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Morphological and Optical properties of ZnO thin films grown on Si and ITO glass substrates.

N. Ait Ahmed¹, H. Hammache¹, M. Eyraud³, C. Chassigneux³, P. Knauth³, A. lahreche⁴, L. Makhouloufi¹, N. Gabouze²

¹Laboratoire d'Electrochimie, de Corrosion et de Valorisation Energétique(LECVE), Université de Bejaia, 06000 Bejaia, Algérie.

²Centre de Recherche en Technologie des Semi-conducteurs pour l'Energétique (CRTSE), 2, bvd. Frantz Fanon, B.P. 140 Alger 7 Merveilles, Alger, Algérie.

³Aix-Marseille Université, CNRS, MADIREL UMR 7246, équipe Electrochimie des Matériaux, 13397 Marseille Cedex 20, France.

⁴Laboratoire Matériaux : Elaborations-Propriétés-Applications, Université de Jijel 1800, Jijel, Algérie.

Abstract:

In this study, ZnO thin films have been electrodeposited from zinc nitrate solution without using any catalyst, additive or seed layer on two kinds of substrates (Si and ITO glass). Using cyclic voltammetry and chronoamperometry, it was shown that the mechanism of ZnO deposition strongly depends on the substrate used and its overpotential for nitrate reduction. On Si, the nitrate reduction into nitrite occurs before that of Zn^{2+} . This reaction induces an increase of the local pH leading to ZnO precipitation. In contrast on ITO, the Zn^{2+} reduction brings first metallic Zn deposition, which is then chemically oxidized by nitrate into ZnO phase. The effect of deposition time on morphology, structure and photoluminescence properties was studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) measurements. The chemical nature of the substrate has no influence on the orientation of nanorods, but really impacts their morphology and the optical emission properties. X-ray diffraction analysis always revealed ZnO wurtzite phase with a (002) preferential orientation enhanced with increasing deposition time. A well-defined ZnO morphology was generated under -1.4 V for 60 min on Si and ITO glass. ZnO nanorods that composed the nanoflowers grown on ITO glass tend to be shorter, wider, with higher aspect ratio than on Si. ZnO nanostructures prepared on ITO showed an intense UV emission without spreading in the visible region, thus demonstrating the formation of a defect free structure.

Keywords: Zinc oxide; Si and ITO glass substrates; thin films; electrochemical deposition; photoluminescence.

1. Introduction

ZnO is a wide band gap semiconductor whose band gap energy lies typically between 3.1 and 3.4 eV at room temperature. ZnO thin films are widely studied for their interesting optical properties; they generally present the stable wurtzite structure and are suitable for a wide range of applications, such as solar cells and gas-sensors.

ZnO thin films with different nanomorphologies such as nanorods [1], nanosheets [2], nanowires [3], nanospheres [4], nanotubes [5] and nanoflowers [6] have been synthesized by various fabrication methods. These techniques include pulsed laser deposition [7], chemical vapor deposition [8], molecular beam epitaxy [9], spray pyrolysis [10], chemical bath deposition (CBD) [11], hydrothermal synthesis [12], microwave method [13], thermal oxidation [14] and electrochemical deposition (ECD) [15]. CBD and hydrothermal synthesis are the most common methods. However, the deposition rate of CBD is low, while hydrothermal synthesis needs high temperature and pressure [16]. Electrochemical deposition (ECD) is a very simple and economic process through which the film composition can be easily controlled and deposited over a large area with consistent properties [17].

The generally accepted electrochemical formation mechanism of ZnO [18, 19] is initiated by the reduction of nitrate ions into nitrite and hydroxide ion production. This increase in pH leads to Zn(OH)_2 precipitation. The conversion of Zn(OH)_2 into ZnO occurs in an ultimate thermal treatment step [20]. If many papers focus on ZnO thin films and their applications, only few of them deal with the influence of the substrates and experimental parameters during ZnO electrodeposition. J. Yang et al [21] studied the effects of the substrates (Si, glass and ITO-coated glass) on the morphological, structural and photoluminescence properties of ZnO coatings obtained by CBD. J. Cembrero et al [22] did a comparative study for ZnO electrodeposition on Si and ITO by means of a statistical analysis of the main process. They demonstrated that the percentage of substrate area covered by the ZnO deposit is higher on ITO than on Si, probably due to the better conductivity of the former.

In this study, zinc oxide thin films were electrochemically deposited on two substrates Si and ITO glass at high cathodic potential of -1.4V for different deposition times. Our attention was focused on evaluating the effect of substrate and deposition time on the morphology, structure and photoluminescence properties of ZnO thin films.

2. Experimental

ZnO thin films were grown on n-type Si (100) and ITO coated glass by an electrochemical process. The electrodeposition was performed using a potentiostat/galvanostat (Autolab PGSTAT30).

The electrodeposition was carried out in a classical three-electrode system, where Pt served as the counter electrode, a saturated calomel electrode (SCE) as reference, n-type Si (100) or ITO-conducting glass as working electrode. All the potentials mentioned in this paper are indicated versus SCE. The aqueous electrolyte used here contained $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0125 M) and KNO_3 (0.1M) with an initial pH of 6.5; the growth temperature was set at 70°C. Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and KNO_3 were purchased from Sigma-Aldrich (98%) and Fluka (98%), respectively, and were used as received. All solutions were prepared with deionized water purified with a Millipore Milli-Q purification system (18 Ω cm).

Before electrodeposition, the ITO substrate was cleaned in ultrasonic baths with detergent, acetone, and ethanol for 15 min. The treated substrate was then impregnated ultrasonically in distilled water and dried in air. The silicon wafers were cleaned sequentially with acetone (5 min), ethanol (5 min), deionized water (2-3 min), and $\text{H}_2\text{SO}_4 / \text{H}_2\text{O}_2$ (1/3 H_2SO_4 (97%) / H_2O_2 (30%), 10 min); the wafers were then thoroughly rinsed with deionized water (10 min) and dipped 1 minute into a solution of HF [23, 24].

The influence of the growth period (i. e. 10, 20, 40 and 60 min) and the nature of the substrate were investigated. The deposition of ZnO nanoflowers was performed at a fixed potential of -1.4V versus SCE reference electrode.

The surface morphology of the ZnO nanostructures was examined by scanning electron microscopy (SEM) using a Philips XL 30 ESEM. X-ray diffraction (XRD) was performed on a Siemens D5000 diffractometer using $\text{CuK}\alpha$ ($\lambda_0 = 0.15406$ nm) radiation for scattering angles between 25° and 65°. The photoluminescence measurements were carried out at room temperature using a Perkin-Elmer LS-50B luminescence spectrometer with an excitation wavelength of 325 nm (Xe lamp) and a scan rate of 300 nm min⁻¹.

3. Results and discussion

The ZnO electrodeposition mechanism was first investigated by cyclic voltammetry on both substrates. Fig. 1a and b illustrates the cyclic voltammograms recorded on silicon and ITO glass respectively, in the nominal zinc nitrate solution. For comparison, cyclic voltammograms

recorded on these substrates in blank electrolyte (KNO_3 0.1 M only) are presented in **Fig. 2**. It is obvious that from both electrolytes, higher cathodic current densities are observed on ITO glass with regard to Si due to the higher conductivity of ITO. A slight current increase is observed in the cathodic curve on Si (**Fig. 1a**), for potentials below -1.15V . This increase in current can be correlated to the reduction of Zn^{2+} into metallic Zn [25]. Indeed the equilibrium potential for this reaction considering the zinc concentration is -1.06 V/SCE , close to the experimental value. Moreover, the forward current being lower than the backward one, the shape of the curve indicates a deposit formation induced by a nucleation mechanism. A large overpotential is then necessary to reduce NO_3^- ions while the equilibrium potential evaluated neglecting the NO_2^- concentration is 0.17V/SCE , showing that the reduction of anionic species on the cathode is not favorable from an energy point of view. No significant current can be observed until -1.5 V , which corresponds to the H^+ reduction with a very slow rate too (the equilibrium potential is -0.64 V in this solution).

On ITO glass (**Fig. 1b**), the shape of the voltamogram is different. A steep variation in current is first observed below -0.65V , followed by a plateau between -0.8 and -1.2V . For higher cathodic potentials, a new increase in current is then noticeable. The first cathodic peak that appears around -0.8V is located in a potential area where Zn^{2+} cannot be reduced, showing that a different mechanism is involved in this case. On the corresponding nitrate blank curves from **Fig. 2b** these two current increases are visible again with a lower intensity; the first one at about -0.65 V corresponds to the electrochemical reduction of nitrate ions into nitrite, followed by the proton reduction.

We also note that on both substrates, no oxidation peak appears on the backward scan, showing that probably only ZnO was formed over the potential range investigated. The deposits obtained on the electrodes after the voltammetry experiment are too thin to be analyzed by XRD. However analyses made on thicker deposits obtained at -1.4 V for deposition times between 10 to 60 min proves that we only get pure ZnO deposits on both substrates (see Fig 5 and associated comments below)

According to these observations, two different mechanisms can be proposed in function of the substrate used. In the case of ITO that presents a low overpotential for nitrate reduction, the well-known mechanism [26] can be proposed: the electrochemical formation of ZnO is initiated by the reduction of nitrate ions that produces hydroxide ions, followed by the precipitation of $\text{Zn}(\text{OH})_2$. The conversion of $\text{Zn}(\text{OH})_2$ into ZnO occurs in an ultimate step due to a thermal treatment. The sequence of the ZnO deposition can be summarized by the following equations:

On substrates that present a high nitrate reduction overpotential, such as Si, the Zn^{2+} reduction leads to metallic Zn deposition which is then chemically oxidized by nitrate ions to form the stable ZnO phase, following:

This mechanism is quite new and was proposed for the first time in [25].

Chronoamperometry experiments (Fig.3) were performed at -1.4 V vs. SCE on (a) Si and (b) ITO glass. In Fig. 3b, a rapid increase in current density up to -4 mA.cm^{-2} is followed by its decrease after 5 s (see the inset in this figure) assigned to a nucleation process of film before it fully covers the ITO substrate. The presence of this wave is typically observed for films of good crystallographic quality and coverage [27-29]. To have a better insight into the nucleation mechanism involved, the experimental curves were transformed following $(i/i_{\max})^2$ vs. $t/t_{\max}$ and compared with the theoretical curves obtained from the Scharifker and Hill (S-H) model of nucleation [30]. Indeed, according to this model the instantaneous nucleation follows the relationship:

$$\left(\frac{i}{i_{\max}}\right)^2 = 1.9542 \left(\frac{t_{\max}}{t}\right) \left[1 - \exp\left(-1.2564 \frac{t}{t_{\max}}\right)\right]^2 \quad (7)$$

and the progressive nucleation:

$$\left(\frac{i}{i_{\max}}\right)^2 = 1.2254 \left(\frac{t_{\max}}{t}\right) \left[1 - \exp\left(-2.3367 \frac{t}{t_{\max}}\right)\right]^2 \quad (8)$$

(Fig. 4 (a)) on Si, clearly shows that the nucleation does not follow neither instantaneous nor progressive mechanism. At the early stage, a very slow nucleation rate is obtained that increases with time. This suggests a very small numbers of nucleation sites at the beginning and when the first atomic layer of ZnO is deposited; it serves as nucleation site and consequently the nucleation rate increases with time. In contrast on ITO (Fig. 4(b)), the nucleation at the early stage (short time $t < t_{\max}$) follows an instantaneous law switching to progressive nucleation for longer time ($t > t_{\max}$). This result is in agreement with previous studies [31, 32].

Typical XRD patterns of the as-deposited films grown on Si and ITO glass deposited at -1.4 V for different deposition times (10, 20, 40 and 60 min) are shown in Fig. 5(a and b). Whatever the substrate used, XRD measurements revealed only peaks corresponding to the ZnO planes (100), (002), (101) and (102) confirmed by the standard JCPDS (No. 36-1451) files [33], indicating the polycrystalline nature of the films. No characteristic peaks of other phases were observed. It is worth noting that both samples deposited for 10 min on Si and ITO glass, have a polycrystalline structure with a random orientation. When the deposition time increases, the (002) peak becomes gradually more intense compared to the others, indicating a preferential direction of growth along the c axis. This result gives a clue about the formation of a better crystallographic structure of the films deposited for longer deposition time on Si and ITO glass. Previous researches have shown similar results [34–38]; however, Gu et al found a decrease of the (002) orientation with the increase of deposition times [39]. The preferential growth orientation was determined using a texture coefficient $TC(hkl)$ calculated using the following relation [38]:

$$TC_{(002)} = \frac{\frac{I_{(002)}}{I_{(002)}^0}}{N \sum_{i=1}^n \frac{I_{(hkl)}}{I_{(hkl)}^0}} \quad (9)$$

Where $I_{(hkl)}$ corresponds to the measured XRD intensity for the corresponding (hkl) peak, $I_{(hkl)}^0$ is the reference intensity in JCPDS file, $TC_{(002)}$ the texture coefficients of the (002) plane, $I_{(002)}$ the corresponding measured intensities, $I_{(002)}^0$ the intensity of this plane according to the JCPDS 036-1451 card, N the refraction number and n the number of diffraction peaks.

The calculated texture coefficients TC are presented in Table 1. It can be seen that the highest TC is obtained for the (002) plane of the ZnO thin film at -1.4V for 60 min on Si. It can also be seen from Table 1 that the texturation of the films increases with the deposition time.

Table 1

Values of texture coefficient of ZnO electrodeposited on Si and ITO glass at -1.4 V for 10, 20, 40 and 60 min, from 0.0125 M [Zn (NO₃)₂, 6H₂O] and 0.1 M [KNO₃] solution

	TC(002)			
	10 min	20min	40min	60min
ZnO/Si	2.18	2.60	2.76	3.65
ZnO/ITO	1.13	2.05	2.39	3.1

Fig. 6 shows SEM images of ZnO thin films grown on both substrates for several deposition times. The coverage and morphology of the ZnO thin films are both significantly dependent on the substrate and electrodeposition time. On Si, after 20 min (**Fig6 (a)**) scattered ZnO nanorods are obtained. By increasing the electrodeposition time (40 and 60 min) (**Fig 6(d-f)**), the deposits become denser and nanorods tend to turn into flowers. Each flower contains a multitude of nanorods with uniform hexagonal ends pointing in different directions better seen in the high magnification images (**Fig.6 (e-f)**).

In contrast, the ITO glass is totally covered by different sized crystallites after 20 min (**Fig. 6(h)**), indicating a fast growth rate in comparison with Si. The grains are here packed closely and well distributed on the substrate. Each grain is made by an aggregation of very small crystallites. The aggregates tend to cauliflower morphological. For longer times (**Fig.6 (i-k)**), the deposits become denser, consisting of flower-shaped crystallites. Higher magnification (**Fig.6 (k)**) confirms the existence of only "flower sand" crystallites. We noted that the deposited obtained on ITO glass shows morphologies quite different from those obtained on Si, which highlights the effect of the substrate. Simimol et al [40] attributed the ZnO morphologies to the difference in conductivity of the substrate.

Fig.7 (a and b) shows the room-temperature PL spectra of the ZnO films electrodeposited at -1.4 V for different deposition times on Si and ITO substrates. We can be observed that on silicon three main emission regions can be seen(peaks at 386 nm, 434 nm and a broad peak at 532 nm) compared to a single peak at 393 nm on ITO.

As seen in **Fig. 7(a)**, the first region around 386 nm (3.2 eV) can be related to the bound excitons [41, 42]. It provides information about the crystalline quality of the films. Several authors attributed the UV luminescence to radiative recombination of excitons from the excitonic levels that are close to the conduction band levels [43, 44]. The second region in the visible range at 434 nm (2.85 eV) is assigned to Zn levels for (Zn_i) transitions [45]. The energy involved here is in good agreement with that calculated between the Zn_i level and the valence band (2.9 eV) [46]. The third emission at about 532 nm (2.33 eV) can be attributed to crystal defects [47-49] such as O vacancy (V_O), Zn vacancy (V_{Zn}), antisite defect, O on Zn sites (O_{Zn}), and Zn interstitial (Zn_i) [50] due to the poor stoichiometry of ZnO. The intensity of this band decreases with increasing deposition time indicating that the layer exhibits a better crystallinity and less defects. Dijken et al [51] attributed the luminescence of ZnO nanocrystals in the visible to two possible processes: a recombination of an electron with a hole of a deep level or an electron-hole recombination.

In **Fig. 7 (b)**, the spectra present only a strong single emission band located at 393 nm. The intensity of this band increases with the electrodeposition time. Similar results at 384 nm [52] and 398 nm [53] have been reported in literature for ZnO films. Li et al [54] observed the same energy values. The disappearance of the larger band obtained at lower energy on Si, leads us to conclude that ZnO coated on ITO presents a higher crystalline quality with reduced defect density. The nanocrystal size being lower on ITO than on Si, a PL spectra shift to shorter wavelengths is obtained which is in agreement with the theory of quantum confinement [55], compared to the direct band to band radiative transition mechanism.

Conclusion

Highly oriented ZnO thin films with a hexagonal wurtzite structure are grown on both Si and ITO substrates by an electrodeposition method. The influence of the substrate on the nucleation and growth mechanism was studied using cyclic voltammetry and chronoamperometry. It is obvious that the mechanism involved strongly depends on the overpotential for nitrate reduction. On Si, that presents a low overpotential for this reaction, the reduction of nitrate into nitrite ions occurs first leading to ZnO precipitation. On ITO, that presents a higher nitrate overpotential, Zn^{2+} reduction leads to metallic Zn deposit that is then oxidized to ZnO by nitrate species. The XRD results indicate a hexagonal wurtzite structure for ZnO deposits with a preferential orientation along the c axis, which increases with deposition time. However, the morphology of ZnO grown on these two substrates is quite different

highlighting a difference in the growth mechanism already seen in chronoamperometry experiments. Room temperature photoluminescence measurements show ultraviolet PL activity in the case of ZnO grown on the ITO glass substrate and three emission regions in the case of the Si substrate. The obtained results confirm the formation of nearly defect-free ZnO on ITO glass compared to that on Si.

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Fig.1 *Fig.2*

Fig.3

Fig.4

Fig.5

$t = 60 \text{ min}$

5 μm

$t = 60 \text{ min}$

1 μm

500 nm

200 nm

$t = 20 \text{ min}$

10 μm

$t = 40 \text{ min}$

10 μm

Fig.6

Fig.7

Figures Captions:

Fig.1 Cyclic voltammograms measured at: **(a)** Si electrode and **(b)** ITO glass in $[\text{Zn}(\text{NO}_3)_2, 6\text{H}_2\text{O}] = 0.0125 \text{ M}$ and $[\text{KNO}_3] = 0.1 \text{ M}$. $T = 70^\circ\text{C}$, scan rate $= 5 \text{ mV/s}$.

Fig.2 Cyclic voltammograms measured at: **(a)** Si electrode and **(b)** ITO glass in $[\text{KNO}_3] = 0.1 \text{ M}$. $T = 70^\circ\text{C}$, scan rate $= 5 \text{ mV/s}$.

Fig.3 Chronoamperometric curves recorded on **(a) Si electrode and (b) ITO glass** in $[\text{Zn}(\text{NO}_3)_2, 6\text{H}_2\text{O}] = 0.0125 \text{ M}$ and $[\text{KNO}_3] = 0.1 \text{ M}$; $E = -1.4 \text{ V}$ vs. SCE, $T = 70^\circ\text{C}$. inset: magnified view at short deposition time.

Fig.4 Theoretical models for ZnO nucleation deposited on: (a) Si and (b) ITO glass compared to experimental data.

Fig.5 X-ray diffraction patterns of ZnO obtained at different electrodeposition times on: (a) Si (100), (b) ITO glass; from $[\text{Zn}(\text{NO}_3)_2, 6\text{H}_2\text{O}] = 0.0125 \text{ M}$ and $[\text{KNO}_3] = 0.1 \text{ M}$; -1.4 V vs. SCE, $T = 70^\circ\text{C}$.

Fig.6 SEM images of ZnO under different electrodeposition times on: Si (100) (a, b, c, d, e, f), and ITO glass (h, i, j, k); $[\text{Zn}(\text{NO}_3)_2, 6\text{H}_2\text{O}] = 0.0125 \text{ M}$ and $[\text{KNO}_3] = 0.1 \text{ M}$; $E = -1.4 \text{ V}$, $T = 70^\circ\text{C}$.

Fig.7 Room temperature PL spectra of ZnO for different electrodeposition times on: (a) Si substrate, (b) ITO glass; $[\text{Zn}(\text{NO}_3)_2, 6\text{H}_2\text{O}] = 0.0125 \text{ M}$ and $[\text{KNO}_3] = 0.1 \text{ M}$; $E = -1.4 \text{ V}$, $T = 70^\circ\text{C}$.

Answer to reviewer #1

Thank you a lot for the careful reading and comments improving the quality of the manuscript.

We considered carefully your comments (see the answers below).

To improve the paper, numerous parts were rewritten (see the highlighted areas in the text)

Comment 1) about the temperature

A heated solution is needed to get the dehydration of $\text{Zn}(\text{OH})_2$ into ZnO that is the third step of the mechanism proposed in page 4..

Comment 2) the chemical composition of ZnO films are the same on both substrates at least according to XRD analysis, where only the ZnO wurtzite phase was observed, and EDS analysis where only Zn and O elements were found in quite the same proportion (in addition to them coming from the substrate). Concerning the mechanical properties, the deposits are quite brittle especially for longer deposition time, because the preferential orientation increases with the time.

Answer to reviewer #2

Thank you a lot for the careful reading and comments improving the quality of the manuscript. We considered carefully your comments (see the answers below).

To improve the paper and respond to your comments N° 2 and 5, numerous parts were rewritten (see the green highlighted areas in the text)

Comment 1: the sections in “Abstract” and “Conclusion” paragraphs were removed.

Comment 3: the paragraph concerning the discussion about voltammetry results was rewritten and the equilibrium potential was added.

Comment 4: According to us the discussion of the mechanism has to be close the voltmetry experiments to keeps its meaning. The deposits obtained on the electrodes after the voltammetry experiment are too thin to be analysed by XRD. We add a sentence, explaining that the deposit obtained at $E=-1,4V$ was composed only of ZnO crystallites and referred to the corresponding paragraph and figure below.