

SIMULATION AND SYNTHESIS OF ZnO NANORODS ON AAO NANO-POROUS TEMPLATE FOR USE IN A MEMS DEVICES

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The advancement in nano-technology imposed great impact on human life due to its vast variety of applications in various fields like medical and healthcare, sports industry, textile industry, agriculture industry, food industry, cloth industry, electronic devices and energy sector. This advancement is based on versatile nano materials, those have attained gigantic reputation because of its superior properties and applications. By using smart and advanced nanomaterial, various types of nano-structures like nano-pores membrane/template, nanoparticles, nano-wires, nano-rods, nano-tube, nano-fibers can be synthesized by adopting eco friendly strategy. Among these nanostructures, anodized aluminum oxide (AAO) template has vast applications in filtration and purification, microelectromechanical system (MEMS) and for use in a template in electronics devices. In this work, Firstly authors have studied the mechanical behavior of AAO nano-porous template by performing finite element analysis using ANSYS. The results depicted that the porous template produced maximum deflection of 1.56 μm at the middle when a pressure of 5 kPa is applied. Secondly, AAO templates were fabricated in two step anodization by using self-designed anodization setup. Field emission scanning electron microscopy was performed to investigate the pore size that is in the range of 60, 80 and 100 nm. After successful template/membrane fabrication the chemical bath deposition method were adopted to grow the zinc oxide (ZnO) nano rods on AAO template. These templates can be used to develop MEMS devices.

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1. Introduction

During the last few decades, science and technology has gain massive consideration with the foremost goal is to enhance human life [1]. Among various technologies, nano-technology is the most prominent one possessing to its higher capability and applications in the field of medicine, bio-medical, electronics, energy, industrial and purification processes [2-7]. Nano-materials are the foundation of nano-technology with broad and wide range of application owing to its superior properties including physical properties, large surface area to volume ratio, small size (nano scaled) which allows potentials for manipulation and handling of multiple functionalities [8-11]. Nano-structured materials include nano-pores, nano-wires, nano-rods, nano-tube, nano-fibers, nano-particles have vast application with their superior and improved physical, chemical, mechanical and optical properties [12-17]. These highly ordered structures have immense applications in the field of medical to high level technology including electronics devices, energy generation and harvesting, water filtration and gas sensing [18]. Nano-porous anodized aluminum oxide membrane/templates have gained much attention due to their highly ordered and regular structural arrangement [19-21]. The structures give large surface area to volume ratio, exceptional thermal stability and low manufacturing cost which provide wide-ranging of applications for these nanostructures like cell culturing, high resolution bio-imaging, drug delivery, energy generation, conversion and storage, mono-disperse filters and membrane, platform for chemical and

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bio-sensing, gas sensing, high surface area catalytic support, photonic, plasmonic and bio-MEMS device [22-24]. In the field of bio-medical, water filtration and energy, porous anodic aluminum oxide membranes are widely used as a template or as a filter. For various applications, pressure is applied on the AAO structure to foresee the strength. In various applications the pore size and structure of the anodized aluminum oxide is of great concern. In this work, we have simulated a portion of AAO membrane/template to study the deflection, stress and strain produced in the structure due to applied pressure. After performing simulation the actual development of nano-porous membrane/template was carried out by changing the parameters to study the effect of pore-size/diameter. Then zinc oxide (ZnO) nano-rods layer was grown on fabricated structure by using self-designed chemical bath setup.

2. Structural simulation using ANSYS

Structural analysis of anodic aluminum oxide template was carried out Using ANSYS. A solid 3D geometry including pore with both side was created in ANSYS mechanical APDL. AAO material properties were defined. Solid 20node 186 Element was used to perform structural simulation to foresee the uniform effect of loads. Then Meshing was performed and sides were fixed with degree of displacement set to zero with top surface area of $2\ \mu\text{m} \times 2\ \mu\text{m}$. The 3D model and the mesh model are shown in Fig. 1. After meshing, boundary conditions were defined. The Pressure ranging from 1-5 kPa was applied on the top surface of porous structure. Stress, strain and deflection in the film due to applied lode were studied.

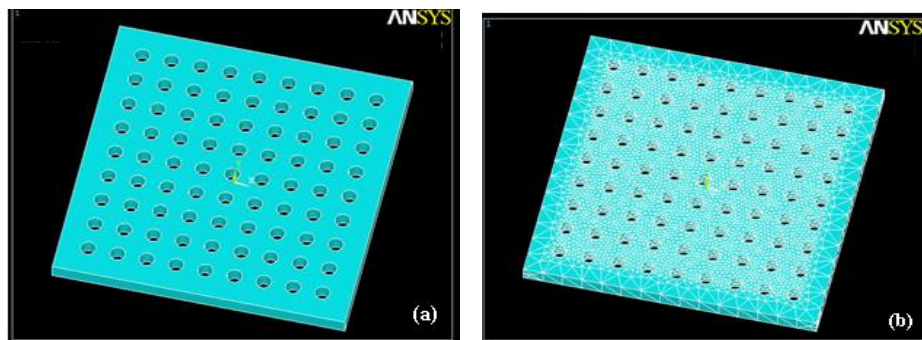


Fig. 1 AAO Template (a) 3D model (b) Mesh Model.

When load is applied the structure bends to opposite side that leads deflection, stress and strain in the structure. The Stress through the length of the template was studied in all three axis with applied pressure of 5 kPa. The stress in all three axis are shown in Fig. 2. The stress in x-axis is highest in the center of the template that is 11331.5 Pa. In y-axis and z-axis, the stress is highest at the sides ranging from 11324.8 Pa and 4419.9 Pa respectively.

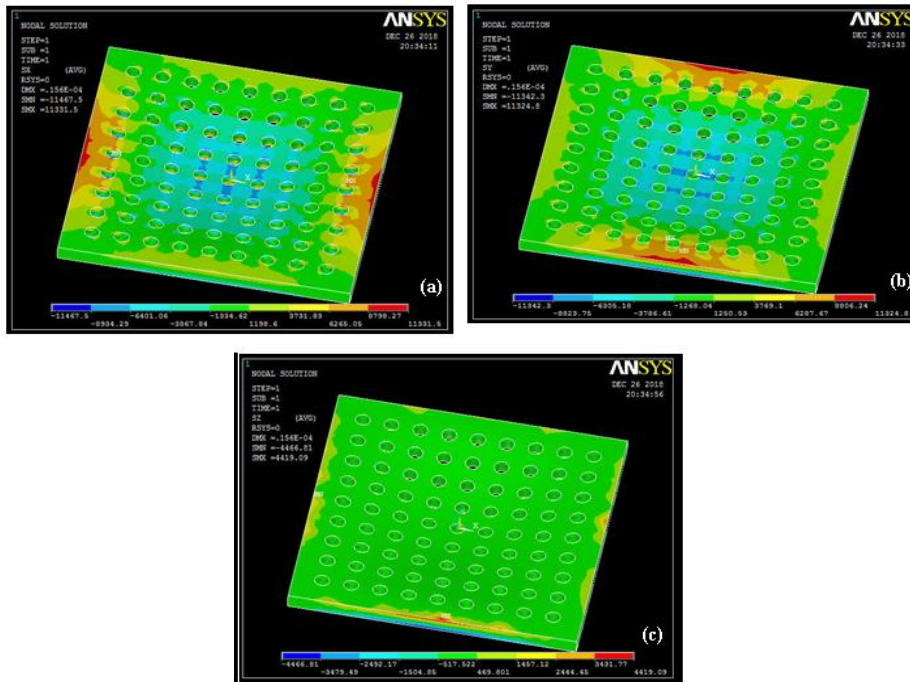


Fig. 2. Stress (a) x-axis (b) y-axis (c) z-axis.

Similarly elastic strain was also studied with applied pressure of 5 MPa. The applied pressure results in elastic strain in all three axes. Maximum strain of $6.55e^{-06}$, $6.51e^{-06}$ and $2.22e^{-6}$ was observed at the sides in x, y and z axis as shown in Fig. 3.

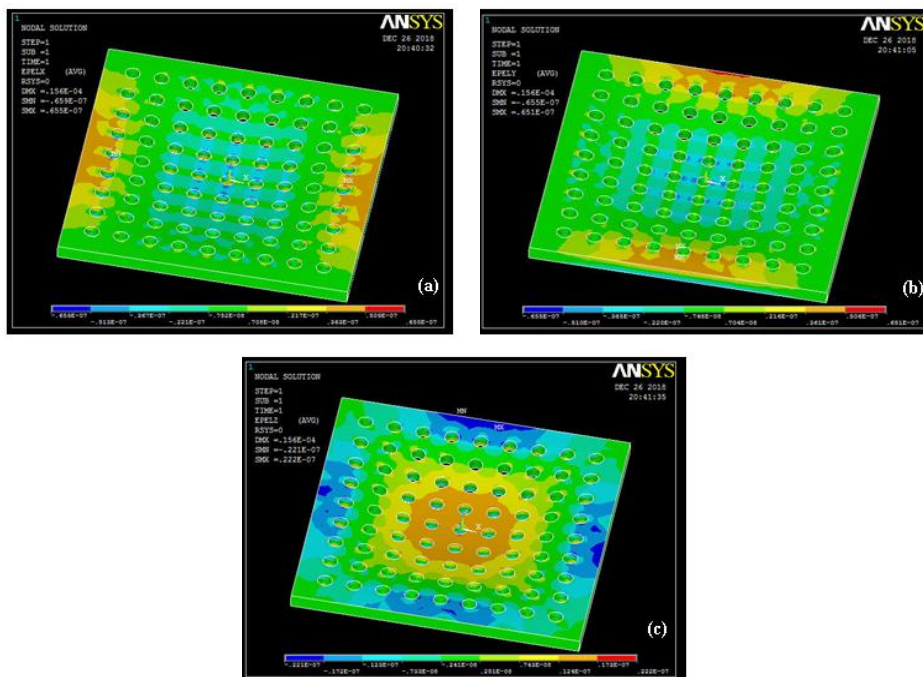


Fig. 3. Elastic Strain (a) x-axis (b) y-axis (c) z-axis.

The effect of deflection due to applied pressure of 5 kPa is shown in Fig. 4. In X and Y-axis the maximum deflection is 1.119 μm , z-axis the maximum deflection 1.73 μm and sum along XYZ the maximum deflection 15.6 μm was observed.

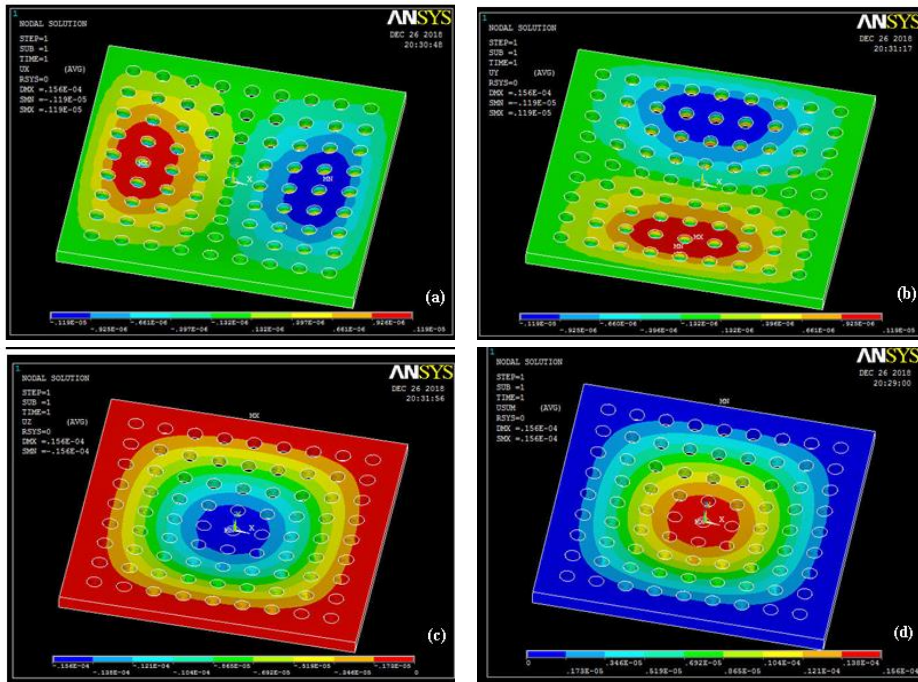


Fig. 4. Deflection (a) x-axis (b) y-axis (c) z-axis (d) sum.

It is clear from the above figure at applied pressure of 5 MPa the maximum deflection of 15.6 μm is observed at the center due to boundary condition displacement degree of freedom and minimum deflection can be seen at the corners. Fig. 5 shows the vector plot of deflection.

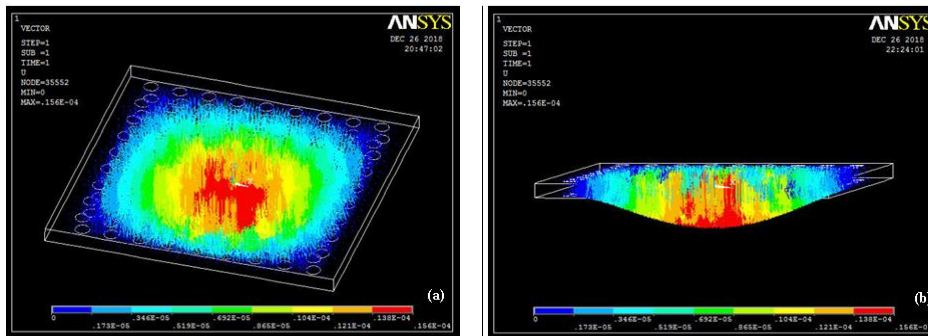


Fig. 5. Vector plot of deflection (a) front view (b) side view.

It has been observed the bending of membrane/template leads to stress and that found under the elastic limits. The deflection varies along the length of nanopours template uniformly. From coroners to center it increased gradually and reaches it maximum values as shown in graphically in Fig. 6.

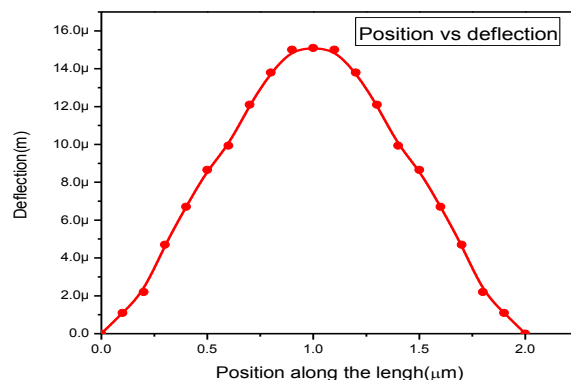


Fig. 6. Graph between deflection vs length of the template.

3. Materials and methods

All the substrates, glass wares and equipment were thoroughly cleaned. The aluminium substrates were cut in 1cm x 1cm area. The substrates have a thickness of 0.3 mm and initially washed with distilled water and acetone. It was further electro-polished using per chloric acid and ethanol. Then these samples were cleaned in distilled water using sonicated method with two chemicals like acetone and ethanol giving treatment 15 minutes. Then samples were treated in oven for air drying at 100 °C. Then anodization procedure was performed. Step 1 of anodization is referred to as mild anodization. At this stage oxalic acid electrolyte solution with molarity of 0.4 M was used, the aluminium substrate was used as anode and lead sheet is used as a cathode as shown in figure 7. The first step was carried out at 40 V for 25 minutes. The voltage was gradually increased to 110 V. The anodization at 110 V was carried out for 30 minutes. The prepared sample was then etched using 4% phosphoric and chromic acid for 25 minutes at 80 °C. Step 2 of anodization is referred as hard anodization. Same electrolyte with similar material cathode was used in the mild anodization. However, the process was conceded out at 110 V for 3, 3.5, 4 hours. The layer that form barrier was detached by varying the electrolyte to 0.3 M potassium chloride with negative voltage. Then etching the samples were performed after stage two of anodization. The mercuric chloride solution was used and time was considered 20 minutes to remove all unwanted impurities. The schematic of the anodization procedure is shown in Fig. 7.

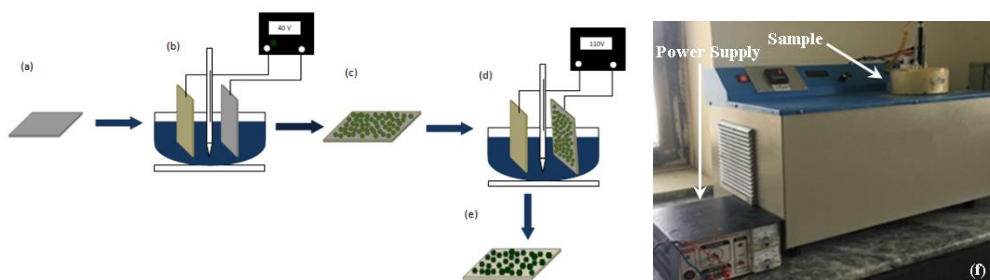


Fig. 7. Schematic and real setup: (a) Aluminum substrate (b) First step of anodization (c) Membrane/template after soft anodization (d) 2nd step of anodization (e) template second step of anodization (f) self-design setup for AAO fabrication.

The prepared anodized aluminum oxide nano-porous template was characterized using Scanning electron microscopy to study its pore size and structure. The porous template formed after the 2nd step of anodization was further used as template to synthesis the ZnO nano structures. These structures further can be used in nano generators as ZnO exhibit piezo-electric properties. Then ZnO nanorods have been synthesis on AAO using chemical bath deposition set-up that were self-designed with low cost. Zincacetate di-hydrate 20 mM solution with hexa-amine was prepared in deionized water. The porous template was treated with dodecanethiol solution to increase the sticking. Then synthesis of ZnO nano-rods was carried out for 6 hours at 95 °C. The solution was changed after every 2 hours to avoid the decay of the solution. After the deposition process, the samples have been washed using deionized water. Then annealing was performed at 400 °C for 2 hours. The schematic diagram and real setup are shown in Fig. 8.

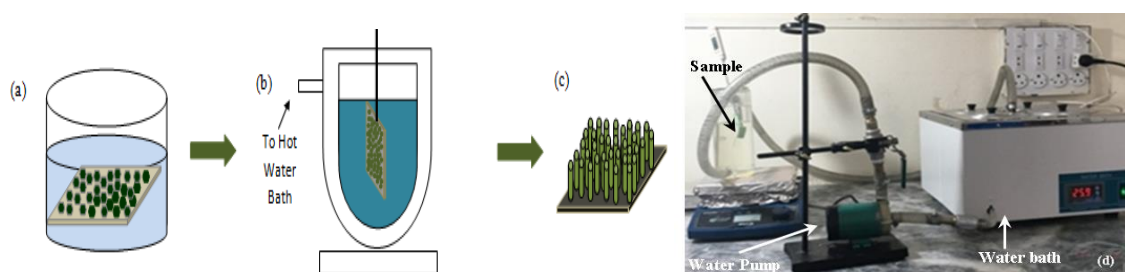


Fig. 8. Synthesis of ZnO Nanorods on AAO template/membrane (a) Anodized aluminium oxide membrane/template (b) Chemical bath deposition (c) Prepared nano-rods on aluminium substrate (d) Self-design chemical bath deposition.

4. Results and discussion

The prepared template samples were studied using scanning electron microscopy for its structural features. The SEM micro-graphs in the images show the continuous highly ordered and aligned nano-porous template. The nano-porous template was highly systematic and nano-pores can be easily seen in Fig. 8. The pores diameter varies from 60 nm to 100 nm depending upon the time of variation of 2nd step of anodization. For 3, 3.5 and 4 hours of mild anodization (2nd step of anodization) the pore size was observed to be 60 nm, 80 nm and 100 nm respectively as shown in Fig. 9. The well-ordered different pore size template can be further use for various applications including bio-medical, electronics, photo-catalysis, cell culturing and bio-imaging [25].

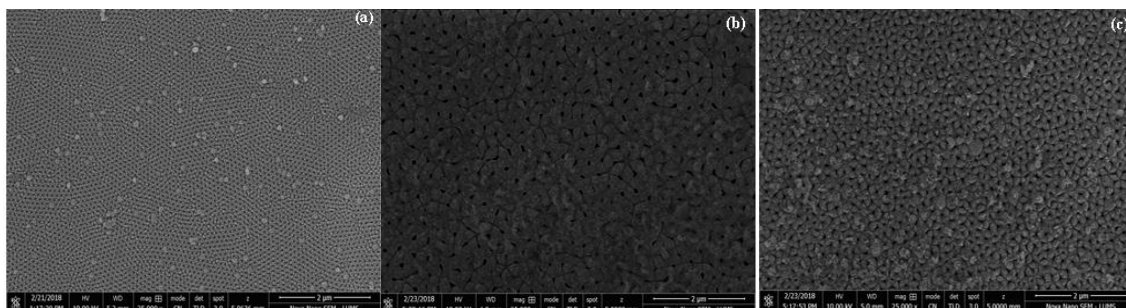


Fig. 9. SEM Micro-graphs of AAO nano-porous template formed after 2nd step of anodization with time (a) 3 hours (b) 3.5 hours (c) 4 hours.

This prepared membrane/template can be further utilized in various applications including its significant applications in the field of biomedical, bio-imaging, cell culturing, water filtration, drug delivery, gas sensing, piezo-electric sensors and MEMS energy harvester. Table 1 shown the nano-porous template used with various pore sizes reported with different applications.

Table 1. AAO nano-porous membrane/ template with different pore size and their applications.

References	Pore Size (nm)	Application
Petrochenko PE etal [26]	20-200	Biomedical
Mahadi Md [27]	50-60	3D Micro-channel
Tomassi [28]	100-300	Template for formation of metal surfaces
Patrick [29]	34-117	Cellular devices
Zeng Z [30]	50-70	Template for graphene nano-mesh
Chen W [31]	200	Pressure Sensor
Kyotani t [23]	50-100	Membrane filter
Thormaan A [32]	185	Filtration and bio functionalization
Zhang Q [33]	20-50	Template for silver nanowire array
Shi W [34]	50-150	Affinity protein separation
Current Study	60-100	MEMS/NEMS Devices

Table 3 provides a scope of nano-porous membrane/template reported in literature and its application in different research areas [35]. While here we have fabricated template with pore size of 60 to 100 nm range and can be used as template of MEMS energy harvester. Furthermore, the porous template was used for growth of ZnO nano-rods on it. The SEM images of nano-rods grown on anodic aluminum oxide substrate shown in Fig. 9 and clearly depicts the formation of nano structured rods on the substrate material. The grown material is highly ordered and systematic, highly symmetrical, uniform and continuous. FE-SEM micrograph shows smooth growth of hexagonal ZnO nano-rods on AAO substrate. The periodic arrangement on ZnO nano-rods with a diameter of 200 nm were orderly spread with great uniformity.

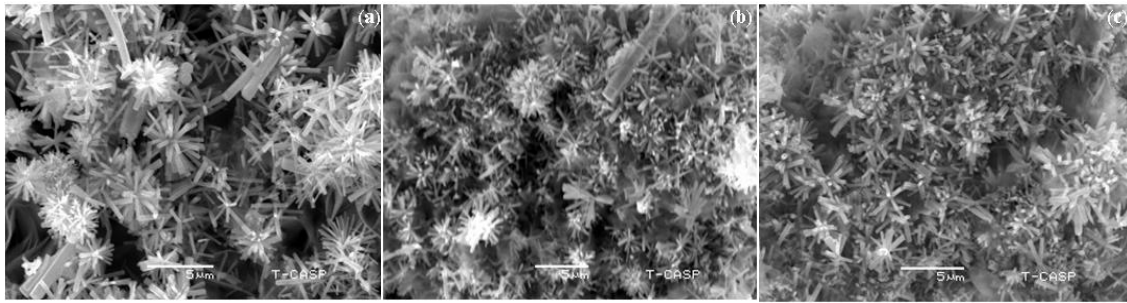


Fig. 10. ZnO nano-rods on AAO template (a) Nanorod on AAO template with pore diameter 60 nm (b) Nanorod on AAO template with pore diameter 80 nm (c) Nanorod on AAO template with pore diameter 100 nm.

The SEM micrograph of ZnO nanorods shows uniformity with hexagonal flower types structures. It has been observed that with increase of pore size the density of rods on AAO template has been increased.

5. Conclusions

This work reflects the structural simulations, fabrication of AAO nano pore template and synthesis of ZnO nanodrods. ANSYS mechanical APDL was used for structural simulation. Stress strain and deflection of template have been studied with applied pressure. Then templates were fabricated by two step anodization by using self-design low cost setup. A highly porous, ordered, symmetrical and homogeneous nano-porous were observed in FE-SEM micrograph.

The results depicts that the prepared nano-porous aluminum oxide template can be used in large variety of applications due to its various pore- size and illustrated uniformity. Pore-size was reported from 60-100 nm. Then synthesis of ZnO nanorods was performed in chemical bath deposition. It has been observed that with increase in pore sized AAO structures lads to high density of nano rod. These rods further can be used to form MEMS energy harvester.

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