THE FABRICATION OF TiO_2 NANOSTRUCTURES ON POROUS SILICON FOR THERMOELECTRIC APPLICATION

NURHAYATI BINTI MUHD RAMLI NARAYANAN

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Universiti Tun Hussein Onn Malaysia

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged.

Student : …..…………………………………………………………………………
NURHAYATI BINTI MUHD RAMLI NARAYANAN

Date : ………………..14 MARCH 2021……………………………...

Supervisor : …..…………… ……………………………….
ASSOC. PROFESSOR DR. MOHD KHAIRUL BIN AHMAD

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ABSTRACT

In the era of globalization, heat is a no doubt to be found in nearly all devices and applications of energy. However, that lost heat is actually representing a substantial portion of energy losses that need to be recovered. The recovery of lost heat is a crucial step in reducing our energy requirements. Therefore, the needs for high-performance thermoelectric (TE) materials to convert heat into electricity and vice versa is become compelling. Nowadays, the leading TE materials are Bi_2Te_3-based alloys, PbTe, PbSe, SiGe, Mg_2X (X = Si, Ge, Sn), skutterudite, and half-Heusler alloys. However, there are some problems arise since most of these rare earth alloy-based TE materials, such as Bi_2Te_3 and PbTe, suffer from thermal and chemical instabilities. Besides, it is also high toxicity, relatively low availability and high cost. On the other hand, transition metal oxide materials have received attention such as TE materials as they are cost-effective, environmentally friendly, and available over a range of compositions. Titanium Dioxide (TiO_2) is among the most widely used transition metal oxides, which takes advantage of its versatility. In this project, a novel and facile method of low temperature hydrothermal method was implemented for the growth of TiO_2 nanostructures on porous silicon by using Titanium (IV) Butoxide (TBOT) and Hydrochloric acid (HCL) electrolytes. As a substrate, porous silicon samples were fabricated by electrochemical-etching (ECE) process which helps in providing large internal surface that can induce large absorption of TiO_2 nanostructures. Optimization of etching time and current density supplied during the ECE process can alter the morphological properties of the porous silicon sample produced. Next, variation in reaction times during hydrothermal process is also studied since it can affect both the growth pattern and coverage area of TiO_2 nanostructures on the porous silicon substrate. Finally, Hall Effect measurement was conducted to calculate the electrical conductivity, carrier concentration and mobility of the TiO_2 materials on the porous silicon sample produced. In conclusion, there is a possibility for porous silicon with a high porosity to be a good adhesive template for the growth of TiO_2 nanostructures to be contributed as TE materials.

ABSTRAK

Dalam era globalisasi, haba tidak diragui ditemui dalam hampir semua peranti dan aplikasi tenaga. Walau bagaimanapun, haba yang hilang itu sebenarnya mewakili sebahagian besar kerugian tenaga yang perlu pulih. Pemulihan haba yang hilang adalah langkah penting dalam mengurangkan keperluan tenaga kita. Oleh itu, keperluan untuk bahan termoelektrik (TE) berprestasi tinggi untuk menukarkan haba menjadi elektrik dan sebaliknya menjadi menarik. Pada masa kini, bahan TE terkemuka adalah aloi. Walau bagaimanapun, terdapat beberapa masalah yang timbul kerana kebanyakan bahan-bahan TE berasaskan aloi nadir bumi ini, seperti Bi2Te3 dan PbTe, mengalami ketidakstabilan terma dan kimia. Selain itu, ia juga merupakan ketoksikan yang tinggi, ketersediaan yang agak rendah dan kos yang tinggi. Sebaliknya, bahan-bahan logam oksida peralihan telah mendapat perhatian seperti bahan TE kerana ia kos efektif, mesra alam, dan tersedia di atas pelbagai komposisi. Titanium Dioxide (TiO_2) adalah antara oksida logam peralihan yang paling banyak digunakan, yang mengambil kesempatan daripada serba boleh. Dalam projek ini, satu kaedah hidroterma suhu rendah dan mudah digunakan untuk pertumbuhan struktur nano TiO_2 pada silikon berliang dengan menggunakan elektrolit asid Titanium (Butoxide) (TBOT) dan asid hidroklorik (HCL). Sebagai substrat, sampel silikon berliang dihasilkan oleh proses electrochemical-etching (ECE) yang membantu dalam menyediakan permukaan dalaman yang besar yang boleh menyebabkan penyerapan besar nanostruktur TiO_2. Pengoptimuman masa etsa dan kepadatan semasa yang dibekalkan semasa proses ECE dapat mengubah sifat morfologi sampel silikon berliang yang dihasilkan. Seterusnya, variasi dalam masa reaksi semasa proses hidroterma juga dikaji kerana ia boleh menjejaskan kedua-dua corak pertumbuhan dan kawasan perlindungan TiO_2 struktur nanos pada substrat silikon berliang. Akhirnya, pengukuran Hall Effect telah dijalankan untuk mengira kekonduksian elektrik, kepekatan carrier dan mobilitas bahan TiO_2 pada sampel silikon berliang yang dihasilkan. Kesimpulannya, ada kemungkinan silikon berpori dengan keliangan tinggi menjadi templat pelekat yang baik agar pertumbuhan struktur nano TiO_2 dapat disumbangkan sebagai bahan TE.

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LIST OF SYMBOL AND ABBREVIATIONS

2D	-	2 dimensions
3D	-	3 dimensions
Å	-	Angstrom
°C	-	Degree Celcius
eV	-	Electron Volt
h	-	Thickness of the sample
μ	-	Mobility
μH	-	Hall mobility
ρ	-	Resistivity
ρsheet	-	Sheet resistivity
σ	-	Conductivity
q	-	Electron charge
n	-	Electron concentration
cm	-	Centimeter
mA	-	Milliampere
min	-	Minute
ml	-	Milliliter
nm	-	Nanometer
µm	-	Micrometer
nsheet	-	Sheet carrier concentration
pSi	-	Porous silicon
A	-	Cross-sectional area
AFM	-	Atomic Force Microscope
Bi	-	Bismuth
BOE	-	Buffered Oxide Etch
CO_2	-	Carbon Dioxide
DC	-	Direct Current
DI	-	Deionized water

DSSC	-	Dye-synthesized Solar Cells
ECE	-	Electrochemical Etching
FESEM	-	Field-Emission Scanning Electron Microscope
FL	-	Fluorometer
FTO	-	Fluorine-doped Tin Oxide
FWHM	-	Full Width Half Maximum
GaAs	-	Gallium Arsenide
HCL	-	Hydrochloric acid
HF	-	Hydrofluoric acid
LED	-	Light Emitting Diode
Mg	-	Magnesium
O_2	-	Oxygen gas
Pb	-	Lead
R	-	Resistance
RHsheet	-	Sheet Hall coefficient
RMS	-	Root Mean Square
Rs	-	Sheet resistance
S	-	Seebeck coefficient
Se	-	Selenium
Si	-	Silicon
SiC	-	Silicon Carbide
Sn	-	Tin
T	-	Temperature
Te	-	Tellurium
TE	-	Thermoelectric
TBOT	-	Titanium (IV) Butoxide
TiO_2	-	Titanium Dioxide
V	-	Voltage
VH	-	Hall Voltage
XRD	-	X-ray Diffraction
ZnO	-	Zinc Oxide
ZT	-	Figure of merit

CHAPTER 1

INTRODUCTION

1.1 Overview

Direct conversion of heat into electricity through advanced thermoelectric (TE) materials has been one of the most attractive solutions to overcome waste heat issues. Heat is found in nearly all applications of energy, and lost heat represents a substantial portion of energy losses. Therefore, thermoelectric oxides, which are naturally abundant, nontoxic and low-cost elements, are introduced in order to recover the problem of heat being wasted.

1.2 Research background

With an abundant amount of heat being lost as waste heat, the needs for high-performance thermoelectric materials is becoming compelling. Thermoelectric materials can convert heat into electricity directly and *vice versa*. In recent years, great progress has been made in improving their dimensionless figure of merit (ZT), which determines the conversion efficiency of TE devices.

ZT is related to three "interlocked" factors—Seebeck coefficient, electrical conductivity and thermal conductivity [1]. Generally, the concept of increasing electrical properties but decreasing thermal conductivity is of great importance for thermoelectric materials. In this project, titanium dioxide (TiO_2) is studied to investigate its potential as a thermoelectric material. Moreover, TiO_2 is less expensive, chemically stable and non-toxic material.

TiO_2 is an important n-type semiconductor with a wide band gap of 3.02 eV and 3.20 eV for rutile and anatase phases, respectively. Rutile, anatase and brookite are the three phases of TiO_2 semiconductor [2]. An experiment is conducted by growing TiO2 nanostructures on a porous silicon (pSi) substrate by the low-temperature hydrothermal method. Generally, a high surface area of silicon nanostructures is formed by the corrosion process of silicon crystallite. By manipulating the parameters, this corrosion process is able to control the size of pores, as well as the thickness and porosity of the porous silicon. It has the ability to combine silicon-specific advantages such as abundance and process-ability with a simple and scalable fabrication process since the porous silicon is a different form of nanostructured silicon [3].
A previous study has shown that the investigation and introduction of porous silicon began at Bell Laboratories by Arthur Uhlir Jr. and Ingeborg Uhlir with their work on silicon (Si) and germanium (Ge) in the 1950s [4]. In recent years, the study of nanostructured silicon as one of the thermoelectric materials has been conducted by many researchers all over the world. The focus is on the rare characteristics of porous silicon since there is a possibility of this material to be used in many applications. Therefore, in this research, the growing of TiO_2 nanostructures on a porous silicon substrate is fabricated in order to study its electrical conductivity.

1.3 Problem statement

By harvesting and converting waste heat into electricity, global climate warming problems are assumed to be solved with TE power generation technology. More than 60% of the energy produced in the U.S. is never utilized, most of it in the form of waste heat [5]. The recovery of lost heat is a crucial step in reducing our energy usage. Nowadays, Bi_2Te_3-based alloys, PbTe, PbSe, SiGe, Mg_2X (X = Si, Ge, Sn), skutterudite, clathrate, Zintl and half-Heusler alloys are known as TE materials. However, most rare earth alloy-based thermoelectric materials, such as Bi_2Te_3 and PbTe, suffer from chemical and thermal instabilities and are expensive, high in toxicity as well as low in their availability [1].

In addition, their limitations in large-scale commercial applications could be the consequences of their toxic and rare compounds. Moreover, problems faced by the manufacturers in converting the materials for engineering devices have limited the materials' use in the thermoelectric field. Therefore, nowadays, transition metal oxides are abundantly studied by researchers all over the world regarding the materials' possible contribution as thermoelectric materials. Being environmentally friendly, cost-effective and high availability are the reasons for the studies. Some oxide elements such as cobalt, zinc rhodium, titanium, copper, manganese, molybdenum, tungsten and vanadium offer a wide range of electronic properties ranging from conducting, semiconducting as well as insulating [6]. TiO_2 is among the most intensively studied and the most widely used transition metal oxides, which takes advantage of its versatility. Anatase, rutile and brookite are three most common polymorphs of TiO_2. Of these, rutile is a stable phase under ambient conditions, while both brookite and anatase are metastable [7].

1.4 Research objectives

Regarding the problems stated above, TiO_2 is considered as one of the potential TE materials. The study in this project is more focused on the electrical properties of the sample. Therefore, the growth of TiO_2 nanostructures on a porous silicon substrate is fabricated based on the three objectives as stated below:

i. To fabricate a porous silicon thin film by electrochemical etching (ECE) process and characterise the properties of the thin film.
ii. To fabricate rutile-phased TiO_2 nanostructures on the porous silicon thin film by a low-temperature hydrothermal method and characterise the properties of the thin film.
iii. To calculate the electrical conductivity of the TiO_2 nanostructures on porous silicon by Hall effect measurement.

1.5 Scope and limitation

i. In this project, an electrochemical etching process is introduced to produce a porous silicon thin film. The ECE process is conducted in a standard room-temperature condition of 27 ºC as a fixed variable with a constant volume of electrolyte consisting of 3 ml hydrofluoric acid (HF) and 5 ml ethanol (C_2H_5OH).

ii. The first set of experiment is to study the effects of different etching times during the ECE process of between 3 to 40 minutes with a constant 10 mA/cm^2 of current density supplied.

iii. The second set of experiment is to study the effects of different current densities supplied during the ECE process ranging from 10 mA/cm^2 to 30 mA/cm^2 with a constant etching time optimized from the first experiment.

iv. The optimal surface area of porous silicon thin film produced will be used to grow rutile-phased TiO_2 nanostructures by a low-temperature hydrothermal method at 150 ºC.

v. In addition, the electrolyte is synthesized with the volume ratio of 80:80 ml of hydrochloric acid (HCL) and deionized water (DI), respectively. A previous study has shown that the ratio leads to surface area improvement for the formation of TiO_2 nanostructures.

vi. The reaction time of the hydrothermal process is varied at 3, 10 and 20 hours to study the formation of the TiO_2 nanostructures. The large and rough surface areas of TiO_2 nanostructures contribute to the high efficiency of photo scattering and the improvement of light absorption.

1.6 Result contributions

TiO_2 has great potential to be a high-performance oxide TE material. The study on the electrical conductivity of TiO_2 nanostructures grown on porous silicon could contribute to the application in TE devices. Additional insight is also gained through the knowledge of carrier concentrations and mobility in the material. In the future, researchers possibly could study the strategy of reducing thermal conductivity and finding the Seebeck coefficient of TiO_2. Moreover, in the thermoelectric field, the figure of merit of new materials is based on the electrical conductivity [8]–[12], thermoelectric power [13], [14] and thermal conductivity [8], [9], [15] of the sample. In addition, for the substrate, the porous silicon has special properties of a controllable size of the pores as well as a high surface area, which has inspired the studies on its applications in various disciplines [16].

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This chapter presents the current state of knowledge about the fabrication of porous silicon and the growth of TiO_2 nanostructures on porous silicon surfaces. Also presented are discussions on porous silicon's characteristics and properties since it has benefits in thermoelectric applications. In addition, TiO_2 nanostructures are reviewed, including their properties and applications. Furthermore, this chapter describes the methodology used to produce the sample. Last but not least, the working principles of Field-Emission Scanning Electron Microscopy (FESEM), Raman spectroscopy, Atomic Force Microscopy (AFM) and Fluorometer are also discussed.

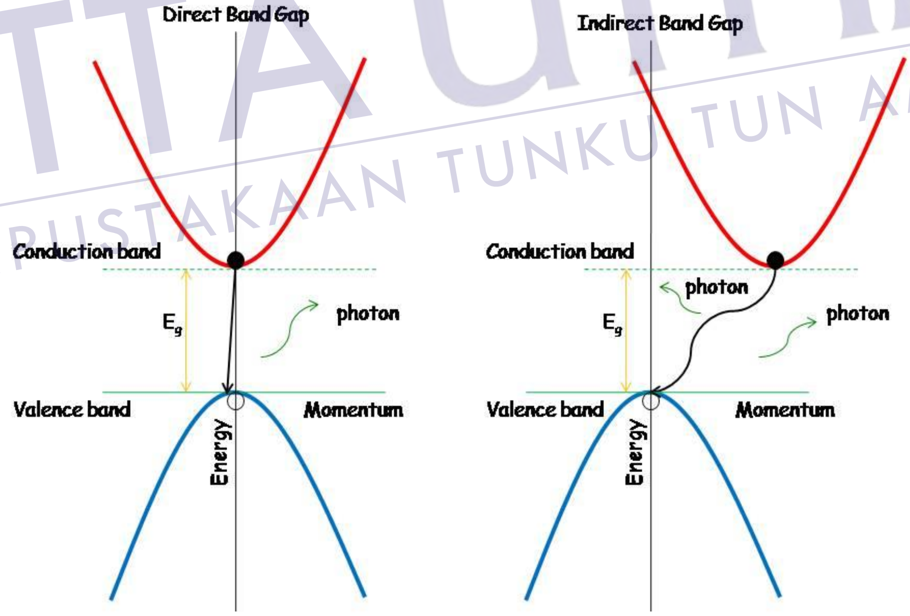
2.2 Semiconductor's properties

Various important properties of nanostructured materials are discussed when considering the behavior of electrons within an energy band. In research, the basic concept of band diagram is required to be clearly understood, including the detailed explanations about the direct or indirect band gap, band gap energy, holes and excitons [16], [17]. Table 2.1 shows a brief explanation and the differences between both types of band gap [18]. There are two types of band gap in semiconductors, which are direct and indirect band gaps. Both types of band gap are different in their characteristics and their electron and hole behaviors.

Table 2:1 Comparison of direct and indirect band gaps

Types of Band Gap	Direct Band Gap	Indirect Band Gap
Concept	The lowest energy of the conduction band and the highest of valence band occur at the same value of momentum as shown in Figure 2.1(a).	The lowest energy of the conduction band and the highest of valence band occur at a different value of momentum as shown in Figure 2.1(b).
Energy	Two conditions occur during the process: 1) Enough energy is supplied from photons (light energy) for electrons to climb to the conduction band from the valence band. 2) Photons are emitted (no phonons involved) during the movement of electrons from the valence band to the conduction band. Very efficient electron transfer since the direct band gap requires less energy.	By the law of conservation of momentum, the momentum of conduction band cannot be directly changed to the momentum of valence band. The recombination process in these semiconductors occurs via a recombination centre and an energy level within the band gap. Less efficient electron transfer since the indirect band gap requires high energy.

Holes and electrons	The electron-hole pairs can recombine directly and emit a photon.	The electron-hole pairs' recombination process takes place indirectly at the recombination centre and results in photon emission.
Examples	Gallium arsenide (GaAs) is an example of III-V compound semiconductor with a direct band gap. It is very useful in optoelectronic applications.	Silicon and germanium are examples of indirect band gap semiconductors. They have very limited usage in optoelectronics applications.



(a) (b)

Figure 2.1: The illustration of band diagrams:
(a) Direct band gap and (b) Indirect band gap

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