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The effect of addition of Tiron as a surfactant on the microstructure of chemically deposited zinc oxide

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Abstract

The effect of one of the surfactants such as Tiron, a compound based on the benzene molecule, on the morphology and chemical composition of zinc oxide deposits, produced from a zinc complex solution using two-stage chemical deposition (TSCD) technique, has been investigated. TSCD technique is a novel and simple chemical route for the deposition of ZnO film from aqueous solution. Zinc oxide films deposited on high purity alumina (HPA) as a substrate. The results show that the addition of Tiron changes the surface morphology and causes to form the fine-grained structure. With a dense and nodular-shape appearance, the film produced from the precursor of zinc complex-containing Tiron, is composed of ZnO particles in even size of 90–160 nm and therefore, is suitable for gas sensors. Also the effect of the number of dipping on the surface morphology has been studied. The obtained results indicate that increasing the number of dipping causes to progress the deposition process. This is attributed to the fact that TSCD method involves both nucleation and growth steps. In addition, the mechanism for the deposition process of ZnO from aqueous solution was preliminarily discussed.

Keywords: Surfactant; Tiron; Two-stage chemical deposition; Morphology; Nucleation; Growth

1. Introduction

Zinc oxide thin films offer a variety of applications. The low conductivity, highly oriented film can be used as an ultrahigh frequency electroacoustic transducer because of its piezoelectric property [1,2]. The medium conductivity thin film is an n-type semiconductor and can be used with an appropriate p-type semiconductor as a heterojunction in the field of photovoltaic conversion of solar energy. The high conductivity ZnO thin film with high transparency in the visible spectrum can be used as a transparent electrode in the field of optoelectronic display and in the field of photovoltaic solar energy conversion as well [3,4]. ZnO thin films can be used in electrophotography and also as a gas sensor [5].

There are numerous methods for the preparation of ZnO thin films, such as sputtering, electron beam evaporation [6,7], spray pyrolysis [8,9], MOCVD [10], electroless bath deposition [11], PLD [12] and chemical deposition [13,14]. Chemical deposition of thin films from aqueous solutions is a very promising method because of its simplicity and economy. Chemically deposited ZnO thin film was obtained as a byproduct in an attempt to prepare the composite $Cd_xZn_{1-x}S$ [15]. The method described here the deposition of ZnO film with a thickness and conductivity which can be controlled during the preparation procedure. Deposition is performed onto any substrate non-reactive with the chemicals used for deposition.

Two-stage chemical deposition (TSCD) is used here to produce ZnO films. The substrate was first immersed into a cold aqueous solution containing a complex compound consisting of Zn^{2+} ions. The substrate was first covered with a layer of the complex. It was then dipped into a distilled boiling water bath to facilitate the decomposition of the complex into the desirable ZnO layer.

Although a large volume of literature is available on the deposition of ZnO, very little attention has been given to the two-stage chemical deposition of these coatings. Furthermore, no previous studies have been conducted on the influence of the surfactant on the characteristics of chemical-deposited ZnO films. It is interesting to know how the microstructure of chemical-deposited

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Table 1
Bath conditions and chemical deposition parameters with their various ranges for ZnO deposition

Variable	Range
$ZnCl_2$ ($g\,l^{-1}$)	20–100
NH_3 (ml)	10–50
Additive	1 drop per liter
Tiron	4 drops per liter
pH	8–11
Temperature (°C)	
Complex solution	10–20
Hot water	90–105

coatings changes with the addition of surfactant. Therefore, the purpose of this paper is to present results of such studies for chemical-deposited ZnO films.

2. Experimental

HPA plates with 25 mm × 15 mm × 1 mm dimensions were used as the solid substrate for film growth. After degreasing, the plates were washed with deionized water and dried in a steam of hot air. The final solution composition and the bath conditions that were used in this work, are shown in Table 1. The zinc complex solution having the composition shown in Table 1 was prepared by mixing concentrated NH_4OH with 0.2 M $ZnCl_2$ until white $Zn(OH)_2$ was precipitated. Further addition of NH_4OH resulted in dissolving of the precipitate. The solution was diluted up to appropriate concentration of Zn^{2+} complex. This was found to be the most convenient concentration for production of a good quality film on the substrate. Cleaned substrates were first immersed into a cold complex-containing solution and then in hot water for 2 s. After a required number of dipping, the substrate with the deposited ZnO film was annealed at 350 °C for several hours.

ZnO thin films produced in this work were characterized for their surface morphology, chemical composition, phase present and preferred orientation. The surface morphology was studied by scanning electron microscopy (SEM) using a Camscan MV2300 operated at 25 kV. The chemical composition of the deposits was determined using the Kevex model energy dispersive X-ray spectroscopy (EDS) system attached to the SEM.

3. Results and discussion

3.1. Morphology and chemical composition

In this work, two-stage chemical deposition of ZnO was studied using HPA substrates. The surface morphologies of the annealed deposits (without the addition of Tiron) after 15, 30, 50, and 100 times dipping deposited on HPA substrates are shown in Fig. 1. As can be shown, at low numbers of dipping, the nuclei of zinc oxide are formed in the preferred sites on the substrate. Low numbers of dipping, such as 15, 30, and 50, result in the formation of non-spherical particles covered on the surface of substrate.

For the numbers of dipping higher than 50, the spherical crystallites started to form within the non-spherical grains. At higher number of dipping stages, they started to spread out further (Fig. 1d). Continuation of the dipping practice up to 100 resulted in the continuous growth of the oxide crystallites and their change from a non-spherical to a spherical structure shape.

Fig. 2 shows the effect of addition of Tiron on the surface morphology of chemically deposited zinc oxide thin films produced after 30 and 100 times dipping process. The SEM micrographs clearly show that the addition of Tiron as a surfactant causes to form the fine-grained structure with a dense and nodular-shape appearance. The film produced from the precursor of zinc complex-containing Tiron, is composed of ZnO particles in even size of 90–160 nm. It is concluded that the surfactants such as Tiron, affect the surface morphology and cause to lower the mean grain size. To increase the gas sensitivity, the films must have a high electrical resistivity associated with a small crystallite size and thickness [16]. Therefore, the precursor containing Tiron is an appropriate starting solution which can be suitable for preparing ZnO thin films used in gas sensors. Electrical properties and sensing behavior of these deposits will be the subject of further studies.

Fig. 3 demonstrates the EDAX elemental analysis of the particles on the surface. The peak of Al belongs to the substrate. In order to verify the accuracy of the EDS analysis, one deposit was also analysed by wet chemistry using atomic absorption spectroscopy (AAS). The deposit was analysed to contain 76.4 wt.% Zn by AAS compared to 78.2 wt.% Zn by EDS.

3.2. Growth mechanism of ZnO film

For Zn^{2+} aqueous solution, the necessary condition for the formation of precipitation is the establishment of ion product higher than solubility product of $Zn(OH)_2$. The degree of supersaturation (S) is the important factor in the examination of the precipitation process in aqueous solution, defined as the ratio of ion product to solubility product. When S is lower than 1, no precipitation is formed in solution. When S is higher than 1 but lower than a critical value, S_c, the heterogeneous precipitation occurs on the wall of vessel and substrate, because the value of S is not sufficient to induce nuclei in the bulk solution. When S is higher than S_c, a large quantity of nuclei will be formed in the bulk solution and the homogeneous precipitation occurs. Based on this theory, the deposition of high quality film from aqueous solution is to control the value of S, to induce the heterogeneous precipitation on the substrates, and to suppress the homogeneous precipitation in the bulk solution.

In this paper, we have made use of the thermal decomposition of $[Zn(NH_3)_4]^{2+}$ which release ions of Zn^{2+} and OH^- into solution and result in the formation of $Zn(OH)_2$ or ZnO particles. Eqs. (1)–(3) illustrate the chemical reaction related to this process. An equilibrium exists in the precursor under the presence of excessive ammonia:

$$Zn(OH)_2 + 4NH_4OH = [Zn(NH_3)_4]^{2+} + H_2O \quad (1)$$

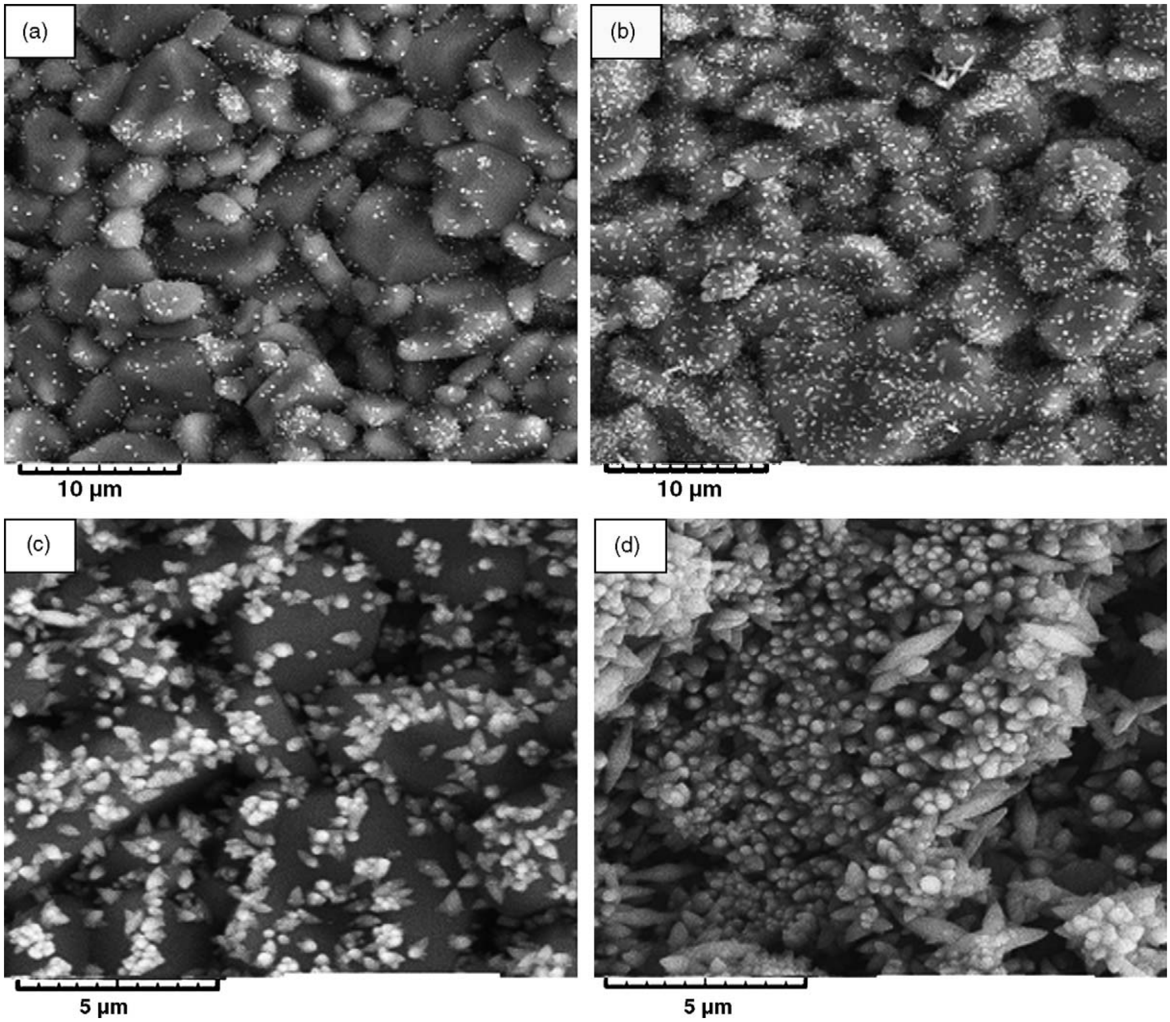

Fig. 1. SEM morphology of the surface for the as-deposited ZnO films with various number of dipping: (a) 15 times; (b) 30 times; (c) 50 times; (d) 100 times.

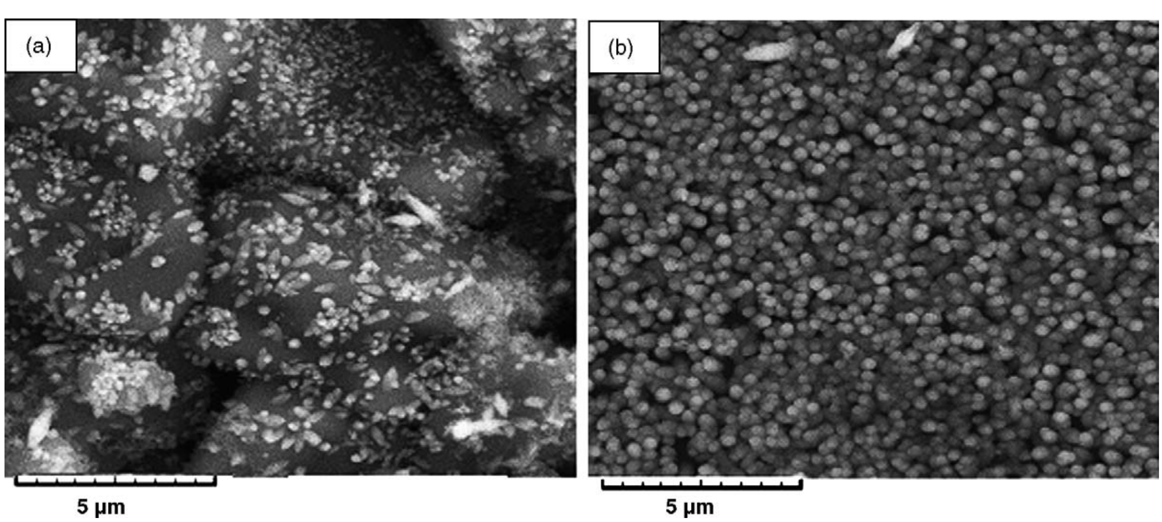

Fig. 2. SEM micrographs of ZnO thin films produced from a precursor containing Tiron after 30 (a) and 100 (b) times dipping.

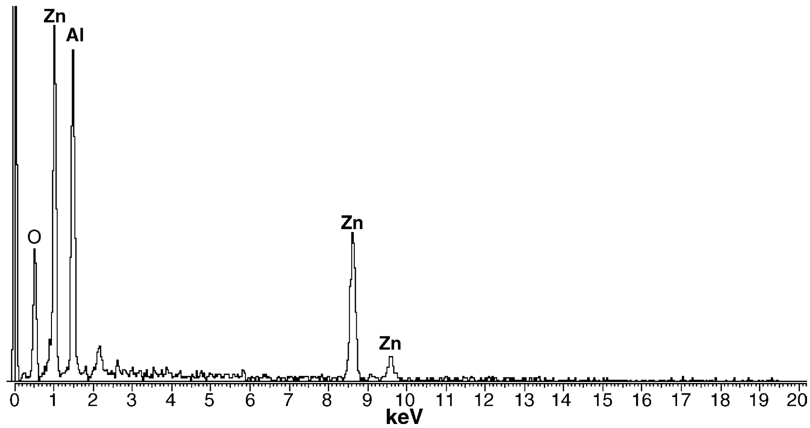

Fig. 3. EDAX elemental analysis of the particles on the surface.

During the reaction process in hot water, $[Zn(NH_3)_4]^{2+}$ complex decomposes with the final formation of zinc hydroxide precipitation:

$$[Zn(NH_3)_4]^{2+} + 4H_2O = Zn(OH)_2\downarrow + 4NH_4^+ + 2OH^- \quad (2)$$

Solid ZnO particles may be formed in aqueous solution when the temperature is over 50 °C [17]:

$$Zn(OH)_2\,(s) = ZnO\,(s) + H_2O \quad (3)$$

It should be noted that the equilibrium deposition temperature has been calculated in this paper for the first time. In order to determine this value, variations with temperature of both pH and weight of the deposited complex were determined and plotted against temperature, as shown in Fig. 4.Concomitant blank tests were also performed in order to determine the general ammonium decomposition effects. Both samples were submerged horizontally into the corresponding solutions so that the partial pressures of the gases could remain invariable. At temperatures below 85 °C, the general ammonium decomposition resulted in a relatively slow slop in the pH reduction as well as the weight gain (Fig. 4). At about 85 °C, both pH decline and weight gain became steep. This indicated that the equilibrium decomposition temperature was around this temperature. Careful examinations indicated that the equilibrium decomposition temperature is equal to 85 ± 2 °C.

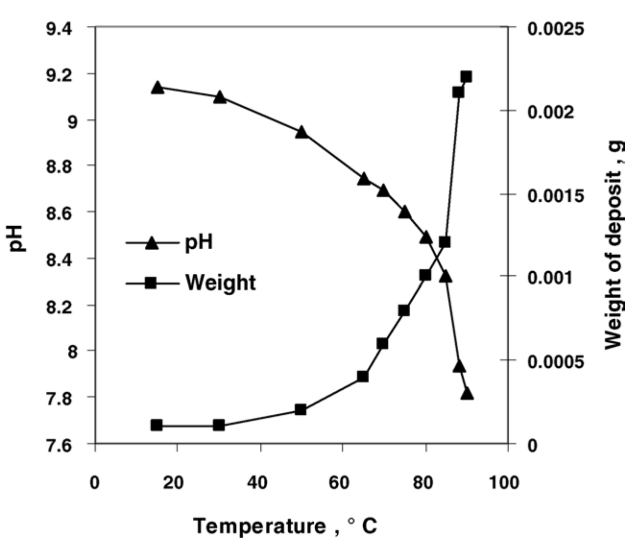

Fig. 4. Effect of temperature on weight of deposit and pH of the solution.

During the chemical reaction process in hot water, with the elapse of the time starting from the initial immersion of substrate in water, here stages will occur subsequently within the liquid film adsorbed on the substrate surface, i.e., the solution stage, the heterogeneous precipitation stage, and the homogeneous precipitation stage. By adjusting the reaction time, the chemical reaction within the liquid film can be terminated in the second stage when the precipitation of zinc hydroxide occurs on the substrate. After a series of successive deposition cycles, ZnO film with certain thickness and high quality will be produced.

4. Conclusions

With the precursor of zinc-ammonia complex, uniform and continuous ZnO films were prepared on high purity alumina (HPA) substrate. SEM and EDS techniques were used to evaluate the effect of addition of Tiron, as a surfactant, on the microstructure and chemical composition of chemically deposited ZnO layers. The surface morphologies of the annealed deposits (without the addition of Tiron) after various numbers of dipping showed that continuation of the dipping practice up to 100 resulted in the continuous growth of the oxide crystallites and their change from a non-spherical to a spherical structure shape. Also, it is shown that the film produced from the precursor of zinc complex-containing Tiron, is composed of ZnO particles in even size of 90–160 nm. Therefore, the precursor containing Tiron is an appropriate starting solution which can be suitable for preparing ZnO thin films used in gas sensors.

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