DEVELOPMENT AND FABRICATION OF CARBON NANOTUBE (CNT) BASED pH SENSOR

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Development and Fabrication of Carbon Nanotube (CNT) Based pH sensor

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LIST OF ABBREVIATIONS

CNT	Carbon Nanotube
Ti	Titanium
Au	Aurum
SiO_2	Silicon Dioxide
SWCNTs	Single-Walled Carbon Nanotubes
MWNTs	Multi-Walled Carbon Nanotubes
DI Water	Deionized water
SDS	Sodium Dodecyl Sulfate
CNT-FET	Carbon Nanotube Field-Effect Transistor
HPM	High Power Microscope
AFM	Atomic Force Microscope
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscopy
1D	One-dimensional
2D	Two-Dimensional
3D	Three-Dimensional
CVD	Chemical Vapor Deposition
PECVD	Plasma-Enhanced Chemical Vapor Deposition
HRTEM	High-Resolution Transmission Electron Microscopy
NEMS	Nano Electromechanical Systems
MEMS	Micro Electromechanical Systems
AC	Alternating Current

DC	Direct Current
TCR	Thermal Coefficient of Resistivity
SAMs	Self-Assembled Monolayers
GAMA	Gas Assisted Microfluidic Alignment
PDMS	Polydimethylsiloxane
DEP	Dielectrophoresis
NADH	Nicotinamide Adenine Dinucleotide
ss-DNA	Single-Stranded DNA
CNFs	Carbon Nanofibres
Si	Silicon
PMMA	Polymethylmethacrylate
IPA	Isopropyl Alcohol
HCl	Hydrochloric Acids
HNO_3	Nitric Acids
DCM	Dichloromethane
Triton-X	Triton X-100
-OH	Carboxylic Acids
Al	Aluminum
EDX	X-ray Spectroscopy
C	Carbon
pH	pH Buffer Solution
H^+	Hydrogen
OH^-	Hydroxide
T	Time

f	Frequency
R	Resistance
V	Potential Difference
N_2	Nitrogen
DNA	Deoxyribonucleic acid
SOI	Silicon on Insulator
NO_2	Nitrogen Dioxide
Cr	Chromium
NH_3	Ammonia
Ar	Argon
CO	Carbon Oxide
He	Helium
I-V	Current-Voltage
WYKO	Wyko NT9100 Optical Profiler
P-type	Positive Type
RCA1	Standard Set of Wafer Cleaning Steps
RCA2	Standard Set of Wafer Cleaning Steps
R_s	Sheet Resistance
-COOH	Carboxylic Functional Group
-OH	Carboxylic Acids
|Sig|	Conductivity
PR	Photoresist

LIST OF SYMBOLS

%	Percent
nm	Nanometer
Pa	Pascal
eV	Unit of Energy
Å	Angstrom
d	Diameter
e	Electron Charge
h	Planck's Constant
M	Apparent Number of Conducting Channels
G	Conductance for CNTs
G_0	Quantum Unit of the Conductance
k	Kilo
Ω	Ohm
E_{gap}	Enerygy Band Gap
γ_0	C-C Tight Binding Overlap Energy
a_{c-c}	Nearest Neighbor C-C Distance
cm	Centimeter
℃	Celsius Degrees
A/cm^2	Current Density
Hz	Hertz
G	Giga
L	Suspended Length

$\Delta\delta/\Delta F$ Slope of the Force Deflection Curve

E_r Young's Moduli

G Shear Moduli

° Degree

µ Micro

µm Micrometer

µl Microliter

Torr Traditional unit of pressure

s seconds

mm millimeter

min minute

ml milliliter

ppm Parts Per Million

rpm Resolutions Per Minute

mg Milligram

V Voltage

Ω/sq Sheet Resistance

nm^2 Nanometer Square

cm^{-1} Wavenumber

Z Impedance

R Ohmic Resistance

X Reactance

t Time

Amp Ampere

S/cm	Conductivity
Q	Capacitance of a Conductor is the Ratio of the Charge
C	Capacitance of Conductor
I	Current
Δt	Delta Time
f	Frequency

Pembangunan dan Fabrikasi Tiub Nano Karbon (CNT) berdasarkan Sensor pH

ABSTRAK

Pembangunan, fabrikasi dan pencirian nanotube karbon tunggal berdinding (SWCNTs) berdasarkan sensor pH menggunakan SWCNT sejajar dilaporkan. Penjajaran SWCNT ditakrifkan oleh tiub nano karbon tunggal sejajar antara fabrikasi elektrod. Kajian ini melibatkan kajian SWCNTs penyebaran, penjajaran SWCNT antara elektrod mikrogap dan pencirian tentang kesan perubahan dalam tahap pH pada galangan, kekonduksian dan kapasitan SWCNT yang sejajar. Dalam kajian penyebaran SWCNT, SWCNTs telah tersebar dalam Isopropyl Alkohol (IPA), Diklorometan (DCM), Aseton dan Triton X-100 larutan. Proses ini telah mendapati bahawa SWCNT bersurai terbaik dalam penyelesaian IPA kerana SWCNTs tersebar kekal yang dan dapat dilihat daripada larutan yang jernih walaupun selepas 14 hari berbanding dengan DCM, aseton dan Triton X-100. Sebaliknya, yang SWCNTs dalam DCM, aseton dan Triton-X 100 telah menunjukkan SWCNT beku selepas 14 hari dari penyebaran. Sebuah topeng krom yang terdiri daripada 6 kumpulan dengan ukuran jurang yang berbeza direka bentuk. Setiap kumpulan mempunyai 5 reka bentuk yang berbeza untuk memudahkan penjajaran SWCNT. Selepas itu, alat-alat yang telah direka menggunakan bahan emas sebagai elektrod untuk meningkatkan kekonduksian elektrik dan ketelusan peranti. Kemudian itu SWCNT sejajar pada peranti direka dan menggunakan kaedah dielectrophoresis AC. Kaedah dielectrophoresis AC yang terlibat dalam kawalan voltan dan kekerapan untuk meningkatkan peluang penjajaran SWCNT antara mikrogap. Alat-alat telah dibawa ke pencirian elektrik sebelum dan selepas penjajaran SWCNT untuk membandingkan kesan ke atas kemuatan peranti dan telah mendapati bahawa kapasitan sebelum penjajaran SWCNT adalah lebih tinggi daripada selepas penjajaran SWCNT peranti. Sebelum penjajaran SWCNT, dielektrik peranti kapasitif adalah udara yang merupakan penebat yang lebih baik daripada SWCNT yang merupakan bahan semikonduktor. Fenomena ini adalah disebabkan oleh hakikat bahawa dielektrik penurunan medan elektrik dan kemuatan adalah berkadar songsang dengan medan elektrik. Sebaliknya, peranti telah diuji untuk impedans dengan menggunakan penyelesaian penampan pH. Sebagai nilai pH telah menurun, impedans juga telah menurun. Ion hidrogen didapati mengikat kepada kumpulan karboxyl SWCNT yang mewujudkan lubang-lubang yang positif dalam SWCNT yang seterusnya meningkatkan kekonduksian itu. Kesimpulannya, kajian ini berjaya menunjukkan proses untuk reka bentuk, fabrikasi dan ciri-ciri sensor berasaskan SWCNT.

Development and Fabrication of Carbon Nanotube (CNT) based pH Sensor

ABSTRACT

The development, fabrication and characterization of single-walled carbon nanotubes (SWCNTs) based pH sensor using aligned SWCNT were reported. The SWCNT alignment is defined by a single carbon nanotube aligned between the fabricated electrodes. This research involves the study of SWCNTs dispersion, alignment of SWCNT between microgap electrodes and characterization on the effect of change in the pH level on the impedance, conductance and capacitance of the aligned SWCNT. In the SWCNT dispersion study, the SWCNTs were dispersed in Isopropyl Alcohol (IPA), Dichloromethane (DCM), Acetone and Triton-X 100. It was found that SWCNT disperse best in the IPA solution because the dispersed SWCNTs have remained dispersed which can be observed from the clear solution even after 14 days as compared to DCM, acetone and Triton-X 100. On the other hand, the SWCNTs in DCM, acetone and Triton-X 100 have shown a thick mass of coagulated SWCNT after 14 days of dispersion. A chrome mask which consists of 6 groups with different gap measurement was designed. Each group has 5 different designs to facilitate the SWCNT alignment. After that, the devices were fabricated using gold material as electrode to increase the electrical conductivity and permittivity of the device. The SWCNT was then aligned on the fabricated devices using AC dielectrophoresis method. The AC dielectrophoresis method involved control in the voltage and frequency to increase the chance of SWCNT alignment between the microgap. The devices were brought to electrical characterization before and after SWCNT alignment to compare the effect on the device capacitance. It was found that the capacitance before SWCNT alignment is higher than after SWCNT alignment of the device. Before SWCNT alignment, the dielectric of the capacitive device is air which is a better insulator than SWCNT that is a semiconductor material. This phenomenon is due to the fact that dielectric decrease electric field and capacitance is inversely proportional to electric field. On the other hand, the device was tested for its impedance using pH buffer solutions. As pH value was decreased, impedance has also decreased. The hydrogen ions were found to bind to the carboxyl group of the SWCNT creating positive holes in the SWCNT hence increasing its conductivity. As a conclusion, this research successfully demonstrated the process to design, fabricate and characterize the SWCNT based sensor.

CHAPTER 1

BACKGROUND

1.1 Introduction

Single-walled carbon nanotube (SWCNT) based sensor is a new sensing materials and technologies. Generally, the detection mechanism was based on the change in electrical field of the SWCNT aligned between the two electrodes gap when a solvent was applied. SWCNT has many distinct properties that may be exploited to develop next generation of sensors. In this research, a Titanium/Aurum (Ti/Au) microgap electrode based sensors were fabricated to obtain higher sensitivity detection using real time measurement. The silicon dioxide (SiO_2) is formed using the dry oxidation process and Ti/Au layer is deposited using the thermal evaporator. The device was then patterned by using a chrome mask through standard photolithography process. After that, the device was brought to SWCNT alignment using the AC dielectrophoresis method. The SWCNT used were purchased from Sigma Aldrich. After the SWCNT was aligned between the electrode pads, a droplet of 10 µl from varying pH buffer solutions was dropped onto the SWCNT to obtain the conductivity, impedance and capacitance of the device. The electrical characterization was done by using the dielectric analyzer probing system.

1.2 Problem Statement

CNT have become the subject of intense investigation on electrical, mechanical, electromechanical and chemical properties. For CNT, it is divided into two major categories which are single walled-carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).

In CNT dispersion, it is hard to be dispersed in liquids like deionized water (DI water), oil, and polymer. It was found that the ultrasonic is a good method to obtain a dispersed CNT solution. Recently, a dispersion study of MWCNT with solvents such as Triton X-100, Tween 20, Tween 80, and Sodium Dodecyl Sulfate (SDS) has shown that Triton X-100 and SDS provide maximum and minimum dispersion respectively (Rastogi, et al., 2008). Another work was done on the dispersion by using Triton X-100 surfactant on functionalized MWCNT in the different mixtures of nitric, sulphuric, and hydrochloric acids (Randhawa, et al., 2012). Even though the number of CNT could be controlled, but most of the MWCNT aligned had metallic properties.

On the other hand, a single CNT aligned device has better sensitivity than a device that is aligned with a bundle of CNTs. Lai et. al. (2004), has shown that about feasible batch fabrication method for functional CNT sensors by using an automated injection system and produced CNT aligned in bundled results (Lai, Fung, Qu, Lei, & Li, 2004).

Recently, there are two categories for CNT attachment method which is direct growth and manual attachment of CNT on electrode pads. Both the methods were found to be effective in attaching CNT in the desired position. First of all, the growth technique of CNT is often applied. However, it requires some patterning of very tiny catalysts and high temperature on the exact position (Jang, Moon, Ahn, Lee, & Ju, 2004). However, it is extremely hard to get a uniform growth of CNT for each catalyst. Meanwhile, the manual attachment of CNT is a low cost and effective method of CNT attachment.

The material used as the electrode pad must have high thermal conductivity, low electrical resistivity and high sensitivity. In this research, the aluminum electrode pad has been used but it was substituted by gold to improve the sensitivity due to its better conductivity.

The microgap structured device was chosen to aid the SWCNT alignment process instead of the field effect transistor due to the shorter fabrication steps were required. Moreover, the CNT alignment process itself is a big challenge which requires long duration of time in order to get the SWCNT properly aligned.

1.3 Research Objective

The aim of this research is to design, fabricate, and characterization CNT sensor device based on Single walled Carbon Nanotube (SWCNT) aligned by using AC Dielectrophoresis Method for electrical testing by different pH buffer solutions.

However, the specific objectives of this research can be summarized as below:

i. To investigate the effect of dispersion of SWCNTs in various type of solvents such as IPA, DCM, Acetone, and Triton X-100.

ii. To study the AC Dielectrophoresis Technique in order to align Single-Walled Carbon Nanotube (SWCNT) between Aurum electrode gaps.

iii. To characterize the alignment of SWCNT sensor device from morphological aspects.

iv. To analyze the electrical characterization for before and after SWCNT alignments by apply different concentration of pH buffer solutions in certain condition.

1.4 Research Scope

This research work is embarked based on the following scopes, and each scope addressed in details.

This research is started with a mask design created using AutoCAD tool software. Then, the design sent over to a manufacturing company to transfer the design onto a chrome mask.

In the second scope, the fabrication process of SWCNT sensor with gap less than 10 μm is developed and optimized. Conventional photolithography technique is used to fabricate the device.

Next, the third scope is dispersion for debundling was studied and determined for alignment process.

The fourth scope for this research is a single strand of SWCNT was aligned properly between the electrode gap by using AC Dielectrophoresis Method through precise control of the voltages and frequencies.

Finally, the last scope is characterization and optimization of the fabricated device. Optical Microscope, Scanning Electron Microscope (SEM), Field Emission Scanning Electron Microscopy (FESEM), Atomic Force Microscope (AFM), Optical Microscope and 3D Profilometer are employed to observe the fabricated structures. The electrical measurement is performed on the fabricated sample using Dieelectric Analyzer to analyze before and after SWCNT alignment with different values of pH buffer solutions.

1.5 Thesis Overview

This thesis consists of 5 chapters. The first chapter provides an introduction of this research to readers. The chapter includes the objectives and the project scopes of this research.

The chapter 2 is the literature review of carbon nanotubes (CNTs) based sensor with emphasis on development of CNTs based sensor, including properties of CNTs, CNTs dispersion, CNTs alignment, CNTs application, and fabrication technologies employed.

The chapter 3 describes the process flow of the fabrication, SWCNTs dispersion, Single-Walled Carbon Nanotube (SWCNT) alignment, morphological characterization and electrical characterization.

The 4 chapter contains the results obtained and data analysis of this research. The results of morphological, dispersion results and electrical characterization of SWCNT sensor with different pH buffer solutions. The data obtained were tabulated and plotted into graph for analysis. Discussion and explanation based on the results are presented in this chapter.

Finally, chapter 5 is the conclusion for this thesis and incorporates the overview of the results in this thesis. There are some future work recommendations for this project as there is huge potential for further development and exploitation.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides the literature review of the development and fabrication of Carbon Nanotube (CNT) based sensor that has been done by some researchers. This chapter also includes the fundamental theories of CNT properties, several method of manual attachment of CNT, development of CNT sensor device and its applications. For CNT manual attachment, several methods such as micro scale fluidic channel (Yan, Li, Chen, Chan-Park, & Zhang, 2006), chemically modified adsorption (LeMieux, et al., 2008), top-down approach (Orofeo, Ago, Yoshihara, & Tsuji, 2009), and external electric field guidance (Ural, Li, & Dai, 2002) & (Zhang, et al., 2001) were explained. However, the method above only can produce in low device yield and still lack some practical application on a large scale.

2.2 Carbon Nanotubes

Carbon Nanotubes (CNTs), is a tube-shaped material, made of carbon, also called a carbon buckytubes with a cylindrical nanostructures. The cylindrical carbon nanotubes have huge potential in development and applications such as nano-electronics, optics and materials application. CNTs was discovered by NEC Corporation of Japan in 1991, Iijima (Iijima, 1991), who specialized in nanostructured materials. CNTs can be grow by chemical