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Role of solute and solvent on the deposition of ZnO thin films

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ABSTRACT

ZnO thin films have been deposited on SnO_2:F coated transparent conducting oxide (TCO) glass substrates, using a simple electrochemical (galvanic) technique, from different electrolytic solutions. A detailed investigation on the effect of different solute and solvent on the deposition process has been made. We have established that galvanically obtained ZnO thin films can be deposited with various morphologies depending on the nature of the solute and solvent used. ZnO formation can happen either directly or through an intermediate mixed phase following different reaction paths. Structural, morphological, compositional and optical characterizations of the films developed under different conditions were carried out to study such effects. The films were also tested for their potential use as methane sensor.

1. Introduction

ZnO is a unique material that exhibits multiple properties, i.e., semiconducting, piezoelectric and pyroelectric. ZnO is a wide band-gap semiconductor whose energy lies typically between 3.1 and 3.4 eV at room temperature. ZnO thin films are being widely studied for their interesting optical properties and uses as solar cell window materials and mainly as a very good gas-sensing material. Presently, several nano-forms of ZnO like nanowires, nanorings, nanocombs, nanosprings, etc., are becoming the points of interest for scientists due to their novel applications in dye-sensitized solar cells, opto-electronics, sensors, transducers and bio-medical science, since ZnO is considered to be bio-compatible [1–10]. The ZnO material is also promising for potential use as a UV light phosphor at room temperature due to free electron excitation, having sufficiently large binding energy to be stable even at room temperature [2,3].

Moreover, what makes ZnO so versatile is that it has been already prepared as bulk and thin film by different methods such as sputtering [11–13], chemical vapour deposition [14], metal-organic chemical vapour deposition [15], molecular beam epitaxy [16], electron beam evaporation [17], pulsed laser deposition [18], spray pyrolysis [19], sol–gel technique [20–22] and even thermal oxidation of metallic Zn films [23,24]. Among all these techniques, electrochemical deposition presents several advantages such as low cost, large-scale deposition and low-temperature processing [25].

As a result of a thorough literature survey, it was evident that, most of the workers, who deposited ZnO thin films by conventional electrochemical techniques, have chosen mainly aqueous $Zn(NO_3)_2$ solution as the electrolyte. For instance, Marotti et al. [3] and Mahalingam et al. [26] have potentiostatically deposited ZnO thin films from an aqueous solution of $Zn(NO_3)_2$; whereas, a hybrid electrochemical/chemical (E/C) synthesis of ZnO nanoparticles and optically intrinsic thin films from $Zn(NO_3)_2$ bath was also reported by Nyffenegger et al. [27]. Marotti et al. [3] have electrochemically deposited ZnO thin films on both opaque (Cu) and transparent (indium doped tin oxide, i.e., ITO) substrates from a 0.1 M aqueous $Zn(NO_3)_2$ solution of pH 6 at 89 °C. They have varied the electrodeposition potential from −700 to −1200 mV (vs. SCE) and reported that, the resulting samples showed the properties of hexagonal ZnO. The surface morphology of the films changed from platelet shape to cauliflower shape with change in electrodeposition potential from −700 to −1200 mV. Whereas, Mahalingam et al. [26] have prepared ZnO thin films from the same electrolytic solution as used by Marotti et al. [3] but at pH 5 and at 80 °C. Mahalingam et al. reported the optimum deposition potential to be −1100 mV (vs. SCE).

Three '*direct*' electrochemical methods, for the purpose of comparison, have been described by Nyffenegger et al. [27]. In *method 1*, they have used a chloride and oxygen free aqueous solution of 50 mM $Zn(NO_3)_2$ in 0.10 M KNO_3 with a deposition potential of −700 mV (vs. NHE). This method was previously thoroughly investigated by Izaki and Omi [28,29]. A second direct deposition method (*method 2*) was from an oxygen saturated solution of 1.0 mM $ZnCl_2$ with 0.1 M KCl at a deposition potential of +40 mV (vs. NHE) and at

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22 °C. *Method 3* was carried out using an oxygen saturated solution of 1.0 mM $Zn(ClO_4)_2$ with 0.1 M $HClO_4$ and at a potential of +40 mV (vs. NHE).

Very recently, R. Chander and A.K. Raychaudhuri reported [30] a potentiostatic deposition of ZnO nanorods from an aqueous solution of 0.03 M $Zn(NO_3)_2$ with 0.03 M hexamethylenetetramine (HMT) at 80 °C on Ag thin films, which were deposited on glass substrates by thermal evaporation. They have scanned the potential range −400 to −1000 mV (vs. SCE) and found that −800 mV was optimum for the growth of ZnO nanorods. The nanorods were found to have a well-defined hexagonal morphology and wurtzite structure.

In this work, the authors have reported the formation of different morphological growths like, platelets or flakes, gravel shaped, as well as, well-defined hexagonal grains with *c*-axis orientation of ZnO on transparent conducting oxide (TCO) coated substrates, deposited from aqueous baths of $ZnSO_4$ and $Zn(NO_3)_2$, respectively. The band-gap energy found by the authors from optical measurements was in the range 3.1–3.4 eV, which is characteristic for ZnO and also reported by other workers who have carried out depositions by the conventional electrochemical technique [3,26,27,30].

The authors had earlier deposited *c*-axis oriented hexagonal ZnO thin films from an aqueous solution of $Zn(NO_3)_2$, using the galvanic technique [31]. Here, we present our findings on the reaction path and mechanism towards ZnO thin film formation by studying the galvanic deposition using various Zn-salts, both in aqueous and organic solutions. It was found that, solute and solvent played an important role on the structural, morphological, optical and other properties of the deposited films. The galvanic deposition technique involves no external bias. The deposition potential is achieved by using an easily oxidisable electrode, in this case Zn. The films were characterized by studying the X-ray diffraction (XRD) patterns, scanning electron microscope (SEM) and atomic force microscope (AFM) images and optical (UV–vis and photoluminescence (PL)) spectra. Compositional analysis was done by an energy dispersive X-ray (EDX) technique.

2. Experimental

2.1. Cell set up

To start with, the substrates were cleaned with detergent and then dipped into concentrated chromic acid solution for about 20 min and washed thoroughly with cold distilled water to remove any adhering impurities. They were then boiled in methanol and after drying, were degreased in a vapour of trichloroethelene. A properly cleaned TCO coated glass substrate and a Zn rod (99.9% purity) were dipped into a beaker containing the working solution. The Zn rod and the TCO glass substrates were short-circuited externally through a metal (Cu) wire. The Zn rod served as a self-decaying (easily oxidisable) anode and the TCO glass substrate as the cathode. The schematic of the cell has been shown elsewhere by us [31]. The pH of the working solution was kept in the range 5–6, which was found to be optimum, depending upon the nature of the solute and the solvent. The working solution was stirred continuously using a magnetic stirrer.

2.2. Preparation of solution

Aqueous and non-aqueous [N,N-dimethylformamide (DMF)] solutions of the electrolytes of equimolar strength (0.01 M) were prepared as the working solutions to study the effect of solute and solvent on the deposition of ZnO films. The solutes chosen were $Zn(NO_3)_2$, $ZnSO_4$, $ZnCl_2$ and $Zn(CH_3COO)_2$, respectively. The solvent DMF was chosen due to its high polarity compared to other non-aqueous aprotic solvents, which is essential to dissolve the ionic solutes chosen. Deposition from solutions with concentration more than 0.01 M (e.g., 0.05 and 0.1 M), were also studied, however, in this case, the rate of deposition was significantly high and films with poor adherence were obtained. Concentration of working solutions below 0.01 M (e.g., 0.005 and 0.001 M) yielded no depositions. As a result, the optimum concentration of the working solution was found to be 0.01 M.

2.3. Characterizations

The deposited films were characterized by their structural, morphological, compositional, and optical properties. X-ray diffraction patterns were recorded by an X-ray diffractometer (SEIFERT 3000P) using Cu Kα radiation of wavelength λ = 0.15406 nm. The film compositions were determined by energy dispersive X-ray analysis (EDX, JEOL JSM 6300 Oxford-ISIS). The morphology of the films was studied by a scanning electron microscope (SEM, JEOL-JSM-6360) and an ambient-based multimode atomic force microscope (AFM, NT-MDT, Solver Pro). All AFM measurements were done in contact mode and a silicon probe having radius of curvature 10 nm, height 15 μm and a standard chip size 1.6 mm × 1.6 mm × 0.4 mm was used for the scanning purpose. The PL spectra of the ZnO thin films were measured by a Fluorimeter (FL 4500, Hitachi) with the excitation wavelength of 300 nm (Xenon lamp, 100 W).

Since, TCO (SnO_2:F), on which the depositions were carried out, is a highly conducting material, it was used as the bottom contact to the ZnO films. A ∼1.0 μm thick layer of Au with 0.3 cm × 0.3 cm area was deposited on the ZnO films by e-beam evaporation method and was used as the top contact. The D.C. voltage was applied along the thickness of the films using a Kithley made 6487 voltage source and the changes in current were recorded by AGILENT 34970A high speed data logger. The thicknesses of the films were kept constant at 0.30 μm for all measurements. Resistivity values for the films under investigation were determined by using the equation

$$\rho = \frac{(R \times A)}{L} = \frac{(V \times A)}{(I \times L)}$$

(where ρ, R, L and A are the resistivity, resistance, thickness of the film and area of contact, respectively).

The gas-sensing characteristics were studied in resistive mode, i.e., by measuring the change in resistivity between the two contacts made on the ZnO film, before and after passing CH_4 gas. Evaporating Pd metal by e-beam technique at a base pressure of 10^{-6} mbar, the contacts were made on the surface of ZnO films. The distance between the two contacts was 1 cm and the area of each was 0.3 cm × 0.3 cm. The metal Pd not only acts as the simple contact material, but also exerts some catalytic activity on the sensing mechanism.

The sensor studies were carried out inside a closed glass tube (10 cm × 4 cm Ø) with inlet and outlet for gases and it was placed coaxially inside a resistively heated furnace with 4 cm constant temperature zone. The temperature was controlled within ±1 °C using copper constantan thermocouple in-built in a precise temperature controller. Electrical connections were taken by using fine copper wire and silver paste for the metallization contacts. High purity (100%) methane gas and IOLAR grade N_2 (carrier gas) in desired proportions were allowed to flow to the gas-sensing chamber through a mixing path via Alicat Scientific mass flow controller & the mass flow meter, respectively. The mass flow rate and thus the relative concentrations of the gases were kept constant throughout the experiment. The gas pressure over the sensor device was 1 atmosphere during the experiment. The current–voltage and resistivity characteristics of the sensors in presence and absence of methane was measured by a Kithley 6487 voltage source picoammeter; applying a constant voltage of 2.0 V. The percentage