

## Effects of substrate etching, Sn<sup>+2</sup> doping and surfactant addition on the morphology of chemically deposited zinc oxide films

Mohammad Reza Vaezi\*

Division of Nanotechnology and Advanced Materials, Materials and Energy Research Center, MERC, Karaj, Iran.

The effect of substrate etching by HF, doping by SnCl<sub>2</sub> and the addition of a surfactant such as Tiron on the morphology and growth rate of zinc oxide deposits is investigated. The layer is produced on a high purity alumina (HPA) substrate by two-stage chemical deposition (TSCD) from a solution containing an ammonium zinc complex. Etching does not affect the structure of films thinner than 400 nm. It has, however, a considerable effect on the structure of films greater than 800 nm. The latter is produced by 70 times dipping of the substrate into the ZnO containing solution. It is seen that 100 times of dipping results in the formation of acicular grains on the initially formed grains. The addition of 2 drops per lit (d/l) of Tiron changes the surface morphology and causes the formation of a fine-grained structure. Further addition of Tiron causes poisoning of the nucleation stage and coarsens the grains. The same effect is observed with Sn-doping of the film. Adding more than 2% Sn as a dopant induces poisoning of the nucleation stage and hinders the formation of fine grains. Combined substrate etching and Tiron addition effects are discussed in this paper.

**Key words:** Surfactant, Tiron, Etching, Two-Stage Chemical Deposition, Zinc Oxide.

### Introduction

Zinc oxide (ZnO) is an important semiconductor having numerous applications in transparent electrodes [1-3], SAW filters<sup>4</sup> and gas sensor materials [5-12]. Utilization of ZnO thin films as a sensitive element in gas sensors instead of traditional tin oxide offers such advantages as lower cost and higher stability. A lower crystallite size with a thinner layer results in a greater gas sensitivity [13].

ZnO films can be produced by numerous methods. One of the techniques used to deposit these films is chemical deposition. Chemical deposition is an advantageous technique for formation of a thin film with a large surface area [14-18]. This method helps the deposition of ZnO films with a controllable thickness and a specified conductivity. Deposition can be performed onto any substrate nonreactive with the chemicals used in the process.

Two stage chemical deposition (TSCD) is used here to produce ZnO films. A clean substrate is immersed first in a cold solution of the Zn<sup>+2</sup> complex and then in hot water for 1-2 s. This way, the substrate is covered with a thin layer of the complex solution which decomposes to ZnO when submerged into hot water.

Although a large volume of the literature is devoted to ZnO deposition, two-stage ZnO chemical deposition is rarely given attention. Furthermore, no previous studies have been conducted on the influence of substrate etching, doping

and the addition of a surfactant on the characteristics of chemically deposited ZnO films. It is interesting to know how the microstructure of the chemically deposited coatings changes with etching, doping and surfactant addition. The purpose of this paper is to elucidate such effects.

### Experimental Procedure

HPA plates with 25 × 15 × 1 mm dimensions were used as a solid substrate for film growth. After degreasing, the plates were washed with deionized water and dried in a stream of hot air. The final solution composition and the bath conditions that were used in this study are shown in Table 1. The zinc complex solution having the composition shown in Table 1 was prepared by mixing concentrated NH<sub>4</sub>OH with 0.2 M ZnCl<sub>2</sub> until Zn(OH)<sub>2</sub> started to precipitate. Further addition of NH<sub>4</sub>OH resulted in dissolving the precipitate. The solution was diluted with water to reach an appropriate Zn<sup>+2</sup> concentration. The most convenient

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

Variable	Range
ZnCl <sub>2</sub> (g·l <sup>-1</sup> )	20-100
NH <sub>3</sub> (ml)	10-50
Additive (Tiron)*	1-12 drop(s) per lit
pH	8-11
Temperature of Complex Solution (°C)	10-20
Temperature of Hot Water (°C)	90-105

\*Corresponding author:  
 Tel : +98-21-88771626  
 Fax: +98-21-88773352  
 E-mail: vaezi9016@yahoo.com

concentration for production of a good quality film on the substrate was thus obtained. Clean substrates were first immersed into a cold complex-containing solution and then in hot water for 2 seconds. After a predetermined number of dippings, the substrate with the deposited ZnO film was annealed at 350 °C for several hours. Fig. 1 outlines these steps.

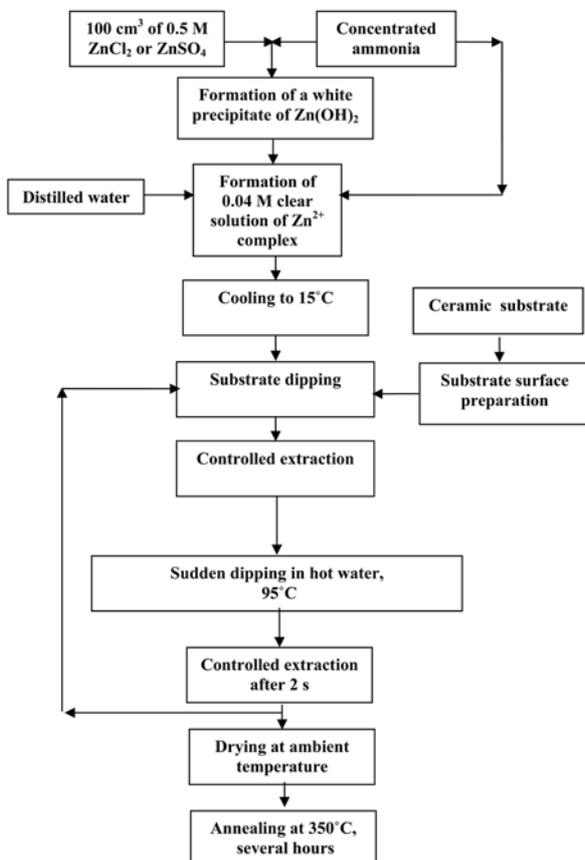
ZnO thin films produced during this research were characterized to find out their surface morphology, chemical composition, prevailing phase and preferred orientation. The surface morphology was studied by scanning electron microscopy (SEM) using a Camscan MV2300 instrument operated at 25 kV. The chemical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

X-ray diffraction (XRD) was used to determine the phase present and the preferred orientation of the deposits. A Philips Xpert-Pro X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418$ ) was employed to obtain XRD spectra using standard  $\theta$ -2 $\theta$  geometry. A computer-based search and match was used for phase identification.

## Results and Discussion

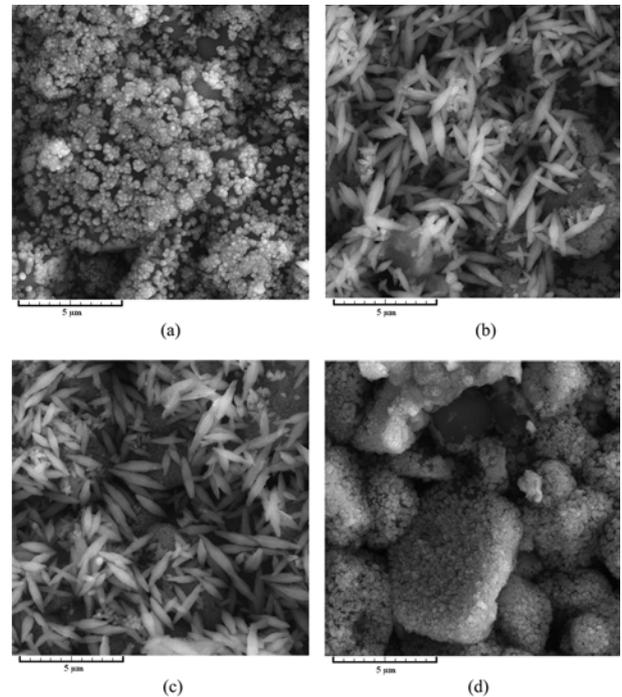
### Effect of substrate etching

Fig. 2 gives SEM micrographs of zinc oxide films

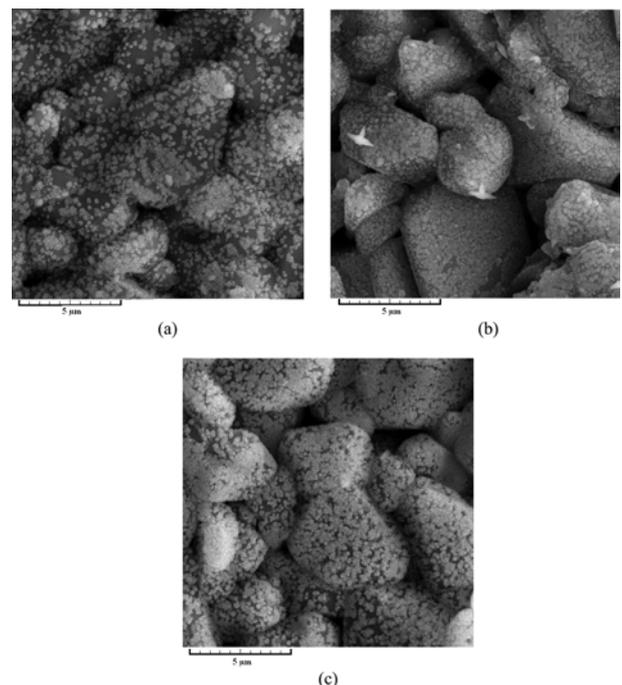


**Fig. 1.** Flowchart of the process used for production of zinc oxide thin film.

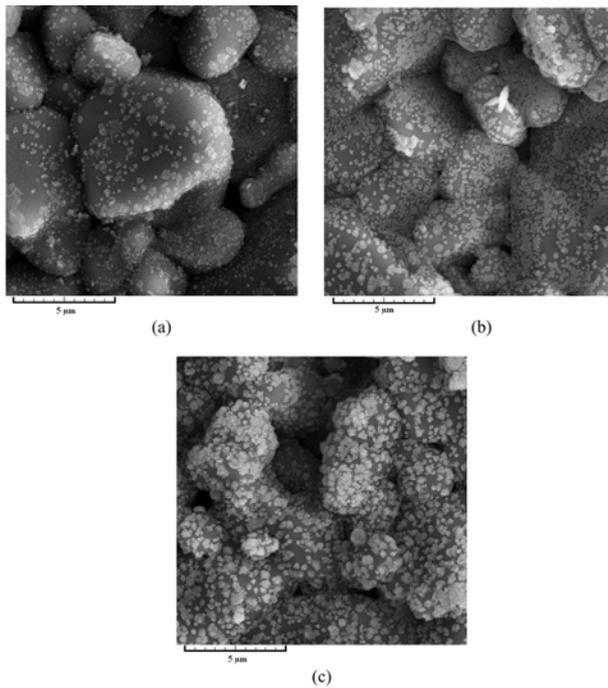
deposited on the HPA substrates after 100 times of dipping and etched for various periods of times indicated in the figure. As is seen, at intermediate times of dipping, i.e. 10 and 15 s, the microstructure of the deposited film changes and acicular grains are produced on the initially formed grains. It is evident from Figs. 2(a) and (d) that etching



**Fig. 2.** SEM micrographs of ZnO thin films (100 times of dipping) produced on the HPA substrates etched for (a) 5 s, (b) 10 s, (c) 15 s and (d) 20 s.



**Fig. 3.** SEM micrographs of ZnO thin films deposited after (a) 30, (b) 50, and (c) 70 times of dipping on the HPA substrate etched for 10 s.

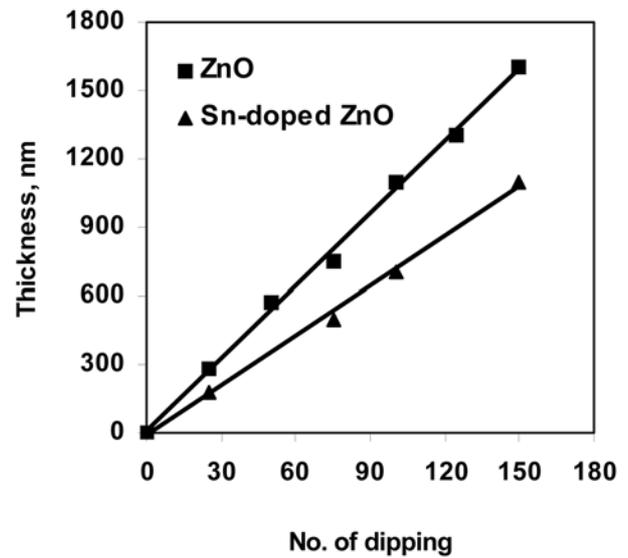


**Fig. 4.** SEM micrographs of ZnO thin films deposited after (a) 15, (b) 30, and (c) 50 times of dipping on the HPA substrate etched for 15 s.

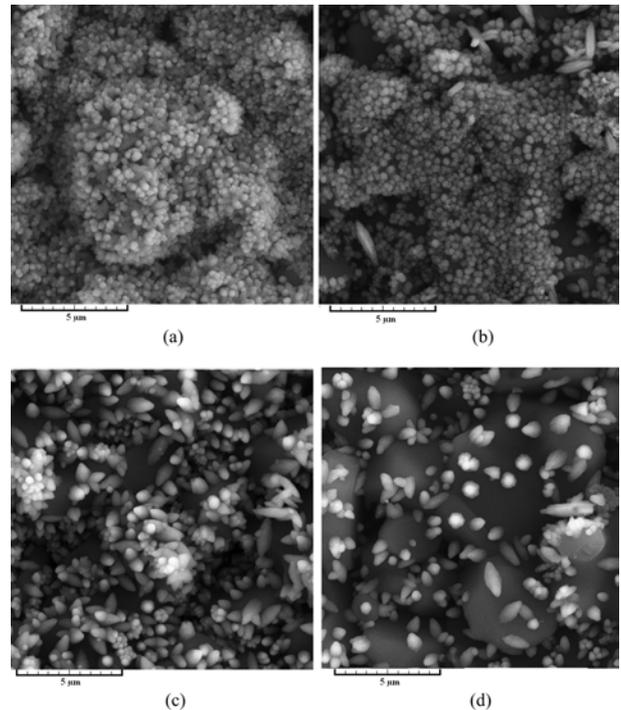
for both insufficient (i.e. 5 s) and long periods of time (i.e. 20 s) does not considerably change the microstructure. This is due to the fact that at insufficient times of etching the surface of the substrate has not been properly etched and at long times, the substrate has been highly etched and there are many micro pores that due to their low size involve no sharp edges. Etching has therefore no significant effect on the microstructure of the film produced on the substrate. Figs. 3 and 4 demonstrate the effect of substrate etching at two different times for low thickness films (less than 70 times of dipping). As is shown in Figs. 3 and 4, the acicular grains have not been produced. This can be explained as follows: At a low number of dipping, zinc oxide nuclei are dispersedly distributed on the surface of the substrate and the role of etching is not easily distinguishable. Further etching results in the formation of microscopic sites for the nucleation of zinc oxide nuclei and the creation of many micro pores. At higher dipping numbers, zinc oxide covers the depth of the pores having sharp edges as appropriate sites for preferred growth. Acicular grains are therefore formed. It is concluded that the effect of substrate etching is not considerable for films of lower thicknesses. Increasing the etching time decreases the grain size. This is due to production of more nucleation sites by the zinc oxide etching process (see Figs. 2-4).

#### Effect of doping

The effect of the addition of  $\text{Sn}^{+2}$  dopant and increasing the dipping number on the thickness of the deposited ZnO film is presented in Fig. 5. It is seen that the doping process decreases the average deposition rate. The average deposition



**Fig. 5.** Effect of number of dippings and Sn doping on ZnO film thickness.



**Fig. 6.** SEM micrographs of Sn-doped ZnO thin films deposited after 100 times of dipping containing (a) 1% Sn, (b) 2% Sn, (c) 4% Sn and (d) 6% Sn.

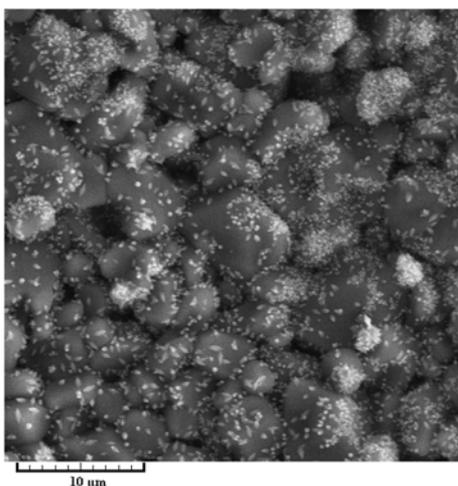
rate per dipping stage was estimated to be  $0.012 \mu\text{m}$  and  $0.008 \mu\text{m}$  for undoped and Sn-doped films, respectively. Fig. 5 shows that the relation between the thickness of the film with the dipping number is linear. The rate of increase of the thickness is therefore constant. An unchanged solution concentration during the growth process seems to be responsible for this effect. Fig. 6 shows the effect of the addition of Sn dopant on the microstructure of the chemically deposited zinc oxide having a constant thickness (100 times of dipping). Less than 2% Sn addition

(e.g. %1) prevents the growth of the zinc oxide nuclei. It poisons the deposit and prevents the growth process. Greater than 2% Sn addition induces poisoning of the nucleation stage and hinders the fine grain formation. The same effect is observed with the addition of other surfactants. With a dense/nodular-shape appearance, the film produced from the precursor of the zinc complex containing 2% Sn is composed of ZnO particles in even sizes of 110-190 nm. It is concluded that the Sn-doped films containing 2% Sn are suitable for a gas sensing application. At lower numbers of dipping, the surface of the substrate is not completely covered with ZnO particles. Growth of the nuclei is not therefore observed. At a low number of dippings, Sn dopant does not significantly affect the microstructure of the doped ZnO thin film formed on a HPA substrate (Fig. 7).

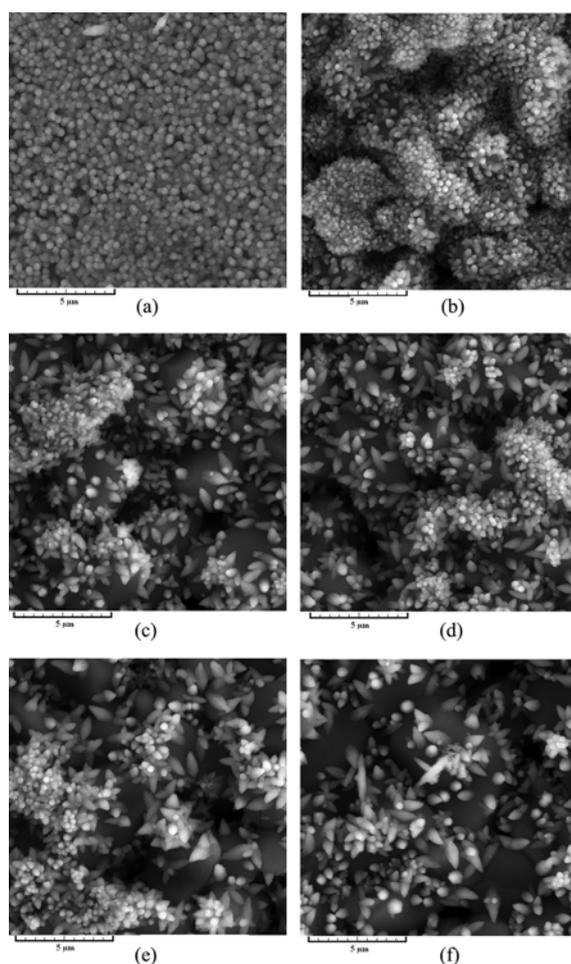
#### Effect of surfactant

Fig. 8 shows the effect of addition of Tiron, as a surfactant, on the microstructure of the chemically deposited zinc oxide layer with a constant thickness (100 times of dipping). The addition of 2 d/l Tiron prevents the growth of zinc oxide particles nucleated on the substrate and poisons the growth stage of the deposition. A further addition of Tiron poisons the nucleation stage and therefore the formation of a fine-grained structure is hindered. It is concluded that the optimum concentration of Tiron which can produce the fine-grained structure is 2 d/l.

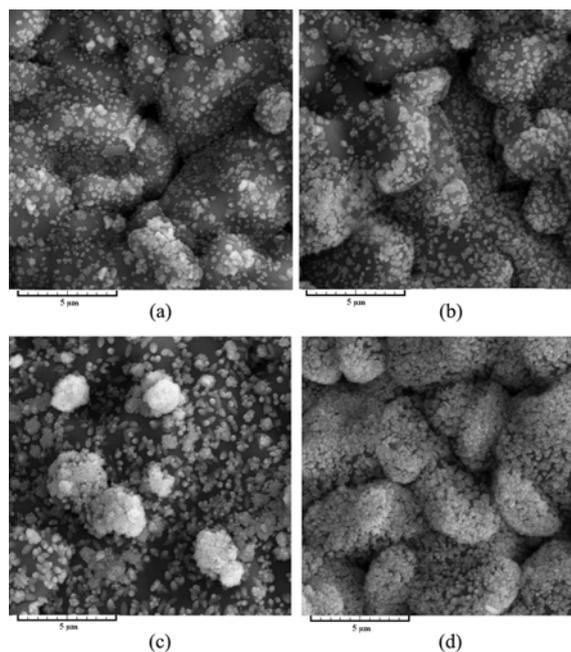
A combination of both substrate-etching and a Tiron-addition effect on zinc oxide microstructures is shown in Fig. 9 for various thicknesses. As was previously mentioned, the substrate etching has no effect on the microstructure of the zinc oxide deposit at low dipping numbers. This is observed in the case of the combined effect of etching and a Tiron addition (Fig. 9). As is shown, the microstructures of zinc oxide at low numbers of dipping do not change (Figs. 9(a), (b), and (c)). A comparison between Fig. 9(d) and Fig. 2(b) shows that Tiron prevents the



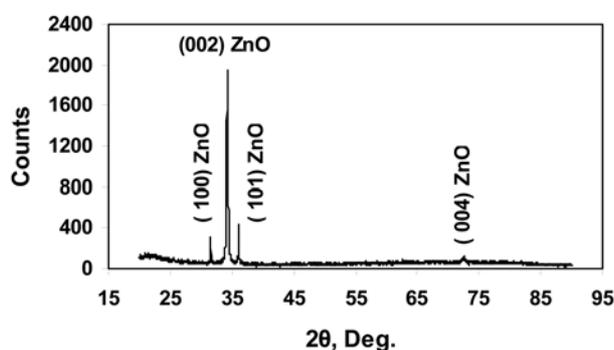
**Fig. 7.** SEM micrograph of a Sn-doped ZnO thin films deposited after 30 times of dipping in a solution containing 1% Sn.



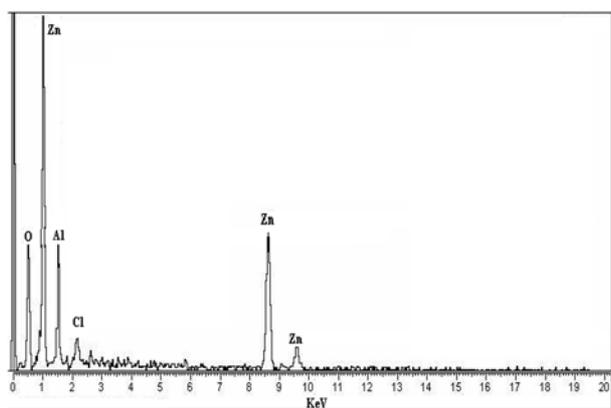
**Fig. 8.** SEM micrographs of ZnO thin films (after 100 times of dipping) produced from precursors containing (a) 2 drops, (b) 4 drops, (c) 6 drops, (d) 8 drops, (e) 10 drops and (f) 12 drops of Tiron.



**Fig. 9.** SEM micrographs of ZnO thin films produced after (a) 30, (b) 50, (c) 70, and (d) 100 times of dipping (precursor contains 2 drops Tiron and the substrates were etched for 10 s).



**Fig. 10.** XRD pattern for a ZnO deposit on an HPA substrate annealed at 350 °C.



**Fig. 11.** EDAX result of a ZnO film after 100 times of dipping.

formation of the acicular grains.

An X-ray diffraction  $\theta$ - $2\theta$  pattern of an annealed ZnO film is shown in Fig. 10. The crystal structure and chemical composition of the phase were determined from this graph. From the presence of the diffraction peaks produced by the film and the angles of the peaks it was concluded that the film prepared from the aqueous solutions containing  $\text{ZnCl}_2$  have the zincite ZnO crystal structure. Other materials such as impurities are below the limits of detection.

Comparing the pronounced peak at  $2\theta = 34.6$  (Fig. 10) with a standard one shows that the preferred orientation of the microcrystals of ZnO films are (002) crystal planes.

An EDAX spectrum of the ZnO film shows the presence of Zn, O, Al and a trace amount of Cl. The source of Al is the substrate (Fig. 11). The Cl species may have come from the aqueous complex solution. As a typical example, one of the samples was also analyzed by wet chemistry using atomic absorption spectroscopy (AAS). AAS analysis showed 76.4 wt.% Zn. EDAX analysis indicated 78.2 wt.% Zn. The difference is within the acceptable range of the experimental estimations.

## Conclusions

ZnO thin films can be easily deposited by successive

immersions of HPA substrates into a cold complex solution and then in hot water. The thickness of the film can be controlled by varying the number of successive immersions. Substrate etching for low thickness films has no effect on their microstructure, but it has a considerable effect on the structure of films prepared after 100 times of dipping and causes acicular grains to form on the initially formed grains. The addition of 2 drops per lit (d/l) of Tiron changes the surface morphology and causes the formation of a fine-grained structure. Further addition of Tiron causes poisoning of the nucleation stage and hence produces a coarse-grained structure. The addition of more than 2% Sn as a dopant induces poisoning of the nucleation stage and hinders the formation of fine ZnO grains. With a nodular-shape dense appearance, the film produced from a zinc containing complex having 2 d/l Tiron and 2% Sn as a precursor, is composed of even sized ZnO particles of 90-160 nm and 110-190 nm, respectively. These films look suitable for gas sensor applications.

## References

1. B.J Jin, S.H. Bae, S.Y. Lee and S. Im, *Mater. Sci. Eng. B*, 71 (2000) 301-305.
2. B. Lin, Z. Fu, Y. Jia and G. Liao, *J. Electrochem. Soc.*, 148 (2001) 110-115.
3. T. Tsuchiya, *J. Non-Crystal Solids*, 178 (1994) 327-329.
4. V. Anisimkin, M. Penza and A. Valentini, *Sensors Actuat. B*, 23 (1995) 197-201.
5. P. Nunes, E. Fortunato, A. Lopes and R. Martins, *Int. J. of Inorg. Materials*, 3 (2001) 1129-1131.
6. K.C. Song and Y. Kang, *Mat. Lett.*, 42 (2000) 283-289.
7. T. Maosong, D. Guorui and G. Dingsan, *Appl. Surf. Sci.*, 171 (2001) 226-231.
8. A. Ahmad, J. Walsh and T.A. Wheat, *Sensors Actuat. B*, 93 (2003) 538-544.
9. GG Mandayo, E. Castano, F.J. Gracia, A. Cirera, A. Cornet and J.R. Morante, *Sensors Actuat. B*, 95 (2003) 90-95.
10. E. Comini, G. Faglia and G. Sberveglieri, *Sensors Actuat. B*, 76 (2001) 270-274.
11. T. Becker, S. Muhlberger, C. Bosch, G. Muller, T. Ziemann and K.V. Hectenberg, *Sensors Actuat. B*, 69 (2000) 108-114.
12. S.M. Lee, Y.S. Lee, C.H. Shim, N.J. Choi, B.S. Joo, K.D. Song, J.S. Huh and D.D. Lee, *Sensors Actuat. B*, 93 (2003) 31-36.
13. Y. Suda, H. Kawasaki, J. Namba, K. Iwatsuji, K. Doi and K. Wada, *Surf. Coat. Technol.*, 174-175 (2003) 1293-1298.
14. J.F. Chang, H.H. Kuo, I.C. Leu and M.H. Hon, *Sensors Actuat. B*, 84 (2002) 258-264.
15. M. Ristov, G.J. Grozdanov and M. Mitreski, *Thin Solid Films*, 149 (1987) 65-71.
16. K. Ramamoorthy, M. Arivanandhan, K. Sankaranarayanan and C. Sanjeeviraja, *Materials Chem. and Phys.*, 85 (2004) 257-262.
17. S.T. Shishiyanu, O.I. Lupan, E.V. Monaico, V.V. Ursaki; T.S. Shishiyanu and I.M. Tiginyanu, *Thin Solid Films*, 488 (2005) 15-19.
18. H.C. Cheng, C.F. Chen and C.C. Lee, *Thin Solid Films*, 498 (2006) 142-145.