Electrodeposition and characterization of ZnO rods films

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ZnO is a metal oxide n-type semiconductor with bandgap of 3.37 eV, the character of n-type semiconductor arises due to the presence of oxygen vacancies and interstitial zinc [1]. Its crystalline form more thermodynamically stable at room temperature is the hexagonal (wurtzite). In this structure the ZnO presents a dense packing of anions, in which zinc ions occupy half of the tetrahedral sites. The presence of zinc is observed in the interstitial structure of ZnO due to its intrinsic ability to accommodate defects as a result of the fact that all octahedral sites are empty [1].

The electron mobility in ZnO at room temperature is 115-155 $cm^2\ V^{-1}\ s^{-1}$, greater than, for example, the material commonly used for these applications as TiO_2 in the anastase form that presents mobility $10^{-5}\ cm^2\ V^{-1}\ s^{-1}$ [2]. In addition, ZnO has a high dielectric constant, long life excited excitons, biological compatibility, high thermal and chemical stability [3]. All these features make ZnO rods, with their large surface area relative to volume, interesting material and versatile for various applications as photocatalysts, gas sensors, biosensors, light emitting diodes (LEDs), field emission device and photovoltaic cells [3].

Several techniques have been applied in obtaining these ZnO structures, including vapor transport, pulsed laser deposition, chemical vapor deposition [4]. Although these methods are capable of producing ZnO structures, they require use of high temperatures and are generally limited by the complexity of the process and products purity, and some are composed of several steps, making the synthesis time consuming and expensive [4].

Thus, in recent years have sought the synthesis of ZnO structures by employing methods low temperatures, such as sol-gel techniques, hydrothermal deposition and electrodeposition [4]. Among which the electrochemical method of obtaining ZnO rods stands out among the other methods that employ low temperatures, because it consists in a technical low-cost, simple, and provides pure structures with lower synthesis times.

Thus the aim of this work is to synthesize and characterize vertically aligned ZnO rods films using electrodeposition technique.

Electrodeposition of ZnO rods was investigated using an electrochemical cell comprising a electrode saturated calomel as reference electrode, a Pt foil as counter electrode and as working electrodes were used polycrystalline gold, gold coated quartz crystals (AuQC), indium tin oxide coated glass (ITO), AISI Type 304 stainless steel and titanium. Electrolyte solutions were used in equimolar concentrations of zinc nitrate ($Zn(NO_3)_2$) and hexamethylenetetramine (HMT). Concentrations studied were 0.001, 0.01, 0.025 and 0.05 mol L^{-1}. Temperature ranged between 60 ° C and 80 ° C and deposition time between 30 and 120 minutes. Chronoamperometry technique was used and cathodic potential of -1.0 V was applied. In order to obtain a better orientation of rods was deposited a seed layer on substrates using the same concentration of HMT and $Zn(NO_3)_2$, temperature and deposition time used in electrodeposition. ZnO films were characterized using scanning electron microscopy (SEM), energy-dispersive X-ray microanalysis (EDX), X-ray diffraction, optical microscopy, diffuse reflectance spectroscopy and current transient with time under light on/off ilumination.

a) b)

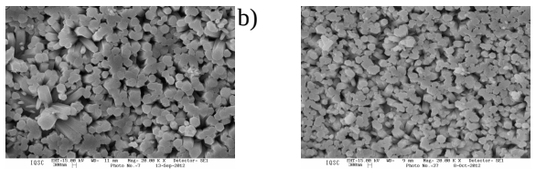

Figure 1. SEM images of ZnO rods films obtained on (a) AuQC and (b) ITO substrates.

SEM images (Figure 1) and EDX analyzes suggested that CQAu and ITO substrates were more efficient in obtaining ZnO rods, and that the best condition for electrodeposition of ZnO rods film is obtained using solutions equimolar $Zn(NO_3)_2$ and HMT at a concentration 0.025 mol L^{-1}, both during deposition of ZnO seed layer as during rods electrodeposition. In addition the electrochemical cell should be maintained at 90 ° C, under magnetic stirring and in the dark. The cathodic potential -1.0 V (vs SCE) must be applied for 90 minutes during the electrodeposition. With these deposition parameters optimized obtain a homogeneous adhesive film consisting of rods bundled and highly aligned with preferential growth perpendicular to the substrate surface, as well as atomic ratio between Zn and O according to stoichiometry 1:1.

Optical microscopy images showed a thickness of 2.22 μm for the film. X-ray diffractograms showed the three peaks characteristic of ZnO wurtzite crystalline form, wherein (002) was the predominant peak of refraction, indicating rods orientation in the c-axis vertical in relation to substrate. Diffuse reflectance spectroscopy characterization afforded absorption coefficient and energy bandgap value 3.43 eV, close to the theoretical value (3.37 eV) [4]. Studies of current transient with time performed at 0.5 V, in a 0.2 mol L^{-1} Na_2SO_4 aqueous electrolyte solution, indicated an anodic photocurrent 12 $\mu A\ cm^{-2}$. The low settling time observed is attributed to good conductivity of the obtained structures.

Thus, the vertically aligned ZnO rods synthesized, characterized as an n-type semiconductor material, promising for applications in photovoltaic devices.

References

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