STRUCTURAL AND OPTICAL PROPERTIES OF SILICON CARBIDE QUANTUM DOTS GROWN BY VERY HIGH FREQUENCY PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION

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DEDICATION

To my greatest blessing Ummi & Ayoh Thank you For the unceasing prayer and the endless love and support

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ABSTRACT

This study presents the synthesis of Silicon Carbide Quantum Dots (SiC QDs) Frequency-Plasma Enhanced Chemical Vapour Deposition (VHFby Very High PECVD) method. Si (100) was used as a substrate where the growth was performed at a much lower temperature (100 $^{\circ}$ C) than previous work. Besides, the growth time has been shorten in order to enhance the SiC QDs growth process. The effect of different Radio Frequency (RF) plasma frequencies (150 MHz, 160 MHz and 200 MHz) on the structural properties of SiC QDs were investigated. The growth parameters such as growth temperatures, growth time and hydrogen flow rates were manipulated in order to study the optical properties of SiC QDs grown at 150 MHz. Silane (SiH₄) and methane (CH₄) were used as precursor gases and both were decomposed by RF plasma excitation to silicon (Si) and carbon (C) respectively at certain temperature for the growth of SiC QDs. The samples were then characterized by Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Microscopy (EDX) and Atomic Force Microscopy (AFM) to observe the morphology and structure of quantum dots. FESEM images show that the dots diameter increased as the RF plasma increased from 150 MHz to 200 MHz and the EDX analysis further confirmed that quantum dots consist mostly of silicon (Si), carbon (C) and oxygen (O) elements. From the crosssectional image, it was suggested that the growth of SiC quantum dots follows Stranski-Krastanow (S-K) mode. Moreover, AFM results revealed that the surface roughness also increased concurrently with the increased of RF plasma frequencies. Raman spectra analysis and X-Ray Diffraction (XRD) pattern further confirmed that some of them composed of crystalline peak of SiC at 780.32 cm⁻¹ with (200) growth plane. For emission properties of SiC QDs, two peaks detected for all samples located at 407 nm and 571 nm which are comparable to the 6H-SiC and 3C-SiC crystal structures. The energy band gap of a sample grown at 160 MHz with growth temperature of 200 °C was 3.19 eV which is approximately the energy band gap of 4H-SiC (3.20 eV). In conclusion, this enhancement method in growing SiC QDs can be applied in future study in terms of its material properties and also its application in nanodevice technology.

ABSTRAK

Kajian ini mempersembahkan sintesis Titik Kuantum Silikon Karbida (SiC QDs) menggunakan kaedah Pemendapan Wap Kimia Peneguhan Plasma-Berfrekuensi Sangat Tinggi (VHF-PECVD). Si (100) telah digunakan sebagai substrat di mana pertumbuhan telah dilakukan pada suhu yang lebih rendah (100°C) daripada kajian sebelum ini. Selain itu, masa pertumbuhan juga dipendekkan untuk meneguhkan proses pertumbuhan SiC QDs. Kesan frekuensi plasma Radio Frekuensi (RF) yang berbeza (150 MHz, 160 MHz dan 200 MHz) ke atas sifat struktur SiC QDs telah dikaji. Parameter pertumbuhan seperti suhu pertumbuhan, masa pertumbuhan dan kadar aliran hidrogen telah dimanipulasi untuk mengkaji sifat-sifat optik SiC QDs yang ditumbuh pada 150 MHz. Silane (SiH₄) dan metana (CH₄) telah digunakan sebagai gas pelopor dan kedua-duanya telah diuraikan oleh pengujaan plasma radio frekuensi (RF) terhadap silikon (Si) dan karbon (C) pada suhu tertentu untuk pertumbuhan SiC QDs. Sampel-sampel kemudiannya dicirikan dengan menggunakan Mikroskopi Elektron Pengimbasan Pelepasan Medan (FESEM), Serakan Tenaga Sinar-X (EDX) dan Mikroskopi Daya Atom (AFM) untuk memerhatikan morfologi dan sifat struktur titik kuantum. Imej-imej FESEM telah menunjukkan bahawa diameter titik-titik meningkat dengan peningkatan frekuensi plasma RF dari 150 MHz kepada 200 MHz. Analisis EDX seterusnya mengesahkan bahawa titik-titik kuantum kebanyakannya terdiri daripada unsur-unsur silikon (Si), karbon (C) dan oksigen (O). Daripada imej keratan rentas, adalah dicadangkan bahawa pertumbuhan titik kuantum SiC mengikuti mod Stranski-Krastanow (S-K). Selain itu, hasil AFM mendedahkan bahawa kekasaran permukaan juga meningkat sejajar dengan peningkatan frekuensi plasma RF. Analisis spektrum Raman dan corak Pembelauan Sinar-X (XRD) selanjutnya mengesahkan bahawa sebahagian daripadanya terdiri daripada puncak kristal SiC pada 780.32 cm⁻¹ dengan orientasi kristal (200). Bagi sifat pancaran SiC QDs, dua puncak dikenalpasti untuk semua sampel yang berada di 407 nm dan 571 nm yang setanding dengan struktur kristal 6H-SiC dan 3C-SiC. Jurang jalur tenaga bagi satu sampel yang ditumbuh pada frekuensi 160 MHz dengan suhu pertumbuhan 200° C ialah 3.19 eV iaitu lebih kurang sama dengan jurang jalur tenaga 4H-SiC (3.20 eV). Kesimpulannya, kaedah peneguhan dalam pertumbuhan SiC QDs ini boleh digunapakai dalam kajian masa depan dari segi sifat bahan dan aplikasinya dalam teknologi peranti nano.

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LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscopy
EDX	-	Energy Dispersive Spectroscopy
HF	-	Hydroflouric acid
RF	-	Radio frequency
R _{rms}	-	Root-mean-square roughness
SiC	-	Silicon Carbide
TEM	-	Transmission electron microscopy
HRTEM	-	High resolution transmission electron microscopy
DI	-	Deionized water
VHF	-	Very high plasma
UV-Vis	-	Ultra-violet Visible
XRD	-	X-ray diffraction
FM	-	Frank-van der Merwe
VW	-	Volmer-Weber
SK	-	Stranski-Kristanov
2D	-	Two dimension
3D	-	Three dimension
RF	-	Radio frequency
ТА	-	Transverse acoustic
ТО	-	Transverse optical
LA	-	Longitudinal acoustic
LO	-	Longitudinal optic
NEMS	-	Nanoelectromechanical System
FWHM	-	Full width at a high maximum
PL	-	Photoluminescence
QDs	-	Quantum dots
XRD	-	X-ray diffraction
TEC	-	Thermoelectric cooling
PECVD	-	Plasma enhanced chemical vapour deposition
FESEM	-	Field emission scanning electron microscopy

LIST OF SYMBOLS

E_g	-	Energy band gap
Ar	-	Argon
CH ₄	-	Methane
H_2	-	Hydrogen
N_2	-	Nitrogen
SiH ₄	-	Silane
α	-	Rhombohedral
Å	-	Lattice parameter
Vsat	-	Saturated drift velocity
β	-	Cubic
μ_e	-	Electron mobility
k	-	Thermal conductivity
T_m	-	Melting point
E_c	-	Critical electric breakdown field
D	-	Crystallite size
θ_{hkl}	-	Bragg angle
v	-	Frequency of incident angle
λ	-	X-ray wavelength
Δx	-	Uncertainty of position
Δp	-	Uncertainty of momentum
γe	-	Surface energy
Yes	-	Interface energy
γ_s	-	Energy of the substrate
μ_s	-	Strain energy
t_c	-	Critical thickness
S	-	Solid phase
8	-	Gas phase

n	-	Number of integer
θ	-	Angle of reflection
h	-	Planck's constant
sccm	-	Standard cubic centimeters per minute

CHAPTER 1

INTRODUCTION

1.1 Overview

This chapter explains the background of study, problem statement, objectives, scope and also significant of the research. Finally the thesis layout will be presented at the end of this chapter.

1.2 Background of the Study

The fabrication of nanostructure materials has been a great interest in the past few years. Nanostructures with nanoscale dimensions have been put so much attention by many researchers due to their interesting characteristics and properties compared to those of bulk materials. Silicon carbide (SiC) materials are among the most popular candidate since their properties are essentially correspond to the available semiconductor production processes.

As a wide bandgap semiconductor materials, SiC has received a great deal of attention due to their application in high frequency, high temperature and high power systems (Lucia *et al.*, 2017). Its outstanding mechanical properties, chemical inertness and thermal stability has gained important for several applications in optoelectronic devices such as light emitting diode, electroluminescent devices, nanoelectromechanical system (NEMS) sensors fabrication and also thermoelectric cooling (TEC) devices for deployment in harsh environments (Zorman and Parro, 2008).

In recent years, zero-dimensional semiconductor such as Silicon Carbide Quantum Dots (SiC QDs) have been studied because of their unique properties for device application. Quantum dots are interesting building blocks for the fabrication of various devices on nanometer scale. Thus, the fabrication and understanding of the properties of SiC QDs are decisive for the development of SiC based nanodevices. Generally, there are various methods that have been used to synthesize SiC QDs for the past few decades.

One of the common method that have been applied to grow SiC QDs is inductively coupled plasma assisted RF magnetron sputtering. For example, Cheng et al. (2007) managed to fabricate SiC QDs by means of low frequency (13.56 MHz) and low substrate temperature of 400°C on Si substrates. They confirmed that by varying the growth time from 20 to 120 minutes, the size and density of the SiC QDs increased from 14 nm to 29 nm. From the observation, the nanosized SiC grains covered the entire Si (100) surface uniformly. (Cheng *et al.*, 2007).

SiC QDs also have been successfully synthesized by electrochemical etching method. Fan et al. (2012) reported the fabrication and photoluminescence properties of SiC QDs stemming from different polytypes (3C, 4H and 6H) of bulk SiC by electrochemically etched for 40 minutes in a HF:C₂H₅OH=2:1 solution. After 30 minutes of ultrasonic treatment in deionized water, the solution become isolated colloidal SiC crystallites. Then, centrifugation take place to remove larger particles and a stable aqueous solution of SiC QDs for each polytype was obtained. The photoluminescence properties had been investigated for these three polytypes of grown quantum dots. The values of full width at half maximum (FWHM) of all spectra lie between 100 and 130 nm. The broad width of the spectrum are caused by the wide size distribution of the particles. From TEM characterization, it reveals that the size distribution of each sample ranging from 1 nm to 8 nm (Fan *et al.*, 2012).

In optoelectronics, SiC QDs are also adapted for bioanalysis application. Beke (2012) used the method of wet chemical etching of SiC microcrystals to form nanosize SiC QDs. In this method, Silicon and graphite powder were first ground and pressed into a pallet before heated in an induction chamber to produce microcrystalline SiC powder. Then, the sample was etched in HF (50%), HNO₃ (68%) and water mixture with volume ratio of 2:1:5 followed by washing with deionized water to make sure the SiC powder are clean from Si and C residue. All the dried sample was annealed at 900 °C for 6 h. Moreover, in order to produce the highest yield, about 2.0 g of clean SiC

powder was placed in 23 mL Teflon-lined acid and annealed for 2 h at 120 °C. Finally, the sample with acid-treated were sonicated for 1 h and centrifuged at 4000 rpm for 1.5 h to produce SiC QDs. The High Resolution Transmission Electron Microscopy (HRTEM) result confirmed that the SiC QDs are nearly spherical and the typical lattice spacing of 0.25 nm corresponds to the (111) plane of 3C-SiC. The average size distribution was 3 nm with relatively small dispersions in size (1–8 nm). With excitation range between 300-400 nm, photoluminescence (PL) of the SiC QDs was observed. The highest band intensity appears at an excitation of 360–370 nm with the corresponding emission in the range of 420–450 nm. In comparing to their previous study, there is a slight blue shift in the emission maximum of PL spectrum between closed and open system of synthesized SiC QDs and the spectrum for the closed reaction chamber is less broad due to the difference size distribution (Beke, 2012).

In other research, Zhu et al. (2014) fabricated 3C-SiC quantum dots by pulsed laser ablation method. The polycrystalline 6H–SiC target was placed into a cylindrical glass with deionized (DI) water. The top of 6H–SiC target to the surface of DI-water is set to 8 mm in distance. The target was then irradiated with 248 mm laser beam with 10 ns of pulse duration and 10 Hz repetition rate. At a power of 320 mJ/pulse, SiC QDs colloidal solutions were prepared after about 2 h of laser irradiation. The TEM images reveal that most of the dots are about 2 nm in size. At the excited wavelength of 260–420 nm, the QDs show violet–blue photoluminescence (PL) emission. The dependence of PL intensity and peak position on the excitation wavelength confirms that QDs with the diameter of ~2 nm are 3C-SiC (Zhu *et al.*, 2014).

As being described before, several of the most common techniques used in fabrication of SiC QDs are revealed. To the best of our knowledge, there were no reports on SiC QDs growth by VHF-PECVD technique at higher frequency of 150 MHz. Initial work reported by Alim et al. (2017) shown that SiC thin films was successfully deposited using VHF-PECVD at temperature of 400 °C. In this study, they investigated the effect of methane flow rates on the luminescence properties of the deposited thin film at 150 MHz. In other work, Azali et al. (2018) studied the crystallinity of the deposited thin film using the same method with different plasma frequencies of 100, 160 and 200 MHz. The results revealed that the crystallinity of the grown thin film increases with frequency (Azali *et al.*, 2018).

1.3 Problem Statement

Silicon carbide (SiC) has many advantages of its characteristics for semiconductor applications such as high thermal conductivity (Goela *et al.*, 2006), wide band gap (Lucia *et al.*, 2017), high electron mobility (Microsemi, 2014) and high-saturated electron velocity (Bhagoji, 2012) and chemically inert (Gutmann *et al.*, 2010). According to those superior properties, SiC is a good candidate to be used for semiconductor devices such as power transistor, thermoelectric, optoelectronics and as coating material. Increasing the surface to volume ratio of the material to nanometer level such as SiC QDs structures will enhance the ability of SiC to operate in high temperature devices (Cheng *et al.*, 2014).

Nowadays, there has been a lot of methods in fabricating SiC QDs for nanodevices application such as RF magnetron sputtering (Cheng *et al.*, 2007), electrochemical etching method (Fan *et al.*, 2012), wet chemical etching (Beke, 2012) and laser ablation method (Zhu *et al.*, 2014).

There are still some lacking point in each method approached. In summary, from the previous study in fabrication of SiC QDs, there are still no approaches to synthesize SiC QDs by VHF-PECVD except for SiC thin film (Alim *et al.*, 2017; Azali *et al.*, 2018). Thus, VHF-PECVD is expected to be able to synthesize SiC QDs with shorter growth time from 1 to 5 minutes at lower temperature of 100 °C and higher frequency plasma of 150 MHz to 200 MHz. From conventional plasma excitation frequency to the higher frequency, it is also expected that it will influence the morphology, structural and optical properties of the grown SiC QDs. From this work, it is also expected that the grown SiC QDs will improve the photoluminescence emission which is tunable from blue to green emission in order to enhance the optical properties of SiC QDs for optical device applications.

1.4 Research Objectives

The objectives of the research are:

- (a) To synthesize the SiC QDs using VHF-PECVD technique at various growth parameters such as RF plasma frequency, growth temperature, growth time and hydrogen flow rate.
- (b) To characterize the morphology and structural properties of SiC QDs grown with different RF plasma frequencies (150, 160 and 200 MHz).
- (c) To determine the effect of growth temperature, growth time and hydrogen flow rate to the optical properties of the grown SiC QDs at optimized plasma frequency in (b).

1.5 Scope of Study

SiC QDs will be synthesized on silicon (Si) (100) substrate using VHF-PECVD at frequency of 150 MHz, 160 MHz and 200 MHz. Then, QDs of 150 MHz RF plasma frequency will be grown with various growth parameters such as gas flow rate, growth time and growth temperature. The surface morphology and the elemental composition of the grown QDs were analysed using FESEM, EDX and AFM. Structural properties of the synthesized quantum dots were observed by using XRD analysis and Raman spectroscopy. While PL and UV-Vis were used to characterize the optical properties of the SiC QDs.

1.6 Significant of Study

From this research, the structural and optical properties of the QDs can be controlled by manipulating the growth parameters of VHF-PECVD method. These characteristics of the grown SiC QDS are important for the application in optoelectronics and microelectronics especially in extreme environment. This research will give better understanding on morphology, structural and optical properties of SiC QDs grown at high RF plasma frequency.

1.7 Thesis Structure and Organization

This thesis is divided into several chapters. Chapter 1 presents some information of previous works that related to this study. The problem statement, objectives, scope and significant of the research are also presented. In Chapter 2, literature review related to this research will be discussed. This will cover in details about silicon carbide nanostructures and its properties, semiconductor quantum dots and its growth modes. Fundamental principle of PECVD method and the precursor gases used by previous researchers involved in growth of SiC QDs will be included in this chapter. Chapter 3 is the methodology which explain the fabrication of SiC QDs. Its present the sample preparation, fabrication of the quantum dots and followed by characterization techniques that will be used to observe the morphology, structural and the optical properties of the SiC QDs. Finally, the growth parameters in this research follows by Chapter 5 which conclude the research work and some recommendations for future research work. References and appendices are also listed at the end of this thesis.

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