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Growth and Optimization of Vapor Phase Stain Etched Porous Silicon for Plant Viruses and Their Protein Sensing Application

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Abstract- Porous Silicon (PS) layer is fabricated by a novel approach to reaction induced vapor phase stain etch (RIVPSE) technique by using Zn dust as sacrificial metal. This simple innovative technique avoids set up cost, special equipments or contacts and capable of producing large scale PS layer. The porous silicon (PSi) layers were formed on P-type silicon wafer. The samples were formed by different oxidation ratio, different etching times and different chemical volume. The structural and optical properties of porous silicon on silicon substrates were investigated by Scanning Electron Microscope (SEM), Optical Microscope, UV- Vis Spectrophotometer. The thickness and porosity of the layers were measured using gravimetric method. The Surface and optical investigations indicate that the PS layers may used as optical sensing platform for plant viruses and their protein sensing application.

Keywords- Porous Silicon, RIVPSE, SEM, UV-VIS spectrophotometer, Optical Microscope.

INTRODUCTION

Biosensors based on nanotechnologies are now widely investigated for the possible applications to monitor environmental pollutants [1]. Detecting plant viruses in agriculture is one of such applications. Since various shapes, sizes and biochemical properties of a large number of different viruses and bacteria are already known [2], the biosensors need to be able to identify different types of biological objects. In this direction, the porous silicon is now widely considered as a candidate for the biosensors [3].Presence of specific biocompounds in crops, fruits and vegetables can lead to their destruction. Hence, there is a huge market potential for reliable and inexpensive biosensors for agricultural and food applications. The sensitivity and performance of such biosensors can be improved by using certain nanomaterials for their construction. Nanoscale materials provide a large and often highly reactive surface area in sensor applications that enables more effective capture and detection of molecules than their bulk counterparts. These nanomaterials due to their physical structure display several unique physical and chemical features.

PS has been successfully yielded to fabricate sensors primarily due to its enlarged surface area as compared to planar surfaces. Several PS based sensors has been reported such as gas sensor [4], biosensor [5], organic vapor and humidity sensor that have used PS as sensing platform. PS based biosensors have a distinct advantage over other biosensors fabricated by nanomaterials like carbon nanotubes, gold nanoparticles and quantum dots as these show evidences of unintended acute or chronic toxicity in the human body during their diagnostic function. Studies also show toxicity levels when multi-walled carbon nanotubes are injected to the body. Buriak in 2002 reported that

PS in contrast to these sensors are biocompatible biodegradable and hence can be degraded to harmless products [6]

Since its discovery PS has been conventionally formed by electrochemical anodisation etching technique with an external electrical bias. Though pore structures can be easily formed by this technique there exist some potential drawbacks in it. Some of the drawbacks include setup cost as the anodisation process requires special equipment such as constant current source and anodisation cell in addition to its inability to process large area PS layers [7]. Interestingly simple stain etch (SE) method do not require any such technical equipments and offers the possibility to form thin PS films. The time delay that occurs between the immersion of the silicon wafer in the etching solution and the onset of the PS formation is referred to as incubation time that results in oxidized pores with impurities incorporated in it leading to unreliable, unstable PS characteristics. Recently SE process has been reported to be modified by avoiding the "incubation" period and hydrogen bubble formation associated with this PS formation process thereby producing uniform homogeneous porous structures. Modified SE processes such as RIVPSE process overcomes these drawbacks without requiring any special set up, electrical contacts or surfactants thereby significantly reducing the fabrication cost of PS films [7]. Modified SE processes such as RIVPSE[4,7] process overcomes these drawbacks without requiring any special set up, electrical contacts or surfactants thereby significantly reducing the fabrication cost of PS films .Instead of immersing the silicon substrate into etch solution as in basic SE process; RIVPSE technique exposes the substrate to acid vapors to obtain uniform PS structure With respect to this RIVPSE different growth optimization has been done here by using these parameters:- different oxidation ratio of etchant, different etching time durations, different container height variation, same container different chemical volume variation. It has been reported that RIVPSE technique could be employed to develop promising platform for enzyme immobilization with reduced cost and improved shelf life that could lead to a cost effective novel sensor [8]. It can also be efficiently used for fabrication of porous silicon/silicon cantilever beams and production of antireflection coatings for silicon solar cells [9,10].

In this work an attempt has been made to fabricate PS structures by a new approach to RIVPSE method. The specific contribution to this work has been to introduce a new metal Zn dust as a sacrificial metal for PS formation. The resulted uniform and homogeneous PS structures fabricated could be effectively used for the development of biosensing platform. PS surface morphology prepared from vapor etching process has been observed by Scanning Electron Microscopy (SEM). Absorbance and PL spectra of the luminescent PS structures formed based on using Zn dust as sacrificial metal. This method developed mesoporous PS based sensor.

EXPERIMENT

All materials used in the studies undertaken by the author for the presented thesis were purchased from EMerck, India and the Si wafers were purchased from Y-Mart, USA. Boron doped P-type c-Si wafers having (100) orientation and resistivity 3-10 ohm-cm (double side polished surface) thickness 300 micro meter were taken as starting material for the formation of PS.

Wafers were cleaned by standard clean procedure. Silicon (Si) wafers were subjected to hot Acetone treatment in ultrasonic agitation for 5 minutes and dipped into Methanol for 3 minutes followed by rinsing in DI water thoroughly. The substrates were thereafter immersed into strong piranha etch solution containing H_2SO_4 (98 % GR) and H_2O_2 (30% GR) in 3:1 volume ratio for 15 minutes to remove the organic contaminants present in the wafer. Finally the wafers were dipped into 10% Hydrofluoric acid (40% GR) of lower concentration to remove native oxide as well as maintaining the surface roughness. Deionised water (Millipore) of resistivity 18.2M ohm-cm was used to rinse the samples then sample drying ambient air after each step.

It has been reported that PS layer is formed by exposing the Si wafer to an etch vapor where Al used as sacrificial metal. In this work Zn is used as sacrificial metal for the preparation of PS layer by RIVPSE method. The result of fabrication in this process is uniform and homogeneous PS structure. The surface area of resulted PS film may be even higher than the electrochemically etched PS films. The specimens immediately after etching showed homogeneous PS films with white crystalline structures observed in naked eyes. Homogeneous PS layers formed by this technique exhibited bright orange luminescence under UV light. The geometries of etched featured and PS properties depend on several fabrication parameters including diffusion of reactants and nature of chemical reaction [11].
Here for growth optimization distinct approaches were applied to RIVPSE method for preparation of PS layer using different parameters, such as- different oxidation ratio, different etching times and different chemical volume.

Zn induced RIVPSE Method

Here the PS formation has been done by same container 100ml,same etching time 4 min but varying different oxidation ratio such as- HF:HNO_3 (4:1,6:1,8:1).

PS fabrication were carried out by the technique where silicon substrates where exposed to an etch vapor resulting from the reaction of Zn metal dust (99.999% pure)
continuously added to HF: HNO_3 (oxidation ratio 4:1) acidic solution. An exposure time of 4 min to these acidic vapors resulted in the formation of PS structures. Therefore the wafer kept into the filter paper. These specimens immediately after etching showed homogeneous PS films with white crystalline structures observed in naked eye. But uniform pore is not observed by UV-VIS spectrophotometer. Homogeneous PS layers formed by this technique exhibited not so bright orange luminescence under UV light.

Now, another volume ratio has been taken. PS fabrications were carried out by similar aforementioned technique where oxidation ratio made to HF: HNO_3 (volume ratio 6:1) acidic solution. An exposure time of 4 min to these acidic vapors resulted in the formation of PS structures. Therefore the wafer kept into the filter paper. These specimens immediately after etching showed homogeneous PS films with white crystalline structures observed in naked eye. Uniform pore is observed by UV-VIS spectrophotometer. Homogeneous PS layers formed by this technique exhibited bright orange luminescence under UV light.

After that the PS formation has been done by another oxidation ratio made to HF: HNO_3 (volume ratio 8:1) acidic solution where the exposure time was 4min. The method was same as stated before. These samples were bit different from others because of its homogeneous PS films seen by naked eye and very much bright orange luminescence under UV light. But uniform pore is not observed by UV-VIS spectrophotometer.

The absorption spectra of PS layers were measured using Perkin Elmer UV-VIS lambda 45 spectrophotometer. PL measurements were carried out on in room temperature has been carried out by using HeAg laser of 224nm as the excitation source. The surface morphology of PS film formed by Zn induced RIVPSE technique was investigated by scanning electron microscope (VEGA II TESCAN) and Optical microscope.

RESULTS AND DISCUSSION

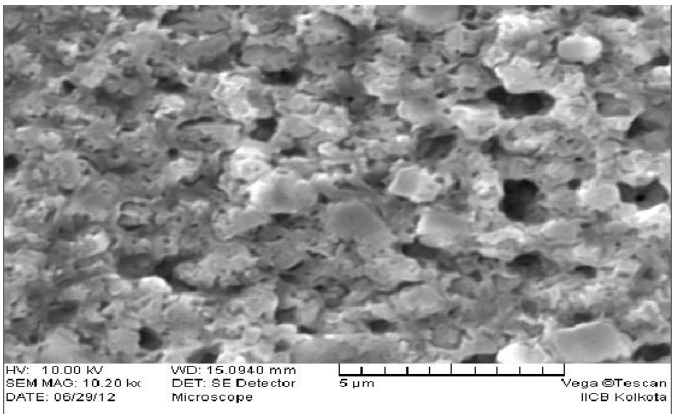

Fig 1 :- SEM image of RIVPSE PS of HF:HNO3 (4:1) (Top view)

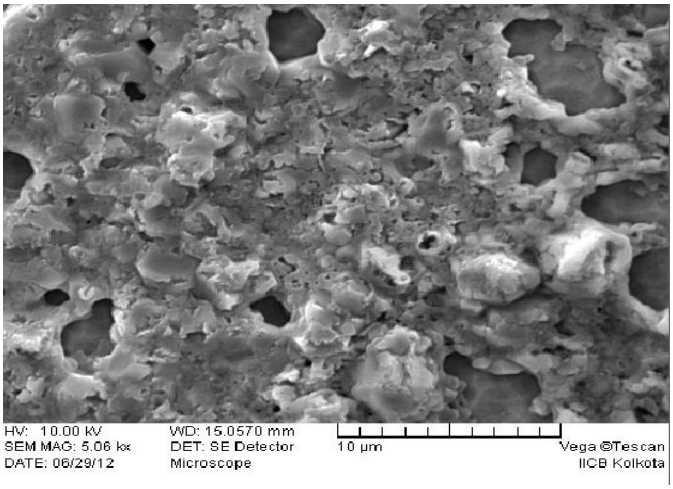

Fig.2 SEM image of RIVPSE PS of HF:HNO3 (6:1) (Top view)

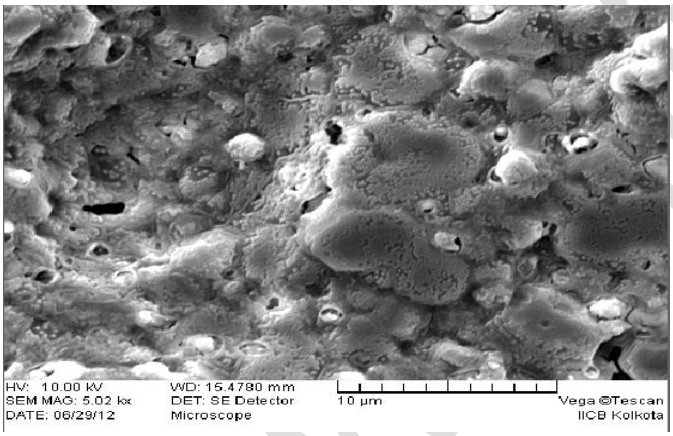

Fig3:- SEM image of RIVPSE PS of HF:HNO3 (8:1) (Top view)

The SEM image shows PS morphological structure that could be formed resulting from the direct localized reaction of etch vapor molecules with the silicon substrate. However beyond a specific etching period acid vapor condensation led to formation of white crystalline structures observed in Figure.

The SEM images displays rough PS surface comprising of white interconnected clusterslike structures. Small dot-like nanoporous structures are observed within these interconnected clusters.

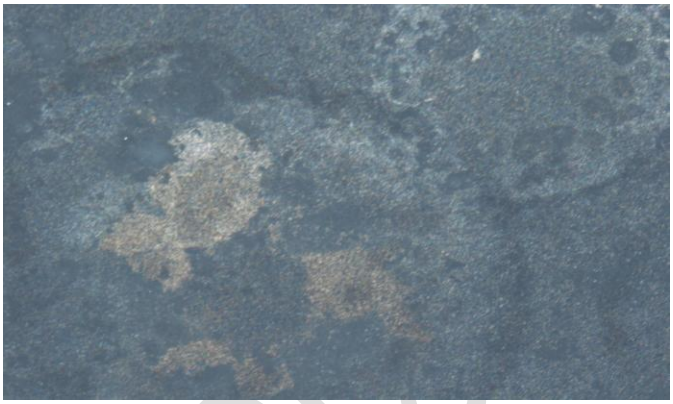

Fig4. OM image of RIVPSE based PS sample HF:HNO_3 (4:1) showing islands

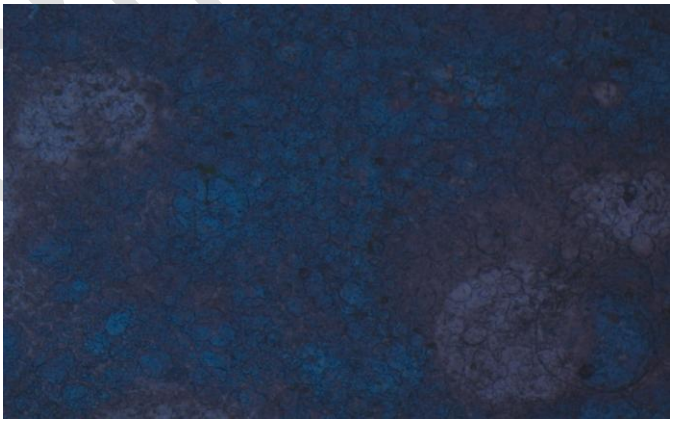

Fig5. OM image of RIVPSE based PS sample HF:HNO_3 (6:1) showing islands

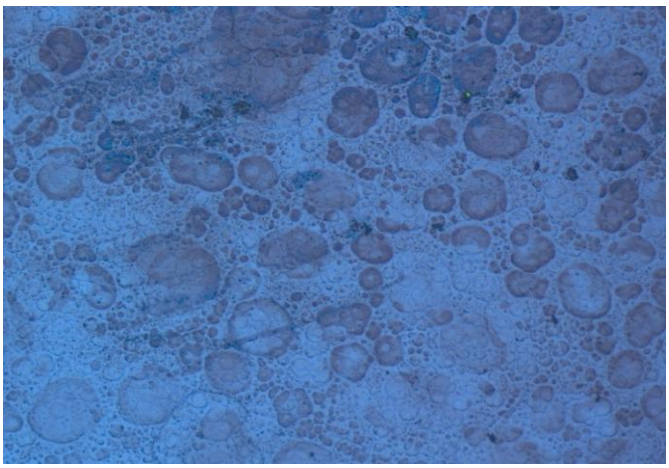

Fig6. OM image of RIVPSE based PS sample HF:HNO_3 (8:1) showing small dots

The fig 4 and 5 show cluster-like isolated PS islands and fig 6 shows small dots like structures.

Hence there exists some reasons for using RIVPSE based PS structures as promising platform for plant viruses and their protein sensing applications. Firstly SEM investigation show that RIVPSE based PS structure are mesoporous and nanoporous. Secondly PS layers with uniform homogeneity could greatly enhance the sensivity of the sensor for better sensor performance.

In oxidation ratio(4:1) the UV-VIS absorption spectra of PS Sample(3-10ohm-cm,PS) obtained. Zn induced RIVPSE based PS structures absorption spectra exhibits characteristic peak at 576nm shown in fig.7 significant absorption peak in Visible light range and suggesting formation of PS structures containing well defined pore structures of different pore dimensions as evident from SEM investigations.

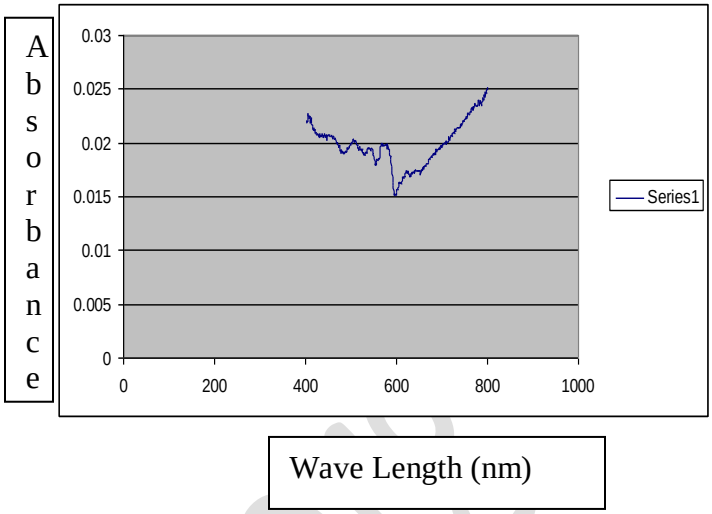

Fig 7. Absorbance spectra of RIVPSE based PS sample HF: HNO_3 (4:1)

In oxidation ratio(6:1) the UV-VIS absorption spectra of PS Sample(3-10ohm-cm,PS) obtained. Zn induced RIVPSE based PS structures absorption spectra exhibits characteristic peak at 782nm and 641nm shown in fig.8 significant absorption peak in Infrared light range and Visible light range and suggesting formation of dual PS structures containing well defined pore structures of two different pore dimensions as evident from SEM investigations.

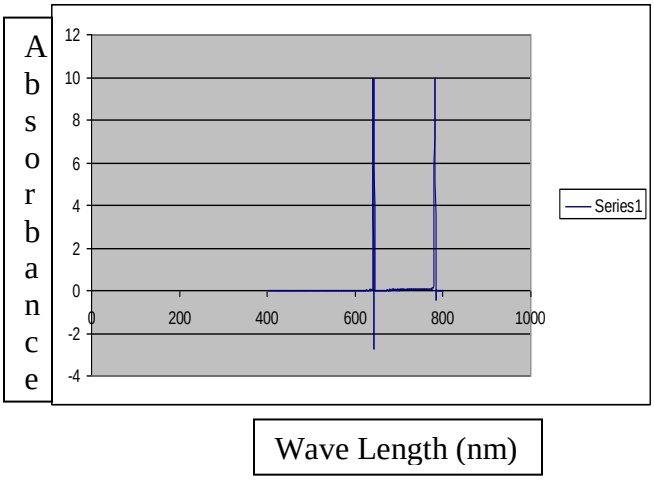

Fig 8. Absorbance spectra of RIVPSE based PS sample HF: HNO_3 (6:1)

In oxidation ratio (8:1) the UV-VIS absorption spectra of PS Sample(3-10ohm-cm,PS) obtain. Zn induced RIVPSE based PS structures absorption spectra exhibits characteristic peak at 564nm shown

in fig.9 significant absorption peak in Visible light range and suggesting formation of dual PS structures containing well defined pore structures of different pore dimensions as evident from SEM investigations.

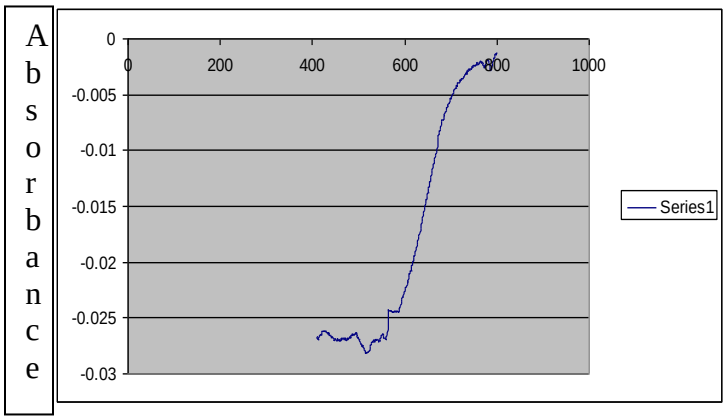

Fig 9. Absorbance spectra of RIVPSE based PS sample HF: HNO_3 (8:1)

have been reported here ade to explain the obtai lts. Spectrophotometric results have been found to be and etch time 4 min same chemical volume may be standardized for biosensor applications. This interesting PS surface morphological feature consisting of dual meso and nano structures on a single PS layer. This demonstrates that PS films could be used as optical sensing platform for biosensors, chemical sensors, humidity sensors ever bearing the fact that the preparation process is fast, simple, less expensive, batch processing and reproducible.

Porosity of RIVPSE PS sample using gravimetric method

The porosity of PS substrate, which is etched in the solution of HF: HNO_3 (4:1) for 4 minute is 81%. The porosity of PS substrate, which is etched for 4 minute in HF: HNO_3 (6:1) solution for is 53%. And the porosity of PS substrate, which is etched for 4 minute in HF: HNO_3 (8:1) solution for 40%.

Thickness Measurement of RIVPSE PS sample

The PS films have been prepared in same etch time 4min same chemical volume but different oxidation ratio HF:HNO_3 4:1,6:1,8:1. The use of Zn metal dust in RIVPSE process has yielded the strongest and uniform pore. The absorption spectra observed in UV-VIS range by the RIVPSE based PS films

reproducible and reliable in this present study. And especially 6:1 ratio

The thickness of PS substrate, which is etched in the solution of HF: HNO_3 (4:1) for 4 minute is18.18micro meter. The thickness of PS substrate, which is etched for 4 minute in HF: HNO_3 (6:1) solution for is 22.32 micro meter. And the porosity of PS substrate, which is etched for 4 minute in HF: HNO_3 (8:1) solution for 17.17 micro meter.

Here the porosity will be maximum when oxidant ratio will minimum and when oxidant ratio will be maximum then porosity will be minimum.

CONCLUSION

In this work PS films has been prepared by new metal dust Zn in RIVPSE method. The Zn dust in acidic solution acted as catalyst in PS formation process avoiding incubation period that enable faster PS formation. This innovative technique formed uniform dual mesoporous and nanoporous structure as revealed by SEM image and validated by spectrophotometer spectra. Achieved 53% porosity and 22.32 micro meter thickness by gravimetric method. The enhanced specific surface area due to the presence of meso structure and

nanoporous structure may be utilize for the optical transduction of biosensor.

Therefore the PS films formed by Zn dust induced RIVPSE process standardized the oxidation ratio 6:1 etch time 4 min and 100 ml container makes it an attractive platform for plant viruses and their protein sensing application. This PS fabrication process may be optimized for better stability and reliability. Zn induced RIVPSE process is a simple new fabrication process that requires no technical equipment, no constant voltage source, no cost effective biosensor.

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