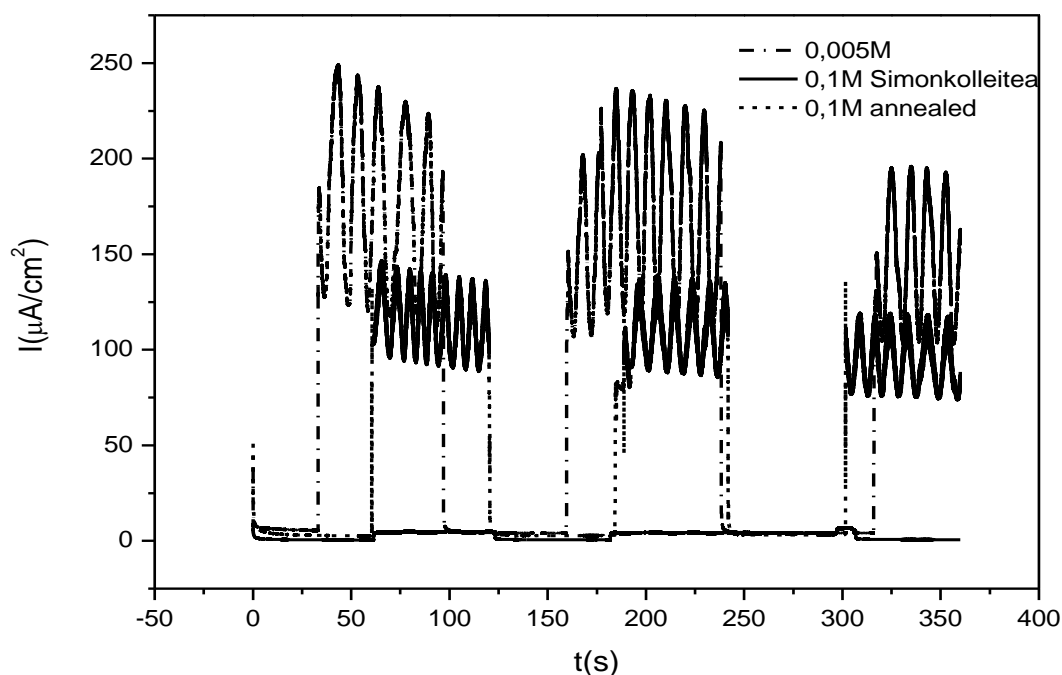


Fig. 5. Photoelectrochemical behavior of electrodeposited films at  $E = -1V$  vs  $Ag/AgCl$ : (-full line) in  $0.1M$  zinc salt (simonkolleitea); (---dashed line) annealed deposit at  $400^{\circ}C$  for 1 hour; (dotted -.line) in  $0.005 M$  zinc salt (as-deposited under  $70^{\circ}C$ ).

Dissimilar behavior for the three films can be remarked. Obviously the simonkolleitea phase is not photosensitive as it presents no photocurrent under illumination see Fig. 5 (full line). Meanwhile both films of ZnO oxide obtained at lower temperature Fig.5 (dashed line) and ZnO obtained at higher temperature after simonkolleitea annealing Fig.5 (dotted line) present important electrophotoactivity. They display an important generated photocurrent under light with sharp increase when light is switched on and an abrupt drop of the current density till an annihilation (zero value) when light is switched off (under dark). Such behavior can be explained by the establishment of Schottky-type contact between the electrolyte and the film, creating a barrier at the electrolyte/film interface. By illumination of the film, carriers are excited and the excited minority carriers diffuse to the surface to participate in the electrochemical reaction at the interface. On the other hand, the majority carriers are expelled from the surface owing to this created Schottky barrier. The positive photocurrent due to the minority carriers (holes) is then observed.

#### 4. Conclusion

In summary the formation of two kinds of ZnO deposits has been carried out via electrodeposition route on indium tin oxide substrate when varying zinc salt oxide proportions and temperature conditions. Using low aqueous mixed bath with lower concentration salt and lower temperature we succeed to deposit polycrystalline ZnO thin films with preferential growth orientation along the (101) direction. The second deposit is obtained at higher temperature in two steps and generated from the simonkolleitea ( $Zn_5(OH)_8Cl_2H_2O$ ) decomposition at  $400^{\circ}C$  for 1h. This later present no preferential orientation and two much smaller grains sizes than the ( $Zn_5(OH)_8Cl_2H_2O$ ) phase deposits. Differences occurred in structural and morphological studies for both deposits were also reported comparatively to the simonkolleitea ( $Zn_5(OH)_8Cl_2H_2O$ ) phase. Spectroscopic impedance measurements informs about the conductive characteristics of the deposits which enhances under UV light. Photoelectrochemical behaviour of three films indicates the ability of both ZnO oxides to generate photocurrents under light.



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