

A new route to grow ZnO seed layer using the SILAR method

E. Galego^{*}, M.M.Serna^{*} and L.V.Ramanathan^{*}

^{*} IPEN-CNEN/SP

Av. Prof. Lineu Prestes 2242, Sao Paulo, SP, Brazil, CEP:05508-000;

E-mail: egalego@usp.br;

ABSTRACT

In dye-sensitized solar cells (DSSC), the SnO₂ film is used as a transparent conducting electrode. Onto this layer, the n-type semiconductor ZnO is deposited to support the dye. The ZnO/SnO₂ interface exhibits electrical resistance due to mis-orientation in the crystalline structures of the two oxides, which is a deleterious factor. In this investigation, the successive ionic layer adsorption reaction (SILAR) method was used to grow the ZnO seed layer with low mis-orientation. In this new process, we used two cationic baths with different compositions. First, the counter-ion Zn(NO₃)₂ solution was used to form the nuclei by adsorption of Zn²⁺ on the substrate. This was then converted to ZnO by immersion in an anionic bath. Subsequently the zinc acetate bath was used for growth. This approach avoids twins parallel to the (0001) plane of the ZnO crystalline structure. The micrographs showed a dense layer and homogeneous petal array, with high orientation in the C axis, which improves electron transport.

Keywords: DSSC, SILAR, ZnO thin-film, solar cell.

1 INTRODUCTION

Zinc oxide (ZnO) is an important n-type semiconductor material which is environment-friendly, is inexpensive and non toxic. ZnO has a hexagonal wurtzite structure with lattice parameter $a = 0.3296$ nm and $c = 0.5206$ nm. Its structure can be described as two polar faces: Zn²⁺ (0001) and O²⁻ (000 $\bar{1}$) and orthogonal non polar faces. The polar faces are unstable energetically where three mechanisms lower their free energy: (1) surface reconstruction or faceting; (2) electronic relaxation and (3) non-stoichiometric surface. ZnO does not exhibit faceting that allows fast growth of polar faces. Besides the $\pm[0001]$ direction, there are two other fast growth directions: the $\pm\langle 2\bar{1}\bar{1}0 \rangle$ ($\pm[2\bar{1}\bar{1}0]$, $\pm[\bar{1}2\bar{1}0]$, $\pm[\bar{1}\bar{1}20]$) and the $\pm\langle 01\bar{1}0 \rangle$ ($\pm[01\bar{1}0]$, $\pm[10\bar{1}0]$, $\pm[1\bar{1}00]$), which form a variety of morphologies and these morphologies have been obtained through control of growth rates in these directions [1,2]. This control is possible by altering growth parameters.

ZnO can be used in many types of opto-electronic devices, due to its physical characteristics such as: higher binding energy (60meV), direct wide band gap (3.37 eV),

high electrochemical stability and good optical characteristics [3]. ZnO can be grown as thin films with different morphologies and in the form of nanowires, nanorods, nanoflowers, nanobelts, etc., and each morphology is suitable for making sensors or devices like thin-film dye-sensitized solar cells (DSSC), gas sensors, piezoelectric transducers, surface acoustic wave filters, etc. [4].

In DSSCs the ZnO is grown on a conductive glass like fluorine doped tin oxide (FTO) or indium tin oxide (ITO). In the case of the FTO (used in this investigation), the SnO₂:F layer (tetragonal litharge-type) does not have the same crystalline structure as ZnO and this hampers its formation [5]. To minimize interfacial defects, it is essential to grow a seed to deposit the entire thin film [3-6].

Nowadays, ZnO seeds are prepared by several techniques, like rf-sputtering [7], spray pyrolysis [8], sol-gel [9] and electrodeposition [10]. These techniques require either high vacuum or high temperatures (or both) which increase processing costs. The successive ionic layer adsorption and reaction (SILAR) technique is a modification of chemical bath deposition (CBD) at near room temperature. In SILAR the cations are adsorbed on the substrate in a specific bath and reaction with the anion occurs in another bath. The substrate is rinsed between each cycle [11-13]. In SILAR, ion by ion deposition takes place, permitting higher control of thickness and morphology than in CBD.

Based on these aspects, the aim of this investigation was to grow a dense seed layer onto FTO glass with an array of nanorods using the SILAR technique, but with the addition of another cationic bath, and then thickening of the layer by CBD.

2 EXPERIMENTAL PROCEDURE

2.1 Glass slide preparation:

The ZnO films were grown on glass slides that were coated with a SnO film on only one side by vacuum metal deposition and provided by *Xop Glass* (TEC 15, 100nm, 12 - 14 Ω \square^{-1}). The SnO film is a good electrical conductor, is transparent and supports the growth of ZnO. The sizes of the slides were typically 2 cm x 1 cm. The substrates were prepared as follows: (1) immersed in ethanol and rinsed for 180s in an ultrasonic bath; (2) immersed in acetone and

rinsed for 180s in an ultrasonic bath; (3) immersed in bi-distilled (BD) water and rinsed for 180s in an ultrasonic bath; (4) dried in flowing N₂ for 2 minutes; (5) the side without SnO film was covered with *Teflon*[®] film. In this last step adherence of the *Teflon*[®] film to the glass slide was achieved due to surface tension.

2.2 Preparation of baths

All the chemicals were purchased from Vetec Quimica Fina LTDA, a subsidiary of Aldrich Chemical Co. LLC and used without further purification. Basically, three baths were used to grow the ZnO seeds: an anionic bath and two cationic baths. The anionic bath was prepared using BD water which was held at 363 K. The first cationic precursor bath was an equimolar bath (0.01M) of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and hexamethylnetetramine (HMT) dissolved in 250ml of BD water and held at 323 K. The second cationic precursor bath was a mixture of 0.02 M zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) and ammonium hydroxide solution (NH₄OH) at molar ratio of 1:20 (Zn:NH₃) and was held at 313 K. Typically, the pH of the first cationic pH bath was 7.15 ± 0.08 and that of the second cationic pH bath, 11.10 ± 0.08. Precision of temperature control was ± 0.1 K.

2.3 SILAR synthesis process

The SILAR growth process is deposition through alternate immersion of the treated substrate in anionic and cationic solutions interspersed with rinsing in BD water at room temperature. Growth of the ZnO seeds was achieved using the following sequence: (1) The substrate was immersed in the first cationic precursor bath, resulting in adsorption of the free Zn²⁺ onto the surface; (2) The substrate was immersed in the anionic precursor bath (BD water at 363 K) and this resulted in conversion of the adsorbed free Zn²⁺ to zinc oxide (ZnO). HMT has been used to obtain nano-rods of ZnO and it acts as a cation buffer [3]. Besides, HMT is innocuous in the initial stages of nucleation; (3) The substrate was immersed in BD water at room temperature to rinse and stop any further reaction. Efficient rinsing was achieved by gentle agitation of the substrate in BD water. (4) The substrate was immersed in the second cationic precursor bath, where growth takes place and the 1:20 ratio between Zn:NHO₃ ensures that all zinc atoms are complexed [4]; (5) The substrate was immersed in the anionic precursor bath achieving the same results as in step 2; (6) step 3 was repeated (7) The substrate was dried in flowing N₂. Usually, the deposition cycles were repeated 40 times and immersion times in the baths are shown in Table I.

2.4 Characterization techniques

The morphology of the nano-structured films was observed in a Philips X-30 scanning electron microscope

(SEM). A Bruker - ASX diffractometer was used to study crystallinity and copper K_α radiation (λ = 0.15406 nm) was used.

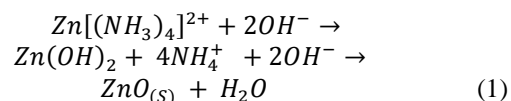
Seq. (#)	Bath (type)	Temperature (K)	Time (s)
01	1 st cationic	323	10
02	Anionic	363	5
03	Rinse	Room(298)	5
04	2 nd cationic	313	40
05	Anionic	363	10
06	Rinse	Room	5
07	Dry	Room	30

Table I – Details of SILAR synthesis.

3 RESULTS AND DISCUSSIONS

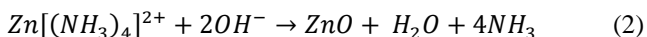
3.1 Anionic precursor bath temperature

In the SILAR method, the anionic bath temperature is the determinant parameter to grow ZnO. There are two possible routes to convert tetraamminezinc-(II) (TE) into ZnO. In the first route, TE is converted to Zn(OH)₂ and then to ZnO, as shown below:



However, the conversion of the Zn(OH)₂ to ZnO is not complete. Consequently the film is heat treated, and this degrades alignment of the nanorods.

In the second route, TE is converted to ZnO directly, as shown below:



The second route is achieved by heating the ultrasonic anionic bath and when the temperature is sufficiently high it breaks down H₂O into free H⁺ and OH⁻ [14-16].

In a previous investigation, the substrate was rinsed in water at room temperature before it was immersed in the anionic bath. In this study the substrate was immersed in the anionic bath immediately after it was removed from the cationic baths. We observed Zn(OH)₂ formation and basal ZnO oriented planes when the anionic precursor bath temperature was less than 360 K. Figure 1 shows x-ray diffraction patterns of the sample sensitized with the anionic bath at 363 K. The peaks in the pattern were indexed as hexagonal ZnO and SnO₂ phases. The stronger peak for reflection from (0002) planes indicated alignment of the ZnO nanorods.

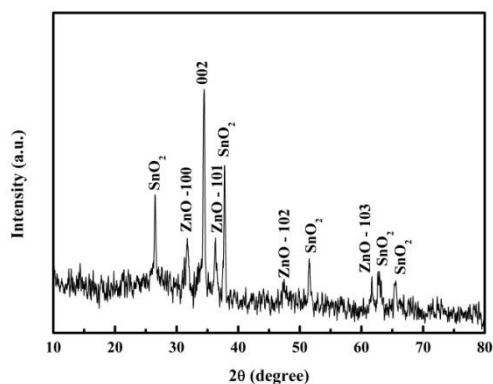


Figure 1: X-ray pattern of a seed layer grown by SILAR method.

3.2 Cationic precursor baths.

In the process used in this study, SEM images (not shown here) suggested that Zn^{2+} contained in the first cationic bath ($Zn(NO_3)_2 \cdot 6H_2O + HMT$) and adsorbed onto the FTO surface was more efficient than $Zn(NH_3)_4^{2+}$. This can be attributed to improved arrangement (allignment) based on size of the cations, on the crystalline SnO_2 structure.

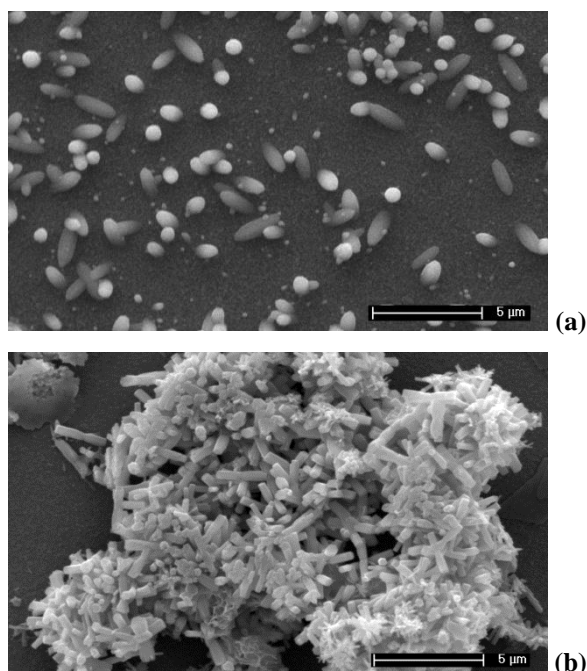


Figure 2: Morphology of ZnO nucleus formed with different precursor concentration (a) 0.01M and (b) 0.05M.

Figure 2 shows SEM images of ZnO nucleus formed with different precursors concentrations: (a) 0.01 M and (b) 0.05 M, without zinc acetate bath in the process. As the concentration increased the initial nuclei grew as random nanorods, and nucleation of new nuclei decreased. In the

0.01M bath, besides the reduced concentration of Zn^{2+} , HMT acts as a non polar chelating agent and inhibits growth of non polar faces [17-18].

In the second cationic bath (zinc acetate), the TE favours growth of the nucleous, which can be described by reaction (2). Growth of the nanorods instead of further nucleation can be attributed to minimization of energy, which is conducive to growth rather than nucleation on SnO_2 . Yamabi and Imai [4] reported that pH of the solution and substrate surface influence morphology. For $(Zn^{2+} : NH_4^+)$ (R) ratio molar of 20 and $pH < 10.5$, heterogeneous nucleation is favoured, where as at $pH 10.5-12.5$, homogenous nucleation occurs. In our study these conditions were not verified. The best results were obtained for $R = 20$ and $pH 11.10$. We ascribe this result to the following mechanism: ZnO nuclei formed in the first bath have high surface energy, appropriate for heterogeneous nucleation with more TE available, since precursor concentration used here is double that used by Yamabi. This indicates that the extent of supersaturation is a controlling parameter for homogenous/heterogeneous nucleation conditions, besides molar ratio at low temperatures. This mechanism finds support in the influence of ammonia concentration reported by Kanmani [19].

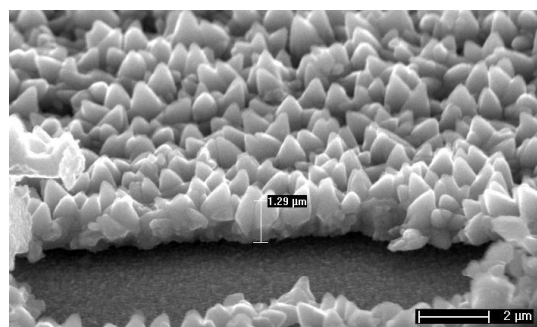


Figure 3: SEM image of ZnO seed layer obtained by SILAR method.

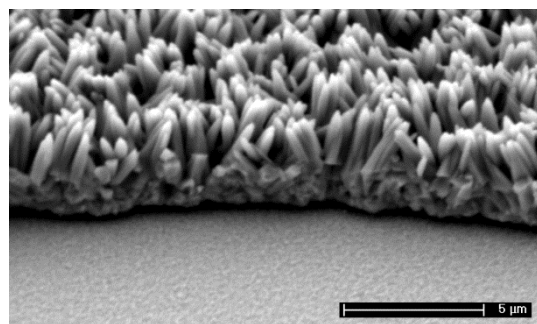


Figure 4: SEM image of ZnO nanorods grown on the seed layer .

A SEM image of ZnO seed is shown in Figure 3 and it reveals that the region near SnO_2 is dense. This suggests that after nucleation on the substrate surface is complete, the first bath promotes dissolution of nanorods that

subsequently grow in the second bath, until they reach the maximum thickness attainable by this method [6]. The roughness of the surface provides oriented growth of ZnO nanorods as shown in Figure 4.

4. CONCLUSIONS

Through control of the counter-ion and concentration of the complexing agents at low temperature, ZnO seed layer was prepared by a new route using the SILAR method. The ZnO seed layer was formed by direct conversion of TE in ZnO in hot water. Experimental results showed that the morphology was determined by the role of both cationic baths. These baths controlled the growth rate of the non polar faces. The seeds layer permitted growth of the nanorods.

ACKNOWLEDGMENT

The authors thank IPEN-CNEN/SP and FAPESP (contract number: 2010/52109-8) for funding this investigation. The authors are also grateful to Dr. Reginaldo Muccillo for the XRD analyses.

REFERENCES

- [1] Wang, Z.L. *Journal of Physics Condensed Matter* 16 (2004) R829-R858.
- [2] Greene, L.E.; Law, M.; Tan, D.H.; Montano, M.; Goldberger, J.; Somorjai, G.; Yang, P. *Nano Letters* (2005) 1231-1236.
- [3] Lockett, A.; Thomas, P.J.; O'Brien, P. *The Journal of Physical Chemistry C* (2012) 116 8089-8094.
- [4] Yamabi, S.; Imai, H. *The Royal Society of Chemistry* 12 (2002) 3773-3778. DOI: 10.1093/b205384e.
- [5] Govender, K.; Boyle D.S.; Kenway, P.B.; O'Brien, P. *Journal of Materials Chemistry* (2004) 14 2575-2591.
- [6] Breedon, M.; Rix, C.; Kalantar-zadeh, K. *Materials Letters* (2009) 63 249-251.
- [7] Dalui, S.; Das, S.N.; Roy, R.K.; Gayen, R.N.; Pal, A.K. *Thin Solid Films* 516 (2008) 8219-8226.
- [8] Breedon, M.; Rahmani, M.B.; Keshmiri, S-H.; Wlodarski, W.; Kalantar-zadeh, K. *Materials Letters* (2010) 64 291-294.
- [9] Zhao, W.G.; Zhang, Q.; Ma, Z.Q. *Materials Science Forum* 685 (2011) 65-70.
- [10] Gao, Y.; Nagai, M.; Chang, T.C.; Shyue, J.J. *Crystal Growth & Design* 7 (2007) 2467-2471.
- [11] Gao, X.D.; Li, X.M.; Yu, W.D. *Journal of Solid State Chemistry* 177 (2004) 3830-3834.
- [12] Kumar, P.S.; Raj, A.D.; Mangalaraj, D.; Nataraj, D. *Applied Surface Science* (2008) 255 2383-2387.
- [13] Gao, X.D.; Li, X.M.; Yu, W.D. *Applied Surface Science* 229(2004) 275-281.

- [14] Gao, X.D.; Li, X.M.; Yu, W.D., Li, L.; Peng, F.; Zhang, C.-Y. *Journal of Crystal Growth* 291 (2006) 175-182.
- [15] Gurav, K.V.; Patil, U.M.; Pawar, S.M.; Kim, J.H.; Lokhande, C.D. *Journal of Alloys and Compounds* S09 (2011) 7723-7728.
- [16] Shinde, V.R.; Gujar, T.P.; Lokhande, C.D. *Solar Energy Materials & Solar Cells* 91 (2007) 1055-1061.
- [17] Vergés, M.A.; Mifsud, A.; Serna, C.J. *J.Chem.Soc. Faraday Trans.* 86 (1990) 959-963.
- [18] Ridhuan, N.S.; Fong, Y.P. Fong, lockman, Z.; Tazak, K.A. *Applied Mechanics and Materials* 83 (2011) 116-122.
- [19] Kanmani, S.; Ramachandran, K. *Journal Material Science* DOI: 10.1007/s10853-012-6981-2.