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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UNIVERSITI MALAYSIA PERLIS

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TABLE OF CONTENTS

CHAPTER 3 NANOGAP STRUCTURE BASED DEVICE: DESIGN AND FABRICATION

LIST OF TABLES

LIST OF FIGURES

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_2O_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 Dithoil

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_3N_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_4OH	Ammonium Hydroxide
H_2O_2	Hydrogen Peroxide

DIW	De-Ionized Water
HCl	Hydrochloric Acid
NH_4F	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
^{o}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
Å	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^o	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

PEMBUATAN DAN PENCIRIAN ELEKTROD NANOGAP MENGUNAKAN 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 pemegunan 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 silicon 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 berjujukan 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 silicon 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 elektrikal untuk mencirikan struktur ruang nano yang terhasil dengan menggunakan penganalisis dielektrik. Walau bagaimanapun, pada mulanya alat *sourcemeter* 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 ubahsuaian-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, *sourcemeter* 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.