Preparation and Characterization of PSi/Si Electrochemically Formed as Photodetectors

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Abstract
Porous silicon were constructed electrochemically with various formation times (5, 10, 15 and 20) min with current density 20mA/cm² on p-type silicon. The influence of formation time on the structural and morphological properties have been presented by using SEM and optical microscopy. The SEM analysis was showed that the porous silicon layer has a uniform structure and this structure varied with increasing the etching time. The optical microscope was carried out to study the thickness, the pore diameter and etching rate of porous silicon layer, we have found the porous silicon thickness is accretion with excess the formation time and pores diameter increased also. The etching rate was found to increase from 1.25 to 1.53 µm/min. The electrical properties of PSi samples which represented by I-V characterization under dark show that when the etching time increased the current which pass through the layer of porous silicon decreased because of increasing the resistivity of PSi surface. From I-V characteristics PSi layer show a good rectification and high responsivity for visible and near IR region.

Keywords: porous silicon, electrochemical etching, photodetector.

Introduction
Silicon have been considered a core substance for microelectronics on hand but it is not palatially utilize in optoelectronics [1]. The crystalline silicon has very indigent luminescence in the region of near infrared of electromagnetic wave [2], due to of its indirect band gap transition the light emitting from silicon material is impractical [3] and have impoverished efficiency for radiative recombination [4]. As a consequence to this, light emitting diodes have been compounded from another semiconductor like GaAs. Latterly, the light could be emission from nanostructured materials and organic compounds [2]. The concept of nano voids like structure could be also make changes in characteristics of bulk material, pitched people to acquaints the property of porous silicon [5]. Porous silicon (PSi) is a materias extensively utilized in applications in different fields [6] which has been tractate great interesting owing to their photoluminescence in the visible band at room temperature [7]. The luminescence is already resulted from quantum confinement for porous silicon in small size crystallites [8]. Porous silicon PSi consists of meshwork in nanoscal sized silicon voids and wires which has been fabricated from etching the crystalline silicon electrochemically in hydrofluoric acid with fixed conditions of anodization such as current density, Si orientation, etching time and HF concentration [9]. Porous silicon is varied from nanostructured silicon which have the efforts to compiles the silicon qualitative advantages such as opulence and ability with an easy and climbable fabrication method [10]. Porous silicon structures have a wellar mechanical starkness, chemical retention and conformance with silicon cannulation hence has a spacious scope of potential employments like waveguides [11], biological testing equipment [12], chemical sensors [13], photo electronic solar batteries [14] and fuel cells [15]. In accordingly for proves the chemical and physical properties of anodized porous silicon, several techniques have been developed among them rapid thermal oxidation [16], photo electrochemical etching [17], photochemical grown [18], stain etching [19] and electrochemical etching [11]. In our research, we have been studied the attributes of PSi samples prepared by electrochemical etching ECE such as morphological properties by using scanning electron microscope SEM, the structural properties like porosity and thickness have been measured by using the
optical microscope and electrical properties have been investigated.

Experimental work

The electrochemical etching ECE has been used to prepare porous silicon at room temperature from single side polished p-type (100) silicon wafer (dopant with boron) with (1.5-4) Ω.cm resistivity in an electrolyte etching dissosulbe with (40%) concentration of hydrofluoric acid and ethanol of 99% under 20mA/cm² constant current density. Photo electrochemical etching has been carried out in an electrochemical cell with two electrode configuration silicon as anode and platinum as cathode by a distance 1cm which immersed in HF solution. Before the anodization process the silicon samples rinsed in de-ionized water and hydrofluoric acid for 2 min to remove the oxidation layer from the surface of silicon. The samples have been fabricated in various anodization time (5, 10, 15 and 20) min. The surface morphology carried out by using scanning electron microscopy SEM (TEScan – Vega II SBH). The thickness of PSi layer investigated by optical microscope (Olympic) with different magnifications and these lead to calculate the etching rate according to relation [20]:

\[
\text{Etching rate} = \frac{\text{PSi Thickness}}{\text{etching time}}
\]

The porosity of samples were estimated by using the equation [21]:

\[
P(\%) = \left( \frac{m_1 - m_2}{m_1 - m_3} \right) \times 100
\]

Where \((m_1)\) the weight of samples before anodization, \((m_2)\) the weight of samples after anodization and \((m_3)\) the weight of samples after dissolution porous silicon in NaOH solution.

For current – voltage measurements under dark and illumination a 25 volts (Farnell power supply) were used and its acheived by a lamp of Halogen120w with a variac and titration with AM illuminator faculty density by Si power meter the voltages were varied from (0 to 5) volt. Spectral responsivites of porous silicon layers were measured by using a monochro meter in the rang (100-800)nm.

Results and Discussion

1. Morphological properties:-

The morphology of samples prepared with anodization methods for different etching times of 5, 10, 15 and 20 min illustrated by SEM images as in figure (1,2,3,4 a). These figures show that porous silicon are irregular and randomly distributed on the surface of crystalline Si. Pedposts and emptiness overhead the roof can be observed and the formed layer of porous silicon visualize the pyramid and surface coarseness as a surface with hillocks. The surface plot by image J program for porous structure illustrates in figure (1,2,3,4b) which shows the cloistered Si shafts with trenchant paries could be seen which proves the acceptability influence of attainability the quantum confinement. For irradiation time of 5 and 10 minutes, a structure of regular pore-like is observed. Thus, on increasing the irradiation time gradually to 15 minutes, a larger number of randomly distributed appear on the surface. On increasing the irradiation time to 20 minutes, high density of pores were seen though the thickness of porous layer was smaller because of the excessive etching of porous layer. When the irradiation time is increased, electrons confined within the thin walls increase, which leads to further etching resulting in an increase in the number of pores with widening of the area of pores which make in reduction in the thikness of layer also walls width that detaches between pores. When the formation time rise a fraction of pores accumulation to enlargementofstructures. In few irradiation time the bigness width of pores may be owing to the count of holes on the silicon electrode surface increase with formation time which evidences to preferred degeneration of pores, and the reducing in the width of walls that separate pores due to are an enlargement of each pore. When formation time became high, arandomly directed and highly pores meshwork interconnected and highly branched were accroach, agreement with litteratures [3,6].
Fig. (1): Porous silicon morphology electrochemically formed with 5 min  
a) SEM image,  b) AFM surface plot.

Fig. (2): Morphology of PSi prepared by electrochemical technique with 10 min  
a) SEM image,  b) AFM surface plot.

Fig. (3): Porous silicon morphology electrochemically prepared with 15 min  
a) SEM image,  b) AFM surface plot.
2. Structural properties:

The main structural parameters of the porous silicon are the size distribution, porosity and porous thickness. The pore distribution analysis reveals that low anodization times produce pores of smaller diameters compared with those which compounded by high anodization time as seen in Fig.(5). The influence of the formation time on etching rate and porous silicon layer thickness were cleared in Fig.(6a and b) respectively. A linear increase in the thickness enhancement from 6.27 to 30.60μm with an increasing etching time can be observed. This lead to increasing in the etching rate which depend on the porous layer thickness and these suggests that etching times led to increasing in pore growth and the underlying reason was thought to be attacking directly of F– ions on Si atoms. However, when the formation time increased, another process of decay, i.e., chemical dissolution began to prevalent. These methods were common at the wall of pores and suppressed the in traction at the pore tip. Consequently, inter-pore distance becomes narrower with an increasing formation time. The surface porosity of PSi layer expantion with formation time which illustrated in Fig.(6c). It is approbate that the porosity variation with layer thickness were owing to the chemical dissolution of poroussilicon material through etching process. Through the reaction of the electrochemical process, and as a function of the formation time, the influence of chemical dissolution were to increase the pores diameter also the average of porosity these results in good agreements with M. Das &I. Mousa [5,11].
Fig. (5): The size distribution of porous silicon prepared by anodization process with time of
a) 5 min  b) 10 min  c) 15 min  d) 20 min.

Fig. (6): The structural measurements of porous silicon compounded by photo electrochemical
techniques as (a) Thickness  (b) Etching rate  (c) Porosity.
3. Electrical properties

A- I-V characteristics:

Fig. (7) show the (I-V) characteristics for porous silicon layer in reverse and forward at forward base in dark at various etching times. The results were very significant for qualify an apparatus satisfaction and whole apparatus parameters relying upon it. In reverse bias, these evident that the curve illustrate two categories: at first one the at low bias the pairs of electron – hole generate when the reverse current is fairly overlay generate where the with the applied voltage. At the second, we could recognize the reverse bias increased essentially. For these cases, through the junction the current coming from dispersion of minority carriers. From the completed result it is prominently that the current generative by time of 20 minutes development of porous silicon layer is not as much as that created from the 5 minutes which is related to a great number of junction resistant which reduce of the current. The enhancement of the junction structures leads to improvement of the reverse current, that owing to lessen the quantity of pairs at the junction interfaces. The potential barrier high reduce because of the forward voltage, in the forward bias. Consequently, majority carriers are competent to pass the potential barrier much simpler than at zero bias. Additionally, the current drift has been smaller than the current diffused. Two regions could be professed, the first idealizes current of recombination, originates the first currents when the generated carrier concentrations is bigger than the concentration of the intrinsic carrier (ni), i.e. (n*p>ni^2). For the second category at high voltage the diffusion layer instantiates that depends on stuffed resistance. From the coordinating between the results acquired for various formation times set it up, is recognizes the estimations of the current values enhancement present because of deficit in the resistivity of porous silicon results in an expansion in the concentration of electrons this causes a deficiency in the concentration of holes [22].

![Fig. (7): The I-V characteristics (forwred and reverse) in dark of PSi/Si.](image)

The (I-V) characteristics for PSi/Si heterojunction in the illumination which prepaed for different etching times could be illustrated in Fig. (8), we could clear the photoelectric behavior of devices under dark and illumination. For p-type silicon, light induced the generation of electron – hole at the depletion layer which refer to the influence of photoelectric and the arranged photons will take an interest to pairs of electron – hole that occurs in the depletion layer under extrinsic reverse bias. In the depletion region each electron – hole will separate from the others because of he internal electric field and when an external bias have been applied this bias becomes larger. When the intensity of incident light increase an increasing in the photocurrent could be recognized, when the intensity becomes large which owing to the numbers of incident photons were large and there are a great amount of isolate dpairs of electron-hole. The behavior of current versus the reverse bias voltage applied with various illumination powers might be shown in these
figures, the depletion region extended when the detector operates under an external revers bias also this causes with transmited great number of photons about the porous silicon layer and the absorption be in the depletion layer, photocurrent generation would make a federate for the pairs of electron–hole. A great number of pairs electron–hole creates when increasing the power density incident and these lead to increase in the photocurrent of porous silicon. The formation of porous silicon layer could be cause in depende of current-voltage properties on the formation time, that when the etching time increased led to an increasing the diameter of pores in the structure of porous silicon, so it is lead to rise the porous silicon resistivity because of trapping the carrier at walls of the pore. Also the thickness of porous silicon layer have been increased when the formation time increasing from 5 to 20 minutes which conduce to increase the porous silicon layer resistivity, so the current of the forward biases reduced when the etching time increased anodization time reduces, because of the mobility of the porous silicon layer is reduced [23].

![Fig.(8): Photocurrent versus of applied reverse voltage for PSi/Si formed at various etching time, (a 5 min, (b 10 min, (c 15 min and (d 20 min.](image)

**B- Responsivity:-**

The responsivity spectral idealize the relation between the incident power and the generated current output that is very significant due to the detector suitable range specifies. The responsivity as a versus of the wavelength for porous silicon devices which formed at various etching time shown in Fig.(9). For all devices, the curve illustrates two different regions, the first category in the short wavelength denotes that the spectral of responsivity has a great increase. Where this increasing are related to absorption coefficient were high, these guides to a recombination process were fast and low value for the depth of absorption in comparative with another category in the material where this is denominated as carrier concentration.
probability, which becomes high from region of surface with the departure. When the process surface recombination be large leads to increase the responsivity in this region supervened by decreasing in responsivity value [24]. For second category from 750-850 nm, we could observe the value of the responsivity dependent wavelength were high at the active region of deplation layer these wavelength were absorbed at the and in minority carriers the length of diffusion are equal to a long distance. In this region, the internal electric field causes with motion of electron-hole generated addition to negligible the process of recombination at that region. The maximum spectral of responsivity shown at 350±50 nm in spite of reality for this region is distance from the cutoff wavelength. Because the porous silicon semiconductor has a wide and direct band gap which made it collect the photons of high energy. If the porous silicon only absorbs in UV and therefore act as a window for sun light the barrier isolated at the interface and should therefore reduce surface recombination and result in larger short-circuit photo current. For clear this impact, because of the quantum confinement effect the band gap of porous silicon increase, when the porosity of porous silicon increased lead to decreases of the structure of porous silicon nanoscale. The photosensitivity were shifted toward the shorter wavelengths could be observed which inan agreement with the presumption quantum size effects causes the emission. The value of photosensitivity decreased away at longer wavelengths (600-900 nm) from the top of photosensitivity could be seen, which ascribe to the photon energy incident were not be enough to generate pairs of electron-hole [25].

Conclusion
We have been formed and characterized the layer of porous silicon to study its morphological, structural and electrical characteristics. Influence of formation time on the structural and morphological properties have been investigated by using SEM and optical microscopy. SEM show that porous silicon layer has a uniform structure and this structure varied with increasing the etching time. The optical microscope were carried out to study the thickness, pore diameter and etching rate of porous silicon layer we have found the porous silicon thickness increases from 6.27 to 30.60 µm with increasing the etching time and the pores diameter increased also. The etching rate were found to be increase from 1.25 to 1.53 µm/min also the porosity of porous layer. The electrical properties of PSi samples which represented by I-V characterization under dark show that when the etching time increased the current which pass through the layer of porous silicon decreased because of increasing the resistivity of PSi surface. From I-V characteristics PSi layer show a good rectification, with high spectral responsivity of 0.27A/W.
References


الخلاصة

السيلكون المسامي تم تحضيره بالطريقة الكهروكيميائية وبأيام تحضير (5 و 10 و 15 و 20) دقيقة ويكافئة تيار 20 ملي أمبير/سم² على السيليكون نوع P. تأثير زمن التشبع على الخصائص التركيبية والطبوغرافية درست باستخدام المجهر الإلكتروني الماسح والمجهر الضوئي. أظهرت نتائج المجهر الإلكتروني الماسح أن السيليكون المسامي الناتج ذو شكل منتظم وطبيعة الشكل تتغير بتغير زمن التشبع. المجهر الضوئي تم استخدامه لدراسة سك السطح، قطر المسام بالإضافة إلى معدل التاكل في طبقة السيليكون وجدنا أن سمك السيليكون المسامي يزداد بزيادة زمن التشبع بالإضافة إلى قطر المسام يزداد كذلك بزيادة زمن التشبع. معدل التاكل وجد أنه يزداد من 0.05 إلى 0.51 مايكرون/ثانية. الخصائص الكهربائية لعينات السيليكون المسامي تمثلت بخصائص تيار - جهد تحت الظلام بينت أن عند زيادة زمن التشبع يقل التيار المار خلال طبقة السيليكون المسامي بسبب زيادة مقاومة سطح السيليكون المسامي. من خصائص تيار - جهد سطح السيليكون المسامي تبين أنه يظهر تجاعيد جيد واستجابة عالية عند المنطقة المرئية وتحت الحمراء القريبة.