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Synthesis and Functionalization of L, DL-Iso, Nor, Leucine on Porous Silicon for Sensing Application

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Abstract: *The etching process of Porous Silicon has been carried out using an electrochemical oxidation technique. Oxidized samples were immobilized with -Leucine, DL-Iso Leucine and DL-Nor Leucine solutions. Surface morphology and optical properties of the samples have been analyzed using scanning electron microscopy and optical absorption analysis techniques respectively. The bonding characteristics on the surface before and after amino acid deposition have been studied using fourier transform infrared spectroscopy. Photoluminescence spectroscopy was employed to determine the enhancement in wavelength shift of the etched porous silicon.*

Keywords: Porous silicon, L-leucine, DL-iso-leucine, DL-nor-leucine

1. INTRODUCTION

Porous silicon (PS) is a kind of sponge structure with interconnected hydrogen covered silicon columns and pores. It is a material having a direct band gap with better light emitting efficiency in the visible region. For the past few years, there is considerable technological interest concentrated on porous silicon due to its extremely large surface to volume ratio and its association with fast oxidation rate [1, 2]. A number of investigations have been carried out to study the effect of enhanced electro and photoluminescence properties which leads to widespread applications in optoelectronics such as light emitting diodes, gas sensors, photodiodes and solar cells [3]. The surface properties of PS depend upon its electrical and optical properties [4]. Surface area of PS has high surface reactivity which enables the immobilization of many kind of analytes. Reactive SiH_x species present in PS have been removed by the process of thermal oxidation and altered the surface layer into SiO_x species. The above mentioned process ensures the stabilization of PS and give better surface passivation of analytes [5,6]. Recently, PS attracted many researchers for the applications of bio sensors, because of its optoelectronic properties with biocompatibility [7-9].

PS is being used for detection of glucose, DNA, bacteria, viruses, proteins in addition with many more biomedical treatments and diagnostics [6, 10, 11, 12]. The present investigation deals with immobilization of amino acid into the lattice of PS. Amino acids are biologically important organic compounds, which made from amine ($-NH_2$) and carboxylic acid (-COOH) as functional groups, along with a side-chain specific to each amino acid. Key elements of amino acid are carbon, hydrogen, oxygen and nitrogen, though

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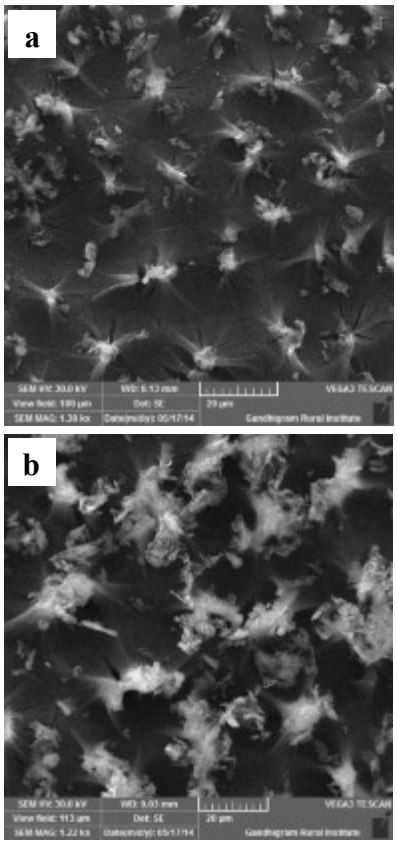

Figure 1. a. SEM image of as prepared porous silicon (PS), b. SEM image of oxidized porous silicon (OPS)

other elements are found in the side-chains of certain amino acids. Surface modification and chemical functionalization of PS are analyzed using Scanning electron microscopy and fourier transform infrared and photoluminescence spectroscopic techniques, respectively. The effect of amino acid immobilization on morphological and optical properties are discussed.

2. EXPERIMENTAL

The PS samples were prepared by electrochemical anodization of boron doped p-type silicon wafers with (100) orientation having resistivity value in the range between 0.5 and 3.0 ohm-cm, thickness value of 150 ± 1 µm and diameter of 250 ± 0.5 mm. The process of anodization was carried out in a composite consisting of Hydrogen Fluoride and Ethanol in the volume ratio 1:2 with current density of 100 mA/cm^2 at a time period of 30 minutes. The current density was kept constant at 100 mA/cm^2 with the help of dc power supply during the process of anodization. Prior to etching, the samples were placed in the etching solution for 1 minute to remove the native oxide layer. The counter electrode was a platinum electrode positioned at a distance around 1.5 cm from Si wafer. The process of etching was carried out at room temperature only. The PS samples were thermally oxidized (Physical adsorption) by heat treatment at 400°C for 2 hours in a muffle furnace and it was allowed to cool at room temperature.

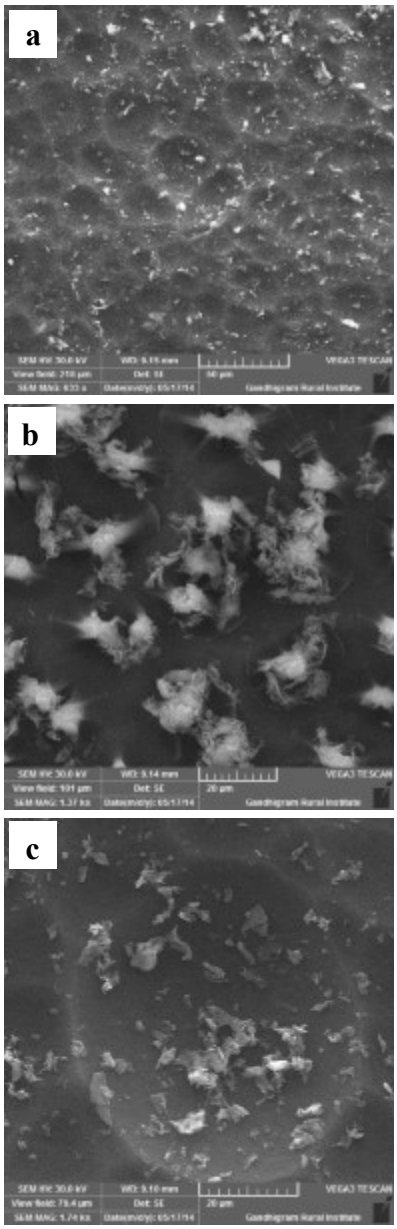

Figure 2. a. SEM image of L-Leucine (LOPS) treated OPS, b. SEM image of DL-ISO Leucine (ISOPS) treated OPS, c. SEM image of NOR Leucine (NOROPS) treated OPS.

It was designated as an Oxidized Porous Silicon (OPS). Amino acid solution (Leucine, Iso-Leucine, and Nor-Leucine) was prepared using water individually with concentration of 0.05 gm per 10 ml**.** The solution was mixed well for two minutes to ensure uniform mixing of amino acid in water. Further, etched PS samples were dipped into individual amino acid solution for time duration of 20 minutes. Thereafter, they were then dried and kept in an air tight container for analysis. Surface morphology, roughness of interface OPS and OPS which must be treated with amino acid was analysed using Scanning Electron Microscope (Philips Model 30XL). Photoluminescence spectroscopic analysis was carried out

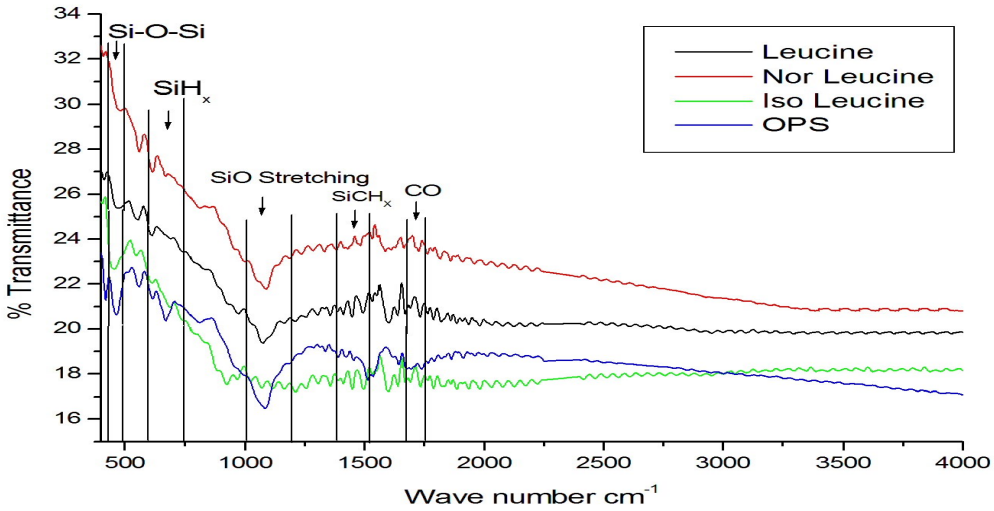

Figure 3. FTIR spectra of OPS and amino acid treated PS

using (LS-50B Perkin Elmer) spectrophotometer with an angle of incidence of 45° using xenon lamp as excitation source. Fourier transform infrared spectroscopic analysis was carried out using (Shimadzu IR Affinity-1) Fourier Transform Infrared spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Surface Morphology

Surface morphology of prepared samples have been analyzed using a scanning electron microscope. Figures 1a and 1b show the SEM image of PS and OPS samples. It is observed that there is uniform distribution of wide pores covering all over the surface. The sizes of the pores were found to be in the range between 10 and 20 µm with porosity greater than 80 %. As a result, overlapping of pores and standing Si columns are formed which must be indicative of a quantum wire structure (Figure 1a). It is found that the pores as well as Si columns are surrounded by an oxide layer which is indicated in Figure 1b. The sizes of the pores are found to be in the range between 10 and 15 µm with porosity greater than 75 % (Figure 1b). The walls of thermally oxidized porous silicon is found to increase when comparing PS with OPS. This may be due to the occurrence of surface modification by the process of thermal oxidation.

SEM image of Leucine, Iso Leucine, and Nor Leucine treated OPS are shown in Figures 2 a-c. It is observed that after immobilization, there are some changes observed on the surface of OPS. The amino acid is spread into the pore region of OPS and the walls of the pore became thick and spread into the pore region which is evident from the SEM images. The above mentioned characteristics for the pore walls indicated that new or modified surface layer developed in amino acid treated OPS samples. Thick and diffused pore walls can be taken as evidence which was indicated by the surface modification of layers leading to produce amorphous structure. Similar results of immobilization of urease on porous silicon matrix has been reported by Prajaka S.Chaudhari et al [2]. Lawrence has reported the surface modified layer on OPS by incorporation of chicken blood plasma and serum as a protein source into thermally oxidized PS layers [6].

3.2. FTIR analysis

The modes of vibrations present in the prepared samples has been analyzed using Fourier Transform Infrared spectroscopy. Figure 3 shows the FTIR spectra recorded for OPS surface before and after immobilization of amino acid. The observation of peaks at 1083 cm^{-1}, 810 cm^{-1}, 464 cm^{-1} and 671, 615 cm^{-1} correspond to SiO stretching, bending modes, Si-O-Si rocking bond, SiH bending modes, respectively. The appearance of SiH bonds in OPS samples indicated incomplete oxidation of PS surface after the process of thermal oxidation. In the case of Leucine treated OPS the appearance of peak at 1074 cm^{-1} depicted reduction in strong SiO bond. The appearance of peaks at 813, 468 cm^{-1} may correspond to SiO bond and formation of Si-O-Si bond, respectively. Almost complete reduction of SiH wagging bond at 671 cm^{-1} and reduction of SiH bond at 615 cm^{-1} are also observed. In addition to that the observation of new strong CH_x, CO bonds at 1463, 1720 cm^{-1} are observed indicating the formation of newly modified carbon layer all over the PS surface by replacing most of the oxide and hydride bonds in the layer.

Similarly appearance of peaks at 1463, 1720 cm^{-1} correspond to the formation of CH_x,CO bonds in the Isoleucine treated modified surface. The appearance of peak at 1074 cm^{-1} indicated the reduced weak SiO bond after the process of immobilization. In Nor leucine treated OPS weak CH_x and CO bonds are observed at 1483 and 1724 cm^{-1} respectively. Also, moderate SiO oxide, Si-O-Si and SiH bonds are also observed in Nor Leucine treated OPS. There is formation of new carbon layer over OPS samples observed for Iso-Nor-Leucine treated OPS. The newly formed carbon layer is not as strong as in Leucine treated OPS. The presence of moderate oxide bonds have reduced the dangling bonds which are tied up with the surface. As a result, reduced intensity was observed in PL spectra for Iso – Nor - Leucine OPS samples. Benyahia [13] has also observed the CH_x bond when porous silicon surface was modified into hydrocarbon layer [13].

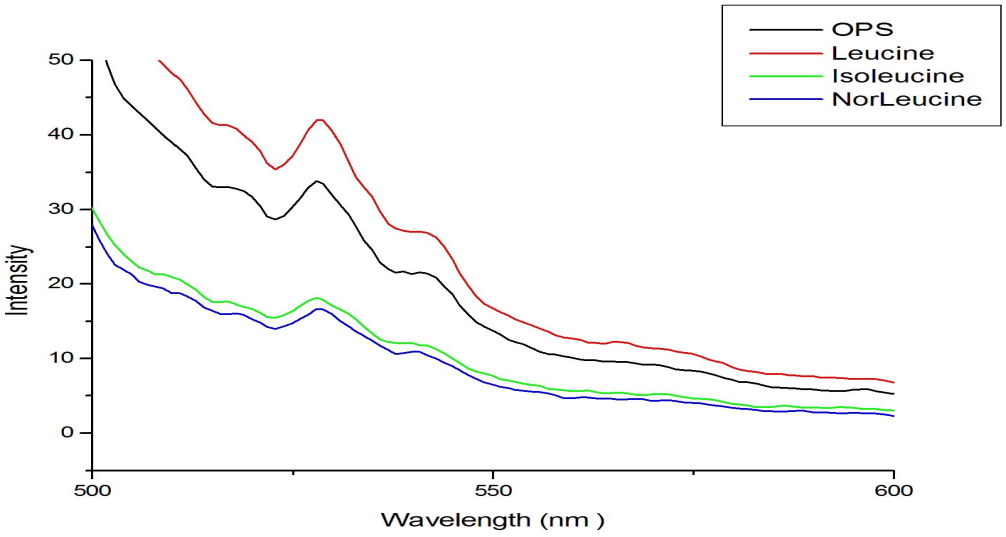

Figure 4. PL spectrum for OPS and amino acid treated OPS

3.3. Photoluminescence analysis

Photoluminescence spectroscopic analysis has been carried out with the help of photoluminescence spectra obtained using a photoluminescence spectrophotometer. Figure 4 shows the photoluminescence spectra of oxidized and amino acid treated OPS samples. The peak with maximum intensity is observed at 526 nm. There is no change in peak position is observed for both OPS and amino acid treated OPS samples. The enhancement in peak intensity is observed in case of leucine immobilized OPS than OPS. The observation of efficient visible photoluminescence in case of leucine immobilized OPS due to_quantum confinement effect and surface states at room temperature. The dangling bonds tied up with SiH bonds covered the internal surface of the sample. The OPS internal surface has been covered mostly internal with SiO bonds than SiH bonds which restrict the tie up process on the surface. After the process of amino acid immobilization, there is formation of a carbon layer all over the surface of OPS. The enhancement process in Leucine treated OPS indicated maximum intensity which may be due to reduction of SiO bonds. The origin of PL enhancement may be due to the formation of high carbon content in the porous layer by CH_X asymmetric and quantum confinement effect of CO bonds. This result is consistent with the IR spectra of the samples. On the other hand, reduction in intensity is observed for Iso-Nor leucine treated OPS. After immobilization process of Iso- Nor Leucine, the carbon layer is not able to be formed as strong as in leucine treated OPS. The presence of moderate SiO bonds which restrict the process and reduces the dangling bonds tie up to the surface which results in reduction in PL intensity.

The enhancement of light emitting behaviour of OPS showed that it may be used as amino acid sensor in the future work. Benyahia [13] have also observed and reported the enhanced photoluminescence for modified porous silicon surface using a hydrocarbon layer [13]. Prajkta S Chaudhari [2] has also observed the enhanced photoluminescence while immobilization of urease in porous silicon matrix.

Table 1.

PeakWave number	Attribution
1083 cm^{-1}	SiO stretching
810 cm^{-1}	SiO bending
464 cm^{-1}	Si-o-Si rocking
671 cm^{-1}	SiH
615 cm^{-1}	SiH beding
1463 cm^{-1}	CH_x bonds
1720 cm^{-1}	CO bond

4. CONCLUSIONS

Porous silicon was etched under optimized conditions. Silicon columnar network was stabilized by thermal oxidization process. Oxidized PS was treated with L-DL-ISO-NOR-Leucine acids. The change in surface morphology and chemical composition was analyzed by SEM and FTIR. They have showed changes in pore and bonds at the surface. The PL spectrum revealed the enhanced light emitting capabilities of amino acid treated OPS; this indicated that the OPS can be utilized as an amino acid sensor. It needs further investigation to understand deeply about the OPS for a better sensor.

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