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***Niyamat Beedri[1], Yusuf Inamdar[1], Suhail Anjum Sayyed[1,2], Arif Shaikh[1], Sandesh Jadkar[1] and Habib Pathan[1]***

# GROWTH OF ZINC OXIDE POROUS FILMS VIA ELECTROCHEMICAL ANODIZATION USING GLYCEROL BASED ELECTROLYTE

[1] *Advanced Physics Laboratory, Department of Physics, University of Pune, 411 007 Pune, India*
[2] *Department of Physics, B.P.H.E. Society's Ahmednagar College, 414 001 Ahmednagar, India*
*pathan@physics.unipune.ac.in*

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**Abstract**. ZnO porous films were successfully anodized on pure Zn sheet *via* electrochemical anodization in the glycerol base electrolyte containing ammonium fluoride salt as a pore enhancing agent. The structural and morphological properties of anodized and annealed films were characterized by X-ray diffraction and scanning electron microscopy, respectively. This shows the formation and growth of ZnO porous structure.

**Keywords***:* anodization, zinc oxide, porous, annealed film.

## 1. Introduction

The preparation of dimensionally controlled zinc oxide nanostructures has drawn much attention in recent years, because of its usefulness in various applications such as chemical sensors, biosensors, solar cells, photo catalysts, and optoelectronics [1, 2]. The porous ZnO films were prepared by a large variety of methods such as wet chemical method [3] hydrothermal method [4, 5] electrochemical deposition [6], electrochemical anodization [7, 8]. The electrochemical anodization is well known as a cost effective method and is widely used to produce very uniform and adhesive oxide films on metals, decorating a metal surface and/or increasing corrosion/wear resistance [9]. Electrochemical anodizations of Zn sheet resulting in the porous structure by using different oxalic acid concentration are explained [7, 10]. There are also reports on the synthesis of various ZnO nanostructures such as nanosheets, nanoparticle, nanoneedles and sunflower like structure by electrochemical anodization in different electrolytes [11, 12]. N. Shrestha *et al.* [13] prepared nanotubular ZnO using sulfide based electrolyte. V. Galstyan *et al.* [14] synthesized self assemble chain-like ZnO nanostructure by using the ethanolic solution of oxalic acid dehydrated as electrolyte *via* electrochemical anodization.

In this article we report two electrode electrochemical anodizations of porous ZnO on Zn sheet by using 20 % dilute solution (0.5 g $NH_4F$ + 90 ml glycerol + + 10 ml DDW). Such porous morphology is useful as a photoanode material in dye sensitized solar cell applications.

## 2. Experimental

### 2.1. Anodization of ZnO Films

The direct current regulated power supply (Radial made model: SVP 100002) was used as the voltage source for anodization. The schematic diagram for the electrochemical anodization set up is shown in Fig. 1.

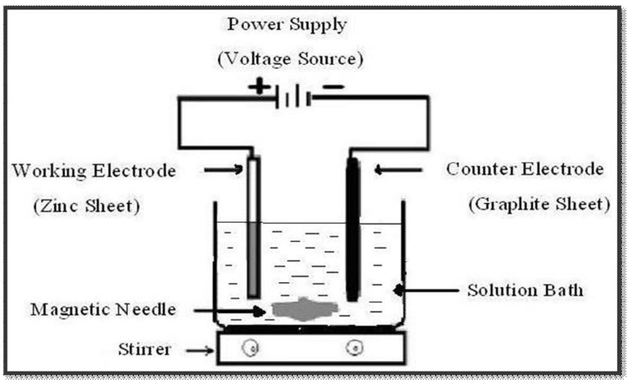



**Fig. 1.** Schematic diagram for the electrochemical anodization setup

Pure Zinc sheet (99.98 % purity, 0.25 mm of thickness, Alfa Aesar) was cut in to the desired size (1x5 cm). Zn foil was ultra-sonicated in acetone for 5 min followed by rinsing in de-ionized water (DIW) to remove the impurity. The anodization process was carried out using two electrode configuration. Zn (anode) sheet was used as the working electrode and graphite sheet (cathode) was used as the counter electrode under the constant potential at room temperature (~ 300 K). Zn sheet was anodized at 2 V for 1 h in electrolyte (pH = 5.2) prepared by using 20 % dilutes (0.5 g $NH_4F$ + 90 ml glycero + + 10 ml DDW). The film thus anodized was washed by DDW, dried in the air and annealed at 523 K for 2 h.

## 2.2. Characterization

The surface morphology studies (SEM) and Energy Dispersive X-ray spectroscopy (EDS) (using scanning electron microscope, JEOL JSM-6360) and X-ray diffraction studies (using X-ray diffractometer, Bruker D8) of as anodized and annealed films were carried out. The optical absorption spectrum (using JASCO V-670 spectrophotometer) was recorded in the range of 200–800 nm.

# 3. Results and Discussion

## 3.1. Growth Mechanism of ZnO Film

The growth mechanism and formation of ZnO layer on the surface of Zn sheet take place under the influence of constant applied voltage. In our method the acidic solution (pH = 5.2) was used as the electrolyte. The reaction mechanism can be described as follows [10]:

Reaction at anode:

$$H_2O \rightarrow H^+ + OH^- \quad \text{(acidic medium)} \qquad (1)$$

$$Zn \rightarrow Zn^{2+} + 2e^- \quad \text{(oxidation)} \qquad (2)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \qquad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad \text{(annealed at 523 K)} \qquad (4)$$

Reaction at cathode:

$$2H^+ + 2e^- \rightarrow H_2\uparrow_{(g)} \quad \text{(reduction)} \qquad (5)$$

Zinc sheet was anodized in 20 % diluted $NH_4F$ electrolyte at 2 V under the constant potential. The zinc sheet (anode) was converted to $Zn^{++}$ ions by releasing two electrons which moved towards the cathode. The water molecules were ionized into $H^+$ and $OH^-$ ions. $H_2$ were liberated at cathode, hence pH of the solution was changed from the acidic to basic one (pH = 8). And remaining $OH^-$ ions move towards the anode resulting in the formation of $Zn(OH)_2$. The anodized film was characterized by XRD. Fig. 2 extensively shows the formation of $Zn(OH)_2$. After annealing in the air at 523 K for 2 h $Zn(OH)_2$ decomposed into ZnO [15].

## 3.2. Structural Study

The anodized and annealed films were characterized using X-ray diffractometry. Fig. 2 shows that XRD pattern of the annealed sample with diffraction peaks at $2\theta$ = 32, 34.6, 36.5, 47.8, 56.8, 63.1 and 68.2$^o$ which were assigned to diffraction from (100), (002), (101), (102), (110), (103) and (112) planes. This confirms the formation of ZnO in the film. The mean size of crystallite calculated using the Scherrer formula is around 16 nm.

## 3.3. Morphological Study

Fig. 3 shows SEM image of anodized and annealed films. The images of the annealed sample show intertwined wire like porous structure. These films have similar morphology as ZnO film produced by wet oxidization method such type of morphology has applications in photocatalysis [16].

## 3.4. EDS Analysis

Fig 4 shows EDS pattern of the annealed film which confirms the presence of the element Zn and O supporting XRD.

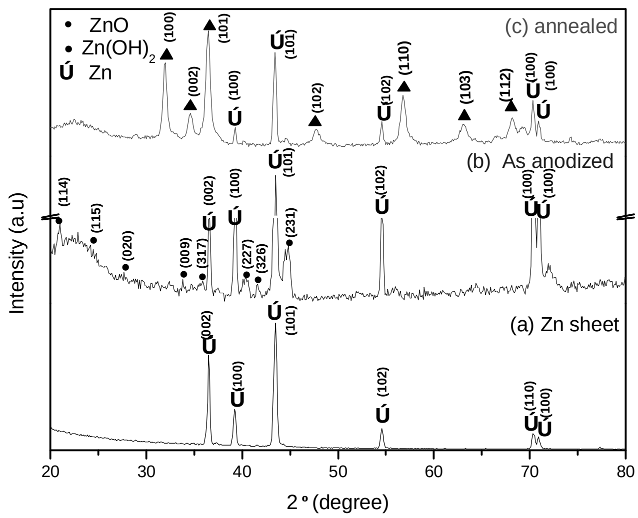



**Fig. 2.** X-ray diffraction pattern of zinc sheet (a); anodized film (b) and annealed film (c) at 523 K

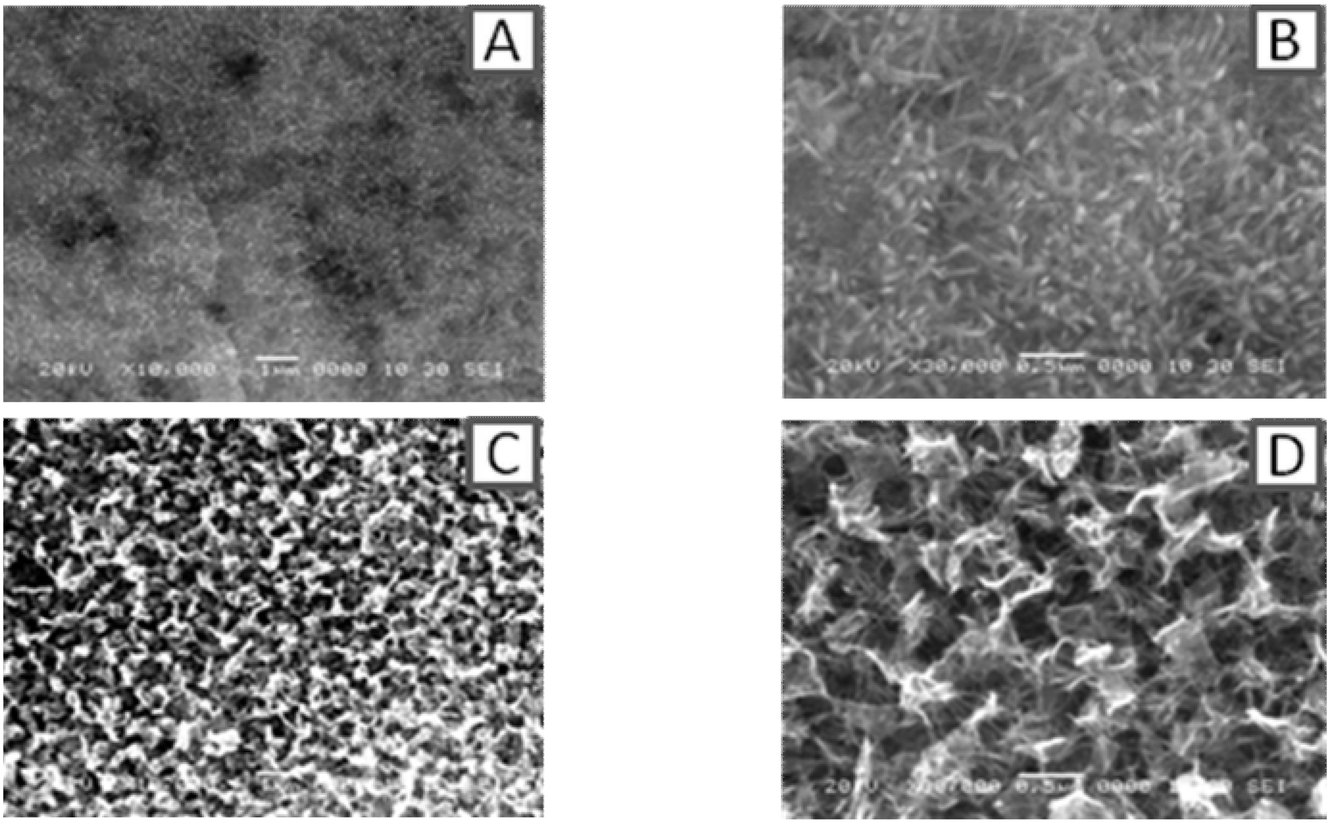



**Fig. 3.** SEM images on zinc sheet: anodized (a, b) and annealed films (c, d) at 523 K

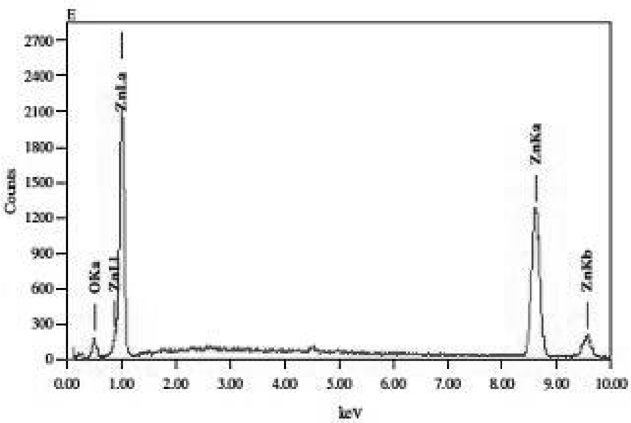



**Fig. 4**. EDS spectra of the annealed film

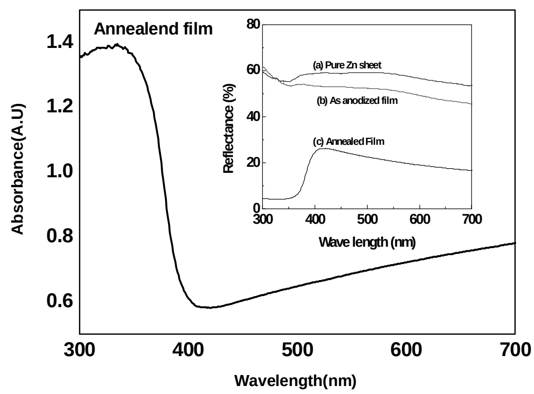


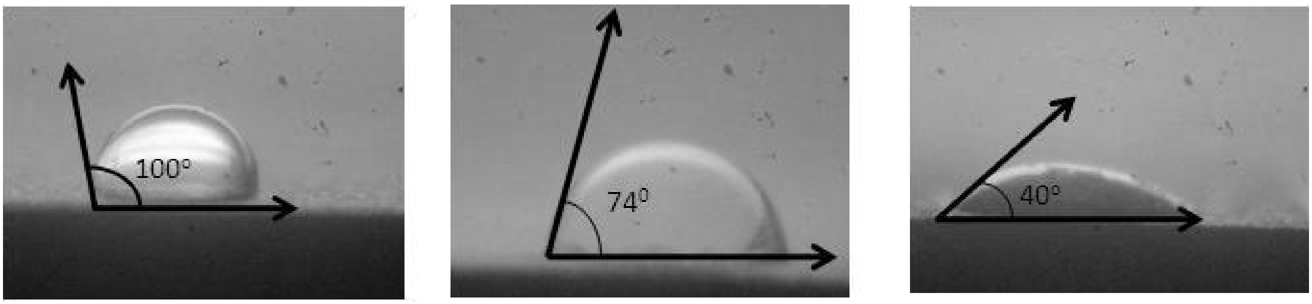

**Fig. 5**. Optical absorption spectra of annealed film (inset: reflectance spectra of pure Zn sheet (a); anodized film (b) and annealed film (c))

## 3.5. Optical Properties

Fig 5 shows optical absorption spectrum of ZnO. The calculated band gap of ZnO film is around 3.2 eV. The sharp absorption feature indicates the presence of very few surface states on the particle surface [17], the inset shows the reflectance spectra of pure zinc sheet, anodized film and annealed film, respectively.

## 3.6. Contact Angle Measurement

Fig 6 shows the contact angle of precleaned pure Zn sheet, anodized film and annealed film. It has been observed that the contact angle of annealed film is less than that of anodized film. This fact confirms that annealed films are more hydrophilic. R. Mane *et al*. [18] measure $TiO_2$ nanocrystalline surface exhibited as hydrophilic surface used in DSSC application.




a) b) c)

**Fig. 6.** Contact angle measurement for: pure zinc sheet (a); anodized film (b) and annealed film (c)

## 4. Conclusions

The present study describes fabrication of porous ZnO film using simple two electrodes electrochemical anodization method. The structural morphological and optical properties of these films were studied. These films are apparently suitable for photoanode application in the third generation solar cells.

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## ПРИРІСТ ПОРИСТИХ ПЛІВОК ОКСИДУ ЦИНКУ ЗА ДОПОМОГОЮ ЕЛЕКТРОХІМІЧНОГО АНОДУВАННЯ З ВИКОРИСТАННЯМ ЕЛЕКТРОЛІТУ НА ОСНОВІ ГЛІЦЕРИНУ

***Анотація***. *На чистому цинковому листі, за допомогою електрохімічного анодування в електроліті на основі гліцерину, що містить фторид амонію як засіб для підсилення пор, анодовано пористі плівки ZnO. Структурні та морфологічні властивості анодованих і відпалених плівок визначено рентгенівською дифракцією та скануючою електронною мікроскопією, відповідно. Встановлено утворення та зростання пористої структури ZnO.*

***Ключові слова:*** *анодування, оксид цинку, пористий, відпалена плівка..*