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Research paper

Investigation of the Nucleation Kinetics of Bi and Δ-Bi_2O_3 During Electro-Deposition on Substrate ITO

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Abstract

Bismuth and there oxide (δ-Bi_2O_3) thin films were deposited on ITO substrates by electro-deposition method. First a cyclic voltammetry study, over a wide range of potentials, with the mounting of three electrodes and an electrolytic solution of 0.01M $Bi(NO_3)_3.5H_2O$, 0.25M tartaric acid and 2.5M KOH. Towards cathode potential -900mV / SCE we observed the peak of reduction of Bi (III) to Bi (0). When scanning towards increasing potentials we observed a nucleation loop on the electrode, which indicates that there is nucleation, followed by an oxidation peak of Bi (0) to Bi (III). Then we carried out a study of the germination kinetics by carrying out transients current at potentials close to that of reduction peak. The comparison of our transients curves obtained by the chrono-amperometric method with the theoretical transients curves of Charifker and Hills allows us to say that the nucleation is three-dimensional and progressive at a poteniel of -940mV and -950mV but, at a potential of -980 that seems rather for small deposition time a progressive nucleation that can change to an instantaneous nucleation. The characterization of one sample was carried out by X-Ray diffraction, showed that the film was pseudo-fluorite structure. The preferred orientation of the crystallites is (200) for the as deposited film.

Keywords: *Bismuth, Bismuth oxide, Nucleation, cyclicvoltametry, Chronoamperometry*.

1. Introduction

Bismuth and there oxide δ-Bi_2O_3 are very interesting semiconductor for researchers for their remarkable properties. Bismuth is the less toxic element than the metals which are close to it in the periodic classification. The bismuth is not a pollutant for the environment and it has an excellent chemical and thermal stability. It has a large magnetoresistance[1], interesting quantum effects [2] and thermoelectric efficiency [3]. These properties allow Bismuth to be used for several high technological applications such as solar cells, electrochromic devices, environmental detection, catalysis, superconductivity, thermoelectrical and piezoelectrical devices [4]. Bismuth oxide Bi_2O_3 exists in several allotropic forms, the δ-Bi_2O_3 phase, stable at high temperature (700°C) [5], is a good ionic semiconductor [6], which can be used as a support electrolyte in Solid Oxide Fuel Cell (SOFC). The initial stages of Bismuth and δ-Bi_2O_3 electrodeposition on substrate ITO from alkaline electrolyte were investigated by cyclic voltammetry and chrono-amperometry. Electrochemical deposition (ECD) is emerging as an important, least expensive, and ready method to prepare thin films such as Bi; this method presents interesting characteristics for large-area, low-cost, generally low-temperature and soft processing of materials. This technique allows also an easy control of the dimensions of nanostructures by means of appropriate growth parameters.The one-step electrodeposition of Bi films has been extensively reported, using perchlorate, lactate, nitrate, and pyrophosphate as electrolytes [7, 8].

2. Experimental

For the electro deposition of Bi and δ-Bi_2O_3 we have used as electrolyte: 0.01M ($Bi(NO_3)_3$, $5H_2O$) with 2.5M KOH and 0.25M tartaric acid. The starting materials were high-purity Bismuth nitrate ($Bi(NO_3)_3$, $5H_2O$) and potassium hydroxide KOH (> 98%). We prepared our solutions with deionized water. The electrochemical measurements including cyclic voltametry CV and Chrono-amperometry CA measurements were performed using a potentiostat/galvanostat PGZ 301 Dynamic-EIS and voltametry chemical Laboratory coupled with computer under Voltalab 40 logiciel. The CV and CA measurements were carried out in a classical three electrod cell with: the glass carbon electrode GCE (1,5 cm in diameter) as a counter electrode, a saturated calomel electrode SCE as reference electrode and as working electrode we have used Indium Tin Oxide ITO (0,25cm^2 in area). Before any measurements ITO electrode was cleaned in an ultrasonic bath of distilled water for 5min. The structure, crystallinity and phase of the δ-Bi_2O_3 thin films were determined by the X-ray diffraction (XRD) analysis, using X' Pert PRO XRD (Panalytical Company, Netherland) operating at 35 kV and 60 mA using Cu Kα radiation (λ = 1.544 Å) in a range 10–80° 2θ with a step-width of 0.02°.

3. Results and Discussion

3.1. Voltammetrycclic results:

Cyclic Voltammetry.CV is a type of potentiodynamic electrochemical measurement which consists in the investigation of electrolysis mechanism [9], used to investigate the chemical reactivity of species. In our work, CV is used to define the potentiel region for deposition and dissolution of Bi on ITO as well as the presentation of a new reversible system. Fig.1 shows the series of cyclic voltammograms for Bi electrodeposition on ITO from alkaline electrolyte at different scan rates. The cyclic voltammograms were consistent with that of typically observed in metal deposition stripping processes. Each curve displays a couple of well-defined cathodic and anodic peaks and a crossover between the going and reverse scans. The presence of this crossover gives rise to what has been called the “nucleation loop”[9] which indicated the formation of Bi nucleation on ITO.

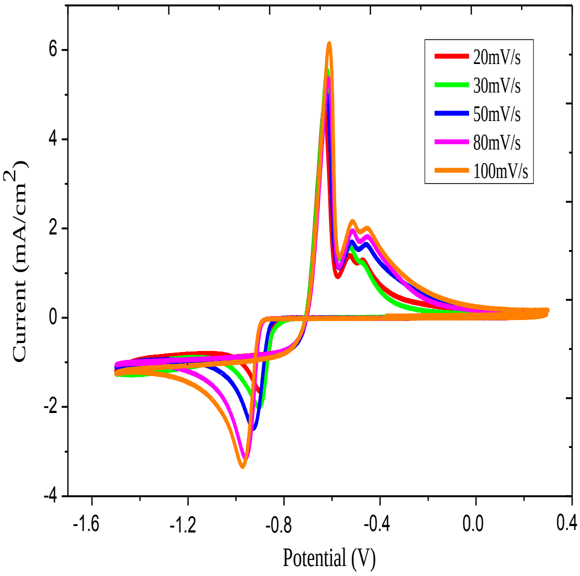

Fig .1: Cyclic voltammograms for Bi electrodeposition on ITO from alkaline electrolyte at different scan rates

According to the Pourbaix Atlas [10], BiO_2^- can only takes place in hot concentrated caustic media at very basic pH close to 14. Bi_2O_3 seems to be the most probable specie in our solution. Moreover, in the presence of the tartrate ion, the stable complex Bi $(T)_2^-$ where T represents the ligand tartrate (pK_d=11,3) is formed. It is grace to this ion that the nitrate is soluble in solution. The oxidation peaks observed in Fig.1 could be explained by the formation of these diffErnt species BiO_2^- and $Bi(T)_2^-$ by oxidation of Bi(0).

Furthermore it can be seen from Fig. 1 that the reduction peak potential shifts to more negative potentials up on increasing the scan rate, which was typically associated with quasi- reversible electrochemical reactions [7].

In order to determine the type of control limiting the deposition process, the cathodic peak current (I_{Peak}) versus the square root of the sweep rate ($v^{1/2}$) for the cyclic voltammograms was plotted and shown in Fig. 2. It can be seen that the plot displays an excellent linear relationship with a correlation coefficient 0,998, indicating a diffusion controlled process [11].

3.2. Chronoamperometry results.

The study of nucleation and growth via electrochemical methods offers a certain advantage over other methods, because the driving force of nucleation can be simply varied by changing the applied potential. Therefore, the mechanism of nucleation and growth can be determined by analysis of transients current from CA measurements [9,11-13]. Fig. 3 shows the series of transients current for Bi electrodeposition on ITO from alkaline electrolyte at different deposition potentials. After applying the potential step, due to the double layer charging, a rise and then fall in current can be observed, which is characteristic of Bi nucleation and growth. In this latter region, the maximum current (I_{max}) increases while the time (t_{max}) required to reach I_{max} decreases with increasing over potential as a result of the higher nucleation densities[7].

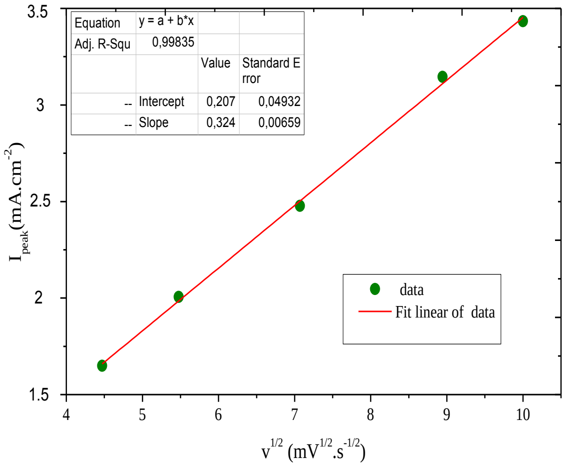

Fig.2: The Plot of the cathodic peak current (I_{Peak}) versus the square root of the sweep rate ($v^{1/2}$) for the cyclic voltammograms presented in Fig.1

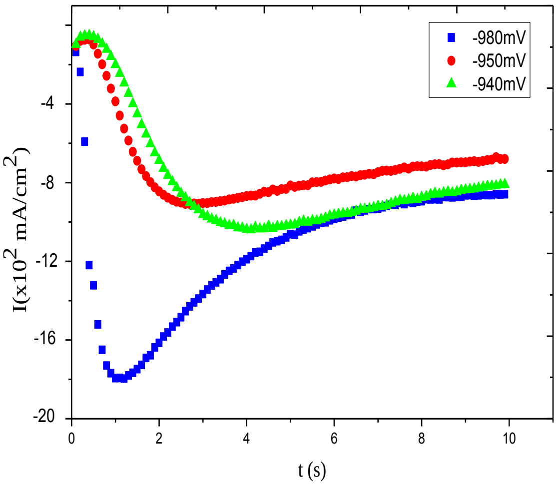

Fig.3: Transients current for Bi electrodeposition on ITO from alkaline electrolyte at different potential

The series of curves giving the transients current I as a function of $t^{-1/2}$ was drawn as shown in Fig. 4. These curves show that the relation between I and $t^{-1/2}$ is linear according to the Cottrell equation [14], which is a typical response of three-dimensional (3D) multiple nucleation with diffusion controlled growth [15-16].

The diffusion coefficient D (table.1) can be deduced from the slopes of the curves in Fig.4, according to the Cottrel equation:

$$i = n.F.C\left[\frac{D}{\pi.t}\right]^{\frac{1}{2}} \qquad (1)$$

Where:

i : is the current,

n: number of electrons,

F: Faraday constant = 96485 (C.mol^{-1}),

C: initial concentration of the reductible analyte in (mol.cm^{-3}),

D: diffusion coefficient in (cm^2.s^{-1})

and t the time in (s).

The Diffusion coefficient values are summarized in Table 1, These observations are in good agreement with the results obtained by Z. Longping *et al* [11].

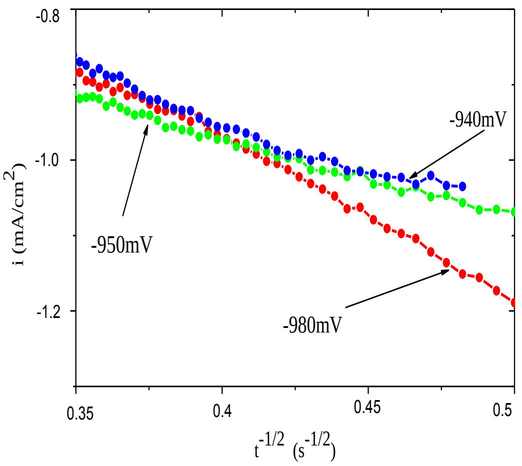

Fig.4: Transients Current (I) versus t $^{-1/2}$ curves for CA measured value presented in Fig. 3

Table 1. Diffusion coefficient of the Bi electrodeposition on ITO from alkaline electrolyte.

E vs SCE(V)	D(x10^{-6}cm^2.s^{-1})
-0.98	1.4
-0.95	0.63
-0.94	0.84

The figure.5 shows the comparison of theoretical non-dimensional $(I/I_{max})^2$ versus t/t_{max} plots for instantaneous nucleation from Eq. (2) and progressive nucleation from Eq. (3) established by B. Scharifker *et al* [14], to the experimental current transients for Bi electrodeposition on ITO from alkaline electrolyte at different deposition potentials.

$$\left(\frac{I}{I_{max}}\right)^2 = 1.9542\left(\frac{t}{t_{max}}\right)^{-1}\left\{1-\exp\left[-1.2564\left(\frac{t}{t_{max}}\right)\right]\right\}^2 \qquad (2)$$

$$\left(\frac{I}{I_{max}}\right)^2 = 1.2254\left(\frac{t}{t_{max}}\right)^{-1}\left\{1-\exp\left[-2.3367\left(\frac{t}{t_{max}}\right)^2\right]\right\}^2 \qquad (3)$$

We observe (Fig. 5) that the experimental curve at -980mV is in agreement with the progressive nucleation model followed by a three-dimensional growth(3D) before the maximum of the current, then it changes to the instantaneous 3D model, this is may be due to the reduction of H^+ ions. On the other hand, the experimental curves at -950mV and -940mV are close to the progressive nucleation model followed by a three-dimensional growth (3D) and especially at the first instants of deposition.

Apriori we can say that the deposition of Bi on the ITO is governed by a progressive nucleation followed by a three - dimensional growth 3D [17].

3.3. Mechanism of formation of δ-Bi_2O_3:

The figure.6 Shows that at the anode branch progressed towards the increasing potentials, we obtained a peak of oxidation probably of $Bi(T)_2^-$ as Bi(III) to Bi(IV) in the form of Bi_2O_5 followed by an oxidation plateau at 1.2V / SCE followed by the oxidation of water. The cyclic voltammetry curve obtained with a solution of tartaric acid and potassium hydroxide without bismuth ions. Fig.7 shows that the oxidation of the tertrate ion is at a potential 0.3V/SCE lower than that 1,25V/SCE observed in Fig.6 which probably justified that $Bi(T)_2^-$ is oxidized to Bi_2O_5 before the tartrate oxidation.

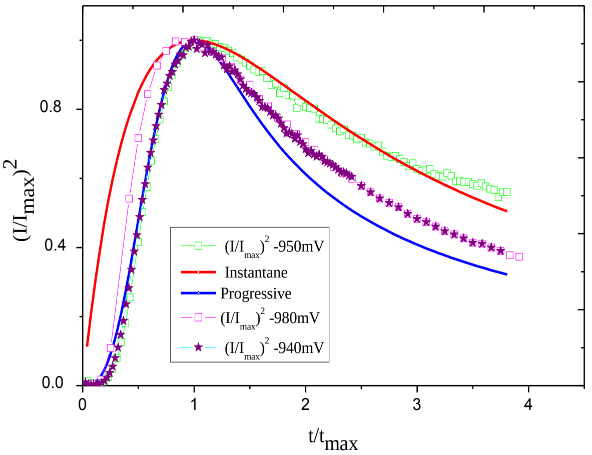

Fig.5: Theoretical non-dimensional $(I/I_{max})^2$ vs. t/t_{max} plots for instantaneous nucleation from Eq. (1) and progressive nucleation from Eq. (2), to experimental transients current of different potential Fig. 3.

The existence of this peak of oxidation followed by a plateau allows us to propose a mechanism for the formation of δ-Bi_2O_3 by oxidation of Bi (0) to Bi (III) and then Bi (V) according to the following equations [11]:

$$Bi + 4HO^- \rightarrow BiO_2^- + 2H_2O + 3e^- \qquad (4)$$

$$2BiO_2^- + 2HO^- \rightarrow Bi_2O_5 + H_2O + 4e^- \qquad (5)$$

The Bi_2O_5 oxide is unstable in water, it spontaneously reduces to δ-Bi_2O_3 with an evolution of the O_2 gas according to:

$$Bi_2O_5 \rightarrow \delta\text{-}Bi_2O_3 + O_2 \qquad (6)$$

This mechanism is in good agreement with that proposed by Switzer *et al* [18].

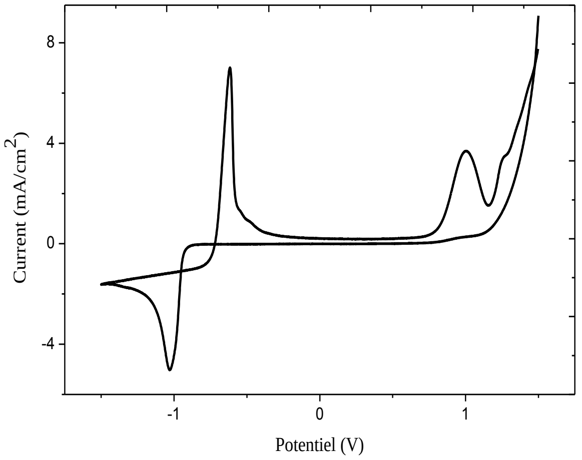

Fig.6: Cyclic voltammogram for Bi electrodeposition on ITO from alkaline electrolyte at potential place (-1.5V to 1.5V/SCE) at scan rate 100mV/s

3.4. Crystal structure determination:

The X-ray diffraction patterns of synthesized sample with electrodeposition method, on ITO realized at 1.2V/ECS, are shown in Fig. 8. From the patterns it is clear that the as deposited thin film all peaks from the diffraction patterns at 2Θ = 27.25°, 33.85°, 53.37° and 58.75° are characteristic of δ-Bi_2O_3 phase, These observations are in good agreement with the results obtained by [20]. The inter-planar spacing values d_{hkl} corresponding to the (111), (200), (311) and (222) diffraction planes are compared with the values of similar compounds reported in theoretical DRX pattern of δ-Bi_2O_3 [19]. These results showed that the crystalline networks have a pseudo-fluorite structure (face-centered-cubic cell, $Fm\bar{3}m$ space group, (ICSD card # 27458)) [20]. The appearance of some XRD peaks reflections corresponding to ITO, and presence of secondary phases. Such as α-Bi_2O_3 and β-Bi_2O_3-type phases, (ICSD card # 41764 and J.C.P.D.S. card #41-1449). The Scherrer equation was used to estimate the particles size from the XRD pattern of the as prepared nanoparticles:

$$D_{XRD} = \frac{k\lambda}{\beta \cos\theta} \tag{7}$$

Where λ is the wavelength of incident radiation (λ = 1.544A°), β is the full-width at half maximum (FWHM) of the preferential orientation diffraction peak and θ is the Bragg diffraction angle. Crystallite size estimation was obtained using the Scherrer formula applied to the separated peaks (111), (200) and (311), and this technique yield values in the range from 8 nm to 11nm.

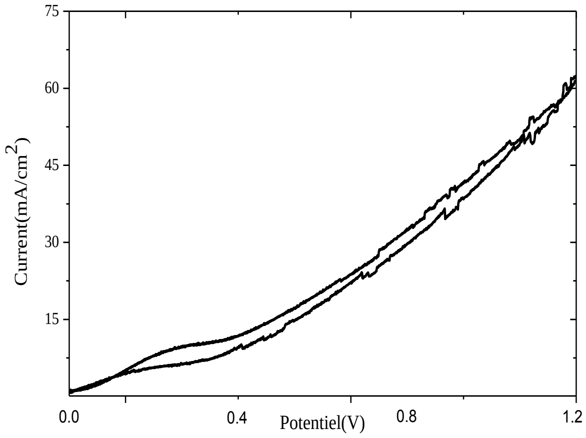

Fig.7: Cyclic voltammogram obtained for a solution 0.25M tartaric acid and 2.5M KOH on ITO at potential place (0 to 1.4V/SCE) at scan rate 100mV/s

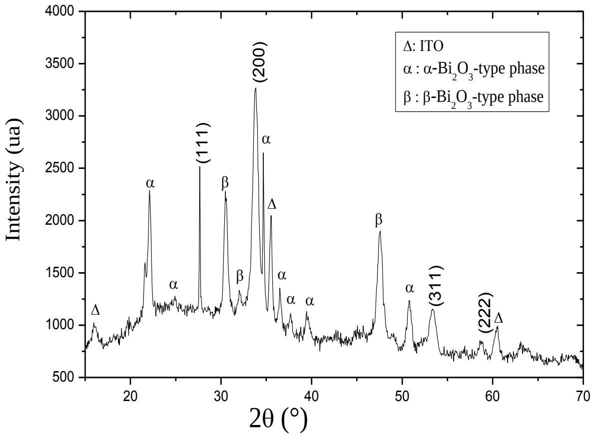

Fig.8: X-ray diffraction patterns of δ-Bi_2O_3 thin film.

4. Conclusion

In this paper, we have studied the electrodeposition mechanism of Bi and there oxide δ-Bi_2O_3 on ITO substrate. The CV and CA studies show that our system is reversible, the early stages of Bi electrodeposition on ITO was carried out a 3D progressive nucleation with diffusion controlled. A comparison between the experimental at -980mV current transients and the theoretical transients current obtained by Scharifker-Hills, showed that the Scharifker-Hills model could be applied with sufficient accuracy in the studied potential range. Nanoparticles of the δ variety of bismuth oxide Bi_2O_3 were successfully prepared. The XRD diffraction results showed that the films were pseudo-fluorite structure. The preferred orientation of the crystallites of these films is (200). The average crystallite size is between 8 and 11nm.

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