



Fabrication and Characterization of Silicon and Polysilicon Nanogaps Electrodes Using Size Reduction Technique for Chemical and Biomolecules Detection

By

Thakra. S. Dhahi

(0841710268)

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TABLE OF CONTENTS

CONTENTS	PAGE
DECLARATION OF THESIS	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xv
LIST OF SYMBOLS	xviii
ABSTRAK	xx
ABSTRACT	xxi
CHAPTER 1 BACKGROUND	
1.1 Introduction	1
1.2 Overview of Nanotechnology	2
1.3 Problem Statements	5
1.4 Research Objective	7
1.5 Research Scopes	8
1.6 Thesis Skeleton	9
CHAPTER 2 NANOGAP STRUCTURE BASED BIOSENSOR	
2.1 Introduction	11
2.2 Overview of Nanostructures	12
2.3 Nanogap Structures	15
2.3.1 Vertical Nanogap	16
2.3.2 Lateral Nanogap	18
2.4 Methods for Fabricating Nanogap Structures	22
2.4.1 Mechanical Controllable Break Junctions	25

2.4.2	Electrochemical and Chemical Deposition for Nanogap Electrodes	28
2.4.3	Electromigration for Nanogap electrodes	32
2.4.4	Shadow Mask Evaporation.	35
2.4.5	Focused Ion Beam and Oxidative Plasma Ablation for Nanogap Electrodes	37
2.4.6	E-Beam lithography Technique	39
2.4.7	Size Reduction Technique	41
2.4.7.1	Thermal Processes	42
2.4.7.1.1	Wet Oxidation	43
2.4.7.1.2	Dry Oxidation	43
2.4.7.2	Etching Processes	44
2.4.7.2.1	Wet Etching	45
2.4.7.2.2	Dry Etching	45
2.5	Methods for Nanogap Characterization	47
2.5.1	Optical Characterization	49
2.5.2	Electrical Characterization	51
2.5.3	Chemical Sensing	53
2.5.4	Biomolecule Sensing	56

**CHAPTER 3 NANOGAP STRUCTURE BASED DEVICE:
DESIGN AND FABRICATION**

3.1	Introduction	61
3.2	Device Design and Chrome Mask Printing	61
3.2.1	Nanogap Design and Chrome Mask Printing	62
3.2.2	Pad Design and Chrome Mask Printing	66
3.3	Nanogap Structures Patterning	68
3.3.1	Process Flow for Silicon Nanogap Patterning	70
3.3.2	Process Flow for Polysilicon Nanogap Patterning	74
3.4	Thermal Oxidation and Pattern Size Reduction	78

3.4.1	Fabrication and Characterization of Silicon Nanogap Structures	79
3.4.2	Fabrication and Characterization of Polysilicon Nanogap Structures	87
3.5	Gold Pad Electrodes Patterning	95
3.6	Chapter Summary	99

CHAPTER 4 NANOGAP STRUCTURE BASED DEVICE:

ELECTRICAL AND CHEMICAL CHARACTERIZATION

4.1	Introduction	100
4.2	Electrical Characterization of the Nanogap Devices	100
4.2.1	Current-Voltage Measurements	101
4.2.2	Capacitance Permittivity and Conductivity Measurements	104
4.3	Chemical Characterization of the Nanogap Devices	111
4.3.1	pH Measurement	112
4.3.2	Yeast Concentration Measurement	117
4.4	Chapter Summary	122

CHAPTER 5 DNA HYBRIDIZATION DETECTION USING THE SILICON AND POLYSILICON NANOGAPS ELECTRODES

5.1	Introduction	123
5.2	Overview of DNA Immobilization and Hybridization Detection	123
5.3	Silicon and Polysilicon nanogaps Electrodes Surfaces Modification	125
5.4	Probe DNA Immobilization and Target DNA Hybridization	127
5.5	Electrical Measurement	128
5.5.1	DNA Immobilization and Hybridization Detection Using Silicon Nanogap Structure	129

5.5.2	DNA Immobilization and Hybridization Detection Using Polysilicon Nanogap Structure	134
5.6	DNA Concentration Optimization	138
5.7	Chapter Summary	140
CHAPTER 6 CONCLUSIONS AND FUTURE WORK		
6.1	Conclusions	141
6.2	Future Development	143
	REFERENCES	145
	APPENDICES	
	LIST OF JOURNAL PUBLICATIONS	160
	LIST OF CONFERENCE PROCEEDING	162
	LIST OF ACHIEVEMENTS	164

LIST OF TABLES

TABLE	CAPTION	PAGE
Table 2.1:	Compares the wet and dry etching process	47
Table 3.1:	Different dimensions of S_d on different designs	62
Table 3.2:	Compositions of RCA-1, RCA-2 and BOE	69
Table 3.3:	Recipe for silicon dry etched	70
Table 3.4:	Recipe for polysilicon dry etched	74
Table 4.1:	pH values for different yeast concentration	118
Table 5.1:	Used oligonucleotides	128

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LIST OF FIGURES

FIGURE	CAPTION	PAGE
Figure 2.1	A vertical nanogap fabricated between two electrodes using e-beam lithography. Shown are schematic of a sacrificial layer sandwiched between a silicon and polysilicon layer (a), SEM image of a vertical gap between a silicon and polysilicon electrodes (b) and two gold electrodes.	17
Figure 2.2	A schematic of lateral nanogap device.	18
Figure 2.3	Prototypes of planar nanogap electrodes for label free biomolecule sensing. Shown are: (a) metal nanogap electrodes and (b) the same after DNA immobilization with self-assembled monolayer (SAM).	20
Figure 2.4	Lateral nanogap fabricated using size expansion technique, before (a), and after (b) thermal oxidation process.	21
Figure 2.5	The sample mounting in a three point bending configuration. The bending beam consists of flexible phosphorus bronze covered with an insulating layer of capton. The junction is formed by breaking the electrode material. This is achieved by bending the beam. The elongation of the unglued section, u , is concentrated on the notch and will result in a fracture of the material. A voltage on the piezo element is used for fine adjustment of the coupling between the two electrodes.	26
Figure 2.6	SEM images of the samples prepared at 3 kHz with different Δt values: a) $\Delta t = 9s$, $d = 26$ nm; b) $\Delta t = 25s$, $d = 16$ nm; c) $\Delta t = 42s$, $d = 7$ nm; d) $\Delta t = 62s$, $d = 1$ nm.	30
Figure 2.7	a) Optical and b) Field Emission Scanning Electron Microscopy (FESEM) images of an array of nanogaps with sub-5nm separations after surface-catalyzed chemical deposition. FESEM images of two-fingered nanogap electrodes with magnifications of c) $\times 40\,000$ and d) $\times 320\,000$.	32
Figure 2.8	SEM image (false color) of the metallic electrodes fabricated by electron beam lithography and the electromigration-induced breakjunction technique. The image shows two gold electrodes separated by ~ 1 nm above an aluminium pad, which is covered with a ~ 3 nm thick layer of aluminium oxide. The whole structure was defined on a silicon wafer. The bright yellow regions correspond to a gold bridge with a thickness of 15nm and a minimum lateral size of ~ 100	33

nm. The paler yellow regions represent portions of the gold electrodes with a thickness of ~ 100 nm. Inset: schematic diagram of single-molecule transistors that contain individual di-vanadium molecules.

- Figure 2.9 Feedback-controlled electromigration (FCE) of a 16-junction array. a) SEM image of an array of 16 junctions made by electron beam lithography and shadow evaporation. Scale bar is 1 μm . b) G - V data from FCE of the 16-junction array. c) SEM images of nanogaps formed by parallel FCE of a 16-junction array that clearly shows the gold removed from the thin overlap junctions. Scale bar is 100 nm. 34
- Figure 2.10 Procedure of the angle-controlled shadow-masking method. The width of the metal mask shown in (e) is actually much wider than that shown in the illustration. 36
- Figure 2.11 a) Precise cutting of SWNTs with oxygen plasma introduced through an opening in a window of poly (methyl methacrylate) (PMMA) defined with e-beam lithography. b) Oxidative opening of a tube produces two point-contacts functionalized on their ends with carboxylic acids and separated by as little as 2 nm. cd) Device characteristics of individual SWNTs connected with DNA. Source-drain current versus V_G at a constant source-drain voltage (50 mV) before cutting (black curve: 1), after cutting (red curve: 2) and after connection with the DNA sequence shown (green curve: 3), for a semiconducting SWNT device (a) and a metallic SWNT device (b). Guanine, G; cytosine, C; adenine, A; thymine, T. 38
- Figure 2.12 TEM image of nanogaps with sizes 0.7 nm (a), 1.5 nm (b), 3 nm (c), 4 nm (d), 5 nm (e) and 6 nm (f). (g) HRTEM image of another 4 nm nanogap. The crystal lattice planes of the electrodes (g) are seen clearly. Inset to (a): SEM image of a full device consisting of electrodes (white lines) on a suspended $50 \mu\text{m} \times 50 \mu\text{m}$ Si_3N_4 membrane (black square) and connected to larger wires. Inset to (c): TEM image of electrodes (black lines) on a suspended Si_3N_4 membrane. 40
- Figure 2.13 Formation of oxide layer on silicon substrate through a dry oxidation process. 44
- Figure 2.14 HPM image for the micro-gap structure. 49
- Figure 2.15 (a) AFM image of a typical graphite nanogap. The scale bar is 1 μm . (b) Aerial view of a zoom-in on the gap area. The scale bar is 100 nm. 51

Figure 2.16	Typical current–voltage characteristic of nano-gap electrode measured at 296 K in vacuum.	53
Figure 2.17	The buffer pH effect on electrokinetic trapping for the preconcentration of β -PE protein after 30 min collection. Note that the pI of β -phycoerythrin protein is ~ 4.3 . Above pI values (pH 5–9), negative charged protein collected proportional with time, while in pH 4, the collection of positive protein is not observed due to positive protein adsorption on PDMS.	55
Figure 2.18	(a) Schematic diagrams of charge transport through a DNA molecule attached between two GNPs, separated by a dithiol spacer. The top diagram represents a fully matched DNA duplex and the bottom one represents a single base-pair mismatch. (b) Real-time resistance changes of the GNP film; (1)—(4) represent the relative changes in resistance of different degrees of mismatch introduced; (1) fully complementary, (2) 1-bp mismatch, (3) 4-bp mismatch, and (4) 11-bp mismatch. (c) Schematic illustrations of single DNA molecule detection. The top diagram represents an arbitrarily shaped ss-DNA molecule, which is stretched and attached to a pair of SWCNT electrodes. The bottom one depicts the double helix. The SWCNT electrodes were separated by a 27-nm gap. (d) The current signals for the ss-DNA molecule and the duplex.	60
Figure 3.1	Schematic of the design specifications for Mask 1.	63
Figure 3.2	The effects of S_d length on nanogap template. Shown are nanogap template with an S_d length of 600 μm (a) and 1100 μm (b).	63
Figure 3.3	The actual design of mask 1 before (a) and after (b) printing on the chrome glass.	64
Figure 3.4	HPM images of the imprints of nanogap designs after transferring from the chrome mask1 onto the different substrate materials for magnification x20: (a) Si substrates (b) Photo resist-layer, (c) Al-layer, and (d) Polysilicon layer.	65
Figure 3.5	Design specification for mask 2 used to fabricate pad electrodes.	67
Figure 3.6	The actual design of mask 2 before (a) and after (b) printing on the chrome glass.	67
Figure 3.7	Specification of wafer substrates: (a) silicon wafer and (b) SOI wafer.	68
Figure 3.8	Shows the PVD (a), and (b) ICP/RIE equipment.	72

Figure 3.9	The process flow for the fabrication of nanogap on silicon substrate. Shown are: SOI wafer (starting material) (a), a deposit of 135-nm Al-layer (b), a coating of photoresist (c), an exposure to Mask1 (d), a resist development (e), a wet etching of Al-layer (f), a nanogap structure after dry etching of silicon layer (g).	73
Figure 3.10	The process flow for the fabrication of polysilicon nanogap structure. (a) Silicon wafer (starting material); (b) deposit of 50 nm SiO ₂ layer; (c) deposit of 150 nm Si ₃ N ₄ layer; (d) deposit of 2000 nm polysilicon layer; (e) deposit of 135 nm Al layer; (f) photoresist (PR) coating; (g) Mask1 exposure; (h) the resist development; (i) wet etching for Al layer; (j) final gap structure after dry etching of polysilicon layer.	76
Figure 3.11	Shows PECVD (a), and LPCVD (b) equipment.	77
Figure 3.12	Shows the furnace for dry oxidation process.	78
Figure 3.13	FESEM image of fabricated silicon pattern before (a) and after (b) thermal oxidation and at the end of BOE (c).	81
Figure 3.14	The FESEM image of the nanopap structure for the 600 nm silicon layer after etching with BOE solution at the end of 40 min thermal oxidation process.	81
Figure 3.15	The FESEM images of the nanopap structure after etching with BOE solution at the end of each thermal oxidation step. Shown are the silicon layers after BOE etching at the end of the 1 st to the 9 th cycles with 20 min of oxidation ((a)-(i)) and the 9 th cycle with 15 min (j) and 10 min (k) of thermal oxidation.	84
Figure 3.16	The thickness of oxide layer (a) and gap-size (b) as a function of the 9 th cycle oxidation time. The relationship of gap-size and oxidation-thickness is shown in (c).	86
Figure 3.17	Photo mask used in exposure process (a) and SEM image of fabricated polysilicon pattern; before (b) and after (c) thermal oxidation treatment and at the end of BOE (d).	88
Figure 3.18	The SEM image of the nanopap structure for the 600 nm polysilicon layer after etching with BOE solution at the end of 40 min thermal oxidation process.	89
Figure 3.19	The SEM images of the nanopap structure after etching with BOE solution at the end of each thermal oxidation. Shown are the polysilicon layer at the end of the first to seventh cycles with 15 min of oxidation, (a)-(g); 7 th cycle with 10 min, (h); and 5 min, (i), of thermal oxidation.	92

Figure 3.20	The thickness of oxide layer (a) and gap-size (b) as a function of the 7 th cycle oxidation time. The relationship of gap-size and oxidation-thickness is shown in (c).	94
Figure 3.21	Process flow for the fabrication of gold pad electrodes on silicon nanogap structures. Shown are: (a) a deposit of Ti/Au-layer, (b) an exposure to mask 2 after depositing a photoresist layer, and (c) final device after resist development and wet etching the Ti/Au-layer.	96
Figure 3.22	Process flow for the fabrication of gold pad electrodes on polysilicon nanogap structures. Shown are: (a) a deposit of Ti/Au-layer, (b) an exposure to mask 2 after depositing a photoresist layer, and (c) final device after resist development and wet etching the Ti/Au-layer.	97
Figure 3.23	SEM images of the complete: (a) silicon, and (b) polysilicon nanogaps devices with gold pad electrode.	98
Figure 4.1	Current-voltages profiles of the: (a) silicon and (b) polysilicon nanogaps structures.	103
Figure 4.2	Capacitance of buffered solution with different concentration; Di water denoted deionized water. PBS is the Phosphate-Buffered Saline and 1000:1 PBS denotedes the solution which is diluted 100 times by adding the deionized water, (a) 6- nm silicon, and (b) 5- nm polysilicon nanogap structures.	105
Figure 4.3	Capacitance of buffer solution with different sizes of gap: (a) silicon, and (b) polysilicon nanogap structures; buffer solution was diluted in 100 times than PBS.	106
Figure 4.4	Schematic of a nanogap capacitor.	107
Figure 4.5	Permittivity profiles of silicon (a) and polysilicon (b) devices with different nanogap sizes.	109
Figure 4.6	Conductivity parameters of silicon (a) and polysilicon (b) devices with different nanogap sizes.	110
Figure 4.7	Capacitance profiles of (a) 6-nm silicon and (b) 5-nm polysilicon nanogaps devices in various buffer solutions of different pH.	114
Figure 4.8	Permittivity profiles of (a) 6-nm silicon and (b) 5-nm polysilicon nanogaps devices in various buffer solutions of different pH.	116
Figure 4.9	Conductivity profiles of (a) 6-nm silicon and (b) 5-nm polysilicon nanogaps devices in various buffer solutions of different pH.	116

Figure 4.10	pH profiles of different yeast solutions.	118
Figure 4.11	Capacitance profiles of (a) 6-nm silicon and (b) 5-nm polysilicon nanogaps devices with yeasts solutions of various concentrations.	119
Figure 4.12	Permittivity profiles of (a) 6-nm silicon and (b) 5-nm polysilicon nanogaps devices with yeasts solutions of various concentrations.	121
Figure 4.13	Conductivity profiles of (a) 6-nm silicon and (b) 5-nm polysilicon nanogaps devices with yeasts solutions of various concentrations.	121
Figure 5.1	Schematic Diagram of nanogap surface modification using NH ₂ - Amino functionalized group to label the AuNPs.	127
Figure 5.2	Schematic diagram of DNA hybridization based on labelling of probe-DNA with AuNPs.	128
Figure 5.3	Electrical measurement setup for: (a) Dielectric Analyzer; (b) Nanogap structure under probing.	129
Figure 5.4	Capacitance profile different situations of silicon nanogap structure under different conditions.	131
Figure 5.5	Conductivity profile different situation of silicon nanogap structure under different conditions.	132
Figure 5.6	Permittivity profile different situation of silicon nanogap structures under different conditions.	133
Figure 5.7	Capacitance profile for different situation of polysilicon nanogap structures under different conditions.	135
Figure 5.8	Conductivity profile for different situation of polysilicon nanogap structures under different conditions.	136
Figure 5.9	Permittivity profile different situation of polysilicon nanogap structures under different conditions.	137
Figure 5.10	Conductivity profiles of Silicon nanogap electrodes under different concentration of target DNA.	138
Figure 5.11	Conductivity profiles of polysilicon nanogap electrodes under different concentration of target DNA.	139

LIST OF ABBREVIATIONS

NG Structure	Nanogap Structure
DNA	Deoxyribonucleic acid
ss-DNA	Single-Stranded DNA
ds-DNA	Double-Stranded DNA
STM	Scanning Tunneling Microscope
AFM	Atomic Force Microscope
HPM	High Power Microscope
SEM	Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscope
DA	Dielectric Analyzer
I-V	Current-Voltage
C-F	Capacitance-Frequency
AuNPs	Gold Nanoparticles
LPCVD	Low Pressure Chemical Vapor Deposition
ISL	Iterative Spacer Lithography
RSL	Reversed Spacer Lithography
Au	Gold
Ti	Titanium
TiO ₂	Titanium Dioxide
UV	Ultra Violet
Ta ₂ O ₅	Tantalum Pentoxide
SiO ₂	Silicon Dioxide
SAM	Self-Assembled Monolayer
EBL	Electron-Beam Lithography
FIB	Focused Ion Beam
NIL	Nanoimprint Lithography
NEMS	Nanoelectromechanical Systems
NSB	Non-Specific Binding
LOD	Limit Of Detection
MCB	Mechanical Controllable Break
BPDN-DT	Bipyridyl-Dinitro Oligophenylene-Ethynylene Dithiol

BP-DT	Bipyridyl Oligophenylene-Ethynylene Dithiol
SERS	Surface Enhanced Raman Scattering
Si	Silicon
We	Working Electrode
Re	Reference Electrode
VGAP	Potential Difference Between the We and Re
SPM	Scanning Probe Microscopy
Pt	Platinum
DC	Direct Current
FCE	Feedback-Controlled Electromigration
PMMA	Poly-Methyl Methacrylate
SWNT	Single-Walled Nanotube
VG	Source-Drain Voltage
TEM	Transmission Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscopy
Si ₃ N ₄	Silicon Nitride
CPL	Conventional Photolithography
RNA	Rebonucleic Acid
HF	Hydrofluoric Acid
SFM	Scanning Force Microscopy
EB	Electron Beam
pH	Hydrogen concentration activity
B-PE	B-Phycoerythrin
PI	Isoelectric Point
PDMS	Polydimethylsiloxane
APTES	3-Aminopropyltriethoxysilane
SWCNT	Single-Walled Carbon Nanotube
Al	Aluminum
BOE	Buffer Oxide Etching
SOI	Silicon-On-Insulator
RCA	Ricinus Communis Agglutinin
NH ₄ OH	Ammonium Hydroxide
H ₂ O ₂	Hydrogen Peroxide

DIW	De-Ionized Water
HCl	Hydrochloric Acid
NH ₄ F	Ammonium Fluoride
N ₂	Nitrogen Gas
PVD	Physical Vapor Deposition
ICP/RIE	Inductive Coupled Plasma-Reactive Ion Etching
PR	Photoresist
RD6	Resist Developer 6
CF ₄	Carbonyl Fluoride
O ₂	Oxygen
Ar	Argon
SF ₆	Sulfur Hexafluoride
PECVD	Plasma-Enhanced Chemical Vapor Deposition
LPCVD	Low-Power Chemical Vapor Deposition
HN ₃	Hydrazoic Acid
PBS	Phosphate Buffer Saline
PCR	Polymerase Chain Reaction
NH ₂	Amine Functional Group
ac	Alternative Current
dc	Direct Current
Pt	Platinum
PdII	Palladium

LIST OF SYMBOLES

T_c	Mid Temperature
K	Kelvin
fs	Femto Second
mM	Mili Mole
$^{\circ}\text{C}$	Celsius Degrees
I	Current
V	Voltage
C	Capacitance
nm	Nanometer
Pm	Picometer
μm	Micrometer
hr	Hour
R_{EXT}	External Resistor
G_0	Conductance Quantum
R_{GAP}	Gap Resistance
Δt	Delta T
s	Second
\AA	Angstrom
Hz	Hertz
Z	Impedance
ng	Nano gram
S_d	Dimension For Side Angle
Ω	Ohm
cm	Centimeter
R^2	Correlation Coefficient
nF	Nano farad
ϵ°	Dielectric Constant
ϵ_r	Relative Permittivity
d	Size of The Gap
A	Capacitor Plate Area
R_C	Capacitive Reactance

f	Frequency
mg/mL	Milligram per Milliliter
min	Minute
bp	Base Pair
σ	Conductivity
ρ	Resistivity

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PEMBUATAN DAN PENCIRIAN ELEKTROD NANOGAP MENGGUNAKAN TEKNIK PENGECILAN SAIZ UNTUK PENGESANAN PENGACUKAN DNA

ABSTRAK

Elektrod ruangnano ditakrifkan sebagai sepasang elektrod yang dipisahkan oleh ruang berskala-nano. Dua kajian penting membolehkan para bukan-saintis untuk membayangkan perkembangan pengesan serta peranti elektronik dan elektronik yang berasaskan ruang nano, untuk pengesanan ultrasensitif DNA. Dalam kajian pertama, DNA berupaya menggerakkan cas dan menyambungkan elektrod yang dipisahkan oleh ruang berskala-nano manakala dalam kajian kedua, pergerakan cas telah terganggu apabila molekul dinyahaslikan daripada penglarasan sekatan dua-lapis kepada sekatan tunggal. Matlamat penyelidikan ini ialah untuk merekabentuk, membuat, mencirikan dan menguji peranti yang berasaskan elektrod-ruang nano, untuk pengesanan bio-kimia serta pemegungan dan pengacukan DNA. Walaubagaimanapun, tumpuan penyelidikan ini ialah untuk melakukan siasatan secara kimia dan elektrik tentang kesan perbezaan bahan dan saiz ruang ke atas rekabentuk elektrod berskala-nano. Pembuatan dan pencirian bagi ruang kurang 10 nm bagi kedua-dua elektrod silikon dan polisilikon merupakan sasaran utama penyelidikan ini. Dua pelitup telah direkabentuk untuk pembuatan ruang nano dan pelapik elektron atas wafer silikon (Si) dan silikon-atas-penebat (SOI) sebagai substrat permulaan masing-masing bagi pembuatan kedua-dua peranti polisilikon dan silikon ruang nano. Peranti elektrod ruang nano telah dibuat menggunakan teknik pengecilan saiz yang melibatkan proses-proses pengoksidaan haba dan punaran basah yang berjjukan dan berulang. Lapisan tebal bahan silikon dan polisilikon telah digunakan untuk memberikan kestabilan peranti sepanjang proses pembuatan ini. Pencirian morfologi permukaan struktur ruang nano yang dihasilkan telah dibuat menggunakan SEM dan FESEM. Keputusan pemerhatian menunjukkan ruang bersaiz 6-nm dan 5-nm masing-masing untuk struktur elektrod silikon dan polysilicon. Pelapik elektrod emas kemudiannya dibuat atas struktur silikon dan polisilikon ruang nano untuk menambah keberaliran elektrik dan kebertelusan peranti terutamanya semasa pengesanan bio-molekul. Kemuatan, kebertelusan dan keberaliran telah diukur secara elektrik untuk mencirikan struktur ruang nano yang terhasil dengan menggunakan penganalisis dielektrik. Walau bagaimanapun, pada mulanya alat *sourcemeeter* digunakan untuk mengukur arus dan mencirikan rintangan struktur ruang nano ini sebagai fungsi voltan yang dikenakan. Keputusan menunjukkan bahawa rintangan menurun apabila saiz ruang mengecil untuk membantu laluan pengaliran arus di antara dua elektrod. Seterusnya, peranti diuji secara kimia untuk pengukuran kepekatan pH dan yis. Keputusan menunjukkan bahawa kemuatan, kebertelusan dan keberaliran meningkat mengikut pH dan menurun mengikut kepekatan yeast. Akhirnya, peranti ini digunakan sebagai pengesan DNA untuk pengesanan pengacukan asid nuklik yang merupakan langkah penting dalam diagnosis molekul, pemprofilan genetik dan pemantauan persekitaran. Kumpulan fungsian Amine digunakan untuk mengubahsuai permukaan silikon dan polisilikon. Prob-Amine telah dilabelkan dengan partikel-nano emas untuk menandakan ujian ubahsuai-thiol DNA ke atas permukaan ruangnano. Pengesan-bio yang telah dibangunkan jelas membezakan pelengkap, bukan pelengkap dan ketidakterpadanan DNA tunggal melalui pengukuran kemuatan, keberaliran dan kebertelusan. Had pengesanan pengesan adalah pada aras 5 nmol/L daripada sasaran DNA. Sebagai kesimpulan, penyelidikan ini telah berjaya menunjukkan proses merekabentuk, membuat, mencirikan dan menguji pengesan-bio berasaskan ruang nano dengan penggunaan teknik pengurangan saiz untuk pengesanan pengacukan DNA.

FABRICATION AND CHARACTERIZATION OF NANOGAP ELECTRODE USING SIZE REDUCTION TECHNIQUE FOR DNA HYBRIDIZATION DETECTION

ABSTRACT

Nanogap electrodes may be defined as a pair of electrodes separated by nano-scale spacing. Two important studies enabled the non-scientists to envision the development of nanogap-based electrical and electronic sensors and devices for the ultrasensitive detection of DNA. In the first study DNA can transport charges and can bridge the electrodes separated by a nanoscale gap whereas for second study, charge transport is interrupted when the molecule undergo denaturation from double-stranded to single-stranded conformation. The aim of this research work is to design, fabricate, characterize, and test nanogap-electrode based device for biochemical detection and DNA immobilization and hybridization detection. However, the focus of this research is to investigate electrically and chemically the effect of different materials and gap sizes on the nanogap electrodes design. Fabrication and characterization of less than 10 nm gap for both silicon and polysilicon nanogap electrodes structures being the main target in this research. Two masks were designed for the fabrication of nanogap and electrodes pad on silicon (Si) and silicon-on-insulator (SOI) wafers as a starting substrate to fabricate polysilicon and silicon nanogap devices respectively. Nanogap electrodes devices were fabricated using a size reduction technique which involves sequential and repeated thermal oxidation and wet etching processes. A thick layer of silicon and polysilicon materials were used to provide device stability throughout the fabrication process. The surface morphology of the fabricated nanogap structure was characterized using SEM and FESEM. The observed results showed the gap size of a 6-nm and 5-nm for silicon and polysilicon electrodes structure respectively. Gold pad electrodes were then fabricated on the silicon and polysilicon nanogap structures to increase the electrical conductivity and permittivity of the devices especially during bio-molecules detection. Capacitance, permittivity and conductivity are measured electrically to characterize the fabricated nanogap structures using a dielectric analyzer. However, *sourcemeeter* equipment was first used to measure the current and characterize the resistivity of the nanogap structures as a function of applied voltage. It was found that the resistivity decreases with the reduction in gap sizes to aid the passage of current flow between the electrodes. Furthermore, the devices were chemically tested for the measurement of pH and yeast concentrations. It was found that the capacitance, permittivity and conductivity increased with pH and decreased with yeast concentrations. Finally, the devices were used as a DNA sensor for nucleic acid hybridization detection which is a key step in molecular diagnostics, gene profiling and environmental monitoring. Amine functionalized group from APTES were used to modify the silicon and polysilicon electrodes surface. Amine- groups (NH_2) were labeled with gold nanoparticles to tag a thiol-modified DNA probe onto the nanogap surfaces. The developed biosensors clearly differentiated complementary, noncomplementary and single mismatched DNA targets through the measurements of capacitance, conductance and permittivity. The detection limit of the sensors was 5 nmol/L of target DNA. As a conclusion, this research successfully demonstrated the process to design, fabricate, characterize and test nanogap based biosensor using size reduction technique for DNA hybridization detection.

CHAPTER 1

BACKGROUND

1.1 Introduction

Nanogap electrodes may be defined as a pair of electrodes separated by nano-scale spacing. They are the fundamental building blocks for the fabrication of nanometer-sized devices and circuits (Li et al., 2010). Two important discoveries enabled the nanoscientists to envision the development of nanogap-based electrical and electronic sensors and devices for the ultrasensitive detection of DNA: (1) DNA can transport charges and can bridge the electrodes separated by a nanoscale gap (Porath, Bezryadin, de Vries, & Dekker, 2000), and (2) charge transport is interrupted when the molecule undergo denaturation from double-stranded to single-stranded conformation (Iqbal et al., 2005). Thus, a ss-DNA probe is immobilized on nanogap surfaces and target hybridization is detected by direct measurement of electrical signals, such as capacitance/dielectric, resistance/impedance or field effect (Chen, et al., 2010) without the need of any labeling steps. A label free detection scheme is cost-effective and more reliable than a labeled one. A labeling assay is not only cumbersome and laborious but also suffers from ambiguous readout in optical detection due to potential spectral-cross talk and photobleaching between the tagging dyes (Roy, et al., 2009a).

In this chapter, an overview of nanotechnology is presented, followed by the problem statements. Next, the discussion with the objective of this research and the research scopes are described in detail. Lastly, the whole organization of the thesis skeleton is addressed.

1.2 Overview of Nanotechnology

Nanotechnology is the engineering of the functional systems at the molecular scale. This covers both current work and concepts that are more advanced. In its original sense, nanotechnology refers to the projected ability to construct items from the bottom up, or top-down, using techniques and tools being developed today to make complete, high performance products. Nanotechnology can be defined as the development and use of devices that have a characteristic size of only a few nanometers. The ultimate goal is to fabricate devices that have every atom in the right place. Such technology would give the opportunity to minimize the size of a device and to reduce the material, energy and time necessary to perform its task. Potential applications include electrical circuits, mechanical devices and medical instruments.

The topic of nanotechnology was again touched upon by physicist Richard Feynman on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and Van der Waals attraction would become more important, etc. This basic idea appears feasible, and exponential assembly enhances it with parallelism to produce a useful quantity of end products.

In 1965, Gordon Moore, one of the founders of Intel Corporation, made the outstanding prediction that the number of transistors that could be fit in a given area would double every

18 months for the next ten years. This it did and the phenomenon became known as Moore's Law. This trend has continued far past the predicted 10 years until this day, going from just over 2000 transistors in the original 4004 processors of 1971 to over 700,000,000 transistors in the Core 2. There has, of course, been a corresponding decrease in the size of individual electronic elements, going from millimeters in the 60's to hundreds of nanometers in modern circuitry.

Nanotechnology was first defined in a 1974 by Norio Taniguchi of the Tokyo Science University (Taniguchi, 1974). Since that time the definition of nanotechnology has generally been extended to include features as large as 100 nm. Additionally, the idea that nanotechnology embraces structures exhibiting quantum mechanical aspects, such as quantum dots, has further evolved its definition (Efremov, 1975).

Nanotechnology and nanoscience got a boost in the early 1980s with two major developments: the birth of cluster science and the invention of the scanning tunneling microscope (STM). This development led to the discovery of fullerenes in 1985 and the structural assignment of carbon nanotubes a few years later. In another development, the synthesis and properties of semiconductor nanocrystals were studied. This led to a fast increasing number of semiconductor nanoparticles of quantum dots.

In the early 1990s Huffman and Kraetschmer, discovered how to synthesize and purify large quantities of fullerenes. This opened the door to their characterization and functionalization by hundreds of investigators in government and industrial laboratories. Shortly after, rubidium doped C_{60} was found to be a mid temperature ($T_c = 32$ K) superconductor. At a meeting of the Materials Research Society in 1992, Dr. T. Ebbesen described to a spellbound audience his discovery and characterization of carbon nanotubes.