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FABRICATION AND CHARACTERIZATION OF GERMANIUM, ZINC OXIDE AND THEIR COMPOUNDS BY THERMAL EVAPORATION TECHNIQUE

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By

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α	Absorption coefficient
A	Area
M	Atomic/Molecular weight
k	Boltzman constant
A	Contact area
θi	Coverage of hydrogen atoms
D	Crystallite size
J	Current density
I_{air}	Current in ambient air
I_{H2}	Current with hydrogen flow rate
ε	Dielectric constant
I_d	Diode current
N_d	Doping concentration of the semiconductor
d	d-spacing
μ	Effective dipole moment
η	Efficiency
e	Electron
χ_s	Electron Affinity
q	Electron charge
E_{G}	Energy band gap
F	Faraday constant
E_{F}	Fermi Energy
h	Hole
n	Ideality factor
a	Lattice constant
c	Lattice constant
d	Lattice mismatch
a_{epi}	Lattice parameter of epitaxial layer
a_{sub}	Lattice parameter of substrate
ω	Light Frequency
f	Light frequency
m	Mass
ϕ_m	Metal Work Function
N	Number of mole
I_{ph}	Photocurrent
hv	Photon Energy
h	Planck constant
QE	Quantum efficiency
n	Refractive index
R_A	Resistance by ambient air exposure
R_{H2}	Resistance by hydrogen exposure
R	Responsivity
A^{**}	Richardson constant
I_{o}	Saturation current
φ_b	Schottky barrier height
ϕ_s	Semiconductor work function
S	Sensitivity

Rs	Series resistance
ε_a	Strain
T	Temperature
λ_c	Threshold Wavelength
a_o	Unstrained lattice parameter
V_d	Voltage across the diode
V	Volume
λ	Wavelength

LIST OF MAJOR ABBREVIATIONS

Al	Aluminium
a.u.	Arbitrary unit
Ar_2	Argon gas
ALE	Atomic layer epitaxy
BH	Barrier height
CVD	Chemical vapor deposition
CB	Conduction band
D_p	Crystallite size
I-V	Current-Voltage
DC	Direct current
eV	Electron volt
EDX	Energy dispersive X-ray
FETs	Field-Effect-Transistors
FTIR	Fourier-Transform Infrared Spectroscopy
FWHM	Full width at half maximum
GaN	Gallium Nitride
Ge	Germanium
GIs	Germanium islands
GeO_2	Germanium Oxide
GeH_4	Germanium Tetrahydride
Ge-SiO_2 NWs	Germanium-catalysed amorphous silicon dioxide nanowires
$GeCl_4$	Germaniun Tetrachloride
He-Cd	Helium-cadmium
HR-XRD	High resolution x-ray diffraction
HTF	Horizontal tube furnace
H_2	Hydrogen Gas
IR	Infrared
JCPDS	Joint Committee on Powder Diffraction Standards
LEPECVD	Low energy plasma-enhanced chemical vapour deposition.
MOVPE	Metal-organic vacuum phase epitaxy
MOSFET	Metal–oxide–semiconductor field-effect transistor
MS	Metal-semiconductor interface
MSM	Metal-semiconductor-metal
MBE	Molecular beam epitaxy
Ni	Nickel
N_2	Nitrogen gas
O_2	Oxygen gas
V_o	Oxygen vacancy
PD	Photodetector
PL	Photoluminescence
PVD	Physical vapor deposition
QE	Quantum efficiency
RCA	Radio Corporation of America
RF	Radio frequency
RTA	Rapid thermal anneal
RTA	rapid thermal annealing
RHEED	Reflection high energy electron diffraction
SEM	Scanning electron microscope

Si	Silicon
SiO_2	Silicon Dioxide
slm	Standard liter per minute
TE	Thermal Evaporation
TFE	Thermionic-Field Emission
UHV	Ultra high vacuum
UHVCVD	Ultra high vacuum chemical vapor deposition
UV	Ultraviolet
VB	Valence band
VLS	Vapor-Liquid-Solid
VS	Vapour-solid
Zn_2GeO_4	Zinc germanate
ZnO	Zinc Oxide
Zn_2SiO_4	Zinc Silicate
V_{Zn}	Zinc vacancy

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FABRIKASI SERTA PENCIRIAN GERMANIUM, ZINK OKSIDA DAN GABUNGAN SEBATIANNYA MELALUI KAEDAH PERUAWAPAN TERMA

ABSTRAK

Tujuan utama kajian ini adalah bagi mengkaji mekanisma pertumbuhan struktur germanium, zink oksida dan sebatiannya melalui kaedah peruapan terma yang mudah dan berkos rendah. Keduanya, bagi memfabrikasi dan menyiasat potensi struktur yang terpilih untuk aplikasi penderiaan. Dalam bahagian pertama kerja ini, penumbuhan struktur unik germanium oksida (GeO_2) bersaiz zarah tanpa pemangkin telah dikaji. Kesan oksigen dalam pembentukan struktur GeO_2 telah dikaji dan sifat-sifat struktur dan optik serta mekanisme pertumbuhan wap-pepejal (VS) telah disiasat dan dicadangkan. Didapati GeO_2 bersaiz zarah menggunakan oksigen (O_2) daripada persekitaran mempunyai ciri-ciri yang hampir sama sepertimana juga keputusan diperolehi dengan membekalkan aliran O_2 daripada sumber luar. Selain itu, pulau-pulau germanium seragam (GIs) telah ditumbuhkan di atas substrat Si menggunakan nikel (Ni) sebagai pemangkin. Pengaruh jangka masa yang berbeza keatas pertumbuhan dan peranan Ni dalam pembentukan pulau telah dikaji. Satu mekanisme terperinci bagi penumbuhan telah dicadangkan bagi mengkaji peranan Ni dalam pembentukan pulau. Analisis spektrum Fourier inframerah menunjukkan bahawa nilai-nilai jurang jalur optik (*Eg*) pulau germanium berubah mengikut masa pemendapan dari 0.62 ke 0.78 eV berbanding dengan nilai pukal bagi ge (0.66eV). Dalam bahagian kedua kerja ini, struktur bersaiz mikro zink oksida (ZnO) telah disintesis menggunakan satu proses peruapan terma yang diubahsuai dengan mencampurkan serbuk GeO_2 dengan serbuk logam Zn sebagai bahan mentah pemula. Sifat-sifat struktur dan optik serta mekanisme pertumbuhan dan peranan GeO_2 untuk pembentukan struktur ZnO telah dibincangkan secara terperinci dan dicadangkan. Tanpa penggunaan mana-mana pemangkin dan aliran oksigen dalam sistem relau, struktur mikro ZnO telah berjaya ditumbuhkan dengan menggunakan serbuk GeO_2 sebagai sumber oksigen pada julat suhu 500 - 900^0C . Dalam bahagian terakhir, pembentukan struktur hibrid pertigaan struktur berasaskan Ge telah dijalankan dengan mencampurkan serbuk germanium dan zink oksida dengan nisbah jisim yang berbeza (1:2 dan 2:1). Gabungan sebatian struktur berbentuk liang hibrid zink oksida/zinc germanat (ZnO/Zn_2GeO_4) dan struktur germanium / zinc silikat (Ge/Zn_2SiO_4) telah difabrikasikan dan dicirikan, serta mekanisme pertumbuhan telah dicadangkan. Sampel bagi struktur ZnO/Zn_2GeO_4 telah difabrikasikan dengan peranti logam-semikonduktot-logam yang menunjukkan kesan fotoelektrik yang berkesan dalam kedua-dua julat UV-C (0.252 A/W) pada lingkungan 250 nm dan UV-A (0.246 A/W) pada lingkungan 385 nm. Manakala sampel struktur Ge/Zn_2SiO_4 yang diuji juga menunjukkan tindakbalas yang berkesan dalam julat panjang gelombang UV yang lebih pendek iaitu 0.280 A/W dan 0.374 A/W pada lingkungan 290 nm dan 230 nm masing-masing. Ini menunjukkan kedua-dua struktur sangat berpotensi untuk digunakan sebagai pengesan cahaya-UV yang berjarak gelombang pendek. Seterusnya, struktur Ge/Zn_2SiO_4 juga diuji sebagai pengesan gas hidrogen. Nilai kepekaan dan operasi optima pada suhu bilik menghampiri 90% ketika kadar aliran gas hidrogen 150 sccm menunjukkan ianya berpotensi tinggi sebagai pengesan gas H_2 pada masa akan datang.

FABRICATION AND CHARACTERIZATION OF GERMANIUM, ZINC OXIDE AND THEIR COMPOUNDS BY THERMAL EVAPORATION TECHNIQUE

ABSTRACT

This work mainly aims to study the growth mechanism of germanium (Ge), zinc oxide (ZnO), and their compounds through simple and low-cost thermal evaporation. Potential structures were also fabricated and investigated for sensor applications. In the first part, germanium oxide (GeO_2) was grown using a novel one-step method without catalyst. The effect of oxygen (O_2) supply in structure formation and the structural and optical properties of GeO_2 were investigated, and the vapor–solid growth mechanism was proposed. The particle size of GeO_2 grown using ambient O_2 was similar to that obtained with a fixed O_2 flow from an external source. Uniform-sized Ge islands (GIs) were also grown on a Si substrate with Ni catalyst. The influence of different deposition durations on GI growth and the role of Ni in island formation were evaluated, and the growth mechanism was proposed. Fourier transform infrared spectrum showed that the optical band gap (*Eg*) of GIs varies with deposition time from 0.62 to 0.78 eV compared with bulk Ge (0.66 eV). In the second part, ZnO microstructures were synthesized through modified thermal evaporation by using the mixture of GeO_2 and metallic Zn powders as raw material. The structural and optical properties, growth mechanism, and roles of GeO_2 in the formation of the ZnO structures were discussed and proposed. The ZnO microstructure was grown using GeO_2 as oxygen source in a furnace system without any catalyst and oxygen flow at temperature range of 500 – 900^0C. Finally, Ge and ZnO powder were mixed at different mass ratio (1:2 and 2:1) to form the hybrid of ternary Ge-based structures. ZnO/zinc germanate (Zn_2GeO_4) with porous-like structure and Ge/zinc silicate (Zn_2SiO_4) were fabricated and characterized, and their growth mechanisms were proposed. ZnO/Zn_2GeO_4 structure was used to construct metal–semiconductor–metal devices, which exhibited significantly strong photoelectric effects under both UV-C (0.252 A/W) at 250 nm and UV-A (0.246 A/W) at 385 nm regions. The Ge/Zn_2SiO_4 structure also exhibited similar response to deep UV (0.280 A/W and 0.374 A/W) at 290 nm and 230 nm regions. Hence, the study demonstrated that both structures can be potentially used as UV-photodetectors for applications requiring short wavelengths. Subsequently, a hydrogen-sensing properties based on Ge/Zn_2SiO_4 structure was also performed. The sensitivity and the optimal operation at room temperature of the sensor are nearly 90% at 150 sccm flow rate of hydrogen gas which heightens potential interest in future H_2 gas sensor devices.

CHAPTER 1

INTRODUCTION

1.1 Historical Overview

Germanium (Ge) was first detected and named as eka-silicon by a Russian chemist, D. I. Mendeleev, in 1871 (Haller, 2006). In 1886, Clemens Winkler, a German chemist, first initiated and characterized this element. The electrical properties of Ge fall between those of a metal and an insulator, and Ge is a chemical element in subgroup IVA of the periodic table (C–Si–Ge–Sn–Pb). Ge possesses a metallic appearance, but it presents a diamond cubic crystal structure and is fragile similar to glass. In addition, Ge is metallic in terms of several physical properties, such as its greyish-white appearance and metallic color.

In subsequent years, the interest for investigating germanium has been motivated by its novel applications in electronic and optoelectronic devices. A Ge material was used in the first transistor created in 1947 by Bardeen and Brattain (1948). Over the last two decades, Ge-based electronic devices are gaining new interest since the continuation of scaling down of transistor dimensions driven for higher performance at a lower cost per function. Ge is widely used as a dopant in fiber optic glasses and semiconductor devices, both as an active layer and as a substrate for III to V epitaxy. Ge use is also widespread in infrared (IR) detection and imaging and as a polymerization catalyst for polyethylene terephthalate (PET) (Bosi et al., 2010; Masini et al., 2005; Nidhi et al., 2014; Sumesh et al., 2013).

Its advantageous properties in comparison with Si make Ge more applicable in many applications. Table 1 shows the comparison of Ge and Si properties, such as hole and electron carrier mobility. The carrier mobility (1900 and 3600 cm^2/Vs for holes and electrons, respectively) of Ge is higher than that of Si. This property is advantageous for application in high-speed devices, in which larger mobility provides a higher source injection velocity that can potentially provide higher drive current and smaller gate delay. These exceptional characteristics are suitable for high frequency operation and permit the design of faster devices with respect to Si. However, Ge also allows operation at lower voltage, even if the thermal noise must be correctly handled and minimized because of the lower bandgap (0.66 eV).

Table 1.1: Properties of germanium compared with silicon

	Ge	**Si**
Crystal structure	Diamond	Diamond
Bandgap energy (eV)	0.66	1.12
Lattice constant (Å)	5.6579	5.43095
Intrinsic carrier concentration (cm^{-3})	2×10^{13}	1×10^{10}
Electron mobility (cm^2/Vs)	3900	1500
Hole mobility (cm^2/Vs)	1900	450
Minority carrier lifetime (s)	10^{-6}	10^{-6}
Lattice thermal expansion (10^{-6}/K)	5.9	2.6

Furthermore, combining higher carrier mobility and higher absorption coefficient (wavelength range: 800 nm to 1550 nm) compared with silicon (Si) makes Ge a feasible candidate for modulators on complementary metal–oxide semiconductor circuits for optical interconnection and the integration of optical detectors (Dosunmu et al., 2004). The lattice constant of Ge (5.4307 Å) in comparison with that of Si (5.6657 Å) is hindered by the 4% lattice mismatch between Ge and Si, which results in growth dominated by "islanding" and misfit dislocations. This factor is also being considered in the semiconductor industry to maximize the properties of Ge and Si, the heterogeneous integration of Ge and Si must be made possible because using bulk Ge is not viable. Another advantage is that the excitonic Bohr radius of bulk Ge (24.3 nm) is considerably larger than that of Si (4.9 nm) (Maeda et al., 1991). Therefore, the quantum size effect will be more prominent in Ge.

1.2 Problem Statement

The development of most electronic and optoelectronic devices depends on epitaxial growth. The following two epitaxial processes are normally consumed: (1) homo-epitaxy and (2) hetero-epitaxy. Homo-epitaxy includes growth on the substrate of the same material (native substrate), whereas hetero-epitaxy involves the growth of single crystalline materials on non-native substrates. Prior to epitaxy, homo-epitaxy and hetero-epitaxy substrate surface preparation and nucleation conditions in Ge are critical in obtaining good deposition quality and reproducible results. Several familiar difficulties reported in the literature focus on surface contamination and its analysis (particularly carbon), oxide elimination with chemical etches, surface reconstruction, and roughening/smoothing mechanisms (Gabás et al., 2012; Gan et al., 1999; Gan et al., 1998; Hovis et al., 1999; McMahon et al., 2006; McMahon et al., 1999; Pukite et al., 1987; S. Zhang et al., 2001).

Several groups have expended efforts to grow Ge epitaxially with different morphologies, as well as with different optical and electrical properties, using various growth techniques. One of the most common methods for Ge epitaxial growth is chemical vapor deposition (CVD), which includes certain recent advances, such as atomic layer deposition and low energy plasma-enhanced chemical vapor deposition (C. B. Li et al., 2011; Rudder et al., 1986), molecular beam epitaxy (MBE) (Barski et al., 2000; Eaglesham et al., 1990) and atomic layer epitaxy (Sugahara et al., 1994; Tillack et al., 2009). In many cases, the widely studied techniques for Ge epitaxy or film growth require complex materials and complicated experimental procedures. Among these techniques, thermal evaporation via vapor phase transport has shown the most potential because of its comparatively straightforward experimental process and its inexpensive, non-hazardous method, which uses only powders as source materials (Akl et al., 2009). Another advantage of thermal evaporation method is that the grown structures can be controlled by precursor and their melting point (Zhi et al., 2005).

The mainly used Ge precursors are germanium tetrahydride (GeH_4) and germanium tetrachloride ($GeCl_4$), which are suitable for deposition at low and high temperatures, respectively. The SiGe layer growth of different compositions on strained Si layers is commonly achieved with Ge and Si deposition in the vapor phase with GeH_4, which is costly and toxic. Hazards of GeH_4 use are also widely reported in the literature. $GeCl_4$ and other metal–organic compounds with Ge atoms, such as trimethyl germane or monomethyl germane, are alternatives to the hydride form, but present high cracking temperatures. Several new precursors, such as Ge-based powder and Ge base mixed with Zn-based powder, have become increasingly important exploration subjects in epitaxial Ge deposition growth.

Using Ge-based powder and tailoring with Zn-based powder as precursors in thermal evaporation technique are becoming increasingly important because different structures based on Ge and zinc oxide (ZnO), as well their compounds, are easily formed. Several attempts have been conducted to grow structures using Ge-based powder, but few have focused on Ge mixed with Zn-based powder. One of the reasons is that Ge is easily vaporized after reaching its melting point in thermal evaporation technique, and predicting its structural formation and growth mechanism is difficult. To date, no studies in the literature have focused on modeling the growth mechanism of Ge-based compound, little information is known regarding its structural formation, particularly by a simple thermal evaporation technique. Therefore, growth mechanism becomes an important scope to be investigated.

1.3 Research Objectives

This research primarily aimed to fabricate and characterize, as well as to study, the growth mechanism of Ge, ZnO, and their compounds by simple thermal evaporation technique. The aims were achieved by dividing the work into several components that carried principal objectives, which can be summarized in the following points:

i. To study the growth mechanisms of germanium-based structures on Si substrate using Ge powder by a simple thermal evaporation technique.

ii. To study the growth of ZnO structures on Si substrate by mixing the GeO_2 and Zn powder at different deposition temperature.

iii. To study the growth of Ge-based ternary structures on Si substrate by mixing of Ge and ZnO powder.

iv. To study the potential use of the fabricated Ge-based ternary structures for sensing applications.

1.4 Originality of the Study

Dielectric oxides, such as germanium dioxide (GeO_2), can be used in various applications. In recent years, GeO_2 crystals are typically produced by any physical evaporation or thermal oxidation method. Inorganic materials with different morphologies and sizes can exhibit different properties (Charlier et al., 1997), despite including the same elements; thus, fabricating new germanium oxide (GeO_2) structures with different techniques is advantageous. GeO_2 is mostly grown by using a tube furnace with catalysts, such as gold (Au), under flowing oxygen. In this study, particle-sized GeO_2 structures were fabricated by simple thermal evaporation in the absence of any catalyst.

The formation mechanisms and properties of GIs on Si substrate are of great interest for use in new optoelectronic devices. However, finding a method to satisfactorily achieve uniform island sizes with normal spatial distribution remains to be a challenge. Growth phenomena by metal-modified nucleation are normally used to modify the characteristics of epitaxial islands. One of the processes discovered involves GIs that are structured on a Si substrate patterned simply by Au evaporation through a stencil mask (Hovis et al., 1999). Given that Au forms deep electronic traps in Si and Ge, Au-seeded islands are relatively undesirable for electronic applications, and other metals are more applicable as seeds. Nickel (Ni) has been shown to be a promising metal catalyst. In this work, uniform GIs were successfully fabricated by a simple thermal evaporation technique with a Ni catalyst.

In thermal evaporation method, ZnO and Zn powders are normally used as raw materials to fabricate ZnO structures. The use of ZnO powder as raw material by thermal evaporation requires a more complex process because of its high melting point. Most growth methods using Zn powder in thermal processes require an oxygen source to control the formation of ZnO structures. Exploring new methods for synthesizing the ZnO nanostructure using Zn powder without introducing an oxygen source remains a challenge, especially for simple, cheap, contamination-free, and catalyst-free structures. With certain modifications, GeO_2 powder will decompose and release a small amount of oxygen that is sufficient for evaporated Zn to form the ZnO structure. In this work, micro- and nanoscale ZnO were fabricated by using GeO_2 and Zn powder without the presence of an oxygen source, and a growth mechanism was proposed.

Numerous researchers have attempted to enhance the ultraviolet (UV) emission of ZnO thin films, either by varying the depositional methods and post-treatment methods or by doping with various dopants, such as Ga, In, Ag, Cr, and Ni. Ge is another possible material for doping with ZnO. Among the different fabrication methods of ZnO-doped Ge thin film, thermal evaporation is of particular interest as a simple method of producing large quantities of ZnO/Zn_2GeO_4 compound. The Ge/zinc silicate (Zn_2SiO_4) mixture is another promising by-product compound with doped ZnO and Ge. In this work, a combination of ZnO/Zn_2GeO_4 and Ge/Zn_2SiO_4 compounds was deposited on the Si substrate by evaporation process from the mixed powder of Ge and ZnO. The potential application of ZnO/Zn_2GeO_4 and Ge/Zn_2SiO_4 compounds as deep UV photodetectors and gas sensors was successfully tested.

1.5 Outline of Thesis

The thesis consists of six chapters that describe studies on the fabrication of Ge-based powder structures by simple thermal evaporation method. The thesis outline is as follows.

Chapter 1 provides an overview of the study and the motivation for growth, discussing introduction to originality and objectives of the research. Chapter 2 involves a literature review of the growth of Ge and Ge-based powder mixed with Zn-based powder. The principles of the thermal evaporation technique and mechanism of Ge growth, the process of growth from vapor phase, and the basic principles of several devices (which have been fabricated in this thesis) are also presented in this chapter. In Chapter 3, the methodology and instrumentation involved in this research work are presented comprehensively. The results achieved from the research works are analyzed and discussed in Chapters 4 and 5. Chapter 4 elaborates on the properties of GeO_2 and GIs growth on the Si substrate using a physical vapor deposition via thermal evaporation of Ge powder under different parameters and conditions. Chapter 5 presents the unique structure of ZnO growth by using Zn mixed with GeO_2 powder under different temperatures, and the results of experiments conducted on the thermal vapor deposition of Ge mixed with ZnO powder and their application are also presented. Finally, Chapter 6 summarizes the findings in this work and concludes the study by suggesting a number of possible directions for future work.

CHAPTER 2

LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 Introduction

In this chapter, relevant literature review and theories of all work involved in this study are presented. The section begins with an overview of Ge epitaxial growth techniques and an overview of the thermal evaporation process of Ge-based powders. In addition, an overview of GeO_2 and GIs growth are presented. An overview of ternary oxide Ge-based materials and ZnO growth using Ge-based powder is also addressed. Several Ge-based material applications and basic concepts of the devices fabricated in this work, which include a metal–semiconductor–metal (MSM) photodetector and a gas sensor, are briefly described in this chapter. The general principles and theories of all subjects involved in this work are also presented.

2.2 Background of Ge Epitaxial Growth Techniques

The word “epitaxy” refers to the growth of a crystalline structure layer on a crystalline substrate. The layer is called an epitaxial film or epitaxial layer. The epitaxial layer can be classified into different categories, such as homo-epitaxial and hetero-epitaxial. A homo-epitaxial layer is performed with only one material, in which a crystalline film is grown on a substrate or film of the same material. A hetero-epitaxial layer is a crystalline film that grows on a crystalline substrate or film of a different material.

In the case of homoepitaxial deposition, the substrate and the film possess the same crystal lattice with the same atoms: $d = 0$, presenting the best possible scenario in which a virtually defect-free layer may be obtained. A substrate and a film of two different materials are commonly applied to achieve greater freedom in designing epitaxial structures. In this case, a difference in lattice parameter typically exists, and the mismatch is not zero. The lattice mismatch exerts a strong influence on the mode in which the epilayer grows on the substrate. Three different models of epitaxial growth are usually reported: 2D or Frank-van der Merwe, 3D with island nucleation or Volmer–Weber, and an intermediate case between the previous two modes or Stranski–Krastanov, in which a 2D layer is initially nucleated and then 3D islands develop (Oura et al., 2003; Pimpinelli et al., 1998).

2.3 Overview of Growth Techniques for Ge Epitaxial.

Utilizing Ge application in Si-based device materials requires the growth of high-quality epitaxial structures. Consequently, several particular techniques, including vacuum pyrolysis (Zanio et al., 1978), sputtering and evaporation (Krikorian et al., 1966), close spacing chemical transport (Nicoll, 1963), gas source and electron beam MBE (Aharoni, 1986; Larciprete et al., 1998; Schmidtbauer et al., 2014; Strite et al., 1990), atomic layer epitaxy (ALE) (Goodman et al., 1986; Sugahara et al., 1994; Takahashi et al., 1989; Tillack & Yamamoto, 2009) and chemical vapour deposition (CVD) (Bosi et al., 2008; Cunningham et al., 1991; Fitzgerald, 2005; Ginige et al., 2006; Kamins et al., 1997; Kummer et al., 2002; Mo et al., 1991; Rudder et al., 1986) have been developed.

Among the techniques mentioned, the CVD-related processes are the most common in Ge epitaxial growth. Kaminis et al (1997) initially reported CVD-based techniques. These techniques involve the deposition of 3D GIs on Si at atmospheric and reduced pressures. A pseudomorphic coverage of up to 3.5 Ge monolayers was achieved, followed by the nucleation of islands with a constant aspect ratio (11:1 between diameter and height) but no distinct facets. In addition, Cunningham et al. (1991) observed how growth conditions, temperature, and alloy composition determined the size, shape, dimension, and homogeneity of islands. Mo et al. (1991) stated that nucleation is critically dependent on surface purity and physical perfection, involving steps and substrate misorientation. Bosi et al. (2008) also reported that certain variants of CVD techniques, such as metal–organic vacuum phase epitaxy, are realized to obtain the homoepitaxial Ge layers. In addition, Rudder et al. (1986) reported that ultra-high vacuum CVD or plasma-assisted CVD technique can be used to study the roughening mechanisms of Ge surfaces and to identify a transition temperature. Low-energy plasma-enhanced CVD techniques were developed to improve the deposition process and obtain thick Ge_xSi_{1-x} graded layers to be used as virtual substrates. However, low pressure processes are often used to minimize the contamination of the growth chamber and prevent unwanted deposition on chamber walls (Fitzgerald, 2005; Ginige et al., 2006; Kummer et al., 2002).

The method used in depositing SiGe layers (Kasper et al., 1975) involves the MBE technique, which remains widely used as a research tool for fundamental studies and for designing novel device structures. Crystal quality and layer thickness can be monitored by reflection high-energy electron diffraction (RHEED) during crystal growth. Eaglesham et al. (1990) explained island growth in terms of elastic deformation around the islands, which accommodates mismatch, by using RHEED in MBE deposition equipment. The growth of extremely high-quality thin films by MBE process is not commercially feasible because of their high cost and low growth rate contributed by the method. In the case of deposition of high-*k* oxides for microelectronic devices, ALE is becoming a highly common technique, considering that the technique is usually adopted for binary or ternary compounds to prevent parasitic reactions between different species and to exert precise control over stoichiometry (Sugahara et al., 1994; Takahashi et al., 1989; Tillack & Yamamoto, 2009). Despite growth occurring in separate steps in the ALE process of elemental semiconductors, such as Ge and Si, has not been given wide interest, several works regarding Ge film preparation are still using this technique.

In the case of integrating future devices with the developed Si-integrated circuit technology, relying on simple and cheap fabrication techniques is essential. The thermal evaporation of solid materials using a horizontal tube furnace and employing conventional powders is a low-cost and simple heating technique that will contribute to the potential commercialization of products (H. Kim et al., 2009; Kovačević et al., 2007; Sorianello et al., 2011). Another advantage of thermal evaporation method is that the grown structures can be controlled by the starting material source content and their melting point (Zhi et al., 2005).

Numerous researchers have extensively investigated and studied the growth of semiconductor materials by thermal evaporation method. Thermal evaporation technique has been widely used recently for the growth of metal oxide structures, such as ZnO and gallium nitride (GaN). The growth of perfectly hexagonal-shaped ZnO nanorods has been achieved on a Ni-coated Si(100) substrate by thermal evaporation (Umar, Karunagaran, et al., 2006). In addition, Abdulgafour et al. (2010a; 2010b; 2013; 2011; 2013) successfully fabricated well-aligned ZnO nanoflower structure arrays, hexagonal tube-like ZnO nanostructures, coral reef-like ZnO nanostructures, and ZnO NWs by a simple thermal evaporation technique without catalysts. Saron et al (2013a) also reported the productive growth of GaN structures by thermal evaporation technique. Among the reported study subjects, GaN NWs were grown on catalyst-free Si substrates using the thermal evaporation of GaN powder at 1150 °C in the absence of NH_3 gas (Saron, Hashim, et al., 2013). Another reported method involves the catalyst-free growth of GaN nanostructures on *n*-Si(111) substrates, (Saron & Hashim, 2013b) as well as GaN NW flowers on Si (111). Therefore, this technique should be applied for Ge-based structure growth.

2.4 The Growth of Ge-based Structures

An overview of Ge-based structures fabricated on this work, such as GeO_2, GIs, ZnO, and Ge-based ternary oxide, are explained in this section.

2.4.1 Overview of Germanium Oxide (GeO_2) Structures Growth

Germanium dioxide (GeO_2) is a dielectric oxide that is considered to be a promising material for a variety of applications. GeO_2 is an important material that exhibits visible luminescence (M Zacharias et al., 1998). Meanwhile, GeO_2-based glass is known to present a higher refractive index and higher linear coefficient of thermal expansion than SiO_2 (X. Wu et al., 2001), suggesting potential applications in future optical wave guides (Yin et al., 1982) and nanoconnections in optical devices and systems. Another important application of GeO_2 is in the area of vacuum technology (Margaryan et al., 1993). Fabricating materials with novel morphologies is an interesting and urgent challenge in the area of materials science. Given that inorganic materials with different morphologies and sizes can exhibit different properties (Hulliger, 1994), despite comprising the same elements, fabricating new GeO_2 structures with different morphologies is valuable.

2.4.2 Overview of Germanium Island (GI) growth

The formation mechanisms and properties of GIs on Si structures are of considerable interest for use in new optoelectronic devices. Several methods are employed to fabricate GIs with different sizes, such as CVD (Borgström et al., 2003; Capellini et al., 1997), radio frequency magnetron sputtering (Das et al., 2007; Samavati et al., 2012), molecular beam epitaxy (Goldfarb et al., 2004; Merdzhanova et al., 2006; K.-F. Wang et al., 2012), and thermal evaporation (Kovačević et al., 2007). However, establishing a method to achieve sufficiently uniform island sizes with regular spatial distribution remains a critical issue. Substantial research focused on the size distribution of islands because such islands are an important aspect in practical application (Dvurechenskii et al., 2005). The conventional method of controlling island formation (size, shape, and density) involves varying growth conditions by altering substrate temperature and molecular flux (Dvurechenskii et al., 2005).

Metal-modified nucleation and growth phenomena are normally used to tune the characteristics of epitaxial islands. Robinson et al. (2007) demonstrated that patterned metal over layers enables to control over large areas of GI position and shape on a Si model heteroepitaxial system. Stencil masks were used to show that the surface is highly preferred in comparison with other patterning routes. One discovered process involved GIs being ordered on a Si substrate that has been patterned simply by Au evaporation through a stencil mask. Nickel (Ni) is a material that presents promising use as a metal catalyst. For instance, Tuan et al. (2005) and Hsu et al. (2006) successfully synthesized Ge and Si NWs using Ni catalysts. Kolahdouz et al. (2012) recently used Ni as a metal catalyst to form islands based on substrate engineering to control the diameter of carbon multi-walled nanotubes. More recently, Thombare et al. (2013), successfully synthesized vapor–solid–solid Ge NW growth using a Ni-based catalyst.

2.4.3 Overview of ZnO growth using Ge-Based powder

In thermal evaporation method, ZnO and Zn powders are normally used as raw materials to fabricate ZnO structures. The use of ZnO powder as raw material in thermal evaporation requires a more complex process because of the material's high melting point. The carbon group [i.e., graphite (C), Si, Ge, tin (Sn), and lead (Pb)] and metallic elements have been effectively used to reduce the melting point of ZnO powder to achieve pure ZnO nano/microstructures (H. D. Li et al., 2008; Lv et al., 2010; C. Xu et al., 2004; B. Yao et al., 2002). In addition, previous studies reported that the use of Zn powder as a raw material does not require any reducing agent for synthesizing ZnO nanostructure and that the nanostructure can be grown either with the use of catalyst or catalyst-free at lower temperature (Cheng et al., 2011; Y. S. Liu et al., 2006; Rusu et al., 2007; Senthil Kumar et al., 2011). Most of the growth methods using Zn powder in thermal processes need an oxygen source to control the formation of ZnO structures. Exploring new methods for synthesizing the ZnO nanostructure using Zn powder without introducing an oxygen source remains a challenge, especially for simple, cheap, contamination-free, and catalyst-free structures. Shen et al. (2006) introduced an adiabatic layer without using oxygen to provide an abrupt temperature decrease and high gas concentration for the growth of ZnO structures. Another possible method to synthesize 1D ZnO structures without introducing any oxygen flow in the tube furnace involves mixing GeO_2 powder with Zn powder as raw material. The use of GeO_2 powder is unique because the powder thermally decomposes to GeO and releases a small amount of oxygen at 500 °C. The oxygen produced from this decomposition can be used by Zn (melting point ~420 °C) to form a suboxide (ZnO_x, $x < 1$) gas that will be vaporized, condensed, and accumulated into a substrate for the formation of ZnO structures. The oxygen generated by the decomposition of GeO_2 could promote impurities (Brazhkin et al., 2003). However, such impurities can be minimized through careful selection of growth temperature. Hence, developing novel methods capable of synthesizing ZnO nanostructure using in the absence of an oxygen source is still a challenge, particularly for uncomplicated, inexpensive, impurity-free, and catalyst-free structures.

2.4.4 Overview of Ternary Oxide Growth

Ternary oxide structures have various applications because of its compelling optical properties. Compared with the extensive research on binary oxide materials, investigations on ternary oxide NWs are relatively limited. In most cases, complex ternary oxide materials are technologically important because their properties, and hence functionalities, can be efficiently tuned by adjusting the ratio of doping or alloying components (Chaoyi et al., 2010). Ternary oxide nanostructures of Ge-based materials, such as indium germanate ($In_2Ge_2O_7$) and zinc germanate (Zn_2GeO_4), were successfully synthesized by a chemical vapor transport method. Prior to the synthesis of these materials, 1D nanomaterials of several ternary oxides were successfully synthesized, especially for ZnO-based ternary compounds (Fan et al., 2009).

ZnO presents a broad bandgap energy of 3.37 eV and large exciton binding energy of 60 meV at room temperature. This material has attracted much attention because of its numerous prospective applications in multiple fields. ZnO films with various doping, such as Er and Ga, were studied to satisfy different requirements in optoelectronic devices (Cho et al., 2001; X. T. Zhang et al., 2002). Modified ZnO can be used as gas sensors, photocatalysts, solar cells, light-emitting materials, and field-effect transistors (Anandan et al., 2007; X. L. Chen et al., 2007; Gao et al., 2005; Ryu et al., 2007; Teng et al., 2006; Z. X. Xu et al., 2007).

Many researchers attempted to enhance the UV emission of ZnO thin films either by varying the depositional methods and post-treatment methods or by doping with various dopants, such as Ga, In, Ag, Cr, and Ni (Duan et al., 2006; Jun et al., 2008; T. Y. Kim et al., 2004; Pál et al., 2008; Singh et al., 2008). However, only few reports focused on ZnO-doped Ge. Ge is an indirect band gap semiconductor with smaller energy difference between the indirect gap and direct gap ($\Delta E_g = 0.12$ eV). In addition, a small ionic radius difference is found between Ge ion (0.53 Å) and Zn ion (0.74 Å), increasing the probability of Ge ion replacing the Zn ion vacancy. All these characteristics lead to the expectation that changing the optical properties of Zn-based materials through modifying the electronic structure around the band edge is considerably easier for Ge than for any other type of dopant.

Yu et al. (2004) prepared ZnO:Ge compound by solid-state reaction method. They discovered that the Zn_2GeO_4 phase was formed by heavy doping of Ge atoms and obtained their PL spectrum. They ascribed the luminescence center to the inherent effects of ZnO and impurity effects of GeO_2. Zheng et al. (2006) deposited Ge/ZnO multilayer films by RF magnetron sputtering and obtained a Zn_2GeO_4 thin film from annealing Ge/ZnO multilayer films. The characteristics of the PL spectra for Ge/ZnO multilayer films annealed at various temperatures were recorded at room temperature and showed a strong green band (532 nm) and a broad red to infrared bands. Fan et al. (2005) prepared Ge-doped ZnO on Si substrates by alternate radio frequency magnetron sputtering. They also investigated the effects of doping and annealing on structural and optical properties and found that the crystalline quality of the film improves with annealing temperature. A recent report involved fabricating Zn_2GeO_4 nanorod photocatalysts with Ag doping and Ag decorating (Ag-modified Zn_2GeO_4) synthesized by a mild solvothermal method (G. Jiang et al., 2014).

Attempts to develop uncomplicated and inexpensive methods for efficiently synthesizing ternary Ge-based material are still a challenge. Thermal evaporation is of particular significance because of the simplicity of its mechanism in producing ternary microstructures, its cost effectiveness, and non-hazardous nature, given that it utilizes only powders as source materials. Growing interest in the synthesis of Ge-based ternary structures are stimulated due to promising devices application.

2.5 Overview of Ge-Based Material Devices Applications

In recent years, the increasing amount of literature focused on ternary oxide materials is technologically important because their properties, and thus their functionalities, can be efficiently tuned by adjusting the ratio of doping or alloying components. Among these materials, Ge-based Zn_2GeO_4 and Zn_2SiO_4, ternary oxides with a wide bandgap, have attracted considerable attention for various applications because of their compelling optical properties. In the following sub-section, a brief description of the most recent devices and applications of Ge-based and ZnO-based structures, especially Zn_2GeO_4 and Zn_2SiO_4, will be presented.

2.5.1 Overview of Ternary Oxide UV-MSM Photodetector

UV photodetectors perform highly important functions in multiple fields, such as missile tracking, ozone monitoring, flame detection, imaging techniques, and lightwave communications (Chang et al., 2007b; C.-H. Chen et al., 2009; De Cesare et al., 2006). Various wide band gap semiconductors, such as GaN, AlGaN, diamond, SiC, III to V compounds, and II to VI compounds (Carrano et al., 1997; Han et al., 2004; Monroy et al., 2001) are used to fabricate UV photodetectors. Among these compounds, ZnO-based UV detectors have recently gained attention because of their properties, such wide band gap (3.34 eV), high exciton binding energy (60 meV), non-toxicity, high radiation hardness, and higher transparency in the visible region. The conductivity of ZnO can be dramatically increased under UV illumination, and this fact has been used in UV sensor applications.

However, less attention has been focused to more complex materials, including ternary oxide, because of the difficulty in obtaining high-quality thin films or NWs. Extensive research on Ge-based ternary oxides, such as zinc germanite (Zn_2GeO_4), has been carried out to make them suitable for applications, such as visible-blind deep-ultra violet photodetection (C. Li et al., 2010; Yan et al., 2010), high-capacity anode material of lithium battery (Feng et al., 2011), bright white-bluish luminescence (Z. Liu et al., 2007), water-splitting by photocatalysis (Huang et al., 2008; L. Zhang et al., 2010), photocatalytic reduction of CO_2 into renewable hydrocarbon fuel (Q. Liu et al., 2010). Ternary oxide NWs are chemically and thermally stable as well as superior in deep UV detection because of their large bandgap, thereby resulting in high wavelength selectivity. For example, ZnO (E_g = 3.4 eV) responds to the whole UV band (200 nm to 400 nm), but Zn_2GeO_4 (E_g = 4.68 eV) is expected to be UV-A/B (~290 nm to 400 nm) blind and only responsive to

UV-C band (~200 nm to 290 nm (Fang et al., 2009). Yan et al. (2010) reported the deep-UV photodetection performance of Zn_2GeO_4 nanonetworks with good wavelength selectivity.

Another ternary oxide from ZnO-based material by simple thermal evaporation technique is Zn_2SiO_4. Zn_2SiO_4, with its wide band gap of 5.5 eV, is widely used as a host material in cathode ray tubes and electroluminescent devices (Fan et al., 2009). This ternary oxide can also serve as an electronic insulator, a crystalline phase in glass ceramics, and as catalyst and catalyst supports (Fan et al., 2009). Zn_2SiO_4, especially $Zn_2SiO_4:Mn^{2+}$, is one of the most practical and attractive materials that has been identified and widely researched over the last 180 years (Takesue et al., 2009). However, $Ge:Zn_2SiO_4$ compound applications, such as photodetectors, have not yet been explored and reported.

Various types of photodetectors have been widely studied, including photoconductive, avalanche, Schottky barrier, *p–n* junction, *p–i–n* junction, phototransitive, and MSM photodetectors. Among these devices, MSM-based photodetectors offer various advantages, such as simplicity of fabrication, compatibility with field-effect transistors in optoelectronic integrated circuits (Rogers, 1991), low capacitance, low dark current, high speed operation, and high sensitivity.

2.5.2 Overview of Ge-Based Material Hydrogen Gas Sensor

Sixty years ago, Brattain et al. (1953) discovered that gas adsorption onto a semiconductor produces a conductance change. Since the discovery, a considerable amount of research has been carried out to realize commercial semiconducting devices for gas detection. Over the past decade, semiconducting metal oxide-based gas sensors have become a primary technology in several domestic, commercial, and industrial gas sensing systems. Three different types of solid-state gas sensors are widely available (Korotcenkov, 2007; Moseley, 1997). Among the available gas sensing methods, semiconducting metal oxide gas sensor devices present several unique advantages, such as low cost, small size, measurement simplicity, durability, ease of fabrication, and low detection limits (< ppm levels). Given these reasons, these devices have been increasingly known, becoming the most widely used gas sensors available at present.

Extensive investigations have been conducted on binary metal oxides nanostructures in several applications (Dai et al., 2013; Sen et al., 2010). A continuing need for specially designed semiconductors exists, leading to an interest in ternary oxides, such as Zn_2TiO_4 (Y. Yang et al., 2009), $CdSnO_3$ (L. Wang et al., 2014), $ZnSnO_3$ (J. M. Wu et al., 2012), $LiNbO_3$ (Yun et al., 2014), Cd_2SnO_4 (Kelkar et al., 2012), Zn_2SnO_4 (Y. Q. Jiang et al., 2012; Z. Li et al., 2012; Lim et al., 2012), $BaTiO_3$ (Ma et al., 2012), $CdIn_2O_4$ (Cao et al., 2008), $CuFe\text{-}O_2$ (Read et al., 2012) and $SrTiO_3$ (Ma et al., 2012). Ternary oxides provide greater flexibility in tuning the chemical and physical properties of materials by varying the compositions (D. Chen et al., 2011). Among these ternary oxides, Zn_2SnO_4 is frequently reported as the most promising material for gas sensing applications. Recently, Tharsika et al. (2015) used a carbon-assisted thermal evaporation process to grow Zn_2SnO_4 NWs under ambient pressure and found it suitable for practical applications, such as gas sensing.

Hydrogen (H_2) gas is hard to detect because it is tasteless, colourless and odourless. However, it requires special caution in its handling because of its inflammable and explosive nature. Thus, precise hydrogen detection and constant observation is crucial for safe production, storage and exploitation of hydrogen in industry. Zn_2SiO_4-based nanostructures have been widely studied because of their considerable potential applications and importance in the study of size- and dimensionality-dependent chemical and physical properties (Rhoderick et al.; Soole et al., 1991). However, Ge/Zn_2SiO_4 hybrid compound applications, such as H_2 gas sensors have yet to be explored and reported.

2.6 Growth Mechanisms of Thermal Evaporation Technique.

Thermal evaporation (TE) technique has been extensively used for growing semiconductor materials in vacuum chambers or in furnace tubes. The TE mechanism is based on a vapor transport process, in which a material is physically released from a source material by heating and transformed into a substrate by gas carriers. No chemical reaction occurs when vapors directly solidify onto a surface. According to the difference in structure formation mechanisms, the widely used vapor transport process can be classified into two different categories, namely, the catalyst-free vapor–solid (VS) and catalyst-assisted VLS process.

2.6.1 Vapor-solid (VS) process

Synthesis utilizing the VS process is usually capable of producing a rich variety of nanostructures (Z. L. Wang, 2008, 2009), including NRs, NWs, nanobelts, and other complex structures. Without the aid of metal catalysts, VS growth is mainly used to synthesize metal oxides and certain semiconductor nanomaterials. According to the classical theories of crystal growth from liquid or vapor phases, the growth fronts perform a crucial function in atom deposition. Two kinds of microscopic surfaces exist, the first of which includes rough surfaces on which atoms of about several layers are not well arranged. The deposition of atoms is relatively easy compared with that on a flat surface, and crystal growth can continue if enough source atoms are continuously provided. The second surface involves atomically flat surfaces, on which atoms are well arranged. Atoms from the source present weak bonding with flat surfaces and can easily return to the liquid/vapor phase.

2.6.2 Vapor-liquid-solid (VLS) process

The VLS process is a growth mechanism using catalyst assistance. The VLS mechanism is the most widely used mechanism for NW growth (Wagner et al., 1964). Mohammad (2006) proposed a familiar mechanism to produce micrometer-sized whiskers in 1960 to explain the growth of Si whiskers using Au as metal catalyst. Three well-known phases of the growth mechanism occur. The first phase is the formation of molecules (metal alloys) as catalyst and source materials. The second step involves the formation of liquid droplets on the substrate surface and/or at polycrystalline mounds, and the last step is crystal nucleation and axial growth of NWs

In this process, various nanoparticles or nanoclusters are used as catalysts, such as Au, Cu, Ge, and Sn (Z. Fan et al., 2005). The formation of a eutectic alloy droplet occurs at each catalyst site. The alloy droplets absorb the vapor phase, resulting in supersaturated structures. Consequently, crystal growth occurs at the liquid–solid interface by precipitation, and NW growth commences. Thus, such a growth method inherently provides site-specific nucleation at each catalytic site. Based on the VLS mechanism, the diameter of NWs can be tuned by using different sizes of nanoparticles or nanocluster catalysts. In addition, the control of NW growth location and alignment has been realized by using patterning techniques and selecting proper epitaxy substrates.

2.7 Theory of X-Ray Crystallography

X-ray crystallography is a method used to examine the coordination of atoms in a crystal, whereby an incident X-ray beam on a crystal is reflected into numerous specific directions. Based on the intensities and diffraction angles of the beams, a three-dimensional (3D) image of the density of electrons in the crystal can be acquired. In turn, the electron density determines the mean locations of the atoms in the crystal, in addition to their disorder, chemical bonds, and several other details.

2.7.1 Bragg's Law

X-rays are waves of electromagnetic radiation, while crystals are regular arrays of atoms. Atoms scatter X-ray waves mainly by their electrons. This phenomenon is referred to as elastic scattering, and the electrons are called scatterers. Regular arrays of scatterers generate regular arrays of reflected waves. Although these waves disrupt each other in random directions through destructive interference, these add constructively in a few specific directions as resolved by Bragg's law, which was discovered by physicist Sir William Lawrence Bragg in 1912:

$$2d\sin\theta = n\lambda \tag{2.1}$$

where d (termed d-spacing) is the distance separating the diffracting planes, θ is the angle of incident photons, n is any integer, and λ is the wavelength of the X-ray beam. The constructive directions emerge as spots on the diffraction pattern referred to as reflections. Thus, X-ray diffraction (XRD) is derived from an electromagnetic