



**UNIVERSITI PUTRA MALAYSIA**

***STRUCTURAL, OPTICAL AND THERMAL PROPERTIES OF  
AS-PREPARED AND ANNEALED GOLD COATED POROUS  
SILICON***

**KASRA BEHZAD**

**FS 2012 55**

**STRUCTURAL, OPTICAL AND THERMAL PROPERTIES OF  
AS-PREPARED AND ANNEALED GOLD COATED POROUS  
SILICON**



By  
**KASRA BEHZAD**

**Thesis submitted to the School of Graduate Studies, Universiti Putra  
Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of  
Philosophy**

**December 2012**

*I dedicate this thesis to my wife, parents, sisters, brother and my daughter Andia for nursing me with affections, love and their dedicated partnership for success in my life.*



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

**STRUCTURAL, OPTICAL, AND THERMAL PROPERTIES OF  
AS-PREPARED AND ANNEALED GOLD COATED POROUS  
SILICON**

By

**Kasra Behzad**

**December 2012**

**Chairman: Professor Wan Mahmood Mat Yunus, PhD**

**Faculty: Science**

In this study, porous silicon (PSi) layers were prepared on n-type silicon (Si) substrates using the anodization method. Three sets of PSi samples were prepared under different current densities (10, 20, and 30 mA/cm<sup>2</sup>), where each set consisted of six samples that were prepared at different etching times (10, 20, 30, 40, 50, and 60 min). Gold was coated at different thicknesses (5, 10, and 20 nm) on PSi, Si, and glass substrates. Gold coated porous silicon (Au/PSi) with 20-nm thick gold layers, were selected for annealing at different temperatures (360, 600, 800, and 1000 °C).

The structural characterizations were performed by gravimetric method, Field Emission Scanning Electron Microscope (FESEM), and Energy Dispersive X-Ray Analyser (EDX). The porosity initially increased and then leveled off after attaining a certain value (47%–94%), but the thickness increased linearly with an increase in the etching time and current density (3.8–104  $\mu\text{m}$ ). For PSi samples, FESEM images showed that pores were formed on the surface. In the Au/PSi samples, a thin film of Au was coated on the porous structure. In the annealed Au/PSi samples, after annealing at a temperature higher than 360 °C, the surface of the samples were covered by silicon nanorods (SiNRs). The length of these nanorods varied between 110 and 1500 nm, and their diameter was tuned from 60 to 106 nm.

Photoluminescence (PL) and photoacoustic spectroscopy (PAS) were carried out as optical characterizations. PL spectra show a peak for PSi and Au/PSi samples that is blue shifted towards higher energy, in the range of 700 to 600 nm, as the porosity is increased from 47% to 94%. The intensity of PL peaks raised around 50% by increasing the porosity and decreased (92 to 98%) by coating the gold layer (5 to 40 nm). The absorbance spectra achieved by PAS at modulation frequency of 73 Hz. It shows that the optical absorption raised by increasing the porosity. Gold deposition increased the absorbance and also pushed them up in the range of 500-800 nm. The band gap was calculated from PL and PA spectrum

and the results are in good agreement with each other. The band gap increased linearly from 1.76 to 2.15 eV with porosity.

Thermal characterization was fulfilled by PAS with chopping frequency, 20-240 Hz. The thermal diffusivity (TD) measured for PSi, Au/PSi and annealed Au/PSi samples. The TD reduced (0.33-0.08 cm<sup>2</sup>/s) with raising the porosity due to limitation of phonon mean free path. By gold deposition due to the additional metal layer, the TD increased to more than 25-38% of the PSi. After annealing the Au/PSi samples the TD decreased to the lowest value (0.23 to 0.27 cm<sup>2</sup>/s) at 360 °C. By growing the nanorods the TD increased (0.4 to 0.53 cm<sup>2</sup>/s) at 600 °C to the maximum value. It decreased (0.36 to 0.50 cm<sup>2</sup>/s) by increasing the annealing temperature to 800 and 1000 °C.

Based on the first objective of dissertation; PSi samples were prepared, deposited and annealed under different conditions. By following the next three objectives, the structural, optical, and thermal investigations have been done on the samples to find the applicable applications for these samples. These investigations promote a novel field of study and can extend the applications of PSi as an interesting material in the nanotechnology and optoelectronics fields.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia  
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**STRUKTUR, SIFAT OPTIK DAN TERMA SILIKON TERSEDIA DAN  
ANIL EMAS BERSALUT SILIKON BERLIANG**

Oleh

**KASRA BEHZAD**

**Dicember 2012**

**Pengerusi: Profesor W. Mahmood Mat Yunus, PhD**

**Fakulti: Sains**

Dalam kajian ini, lapisan berliang silikon (PSi) telah disediakan keatas substrat silikon jenis-n (Si) dengan menggunakan kaedah penganodan. Tiga set sampel PSi telah disediakan di bawah ketumpatan semasa yang berbeza (10, 20, dan 30 mA/cm<sup>2</sup>), di mana setiap set terdiri daripada enam sampel yang telah disediakan pada masa punaran yang berbeza (10, 20, 30, 40, 50, dan 60 minit). Emas disalut berbeza ketebalan (5, 10, dan 20 nm) pada PSi, Si, dan substrat kaca. Silikon berliang bersalut emas (Au/PSi) dengan lapisan emas yang bertebalan 20 nm, telah dipilih untuk penyepuh Lindapan pada suhu yang berbeza (360, 600, 800, dan 1000 ° C).

Pencirian fizikal telah dilakukan dengan mengukur keliangan, ketebalan, mikroskop pengimbas elektron pancaran medan (FESEM) dan spektroskopi sinar-X penyebar tenaga (EDX). Keliangan pada mulanya meningkat dan kemudian mendatar selepas mencapai nilai tertentu (47% - 94%), tetapi ketebalan meningkat secara linear dengan peningkatan dalam masa punaran dan ketumpatan semasa (3.8-104  $\mu\text{m}$ ). Bagi sampel P*Si*, imej FESEM menunjukkan bahawa liang telah terbentuk di permukaan. Dalam sampel Au/P*Si*, filem nipis Au disalut pada struktur berliang. Dalam sampel Au/P*Si* disepuh lindap, selepas penyepuhlindungan pada suhu yang lebih tinggi daripada 360 °C, permukaan sampel telah dilindungi oleh nanorod silikon (SiNRs). Panjang nanorod ini adalah berbeza-beza antara 110 dan 1500 nm, dan diameternya telah siap sedia antara 60-106 nm.

Fotopenyinaran (PL) dan spektroskopi fotoakustik (PAS) yang telah dijalankan sebagai pencirian optik. PL spektrum menunjukkan puncak bagi P*Si* dan Au / P*Si* sampel yang biru beralih ke arah tenaga yang lebih tinggi, dalam lingkungan 700-600 nm, apabila keliangan meningkat daripada 47% kepada 94%. Keamatan puncak PL menaik sekitar 50% dengan meningkatkan keliangan dan menurun (92-98%) oleh salutan lapisan emas (5-40 nm). Spektrum keserapan yang dicapai oleh PAS pada frekuensi pemodulatan 73 Hz. Ia menunjukkan bahawa penyerapan optik yang dibangkitkan oleh peningkatan keliangan. Pemendapan emas meningkat keserapan dan juga menolak mereka dalam julat 500-800 nm.



Jurang jalur dikira dari spektrum PL dan PA dan keputusan adalah di dalam perjanjian yang baik. Jurang jalur meningkat secara linear dari 1.76 2.15 eV dengan keliangan.

Pencirian terma telah dipenuhi oleh PAS dengan frekuensi mencincang, 20-240 Hz. Kemerresapan terma (TD) diukur untuk PSI, Au / PSI dan sepuhlindap sampel Au/PSi. TD berkurangan (0.33-0.08 cm<sup>2</sup>/s) dengan meningkatkan keliangan yang disebabkan kepada had fonon laluan bebas. Disebabkan oleh pemendapan emas oleh lapisan logam tambahan, TD meningkat kepada lebih daripada 25-38% daripada PSI. Selepas penyepuhlindapan sampel Au/PSi TD berkurangan kepada nilai yang terendah (0.23-0.27 cm<sup>2</sup>/s) pada 360 °C. Dengan pertumbuhan nanorods TD meningkat (0.4-0.53 cm<sup>2</sup>/s) pada 600 °C kepada nilai maksimum. Ia menurun (0.36-0.50 cm<sup>2</sup>/s) dengan meningkatkan suhu penyepuhlindapan 800 °C dan 1000 °C.

Berdasarkan sampel objektif pertama disertasi; silikon berliang (Psi) telah disediakan dengan didepositkan dan disepuh lindap di bawah keadaan yang berbeza. Tiga objektif seterusnya adalah penyelidikan terhadap struktur, optik, dan terma telah dilakukan ke atas sampel untuk mencari aplikasi yang boleh diguna pakai untuk sampel ini. Penyelidikan ini menggalakkan satu bidang kajian novel dan boleh memanjangkan aplikasi PSI sebagai bahan yang menarik dalam bidang nanoteknologi dan optoelektronik.

## ACKNOWLEDGEMENTS

First of all, I would like to express my deepest praise to **God** who has allowed and give me strength, confidence, and patience to complete this project. Keep me in a way that I love you, worship you, and think about your creatures forever.

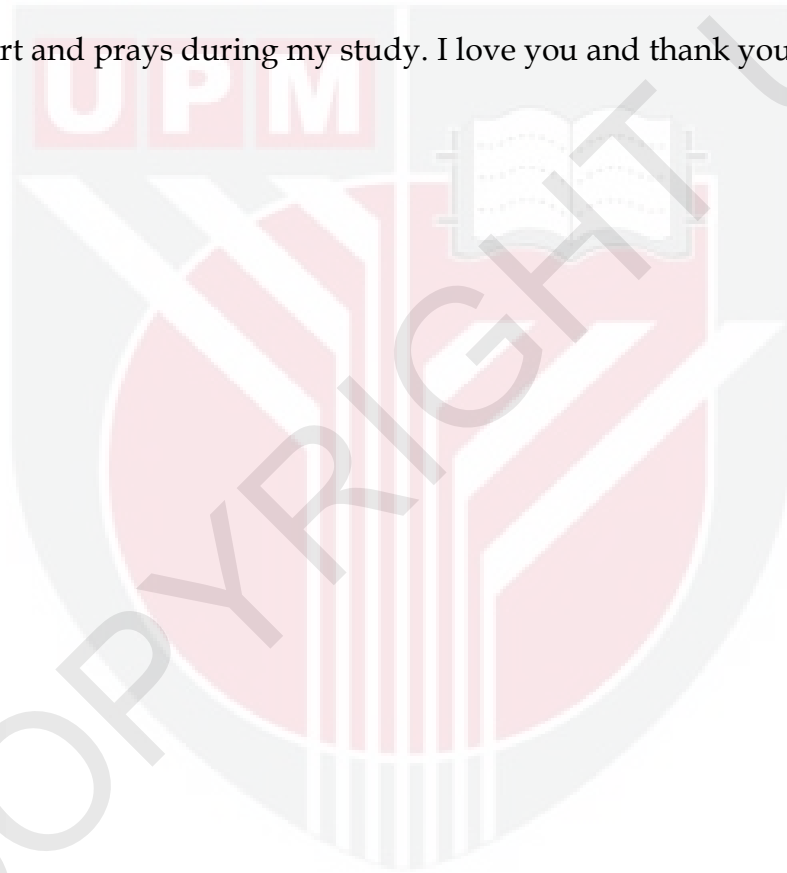
I wish to express my sincere thanks to Prof. Dr. Wan Mahmood Mat Yunus, my supervisor, for his guidance, supervisions, supports, valuable advise and providing me with all the necessary facilities. I would like to extend my sincere appreciation to my co-supervisors Prof. Dr. Zainal Abidin Talib and Prof. Dr. Azmi Zakaria for their assistance, guidance, and suggestions to keep me on track and focus during the research.

I am grateful to all the lecturers and staff of the science faculty for helping me feel home here at UPM. Special thanks are credited to Mrs. Norhaslinda Noruddin, Mrs. Kamsiah Alias, Mr. Muhamad Zamri, Dr. Ismayadi Ismail and the others whose names are not mentioned in this section for their kindly assistance in analysing the samples and their valuable effort and time.

I take this opportunity to record my sincere thanks to all my dear friends Amirreza Sadrolhosseini, Esmail Shahriari, Hamidreza Bahari, Yap Wing Fen, Roslina Mat Husin, Firas Al-asfoor, Abdullah Ahmad Ali, Manijeh Navaseri, Fasih Uddin, Reza Zamiri, Farhad Larki, Ahmad Kamali, Josephine Liew Ying, Nayere Soltani, Khor Shing Fen, Mahmoud

Goodarz Naseri, Mohd Sabri Mohd Ghazali, Firdaus, Nastaran Faraji, Alireza Kharazmi, Mohd Shahril Husin, and Nordin Bin Sabli for their help, encouragement and support. They share their knowledge, skills and experiences.

Last but not least, I would like to express thanks to my wife, father, mother, sisters, brother, niece, nephews and specially Marjan for their support and prays during my study. I love you and thank you.



I certify that a Thesis Examination Committee has met on 21 December 2012 to conduct the final examination of Kasra Behzad on his (or her) thesis entitled "Structural, optical and thermal properties of as-prepared and annealed gold coated porous silicon" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Abdul Halim Shaari  
Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

Elias Saion  
Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Internal Examiner)

Zulkifly Abbas  
Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Internal Examiner)

Joao Cardoso de Lima  
Professor  
Physics Department  
Santa Catarina Federal University (UFSC)  
Brazil  
(External Examiner)

---

SEOW HENG FONG, PhD  
Professor and Deputy Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date:

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

**Wan Mahmood Mat Yunus, PhD**

Professor  
Faculty of Science  
University Putra Malaysia  
(Chairman)

**Zainal Abidin Talib, PhD**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**Azmi Zakaria, PhD**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

---

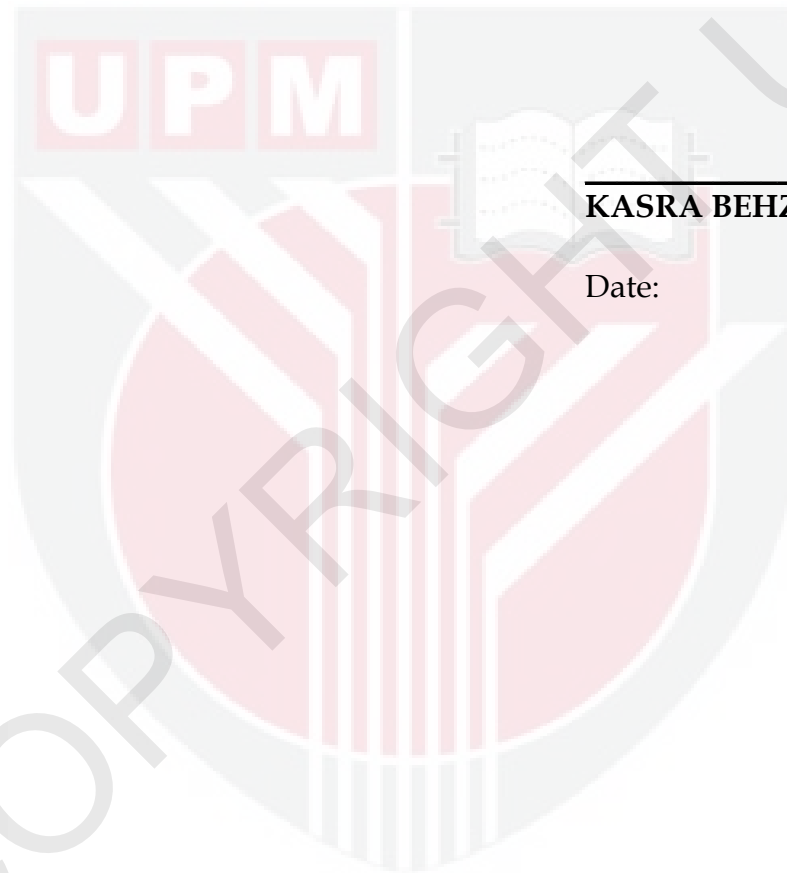
**BUJANG BIN KIM HUAT, PhD**

Professor and Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date:

## DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently submitted for any other degree at Universiti Putra Malaysia or other institutions.



**KASRA BEHZAD**

Date:

## TABLE OF CONTENTS

	Page
<b>ABSTRACT</b>	<b>III</b>
<b>ABSTRAK</b>	<b>VI</b>
<b>ACKNOWLEDGEMENTS</b>	<b>IX</b>
<b>DECLARATION</b>	<b>XIII</b>
<b>TABLE OF CONTENTS</b>	<b>XIV</b>
<b>LIST OF TABLES</b>	<b>XVI</b>
<b>LIST OF FIGURES</b>	<b>XVII</b>
<b>LIST OF ABBREVIATIONS</b>	<b>XXII</b>
<b>1 INTRODUCTION</b>	<b>1</b>
1.1 Porous Silicon (PSi)	1
1.2 Applications of Porous Silicon	3
1.2.1 Interference Filters	5
1.2.2 Distributed Bragg Reflectors (DBR)	6
1.2.3 Microcavities	8
1.2.4 Omnidirectional Mirrors	9
1.2.5 Waveguides	9
1.2.6 Sensors	10
1.2.7 Biosensors	11
1.2.8 Other Applications	12
1.3 Photoacoustic Spectroscopy (PAS)	12
1.3.1 Radiation Sources	14
1.3.2 Experimental Chamber	15
1.3.3 Data Acquisition	16
1.4 Photoluminescence Spectroscopy	17
1.5 Problem Statement	18
1.6 Objectives	19
1.7 Outline of Thesis	20
<b>2 LITERATURE REVIEW</b>	<b>22</b>
2.1 Porous Silicon; history, formation, and characterizations	22
2.2 Photoacoustic Spectroscopy	30
<b>3 THEORY</b>	<b>43</b>
3.1 Introduction	43
3.2 Fundamentals of Porous Silicon Preparation	43
3.3 Experimental Setup for Electrochemical Etching of Porous Silicon	50
3.4 Drying of the samples	54
3.5 Photoluminescence Spectroscopy	56

3.6	Photoacoustic Spectroscopy in Solid	59
3.6.1	Rosencwaig- Gersho Theory	60
3.6.2	Photoacoustic Signal Production	64
3.6.3	Six Special Cases	66
3.6.4	Thermal Expansion	72
3.6.5	Thermal Diffusion Model	72
<b>4</b>	<b>METHODOLOGY</b>	<b>76</b>
4.1	Introduction	76
4.2	Sample preparation	76
4.2.1	Preparation of Porous Silicon	77
4.2.2	Preparation of Gold Coated Porous Silicon	79
4.2.3	Annealing the Gold Coated Porous Silicon	80
4.3	Morphological Investigations	80
4.4	Photoacoustic Spectroscopy System for Optical Investigations	82
4.5	Photoacoustic Spectroscopy System for Thermal Investigations	84
4.6	Photoluminescence Spectroscopy	87
<b>5</b>	<b>RESULTS AND DISCUSSIONS</b>	<b>89</b>
5.1	Introduction	89
5.2	Physical and Structural Characterizations	90
5.2.1	Porous Silicon (PSi)	90
5.2.2	Gold Coated Porous Silicon (Au/PSi)	99
5.2.3	Annealed Gold Coated Porous Silicon	101
5.3	Optical Characterizations	107
5.3.1	Porous Silicon (PSi)	107
5.3.2	Gold Coated Porous Silicon (Au/PSi)	122
5.3.3	Annealed Gold Coated Porous Silicon	130
5.4	Thermal Characterizations	147
5.4.1	Porous Silicon (PSi)	147
5.4.2	Gold Coated Porous Silicon (Au/PSi)	152
5.4.3	Annealed Gold Coated Porous Silicon	155
<b>6</b>	<b>CONCLUSIONS</b>	<b>159</b>
	<b>REFERENCES</b>	<b>164</b>
	<b>APPENDICES</b>	<b>178</b>
	<b>LIST OF PUBLICATIONS</b>	<b>183</b>
	<b>BIODATA OF STUDENT</b>	<b>185</b>