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Etching Effect on Sensing Behavior of ZnO/PS Gas Sensor

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Abstract— Pulse laser deposition was used in this research by Nd:YAG laser with λ=1064 nm average frequency 6 Hz and pulls duration 10 nm) to deposit ZnO thin films with thickness 100 nm. From Atomic Force microscope of prepared samples show an decrease in average diameter with increase etching time. From FTIR spectra of porous silicon with constant current 40 mA and different etching time .The peaks at around 626 cm-1 for Si-Si , 875 cm-1 wagging mode,1073 cm-1 stretching mode and the transmittance peak at 2097 cm-1 reveal to bending mode (Si3SiH). The photolumincense spectroscopy shows that the blue shift with increasing etching time. The operation temperature of gas sensor was studied for different temperature and found the maximum sensitivity (85.3) for 30 min porous silicon time.

Index Terms— Metal Oxide, Pulsed Laser Deposition, Gas Sensors, Atomic Force Microscope.

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1 Introduction

Porous silicon (PS) can be defined as a silicon crystallite having a bunch of nanosized pores in it. It has been proven that porous silicon is one of the most promising materials, because it can emit visible range of light at room temperature. One of the most important characteristics of the PS layers is its very large and reactive internal surface So that, one should expect, that this internal surface would play an important role in those specific properties of PS layers which make this material so different from bulk one [1]. Porous silicon (PS) has many unique characteristics such as direct and wide modulated energy band gap, high resistivity, and the same single-crystal structure as bulk. Distinction in absorption of the light by PS and crystalline silicon is that in PS the pores can play a role of waveguides. The optoelectronic applications such as light-emitting devices, Photo detectors, solar cells and sensing devices using PS active layer require proper understanding of electronic transport behavior of PS layers in device structures, especially the junction properties [2]. PS has the potential to replace bulk silicon commonly used in micro-electronics. Other promising applications include environmental and in-vivo biological sensing. Gas sensors based on porous silicon have been developed [3].

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There are four important methods for fabrication of PS layer, electrochemical, photo-electrochemical, photochemical and stain etching processes. the most common of them are stain etching and electrochemical etching of the silicon wafer. The fabrication of Porous Silicon (PS) is a comparatively simple process that only requires a small amount of equipment. PS is formed by electrochemical etching that takes place at the interface of the Si substrate. When the current density is lower than the threshold value, holes will arrive at the surface at a slower rate so that sufficient amounts of fluorine $\mathbf{F}^{-}$ ions are already available at the surface to recombine with a hole at all times [4]. As n-type metal oxide semiconductor, zinc oxide (ZnO) has attracted intensive research attention owing to its diverse interesting properties such as electro-optical, piezoelectric, and magnetic properties [5-6]. With a direct wide band gap (3.37 eV) and relatively large exciton binding energy of (60 meV) ZnO has been widely investigated for many optoelectronic, chemical and bio sensing applications [7-8].In this research we want to study the effect of etching time on the structure, photoluminescence and sensing behavior of ZnO/porous Silicon. Experimental Setup

2 Experimental Setup

Porous silicon prepared by electrochemical Etching was the silicon wafer serves as the anode. The cathode is made of platinum or any HF-resistant and conducting material. Si wafer p-type with (111) orientation was used as a starting substrate in the electrochemical etching. The samples were cut from the wafer and rinsed with acetone and methanol to remove dirt. In order to remove the native oxide layer on the samples, they were etched in diluted HF acid (1:1) with

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constant current 40 mA and different etching time (10and 50) min .

Zinc Oxide powder pressing it under 5 Ton to formed a target with 2.5 cm diameter and 0.2 cm thickness. It should be as dense and homogenous as possible to ensure a good quality thin films were prepared by PLD technique. The pulsed laser deposition experiment is carried out inside a vacuum chamber generally at (10^{-3} Torr) vacuum conditions. The focused Nd:YAG Q-switching laser beam coming through a window is incident on the target surface making an angle of 45° with it. The substrate is placed in front of the target with its surface parallel to that of the target.

The morphological surface analysis is carried out employing an atomic force microscope (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBSfrom Angstrom Ad-Vance Inc.

The (Bruker tensier 27) scans of the FTIR measurements are performed over range between (500- 3500)$cm^{-1}$for prepared sample.

3 RESULT AND DISCUSSION

3.1 Atomic Force Microscopy (AFM)

The surface morphology of the oxidized PS layer was investigated using atomic force microscopy (AFM) studies focus entirely on the nanoscale characterization of PS films. When etching time increases a part of pores coagulate to larger structures .Figures (1) to (5) show AFM images of porous silicon at constant current 40 mA and different etching time (10,20,30,40 and 50) min . AFM parameters (average diameter, average roughness and peak –peak) for these samples have been shown in table [1] .The average diameter decreased with increase etching time. A change of microstructure of the porous silicon surface are observed for different etching time (10-50)min where pore sizes varied significantly as shown in the AFM pictures .

This roughness is expected to be caused by inhomogeneous of the substrate and electrolyte composition, and seems to increase with layer thickness.

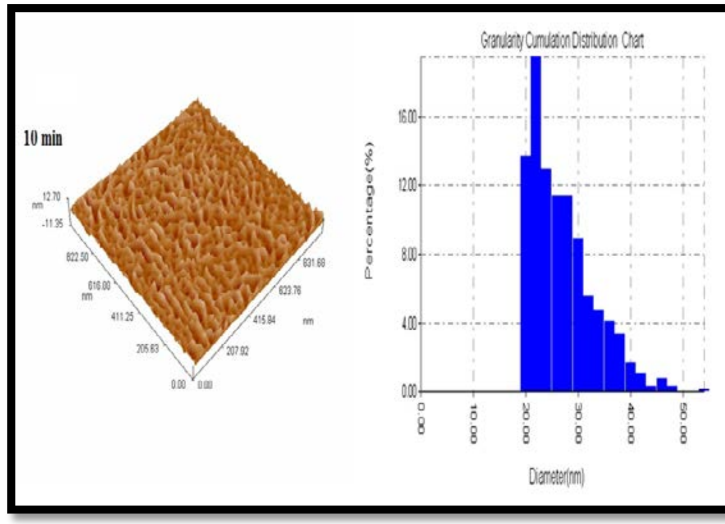

Figure (1) Atomic force microscopy pictures for porous silicon with current 40 mA and etching time 10 min

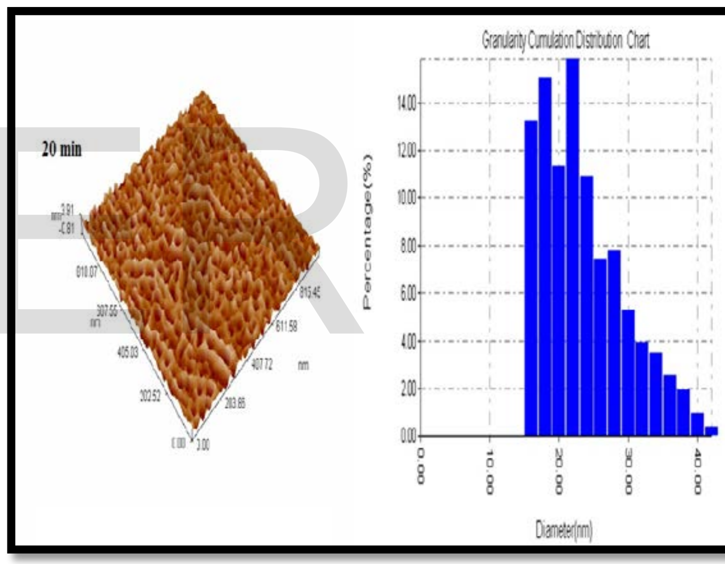

Figure (2) Atomic force microscopy pictures for porous silicon with current 40 mA and etching time 20 min.

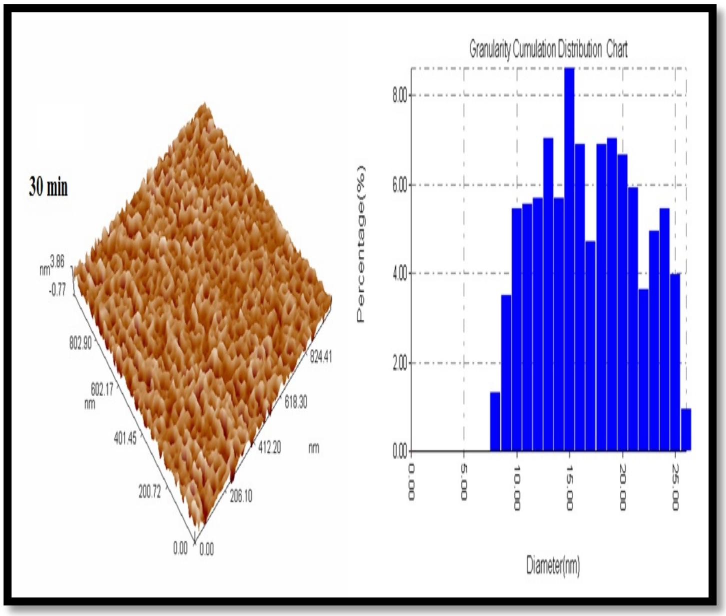

Figure (3) Atomic force microscopy pictures for porous silicon with current 40 mA and etching time 30 min.

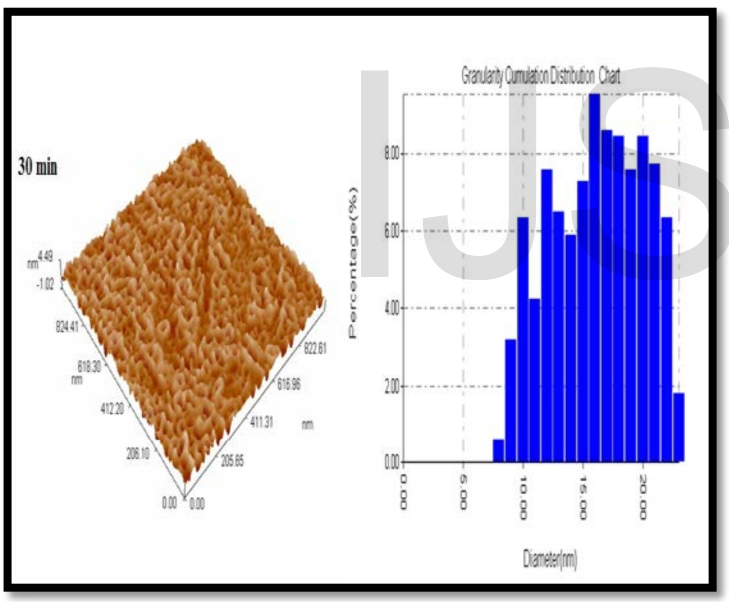

Figure (4): Atomic force microscopy pictures for porous silicon with current 40 mA and etching time 40 min.

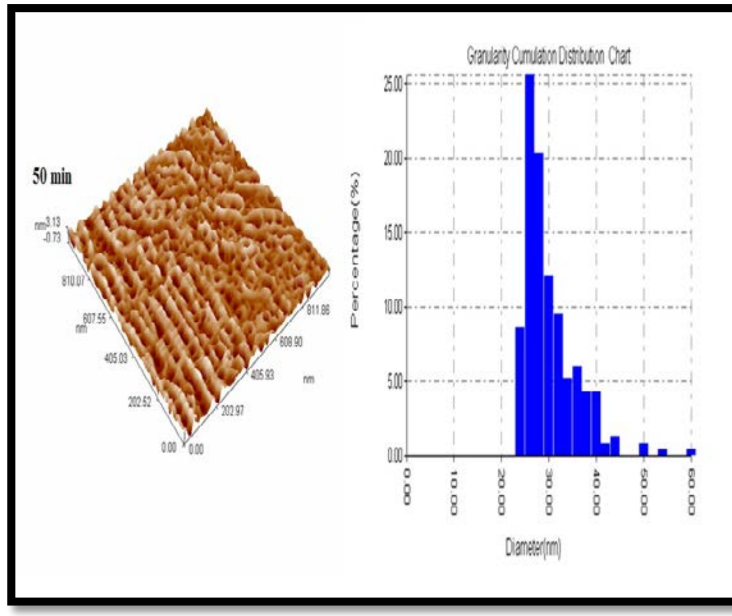

Figure (5) :Atomic force microscopy pictures for porous silicon with current 40 mA and etching time 50 min.

Table (1): AFM parameters for porous silicon wafer with constant current and different etching time.

sample	Average diameter (nm)	Average roughness (nm)	Peak –Peak (nm)
10	29.29	0.559	3.47
20	26.00	2.04	14.5
30	22.51	0.568	3.1
40	16.34	0.523	4.17
50	15.66	0.515	4.03

3.2 FTIR Transmittance spectra

Figure (6) shows the FTIR data for PS, synthesized by 40 mA/cm^2 etching current density at (10, 20,30,40 and 50) minutes etching time, it is clear that there are four distinct peaks with different intensities. The peak with intensity at 626 cm^{-1} indicates the presence of Si-Si stretching. A small peak at 875 cm^{-1} can be associated with the Si-H_2 Wagging mode[9,10]. While a peak at 2097 cm^{-1} suggests the Si-H stretching[11]. A strong broad band is observed at about

1073 cm^{-1} due to Si-O-Si asymmetry stretching vibrations mode in p-Si type.

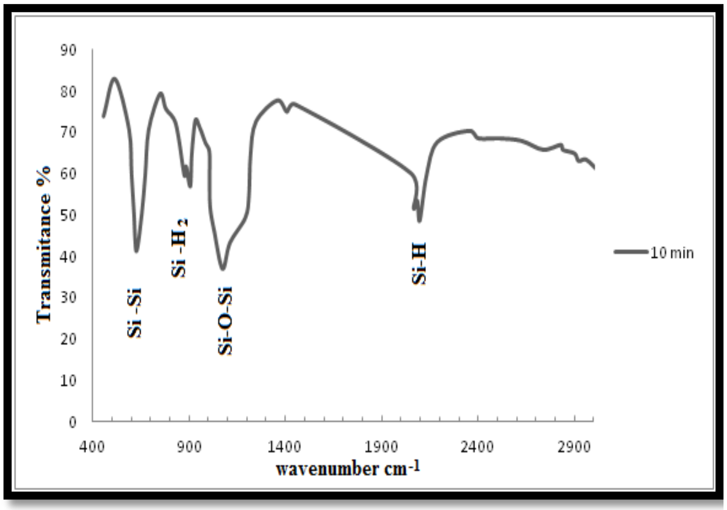

Figure (6): FTIR spectra for porous silicon with current 40 mA and 10 min etching time.

3.3 Photoluminescence Spectroscopy

Fig.(7) shows, the excited wavelength is at 210 nm which is the maximum absorption peak observed in UV spectra of PS, fluorescence spectrum of PS nanostructure consist the presence of a strong UV emission peak centered at 289 and 291nm for PS at current density 40 mA and(10,20,30,40 and 50) min etching time respectively, this blue shift could be attributed to decreasing in grain size.

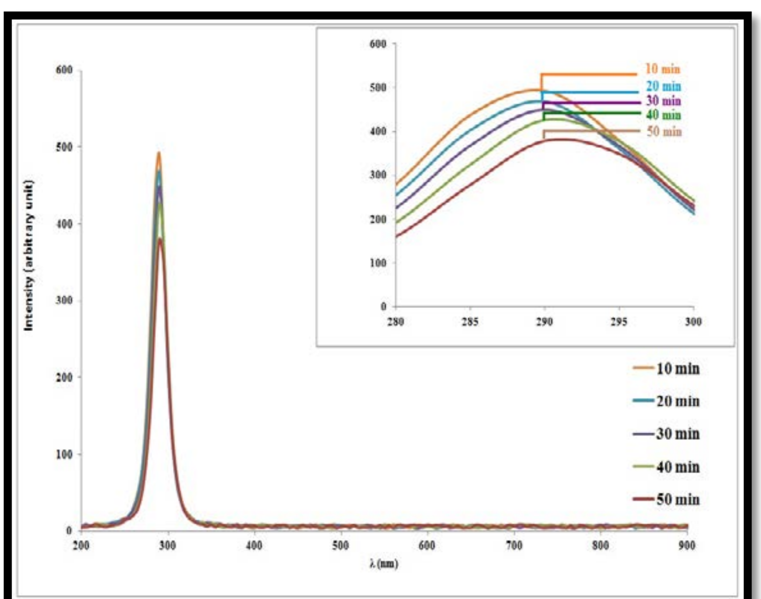

Figure (7): PL spectrum of porous silicon with constant current and different etching time (10,20,30,40 and 50)min.

3.4 Gas Sensor Measurement

Figure (8) shows the sensitivity as a function of operating temperature in the range (RT-350 °C) for pure ZnO which is deposited on the porous silicon substrate. The porous silicon substrate formed with constant etching current (40mA) and different etching time (10, 20, 30, 40, and 50min). The gas sensitivity tests were performed at room temperature and increased to 350 °C by 50 °C step, where the 3 % NO_2 : air mixing ratio the bias voltage of 3 Voltage were applied on the all samples .Figures (8)Show the sensitivity as a functions of operation time at different temperature for ZnO/PS films under 10 ppm NO_2 concentration. The variation of the sensitivity with operation temperature decreases as the temperature increases from room temperature to 350^{o} C showing a typical negative temperature coefficient of resistance (NTCR) due to thermal excitation of the charge carriers in semiconductor.

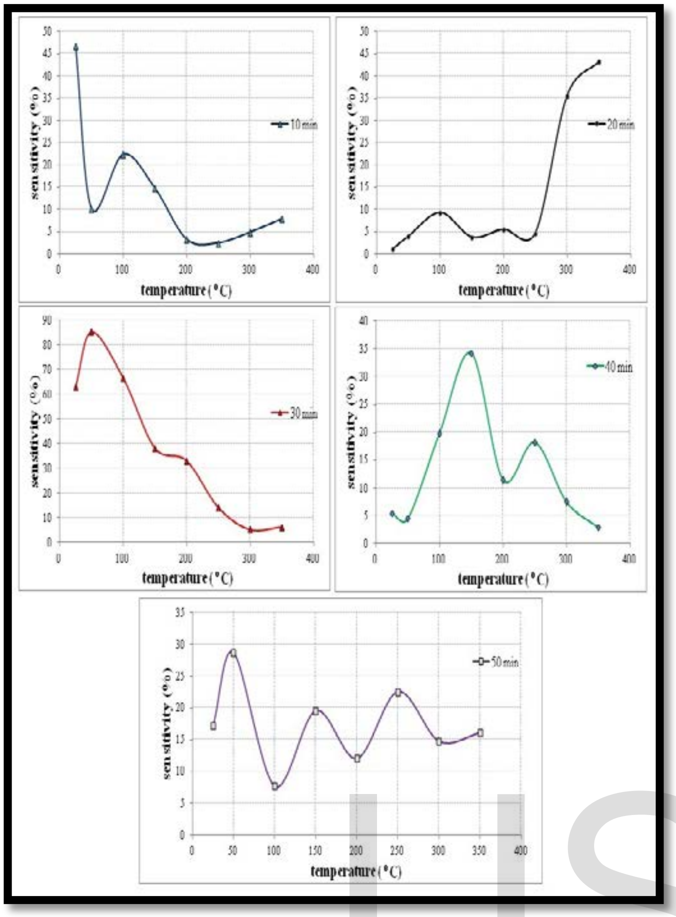

Figure (8): The variation of sensitivity with the operating temperature of ZnO for different porous time on porous silicon.

Figures (9) shows the relation between the response time and the Recovery time as a function of operation temperature with (40min) etching time of the pure ZnO deposited on porous silicon wafer (111) for 3 % NO_2 :air and bias voltage of 5V . These figure shows that the decrease of response \recovery time with increasing operation temperature and also with increasing doping ratio.

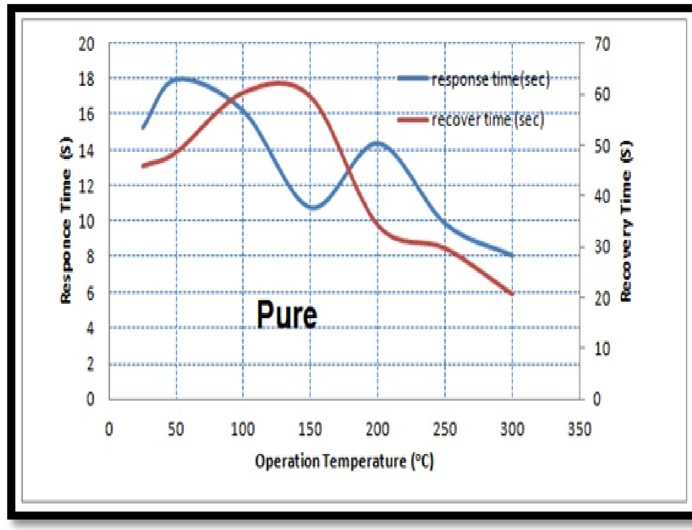

Figure (9) : The variation of Response time and Recovery time with operating temperature of the pure ZnO deposited on porous silicon wafer

4 Conclusions

- A polycrystalline structure of ZnO prepared successfully by PLD.
- Topography of porous Si shows a decrease in average diameter with increase of etching time.
- PL emission spectrum has abroad blue range with increasing porosity time.
- The sensitivity of sensor decreased by increased the time of porous silicon above 30 min.

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