Republic of Iraq
Ministry of higher education
and scientific research
University of Kerbala
College of education for pure sciences
Chemistry department

Study the Properties of Porous Silicon for P- type and N-type Bulk Silicon

A thesis

Submitted to the college of Education for Pure Sciences-University of Kerbala it is part of the requirements for obtaining a master's degree in chemistry.

By

Noor Mohammed Kadum

(B.Sc.2015)

Supervisor

Prof. Dr.Hamida Idan Salman
Assist Prof .Dr.Ahmed.K.Al-Kadumi

1442 A.H 2021 A.D

بسم الله الرحمن الرحيم

يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ

صدق الله العلي العظيم

(سورة المجادلة /الآية11)

Supervisor's Certificate

I certify that this thesis entitled titled "Study the Properties of Porous Silicon for P-type and N-type Bulk Silicon" was prepared by (Noor Mohammed Kadum) under my supervision at the College of Education fore pure sciences of the University of Karbala in a partial fulfillment of the requirements for the degree of master in chemistry .

Signature:

Prof. Dr. Hamida Idan Salman

Date:

Signature:

Asst. Prof. Dr.Ahmed .K. AL-kadumi

Date:

In view of the available recommendations, I forward this thesis for debate by the examining committee.

Signature:

Name:**Dr. Sajid Hassan Guzar**

Sci. Title: Assistant Professor

Date:

Head of Chemistry Department

Amendment Report

This is the to certify that the thesis entitled (Study the Properties of Porous Silicon for P-type and N-type Bulk Silicon) and corrected the grammatical mistakes I found .the thesis is ,therefore ,qualified for debate .

Signature:

Name: **Dhiya.K.Nile**

Sci. title: Instructor

Address: University of Kerbala

Date:

Committee Certificate

We certify that we have read this thesis entitled "Study the Properties of Porous Silicon for P-type and N-type Bulk Silicon" and, as an examining committee, examined the student (Noor Mohammed Kadum) in its content and that in our opinion; it is adequate with standing as a thesis for the degree of Master in chemistry.

<u>Chairman</u>

Signature:

Name:Dr. Saad Aziz Hassan

Sci.Title: Professor

Adress: University of Kufa

Date:

<u>Member</u>

Signature:

Name: Dr. Ayad .F.Alkaim

Title: Professor

Address: University of Babylon

Date:

<u>Member</u>

Signature:

Name: Dr.Rajaa .K. Mohammad

Title: Assistant. Professor

Address: University of kerbala

Date:

<u>Supervisor &Member</u>

Signature:

Name: Dr. Hamida Idan Salman

Title: Professor

Address: University of kerbala

Date:

<u>supervisor &member</u>

signature:

Name: Dr.Ahmed .K.AL-kadumi

Title: Assistant .Professor

Address: University of kerbala

Date:

Approved by the Collage of Education for pure Sciences, University of Karbala .

Signature:

Name:Prof .Dr.Hamida Idan Salman

Date:

Acknowledgment

Praise be to Allah, the best grader, who is alone with powerlessness and will. I thank him and thank him in recognition of the grace that he opened to me from the vast and generous virtues of which countless servants like me, and prayers and peace be up on the most honor able being Muhammad (may Allah prayers be upon him and upon his pure household).

Iam also honored to thank my dear supervisor (Prof.Dr. Hamida idan salman) for her support and for me throughout the completion of this work. we ask Allah for her health and wellness and for us to remain a lamp for science and knowledge .

Iam also honored to extend my sincere thanks and gratitude to my supervisor (Dr. Ahmed Kherallah Al-kadumi), I had a father before he was honorable in his and support for me in every possible way, his positive attitudes that do not promise, and the distinguished and continuous efforts he showed to accomplish this work. We ask that Allah give him double what he wishes

I cannot forget the credit and thanks to my family for their support to me, especially (my dear mother), which has the great merit of my access to this achievement.

I also extend my sincere thanks and gratitude to the dean of my college and the presidency of the chemistry department for the help they have shown me. We ask Allah to grant them continued success and continuous giving.

Finally, I extend my thanks and gratitude to everyone who called for good and facilitation for me to complete this work .I ask Allah to you as much as you have called.

NOOR…

Dedication

-To whom he mentioned is contentment and success (Allah Almighty). And to those who are not disappointed by the hope who supported me in every adversity and gave me their strength and patience and chose the right path for me (the pure imams).

-To the one who gave me life and gave me life to the one who raised me in the faith and love of the most merciful to those who stood beside me until I advanced to success to the one who loved her in my heart until death (my dear mother).

In addition, to the one who was proud of his martyrdom and carried his name to those whom I have missed all my live and my eyes have never seen (my dear father). And to all the martyrs of the formers regime who were martyred unjustly and treacherously, and were deprived of seeing their children in defense of their wounded Iraq.

NOOR…

Abstract

-The thesis includes the preparation of nano porous silicon by the photo electro chemical etching scraping process, using alight with luminous power of (100W) for N-type and electro chemical etching for P- type in the same method of preparation for both types and with the resistivity (R=1-10 Ω.cm) by using different concentrations of hydrofluoric acid/Ethanol at a ratio (39-43%) and ethanol (99%) the operation was carried out with a skimming time of (10 min) and a voltage of (10 volts) .

-Porous silicon has been theoretical studied by means of preparation, physical and chemical properties and applications of porous silicon have been studied .

- We also compared the two kinds by examining the shape and compositional features of porous silicon layers using X-ray diffraction XRD, scanning electron microscope SEM, and gravimetric technique. The X-ray diffraction findings revealed that the difference between the two kinds is minor owing to differences in acid interaction .Either the homogenous is in the medium shape due to their effect with porous silicon. As for the scanning electron microscope images, they showed different shapes. If these shapes change with the change of concentrations, it has been found that the width of the pores and the thickness of the porous silicon layer increases as the acid concentration decreases.

- As for the porosity values of the porous silicon layers measured using the gravimetric method for both types, it was found that the porosity changes due to the strength of the reaction concentration, If it increases as the acid concentration decreases due to the occurrence of more polishing, which leads to an increase in density due to the large amount of voids in the porous silicon layer and decreases with increasing the concentration .A weak porous silicon layer is produced which results in a small amount of voids .

-Also, the optical and electrical properties of both types have been studied .it has been found that both are affected by the thickness of the layer due to their mathematical connection; as the thickness of the layer increases, the relative permittivity and refractive index decrease and vice versa. As for the electrical capacitance, it is affected by the porosity, thickness of the layer, it increases as the porosity layer is smaller, due to the presence of air and the layer thickness is large because there are a lot of ions and charges.

Finally, the applications of porous silicon were study since we saw a rise in the voltage of the solar cell after adding a sample of porous silicon to it, and the findings and measurements we acquired proved its efficiency and capacity to amplify the voltage generated by the solar cell. This gives an outcome meaning that it is possible to improve that solar cell by using a nanostructured layer of silicon and using it as a diode in the solar cell.

Table of content

List of Symbols & Abbreviations

Symbol & Abbreviation	Meaning	Unit
d	Layer thickness of Porous silicon	Cm
Eg	Energy gap of silicon wafer	eV
Cpsi	Capacitance of PSi layer	Farad
K	Boltzmann's constant	J\K
Hv	Photon energy	eV
m_1	Weight of silicon sample before etching process	g
m_2	Weight of silicon sample after etching rate	g

m_3	Weight of silicon sample after removing porous silicon layer	g
A	The area of the freckled surface	Cm^2
T	Etching time	Minute
V	Etching rate	Cm/min
ε_{pore}	Relative Permittivity of air	-
ε_{si}	Relative Permittivity of silicon	-
ε_0	Relative Permittivity of free space	F/cm
ε_{psi}	Relative Permittivity of porous silicon	-
n_{psi}	Refractive index	-
P	Porosity of Porous silicon layer	%
ρ	Silicon density	g/cm^3
J	Current density	mA/cm^2

ʎ	Wave length	Nm
r	Resistivity	Ω.cm
PEC	Photo electro chemical	-
EC	Electro chemical	-
HF	Hydrofluoric acid	-
c-si	Crystalline silicon	-
PSi	Porous silicon	-
PL	Photoluminescence	-
FTIR	Fourier transform infrared spectroscopy	-
EHT	Event Horizon Telescope	Kv
LED	Light emitting diode	-

SEM	Scanning electron microscopy	-
HRSEM	High resolution scanning electron microscopy	-
HRTSEM	High- resolution transmission electron microscopy	-
SPF	Surface porous film	-
XRD	X-ray diffraction	-

Chapter One

Literature Review

1-1 Introduction

The nano is the discovery of new materials processes and phenomena at the nano scale as will be wide in researchers at last century experimental and theoretical techniques for research provides new opportunities for developing in novative nano scale systems and materials with nano structures. Many unique application and materials are expect from nano scale system.

It is expected that this field will open a new branch in science of technology [1].

The nano structures science and technology are large and interdisciplinary area of research’s and development that have grown significantly worldwide in the past year [2].

It has the potential to revolutionize the ways in which materials and products are created and the range and nature of jobs accessible. It already had a major commercial impact that will be confirmed in the future [3].

Silicon is at heart of microelectronics revolution. Its dominance over other semiconductors is intimately tied to its superior characteristics and processing properties and to the tremendous base of technology that has developed around it. Other semiconductors are not likely to displace Si as the material of choice in electronic applications. Si, however, is an extremely inefficient light emitter and for this reason, has not enjoyed the same level of dominance in optical applications [4, 5].

Vincent. From experimental tests, that porous silicon (PSi) can be produce from [PEC] etching process. It is ability to form junctions that using in electronics tests in simpler ways compared with the relatively advanced techniques required solid state processing [6].

Silicon is widely used in today's semiconductor field because of its low price and high process compatibility. However, the application of silicon in the infrared is limited by its higher reflectance and its wide band gap. The emergence of porous silicon has effectively improved these limitations. Porous silicon has a sponge-like structure capable of reducing the reflectance [7]. And exhibits the characteristics of a direct band gap semiconductor .Therefore, It has been widely used in solar cells, photo detectors, and other wide-spectrum applications using visible to infrared light [8].

Porous silicon is mixture between silicon and inserts of nano-porous holes which make micro structure and provide large surface with volume ratio and in history it was discovered [9].

Porous silicon is quickly becoming an increasingly important and versatile electronic material in today's fabrication technology [10].

The porous silicon consists of a network of sized nano meter silicon region surrounded by void space. In the other hand on of the most popular techniques that is used to produce porous silicon nano structures which is the photo chemical etching process of silicon wafer with hydrofluoric acid [HF][11].

Over the past several years, there has been arising level of research work focusing on improving the efficiency of the light emission from silicon based some materials through various scheme layers to produce artificial structures .

Porous silicon has attracted much attention as a new opto electronic material since the observation of its visible efficiency photoluminescence at room temperature. A lot of one of experimental and theoretical studies have been report so far in order to clarify origin of light emission by (PSi) layers (photoluminescence's). And from that appear some acceptable explanations is the quantum confinement model [12].

Here, electrons are confined in nano meter sized structure where the visible emission originates from electron-hole recombination between discrete energy level inside the quantum wells wires or dots depending on the confinement dimensions[13].

Porous silicon layers are different in properties , there properties depending on the parameters of preparation conditions [14].

Canham in 1990 observed the bright photoluminescence (PL) irradiated from porous silicon material or a new material that became among scientists and technologyists , and has been applied in various fields during the past two decades .From some arrange techniques the porous silicon can be formation. And direct images of the material can be carried out by scanning electron microscopy [15, 16].

In the last years, the nano materials get very important and were give attention from researchers because in addition the small size the responsibility for the many properties (electronic, optical, magnetic, chemical and mechanical) of the nano particles. It makes it suitable for new applications [17].

1-2 Literature Review

Arthur uhlir was working in 1956 on electro chemical (EC) etching of silicon with assisted hydrofluoric acid (HF) solution, this working with intent of polishing to make micro structures in silicon, how over the films are relatively little interest at the time [18].

In the 1970s and 1980s the interest in porous silicon increased because the high surface area of porous silicon was found to be useful as model of the crystalline silicon surface in spectroscopic studies [19, 20].

The first study of the porous silicon in 1991 and 1990 with the study of the electrical properties of (PSi) layer and showed the vapor sensing as direct application of this new material the important structure characteristics of (PSi) layer were investigated by Lehman et al [21].

The photo chemical etching process focused on the studies in 1992, the photoluminescence and electroluminescence characteristics for the silicon nano crystallites layer prepared by laser-induced etching process as follow.

The photo chemical formation of porous silicon in hydrofluoric acid (HF),without external as was firstly reported in 1991 by nouguchi and suemune [22].

Lang, et. al. in 1995 prepared (PSi) from doped foil silicon crystalline (N-type and P-type) with different light assisted conditions (dark, visible, and ultra violet light) [23].

The experimental tests showed that (PSi) can be produced with laser assisted which called laser-induced etching process and make very advantage and dramatic structural in optical properties this shown as D.G Rasheed and its groups in 2001,2005 and 2006 [24].

In 2006, group of scientists studied the porous silicon morphology as a function of condition preparation, that the link let-wean morphology, porosity and surface resistance [25].

In 2008, Izabella studied the porous silicon as application in solar cell that one-dimensional photonic crystal. The results were gradual increase in the spatial period of the structure. Image processing is use to design the porous silicon; the efficiency of almost 14% was reached for those types of reflectors on large area 71cm^2 epitaxial Si solar cell. and give boosting efficiency of 0.6% absolute in comparison with the solar cells containing [26].

In 2009,Nansheng used electrochemical etching to form porous silicon layer which emitter layer of solar cell with very low reflectivity obtained the morphology and reflectivity of (PSi) layer are easily modulated by controlling the electro chemical condition i.e.(the current density and etching time) [27].

Alwan.M.Alwan et al in 2010 reported the morphological properties of porous silicon and oxidized porous silicon prepared by photo electro chemical etching from N-type silicon wafer as a function of experimental parameters [28].

1-3 The Aims of Project

1 -Studying the porous silicon properties which prepared by using photo electro chemical etching and electro chemical etching.

2-Studing the effect of the hydrofluoric acid and ethanol on properties of porous silicon.

3-Study the porosity of porous silicon, layer thickness, relative permittivity, refractive index, and the capacitance.

4- Comparative study between N, P-type for porous silicon.

5- Studying the effect of the porous silicon sample on the solar cell.

Chapter Two

Theoretical Part

2-1 Introduction

This chapter explains the information about silicon crystalline and how the bonds consist of inside it, the quantum confinement model can be shown in this chapter, the preparation of porous silicon from technique; one can study physical and chemical properties of porous silicon, which enter into important applications.

2-2 Silicon Element

Silicon is a nonmetallic carbon-based chemical element (group IV of the periodic table). It is the second most common constituent in the crust, accounting for 27.7% of the earth's crust. Silicon surface has high absorptivity for oxygen and the growth rate of oxide layer [3].

Crystal-clear Silicon is the most common material used in microelectronics, but its use is constrained due to its narrow and indirect band gap of around 0.5 microns (1.12 eV). Single-crystal silicon wafers of high purity are widely affordable and comparatively inexpensive due to their widespread use in microelectronic applications [29].

Since the likelihood of a three-particle reaction is tiny, the photoluminescence lifetime is measure in seconds. Bulk c-Si is a very inefficient light emitting medium under both optical and electrical excitation, as seen in Figure (2-1).

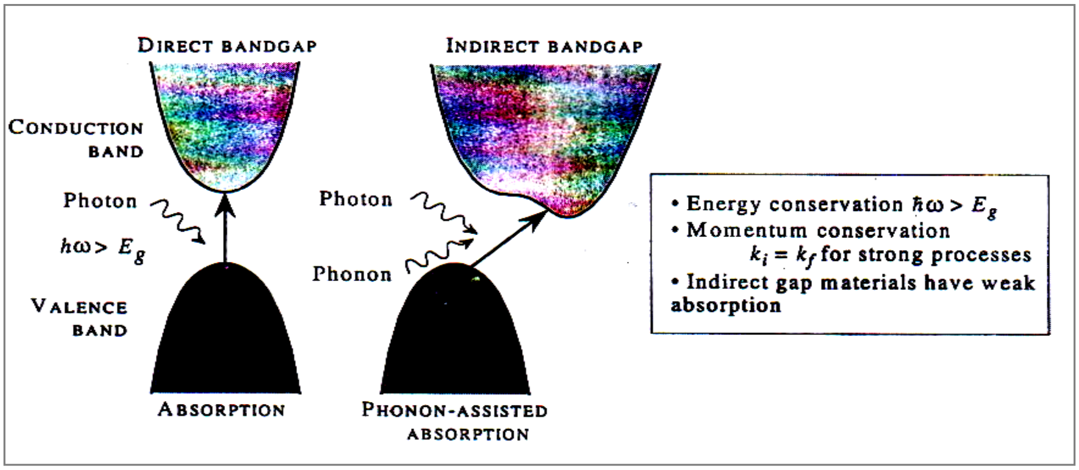
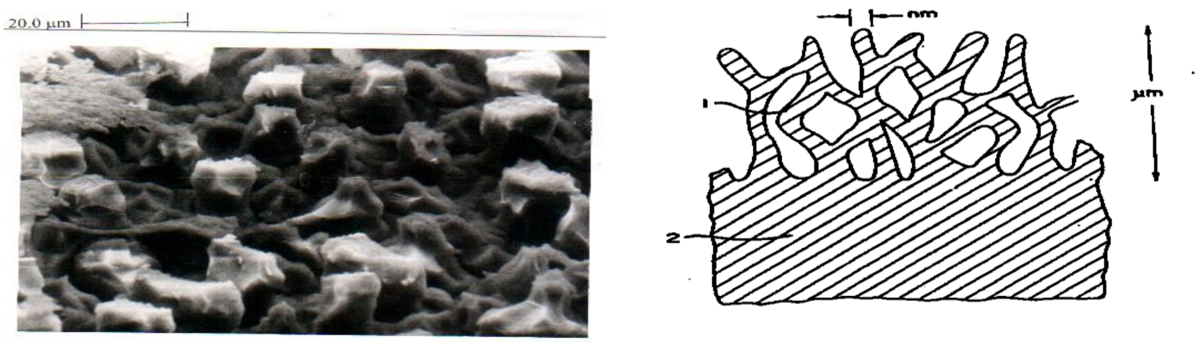


Figure (2-1): Direct and indirect band gap of semiconductors [23].

The bulk of embedded electronic systems are made of crystalline silicon .Bulk silicon, on the other hand, has a very poor luminescence due to its indirect band-gap and electrical composition. As a result, Si has not proven to be a suitable substrate for the production of active optical devices such as light emitting diodes or laser diodes [30].

2-3 Porous Silicon

Porous silicon is a network of pores divided by thin walls that incorporate silicon nano crystalline in the surface morphology. Uhlir, was the first notice porous silicon forming on the surface of crystalline silicon substrates in hydrofluoric acid (HF) under the right anodic bias in 1956 [31]. He looked into silicon electro polishing and discovered that below a certain current density, brownish film forms, which is now known as porous silicon. Turner, further studied porous silicon in depth since it was an annoyance at the time [32]. The etching method transforms bulk crystalline silicon into a sponge structure of entangled and hydrogen-covered silicon columns and pores, as shown schematically in Figure (2-2). The size of the pores and the remaining silicon skeleton is highly dependent on the doping and etching conditions, as well as the lighting conditions during etching.



(a) **(b)**

Figure (2-2) Structure of porous silicon layer (a) SEM image of PSi (b) 1.Schematic of PSi. 2.crystalline bulk silicon [23].

The high surface-to-volume ratio of porous silicon, as well as the related rapid oxidation rate, have piqued the attention of scientists for many years.

2-4 Properties of Porous Silicon

Porous silicon (PSi) layer has unique and dramatic properties, which made this material used in wide range of fields and applications.

2-4-1 The Physical Properties

The shape and diameter of pores, the thickness and relative content of Si, voids, and, in some situations, the relative content of different Si compounds in the formed porous layer are all important factors in determining the physical properties of porous silicon. These parameters are dependent on the preparation conditions, allowing materials with physical properties similar to those of Si and air (or the medium, which fills the pores). Furthermore, when the Si wires' function size is less than a few nanometers, different quantum-size effects arise, making (PSi) much more interesting. (PSi) has been a common material among scientists and technologists due to its durability and tunable properties, and has been used in a variety of fields over the last two decades [33, 34].

2-4-2 The Chemical Properties

X-ray photoelectron spectroscopy and Fourier transform infrared (FTIR) spectroscopy were used to investigate the surface chemical composition of the (PSi) layer. Because of the wide specific field, the (FTIR) signal from (PSi) layer is much stronger and simpler to quantify than that from bulk silicon [35].

Since the pore surface has a high density of hanging silicon bonds with original impurities such as hydrogen and fluorine, which are residuals from the electrolyte, the chemical properties of freshly etched silicon samples are very susceptible to the local ambient, where they vary over time during storage in air [36].

The high specific surface area of (PSi) layer (200 – 600 m^2/cm^3) has been stated to affect chemical properties, which will impact the optical, electrical, and mechanical properties of (PSi) layer, according to Andria [37] .

2-4-3 Structural Properties of PSi

Structural properties of porous silicon (PSi) involves both X-ray diffraction and morphological aspects. The morphological of the measurement of porous silicon layers has specific characteristics such as pore type, shape, and size depending on the preparation conditions [38].

2-4-3-1 X-ray Diffraction

X-ray diffraction (XRD) is a versatile, non-destructive method for determining the existence of various material structures and phases in a sample based on their diffraction activity when irradiated with a known x-ray wavelength .Each different structure of phase can only diffract an incident x-ray at a certain range of angles, which can then be determined. The transparent silicon structure includes nanoscale crystals [39]. This property has a significant impact on each property of the porous silicon substrate, so it has attracted the attention of many researchers. By obtaining x-ray diffraction measurements for porous silicon layers, Hauser et al. have shown that the Si material's structure remains crystalline, but there is a substantial peak broadening[40] which is perceived as a nano crystallite size effect, as seen in figure (2-3).

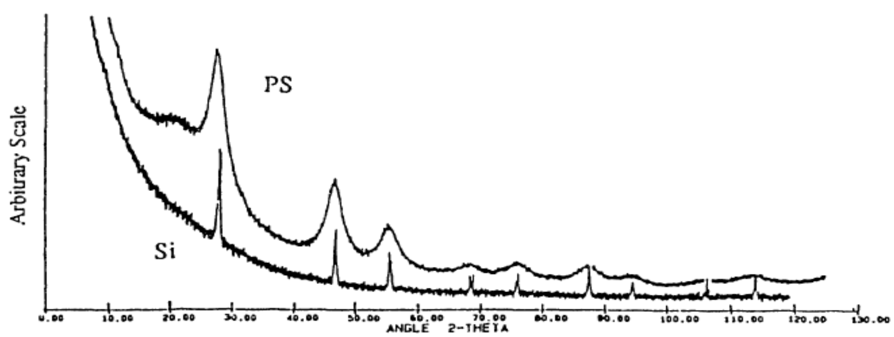


Figure (2- 3) X-ray diffraction of silicon and PSi layer[41].

2-4-3-2 Surface Morphology of PSi

Based on the preparation conditions, the morphology of the porous layer has distinct features such as pore form, shape, and scale.

2-4-3-2-1 Pore Type

As shown in Figure (2-4) , there are many types of pores that can be formed in the porous layer of a silicon wafer (2-4). A pore, in the broadest sense, is an etch pit whose depth exceeds its width, As seen in Figure (2-4, a). Individual pores are usually closed at one end in Figure (2-4, b) and intertwined to a degree as seen in Figure. Most porous Silicon layers are a few m thick and individual pores are generally closed at one end in Figure (2-4, b) (2-4, c). High-resolution transmission electron microscopy (HRTEM) or high-resolution scanning electron microscopy (HRSEM) are the most popular methods for pore analysis. Pores closed at both ends, as shown in Figure (2-4, d), can be realized in porous silicon membranes by capping or thermally-induced reconstruction of the pore network [28] Pores open at both ends, as shown in Figure (2-4, e), can be realized in porous silicon membranes by capping or thermally-induced reconstruction of the pore network. Structures by either extended anodization of wafers [40] , anodization of pre-thinned areas, or the *Turner* 'lift-off ' technique. In the latter case, the current is ramped high enough to go into the electro-polishing mode, which results in, porous over layer detachment from its substrate.

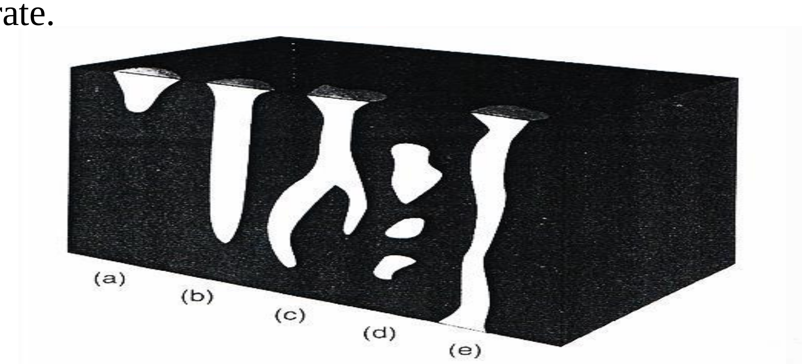


Figure (2-4) Types of pores; (a, b) Blind, Dead end, (c) Interconnected or Branched (d)Totally isolated or Closed and (e) Through pores [40].

2-4-3-2-2 Pore Shape

Figure (2-5) shows schematically the major types of pore shape reported for electrochemically etched silicon. The most common shape by far is that cylindrical pores as shown in Figure (2-5, a) with varying degrees of 'branching' as in Figure (2-5, c) and necking. Early Japanese studies reported an 'ink- bottle' type morphology as illustrated in Figure (2-5, b) where there is a thin surface porous film (SPF) of much smaller pore size than the rest of the layer. This type of morphology is not evident in mesoporous material but can arise in macroporous layers [42]. As clearly shown by the SEM data of *Zhang* [43] What is much more common for mesoporous is likely to be a very gradual decrease in pore size with the depth in the thick layers. This arises via secondary chemical dissolution since the top of the layer is expose to the etchant longer than the bottom of the layer.

Crystallographic effects on pore shape are also well documented, at least for the macrospores and large mesopores [44]. The anodization of (100) oriented wafers can generate pores of square cross-section as in Figure (2-5, d) while (111) oriented wafers can exhibit triangular shaped pores as in Figure (2-5, e).

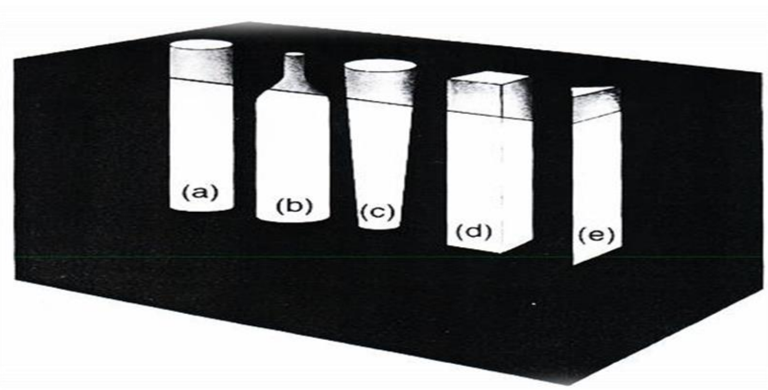


Figure (2-5) Pore shapes (a) cylindrical (b) Ink-bottle (c) Funnel (d) Cuboid or slit and (e) Triangular or Pyramidal [16].

2-4-3-2-3 Pore Size

Pore size defines a lot of the porous silicon's optical and electrical properties. Table (2.1) shows the pore size ranges according to the International Union of Pure and Applied Chemistry (IUPAC) guidelines. The vast majority of electrochemically engraved luminescence silicon analyzed so far is mesoporous due to the quantum confinement effect of porous silicon [45].

Table (2.1) IUPAC classification of pores size [28].

Pore Width (nm)	Type of pore
≤ 2	Micro
2 – 50	Meso
> 50	Macro

2-4-3-2-4 The Porosity

The most critical parameter that characterizes the porous silicon is its porosity. It is known as the percentage of void space inside the porous layer, and it can be easily calculated by measuring the silicon substrate before and after the etching phase (m_1 and m_2), as well as after removing the porous silicon layer with a molar NaOH or KOH solution (m_3) [46]. The following equation calculates percentage porosity [47].

$$P = \frac{m_1 - m_2}{m_1 - m_3} \quad \text{...........} \quad (2.1)$$

Furthermore, the dielectric constant of the porous substrate in (metal/PS/C-Si/metal) systems can be determined by calculating the capacitance of the structure at small reverse. employed this process [48].

2-4-4 Optical Properties

The quantum confinement effects cause a blue change in the optical absorption edges of Nano crystals as compared to bulk silicon.

As seen in Figure (2-6), porous Si has a lower absorption coefficient than bulk Si.

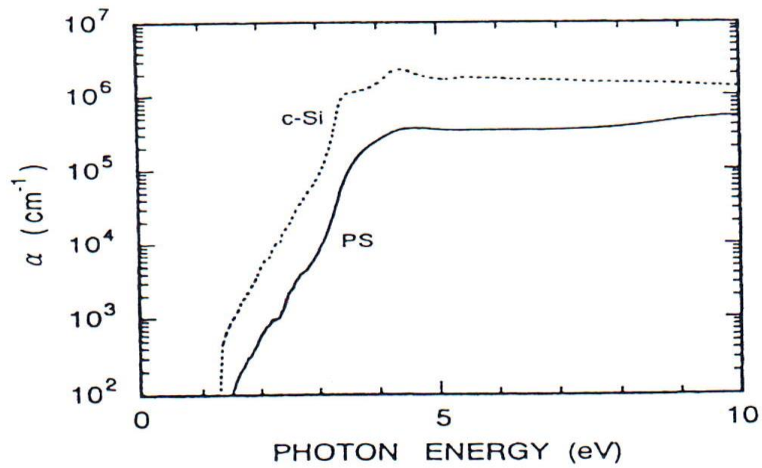


Figure (2-6) Absorption spectra of (PSi) and crystalline silicon [47].

As seen in Figure (2-7) It decreases as porosity increases [49] .The quantum confinement affects the absorption edge of the band-to-band transition, which increases as the confinement energies of electrons and holes rise [50].

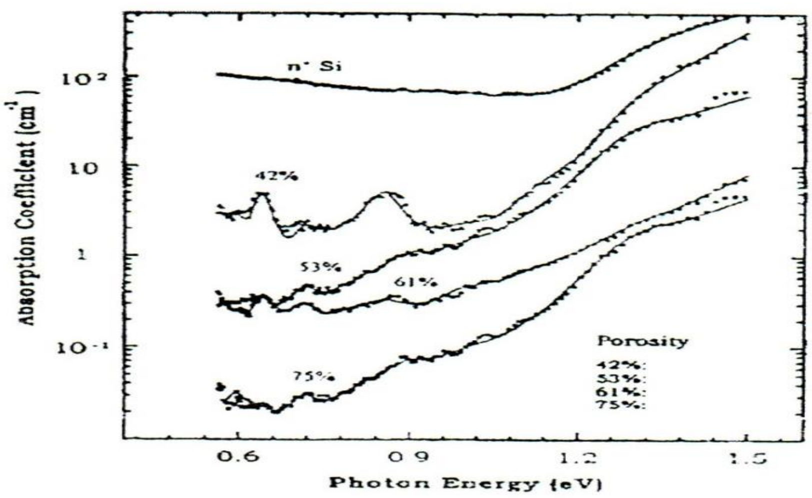


Figure (2-7) Absorption coefficient of porous silicon with different porosities prepared on N-type Si [51].

The relative permittivity ε_{psi}) of (PSi) and hence the refractive index (n_{psi}) are changed due to the reduction in dimensionality, where the nano-scale silicon (porous silicon) is composed of many columnar crystalline silicon particles separated by air Thus, the ε_{psi} is related to the porosity (P) by *Bergman's* effective medium approximation [52].

$$\varepsilon_{psi} = \varepsilon_{si} - P\,(\varepsilon_{si} - \varepsilon_{pore}) \qquad \ldots\ldots\ldots\ldots (2.2)$$

Where ε_{pore} is the relative permittivity of air when the pore filled by air, ε_{si} is the relative permittivity of silicon. Therefore, the relative permittivity of porous silicon is lower than that of crystalline bulk silicon, especially at higher values of porosity and hence the refractive index (n_{psi}) is expected to be lower than that of crystalline silicon and decreases with increasing porosity [53].

2-4-5 Electrical Capacitance of Porous Silicon layer

Capacitance measurements are a useful instrument for studying the electrical properties of (PSi) layers and instruments that include (PSi) layers [54]. The parameters such as built-in potential, width of the depletion layer, and effective carrier density for the M/PSi/c-Si/M sandwich structure can be determined from capacitance measurements [55, 56] .

The capacitance of a (PSi) layer is determined by its morphological properties, as it decreases as layer thickness and porosity increase, as seen in Figure (2-8) [55, 57].

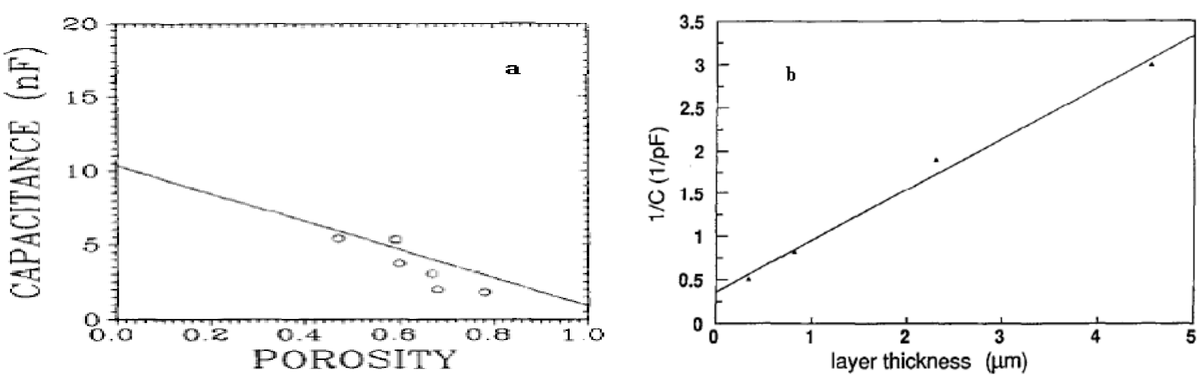


Figure (2-8) The Capacitance of PSi layer as a function of the (a) Porosity and (b) Layer thickness [58].

The capacitance of (PSi) layer C_{PSi} (F) is given by [59].

$$c_{psi} = A.\frac{\varepsilon_{psi} . \varepsilon_0}{d} \ldots\ldots\ldots\ldots\ldots\ldots \text{(2.3)}$$

Where $\varepsilon_\circ$ (F/cm) relative permittivity of free space and ε_{psi} relative permittivity of the porous silicon, A (cm^2) is the (PSi) area and, *d* (cm) is the thickness of (PSi) layer.

2-5 The Preparation Methods Porous Silicon

The etching processes (stain, electrochemical, photochemical, and photo electrochemical) are the four most popular methods for fabricating (PSi) layers. Each of these methods has its own set of characteristics, and the characteristics of the shaped (PSi) layer vary from one process to the next. The common characteristic in both approaches is the lack of complex components opposed to those used in developed and complicated solid-state techniques[60]. ***Etching techniques:*** Can be classifieds into two groups:

2-5-1 Dry Etching

Based on chemical reactions at the gas-solid interface. Fast laser pulses with high power densities from excimer or CW visible lasers are used to etch semiconductor wafers in a gas atmosphere. Dry etching results in higher growth rates and thicknesses of porous silicon than stain etching [61].

2- 5-2 Wet Etching

The liquid-solid interface is where chemical etching takes place. The growth rate and thickness of the porous coating are the most significant differences in the two methods. Kalem and Yavuzcetin have proposed a new technique for porous semiconductor forming that is based on exposing the semiconductor surface to gas phase etchants, which exhibit photoluminescence about 750nm [62]. Different methods for producing porous silicon are use in wet etching.

2-5-2-1 Stain Etching Method

Another method for producing films that are close to anodically treated (PSi) content is stain etching.

During regular etching nitric and HF acids are using to prepare (PSi) films. For stain etching, the most popular etchant is HF: HNO3:H2O is a ratio of HNO3 to H2O [63]. The stain etching method is an important choice in (PSi) forming due to the tacit simplicity of fabrication steps, but it is also consider very slow and the surface of the formed (PSi) layer is very rough. It is particularly appealing when very thin (PSi) films of uniform depth (101–102 nm) are need [64].

2-5-2-2 Electro –Chemical Etching Method

In this method constant current densities in the range of 1-300 mA/cm² in aqueous HF solutions are used in the most popular (PSi) preparation process to convert silicon to large-surface area material [65].

Charge transfer occurs at the semiconductor/electrolyte interface when a silicon wafer is submerged in a solution containing electron accepter species, resulting in band bending at the interface upward in N-type Si and downward in P-type Si as seen in Figure (2-9). Since hydrogen and silicon have equal electronegativity, the surface of N-type Si becomes saturate with hydrogen. Since the induced polarization is minimal, the saturated surface would be shielded from any surface attack [66].

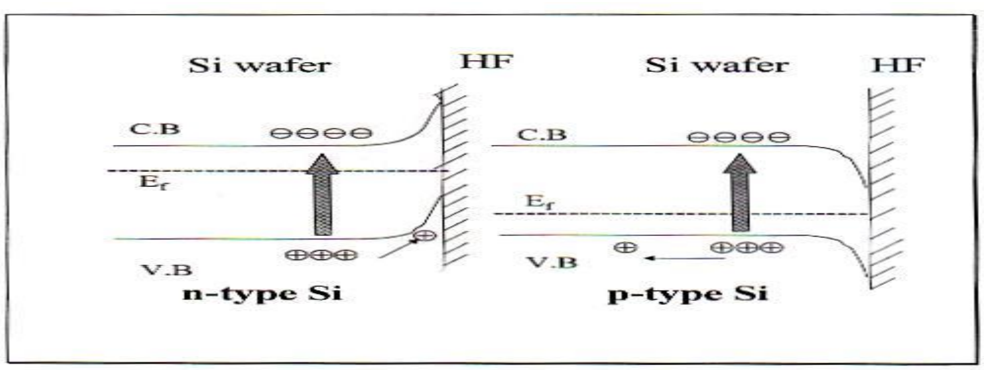


Figure (2-9) Band bending of Si immersed in HF[67].

A hypothesized chemical reaction describes the reaction as follows [68]

$$Si + 6HF \rightarrow H_2SiF_6 + H_2 \uparrow + 2H^+ + 2e^-$$

The final and stable produce for silicon in HF is H_2SiF_6 or some of its ionized forms, it follows that during the pore formation only two of the four available silicon electrons participate in an interface change transfer while the remaining two undergo a corrosion hydrogen formation.

2-5-2-3 Photochemical Etching

In this technique, a photon source such as lasers and intensive light is use to supply the required holes in the irradiated area of silicon wafer to initiate the etching process. Photochemical etching has been use to produce porous silicon (PSi) and nano crystallites of silicon, and has advantages that can be summarize as follows: (1) Simple process (without external potential). (2) Controllable processes that have more accurate processing parameters . This way has some drawbacks such as nonuniformty of illumination distribution and also the etching process in this method is considered slow [23, 46]. In over-view, the prepared (PSi) structure by photochemical etching process has different layer thickness and surface morphology according to wavelength and power of the utilized light [69].

2-5-2-4 Photo-Electro Chemical Etching Method

This technique is consider an ultra-important method in industry of (PSi) material because it is suitable for etching of N-type and P-type silicon in HF solution. This fact based on that the photo electrochemical (PEC) etching process collects between two ways (electrochemical and photochemical) etching processes [28, 70]. Have reported that the illumination of N-type as well as P-type PSi during formation causes dramatic changes in the structure of layers. The N-type (PSi) obtained under illumination by PEC etching process consists of layers of nonporous silicon layer which covers a macro porous silicon layer with pores in the micron size range [71].

2-6 Hydrogen fluoride

Hydrogen fluoride is a chemical compound with the formula (HF),which is considered the main industrial source of fluorine, and it is often in the form of hydrofluoric acid [72]. Therefore, it is considered the precursor to many important compounds such as pharmaceutical compounds and polymers (such as Teflon). hydrogen fluoride is widely used in the petrochemical industries and as a component of many super acids [73]. Hydrogen fluoride boils at a temperature lower than room temperature whereas other hydrogen halides condense at much lower temperatures. The only hydrogen atom in (HF) is linked with the fluorine atom through the formation of a covalent bond (sigma) that occupies on of the hybrid orbitals (2pz) and the remaining three orbitals contain (2px and 2py in addition to 2s).These orbitals contain three pairs of electrons. Thus, the assumed molecular geometry for hydrogen fluoride is as shown in figure (2-10).

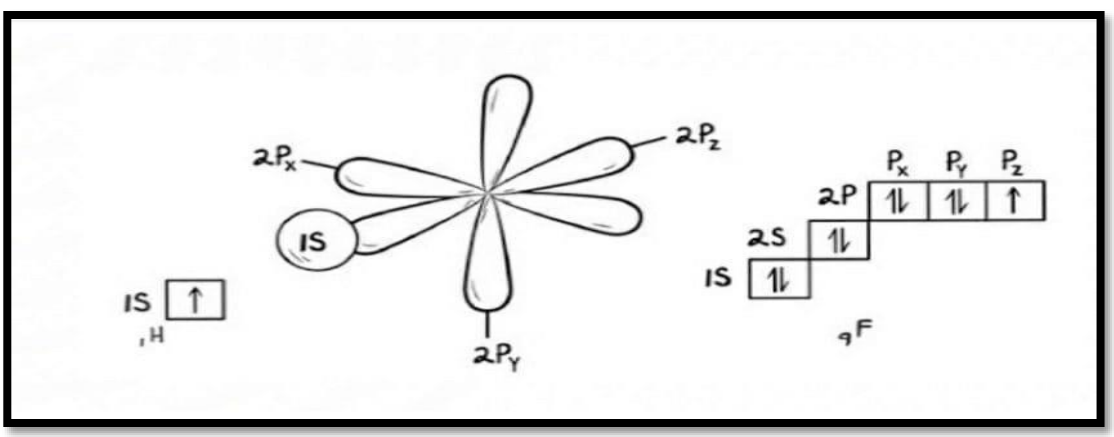


Figure (2-10) Molecular geometry of hydrogen fluoride orbital [74].

Because of its high electronegativity of fluorine, hydrofluoric acid (HF) is consider a weak acid, despite being one of the most voracious acids to react. Because the acid's electronegativity is high, it does not readily give up its only hydrogen, and because we know that, an acid's ionization decreases as its ability to give hydrogen increases, the acid's ionization decreases and the acid is consider weak [75].

2-7 Application of Porous Silicon

Because of its designable materials properties, compliance with traditional Si fabrication and thin film technologies, and special physical and chemical properties, porous silicon is a dielectric substrate with a wide range of applications[76]. Table (2.2) summarizes the possible use areas for porous silicon, and it also showing the properties of porous silicon used in each application.

Table (2.2) Application of Porous Silicon [77].

Application area	Role of porous silicon	Key property
Optoelectronics	LED	Efficient electroluminescence
	Waveguide	Tunability of refractive index
	Field emitter	Hot carrier emission
	Optical memory	Non-linear properties
Micro-optics	Fabry-Pérot Filters	Refractive index modulation
	Photonic bandgap structures	Regular macropore array
	All optical switching	Highly non-linear properties
Energy conversion	Antireflection coatings	Low refractive index
	Photo-electrochemical cells	Photocorrosion cells
Environmental monitoring	Gas sensing	Ambient sensitive properties
Microelectronics	Micro-capacitor	High specific surface area
	Insulator layer	High resistance
	Low-k material	Electrical properties
Wafer technology	Buffer layer in heteroepitaxy	Variable lattice parameter
	SOI wafers	High etching selectivity
Micromachining	Thick sacrificial layer	Highly controllable etching
Biotechnology	Tissue bonding	Tunable chemical reactivity
	Biosensor	Enzyme immobilization

Chapter Three

Experimental Part

3-1 Introduction

This chapter includes description of all instruments and apparatuses that have been employed in the preparation of (PSi) layers as well as the techniques, which have been utilized to study and clarify the characteristics of (PSi) layers.

3-2 Materials and Equipment used in the Study

Table (3.1) Shows the Equipments used in this Study

The device name	Device type and manufacturer	Work place
Device power supply (DC)	YX-1501 AD median -china	University in kerbala
X-ray diffraction meter	Philips-PW1730	University in Tehran
Scanning electron microscopy (SEM)	MIRA3 TESCAN Det: In Beam	University in Tehran
Sensitive electrical balance	Lab. BL210,Sartorius median-Germany	University in kerbala

Table (3.2) Shows the Chemicals used

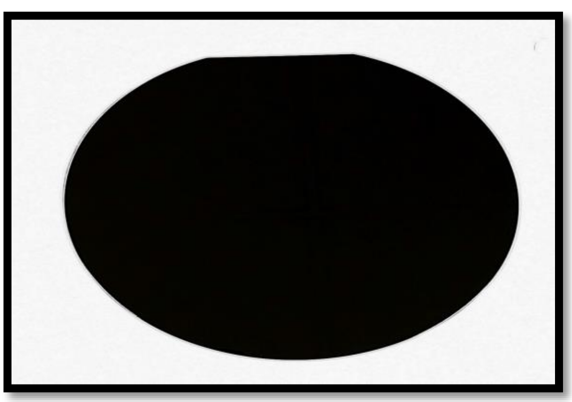
Subject name	Chemical formula	%	The manufacture company
Wafer silicon N,P-type	Si	-	Made in china
Hydrofluoric acid	HF	39-43 %	New Delhi -110002 (India)

Ethanol	C_2H_5OH	99%	Chem-Lab NV B-8210 Zedelgem- Belgium
sodium Hydroxide	NaOH	-	BDH chemicals Ltd, Poole England

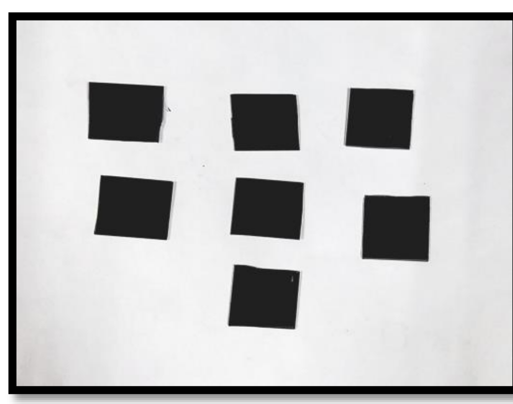
3-3 Sample Preparation

Porous silicon was produced using photo electro chemical etching for N-type bulk silicon (110) model/oriented silicon wafers with (R=1-10 Ω.cm) and size :(1300.5) mm standard-GB in this study. Electro chemical etching (110)/model P-type and (R=1-10 Ω.cm), size :(1250.5) mm standard-GB was used to prepare P-type porous silicon.

The silicon wafer in this figure (3-1, a) has been cut out in to small pieces (3-1, b) (1.3× 1.5) cm as shown in figure (3-1, a,b) .



(a)



(b)

Figure (3-1) Photograph of silicon wafer (a) with before cut the bulk silicon.

(b) After cut with bulk silicon.

These samples are rinsed with (1:10) HF : ethanol to remove dirt, then etched in dilute hydrofluoric acid (39 -43 %) to eliminate the native oxide layer, and then rendered porous silicon with aided photo electro chemical etching for N-type bulk silicon and electro chemical etching for P-type bulk silicon with time etching (10 min) ,(10V). and separate (1:1), (1:2), (1:3), (1:4), (1:5) concentrations (HF): ethanol After the (10min) quick, the sample is rinsed with deionized water and left in the atmosphere to dry for a few minutes before being deposited in a plastic container filled with ethanol to avoid the forming of an oxide layer on the prepared sample, as shown in figure (3-2). Photo electro chemical etching process was done at room temperature.

Figure (3-2) Photograph of the sample with the ethanol.

The sample has been place on a Teflon cell in such a way that current does not flow through the back surface in the schematic diagram of the PEC set-up. Simultaneously, a silicon electrode was place as an anode, and the electrical circuit was complete by placing a platinum electrode as a cathode in a parallel manner to achieve the PSi layers as seen in figure (3-3).

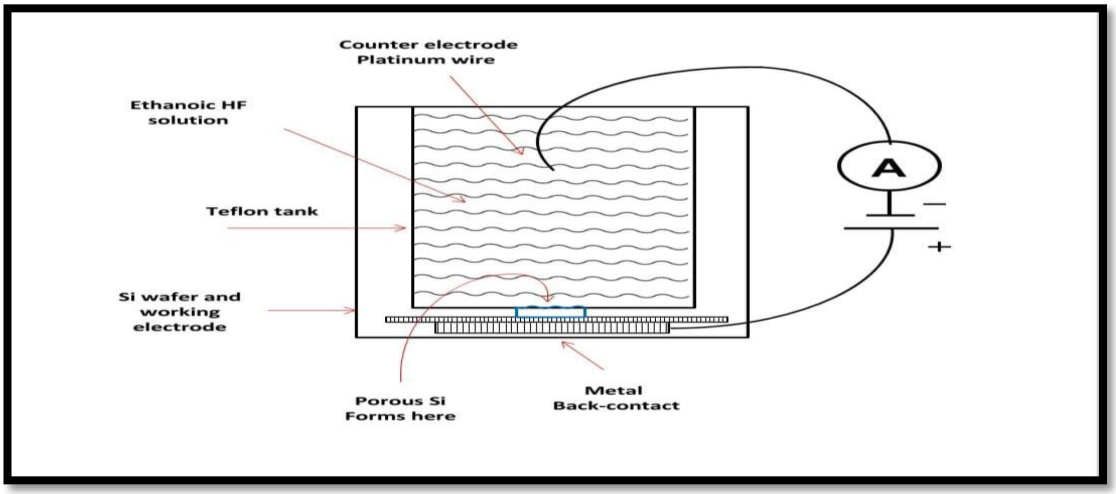


Figure (3-3) Shows the systematic for the photo electro chemical etching and electro chemical etching which using in this work.

3-4 Measurements

The structural of (PSi) layer have been investigate in this work by achieving of some measurements as follows:

3-4-1Gravimetric Measurements

The porosity and layer thickness of (PSi) layer has been calculated by measuring the weight of the samples before and after etching process as well as the weight of sample after removing of (PSi) layer from sample by immersing for (30min). In 1M NaOH which prepared by using (10g) NaOH and (250ml) D.W to calculate molarity law $M = \frac{wt}{M.wt} \times \frac{1000}{Vml}$ ……………(3-1)[78]. And using equation (2-1) and (3-2) to calculate the percentage porosity and layer thickness [79].

$d = \frac{m_1 - m_2}{\rho A}$ ………………. (3-2)

m_1 = the weight of the sample before etching rate.

m_2 = the weight of the sample after etching rate.

ρ= silicon density , A = the area of the freckled surface.

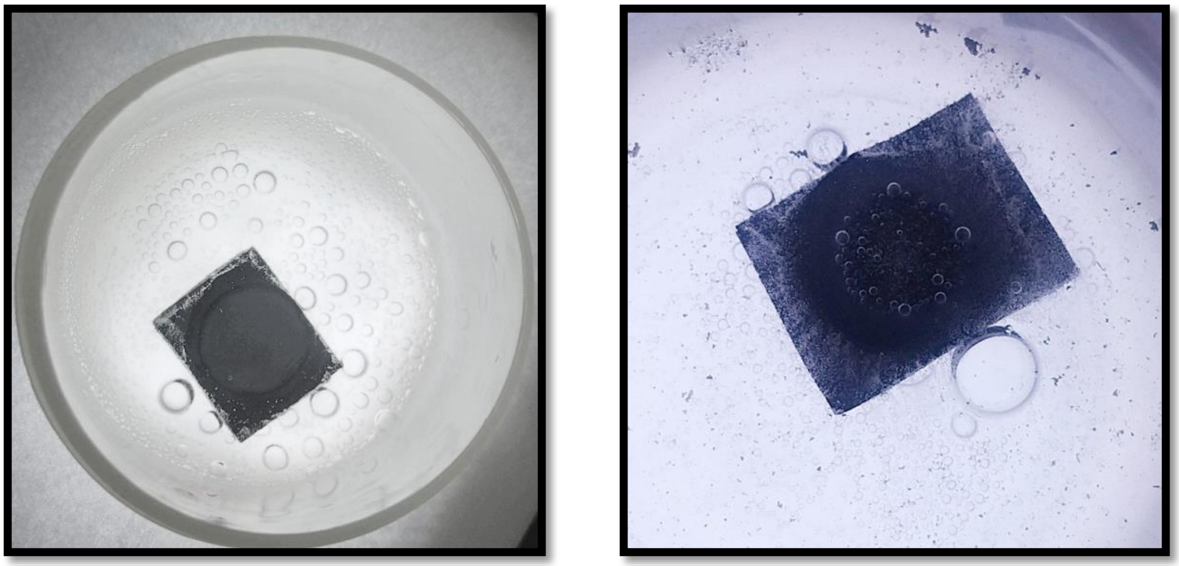


Figure (3-4) Shows photograph when we remove the porous silicon layers in NaOH.

3-4-2 Etching rate Measurements

The etching rate is calculated by measuring the layer thickness and etching time for (10 min) by using the equation [80].

$V=\frac{d}{t}$ ………………. (3-3)

3-4-3 Optical Measurements

The relative permittivity is calculated by measuring the porosity and constant ε_{si}=11.68, ε_{pore}=1 by using the equation (2-2) and measuring the refractive index from the square root of relative permittivity by using the equation [81].

$$n_{psi} = \sqrt{\varepsilon_{psi}} \ldots\ldots\ldots\ldots \text{(3-4)}$$

3-4-4 The Electrical Capacitance of the Porous Silicon Measurement

The capacitance of porous silicon can be calculated by measuring the relative permittivity, which related as a function of layer thickness for porous silicon by using the equation (2-3).

3-4-5 Scanning Electron Microscope (SEM)

The structural measurements of (PSi) layer are carried out by direct imaging of (PSi) layer using a field emission scanning electron microscopy .The morphological aspects like pore width, pore shape and thickness of wall between pores uni formity of the (PSi) layer are studied using (SEM).

The (SEM) measurements with EHT=15.00kv ,signal A=SE_2 are carried out at the university of Tehran.

3-4-6 X-Ray Diffraction Technique

The morphological properties of porous silicon (PSi) layer such as nano crystallite size, the structure aspect of (PSi) layer (crystalline or amorphous) and little constant have been investigated in this work by using X-ray device (Philips-PW1730) supplied from Philips company and carried out at the university of Tehran .

Chapter Four

Result and Discussion

4-1 Introduction

The properties of porous silicon is very important with respect to the applications because these applications reflected to the nano crystalline of silicon characteristics like solar cells or gas sensor according to the morphological properties [82].

The porous silicon properties fabricated by photo electro chemical (PEC) etching for N-type and electro chemical etching for P-type processes of Nano crystalline silicon substrate are presented and discuss in this part. According to that one can described observations, the structural, morphological, optical, and electrical characteristics of the PSi layer were investigate.

4-2 Surface Morphology of Porous Silicon Layer

Porous silicon layer is a very unique structure that is distinguished by the appearance of intertwined pores in a single crystal. The morphological properties of the prepared (PSi) layer, such as porosity, layer thickness, pore depth, pore shape, the wall thickness between two pores, the surface area, and Nano crystallite. The etching conditions have a strong influence on the morphology of the (PSi) layer (crystalline or amorphous), and the size of the Nano crystallites [83].

4-2-1The Porosity

The relationship between porosity percent of the porous silicon and different concentration acid ratio during the preparation can be show in figure (4-1). This Figure shows depicts the relationship between porosity of porous silicon and different acid ratio achieved by this vicissitudes are caused by the Bulk N-type silicon demeanor, that necessitates the use of light when preparing the porous silicon, which make strong reaction between the acid and silicon [84].

The porosity improves with increasing and decreasing result from the strength of the reaction acid ratio so the lower the concentration acid ratio, the more polishing occurs and the smoother the porous layer developed, and the density increases due to the large amount of voids in the (PSi) layer. And increasing acid ratio since a weak porous layer is produce while the acid ratio is high, and it does not polish, resulting in a limited amount of voids in porous silicon layers [85].

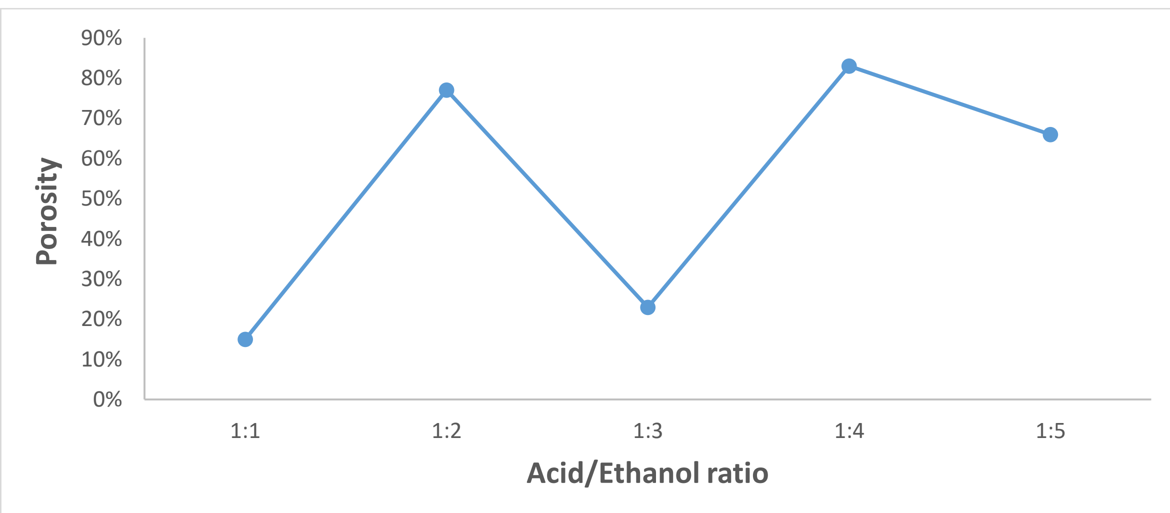


Figure (4-1) Relation between the porosity and different acid/ethanol ratio for N-type.

Figure (4-2) shows the porosity percent as a function of acid ratio to hydrofluoric / ethanol. And this figure varies from figure (4-1) in that the porosity increases with rising concentration acid ratio due to high resistance, and resulting in polishing, and the porosity decreases with decreasing acid ratio because this figure (4-2) show the porosity of porous silicon as a function of concentration acid ratio for the acid to ethanol this figure show some changes in the behavior because of the P-type dependence on holes as charge carriers, which this due to make slow in reaction with little charge carriers reaction and make the porosity increases with respect to the concentration acid ratio resulting in a small number of pores in the porous silicon [45].

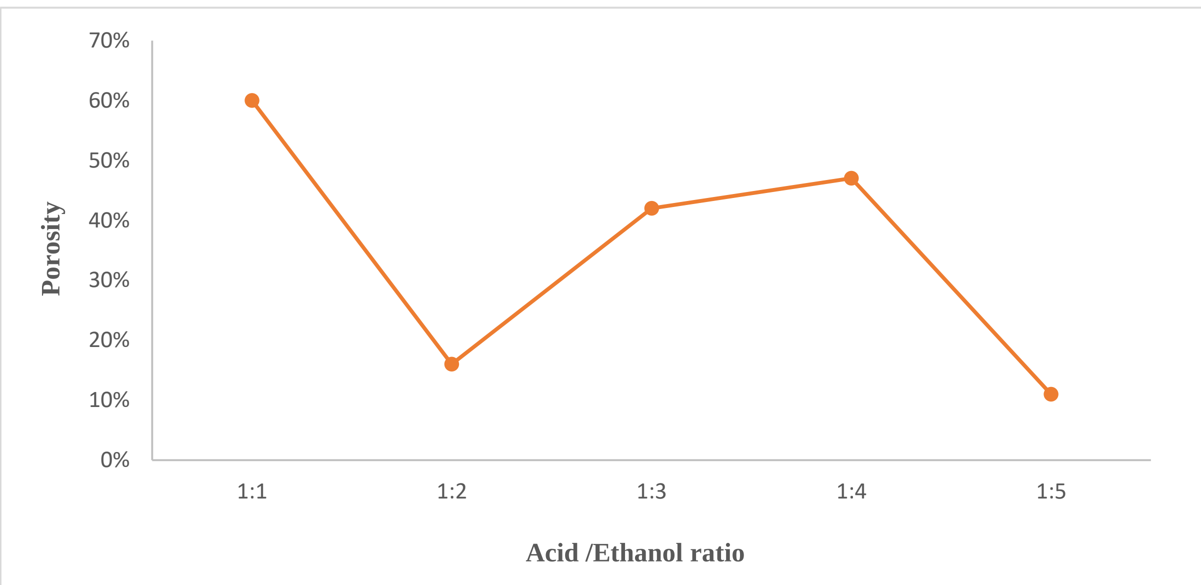


Figure (4-2) Relation between porosity and different acid/ethanol ratio for P-type.

As for the figure, one can see in the aforementioned figure (4-3) that combined the two types N,P-type, which is represented by the connection between acid ratio and porosity for porous silicon, that the N-type has different P-type in terms of rise and decrease reactivity following the comparison between two types . due the N-type requires light, whilst the P-type does not, and the reaction for the two types has not been regulated in terms of increase and decrease [86].

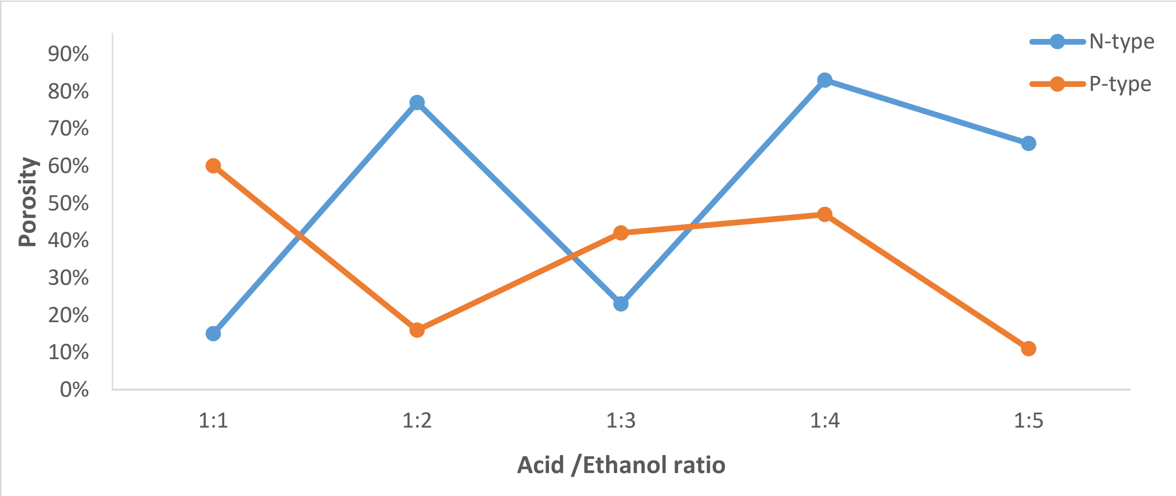


Figure (4-3) Relation between porosity and different acid/ethanol ratio for N, P-type.

4-2-2 The Layer Thickness and Etching rate

The etching rate is associated with the layer thickness because the etching rate is defined as the ratio between porous silicon layer thickness and the etching time, as shown in equation (3-3) [23].

Figure (4-4), shows the fluctuation of layer thickness with acid ratio for N-type PSi due to a heavy reaction with acid [87]. On the other hand, the differing concentration acid ratio of ethanol and HF acid create a decrease in the ions and charges, which effects on the energy levels between acid and ethanol atoms, and therefore the reaction, will change. The thickness of the layers used in the manufacture of porous silicon can vary depending on acid ratio. From this figure, the layer thickness may increase, and decrease. This may be due to the different concentration acid ratio creating new bonds for the mixture, which has a direct effect on the reaction process between the acid and bulk silicon [88], this fluctuation can be shown in many papers and many researcher reported the same results .

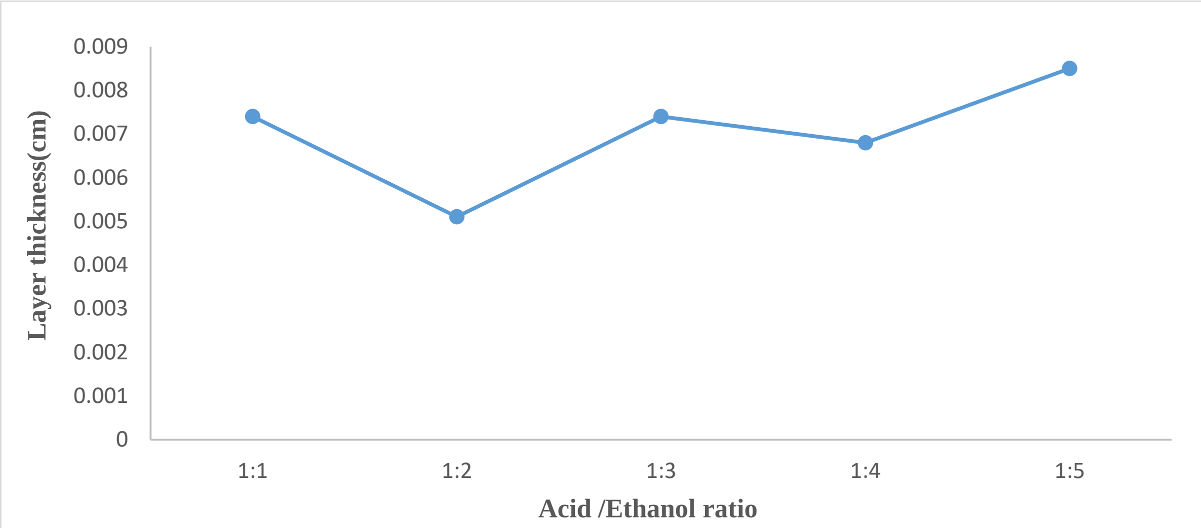


Figure (4-4) Relation between layer thickness and different acid/ethanol ratio for N-type.

Figure (4-5) shows the thickness of the layer for P-type one can easily show the increasing in the layer thickness which differ from figure (4-4) due to the preparation condition for porous silicon and the increasing in the layer thickness because the weak interaction between the acid and the silicon which did not make polishing and remove the porous silicon layer as in the figure one but the reaction continue along ten minute but in the figure (4-4) the reaction forms the porous layer, and since the strong reaction forms the polishing and removal of the porous silicon layer, this case is not seen in figure (4-5) with reason the reaction continues to form the porous silicon, and the low acid ratio enable the charges reaction to form the porous silicon. Many researchers would be able to see the findings of this study [87].

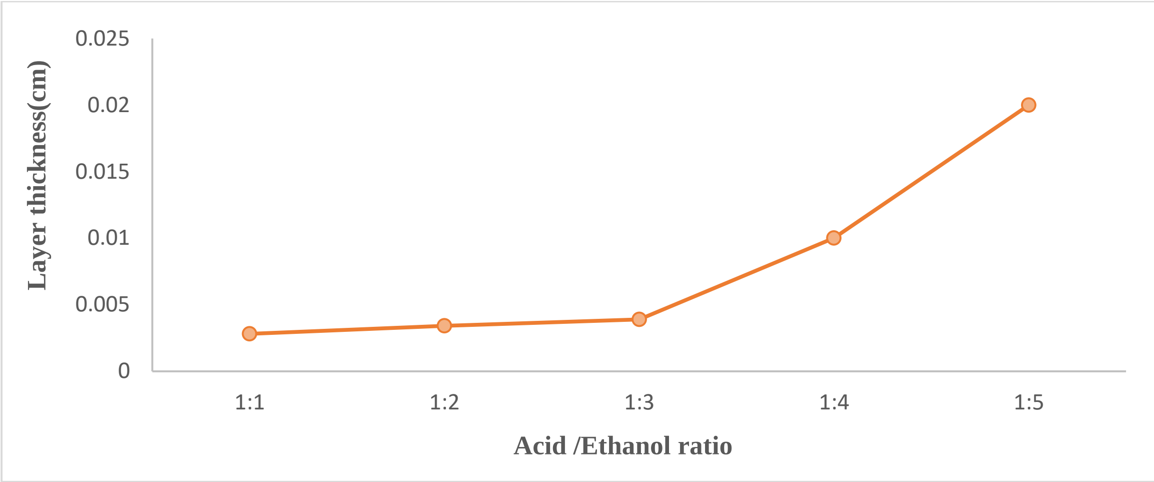


Figure (4-5) Relation between layer thickness and different acid/ethanol ratio for P-type.

The comparison between N-type and P-type bulk silicon is shows in figure (4-6).The increased layer thickness of P-type more than N-type for the same acid ratio may be seen in the layer thickness of porous silicon with regard to acid ratio. This indicates that there is a change in energy levels occurred during porous silicon production due the holes in the P-type are ready to react with acid, but the holes in the N-type require some photons to produce the holes [89].

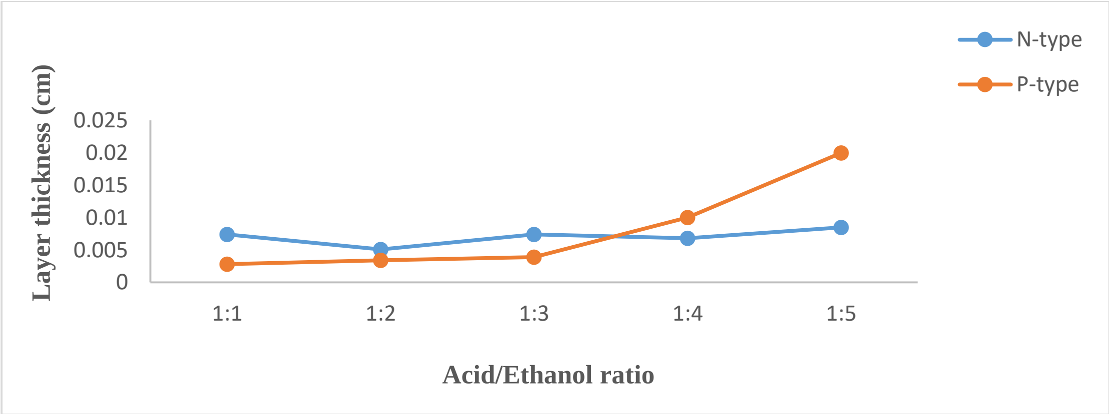


Figure (4-6) Relation between layer thickness and different acid/ethanol ratio for N, P-type.

Figure (4-7) shows the relationship between the different acid ratio and the etching rate of porous silicon, we will notice that there is a similarity between figures (4-6) because the time is constant (10min) and the etching rate relates mathematically to the layer thickness, from that occur perhaps due to an increase or decrease in layer thickness. By this, the etching rate, and in the case of high concentration acid ratio, the thickness of the layer will decrease due to reduce the etching rate. As for the difference between the two types, this may be because the N-type needs light compared to the P-type .The interaction between the acid and bulk silicon is simpler without the need for light, which effects the energy levels between the acid and ethanol, atoms and thus the reaction will change [46].

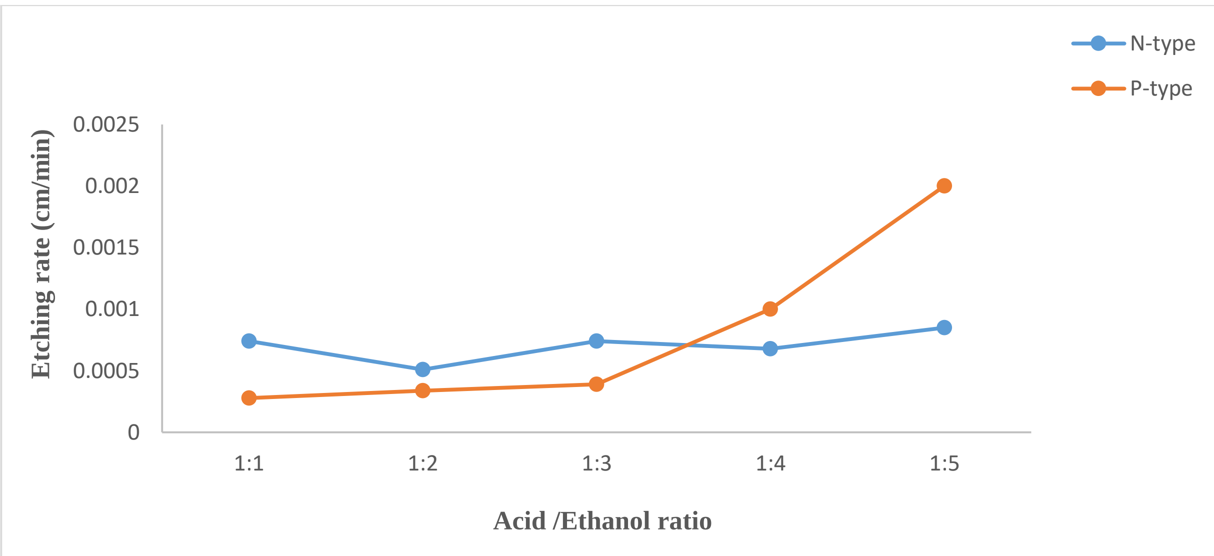


Figure (4-7) Relationship between etching rate and different acid/ethanol ratio for N, P-type.

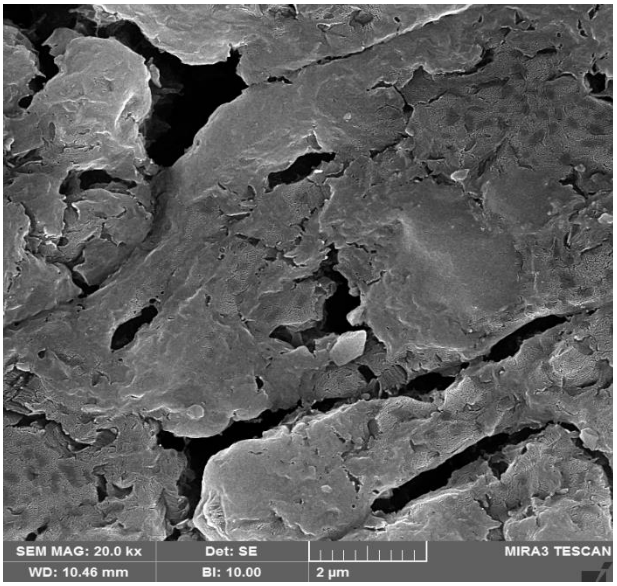
4-2-3 Scanning Electron Microscope (SEM)

The researchers focusing on the walls of porous silicon because these walls are basic of nano crystalline silicon, which the properties of quantum confinement effects were appear [90].

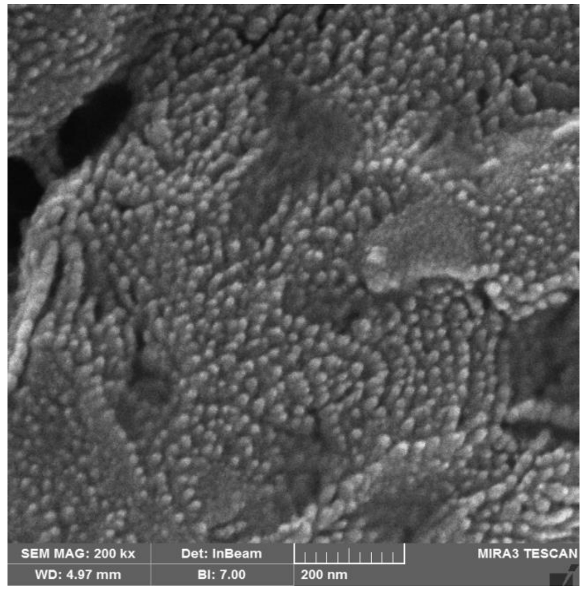
Figures (4-8,a) and (4-8,b) show (SEM) image for samples prepared at ahigh concentration acid ratio (1:1) of HF to ethanol for the N-type of porous silicon by using (10min) and (10V) .Through this figure ,one can see the pores in the form of afew clear cracks,due to high acid ratio which will be a rapid reaction, forming more porous layer, which leads to adecrease in the layer thickness as a result of this. The (SEM) image will have afew slits and thin [91].

Also Figures (4-8,c) and (4-8,d) display SEM images of N-type bulk silicon samples prepared to (1:3) ,(1:4) acid ratio of HF to ethanol and using (10) min and (10V) . The pores in the porous silicon substrate and forming of nano size scale silicon are clearly seen, and the initial polishing can be shown in the figure (4-8,c) [92].

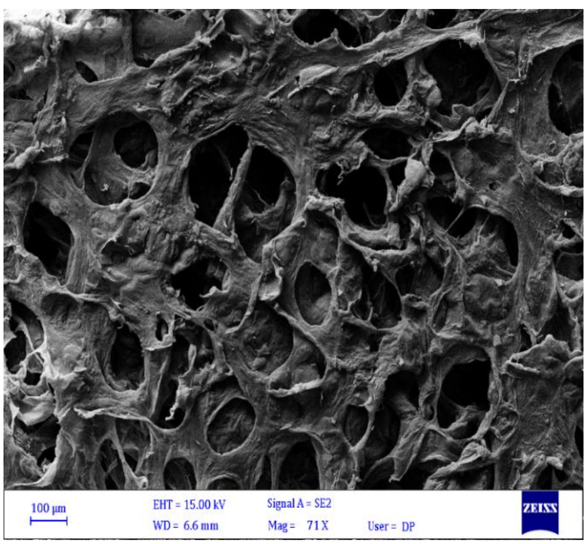
This perhaps because of the low concentration acid ratio, which induces a difference in the energy levels between the acid and the bulk silicon, allowing room for charge contact and eventually removing the porous silicon layer, as seen in figure (4-8,d). The nano walls and pore-like caves that give this layer its nano properties can be seen.



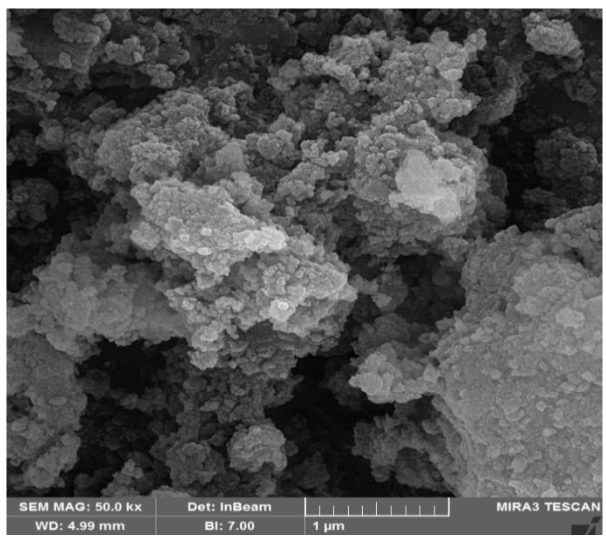
(a)



(b)



(c)



(d)

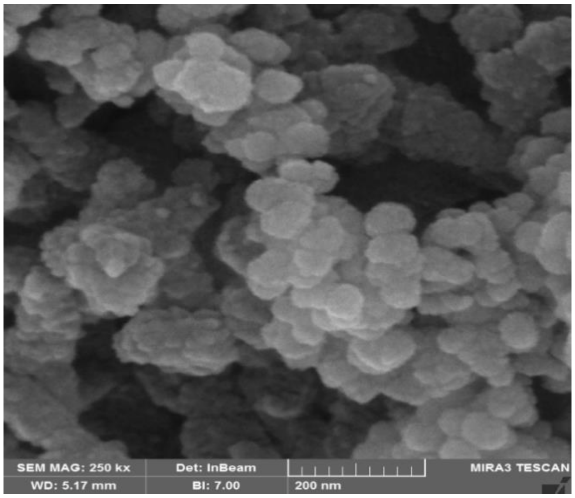
Figure (4-8) SEM images of porous silicon layers prepared by 10 min and 10V at different acid/Ethanol ratio for N-type (a, b) 1:1M (c) 1:3M (d) 1:4 M.

Figures (4-9, a) and (4-9, b) show porous silicon from P-type bulk silicon prepared (1:1) acid ratio of HF to ethanol and using (10 min) and (10V).

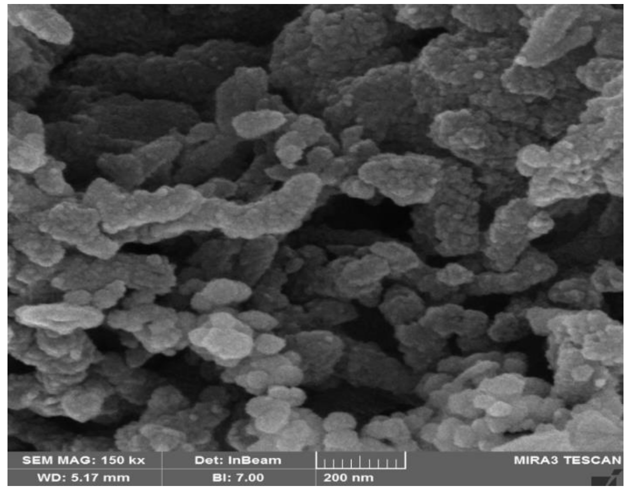
By the ratio because the pores and caves will be see no polishing or removal of the porous silicon coating will be required, as in the N-type case, despite the fact that the low concentration acid ratio may cause the layer thickness to grow. In order to of the porous silicon layer's morphological features, many implementations can be concluded from these situations because the porous silicon layer has many features that have a direct impact on the application [93].

Figure (4-9, c) and (4-9, d) show SEM image of P-type bulk silicon sample prepared at (1:2), (1:3) acid ratio HF / ethanol by using (10min) and (10V). We notice through these figures that the surface morphology reveals the existence of a trench-like structure of different sizes and shapes due to the overlap of neighboring pores as in figure (4-9,d) so that the pores density is much greater than the shape in figure(4-9 ,c) .It allows for an increase in the dissolution of silicon between the pores close to the irregularity of the width values of the pores that arise .By distributing the non-uniform energy density ,which leads to a difference in the width of the pores ,this means that increasing the concentration intensity will lead to modification of the porosity structure into new shapes with different nano scale sizes [94] .

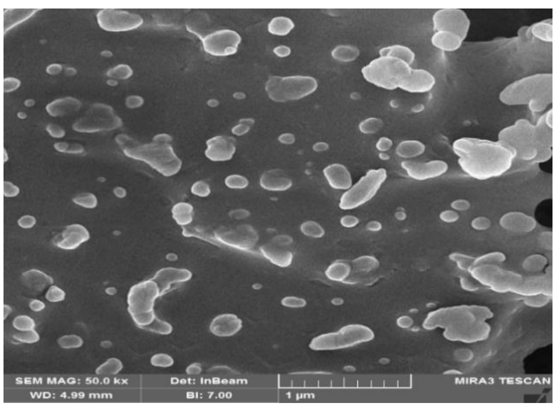
Figure (4-9, e) shows a display SEM image of P-type bulk silicon samples prepared using (10min) and (10V) at (1:4) HF/ethanol acid ratio. We can see the homogeneity of the apertures that make up porous silicon using a scanning electron microscope (SEM) image, as cracks have formed because of the union of silicon nozzles, giving porous silicon unique features. [89] .



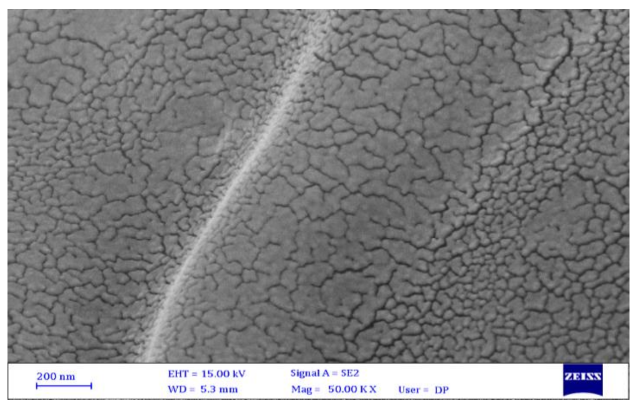
(a)



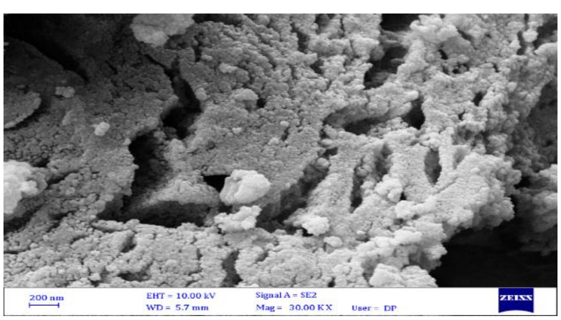
(b)



(c)



(d)



(e)

Figure (4-9) SEM images of porous silicon layers prepared by time 10min and 10V at different acid/Ethanol ratio for P-type (a,b)1:1 (c)1:2 (d)1:3 (e)1:4

4-3 Optical Properties

The relative permittivity and refractive index, which is directly related to electrical properties and are define in the following section, there are two types of optical measurements that have been studied [95].

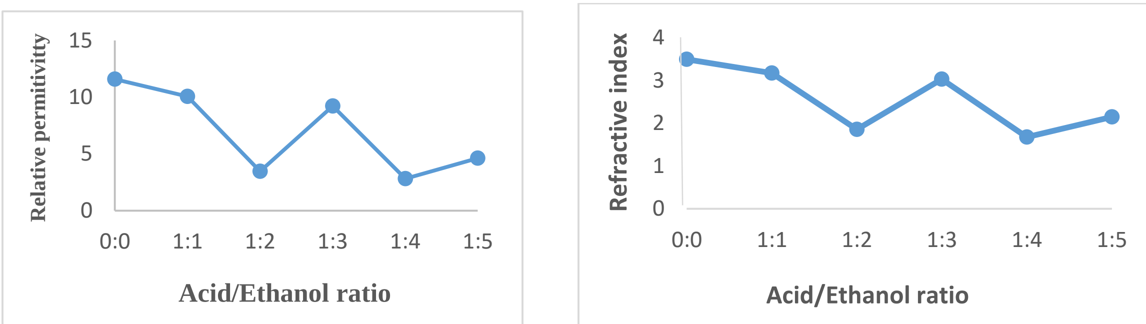
4-3-1 Relative Permittivity and Refractive index

Since relative permittivity and refractive index are functions of morphological properties, especially porosity, they are relate to one another [96].

Relative permittivity of PSi can be calculated by using equation (2-2) while the refractive index by using the equation (3-4).

The relationship between different acid ratio of HF / ethanol and (a) relative permittivity (b) refractive index for N-type is show in Figure (4-10). The increased and decreases in relative permittivity and refractive index, which is the reason for the porosity, and linked mathematically to the optical properties [95].

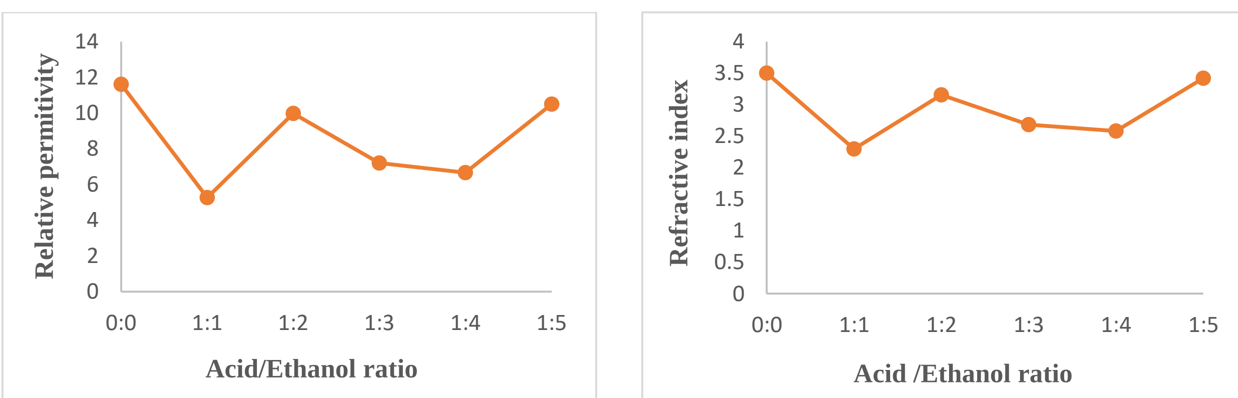
From the two figures one can show the decreasing in the values because of the hole effect inside the porous silicon which make the decreasing this values and effect on the properties of the porous silicon [97].



(a) (b)

Figure (4-10) Relationship between different acid/ethanol ratio and (a) Relative permittivity (b) Refractive index for N-type.

Figure (4-11) shows the relationship between different acid ratio of HF / ethanol and (a) relative permittivity (b) refractive index for P-type bulk silicon. The increase and decrease in characteristics is due to porosity, which decreases relative permittivity, refractive index and vice versa. Because the porosity they are related to the optical properties mathematically so that’s why the relative permittivity ,refractive index change with change porosity [98].

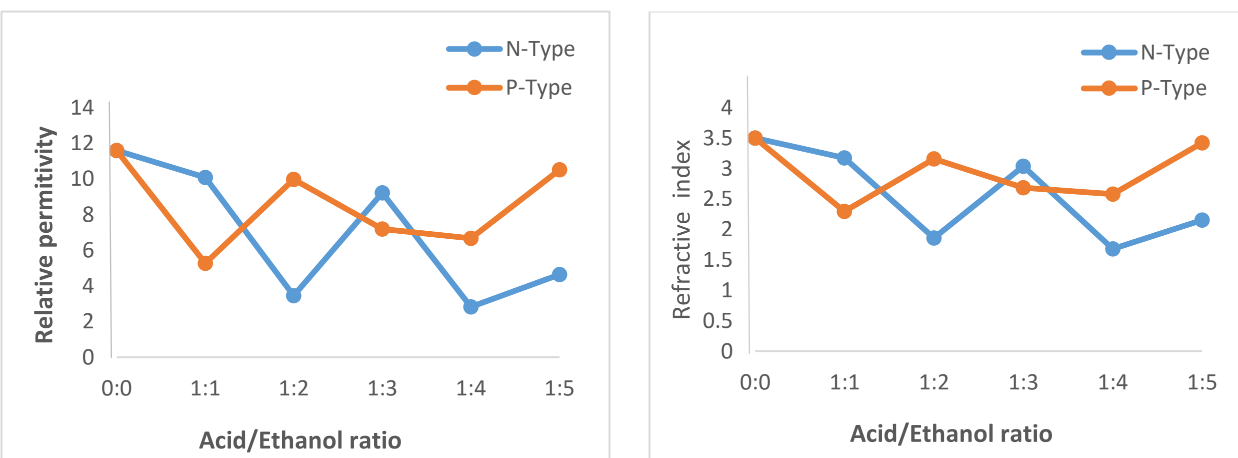


(a) (b)

Figure (4-11) Relationship between different acid/ethanol ratio and (a) Relative permittivity (b) Refractive index for P-type.

There are some differences between figure (4-10),(4-11) this results from the origin interaction during prepare the samples and effect the dopping in the N-type and P-type in addition to that the effect on the different acid ratio for the acid [99] this different can be shown in the figure (4-12).

As for the figure (4-12) which shows the relationship between different acid ratio (HF / ethanol) and (a) relative permittivity (b) refractive index for porous silicon through this figure, we notice a similarity between the (a) relative permittivity and (b) refractive index .Because that the optical properties are related to other mathematically [95]. Moreover, with respect to the N and P-types, and for the fluctuations and the difference that occurs between the two types, it is because the N-type occurs with the help of light .As for the P-type, it does not need light, so the interaction in it is easier. Thus a change in energy levels will occur, which leads to a change in the interaction between Acid and ethanol for bulk silicon.



(a) (b)

Figure (4-12) Relationship between different acid/ethanol ratio and (a) Relative permittivity (b) Refractive index for N, P-type.

4-4 Electrical Capacitance for PSi Layer

The morphology and porosity of the engraved silicon surface influence the capacitance-voltage properties of PSi/c-Si structures.

Figure (4-13) shows the relationship between different acid ratio and capacitance for N-type bulk silicon, the electrical capacitance increases with the increase in the relative permittivity and by reducing the layer thickness, the smaller the porous layer, the porosity will decrease and the electrical capacitance will increase because the morphological properties is related with each other mathematically [95, 100].

The capacitance is relate to the layer thickness and the layer thickness may increase and decrease. This perhaps due to the different acid ratio creating new bonds for the mixture so the reaction is not control terms of increase and decrease, and one can conclusion the capacitance for the electrical charge can be changed for porous silicon with different concentration acid ratio [101].

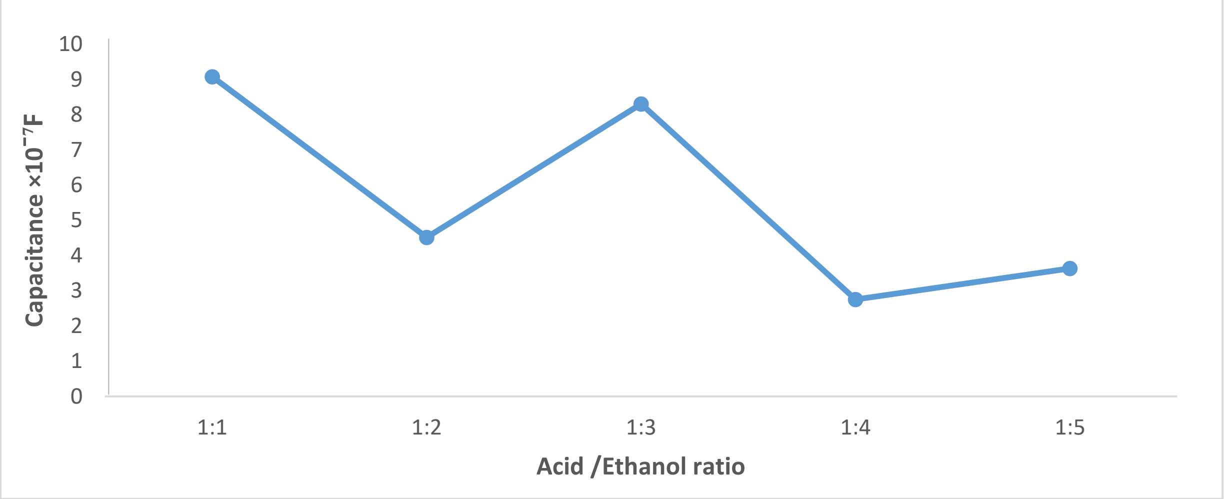


Figure (4-13) Relationship between capacitance and different acid/ethanol ratio for N-type.

Moreover, this figure (4-14) shows the relationship between different concentration of acid ratio and capacitance for P-type bulk silicon, we note the interaction is slow as it continuous to descend due to the increase in the layer thickness of samples and this reaction is not controls terms of increase and decrease [102].

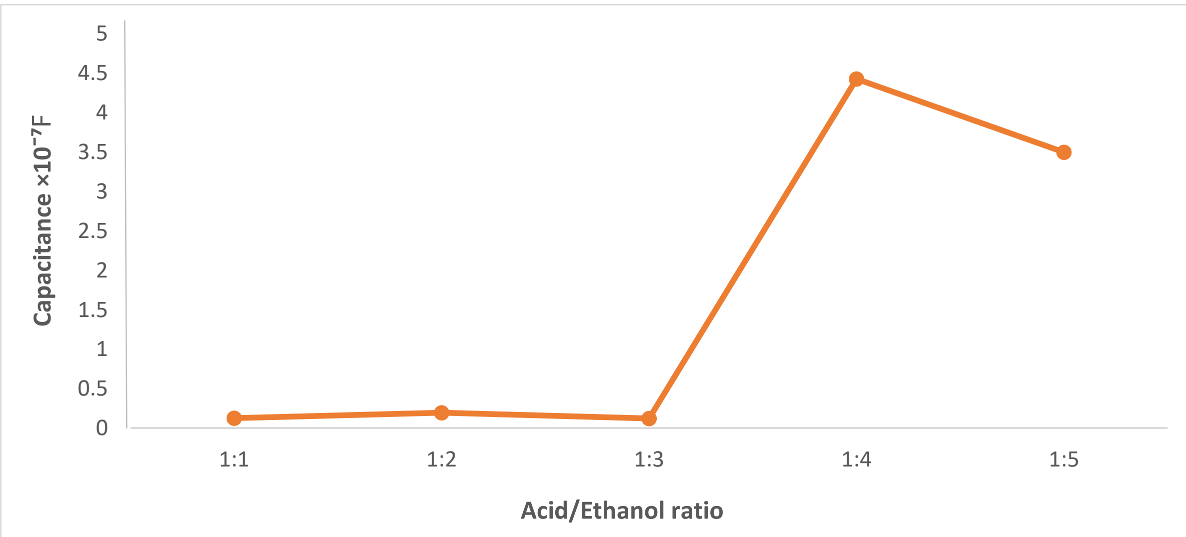


Figure (4-14) Relation between capacitance and different acid/ethanol ratio for P-type.

Also figure (4-15) combines the two types N and P type which, which is the relationship between the different concentration acid ratio and the electrical capacitance when comparing the two types; We notice the fluctuations that occur in terms between two type. Because the N- type work with the help of light, while the P-type works without light and thus will affect the reaction, and new bonds may arise in it that will affect the energy levels between the acid and ethanol atoms, leading to a change in the reaction [55, 103].

And we can see the difference between the capacitance for porous silicon produced from P-type and porous silicon produced from N-type bulk silicon this may be come from the effect of the ratio of the acid on the charge capacitance ,one can conclusion from that, the capacitance for porous silicon produced by N-type are better than P-type [104].

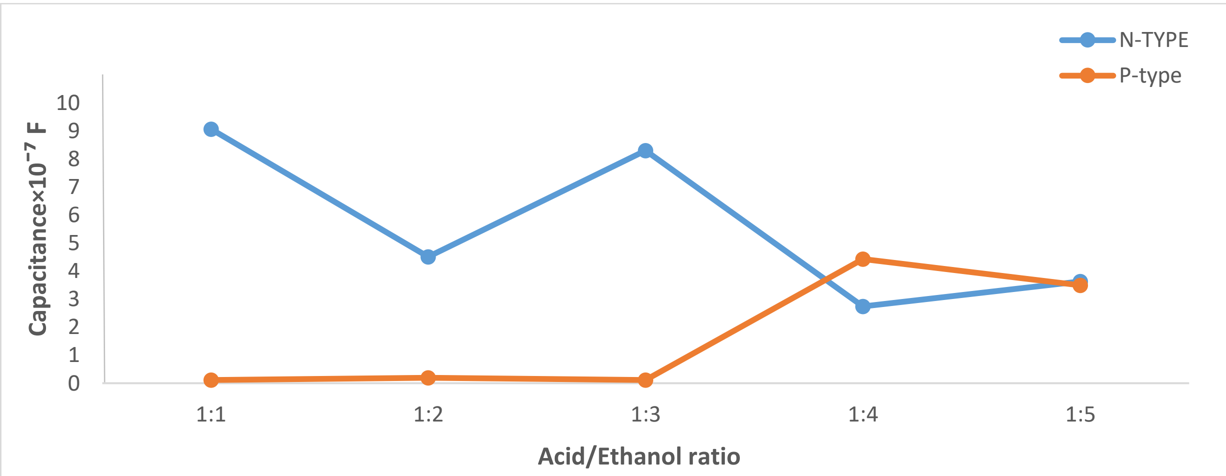


Figure (4-15) Relation between capacitance and different acid/ethanol ratio for N, P-type.

4-5 X-ray Characteristics of (PSi)

The X-ray diffraction test gives a valuable insight into the morphological structure of the (PSi) as a function, as well as calculating silicon nano sizes (PSi). The morphological step of the (PSi) layer (crystalline or amorphous) will provide a clear idea of the material's electrical and morphological behavior [105].

Figures (4-16), (4-17) show the X-ray diffraction of porous silicon made of N,P-type bulk silicon and different concentration acid ratio HF / ethanol in the time (10) min and angle range of (20-70) one can observe through the figure (4-16) is heterogeneous of the porous silicon from N-type and the figure (4-17) is homogenous of porous silicon from P-type due to the difference in the reaction with the acid this was reflected in the morphological characteristics of the porous but the similarity with N, P-type is in the middle due the porous effect this results from the chain reaction between the silicon and the dilute acid .To the periphery, this is the function of the Gaussian distribution which is severe in the middle and represents [106]. It presents effect of the reaction in the middle and its slope at the ends, and therefore we notice the high diffraction of the rays at the edges, which gives new properties to the porous that differ from the properties of the silicon from which it was originally produced .

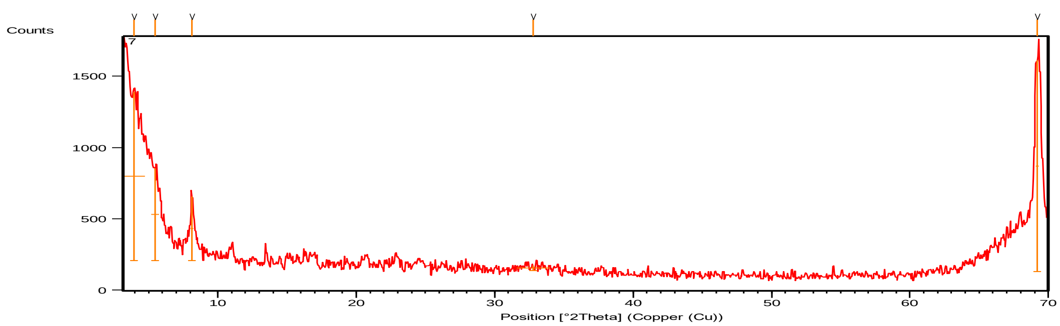


Figure (4-16) X-ray diffraction measurement of porous silicon layer for N-type.

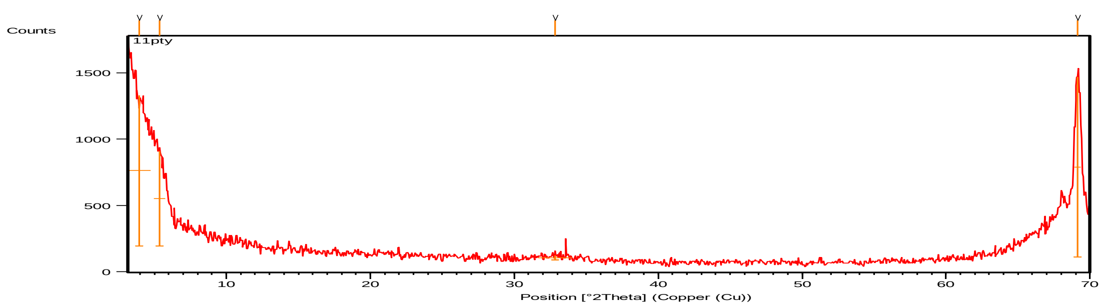


Figure (4-17) X-ray diffraction measurement of porous silicon layer for P-type.

From the two figures, one can show the homogenous structure for the porous silicon due to regular reactions and the same result had been reported can see in some papers [107].

Chapter Five

Application of Porous Silicon

5-1Introduction

Nanomaterial's are thought to open a new branch in the science of technology due to their unique properties such as high strength, amazing chemical reaction, high surface area, and high stability, as well as the fact that they are regarded as a magical point in the dimensional scale. New optical, magnetic, electrical, and a variety of other properties develop as the materials appear [108].

5-2 Solar Cell Components

Silicon nano structures may attract increasing interest in various fields, as it is considered the heart of the electronics revolution, including optical and microelectronics, medicine, chemistry, bio sensing and energy[109].

Porous silicon can make new applications such as solar cells and diode, such as polymer nano fibers .It fills the formation and characteristics a gap in today's literature, introducing knowledge of information and processing [110].

Due to the importance of this topic, there are many studies that dealt with the topic of solar cells and its effect on porous silicon, including.

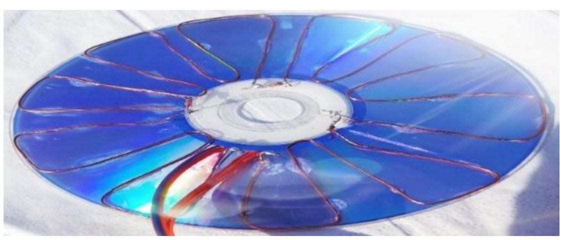
In (1941) American inventor (Russell uhl) was able to produce a solar cell made of silicon and make a solar cell from chemically treated silicon[111].

In (1995 Mena .et. all) formed porous silicon on a Si solar cell by both electro-chemical and photoelectric drilling methods. They created as porous silicon layer as anti –reflective coating (ARC) for a Si polycrystalline solar cell. Resulting from the porous silicon layer about 0.5mw thick formed on the poly crystalline chip has an effective reflection coefficient of less than 5% in the wavelength region of (350-1150 Nm)[112].

In (2004) Nuri and others demonstrated the grain boundaries in polycrystalline silicon solar cells using (PSi) increasing efficiency to about 12% [113].

5- 3 Solar Cell of the Present Work

Solar cells are semiconductors with the ability to convert solar radiation into electrical energy using a quantitative theory of photon energy conversion. When compared to other sources of energy .Solar energy is one of the most important types of energy that humans can use because it does not produce harmful gases for the environment [112]. As a result , we created a solar cell using basic and affordable components by DVD disc and connecting wires to increase the efficiency of cell work as shown in photograph (5-1,a) and we have replaced a zenar diode with a diode composed of nano-porous silicon as an diode by used porous silicon sample from P-type and concentration (1:5) as shown in photograph (5-1,b) and we studied its effect on solar cells . It has been invents or enhanced to increase the efficiency of cell operations. And the addition of the conductive (silver past) substance to the sample, as indicated at it is considered inexpensive addition of cost and quality of work.



a

b

Figure (5-1) Photograph the solar cell (a) without porous silicon (b) With porous silicon as a diode.

We have done the voltage readings produced by the solar cell were take alone without adding porous silicon for different times during the day, and the result was as shown in figure (5-2). We observe the behavior similar to the behavior of the normal caustic distribution based on the amount of radiation received from the sun and the contribution of a DVD in increasing the amount of solar radiation received.

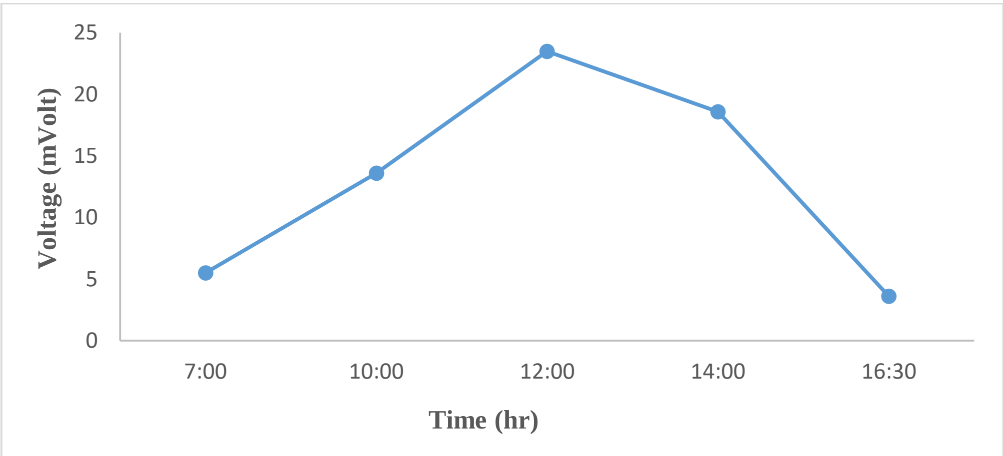


Figure (5-2) Measurements of solar cell without addition of porous silicon.

In addition, we have done the voltage readings resulting from the solar cell were taken by adding a sample of nano-porous silicon as a diode on the solar cell and for the times, and we observed a remarkable rise in the voltage curve of the solar cell as shown in the figure (5-3). We conclude that it is possible to improve the performance of the solar cell by adding nano materials of nano particles as a diode, and the results have proven that it is able to raise or improve the voltage performance resulting from the origin voltage of the solar cell.

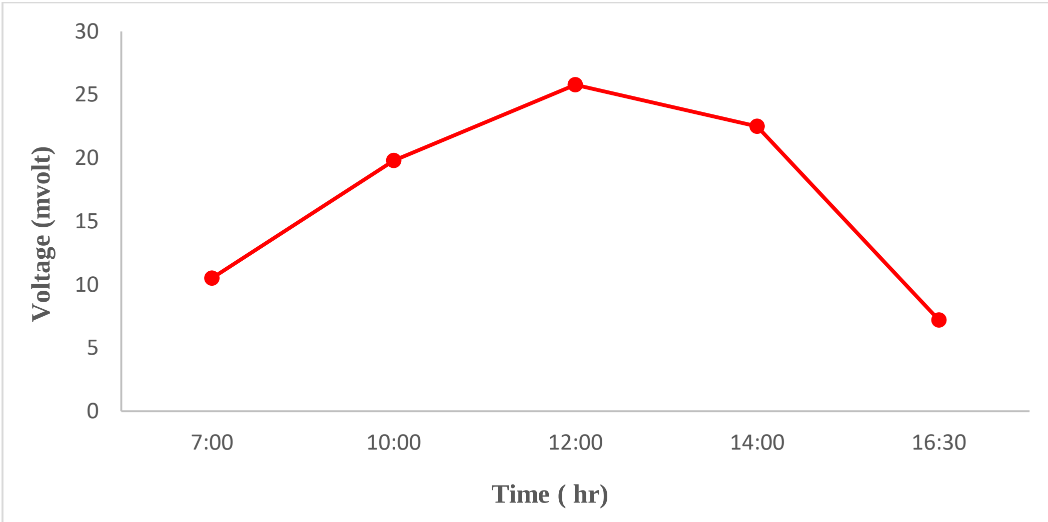


Figure (5-3) Measurements of solar cell in the presence of porous silicon.

Finally, we noticed through this figure (5-4) which shows the difference in the solar cell measurement a significant increase in the area under the curve, indicating that porous silicon can amplify the voltage generated by the solar cell as a resulted of obtaining a quantitative restriction in the size of the silicon particles, implying that the solar cell's performance can be improved by using a nano layer of silicon. Pores and by placing it as a diode in the solar cell.

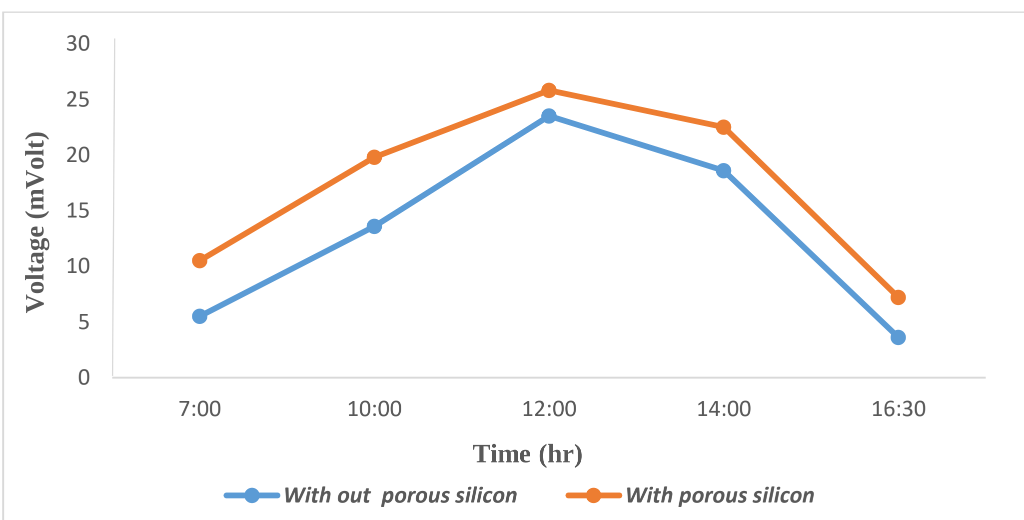


Figure (5-4) The difference is in the solar cell measurements.

Chapter Six

Conclusion and Future Work

6-1 *Conclusions*

In light of these findings and facts, the photo electrochemical etching process could be consider a very useful technique for producing (PSi) materials with desirable properties for a variety of applications. The following are the main conclusions:

1-Photo electrochemical (PEC) etching of N, P-type silicon is being investigate as one of the etching methods accessible today. Its qualities combine properties of electrochemical etching with laser, light -induced etching to provide a simple, low-cost, and controlled etching method. As a result, this approach may be used to etch either type of silicon (N-type or P-type) in a relatively short period.

2- The morphological features of the (PSi) material generated using the PEC etching method were spectacular and extremely sensitive to preparation conditions. In general, the porosity, pore width, and thickness of the (PSi) layer have grown as concentration and substrate resistivity, but the wall thickness between pores and nano crystallite size has dropped as concentration and substrate resistivity have increased. Depending on the random pattern of holes beginning, the pores have almost cylindrical and rectangular forms. Furthermore, the (PSi) layer's structure is crystalline, but the shift of its peak to a tiny diffraction angle indicates that the lattice constant has been somewhat expanded due to strain, which rises with increasing etching and substrate resistivity.

3- Other formation factors like as illumination and current density have a significant impact on the etching process and structural aspects of the resulting (PSi) layer, since light absorption supplies the necessary electron-hole pairs to commence the chemical interaction between the HF acid and the irradiated region.

4- When compared to other techniques, photo-electro-chemical etching takes less time to produce porous silicon surfaces because the laser or light helps to initiate the contact between the silicon and the acid.

5- When the comparison between the two types, that the N-type differ from P-type in terms of increased and decreased reactivity due to the N-type need to light un like P-type it works without light and the reaction for the two type has not controlled.

6-Relative permittivity and refractive index that is the reason for the increase and decrease the porosity is link mathematically to the properties, the higher of porosity the relative permittivity and refractive index will decrease.

7- One can see the difference between the capacitance for porous silicon produced from P-type and porous silicon produced from N-type bulk silicon this may be come from the effect of the concentration of the acid on the charge capacitance ,one can conclusion from that, the capacity for porous silicon produced by N-type are better than P-type .

8- We also conclude that the lower of acid concentration, the better porous silicon layer is form due to the skimming effect.

9- Through our work we conclude that the morphological properties is related to another and the increase and decrease that these properties because relate to the other mathematically.

10-Finally, also we conclude that porous silicon is able to increase the voltage of the solar cell when replacing the diode with a zinar diode of nano particles because of obtaining a quantitative restriction of the size of silicon particles.

6-2 Future Work

It would be interesting and important to carry out the following studies in future:

1- Study the electrical properties of resistivity and calculate the voltage current for the dark areas.
2- Finding the permittivity of other nanomaterial has added to porous silicon.
3- Using mathematical models to find the structural properties and the effect of the preparation conditions.
4- Study the effect of skimming time on structural properties and find electrical properties with the same effect.
5- Study of the effect of optical density on structural properties with low concentrations of N-type silicon.
6- Study the effect of structural properties on the efficiency of solar cells and finding the dark current.

Reference

1. Boul, P.J. and P.M. Ajayan, *Nanotechnology research and development in upstream oil and gas.* Energy Technology, 2020. **8**(1): p. 1901216.
2. Wang, B., Zhang, Z, Chang, K, *New deformation-induced nanostructure in silicon.* Nano letters, 2018. 18(7): p. 4611-4617.
3. Al-Kadumi, D.A.k.s., *Study the characteristic of nano structure porous silicon prepared by photo-electro-chemical etching.* 2012: p. 141.
4. Jiang, Y., Shen H, Pu T, Zheng ,C, Tang Q, Gao ,K, *High efficiency multi-crystalline silicon solar cell with inverted pyramid nanostructure.* Solar Energy, 2017. **142**: p. 91-96.
5. Wang, H.-P., Zhang Z, Ning ,Y, Fang ,X, *Fabrication of silicon hierarchical structures for solar cell applications.* IEEE Access, 2018. **7**: p. 19395-19400.
6. Stepanov, A., et al., *Synthesis of porous silicon by ion implantation.* Rev. Adv. Mater. Sci, 2015. **40**: p. 155-164.
7. Jung, D., Gyeong.S., Cho, Moon.T, *Fabrication and characterization of porous silicon nanowires.* Electronic Materials Letters, 2016. **12**(1): p. 17-23.
8. Ašmontas, S., et al., *Suppression of hot carriers by nanoporous silicon for improved operation of a solar cell.* Ukrainian Journal of Physical Optics, 2020. **21**(4): p. 207-214.
9. Ensafi, A.A., F. Rezaloo, and B. Rezaei, *Electrochemical sensor based on porous silicon/silver nanocomposite for the determination of hydrogen peroxide.* Sensors and Actuators B: Chemical, 2016. **231**: p. 239-244.
10. Bonanno, L.M. and E. Segal, *Nanostructured porous silicon–polymer-based hybrids: from biosensing to drug delivery.* Nanomedicine, 2011. **6**(10): p. 1755-1770.
11. Ismail, R.A., A.M. Alwan, and A.S. Ahmed, *Preparation and characteristics study of nano-porous silicon UV photodetector.* Applied Nanoscience, 2017. **7**(1-2): p. 9-15.
12. Rahmouni, S., et al., *Correlation between photoluminescence and ellipsometric measurements of porous silicon layers.* Optoelectronics and Advanced Materials, 2018. **12**(9-10): p. 5535-5558.
13. Fakhri, M.A., Basam ,G., Rashid, Najwan, H. *Synthesis of nano porous silicon heterostructures for optoelectronic applications*. in *AIP Conference Proceedings*. 2018. AIP Publishing LLC.

14. Torres-Costa, V., Ermei- Mäkilä., Sari -Granr., *Synaptic and fast switching memristance in porous silicon-based structures.* Nanomaterials, 2019. **9**(6): p. 825.
15. Almomani, M.S., Ahmed,N.M., *Broadband visible emission from photoelectrochemical etched porous silicon quantum dots containing zinc.* Materials Chemistry and Physics, 2021. **258**: p. 123935.
16. Alwan, A.M., D.A. Hashim, and M.F. Jawad, *Optimizing of porous silicon alloying process with bimetallic nanoparticles.* Gold Bulletin, 2018. **51**(4): p. 175-184.
17. Shcherban, N.D., *Review on synthesis, structure, physical and chemical properties and functional characteristics of porous silicon carbide.* Journal of Industrial and Engineering Chemistry, 2017. **50**: p. 15-28.
18. Katiyar, A., Tocco J,V., Yuan ,Li, Aggar.V, *Nuclear size changes caused by local motion of cell boundaries unfold the nuclear lamina and dilate chromatin and intranuclear bodies.* Soft Matter, 2019. **15**(45): p. 9310-9317.
19. Björnerås, C., Weyhenmeyer, G, A. Ch., *Widespread increases in iron concentration in European and North American freshwaters.* Global Biogeochemical Cycles, 2017. **31**(10): p. 1488-1500.
20. Sohail, M.G., et al., *Advancements in concrete mix designs: High-performance and ultrahigh-performance concretes from 1970 to 2016.* Journal of Materials in Civil Engineering, 2018. **30**(3): p. 04017310.
21. Chan, K.S. and T.J.E. Dwight, *Photoluminescence, morphological and electrical properties of porous silicon formulated with different HNO3 concentrations.* Results in Physics, 2018. **10**: p. 5-9.
22. Georgobiani, V.A., Georgobiani, V, A.,Gonchar, K, A, Elenl., *Porous silicon nanowire arrays for reversible optical gas sensing.* physica status solidi (a), 2018. **215**(1): p. 1700565.
23. awad, A.a., *Electrical properties of porous silicon prepared by stain etching.* 2008.
24. Rashid, M. and S.F. Ralph, *Carbon nanotube membranes: synthesis, properties, and future filtration applications.* Nanomaterials, 2017. **7**(5): p. 99.
25. Al-kadumi, A.K.S. and R.R. Attab, *The effect of Incorporation Salt and graphite on the relative permittivity, refractive index and capacitance for porous silicon.* journal of kerbala university, 2017. **15**(2): p. 241-249.
26. Feliczak-Guzik, A., et al., *Catalytic isomerization of dihydroxyacetone to lactic acid and alkyl lactates over hierarchical zeolites containing tin.* Catalysts, 2018. **8**(1): p. 31.

27. Dawood, Y.Z., *Preparation of porous silicon and its application in solar cell.* 2009.
28. Alwan, A.M., A.A. Yousif, and L.A. Wali, *A study on the morphology of the silver nanoparticles deposited on the n-type porous silicon prepared under different illumination types.* Plasmonics, 2018. **13**(4): p. 1191-1199.
29. Chen, C., Song,Z., Chuanxiao., *Achieving a high open-circuit voltage in inverted wide-bandgap perovskite solar cells with a graded perovskite homojunction.* Nano Energy, 2019. **61**: p. 141-147.
30. Suri, M., et al., *Enhanced Open-Circuit Voltage of Wide-Bandgap Perovskite Photovoltaics by Using Alloyed (FA1–x Cs x) Pb (I1–x Br x) 3 Quantum Dots.* ACS Energy Letters, 2019. **4**(8): p. 1954-1960.
31. Alwan, A.M., I.A. Naseef, and A.B. Dheyab, *Well controlling of plasmonic features of gold nanoparticles on macro porous silicon substrate by HF acid concentration.* Plasmonics, 2018. **13**(6): p. 2037-2045.
32. Jansen, D., Naber,Ch., Ectors, D. Z. Lu, X.-M. Kong, F., *The early hydration of OPC investigated by in-situ XRD, heat flow calorimetry, pore water analysis and 1H NMR: Learning about adsorbed ions from a complete mass balance approach.* Cement and Concrete Research, 2018. **109**: p. 230-242.
33. Korotcenkov, G., *Porous silicon: from formation to application: formation and properties, Volume One*. 2016: CRC Press.
34. Mekeef, Q.A., *Characteristics of silicon Nanostructures produced by High power Lasers.* 2010.
35. Dwivedi, P., Chauhan, N., Vivekananl. P., *Scalable fabrication of prototype sensor for selective and sub-ppm level ethanol sensing based on TiO2 nanotubes decorated porous silicon.* Sensors and Actuators B: Chemical, 2017. **249**: p. 602-610.
36. Massad-Ivanir, N., et al., *Porous silicon bragg reflector/carbon dot hybrids: synthesis, nanostructure, and optical properties*. Frontiers in chemistry, 2018. **6**: p. 574.
37. Zabotnov,S. V., Kurakina, D. A., Kashaev. F. V., A., *Structural and optical properties of nanoparticles formed by laser ablation of porous silicon in liquids: Perspectives in biophotonics.* Quantum Electronics, 2020. **50**(1): p. 69.
38. Valerii Myndrul, Roman Viter, Maryna Savchuk, N., *Porous silicon based photoluminescence immunosensor for rapid and highly-sensitive detection of Ochratoxin A.* Biosensors and Bioelectronics, 2018. **102**: p. 661-667.

39. Jabbar, A.A., A.M. Alwan, and A.J. Haider, *Modifying and fine controlling of silver nanoparticle nucleation sites and SERS performance by double silicon etching process.* Plasmonics, 2018. **13**(4): p. 1171-1182.
40. Hashim, D.A., A.M. Alwan, and M.F. Jawad, *An investigation of structural properties of monometallic (Ag, Pd) and bimetallic (Ag@ Pd) nanoparticles growth on macro porous silicon.* 2018.
41. Xiao, Q., Meng Gu, Hui Yang, Bing Li, Cu., *Inward lithium-ion breathing of hierarchically porous silicon anodes.* Nature communications, 2015. **6**(1): p. 1-8.
42. Adawyia, J.H., M.A. Alwan, and A.J. Allaa, *Optimizing of porous silicon morphology for synthesis of silver nanoparticles.* Microporous and Mesoporous Materials, 2016. **227**: p. 152-160.
43. Alwan, A.M., A.A. Yousif, and L.A. Wali, *The growth of the silver nanoparticles on the mesoporous silicon and macroporous silicon: a comparative study.* Indian Journal of Pure & Applied Physics (IJPAP), 2017. **55**(11): p. 813-820.
44. Bera, B., *Porous silicon and its nanoparticles: a theoretical study.* International Journal of Applied Nanotechnology, 2019. **5**(1): p. 14-18p.
45. Herino, R., Bomchil,G., Barla,K., Bertrand, C. J. L., *Porosity and pore size distributions of porous silicon layers.* Journal of the electrochemical society, 1987. **134**(8): p. 1994.
46. Abbas, O.A., *Structural,Morphological and electrical properties of porous silicon prepared under laser llumination.* 2007: p. 91.
47. Ali, W.H., *Environmental effects on stored porous silicon.* 2011.
48. Karthik, T., L. Martinez, and V. Agarwal, *Porous silicon ZnO/SnO2 structures for CO2 detection.* Journal of Alloys and Compounds, 2018. **731**: p. 853-863.
49. Searson, P., J. Macaulay, and S. Prokes, *The formation, morphology, and optical properties of porous silicon structures.* Journal of the Electrochemical Society, 1992. **139**(11): p. 3373.
50. Kanemitsu, Y., Uto H, Masumoto **Y**, Matsumoto T, Futagi T, Mimura H.., *Microstructure and optical properties of free-standing porous silicon films: Size dependence of absorption spectra in Si nanometer-sized crystallites.* Physical review B, 1993. **48**(4): p. 2827.
51. Prušáková, L., et al. *Quantum Size Effects in a Si: H Films Prepared by PECVD with Different Hydrogen-Diluted Silane*. in *Advances in Science and Technology*. 2010. Trans Tech Publ.

52. Salonen, J. and E. Mäkilä, *Thermally carbonized porous silicon and its recent applications.* Advanced Materials, 2018. **30**(24): p. 1703819.
53. FaragI, M., et al., *Investigation of dielectric and optical properties of MgO thin films.* Int. J. Adv. Eng., Technol. Comput. Sci., 2014. **1**(1): p. 1-9.
54. Cherif, A., et al., *Electrical investigation of the Al/porous Si/p+-Si heterojunction.* Physica B: Condensed Matter, 2013. **409**: p. 10-15.
55. Hadi, H.A., , Abood T.H. , Mohi A.T. , Karim M.S.l., *Impact of the etching time and current density on Capacitance-Voltage characteristics of P-type of porous silicon.* World Scientific News, 2017. **67**(2): p. 149-160.
56. Chakraborty, P., Naga, B., Gundratia, Chi., *Effect of stress on the capacitance and electric permittivity of three-dimensionally printed polymer, with relevance to capacitance-based stress monitoring.* Sensors and Actuators A: Physical, 2017. **263**: p. 380-385.
57. Sun, N., Zhou,D., Liu,W, Aikl., *Sputtered titanium nitride films with finely tailored surface activity and porosity for high performance on-chip micro-supercapacitors.* Journal of Power Sources, 2021. **489**: p. 229406.
58. Zhanabaev, Z.Z., Turlykozhayeva, D. A .l., *Current and capacitance hysteresis in porous semiconductor nanofilms.* Physical Sciences and Technology, 2020. **7**(3-4): p. 37-43.
59. Manakov, S., Ibraimov, M.K., Sagidolda ,Ye., *Detection of acetonitrile and chloroform using structures on the base of porous silicon.* Eurasian Chemico-Technological Journal, 2019. **21**(1): p. 89-93.
60. Xu, J., et al., *Preparation of porous silicon by electrochemical etching methods and its morphological and optical properties.* Int. J. Electrochem. Sci, 2019. **14**: p. 5188-5199.
61. Škrabić, M., , Kosović, M.,Gotić,M., Lara., *Near-infrared surface-enhanced Raman scattering on silver-coated porous silicon photonic crystals.* Nanomaterials, 2019. **9**(3): p. 421.
62. Roland, A., Dupuy,A., Machon,D., Fré., *In-depth study of annealed porous silicon: Understand the morphological properties effect on negative LiB electrode performance.* Electrochimica Acta, 2019. **323**: p. 134758.
63. Rustamov, F.A., Darvishov, N.H.,Bagiev,V.E ., *Reversible quenching of photoluminescence in stain etched porous silicon at HNO3 posttreatment and role of oxygen bonds.* Journal of Luminescence, 2018. **195**: p. 49-53.
64. Juyal, S., Kumar,Y., Prasad,B., *Stain etching of silicon with V2O5 and FeCl3: Effect of etching time on photoluminescence.* Materials Today: Proceedings, 2020. **26**: p. 3193-3196.

65. Kasim, S.T. and H. Hadi, *Illuminations Condition Effect on Optical Properties of Nanocrystalline Porous Silicon*. 2020, EasyChair.
66. Saverina, E.A., et al., *Porous Silicon Preparation by Electrochemical Etching in Ionic Liquids.* ACS Sustainable Chemistry & Engineering, 2020. **8**(27): p. 10259-10264.
67. Mogoda, A. and Y. Ahmad, *Electrochemical impedance study of porous silicon prepared by metal-assisted chemical etching.* Silicon, 2019. **11**(6): p. 2837-2844.
68. Shi, D., et al. *Backside ultraviolet illumination enhanced metal-assisted chemical etching for high-aspect-ratio silicon microstructures*. in *2020 21st International Conference on Electronic Packaging Technology (ICEPT)*. 2020. IEEE.
69. Volovlikova, O., S. Gavrilov, and P. Lazarenko, *Influence of illumination on porous silicon formed by photo-assisted etching of p-type Si with a different doping level.* Micromachines, 2020. **11**(2): p. 199.
70. Al-Douri, Y., N. Badi, and C. Voon, *Etching time effect on optical properties of porous silicon for solar cells fabrication.* Optik, 2017. **147**: p. 343-349.
71. Park, J., Y. Yanagida, and T. Hatsuzawa, *Fabrication of p-type porous silicon using double tank electrochemical cell with halogen and LED light sources.* Sensors and Actuators B: Chemical, 2016. **233**: p. 136-143.
72. Amrutha, M., F. Fasmin, and S. Ramanathan, *Effect of HF concentration on anodic dissolution of titanium.* Journal of The Electrochemical Society, 2017. **164**(4): p. H188.
73. Bregante, D.T., Bregante, D,T.,Potts, D, S.Ohsung., *Effects of Hydrofluoric Acid Concentration on the Density of Silanol Groups and Water Adsorption in Hydrothermally Synthesized Transition-Metal-Substituted Silicalite-1.* Chemistry of Materials, 2020. **32**(17): p. 7425-7437.
74. Daniau, A.-L.,Mari., *Orbital-scale climate forcing of grassland burning in southern Africa.* Proceedings of the National Academy of Sciences, 2013. **110**(13): p. 5069-5073.
75. Venturini, A.B., Ga, C. P., *Effect of hydrofluoric acid concentration on resin adhesion to a feldspathic ceramic.* J Adhes Dent, 2015. **17**(4): p. 313-20.
76. Kumeria, T., Steven J. P., McInnes, Shaheer, M., *Porous silicon for drug delivery applications and theranostics: recent advances, critical review and perspectives.* Expert opinion on drug delivery, 2017. **14**(12): p. 1407-1422.
77. Pérez, E.X., *Design, fabrication and characterization of porous silicon multilayer optical devices*. 2008: Universitat Rovira i Virgili.

78. Sanderson, T., *Mixology: a tool for calculating required masses and volumes for laboratory solutions*. bioRxiv, 2021.
79. Lascaud, J., Defforge, T., Dominique., *In-depth porosity control of mesoporous silicon layers by an anodization current adjustment.* Journal of Applied Physics, 2017. **122**(21): p. 214903.
80. Sailor, M.J., *Porous silicon in practice: preparation, characterization and applications*. 2012: John Wiley & Sons.
81. Krueger, N.A., Holsteen, A. L., Seung, K., *Porous silicon gradient refractive index micro-optics*. Nano letters, 2016. **16**(12): p. 7402-7407.
82. Gonchar, K.A., Moiseev, D.V., Ivan ,V., *Influence of H2O2 concentration on the structural and photoluminescent properties of porous silicon nanowires fabricated by metal-assisted chemical etching.* Materials Science in Semiconductor Processing, 2021. **125**: p. 105644.
83. Li, W., Y, F., *Tailoring porous silicon for biomedical applications: from drug delivery to cancer immunotherapy.* Advanced Materials, 2018. **30**(24): p. 1703740.
84. Omar, K. and K.A. Salman. *Effects of electrochemical etching time on the performance of porous silicon solar cells on crystalline n-type (100) and (111)*. in *Journal of Nano Research*. 2017. Trans Tech Publ.
85. Ahmed, A.M. and A. Mehaney, *Ultra-high sensitive 1D porous silicon photonic crystal sensor based on the coupling of Tamm/Fano resonances in the mid-infrared region.* Scientific reports, 2019. **9**(1): p. 1-9.
86. Salman, K.A., Z. Hassan, and K. Omar, *Effect of silicon porosity on solar cell efficiency.* Int. J. Electrochem. Sci, 2012. **7**(9): p. 376-386.
87. Rahmouni, S., et al., *Experimental study of porous silicon films prepared on N and P type monocrystalline silicon wafers.* Optoelectronics and Advanced Materials, Rapid Communications, 2017. **11**(1–2): p. 105-108.
88. Yang, X., Chen, F.Xi, X.S. Li, S. Li, X. Wan, W. Ma, P. ., *Porous Silicon Fabrication and Surface Cracking Behavior Research Based on Anodic Electrochemical Etching* ▲. Fuel Cells, 2021. **21**(1): p. 52-57.
89. Al-Rahime, N.M., H.I. Salman, and A.K. Al-Kadumi, *The effect of the acid concentration on morphology of nano crystalline silicon.* Materials Today: Proceedings, 2021.
90. Elia, P.,Nativ-Roth E, Zeiri, Y., Porat. Z., ***D**etermination of the average pore-size and total porosity in porous silicon layers by image processing of SEM micrographs.* Microporous and Mesoporous Materials, 2016. **225**: p. 465-471.

91. Syahidi, I., Prayogo, B. Pratama, K. Triyan., *Porous silicon fabrication on N-type Si (111) electrochemical anodization technique with HF: methanol solution.* Materials Today: Proceedings, 2021. **44**: p. 3430-3433.
92. Gopal, S., Chiappini,C., *Porous silicon nanoneedles modulate endocytosis to deliver biological payloads.* Advanced Materials, 2019. **31**(12): p. 1806788.
93. Abd Al-Hussan, S.M., N.A. Bakr, and A.N. Abd, *Effect of Zinc Oxide on the Efficiency Enhancement of Al/Li2O/PSi/Si/Al solar cell.* 2021.
94. Chiang, C., P. Juan, and T.-H. Lee, *Inhibition effect of a laser on thickness increase of p-type porous silicon in electrochemical anodizing.* Journal of The Electrochemical Society, 2016. **163**(5): p. H265.
95. Kheralla Shaheed Al-kadumi, A. and R. Ramadan Attab, *The effect of Incorporation Salt and graphite on the relative permittivity, refractive index and capacitance for porous silicon.* journal of kerbala university, 2017. **13**(2): p. 241-249.
96. Remache, L., Nychyporuk T., Guermit N., Fourmond E., Mahdjoub A., Lemiti M. Affiliations., *Optical properties of porous Si/PECVD SiNx: H reflector on single crystalline Si for solar cells.* Materials Science-Poland, 2016. **34**(1): p. 94-100.
97. Jane, A., Dronov, R.,Hodg,A., *Porous silicon biosensors on the advance.* Trends in biotechnology, 2009. **27**(4): p. 230-239.
98. Al-kadumi, A.K.S. and M.R. Sharif, *The Fabrication of Porous Silicon by Electrochemical Etching with Photo Assisted.* International Journal of Enhanced Research in Science Technology & Engineering, 2014. **3**(11): p. 167-171.
99. Zhang, M., et al., *Biological detection based on the transmitted light image from a porous silicon microcavity.* IEEE Sensors Journal, 2020. **20**(20): p. 12184-12189.
100. Saha, H., *Porous silicon sensors-elusive and erudite.* International journal on smart sensing and intelligent systems, 2017. **1**(1).
101. Anderson, R.C., R.S. Muller, and C.W. Tobias, *Investigations of the electrical properties of porous silicon.* Journal of the Electrochemical Society, 1991. **138**(11): p. 3406.
102. Rojas-Fernández, Y., M.J. Hernández-López, and A. Ramírez-Porras, *Study of oxide bands in p-type porous silicon layers.* Materials Science in Semiconductor Processing, 2019. **97**: p. 44-47.
103. Tregulov, V., *Features of the Frequency Dependence of Capacitance–Voltage Characteristics of a Semiconductor Structure of a Photoelectric*

Converter Based on ap–n Junction with an Antireflective Film of Porous Silicon. Technical Physics, 2018. **63**(12): p. 1824-1828.
104. Ramadan, R. and R.J. Martín-Palma, *Electrical characterization of MIS Schottky barrier diodes based on nanostructured porous silicon and silver nanoparticles with applications in solar cells.* Energies, 2020. **13**(9): p. 2165.
105. Rabiei, M., Palevicius, A., Monsh,A., *Comparing methods for calculating nano crystal size of natural hydroxyapatite using X-Ray diffraction.* Nanomaterials, 2020. **10**(9): p. 1627.
106. Das, M. and D. Sarkar, *Morphological and optical properties of n-type porous silicon: effect of etching current density.* Bulletin of Materials Science, 2016. **39**(7): p. 1671-1676.
107. Singh, N., M.K. Sahoo, and P. Kale, *Effect of MACE parameters on length of porous silicon nanowires (PSiNWs).* Journal of Crystal Growth, 2018. **496**: p. 10-14.
108. Knežević, N.Ž. and G.N. Kaluđerović, *Silicon-based nanotheranostics.* Nanoscale, 2017. **9**(35): p. 12821-12829.
109. i Morral, A.F., *Nanostructured alloys light the way to silicon-based photonics*. 2020, Nature Publishing Group.
110. Shin, D.H., Kim, J.H.,Chan., *Graphene/porous silicon Schottky-junction solar cells.* Journal of Alloys and Compounds, 2017. **715**: p. 291-296.
111. Šemić, E. and M. Čabaravdić. *Photovoltaic Systems with Sun Tracking Position*. in *International Conference "New Technologies, Development and Applications"*. 2019. Springer.
112. Dzhafarov, T. and A. Bayramov, *Porous silicon and solar cells.* Handbook of Porous Silicon: Second Edition, 2018. **2**(2): p. 1479-1492.
113. Susini, T., Renda I, Giani M, Vallario A, *Changing Trends in Mastectomy and Breast Reconstruction. Analysis of a Single-institution Experience Between 2004-2016.* Anticancer research, 2019. **39**(10): p. 5709-5714.

الخلاصة

- تتضمن الرسالة تحضير السيليكون المسامي النانوي بعملية القشط الكهروكيميائي الضوئي وبأستعمال ضوء ذو قدرة اضاءة (100W) بالنسبة للنوع (N) والقشط الكهروكيميائي للنوع (P) وبنفس طريقة التحضير لكلا النوعين وبمقاوميه R=(1-10 Ω. cm) وذلك بأستعمال تراكيز مختلفة من حامض الهيدروفلوريك/ الايثانول بنسبة (39-43%) والايثانول (99%) وقد تمت العملية بزمن قشط (10min) وبفولتية (10V).
- وقد تمت الدراسة نظريا للسيليكون المسامي من خلال طرق التحضير والخصائص الفيزيائية والكيميائية والتركيبية وأيضا تمت دراسة بعض تطبيقات السيليكون المسامي.
- كما وتمت المقارنة بين النوعين من خلال دراسة الخصائص المورفولوجيا والتركيبية لطبقات السيليكون المسامي باستعمال حيود الاشعة السينية (XRD) والمجهر الالكتروني الماسح (SEM) والطريقة الوزنية. وقد تبينت نتائج حيود الاشعة السينية ان الاختلاف بسيط بين النوعين بسبب اختلاف التفاعل مع الحامض اما التجانس يكون بالوسط بسبب التفاعل المتسلسل للسيليكون المسامي.
- واما بالنسبة لصور المجهر الالكتروني الماسح وقد بينت هناك اشكال مختلفة اذ تتغير الاشكال بتغير التراكيز وقد تبين بان عرض المسام وسمك طبقة السيليكون المسامي تزداد كلما يقل تركيز الحامض.
- وبالنسبة لقيم المسامية لطبقات السيليكون المسامي المقاسة بأستعمال الطريقة الوزنية لكلا النوعين فقد تبين بان المسامية تتغير نتيجة قوة تركيز التفاعل اذ تزداد كلما يقل تركيز الحامض نتيجة حدوث المزيد من التلميع مما يؤدي الى زيادة الكثافة بسبب الكمية الكبيرة من الفراغات في طبقة السيليكون المسامي وتقل بزيادة التركيز حيث يتم انتاج طبقة مسامية ضعيفة مما ينتج عنه كمية قليلة من الفراغات.
- وأيضا تمت دراسة الخصائص البصرية والكهربائية لكلا النوعين وقد تبين ان كلاهما يتأثران بسمك الطبقة فبزيادة سمك الطبقة تقل النفاذية النسبية ومعامل الانكسار وبالعكس.

اما بالنسبة للسعة الكهربائية فتتأثر بالمسامية وسمك الطبقة اذ تزداد كلما كانت طبقة المسامية أصغر بسبب وجود الهواء وسمك الطبقة أكبر بسبب كمية الشحنات والايونات الموجودة.

-وأخيرا تمت دراسة تطبيقات السيليكون المسامي حيث رأينا ارتفاعا في جهد الخلية الشمسية بعد إضافة عينة من السيليكون المسامي، وأكدت النتائج والقياسات التي حصلنا عليها كفاءته وقدرته على تضخيم الفولتية المتولدة من الخلية الشمسية. وذلك نتيجة لحصول الحصر الكمي في حجم جزيئات السيليكون مما يشير الى انه بالإمكان تحسين الخلية الشمسية من خلال استعمال طبقة نانوية من السيليكون واستعمالها كدايود في الخلية الشمسية.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة كربلاء
كلية التربية للعلوم الصرفة
قسم الكيمياء

دراسة خصائص السيليكون المسامي للسيليكون من النوع P والنوع N

رسالة مقدمة
الى كلية التربية للعلوم الصرفة – جامعة كربلاء
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء

من قبل
نور محمد كاظم
بكالوريوس (2015)
بأشراف
أ.د حميدة عيدان سلمان
أ.م.د احمد خير الله شهيد الكاظمي

2021م **1442هـ**