WASTE BIOMASS ASSISTED SYNTHESIS OF SILICON NANOSTRUCTURES FOR PHOTOELECTROCHEMICAL WATER SPLITTING

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FACULTY OF SCIENCE UNIVERSITI MALAYA KUALA LUMPUR

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WASTE BIOMASS ASSISTED SYNTHESIS OF SILICON NANOSTRUCTURES FOR PHOTOELECTROCHEMICAL WATER SPLITTING

ABSTRACT

This work reports on the growth of Si nanostructures (nanorods and nanowires) by a chemical vapor deposition technique. The main interest of this work is to utilize the wastebiomass sources for the application of photoelectrochemical water splitting. This work is initiated to transform the biomass into a value-added product as well as to investigate the optimization conditions of Si nanostructures as photocatalyst for the water splitting application. In this work, the effect of variation of SiO₂ source masses (15 to 150 mg) on the growth, structural and optical properties of the nanostructures are studied at a fixed deposition temperature of 1410 °C. Si nanorods were prepared at low SiO₂ source masses of 15, 25 and 50 mg with an average diameter of about (247 ± 22) , (55.1 ± 5.5) and (221) \pm 28) nm, respectively. An increase in SiO₂ source masses of 100, 125 and 150 mg resulted in the formation of high-density Si nanowires with relatively smaller in average diameter of (31.8 ± 3.0) , (48 ± 4) and (82 ± 17) nm, respectively. The microstructure studies of these nanostructures have revealed the perfect single crystal structure of a highly crystalline Si nanowires with a very thin amorphous SiO_x layer. Therefore, this resulted in the band gap energies of the Si nanowires and nanorods been tailored within the UV and visible light region showing an excellent visible light absorption capability. Apart from that, this work also highlights on the photoelectrochemical behaviour of asgrown Si nanowires with a better photocurrent density of 0.5 mA cm⁻² as compared to asgrown Si nanorods at a potential of 0.6 V in Ag/AgCl aqueous solution. This is attributed to the extremely large surface area and large number of active sites of Si nanowires, which enhancing the water splitting oxidation and reduction reaction processes. The role of silica in facilitating the growth mechanism of these nanostructures were also discussed.

Keywords: Si nanowires, CVD, biomass, photoelectrochemical water splitting

BIOJISIM BUANGAN MEMBANTU SINTESIS NANOSTRUKTUR SILIKON UNTUK PENGURAIAN AIR FOTOELEKTROKIMIA ABSTRAK

Hasil kerja ini melaporkan tentang pertumbuhan struktur nano Si (rod nano dan nanowayar) yang dihasilkan melalui teknik pemendapan wap kimia. Keutamaan kerja ini adalah memanfaatkan sumber biojisim buangan untuk kegunaan aplikasi penguraian air fotoelektrokimia. Kerja ini dimulakan sebagai langkah untuk mengubah biojisim buangan kepada produk yang ditambah nilai dan untuk mengkaji kondisi optimum struktur nano Si sebagai fotokatalis di dalam aplikasi penguraian air. Dalam kerja ini, kesan variasi sumber jisim SiO₂ (15 hingga 150 mg) terhadap sifat-sifat pertumbuhan, struktur dan ciri optik struktur nano telah dikaji pada suhu tetap proses pemendapan 1410 °C. Rod nano Si telah dihasilkan pada sumber jisim SiO₂ yang rendah iaitu 15, 25 dan 50 mg dengan purata diameter (247 ± 22) , (55.1 ± 5.5) dan (221 ± 28) nm. Pertambahan sumber jisim SiO₂ kepada 100, 125 dan 150 mg telah menghasilkan nanowayar Si pada ketumpatan yang tinggi dengan anggaran purata diameter yang lebih kecil iaitu $(31.8 \pm 3.0), (48 \pm 4)$ dan (82 ± 17) nm. Sementara itu, penyelidikan struktur mikro bagi struktur nano tersebut telah menunjukkan nanowayar Si mempunyai struktur kristal tunggal yang tinggi yang terdiri daripada hablur tunggal dan lapisan nipis polihabluran SiOx. Oleh yang demikian, ini telah memberikan kesan kepada jurang kumpulan tenaga nanowayar Si dan rod nano yang disesuaikan dalam lingkungan julat UV dan cahaya yang kelihatan serta telah menunjukkan kemampuan penyerapan cahaya yang kelihatan yang sangat baik. Selain itu, kerja ini turut membincangkan tentang tingkah laku fotoelektrokimia nanowayar Si yang dihasilkan dengan ketumpatan arus foto yang lebih baik berbanding rod nano Si sebanyak 0.5 mA cm-2 pada potensi 0.6 V di dalam larutan Ag/AgCl. Hal ini disebabkan oleh jumlah luas permukaan nanowayar Si dan jumlah kawasan aktif yang menggalakkan penguraian air dan proses reaksi pengoksidaan dan penurunan yang berkesan. Tugas silika dalam membantu mekanisma pertumbuhan struktur nano turut dibincangkan.

Kata kunci: Nanowayar Si, CVD, biojisim, penguraian air fotoelektrokimia

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LIST OF SYMBOLS AND ABBREVIATIONS

α	:	absorption coefficient
Al	:	aluminium
a-Si	:	amorphous silicon
Ar	:	argon
С	:	carbon
СО	:	carbon monoxide
R _{ct}	:	charge transfer resistance
Cu	:	copper
c-Si	:	crystal silicon
e ⁻	:	electron
Au	:	gold
H ₂	:	hydrogen
Fe	:	iron
nc-Si	:	nanocrystalline silicon
N_2	:	nitrogen
1D	:	one dimensional
E_g	:	optical energy gap
0	:	oxide
hv	:	photon energy
Pt	:	platinum
SiH ₄	:	silane
Si	:	silicon
SiC	:	silicon carbide
SiO ₂	:	silicon dioxide/silica

SiO	:	silicon monoxide
SiNWs	:	silicon nanowires
SiO _x	:	silicon oxide
Ag	:	silver
AgCl	:	silver chloride
R_s	:	solution resistance
wt%	:	weight percent
BSE	:	backscattered electron
CB	:	conduction band
CVD	:	chemical vapor deposition
DI	:	deionized
EDX	:	energy dispersive x-ray spectroscopy
EIS	:	electron impedance spectroscopy
FESEM	:	field emission scanning electron microscopy
FFT	:	fast fourier transform
FWHM	:	full width at half maximum
HRTEM	:	high resolution transmission electron microscopy
IPA	:	isopropyl alcohol
LA	:	longitudinal acoustic
LO	:	longitudinal optic
LSV	:	linear sweep voltammetry
NIR	:	near infra-red
PEC	:	photoelectrochemical
PES	:	photoelectron spectroscopy
PL	:	photoluminescence
TA	:	transverse acoustic

TEM	:	transmission electron microscopy
ТО	:	transverse optic
UV	:	ultraviolet
UV-Vis	:	ultraviolet visible spectroscopy
VB	:	valence band
XPS	:	x-ray photoelectron spectroscopy
XRD	:	x-ray diffractometer

CHAPTER 1: INTRODUCTION

1.1 Energy Crisis and Advantages of Hydrogen Generation via Water Splitting

Energy and environmental issues have become increasingly severe since the early twenty-first century (Yuan et al., 2019). Global primary energy consumption is expected to soar at least twice by the year 2050, in tandem with global population growth (Lewis et al., 2006). The analysis on global fossil fuels consumption over years is clearly reported by Our World in Data (2020) as shown in Figure 1.1. The need to expedite the energy transition by substituting fossil fuels with renewable energy sources has demanded the scientific innovation of energy saving technologies. The major key challenge is to provide an environmentally sustainable, clean and secure energy at low cost and improve quality. Motivated by the rising awareness concerning global climate change, efforts are made to innovate alternative energy sources. There are several significant movements towards sustainable energy sources that can be used in the future such as nuclear power, wind, solar energy, biomass and hydroelectric power. Among these resources, solar energy is by far the greatest exploitable resource, free and non-polluting. A multistep approach is followed to first harvesting the solar radiation into electricity and then to generate hydrogen using the electricity by various catalytic processes (Marepally et al., 2019). Photocatalytic water splitting utilizes solar energy and water, offering potential alternatives for hydrogen production. Hydrogen is regarded as one of the most promising secondary energy sources since it is non-polluting, infinitely renewable and efficient energy transporter that may be utilized to minimize the long term reliance on fossil fuels and CO₂ greenhouse gases emission (Zhou et al., 2011).



Figure 1.1: The global fossil fuel consumption over years. Ritchie, H. (2020). *Fossil Fuels*. Our World in Data. Retrieved from https://ourworldindata.org/fossil-fuels.

1.2 Background of Materials

Nanotechnology promotes the fabrication of nanometer scale structures, defines as one dimensional (1D) structure with distinctive features and potentials in wide variety applications. 1D nanomaterials are unique due to their high aspect ratio characteristics as well as excellent structural (Adachi et al., 2010; Nazarudin et al., 2015), electrical (Goh et al., 2014; Shin et al., 2014) and optical properties (Bae et al., 2010; Hamzan et al., 2015). Among these nanostructures, nanowires have received a huge interest in nanotechnology research due to their rigid structures (Chopra et al., 2007). Significance progress in nanotechnology necessitate approaches for observations, characterization and controlling nanoscale phenomena. Generally, nanostructured materials such as nanowires, nanorods and nanoparticles can be classified as structures having one of a dimension less than 100 nanometers. The physical characteristics of these 1D structures

are remarkably different from bulk materials and have led to a variety of potential applications from sensing (Abdul Rashid et al., 2013), photovoltaic solar cells (Yu et al., 2016a), Li-ion batteries (Burchak et al., 2019), supercapacitors (Soam et al., 2017) and to photoelectrodes in water splitting (Dytrych et al., 2018; Liu et al., 2015).

Si has always been the dominating semiconductor materials in the microelectronics industry (Kwon et al., 2018; Peng et al., 2013). However, bulk Si exhibits weak infrared photoluminescence due to its indirect band gap, in which inhibits effective interband radiative recombination (Arzate et al., 2011). Consequently, 1D silicon nanowires (SiNWs) are introduced to allow effective photoexcitation owing to the quantum size effects (Hutagalung et al., 2017). The relatively small dimension will allow even a little input signal to optimally regulate the potential of the nanowire, making the nanowire highly sensitive especially for chemical sensing or bio sensing (Mikolajick et al., 2015). The same feature also allows in the successful power conversion efficiency (PCE) of solar cells recorded at 25 % by Martin Green's group in 1998 (Green et al., 2012), verifying the effective collection of incident solar radiation. On top of that, SiNWs with diameters in the order of visible light wavelengths exhibit significant resonant field enhancement of incident light, making them a viable option for a variety of photonic devices (Quan et al., 2019).

The fabrication of SiNWs from biomass sources is becoming a favourable approach considering the alternative and economical way in converting the agricultural wastes into useful nanomaterials (Chiew & Cheong, 2011; Huang et al., 2020; Li et al., 2012). The studies on these organic type raw materials by thermochemical technologies were extensively investigated due to their low cost, large yield, simple process and eco-friendly (Zhu et al., 2013). Indeed, the utilization of this method is not only capable to fabricate 1D nanomaterials but also has solved the disposal problem of this organic waste. The

synthesize of Si nanostructures from plant-based biomass was firstly reported by Lee and Cutler in 1975, using rice husk ash (RHA) (Chiew et al., 2012) and was studied in depth by others using coconut shell, coconut fibres, sugarcane leaf with rice straw, cotton fibres, bamboo leaves, and palm kernel shell (Voon et al., 2016). In fact, these natural wastes, especially RHA and palm kernel shell are available in large-scale everywhere in Malaysia owing to its industry abundant by-products.

SiNWs materials are believed to be efficient in solar-driven hydrogen generation via water splitting to replace exhaustible fossil fuels in the future (Mohd Daud et al., 2016). The significant natural abundance, environmental safety and the previously stated benefits have enhanced the reliability of Si as a photoelectrode material (Yuan et al., 2019). The SiNWs exhibit a tunable band gap within the UV and visible spectral region (Chong et al., 2012) which is of important for photoelectrochemical (PEC) behaviour and the potential water splitting redox processes. Furthermore, the extremely large surface area of SiNWs could enhance the light absorption efficiency in the UV and visible regions, and additionally give excellent performance in PEC water splitting devices (Chong et al., 2012). Considering the fact that Si nanowires and nanorods have small radius, the photo-generated charge carriers in the nanostructures can diffuse to the semiconductor/electrolyte interface before recombination (Hwang et al., 2012; Stolterfoht et al., 2016). This could enhance the charge separation efficiency, mostly when diffusion length of the photo-excited charge carriers is comparable to the radius of the nanowires or nanorods.

The optical energy gap, E_g of a semiconductor material is crucial in the light-matter interactions. Photons with sufficient energy are absorbed by nanomaterials generating electrons and holes during the recombination process and inducing redox reaction process. In PEC water splitting, semiconductor photocatalysts must satisfy several main requirements to achieve an efficient photocatalytic activity on the basis of following theories:

- 1. Photoelectrodes materials have a suitable energy gap approximately 2-3 eV which allows them to absorb 43 % of total solar irradiance covering the visible light region as illustrated in Figure 1.2.
- 2. The bottom level of conduction band edge must be positioned at a more negative potential than hydrogen reduction potential and the valence band must be located at a more positive potential than the water oxidation potential as shown in Figure 1.3.
- 3. Photoelectrodes materials have a high chemical and physical stability against photocorrosion in dark and illuminated conditions.

The sun transmits light with a variety of wavelengths that include the ultraviolet (UV) (300-400 nm), visible light (400-700 nm) and near infra-red (NIR) (700-2500 nm) electromagnetic spectrum. The maximum intensity of solar radiation is concentrated on a visible light with an irradiance of 43 % as shown in Figure 1.2. Meanwhile, 9% of the solar irradiance is in UV and 48% is in near infra-red (NIR) region. Therefore, the band gap energy of an effective photoelectrode is ought to be approximately 2-3 eV to widen the absorption of light within the visible region and utilizes the solar energy effectively. These energy gaps are equivalent to irradiance wavelength of 413-620 nm, which is within the visible light region.

Additionally, in order to achieve overall PEC reaction, the energy requirements necessitate that the bottom of the conduction band (CB) edge is positioned more negatively than the reduction potential of H^+/H_2 (0 V vs normal hydrogen electrode (NHE) at pH of 0). Meanwhile, the top of the valence band (VB) edge is positioned more positively than the oxidation potential of H_2O/O_2 (1.23 vs NHE). The band positions of

different semiconductor photocatalysts in relation to potential (NHE) for water oxidation and reduction processes are depicted on Figure 1.3. The suitable semiconductors that meet the thermodynamic criteria for overall water splitting are TiO₂, CdS, GaP, SiC, WO₃ and Fe_2O_3 . However, photocatalyst must also be able to generate and separates photo-excited electrons and holes at a low recombination rate (Joy et al., 2018). The transportation of electrons and holes at the photocatalyst surface are highly influenced by the microstructure and photocatalyst surface (Lin et al., 2019; Yerga et al., 2013). The photoactivity of highly crystalline semiconductor photoelectrode rises in general due to the density of defects generated by the grain boundaries which serve as recombination sites for photo-excited electrons and holes (Adamczyk et al., 2018). In a way, this means that reducing the particle size of photocatalysts will impact the possibility of charge carrier reaching the photocatalyst surface. Consequently, the improved microstructure of other photocatalysts such as ZnS, Si, CdSe and MOS₂ with high crystalline degree gives high impact on the efficiency for overall water splitting reaction.



Figure 1.2: Solar irradiance spectrum percentages respected to wavelength. (Cocilovo et al., 2015).



Figure 1.3: (a) Schematic diagram of basic principle of PEC water splitting. (b) Band structure of semiconductor respected to water redox reaction. (Tee et al., 2017).

1.3 Problem Statements

Despite the fact that Si materials have been studied extensively and demonstrates excellent properties in PEC water splitting, yet they suffer from several difficulties in the optical absorption and the band energy configuration of this material. Si has an indirect band gap energy of 1.1 eV (Cao et al., 2016; Tian et al., 2019) and can only absorb approximately 4 % of the total solar spectrum, insufficient to initiate the oxidation and reduction of water. The indirect band gap of Si severely restricts its application in electrical and optoelectronic devices. Designing a highly efficient and stable photoelectrodes practically for water splitting requires the advanced semiconductor materials and fundamental understandings on the photoelectrode materials. These limitations reveal that the photoresponse of Si within the visible light region is critical, hence one method for doing so is by altering the band gap of SiNWs within the ultravisible (UV) and visible light (VIS) region.

Hasan et al. (2013) reported the modification of band gap energy of SiNWs by controlling the nanowires diameter. Electronic band gap width is dependent with the size of SiNWs irrespective to wire growth direction. The decrease in size of nanowires will widen the band gap energy, deviating it from bulk Si. Therefore, the optimization growth parameters of SiNWs for an ideal photocatalysts is an important motivation to defeat the problems mentioned earlier.

1.4 Motivations and Research Objectives

Band gap tuning of SiNWs has opened the doorway to enhance the absorption of light into visible region for the redox chemical reactions. Semiconductor materials with wide band gap energy allow devices to conduct at higher voltage and temperature. The band gap width is the crucial factors for most nano photocatalytic phenomena to determine the amount of solar energy been absorbed (Preethi et al., 2013). This wide band gap material covers the electronic transition of valence band and conduction band within the range of visible light region.

The successful works on band gap tuning of SiNWs was also previously reported by Ma et al. in 2003. Small diameter of SiNWs were observed ranging from 1 to 7 nm. The electronic energy gap of SiNWs showed an increment from 1.1 eV to 3.5 eV as the diameter of SiNWs was controlled from 7 nm to 1.3 nm, respectively (Ma et al., 2003).

According to Vidur et al. (2010), the utilization of nanowires offers an advantage similar as quantum dots, in which the band gap can be tailored to a specific region in the solar spectrum. Hence, quantum confined Si nanostructures with SiO₂ or SiC barriers might possibly meet these conditions and enable simultaneous cell configurations.

The objectives of this research are to demonstrate a high quality and efficient photoelectrode materials at low cost as a resolution for environmental issues. The three main research objectives can be summarized as follows:

- 1. To grow single crystalline Si nanostructures via CVD technique.
- 2. To investigate the morphological, structural and optical properties of Si nanostructures.
- To evaluate a photoelectrochemical (PEC) water splitting performance by Si nanostructures.

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1.5 Outline of Thesis

The thesis covers five main chapters basically including the literature review studies of Si nanostructures (Chapter 2), preparation technique and sample characterization of Si nanostructures (Chapter 3), results and discussions for each characterization analysis in terms of morphology, structural and optical properties and PEC performance properties (Chapter 4) and ends up with conclusions and future works suggestions (Chapter 5).

Chapter 1 briefly presents the background of materials and their properties in PEC water splitting, follows by research problem statements, motivations and objectives of the work. Chapter 2 highlights the literature review on the structural and optical properties of Si nanostructures. The growth mechanism model and deposition techniques of Si nanostructures were reviewed in this chapter. Furthermore, the utilization of waste biomass from palm kernel shell to produce SiNWs was also clarified. From the literature reviews, the effects of morphologies and optical energy gap for PEC water splitting was discussed at the end part of this chapter. Chapter 3 demonstrates the CVD experimental setup and procedures to grow SiNWs and the optimization parameters implemented in this work. The fundamental theories on the characterization analysis are presented. Next, chapter 4 discusses the results of morphological, structural, elemental composition and optical properties of SiNWs grown at varied SiO₂ and C source masses. The PEC performance of the as-grown sample was also demonstrated in this chapter. This thesis ends with chapter 5 that presents the summary and conclusions of this work including the suggestion for future works.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

The previous Chapter 1 introduced the excellent performance of Si nanostructures (nanorods and nanowires) in many research areas, despite their challenges in light absorption capabilities. This chapter briefly describes the outstanding structural and optical features of Si nanostructures that have struck a conspicuous attention over the years. Various deposition techniques of Si nanorods and nanowires have been well discussed in the first part of this chapter which compares the laser ablation and CVD growth techniques. Further discussion on the growth mechanism models of these 1D nanostructures has also been reviewed involving the VLS and OAG mechanisms. This is followed by the recent progress on the fabrication of Si nanostructures as photocatalyst in PEC application.

2.2 Si nanostructures

2.2.1 Introduction

Silicon (Si) has been recognized as a preferred material in the microelectronic, nanoelectronics and photovoltaics devices for ages. However, the optical properties of bulk Si turns out to be the critical constraints in optoelectronic applications due to its indirect band gap which prevents the effective light emission and absorption. In this case of indirect band gap, the atomic transition of electron from maximum valence band to minimum conduction band is mediated by phonons in order to gain or lose momentum (Cao et al., 2016). Therefore, high optical performance is required in optoelectronic integration, a technique of creating highly functional circuits by the combination of optical components and electrical components (Priolo et al., 2014). The transition of indirect to direct band gap is highly desired for not only widens their light absorption range to visible light region, but it also considerably increases their absorption intensity.

This could open up the opportunities for a better, cost-effective and highly integrated photovoltaic or photocatalytic devices.

The functionalization of Si nanostructures validates the improvement of these optoelectronic devices properties. In fact, Si nanostructures has become the cornerstone of one-dimensional (1D) semiconductor materials because of their small and unique structures. The one-dimensional (1D) Si nanostructures such as Si nanorods and nanowires have unique structural (Chong et al., 2011; Naffeti et al., 2020), optical (Bae et al., 2010; Quan et al., 2019) and electronic (Goh & Rahman, 2014; Xue et al., 2018) properties. These include that the 1D structure generally possesses an extremely large surface area, high charge trapping volume, and very high electron transport literally compared to bulk semiconductor material (Chiew et al., 2011; Constantinou et al., 2016). The excellent properties of Si nanorods and nanowires have tremendously solved technical challenge in Si thin film materials (a-Si or nc-Si or c-Si). For example, interfacial lattice mismatch of optically active materials has been overcome by relaxing lattice strain at the interface of the nanowire resulting in the dislocation-free growth on the lattice mismatched substrate (Goktas et al., 2018). Furthermore, 1D Si nanostructures with its band gap tunability, high chemical stability, excellent mechanical and thermal properties (Yu et al., 2016b), and high charge carrier mobility (Bollani et al., 2019) provide great advantages for specific applications in electronics, optoelectronics, sensors, and thermoelectric devices (Mohd Daud et al., 2016; Shao et al., 2010).

2.2.2 Structural properties

TEM analysis revealed that straight wires might have stacking fault commonly in large diameter nanowire (Hocevar et al., 2012). Hyun et. al (2009) reported the TEM image of SiNWs by VLS method with a kinking structure and extensive branching. The kinking in nanowires is a direct outcome of the shifting in the growth direction from (111) to (112)

orientation plane driven by the sudden enhancement in the total pressure. The TEM image of the kinking in SiNWs are shown in Figure 2.1 (a). Furthermore, the formation of kink in the growth of SiNWs is likely to be driven by some irregularities at the liquid/solid interface as reported by Westwater et al. (1997). Figure 2.1 (b) displays a hexagonal cross section TEM image of the kinked nanowires with a vertical (112) facets parallel to the (111) growth orientation of SiNWs. Meanwhile, the lattice spacing of SiNWs with a welldefined single crystal structure was observed at a crystalline lattice spacing of 0.314 nm (Figure 2.1 (c)). This lattice constant was corresponded to crystallographic orientation of Si (111). On the other hand, the difference in Si morphology based on the pyrolysis temperature is demonstrated by Jeong et al. (2020). The TEM image shown in Figure 2.1 (d) exhibited a SiNWs cluster particle. The thick dendritic crystals may be seen on the right bottom of the cluster, marked by a circle. A cluster of thick dendritic crystals seems to be the core and surrounds by many kinked SiNWs. The transformation of Si morphology from spherical shape Si nanoparticles to kinked shape SiNWs demonstrated the growth rate increment of the reaction temperature. The selected area electron diffraction (SAED) pattern presented the formation of a homogenous rings referred to silicon crystals as a core surrounded by randomly oriented kinked Si nanowires as shown in the inset of Figure 2.1 (d).



Figure 2.1: (a) TEM image of kinked SiNWs with branches. (b) The cross-sectional TEM image of SiNWs with hexagonal facets. (c) The respected crystalline lattice spacing of Si (111). (d) TEM image of SiNWs cluster particle with kinked SiNWs. Thick dendritic crystals are marked by circle. Inset represents the SAED pattern of crystal Si core and randomly oriented kinked SiNWs. (Hyun et al., 2009; Jeong et al., 2020).

The typical Raman scanning spectra of SiNWs with crystalline and amorphous characteristics are shown in Figure 2.2 (a). The Raman peaks were clearly seen at 148, 342 and 485 cm⁻¹ corresponded to active phonon modes of amorphous Si (Jangid et al., 2018). According to Yogi et al. (2017), a sharp Raman peak located at ~520 cm⁻¹ was perfectly assigned to the optical phonon Raman scattering. The symmetrical and high intensity of the Lorentzian Raman spectra indicates the high crystallinity of SiNWs. Figure 2.2 (b) illustrates the Raman spectra of SiNWs prepared on p-type Si wafer with different resistivity of 0.01 and 0.001 Ω respectively. Agarwal et al. (2019) demonstrated the Raman excitation bands of SiC nanowires prepared at different scan position to characterize the ion irradiation damage with the dependency of depth surface. The spectra are shown in Figure 2.3. The wide Raman spectra of SiC nanowires was displayed in Figure 2.3 (a). Two noticeable peaks are observed at 794 cm⁻¹ and 970 cm⁻¹ which are perfectly assigned to Si-C bond with a cubic structure as shown in the magnified Raman spectra ranging from 650 to 1000 cm^{-1} in Figure 2.3 (b). The characteristics of these peaks represent the transverse optical (TO) and longitudinal optical (LO) vibration of phonon modes. Meanwhile, the peaks between 1000 and 1600 cm⁻¹ as illustrated in Figure 2.3 (c) are related to C-C vibrations (D band and G band) implying the carbon structural disorder.


Figure 2.2: (a) Typical Raman spectra of Si nanostructures. (b) High intensity of Raman peak corresponds to highly crystalline Si structure. (Jangid et al., 2018; Yogi et al., 2017).



Figure 2.3: (a) The wide Raman spectra of SiNWs. (b) The magnification spectra of TO and LO peak. (c) The magnification spectra related to C-C phonon vibrations. (Agarwal et al., 2019).

Comedi et al. (2006) reported the XRD patterns of Si nanostructures with four prominent peaks resolved at $2\theta = 22^{\circ}$, 28.3 °, 47.5 ° and 55.9 ° as shown in Figure 2.4 (a). The first peak at angle 22 ° with broad hump features was attributed to the amorphous SiO₂. Meanwhile, the other three peaks were assigned to cubic Si with orientation planes of (111), (220) and (311) which were really close to the expected Braggs peaks of Si [JCPDS card number 27-1402] (Sun et al., 2016). Meanwhile, the XRD patterns of SiC nanostructures were observed at three diffraction angles at 35.7 °, 60 ° and 71.8 ° which corresponding to 3C-SiC as depicted in Figure 2.4 (b). These peaks were correlated with orientation planes of (111), (220) and (311) respectively. Indeed, these peaks indexed are in accordance with the standard pattern of 3C-SiC [JCPDS card number 29-1129] (Shariatmadar Tehrani, 2015; Yang Yang et al., 2014).



Figure 2.4: XRD patterns of (a) Si and (b) 3C-SiC nanostructures. (Comedi et al., 2006; Shariatmadar Tehrani, 2015).

Hamzan et al. (2017) reported the chemical bonding state of heterostructures NiSi/SiC core-shell nanowires analyzed by XPS spectra. Figure 2.5 (a) shows the general wide scan elemental spectra consisting of the main elements in the nanowires which are Si, C and O at respected photoelectron energies. The deconvolution of XPS spectra was based on the Gaussian function respectively. The narrow scan spectra of Si 2p band revealed four components as shown in Figure 2.5 (b). The first component was detected at 98.5 eV representing the Si-Si bond, followed by Si-Ni bond at 99.5 eV. A high intensity peak at 100.7 eV indicated the Si-C bond while the peak at 102.7 eV corresponded to Si-O_x chemical states, respectively. On the other hand, narrow scan of C 1s spectra is shown in Figure 2.5 (c). The C 1s spectra can be deconvoluted into four main component of C-Si, C=C, C-C and O-C=O, which are located at 283.2, 284.4, 285.9 and 288.8 eV respectively. The appearance of C-Si chemical states verifies the formation of SiC shell. Figure 2.5 (d) presents the deconvolution components of the O 1s band at 531.2, 532.6 and 533.8 eV corresponding to O=C, O=Si and O-O chemical states. The presence of these oxide-related bands is associated to the formation of SiO_x layer on the nanowires surface.



Figure 2.5: (a) General XPS scan spectra of NiSi/SiC nanowires and XPS deconvoluted spectra of (b) Si 2p, (c) C 1s, and (d) O 1s. (Hamzan et al., 2017).

2.2.3 **Optical properties**

Silicon is well known as a bedrock material in most electronic system. However, due to its poor efficiency in light emission restricts the potential of bulk silicon in optoelectronic devices. This is owing to the indirect band gap of 1.1 eV of bulk Si which limits the absorption of photon within the visible and near infra-red region (Late et al., 2019). The downside of bulk Si has revealed the importance of Si nanostructure semiconductor material owing to its superior efficiency in optical transition. In addition, semiconductor nanowires are unique nanoscale structure with the dimensions typically in the range of visible light wavelength. This makes nanowires perform as an optical antenna feasible to change the absorption and emission properties due to the high refractive index of nanowires (Zhang et al., 2019). The fabrication of nanowires by bottom-up approach promotes formation of nanowires layers with different sizes, densities, and positions. Nevertheless, the optical properties of this material can be tuned by altering their physical dimensions. The low dimensional structure of nanowires revealed a quantum confinement effect causing a notable improvement in the optical properties (Jia et al., 2020). SiNWs with thick layers develop a stable scattering medium and are extremely opaque due to multiple light scattering and trapping (Holmberg et al., 2012). This can be explained by the presence of inhomogeneities structure in the medium such as the growth of Si nanostructures on top of the substrate that disrupt the propagation of light in a straight line. Figure 2.6 illustrates the light trapping action by Si nanowire arrays.



Figure 2.6: Light trapping effect by Si nanowire with the array periodicity, *P*. The incident light is in parallel with SiNWs axis.

Li et al. (2009) previously reported the optical properties of SiNWs contributed by the low dimensional structure based on quantum confinement model. The absorption (*A*), reflection (*R*), transmission (*T*) and ultimate efficiency spectra (η) of SiNWs at different periodicity, *P* of SiNWs arrays are shown in Figure 2.7. The absorption spectra in Figure 2.7 (a) shows a significant increase in energy (>2.5 eV) at lowest periodic array of SiNWs as in agreement with Hu et al. (Hu et al., 2007). Further increase in the periodic array of SiNWs to *P* = 600 and 1300 nm contributed to lower absorption at higher energies because of the increment in reflection as shown in Figure 2.7 (b). Low Si periodic array at 100 and 300 nm exhibited high light transmission at higher energies (Figure 2.7 (c)). The ultimate efficiency (η) of SiNWs rather than Si thin film at various *P* is shown in Figure 2.7 (d). The η of SiNWs increases significantly as *P* is also increased, overtook the 5 µm thick Si film at periodicity array of ~250 nm and has gained maximum efficiency of 24% at P = 600 nm. Subsequently, the increase in reflection at P > 600 nm as mentioned earlier, results in a reduction in η respectively (Adachi et al., 2013). Since the wavelength of light was considerably longer than the SiNWs arrays with short periodicities such as P = 100 nm, the incident light may readily permeate through the SiNWs, leading to excellent light transmission (Li et al., 2009).



Figure 2.7: (a) Absorption, A, (b) reflection, R, and (c) transmission, T spectra of SiNWs at various periodicity arrays, and (d) ultimate efficiency, η spectra of SiNWs and Si film respected to SiNWs array periodicity. (Li et al., 2009).

Previously in 2012, Chong et. al reported the transmittance, *T* spectra of SiNWs which is highly correlated with the density of nanowires as shown in Figure 2.8. Generally, both SiNWs prepared at rf power of 40 and 80 W present low *T* in the low wavelength region. SiNWs prepared at 40 W show a notable decrease of $T \sim 48.7$ % at wavelength, λ of 2200 nm. Meanwhile, less than 5% of light were transmitted at the same wavelength for SiNWs prepared at higher rf power. The reduction of *T* at rf power of 80 W is attributed to the high density of SiNWs and the presence of amorphous Si layer surrounding the crystalline Si core. The high density of SiNWs may potentially enhance the interactions of light that occurrs within the surface of nanowires. Consequently, more re-absorption and reflection of light happen internally. The low *T* value of Si nanowires in the lower wavelength region reveals a strong and efficient light absorption properties of the nanowires.

Meanwhile, the *A* and α spectra of SiNWs prepared at different rf power of 40 and 80 W are plotted in Figure 2.8 (b) and (c). SiNWs prepared at 40 W shows ~99% of *A* at lower wavelength from 220-500 nm and dramatically decrease in *A* from 500 nm to over the wavelength. Meanwhile, SiNWs prepared at 80 W show higher *A* (>99%) at broad wavelength range of 220 to 1500 nm and decrease to ~86% at 2200 nm respectively. In sum, the high *A* demonstrated throughout a broad wavelength range is credited to the high light absorption of SiNWs. On the other hand, the α spectra of SiNWs were divided into two classes comprised of high energy region (E > 1.8 eV) and lower energy region (E ≤ 1.8 eV). SiNWs prepared at 40 W revealed high α as compared to 80 W, showing strong light trapping ability within the high energy region owing to their smaller diameter and high crystalline structure. The broad α as observed at (E ≤ 1.8 eV) for SiNWs grown at 80 W was related to amorphous band. Furthermore, the remarkable enhancement in α was shown by both SiNWs at the infrared region (E < 1.7 eV) as in contrast to bulk Si.



Figure 2.8: (a) Optical transmission, T (b) absorption, A and (c) absorption coefficient, α spectra of SiNWs prepared at different rf power of 40 and 80 W. (Chong et al., 2012).

Basically, the PL optical properties of a material can be clarified based on two viewpoints which are the quantum confinement model that assigned the PL to quantum size effects and the surface defect model which ascribed the PL to oxygen-related defect centers (Abdullah et al., 2018; Zheng et al., 2018). Dasog et al. (2014) reported the tailoring of PL for Si nanostructures obtained by dodecyl functionalized Si nanocrystals in air and inert atmosphere. The PL spectrum observed for sample grown in air exhibits a blue-shifted with a broad emission band centered at 630 nm as shown in Figure 2.9 (a). Meanwhile, the dodecyl functionalized Si nanocrystals in inert atmosphere illustrates red PL spectrum with peak centered at 730 nm as shown in Figure 2.9 (b). The red PL arises from the defect states at the interface between the SiNWs core and the surrounding SiO₂ (Toda et al., 2010). The excited state lifetime measurements of Si nanocrystals prepared in air show a short-lived excited states to be in nanosecond order while the Si nanocrystals prepared in inert atmosphere was measured to be in microsecond order. Based on simulation model, the short-lived excited states and blue-shifted PL are ascribed to oxide defects Si=O component (Dasog et al., 2014). Nevertheless, the red emission band observed for Si nanocrystals produce at inert atmosphere are correlated with surface radiative recombination at crystalline Si core and amorphous Si oxide layer (Hamidinezhad et al., 2017).



Figure 2.9: Photoluminescence spectra of Si nanocrystals prepared at (a) air and (b) inert atmosphere at respected excitation wavelengths. (Dasog et al., 2014).

2.3 Deposition Techniques

Several common deposition techniques have been reviewed to independently regulate the growth, diameter and shape of nanowires. These parameters controlling are indeed affecting their physical, electrical and optical properties. In principle, nanowires can be synthesized based on the top-down and bottom-up approaches. Top-down approach which includes the laser ablation, thermal decomposition and chemical etching involves the breaking of bulk starting material into smaller fragments by ion beam or photolithography (Noah, 2020). Meanwhile, in bottom-up approach, nanowires are synthesized by the interaction of atoms or molecules to form nanostructures via a series of chemical reactions or by application of heat (Ramanujam et al., 2011). The techniques used in the bottom-up approach includes CVD and sol-gel method. In this part, the two most common nanofabrication method which are laser beam and CVD growth techniques based on top-down and bottom-up approaches are reviewed in depth to synthesis high quality nanowires for applications.

2.3.1 Laser Ablation

The first theory of laser was proposed in 1960 by Maiman et al. (1960). Since then, lasers have been widely employed in various scientific and technical sectors, with laser-assisted manufacturing of functional materials being one of the most important applications. The research continued in 1965 for the laser-target interaction to produce wide variety of materials. Initially, the laser was introduced in a vacuum chamber, the materials get vaporized in the presence of ultra-high vacuum pressure and ambient gas resulted in the formation of plasma plume. The plasma plume is then deposited as thin films on the substrate. This technique can be referred as pulsed laser deposition (PLD) (Smith et al., 1965).

The size control of nanowires is a crucial topic for many applications and for studying the quantum confinement effects. Mainly, laser ablation method was studied over the years to synthesis semiconducting SiNWs. The size control of SiNWs by laser ablation was synthesized by Fukata et al. (2005). The relation between the metal catalyst content and the size of SiNWs at respected laser power are studied. Fe is used as a catalyst and its content is kept varied throughout the experimental work. The dependency of Fe catalyst content with the growth of SiNWs are shown in Figure 2.10 (a), in which the diameter decreases with decreasing Fe content. The SEM images showed the assynthesized SiNWs prepared at Si:Fe of 90:10 (top image of Figure 2.10 (a)) and Si:Fe of 98:2 (bottom image of Figure 2.10 (a)). During laser ablation, Si atoms and Fe metal catalyst evaporate at high pressure with the presence of inert gases and produce Si-Fe liquid alloys. The Si-Fe liquid alloys then become supersaturated with continuous addition of Si and acts a nucleation seed of SiNWs. On the other hand, the diameter of SiNWs is highly dependent with the laser power as shown in Figure 2.10 (b). The amount of ablation atom increases as the laser power was also increased. The rise in the laser power thus impacts the size of supersaturated Si-Fe liquid alloy, resulting in SiNWs growth diameter.



Figure 2.10: (a) The dependency of Fe catalyst content with the diameter of SiNWs prepared at different Fe ratio of 10 at% (top FESEM image) and 2 at% (bottom FESEM image), respectively. (b) The dependency of laser power with the diameter and length of SiNWs growth. (Fukata et al., 2005).

Zeng et al. (2012) reviewed the critical requirements require for laser ablation procedures. During the ablation of laser onto target material, the incident laser pulse penetrates the target material surface in a particular depth penetration. The penetration rates are in dependence of the wavelength of laser used and the refraction index of the target material. The strong electric field created by the laser light is adequate enough to remove the electrons from the material in less than 10 ps (Hashida et al., 2009). The free electrons oscillate inside the electromagnetic field then collide with the atoms of the materials. Some of the energy is passed to the lattice during the colliding action. The material then generally turned into plasma which contains a variety of energetic species such as atoms, molecules, electrons, ions and clusters at sufficient laser intensity. The plasma possesses some distinct properties such as high temperatures, high pressure and high density (Chakraborty et al., 2007). The plasma species will nucleate and develop into desired nanostructures either on a substrate or in a cool liquid medium under proper condensation conditions such as temperature and pressure. Laser ablation is usually performed with tube furnace or vacuum chamber, such that tube furnace provides a uniform and controllable growth temperature and gas flow. The pulsed laser ablation arrangement (PLA) combines the benefits of laser and furnace, which is useful in the synthesis of 1D nanomaterials.

Current studies on the SiNWs decorated Au or Cu (AuNPs@SiNWs and CuNPs@SiNWs) by pulsed laser ablation was scientifically reported by Casiello et al. (2018). Pulsed laser deposition (PLD) technique is used to decorate SiNWs sidewalls by ablating an oxide target with high power laser pulse. The procedure took place in high vacuum chamber with a base pressure of 10⁻⁴ Pa. The Si nanoparticles formation are induced by the interaction of ambient gas (Ar) with the laser generated plasma (Bailini et al., 2007). Higher Ar pressure was required to confine the Au plasma as compared to Cu plasma due to their difference in atomic mass value (Au = 196.9 amu, Cu = 63.5 amu). The plasma is transferred through the ambient Ar gas at the specific deposition parameters, forming shock waves at the plasma and Ar interface (Spadaro et al., 2015). The shock waves are usually occurred at high plasma temperature as the plasma becomes collision free. The density and pressure of the gas encourage the development of clusters in air, which then settle on the substrate surface and produce the decorated SiNWs. Figure 2.11 and Figure 2.12 show the cross-section FESEM images of the successful growth of AuNPs and CuNPs decorated SiNWs scanned at top, center and bottom region with the statistical analysis radius of the nanoparticles produced at each cross-section images. The FESEM image of AuNPs at the top region shows a dense and bigger radius size of $5.6 \pm$ 0.8 nm (Figure 2.11 (a)). Meanwhile, the AuNPs radius as observed at the center and bottom region are 4 ± 0.6 nm and 3.5 ± 0.5 nm respectively. On the other hand, the presence of small CuNPs was clearly observed at the tip of the SiNWs as shown in Figure 2.12 (c) with the radius of 3.4 ± 0.5 nm. The radius of CuNPs can only be measured at the tip of the nanowires since its dimension is relatively close to the SEM resolution limit contradicting with center and bottom region of SiNWs.



Figure 2.11: Cross-section FESEM images at (a) top (b) center and (c) bottom of the SiNWs decorated with AuNPs. The radius of AuNPs was measured at (d) top (e) center and (f) bottom region, respectively. (Casiello et al., 2018).



Figure 2.12: Cross-section FESEM images at (a) bottom (b) center and (c) top of the SiNWs decorated with CuNPs and the mean radius of CuNPs measured at (d) top region, respectively. (Casiello et al., 2018).

2.3.2 Chemical Vapor Deposition (CVD)

The bottom up approach for 1D semiconductor nanomaterials by CVD technique has arouse attention for fundamental physics and possible device applications (Chen et al., 2019; Sun et al., 2021). CVD is well-known as the most researched SiNWs synthesis technique over the years. Generally, the growth of SiNWs is initiated by the decomposition of precursor gas on a semiconducting material nanoparticle. The CVD bottom-up approach yields less defect nanoparticles with a homogeneous chemical composition. In fact, the alignment and directional growth of SiNWs can be easily controlled.

The multiple routes of deposition techniques to produce SiNWs via vapor-liquid-solid (VLS) method were reviewed by Colli et al. (2007). The first deposition route utilized Au metal catalysts which commonly used in CVD growth of SiNWs due to the popularity that Au does not easily oxidized during the reaction and easily formed liquid Au-Si alloy (nucleation sites) at quite low eutectic temperature of 363 °C (Henry et al., 2012). The VLS mechanism suggests that the nanowires are produced when catalyst droplets get supersaturated with the precursor and then precipitates from the liquid/solid interface and grow nanostructures (Maliakkal et al., 2021). The size of metal droplets usually determines the end size of SiNWs. The result demonstrated the low growth temperature of SiNWs at 300 °C, such that a relatively low temperature limits the undesired effects such as catalyst diffusion and surface migration (Hannon et al., 2006). The second route employed the thermal CVD technique to grow SiNWs with pure SiH₄ precursors. A straight and small diameter of SiNWs were observed to grow from Au-coated surface. The length and density of SiNWs increased with increasing SiH₄ pressure (1 to 10 Torr) as shown in Figure 2.13 (a) and (b). There was an unshaped Si nanostructure observed and no SiNWs grow at low SiH₄ pressure. However, the morphology of SiNWs changed dramatically as plasma was introduced at SiH₄ pressure of 10 Torr, showing a thick and

tapered shape SiNWs with a length of 100-300 nm as shown in Figure 2.13 (c). The results persuade that SiNWs showed great growth enhancement by PECVD rather than thermal CVD (Colli et al., 2007).



Figure 2.13: FESEM image of SiNWs grown at different SiH₄ pressure of (a) 1 Torr and (b) 10 Torr. (c) FESEM image of SiNWs at SiH₄ pressure of 10 Torr with the presence of plasma. (Colli et al., 2007).

Schmidt et al. (2009) discussed the aspects ratio of SiNWs growth via CVD and the outstanding favors of CVD as compared with other SiNWs growth techniques. Generally, a volatile silicon precursor gaseous such as silane (SiH₄) or silicon tetrachloride (SiCl₄) act as Si source in CVD growth method. As shown in Figure 2.14, the Si source is brought to the deposition surface where the precursor started to react and split accordingly to its parts. CVD techniques have a wide range of variations, categorized based on the base/operating pressures and gas precursor's treatment. Si is known to oxidize rapidly when exposed to oxygen at high temperatures hence, the oxygen background pressure should be reduced in order to grow an epitaxially uniform SiNWs. It is also important to lower down the CVD reactor's base pressure to high vacuum (10⁻¹ to 10⁻⁵ Pa) or ultrahigh vacuum (10⁻⁵ to 10⁻¹⁰ Pa) to eliminate undesired contaminants and enables SiNWs to grow at low temperature (Akhtar et al., 2008). CVD growth technique is specifically designed for the deposition of high purity films which allows the epitaxial growth of SiNWs depending on the temperature and Si precursor type used. In addition, CVD also provides a wide range options for controlling the characteristics of SiNWs for example by ion doping (Iacopi et al., 2007). Another big benefit of CVD as a bottom-up synthesis technique is due to its flexibility in terms of wire size. The SiNWs grown by CVD technique was previously reported by Cui et al. (2001) to have a diameter in range from 10 nm up to hundred micrometers. As surface diffusion plays such a minimal role in CVD, the nanowires length may be adjusted simply by increasing or reducing the growth time. CVD technique allows to change not only the wire size but also its characteristics.



Figure 2.14: Schematic diagrams setup of CVD technique for SiNWs growth. (Schmidt et al., 2009).

The large-scale production and low production cost of SiNWs by hot wire chemical vapor deposition (HWCVD) technique observed by Goh et al. in 2011 boosted more research on this technique due to the outstanding features of as-grown SiNWs. As contrast with the conventional PECVD, the HWCVD technique does not use high energy ions, therefore the nanowires is believed to generate superior crystallinity structure (Rath et al., 2003). Nazarudin et al. (2015) reported the HWCVD as one of most promising methods for low temperature, high deposition rate and large area-deposition for Si nanostructures. A cubic SiC thin films was successfully grown by this technique at ultimately low temperatures (~ 300 °C). The Si/SiC core-shell nanowires were produced at varied deposition pressure of 0.5 and 1.0 mbar with the assistance of Ni catalyst. The morphologies of Ni-catalyzed Si/SiC core-shell nanowires are represented in Figure 2.15. The nanowires showed a tapered morphology and uniform distribution at pressure of 0.5mbar (Figure 2.15 (a)). The agglomerated grains are observed at the nanowires roots as the pressure was increased to 1 mbar as shown in Figure 2.15 (b). The formation of agglomerated grains are actually due to the vapor phase reaction in HWCVD (Klein et al., 2005). TEM image and dark field STEM images revealed a core-shell structure as

shown in Figure 2.15 (c). The nanowires showed a tapered morphology with small tip (diameter of ~ 10 nm) and large nanowire diameter ranging from 15 to 72 nm, respectively. The tapered shape of nanowire is assigned by the radial growth of SiNWs. The bright nanowires tips are observed, indicate the existence of Ni catalyst that induce the Si/SiC nanowires growth.



Figure 2.15: FESEM image of Si/SiC core-shell nanowires at (a) 0.5 mbar and (b) 1.0 mbar. (c) TEM image of nanowires prepared at 0.5 mbar. (Nazarudin et al., 2015).

2.4 Growth Mechanism Models

Despite the challenges in growing various properties of nanowires by different techniques, the growth model is also essentially important. A comprehensive understanding on the growth dynamic and growth model is required to effectively control the size, morphology and chemical composition of the nanowires. Several attempts have been made to synthesis nanowires by different growth mechanism. These include the famously known vapor-liquid-solid (VLS), vapor-solid (VS), solid-liquid-solid (SLS) and oxide-assisted growth (OAG). Metal catalyst such as Au is introduced to mediate the VLS growth whereas the OAG has been proposed as an alternative model, which is corroborated by the fact that metal catalyst is not generally necessary throughout the synthesis process. The general concepts of VLS and OAG growth are comprehensively reviewed in this chapter.

2.4.1 Vapor-Liquid-Solid (VLS)

One-dimensional (1D) crystals growth, including whiskers, rods and wires are studied extensively in many applications. The vapor-liquid-solid (VLS) technique has always been the method of choice for growing Si nanowires since Wagner's early works in 1964 (Li et al., 2018; Shi et al., 2020; Wagner et al., 1964). Wagner's has successfully employed Si whiskers from VLS mechanism. The subsequent reviewed by Givargizov et al. demonstrated the VLS mechanism via CVD growth technique which revealed the kinetic studies of the crystal growth and the diameter of Si whiskers. The kinetics' growth are highly dependent with the growth rate according to Gibbs-Thompson effect and whiskers are mainly to grow by direct diffusion rather than by side facets diffusion (Givargizov et al., 1975). Research on whiskers continued to be fruitful in the early days, although the large size of whiskers (> 0.1 μ m) grown provide limited practical advantages. Later, the experimental demonstration by Morales et al. (1998) opens new opportunities of Si wires produced in nanometer scale by laser ablation method. The

successful discoveries by Morales et al. have spurred scientific curiosity in nanowire research and has motivated many researchers due to the great advantages of 1D nanowires in device applications (Arora et al., 2013; Lieber et al., 2003).

During the VLS growth, Si from vapor phase assimilate with liquid catalyst such as Au (Wagner et al., 1964), Ni (Kuykendall et al., 2003), Cu (Arbiol et al., 2007) and Fe (Morales et al., 1998) at metal alloy tip that form on the silicon substrate. This liquid appears as tiny droplets and does not wet the Si surface. Si then combines with these droplets resulted in the formation of Si wires and whiskers with a diameter in a unit of nanometer. The diameter of nanostructures formed are influenced by the size of the droplets (Kodambaka et al., 2006). The schematic diagram of typical VLS mechanism is shown in Figure 2.16. During the process, the Au metal nanoparticles is heat up above the eutectic temperature (363 °C) to form a liquid-metal eutectic alloy. The eutectic alloy (e.g., Au-Si) then continue to integrate with semiconductor material (Si) in vapor phase across the vapor/liquid interface, causing supersaturation of the semiconductor material. Continuous addition of Si into eutectic Au-Si alloy at the melting point of Si (1414 °C) will ultimately cause nucleation and Si atom will precipitates from the supersaturated droplets and forms a liquid/solid interface or define as growth interface of nanowires. The metal catalyst will remain at the nanowire tip as the nanowire continues to grow. The VLS growth mechanism is widely chose due to the direct control of diameter and length of the nanowires, as well as for a wide variety of materials covering the elemental and compound semiconductor which combine Group III and V elements and Group II and VI elements for example, GaAs, SiC and InP (Paiman et al., 2009).



Figure 2.16: (a) Schematic diagram of Si nanowires grown via VLS mechanism, and (b) phase diagram for the Au-Si system. (Lu et al., 2006).

2.4.2 Oxide-assisted Growth (OAG)

Oxide-assisted growth (OAG) is known as one of successful Si nanowire growth mechanism aside from the famous VLS technique. This technique utilized the semiconductor nanowires without the use of conventional metal catalyst, yet by the reaction with metastable oxide (i.e., CO and SO). In this OAG method, the metastable oxide plays a crucial role as a nucleating center for the nanowire growth (Lee et al., 2000). The OAG mechanism model's approach is demonstrated in a variety of semiconducting nanowires, including Ge, SiC, GaAs, GaN, GaP and ZnO nanowhiskers. In late 1990's, Zhang et al. reported the growth of Si nanowires by high temperature laser ablation using a mixture of silicon dioxide and silicon powders with the presence of Fe catalyst. The initial aim was to grown Si nanowires via VLS mechanism at a temperature reached to approximately 900 °C, Zhang et al. (1998) discovered that the nanowires were grown without any catalyst particles at the nanowires tip. In fact, the oxide sheath is spotted surrounding their lateral surface, in which oxide is expected to mediate the nanowires growth (Mohammad et al., 2008).

The high yield production and ultralong SiNWs via OAG method has demonstrated that Si nanowires produced from SiO₂-containing Si targets yielded up to 30 times (at 50 wt.%) more than the conventional metal-containing Si targets as reported by Lee et al. (1999). The production of SiNWs is limited if only pure Si powders are used as target. However, Si target is easily oxidized in air in which it suggested that Si oxide may influence the development of SiNWs. TEM image in Figure 2.17 showed the high density and uniform diameter of SiNWs grown by OAG. The high intensity as observed in SAED pattern ring indicates a strong Si (111) diffraction pattern. This signifies that the Si nanowire's cystals have a same orientation and same growth direction. The nanowires growth is inhibited, and re-nucleation occurs if the nuclei grow in unfavorable orientation.

Hence, this may induce kinking in nanowires or further re-nucleation if the newly formed nuclei are likewise unfavorable (Lee et al., 1999).



Figure 2.17: TEM image of the morphology of SiNWs grown from SiO₂-containing target. Inset shows the SAED pattern ring image of Si (111). (Lee et al., 1999).

Meanwhile, the formation of Si nuclei at the early stage was presented by TEM shown in Figure 2.18 (a). The Si nanoparticles are initially precipitated into the deposited SiO_x matrix. Some of the nanoparticles are then accumulated and piled up on the SiO_x surface. Specifically, the Si nuclei that stand apart with their growth orientations tend to develop rapidly. An individual nucleus is made up of a crystalline Si core and amorphous SiO_x outer layer as marked by arrow in Figure 2.18 (a) and (b). No metal catalyst was detected at the tips of Si nuclei (Lee et al., 1999).



Figure 2.18: TEM image of (a) the initial growth stage of Si nuclei and (b) the accumulated Si nanoparticles piled up on the SiO_x surface. The marked arrow indicates the formation of Si core and SiO_x amorphous shell. (Lee et al., 1999).

The temperature dependence study on the morphology of SiNWs was successfully reported by Peng et al. (2001). The diameter of the as-grown SiNWs is controlled by the temperature of the substrate. Figure 2.19 shows an optical image of SiNWs grown on alumina substrate. There are six distinct zone as observed. As the temperature dropped from 1200 to 850 °C, the substrate color changed from dark yellow (I 1) to blue with some yellow spots (I 2, I 3) and then to pink (II 1) and light yellow (II 2, II 3). Further research revealed that the first three zones (I 1, I 2 and I 3) denoted as region I consisted of SiNWs grown by VLS mechanism. The remaining three zones (II 1, II 2 and II 3) referred as region II consisted of SiNWs grown by OAG method. Region I covered the temperature in range of 1200-1100 °C, while region II is in range of 1100-850 °C.



Figure 2.19: Optical micrograph of SiNWS growth on the alumina substrate at respected region I and region II temperatures. (Peng et al., 2001).

TEM analysis was then carried out for three samples (I 1, I 2 and I 3) in region I indicated by their position on the alumina substrate. Sample I 1 prepared at 1190 °C showed uniform SiNWs with diameter approximately 200 nm (Figure 2.20 (a)). As the growth temperatures were reduced to 1160 and 1130 °C, the diameter of the SiNWs gradually decreased while the morphology transformed from uniform nanowires to

tadpole-like shape as observed in Figure 2.20 (c). The variation in SiNWs diameter is attributable to the droplet diameter nucleated at different temperature parallel with the nanowires grown by VLS method. The small nanoparticles catalysts (marked by the arrow) were also observed at the tip of the SiNWs shown in Figure 2.20 (a & b). The HRTEM image confirmed that the head of tadpole was crystalline Si, and the tadpole tail consisted of amorphous SiO_x. The morphology evolutions of SiNWs grown by VLS model from nucleation, growth and annealing were illustrated in Figure 2.20 (d1-d3).

Figure 2.21 demonstrates the TEM analysis scanned at position II 1, II 2 and II 3 of region II prepared at 1050, 950 and 900 °C respectively. The morphology changes from tadpole-like (Figure 2.21 (a)) to chain-like (Figure 2.21 (b)) and then to more uniform wire-like structure as shown in Figure 2.21 (c) at low temperature. The diameter of the as grown SiNWs (~ 20 nm) were uniformly distributed in all three samples. This observation leads to a crucial finding that, under certain growth conditions, the diameter of SiNWs grown by OAG is independent of the growth temperature. Figure 2.21 (d1-d3) presents the schematic diagram of SiNWs growth evolution by OAG model initiated by nucleation, growth and annealing (Peng et al., 2001; Wang et al., 1998).



Figure 2.20: TEM image of SiNWS grown at (a) 1190, (b) 1160, and (c) 1130 °C according to VLS growth mechanism. The nanoparticles catalysts grown on the tip of SiNWs is marked by arrow. (d) Schematic diagram of SiNWs morphology evolution: (1) nucleation, (2) growth and (3) annealing. (Peng et al., 2001).



Figure 2.21: TEM image of SiNWs grown at (a) 1050, (b) 950, and (c) 900 °C according to OAG growth mechanism. (d) Schematic diagram of SiNWs morphology evolution: (1) nucleation, (2) growth and (3) annealing. (Peng et al., 2001).

Zhang et al. (2003) extensively reviewed the coexistence of OAG and VLS growth correlated by temperature in terms of morphology, which previously studied by Peng et al. in 2001. Similarly, the morphology growth of SiNWs can be identified corresponding to region I (1100-1200 °C) and region II (850-1050 °C). Metal was detected at the SiNWs tip as observed from TEM analysis and indicated that these SiNWs grown in region I followed the metal catalytic-VLS method as shown on the right-side diagram in Figure 2.22. The SiNWs produced by VLS are mainly in (111) orientation. The VLS process was according to the flow of vapor (collected by metal) to liquid (Fe-Si alloy) and finally to solid (SiNWs produced at liquid/solid interface). On the other hand, no metals catalyst was observed in the samples grown in region II, suggesting the growth of SiNWs were likely by OAG mechanism. The SiNWs growth are assisted by SiO_x diffusion and SiO₂ are usually present as amorphous shell covering the SiNWs. The schematic diagram of OAG method is shown on the left-side of Figure 2.22. In this region, the growth temperature does not affect the diameter of SiNWs. However, the VLS and OAG growth mechanisms coexist at 1100 °C (Peng et al., 2001; Zhang et al., 2003; Zhang et al., 1998).



Figure 2.22: Schematic diagram of OAG (left-side) and VLS (right-side). (Zhang et al., 2003).

The role of oxide in the OAG growth mechanism was demonstrated by Agati et al. (2016). The formation of SiNWs is first activated by silicon suboxide clusters (SiO_x) present in vapor phase. Some of the highly reactive Si atoms in the SiO_x deposited on the substrate are covered by silicon oxide. The dangling bonds of SiO_x will form bonds with Si substrate atoms and serve as nucleation site to facilitate the SiNWs growth. The SiO_x clusters supplies oxygen atoms which are laterally ejected by Si atoms to the boundaries during the formation of SiNWs, resulted in the creation of chemically inert SiO₂ shell. The SiO₂ outer shell covering the SiNWs eventually limits the lateral development, allowing only perpendicular growth of SiNWs (Zhang et al., 2001; Zhang et al., 2006).

In sum, OAG was discovered to be a general technique for mass production (Wang et al., 1999) of a variety of semiconducting nanowires with a high density, clean and high purity (Namdari et al., 2016; Shao et al., 2008). Besides, the nanowires grown by this technique exhibit ultra-long in diameter and uniform in size (Lee et al., 2004; Yang et al., 2013).

2.5 Nanostructures from Waste-Biomass Sources

The production of Si nanostructures using biomass sources is becoming a favourable approach considering the alternative and economical way in converting wastes into useful nanomaterials (Chiew et al., 2011; Li et al., 2012). Biomass is described as the agricultural waste resources, mainly of animals, plants and microorganisms that have no values for consumer goods but may benefit in industrial usage. These biomasses are usually made up of complex mixtures of organic materials such as carbohydrates, fats, proteins and a minor amount of minerals for example calcium, phosphate and iron. The agricultural industry, which occupies almost 25 % of total land has generated a large quantity of after-treatment waste comes from oil palm and rubber wood.
Today, these wastes are ploughed to the soil as organic fertilizers and animal feed, or else permitted to degrade naturally, dumped or burned. However, the chemicals produced by burning or composting such as carbon monoxide and nitrogen oxide gaseous are pollutants and have negative impacts on the ecosystem. Hence, the studies on the waste management of these organic raw materials by thermochemical technologies are extensively investigated due to their low cost, large yield, simple process and eco-friendly (Zhu et al., 2013). Indeed, the utilization of this method is not only capable to fabricate nanostructures but also has solved the disposal problem of these organic wastes. Plantbased biomass in synthesize Si nanostructure was firstly reported by Lee and Cutler in 1975, using rice husk ash (RHA) (Chiew et al., 2012) and was studied in depth by others using coconut shell, coconut fibres, sugarcane leaf with rice straw, cotton fibres, bamboo leaves, and palm kernel shell (Voon et al., 2016). Recent research has been reported by Li et al. (2019) that revealed the formation of n-butanol which is a potential biofuel via the usage of lignocellulosic biomass fibres present in corn fibre, cotton stalk and soybean hulls via fermentation. Besides, a superabsorbent bioactive aerogels for food packaging has been developed from A. donax stems by the extraction of polysaccharides and polyphenols (Fontes et al, 2019).

Mi et al. (2012) reviewed the synthesis of coconut shell derived granular micro/mesoporous carbon electrode which exhibits superior high capacity performance as supercapacitors. An advance research in biomedical application on the microbial inhibition of *E. coli* and *S. aureus* was successfully demonstrated by the utilization of biogenic silica (b-SiO₂) derived from RHA (Capeletti et al., 2014; Sharma et al., 2019). RHA and palm kernel shell are popularly studied since they are available in large-scale everywhere in Malaysia owing to its industry abundant by-products. These plant-based biomasses are composed of cellulosic components that consist of 75 wt.% carbon and a

small amount of silica (SiO₂) at the outer epidermis of the cell wall, which retains useful structural and characteristics.

The production of 3C-SiC nanowires via pyrolysing of acid-treated oil palm empty fruit bunch fibres and RHA (TOP/RHA) was reported by Chiew et al. (2012). The effects of RHA amounts and pyrolysis temperature on the morphology growth of the nanowires are shown in Figure 2.23. The sample morphology changed from nanowires to nanocones with an increased in the diameter and length of the nanowires as the amount of RHA and pyrolysis temperature were raised respectively. The nanocones were observed with broad tip and spherical caps which then tapering down along the sidewalls to the bases. This phenomenon suggested that the SiC nanowires are grown by VLS mechanism. The green synthesis of palm kernel shell was then continued by Itam et al. (2016) as a potential to produce an affordable and sustainable alternative in the lightweight concrete industry. In sum, the utilization of waste-biomass and phytochemical (compounds produced by plants) in the synthesis and development of nanomaterials establishes a strong link between natural waste and nanoscience, dubbed "green technology" (Zamani et al., 2019).



Figure 2.23: FESEM image of pyrolysed TOP/RHA at different RHA amounts of (a) 0.2, (b) 0.4, (c) 0.6 and (d) 0.8. The insets of (a-c) represents the higher magnification image. (e) The nanocones structure formed at 0.8 RHA. The red circle shows the spherical cap at the tip of the nanocones. (Chiew et al., 2012).

2.6 Si nanostructures as Photoelectrodes in Photoelectrochemical Water Splitting

The evolution of nanomaterials as photoelectrode in PEC water splitting has arisen as a promising sustainable energy to perform the solar-to-hydrogen transformation process (Landman et al., 2017; Yao et al., 2019). Hydrogen is regarded as one of the most potential energy sources (van Renssen, 2020). It is clean, inexhaustible, practical and economical transporter that can help minimize the long-term reliance on fossil fuels (Dawood et al., 2020; Zhou et al., 2011). In fact, this scientific technology is also believed to defeat the long-lasting greenhouse gas emissions (CO₂) derived from the fossil fuels that are currently not caught or removed. Nanostructured photoelectrodes possess outstanding advantages in contrast to conventional bulk materials due to the large surfaceto-volume ratio. Joy et al. (2018) previously reported the vital role of semiconductor nanomaterials in PEC water splitting considering that the nanometer-scale dimension is relatively small compared to the scattering lengths of a charge carriers, resulted in the high efficiency in carrier collection. Besides, the low mass and fast charge transfer within the semiconductor/electrolyte interfacial area promote high light trapping and low light scattering. Basically, from the architectural point, PEC water splitting system contains monochromatic light source, photoelectrodes (photoanodes and photocathodes) and an electrolyte.

Jeong et al. (2018) reported a simplified PEC water splitting process consisting of the electrolyte, photoanode and photocathode as shown in Figure 2.24. Generally, when a photon of energy equals to or higher than the band gap of a material irradiates the semiconductor photocatalyst, photons get absorbed by the photoelectrode material and electrons get excited and jump into the conduction band creating holes in the lower valence band. The minimum amount of energy required to excite an electron is called band gap energy, E_g . The charge carriers (photoelectrode by internal and external bias. Oxidation of water then occurs at the anode and reduction of H⁺ ions into hydrogen gas evolve at the cathode, indicating the water splitting into hydrogen and oxygen gaseous. The chemical reactions involved through the water splitting mechanism can be clearly shown as follows:

At photoanode :
$$H_2 0 + 2h^+ \to 2H^+ + \frac{1}{2}O_2$$
 (2.1)

At photocathode : $2H^+ + 2e^- \rightarrow H_2$ (2.2)

Overall water splitting reaction: $H_2 0 \rightarrow H_2 + \frac{1}{2}O_2$ (2.3)

Both oxidation and reduction reactions must involve simultaneously to achieve a stable photoactivity. The efficiency of PEC water splitting system is measured by two key parameters which are the effective charge carrier transportation and rapid water redox (reduction and oxidation) reactions.



Figure 2.24: Schematic diagram of PEC water splitting process. (Jeong et al., 2018).

Photocatalyst such as CdS and metal oxides photocatalysts including TiO₂, SiO₂, SnO₂, WO₃, ZnO, Nb₂O₃, Fe₂O₃ are widely investigated over the past years. However, TiO₂ photocatalysts has been used extensively since the demonstration at the early stage of PEC water splitting device in 1972 by Fujishima and Honda due to the low cost, high physical and chemical stability, high photocatalytic activity and environmentally safe (Fujishima & Honda, 1972; Roy et al., 2019). However, because of its wide band gap of 3.2 eV, TiO₂ can only absorb solar energy that lies in the UV light range ($\lambda < 400 \text{ nm}$), which makes up only 5 % of the solar spectrum (Dong et al., 2015) (shown in Figure 1.3). In fact, most oxide materials used previously have a wide band gap energy which restricts the light absorption causing poor PEC water splitting performance.

In PEC water splitting device, semiconductor electrode must satisfy certain criteria to overcome the limitations, achieving a desired characteristics for the large-scale utilization of solar energy. Photoelectrodes are required to have a suitable band gap covering the UV-Vis region and high absorption capability. Photoelectrode materials with low band gap are more sensitive to photo corrosion than those with a wider band gap. Besides, an appropriate band-edge alignments respected to redox reactions and thermodynamic potentials is also crucial to perform water splitting reactions. The valence band and conduction band edge positions must cross the water oxidation and reduction potentials for an optimum overall water splitting mechanism. The bottom level of conduction band should be more negative than the redox potential of hydrogen evolution $(E_{H_2/H_20}, 0V vs normal hydrogen electrode; NHE)$ and the top level of valence band needs to be more positive than the water oxidation potential $(E_{O_2/H_2O}, 1.23V vs NHE)$. Thus, the minimum band gap energy for efficient water splitting reported is 1.23 eV (Smith et al., 2015).

Figure 2.25 shows the comparison of semiconductor band edge positions respected to water redox potential (Tamirat et al., 2016). The band gap energy of a material must be lower than 3 eV for ideal visible light absorption (Afroz et al., 2018). In addition, a good photoelectrode materials should have high chemical and physical stability in dark and illuminated conditions. For example, CdS has a suitable band gap energy and band edge positions. However, CdS itself tend to oxidize easily under photoexcitation, leading to a photo corrosion of the materials. Therefore, oxygen evolution are not able to take place during the process (Laursen et al., 2015). Same cases as CdS, typical semiconductor such as ZnO and SiC also suffer from photo corrosion due to the oxidation of anions instead of H_2O by photogenerated holes (Marepally et al., 2019).



Figure 2.25: Semiconductor band positions and band edge positions at pH = 0 relative to NHE and vacuum level. (Tamirat et al., 2016).

To date, the bottleneck of current photocatalysts is due to several reasons. Most photocatalytic materials discovered are only active under UV irradiation while UV region accounts for only ~ 4 % of the solar spectrum (Laursen et al., 2015). Hence, the key challenge is to select the fit photocatalysts that possess high photoactivity within UV and visible region of electromagnetic spectrum. Various strategies such as nanostructuring, ion doping and noble metal integration have been explored to reform the light absorption capability of these photocatalysts by altering the absorption limits to longer wavelengths into the visible region. These efforts are essential to slow the electron/hole recombination rate hence grant more charge carriers to diffuse to the surface (Moma et al., 2018). The ultimate requisite of the charge separation and transportation of photogenerated carriers can be deploy in nanostructuring the semiconductor materials by modifying their structure and dimensions (Kudo et al., 2009). Figure 2.26 illustrates the schematic diagram of the particle size and boundary in photocatalytic activity. Crystallinity, crystal structure and size of particle are the three main components that can affect water splitting process. The higher the crystallinity of a structure, the lower the defects amount. Defects or vacancies serve as photoelectrons and photo holes trapping and recombination centers that speed up the recombination of carriers and shorten the excited state lifetimes, thus result in weak photocatalaytic activity (Hoch et al., 2016). Research on efficient materials for photocatalysts has been extensively studied since then. Even so, no findings have revealed the perfect candidate of photoelectrode materials.



Figure 2.26: Effects of particle size and the recombination of charge carriers at boundaries in photocatalytic activity. (Kudo et al., 2009).

In general, the semiconductor nanomaterials for PEC photoelectrodes may be categorized into two groups based on the arrangements of crystal atoms which are the polycrystalline and single crystalline. Polycrystalline semiconductor materials include metal oxides, nitrides and oxynitrides such as TiO₂, WO₃, ZnO, Cu₂O, CuFeO₂ and BiVO₄. However, these polycrystalline materials have low carrier mobility and finite carrier diffusion length with lots of lattice mismatch and defects that affect the lifetime of charge carriers (Abdi et al., 2013; Spitaler et al., 2018). Conversely, single crystalline photoelectrode materials (i.e., Si, GaAs, GaN and InP) are commonly used in photovoltaics (PV) devices owing to their high carrier mobility and outstanding charge transport (Latunussa et al., 2016). They are usually perfect with highly crystallized structure and low lattice mismatch (Li et al., 2020). Si, on the other hand is abundant and economical since it is the second most prevalent element in the Earth's crust. The broad knowledge base of Si has made it the most effective material in optoelectronics and microelectronics. The energy structure of nanomaterials is greatly affected by the size of the nanostructure due to quantum confinement as reported by Priolo et al. (2014). In addition, the surface provides additional options in which when the surface-to-volume

ratio decreases with size reduction, the arrangements of atoms on the surface become increasingly significant. These give a positive impact to the band structure of a material where the optical band gap and the recombination rates may be regulated, and to some extend the indirect band gap can be transformed into direct band gap. Concisely, the surface morphology engineering is employed to design and modify the photoelectrode surface and physical features to increase the PEC performance of the nanostructured photoelectrode (Kment et al., 2017; Luo et al., 2017; Zhou et al., 2017).

Joe et al. (2019) reported the variations of several semiconductors of Group IV, III-V Semiconductors and their integrated fraction of light absorption in solar spectrum. Si, GaAs and MoS₂ exhibit appropriate redox potential for PEC water splitting. Figure 2.27 illustrates the solar irradiance spectrum and the ratio of absorbed light irradiance over light wavelength. The optical band gap energy of a semiconductor is interrelated with the absorbed wavelength defined by Planck-Einstein Relation as follows:

$$E_g = hc/\lambda \tag{2.4}$$

where E_g is the band gap energy in joules (J), *h* is Planck's constant (6.626 x 10⁻³⁴ J s⁻¹), *c* is the velocity of light (3 x 10⁸ ms⁻¹) and λ is the wavelength of the absorbed light.

Si is an indirect band gap material with E_g of 1.1 eV. According to Planck-Einstein Relation, this signified that Si can absorbed light spectrum with a wavelength less than 1127 nm. Meanwhile, GaAs and MoS₂ with E_g of 1.4 eV and 1.8 eV showed a light absorption capability at wavelength of 886 nm and 689 nm respectively. Apart from that, Si showed a strong light absorption of about 80 % while both GaAs and MoS₂ exhibit 62 % and 50 % of the total portion of solar spectrum. Despite the aforementioned minimum E_g of an ideal photocatalysts of 1.23 eV at 1008 nm, Si showed the largest light absorption portion of solar spectrum making it a perfect candidate to intensify the hydrogen evolution by PEC water splitting.



Figure 2.27: Solar irradiance spectrum and the integrated fraction of absorbed light relative to wavelength. (Joe et al., 2019).

The electronic structural modulation in Si is rather challenging because of the densely packed arrangement and strong covalent Si-Si interactions. Besides, phonons are required to mediate the transition of electron from valence band to conduction band, attributed to the indirect band gap of Si (Cao et al., 2016). All these reasons limit the utilization of Si in optoelectronic devices such as in photovoltaic or photocatalytic application which required direct band gap material. Surface engineering is an effective technique to activate the chemical activity of Si and produces various Si allotropes with direct band gap (Lin et al., 2013). The implementation of this technique produces an electronic structure that can be easily modulated by strain, atom decoration and electric field in which the indirect band gap of Si can be tuned to direct band gap easily (Ni et al., 2012). Therefore, the electrical and optical properties of SiNWs can also be tailored to improve the PEC efficiency of nanostructured material respectively.

Oh et al. (2012) previously reported the growth of p-type SiNWs by the adoption of nanostructuring technique for PEC device. The SiNWs were fabricated by metalcatalyzed electroless etching (MCEE) impregnated with Pt catalyst. The vertically aligned SiNWs arrays absorbed the incident photons and produced minority charge carriers which then traveled along the nanowires length before being assembled at the junction. As a result, the nanostructured photoelectrode demonstrated significantly large semiconductor/ electrolyte interface regions which can minimize the overpotential caused by the poor H₂ generation at the photoelectrode. Besides, the SiNWs arrays have a dimension comparable to the visible light wavelengths, which could perform as light trapping layer for efficient photocatalytic process. The basic configuration of PEC includes three electrode arrangements with SiNWs sample as working electrode, Pt as counter electrode and a standard calomel as reference electrode. Figure 2.28 (a) presents the current density-potential (J-V) measurements for SiNWs under dark and visible light as well as the reference planar Si. The identical PEC measurement is also done using planar p-type Si photocathode as reference. The as-grown SiNWs exhibited almost zero photocurrents under dark condition, confirming that the current produced upon illumination on the SiNWs is photogenerated. Meanwhile, upon illumination, SiNWs absorbed more light and generated high photocurrent density in contrast with the reference planar Si. The current density-potential measurements of Pt-impregnated SiNWs under dark and visible light together with the reference Pt/Si planar are shown in Figure 2.28 (b). The photovoltage of Pt/SiNWs is significantly higher than the Pt/Si planar upon illumination. The onset potential value of Pt/SiNWs photoelectrode showed a great enhancement at 0.42 V, much larger than the Pt/Si planar photoelectrode at 0.33 V. The inset of Figure 2.28 (b) presents the dark current density plot showing that the high current density of Pt/SiNWs was attributed to the large surface area of Pt/SiNWs.



Figure 2.28: Current density-voltage measurement of (a) SiNWs photoelectrode and (b) Pt-impegranted SiNWs under dark and upon illumination. The inset in B represents the dark current densities of Pt/SiNWs and Pt/Si planar. (Oh et al., 2012).

CHAPTER 3: MATERIAL SYNTHESIS AND CHARACTERIZATION

TECHNIQUES

3.1 Introduction

This chapter briefly describes the growth of Si nanostructures (nanorods and nanowires) by chemical vapor deposition (CVD). CVD plays a crucial role in growing nanostructures by depositing volatile materials on the substrate surface under vacuum environment. The first part of this chapter describes the deposition system and the sample preparation procedures. Meanwhile, the second part of this chapter presents the analysis and calculation techniques used in nanostructures characterization. These characterization techniques include field emission electron microscope (FESEM), high resolution transmission electron microscope (HRTEM), Micro-Raman scattering spectroscopy, X-Ray Diffraction (XRD) technique, X-Ray photoelectron spectroscopy (UV-VIS-NIR) (XPS), Ultraviolet-Visible-Near-Infrared spectroscopy and photoluminescence (PL) spectroscopy.

3.2 Chemical Vapor Deposition System

The growth and fabrication of Si nanostructures were synthesized in the home-built CVD system as shown in Figure 3.1 (a). The system mainly consists of three parts, which are the furnace and reaction tube, vacuum pump and control system.





Figure 3.1: (a) Photograph image of the home-built CVD system. (b) Schematic diagram of the reaction tube.

3.2.1 Tube

The tube modelled STF 16/180 (Carbolite Furnace Ltd, United Kingdom) is a heating device with integrated monitoring system used to synthesis inorganic samples. Basically, the tube consists of a cylindrical stainless-steel chamber with an outer tube diameter of 60 mm and a length of 120 cm, made up of high-quality ceramic. The horizontal configuration of the tube is compulsory as for the easy sample placement. The tube chamber is controlled by a programmable system with a retransmission of set point, ramping and a process timer. The heat up ramping rate (rate of period at setpoint temperature changes) was set at 5 °C/min. Meanwhile the dwell time (period at setpoint temperature remains constant) was fixed for 3 hours. The schematic diagram of the tube furnace system is shown in Figure 3.1(b). The chamber comes with three zoned design to promote good temperature uniformity. The heated zone where the deposition process is conducted is the central zone while the two ends of the tube are the cold zone. The cylindrical tube is also surrounded by heating coils embedded in a thermal insulated material with the presence of R type thermocouple. Additionally, this tube is designed with a reserve power at the end zones to compensate the heat loss from the ends of the furnace. These end tubes are well-sealed with Viton O-rings and is closely attached to rotary pump at the right end to prevent leakage during the pumping process. The maximum operating temperature of the system can reach up to 1600°C. A 13 x 3 cm of alumina (Al₂O₃) boat is being used as a substrate holder to place two pieces of Si substrate with diameter of 1 x 1.5 cm each respectively. The alumina boat was then placed at the center zone with an approximately distance of 54.5 cm from the tube ends.

3.2.2 Vacuum

Vacuum is essential in deposition process to reduce the surface contaminations by removing air molecules from an enclosed sealed reaction chamber or confined volume in a ceramic tube. The vacuum level is always dependent with the pump used for the evacuation process. A clean deposition atmosphere will be created by the axial flow pump yielding high quality of nanostructures. In this work, a dual stage rotary mechanical vacuum pump modelled Edwards E2M5 was used and directly connected at one end of the tube. This mechanical pump has a good pumping speed of 3.75 cfm at 60 Hz and was capable to evacuate the pressure level down to 10⁻³ mbar. The pressure level was measured by Leybold pirani gauge which was connected to the ceramic tube chamber. The ideal vacuum pressure (1 mbar) was maintained and kept constant during the deposition process by controlling the diaphragm valve. The photograph image of the rotary mechanical pump is shown in Figure 3.2.



Figure 3.2: Photograph image of vacuum pumping system.

3.2.3 Substrate Heating Supply

A high heat treatment process is crucial to fabricate high quality Si nanostructures using CVD system. In general, the tube furnace consisted of a cylindrical chamber encircled by silicon carbide heating coils (as illustrated in Figure 3.3) embedded within a heat insulated model for a uniform distribution of heat. The heating coil portrayed an important role in converting the electrical energy into heat that flows through the coil and regulating the temperature of the furnace by a thermocouple. This heating coil required 240 V to supply a maximum heating power up to 2500 W. In addition, the tube furnace also came with a special features of over-temperature protection to keep samples safe and allow unsupervised operation. A thermocouple (type R thermocouple) was installed at the rear panel of the tube furnace and connected to a temperature controller to monitor the temperature during the annealing process. Ceramic tube with a dimension of (4.5 x 120 cm) was inserted into a tube furnace, with the alumina boat containing the SiO₂ and C sources placed at the center.



Figure 3.3: Illustrations of heating coils embedded within a thermally insulated model.

3.3 Deposition Procedures

The deposition procedures basically include three steps, the pre-deposition, deposition and post deposition. The illustration of the flow chart of the deposition procedures is shown in Figure 3.4. The pre-deposition involved the substrate cleaning and evacuation of pumping process. Meanwhile, the deposition was mainly on the variations of the SiO₂ and C source masses to grow Si nanostructures. Finally, the post deposition took in the cooling process of the tube furnace upon samples collection and tube furnace cleaning.



Figure 3.4: Flowchart of research methodology of the work.

3.3.1 Pre-deposition

P-type crystal silicon (c-Si) with an orientation of (111) is used as substrate in this work. The c-Si wafers were first cut into two small pieces with a dimension of (1 x 1.5 cm) each to place the SiO₂ and C powders. Besides, a long rectangular-shaped Si wafer substrate (13 x 3 cm) is also prepared to cover the alumina boat throughout the experiment. These Si substrates were chose as it has relatively low background, essential for all characterization techniques.

Basically, the cleaning process is crucial to remove contaminants or residues such as dust, oil and fingerprint that might affect the properties of the nanostructures grown on the substrates. The c-Si substrates were cleaned by following the method of Radio Corporation of America RCA I and II cleaning procedures (Kern, 1970). The RCA procedures are the standard cleaning procedures popularly known for silicon wafer substrates before these substrates undergo deposition process in the reaction furnace. Initially, the substrates were rinsed with deionized (DI) water to remove dust particles from the substrate surface. The substrates were then immersed for 5 minutes in $H_2O:H_2O_2:HCI$ (ratio of 6:1:1) solution in order to remove metal contaminations. The substrates were then rinsed with DI water for 3 times. The next step was to remove organic contaminations and oxide layer from the surface by immersing the Si substrates in $H_2O:H_2O_2:NH_4OH$ (ratio of 5:1:1) solution, then rinsed again with deionized water before been immersed in $H_2O:HF$ (ratio of 10:1) solution respectively. Finally, the substrates were rinsed with DI water, dried and purged using N₂ gas.

SiO₂ (99.8%) and palm kernel shell derived carbon (C) powders are both mixed with graphite powders separately. The materials were first weighed by varying the amount of SiO₂ and C powders at a fixed ratio of 4:3. Hence, the SiO₂:C used in this work are 15:11.25 mg, 25:18.75 mg, 50:37.5 mg, 100:75, 125:93.75 mg and 150:112.5 mg

respectively. Meanwhile, the graphite mass was fixed at 5 mg for both powders and for all parameters. The mixed SiO₂ and C powders were then separately spread on the Si substrates on the bottom of the alumina boat as shown in Figure 3.5. This alumina boat was subsequently covered with Si substrate $(13 \times 3 \text{ cm})$ and then inserted inside the tube furnace, with the alumina boat positioned at the centre of the furnace. The polished side of Si substrate was placed facing down to the bottom of the boat. The steps are then followed by the evacuation of the tube furnace by controlling the diaphragm valve of the rotary mechanical pump to its maximum. The pumping process usually took almost an hour to reach its base pressure of 0.5 mbar. Indeed, this process was compulsory to maintain a clean and free active and reactive constituent such as air and water vapor.



Figure 3.5: Photograph of (a) SiO₂ and C source powders together with graphite placed at the bottom of alumina boat and (b) the alumina boat been covered with Si substrates.

3.3.2 Deposition

Generally, the deposition process involved the material deposition of Si nanostructures at different SiO_2 and C source masses. Meanwhile, most of the deposition parameters such as the growth pressure, deposition temperature and ramping rate are remained constant during the work.

During the deposition, the growth pressure was maintained at 1 mbar throughout the process. The tube furnace was set to ramp slowly from room temperature at a rate of 5 °C/min for a precise sample temperature control. This process was usually carried out for 4 hours for the tube furnace to reach the selected deposition temperature. Meanwhile, the deposition temperature was fixed at 1410 °C since the melting point of Si is 1414 °C so as to turn Si into vapors for the chemical reactions to occur. The tube furnace was then set to keep at the similar deposition temperature for 3 hours. The details of the deposition parameters used in this work were classified in Table 3.1.

Sample	Nanostructure	Deposition parameters		
		Variation of SiO ₂ and C source masses		Fixed parameter
		$SiO_2(mg) + Graphite (5 mg)$	C(mg) + Graphite (5 mg)	Temperature: 1410 °C Pressure: 1 mbar Time: 3 hours
А	Si nanorod	15	11.25	
В		25	18.75	
С		50	37.5	
D	Si nanowire	100	75	
Е		125	93.75	
F		150	112.5	

Table 3.1: Details on deposition parameters of Si nanostructures.

3.3.3 Post-deposition

After the successful completion of Si nanostructures growth process, the tube furnace is cooled down to room temperature before the air flowed into the tube. The Si nanostructures were expected to grow on the polished side of the Si substrate. The substrate surface changed to brownish colour after the deposition as shown in Figure 3.6. Finally, the system was shut, and the samples were ready to be collected for analysis and characterization studies. After that, the tube was cleaned thoroughly in preparation for the next deposition.



Figure 3.6: Image of deposited samples on the c-Si substrate at SiO₂ source masses of (a) 15 and (b) 100 mg.

3.4 Characterization Techniques

The properties of the Si nanostructures were studied extensively from spectroscopy and microscopy perspectives which covered the morphology, structural, chemical composition and optical studies. In general, electron spectroscopy was used during the analysis due to its high magnification and better resolution, which is 1000 times more specific and precise than the light microscope. The morphological study of the nanostructures was characterized by field emission scanning electron microscopy (FESEM) to investigate the distribution of the samples. The elements compositions of the samples were analyzed by energy dispersive X-ray spectroscopy (EDX) mapping. The relationship between element composition and the crystal lattice of the nanostructures are further investigated by high resolution transmission electron microscopy (HRTEM). Meanwhile, Raman spectroscopy and X-ray diffraction (XRD) technique was done to figure out the crystallinity structure such as orientation and molecular interaction of the samples. The chemical composition as well as the chemical bonding state were studied by X-ray photoelectron spectroscopy (XPS). Additionally, the optical properties and energy gap of the nanostructures were examined by ultra-violet - visible - near-infrared (UV-VIS-NIR) spectrophotometer and photoluminescence (PL) spectra, respectively. Finally, the photocurrent response of the as-grown Si nanostructures was obtained by the potentiostat measurement analysis.

3.4.1 Morphological and Elemental Studies

3.4.1.1 Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX) Spectroscopy

FESEM is an imaging tool used for morphological characterization of nanostructures. This technique often used ultra-high energy electrons and provides broad information of the sample such as the microscopic measurement of fine features. The topography and morphology of the samples such as the sample surface textures, shape and size could also be determined by FESEM. Besides, this instrument is surface sensitive without requiring pre-treatment process. Briefly, FESEM acquired high resolution and high magnification up to 500,000 times due to the very fast-moving electron as compared to conventional optical spectroscopy.

Figure 3.7 (a) illustrates the schematic diagram of the FESEM component. Basically, this instrument consisted of field emission (FE) gun which is the source of the electron beam (primary electron) by applying a strong electric field. The FE gun is made up of two anodes and a cathode attached at the field emitting tip. This tip with a needle point ($<0.1 \mu$ m) was usually made up of tungsten to obtain high order strength for electron emission. Meanwhile, the two anodes play a role as extraction and acceleration anodes. The extraction anode pull the electrons from the tip while the acceleration anodes speed up the electrons to 100 kV and more. This process operated at ultra-high vacuum environment to reduce contaminations and oxide. These high energy electrons then passed the system apertures and electromagnetic lenses with a focused and minimal distribution of energy. Furthermore, the electron microscopy lenses are made up of a coil-shaped electromagnet for the electron beams to travel in X and Y direction resulting in a fine electron beam. The accelerated electrons then focus by objective lens and enter the surface of the sample, generating signals called secondary electrons (SE), backscattered electrons (BSE), photons (characteristics X-ray), auger electrons and visible light

cathodoluminescence as presented in Figure 3.7 (b). Secondary electrons provide data on the surface morphology and topography while backscattered electron help to determine the elemental distribution of the sample by contrasting the image. The intensity of the backscattered electrons was strongly liable to the atomic number of the material. Higher atomic number element shows brighter image than the lower atomic number element. The resulted SEM images of the as-grown Si nanostructures were shown on the TV screen in 3D view. In this work, the FESEM images of the as-grown Si nanostructures were obtained using Hitachi SU8230 Cold Field UHR FESEM at low electron- accelerating voltage of 2 kV as shown in Figure 3.7 (c).



Figure 3.7: (a) Schematic diagram of FESEM main component. (b) Interaction between sample and beam in FESEM. (c) Photograph of Hitachi SU8230 Cold Field UHR FESEM.

The elemental spectra of the samples are obtained by an energy dispersive X-ray spectroscopy (EDX) in conjunction with FESEM analysis. EDX analysis is commonly used to identify the X-ray spectrum emitted from the sample by the high energy electron beam irradiation (10-20 keV). Conceptually, the high energy electron beam (primary electron) hits the inner orbital of an atom and kick out the electron from the inner orbital leaving a positive charged hole. Eventually, another electron from the outer orbital then fills the vacancy hole. The movement of electron from outer orbital (higher energy) to inner orbital (lower energy) produce an energy difference and released as X-rays form as shown in Figure 3.8. The image of each element exists in the sample ias obtained by spreading the electron beam over the material. The chemical information of the sample is then visualized by elemental mapping and line scans that present the elemental percentage of element in the sample.



Figure 3.8: X-rays generated by the electron movement from outer orbital to inner orbital.

3.4.2 Structure Properties

3.4.2.1 High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM technique was the most favoured technique used to study the internal structure of the material. This technique used electrons to provide sample imaging similar to FESEM technique. Furthermore, this microscopy technique also required high energy vacuum to create a room for electrons to travel. In general, the structural defects and impurities such as lattice dislocation and atomic crystal lattice information can be attained in this analysis. Additionally, this technique has been widely used to characterize the plane orientation and the growth directions of the nanostructures as well as to study the core and shell structure of the nanowires.

Figure 3.9 (a) shows the schematic diagram of HRTEM that consisted of three main parts: electron gun and condenser lens system, objective lens and apertures and imaging system. Initially, high energy electrons are induced by the field emission tip at high accelerating voltage (10 to 1000 kV) and passed through the condenser lens that focused the electron beam. The condensed electron beam is then transmitted through very thin samples and passed the objective lens. The objective lens consisted of aperture with a very small hole centred to filter the high intensity of electrons scattered by the sample before reaching the detector plane. The different intensity of electrons created an image contrast on the microscope. Next, the transmitted electrons are magnified more than 50 million times by a several electromagnetic lenses. Finally, the transmitted electrons are detected by the electron detector as a 2D monochromatic image formed on a fluorescent screen or PC screen.

The basic interactions between electron beam and the atom in the sample were illustrated in Figure 3.9 (b). The fast-accelerating electrons struck the sample and generated a large number of signals. These signals included visible light (cathodoluminescence), backscattered electrons and secondary electrons that indicated the electrical and topographical information of a material. Besides, Auger electrons and X-rays are also released during the process revealing the sample's compositional information. There are also signals observed below the sample which were elastic and inelastic scatterings as well as transmitted primary electrons signals with a restriction that the sample was small enough (~100 nm) for the penetration of incident beam. The transmitted and elastic scattering signals are the most used signals in HRTEM characterization.

In this work, the HRTEM images of the as-grown Si nanostructures were recorded using a TEM (JEOL JEM-2100F) with an accelerating voltage of 200 kV as shown in Figure 3.9 (c). Samples usually required special procedure before scanning to obtain high resolution image. In the sample preparation, the sample was immersed in isopropanol solution and was put in water bath sonicator for about 15 minutes to extract the nanostructures from the substrate. The diluted nanostructure in the isopropanol solution was then transferred onto a copper grid by using a cleaned pipette. The carbon-coated copper grid (Lacey 300 mesh Cu) was used, thin enough for electron beam to be transmitted. The copper grid was then put in the dry cabinet with temperature of 37 °C to let it dry for a few hours.



Transmitted (primary) electrons



Figure 3.9: (a) Schematic diagram on the basic part of HRTEM instrument. (b) Interaction between sample and electron beam in HRTEM analysis. (c) Photograph of TEM (JEOL JEM-2100F).

3.4.2.2 Raman Spectroscopy

Raman spectroscopy was a chemical analysis technique used to investigate the structural properties, crystallinity and phase. Raman spectrometer used laser as light source that interacts with molecular vibrations (phonons) based on the interaction of light with the chemical bond of a material. The high intensity laser beam irradiated the sample and generated two types of scattered light as illustrated in Figure 3.10 (a). Most of the scattered light have similar wavelength or colour in all directions and known as Rayleigh scattering (elastic scattering). However, a small fraction (one per million photon) of the incoming light is scattered at different wavelengths than the incident laser. This scattering process is called Stokes and anti-Stokes Raman inelastic scattering. Stokes scattering usually occurred at lower frequency or lower energy while anti-Stokes scattering occurred at higher frequency (or higher energy) of the incident irradiation. The shifting in the wavelengths depends on the vibrational and rotational energy of the molecules. The energy of the scattering light is less than the incident light for Stokes scattering while the energy of the scattering light is higher than the incident light for anti-Stokes irradiation. Figure 3.10 (b) represents the simplified energy diagram of Raman scattering consisted of Rayleigh scattering, Stokes and anti-Stokes scattering respectively.

In this work, the Raman spectra of the Si nanostructures was characterized by InVia Raman Microscope with an Argon-ion visible green laser with excitation wavelength and laser power of 514 nm and 100 % respectively as shown in Figure 3.10 (c). The diffraction grating was set to 2400 lines/mm. The Raman spectra was detected using a CCD camera and shown on the screen monitor.



Figure 3.10: (a) Basic principle of interactions in Raman. (b) Energy level diagram involved in Raman spectra. (c) Photograph of In Via Raman Microscope.
3.4.2.3 X-ray Diffraction (XRD)

X-ray diffraction is an analytical technique used to identify the crystallinity, phase and orientation plane of an element. The crystallinity structure of the samples can be demonstrated by the intensity of the diffraction peak. Meanwhile, the element phase and the orientation plane can be obtained from the peak position. There are three essential parts of XRD spectroscopy consisted of X-ray light source, sample holder and X-ray detector as illustrated in Figure 3.11 (a). XRD works by introducing X-ray source generates by filament heating in a cathode ray tube to release electrons. The electrons are then accelerated towards a target by applying a voltage before interacting with the sample. Basically, the electrons with sufficient energy will hit the inner shell atom, kick out the electron and create a hole. As a result, characteristics X-ray spectra are produced with several components of K_{α} and K_{β} . The sample holder and the X-ray detector were mechanically rotated at the angle of θ and 2θ . The intensity of reflected X-ray was then recorded simultaneously during the rotation. Therefore, the angle of incident beam was always the same as the angle of diffracted beam. Figure 3.11 (b) illustrates the schematic diagram of Braggs law. The XRD signals were produced based on the constructive interference of monochromatic X-ray and crystallinity of sample satisfying the Braggs Law:

$$2d \, \sin \theta = n\lambda \tag{3.1}$$

where d is the interatomic spacing in angstrom, θ is the diffraction angle in degree, n is positive integer and λ is the wavelength of radiation beam in angstrom. From Braggs Law, the X-ray scatters by atoms are completely in phase, generating constructive interference with maximum intensity of X-ray diffracted. The intensity of the diffraction peak is relatively dependent to the crystallinity degree of the sample. Further calculation on the lattice constant, a was done to equate the theoretical value to the grown crystal structure using the following equation:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
(3.2)

where d is the interatomic spacing and h, k, l are the crystalline plane values.

In this work, XRD patterns were collected using a PANalytical Empyrean X-ray diffractometer over the 2 θ scan range of 20 ° to 80 ° with a fixed grazing incidence angle of 5 ° (Figure 3.11 (c)). The step time and step size were fixed at 3 s and 0.02 °, respectively. Copper is used as the target material with CuK_{α} radiation wavelength of 1.5418 °. The raw data measured by the XRD machine was then transferred to PANalytical X'pert Highscore software for further analysis.



Figure 3.11: (a) Main component of XRD technique. (b) Interaction between incident beam and diffracted beam which obeys Bragg's Law. (c) Photograph of PANalytical Empyrean X-ray diffractometer.

3.4.3 Chemical Composition and Binding Energy

3.4.3.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy or known as Electron Spectroscopy for Chemical Analysis is widely used to analyze the chemical composition and electronic state of the sample. It is basically a measurement technique based on the principle of photoelectric effect. XPS process involved the irradiation of photons (monochromated X-ray) of a specific energy when it bombards the core-level atoms in a material (Figure 3.12 (a)). This high energy electrons become excited and get ejected from the surface. The emission of photoelectrons revealed the orbital shells (1s, 2s, 2p, etc). In photoelectric effect, some of the energy transmitted by the incident photon is used for the photoelectron ejection to overcome the binding force of atom or molecule. Meanwhile, the remaining energy appears as the maximum kinetic energy of the emitted electron and can be explained by the following Einstein's photoelectric equation:

$$K_{max} = E - \emptyset \tag{3.3}$$

where K_{max} is the maximum kinetic energy of ejected electron, denoted as $K_{max} = \frac{1}{2}mv_{max}^2$ (m is the mass of electron = 9.1 x 10⁻³¹ kg and v_{max} is the maximum speed of the photoelectron). Meanwhile, \emptyset is the binding energy or work function of the material. Photoelectrons require a work function larger than the photon energy for the emission to occur accordingly.

XPS spectrum is obtained by counting the ejected electrons that escape from the material's surface over the range of their kinetic energies. The kinetic energy of the electrons helps to determine the chemical states and binding energy of the electrons. Meanwhile, binding energy can be determined as a minimum energy required to free the electrons from the metal surface. In addition, narrow scan with high resolution XPS

analysis was also obtained to identify the bonding state of element from the position and shape of the XPS peak.

Figure 3.12 (b) illustrates the basic schematic diagram of the XPS instrument which comprised of high energy photon of $Al K_{\alpha}$ X-rays radiation, an electron optic, a hemispherical energy analyzer and a detector. The irradiation of X-rays on the sample generates electrons with a different range of energy and directions. The electron optic which consists of electrostatic and magnetic lens will collect and focus the electrons at the entrance slits of the hemispherical energy analyzer. The electrostatic field then allows these electrons of a specific energy to pass through the energy analyzer and be detected at the end.

XPS analysis was carried out at the Synchrotron Light Research Institute (SLRI) in Thailand. Figure 3.12 (c & d) shows the photograph of XPS instrument at beamline BL3.2a (PES beamline) and the real size electron gun used in this analysis. The PES system consisted of Thermo VG Scientific CLAM2 electron spectrometer operated at maximum photon energy of 600 eV and energy step of 0.1 eV respectively. The obtained binding energies data were calibrated using the C 1s binding energy of 284.6 eV attributed to the unavoidable presence of carbon in all exposed material. The XPS spectra was deconvoluted into their assigned peaks to identify the chemical bonding in the material. Figure 3.13 demonstrates the four main deconvolution peaks of Si 2p which is Si-Si, Si-C, Si-O_x and Si-SiO₂ peaks respected to 284.6 eV, 101.3 eV, 102.8 eV and 103.2 eV binding energies.



Figure 3.12: (a) Illustrations on the photoelectric effect process. (b) Schematic diagram of a typical XPS setup. (c & d) Photograph of XPS instrument beamline BL3.2a (PES beamline) and the electron gun used in the analysis.



Figure 3.13: Typical XPS deconvolution spectra of Si 2p.

3.4.4 **Optical Properties**

3.4.4.1 Ultraviolet-Visible-Near-Infrared (UV-Vis-NIR) Spectroscopy

Ultraviolet -Visible – Near-Infrared (UV-Vis-NIR) spectroscopy is a useful technique to determine the light absorbance and transmittance across the ultraviolet and visible ranges in an electromagnetic spectrum of light. Atoms and molecules undergo electronic transition in this spectrum region. This technique can be used for liquids, solids, thin films and glass sample types. When incident light hits the sample, it can either be absorbed, reflected or transmitted. Atomic excitation is caused by the absorption of UV-Vis radiation promoting the transition of electrons from ground state to higher molecular state. The energy difference between both levels is known as band gap. The absorption of UV and visible radiations do not only cause a change in electronic state, but it also induces the potential change in the vibrational energy. The vibrational energy levels are expressed by a series of lines that reflect the superposition of each energy levels. Meanwhile, the absorption of infra-red radiation only activates changes in vibrational energy levels. Electrons get excite and jump from one vibrational level to another or vibrates with higher amplitude as illustrated in Figure 3.14 (a).

Theoretically, UV range extends from 200-400 nm and the visible range from 400-800 nm respectively. Figure 3.14 (b) shows the schematic diagram of UV-Vis spectrometer. These visible and UV radiations are supplied by a light source which is a combination of tungsten filament or hydrogen-deuterium lamps. The beam is then focused on the prism or gratings which separates the various light source wavelength to produce monochromatic light. The output light reaches the beam selector and passes through the reference and sample solution. The reference and sample holder are usually transparent for light source to pass through efficiently. Quartz cuvettes with a rectangular shape and flat ends is commonly used in this characterization. Both beams from the reference and the sample were observed at the detector and the intensities of light passing through the

reference (I_o) and the sample (I) were also measured. The band gap energy, E_g of a material can also be achieved from this analysis. The E_g value was measured from the transmittance (T) and absorption coefficient (α) spectra of the nanostructures. The relationship between the transmittance (T) value and the ratio of light intensities can be denoted as follows:

$$T = I/I_o \tag{3.4}$$

where *I* is the intensity of transmitted light by the sample and I_o is the intensity of incident light. If the value of *I* is less than I_o , it can obviously say that some of the light has been absorbed by the sample. Meanwhile, the absorbance (*A*) and transmittance (*T*) values of a sample could be interrelated and expressed using the equation below:

$$A = \log_{10} \frac{1}{\tau}$$
(3.5)

The absorption coefficient, α was also calculated consecutively by the following expression:

$$\alpha = \frac{1}{t} \ln \frac{(1-R)}{T} \tag{3.6}$$

where t is the thickness of the film (approximately 2.6 μ m and was determined by profilometer), R is the reflectance of the sample which assumed to be zero and T is the transmittance value in percentage, T (%) = 100T. Hence, from the obtained value of α , the value of E_g could be deduced from the Tauc plot relation (Davis et al., 1970):

$$(\alpha h\nu)^2 = B(h\nu - E_g) \tag{3.7}$$

where B is a constant and hv is photon energy in eV. Therefore, the E_g value can be obtained from the extrapolation of linear region at x-axis. The gradient slope, m and the intercept value, c were then measured from the graph thus the value of E_g can be calculated following the general linear equation of y = mx + c. The photograph of Lambda 750 UV-Vis-NIR spectrometer used in this work is visualized in Figure 3.14 (c).

In addition, the light absorption capability of a material is further investigated by the calculation of Urbach energy. Urbach energy can be defined as the degree of absorption edges that determines the types of crystalline defects or disorders. The equation of linear absorption according to Urbach energy are as follows:

$$\alpha = \alpha_o \exp \frac{E}{E_u} \tag{3.8}$$

where, α is the absorption coefficient, α_o is a constant, *E* is the photon energy (*hv*) and E_u is Urbach energy. By rearranging the equation, we could obtain a linear relationship of:

$$\ln \alpha = \frac{E}{E_u} + c \tag{3.9}$$

where c is a constant. The plot of $\ln \alpha$ and E (hv) gave a straight line while the inverse of the slope provided the Urbach energy, E_u . When the slope amount is large, the density of states is high thus resulted in a narrow Urbach tail.



Figure 3.14: (a) Electronic and vibrational energy levels of UV-Vis and IR. (b) Schematic diagram of UV-Vis spectrometer. (c) Photograph of Lambda 750 UV-Vis-NIR spectrometer.

3.4.4.2 Photoluminescence (PL) Spectroscopy

Photoluminescence spectroscopy is a contactless, non-destructive method used to analyze the electronic structure, the impurities level and defects in a material. Figure 3.15 (a) illustrates the schematic diagram of the principle in PL spectroscopy. The spectroscopy comprised of three basic components which are the laser source, monochromators and a detector. There are two types of monochromator involved which are the excitation and emission monochromators. These monochromators acted as a wavelength selector to maintain high resolution spectrum. Photons, a form of electromagnetic radiation has been absorbed by the sample with an energy larger than the band gap energy of a material. It then transfers the energy to a molecule by a process called photoexcitation. This is a spontaneous process where electrons get excited to a higher state of energy level in an atom. Due to the properties of electrons get unstable at the conduction band, this electron undergoes relaxation transition in an atom, falls back to its equilibrium or ground state and dissipates the excess energy in a form of light called photoluminescence. The schematic diagram on the excitation and relaxation processes of electrons is simplified in Figure 3.15 (b). The photoluminescence spectra of the Si nanostructures are then recorded by evaluating the intensity of the emitted radiation.

In this work, the same spectrometer for Raman measurement was used to study the photoluminescence (PL) spectra of the Si nanostructures. A monochromatic HeCd laser with an excitation wavelength and laser power of 325 nm and 5 mW were also selected, respectively.



Figure 3.15: (a) Schematic diagram of photoluminescence spectroscopy components. (b) Illustrations of excitation and relaxation of photoluminescence process.

3.4.5 Photoelectrochemical Water Splitting Measurement

Figure 3.16 (a) shows the real image set-up for photoelectrochemical (PEC) water splitting. The set-up basically consisted of potentiostat, electrochemical cell, solar simulator and computer. A potentiostat modelled Autolab PGSTAT204 was used in this work. The photoelectrochemical cell was configured as shown in Figure 3.16 (b) with three electrodes used where the Si nanostructures was used as the working electrode, a platinum (Pt) wire as the counter electrode and Ag/AgCl as the reference electrode. The tests were conducted at room temperature with a supporting electrolyte of 0.1 M Na₂SO₄ aqueous solution and a pH value of 7. A UV-visible light source was provided by a 300 W Xe arc lamp modelled Newport 66901 and was equipped with a beam turner (Newport 66245) and mirrors to activate the AM 1.5G light which approximating the spectrum of the natural sun light. The as synthesized photoanode was fixed at 1.5 cm² and the defined area was coated with the water dispersible epoxy resin. The photoanode was dried thoroughly before been immersed in the electrolyte solution.

The photocurrent responses of the as-grown Si nanostructure photoanodes deposited at different source masses were recorded by the potentiostat. The scan rate of the linear sweep voltammetry (LSV) was fixed at 2 mV s⁻¹ over a range of -0.6 to 0.6 V. The PEC stability of the as-grown Si nanostructures was measured by evaluating their photocurrent densities under the chopped visible light irradiation (light on/off cycles of 20 s) as shown in Figure 3.16 (c). The measurement was carried out for a period of 5 minutes at a fixed electrode potential of 0 V vs RHE. The illustration of the photoelectrochemical cell and the image of the working electrode with the deposited Si nanostructures were clearly shown in Figure 3.16 (d & e). The three electrodes were wired to a potentiostat, which determined the current flow between the working electrode and the reference electrode while supplying potential between the working electrode and the reference electrode. The resulting current passing the working electrode had been measured while the potential between the working electrode and reference electrode was swept linearly throughout the scan. Generally, the scan started on the left side of the current/voltage diagram, where there is no current flowing. Current will begins to flow when the voltage was swept further to the right of the diagram or to more reductive levels and finally reached a peak before falling. Chronoamperometry measurement was recorded under same experimental setup to measure the current of the electrode as a function of time by stepping the potential of the working electrode. The potential was change instantaneously from non-faradaic (or capacitive current) reaction to a value at which the surface concentration is zero. Further analysis on the impedance of the electrochemical system was carried out by the Electrochemical Impedance Spectra (EIS)-Nyquist plot under dark condition. An arc or semicircle could be seen from the EIS-Nyquist plot where the solution resistance (R_{s}) between the working electrode and reference electrode and the charge transfer resistance (R_{ct}) were calculated respectively. The doping type and flat band potential (V_{fb}) of the nanostructures were examined by Mott-Schottky plot.



Figure 3.16: (a & b) Photograph of PEC measurement set-up and the photoelectrochemical cell basic configuration. (c) Photograph of real time measurement under chopped visible light. (d) Schematic diagram of the basic configuration of the working, reference and counter electrodes. (e) Real image of the working electrode with the deposited Si nanostructures.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter discusses the results of Si nanostructures grown by chemical vapor deposition (CVD) technique. Six different sets of parameters were successfully prepared by varying the SiO₂ and C source masses. The details on the growth parameters have been clarified in Table 3.1 in Section 3.2.2. The morphology of the as-grown Si nanostructures was investigated in detail by FESEM and TEM. Meanwhile, the structural and chemical composition of the nanostructures were determined by EDX, Raman, XRD and XPS analysis. The optical properties of the samples were also studied by UV-Vis-NIR and PL analysis. Additionally, the growth mechanism of Si nanostructures was proposed to have a profound understanding on the morphology changes and structural properties of the samples were splitting application.

4.2 The Morphological Studies of Si nanostructures

The morphological properties of the as-grown Si nanostructures prepared at different SiO₂ source masses are shown in Figure 4.1. The FESEM images of the nanostructures grown at the lowest SiO₂ source mass of 15 mg showed needle-like Si nanorods which are sparsely grown on top of agglomerated bunch of micro-grains (Figure 4.1 (a)). The needle-like Si nanorods are clearly depicted in Figure 4.2 (a). The estimated average diameter of these nanorods is approximately 247 ± 22 nm with an average length of 19.8 \pm 3.0 µm. The estimated aspect ratio of nanorods length-to-diameter is 80. The high densities of agglomerated micro-grains were obviously visible and randomly distributed on the surface substrate. These Si micro-grains had an irregular shapes and sizes. They consisted of various facets mainly circle, square and octahedral shapes (as depicted in Figure 4.2 (b)). However, the octahedron shape micro-grains are dominant on the substrate surface with an estimated average diameter of 0.21 \pm 0.05 µm. The growth of

different facets suggested that the structure of these Si micro-grains are mainly crystalline. The formation of these agglomerated micro-grains could be due to less amount of oxide presence in the reactor during the deposition process. According to Li et al. (2019), the formation of oxide is highly influenced by the thermodynamic and kinetic stabilities of an O adatoms on the surface of the substrate. The lack diffusion rate of oxide leads to low kinetic stabilities of O adatoms on the surface. Hence, the low mobility of SiO vapors into the catalyst droplets could eventually leads to coalescing of catalyst particles in forming large or crystalline micro-grains instead of growing Si nanorods (Phiri et al., 2018).

The sample prepared at SiO₂ source mass of 25 mg revealed the formation of SiNWs and Si nanorods (Figure 4.1 (b)). The SiNWs are grown with rough surface as depicted in Figure 4.2 (c). The average size of the SiNWs is approximately 55.1 ± 5.5 nm and the length is $3.2 \pm 1.0 \,\mu\text{m}$ with an aspect ratio of 58.9. The surface diffusion rate of O vapors into Si contributes to the formation of solid Si seeds (nanoparticles) on the substrate surface. Theoretically, the seeds are formed by annealing process at an appropriate temperature (Mohammad, 2008). These seeds develop over time, eventually serving as well-distributed nuclei which initiate the growth of SiNWs. On the other hand, a small amount of Si nanorods are observed with a diameter and length of 67.8 ± 7.4 nm and $0.27 \pm 0.04 \,\mu\text{m}$ (estimated aspect ratio of 4). The nanorods have spherical and octahedron facets and were randomly grown over the substrate as demonstrated in Figure 4.2 (d).

Figure 4.1 (c) shows the randomly distributed SiNWs grown on top of the Si micrograins prepared at SiO₂ (50 mg). The surface of the nanowires is relatively smoother than the nanowires prepared at SiO₂ source mass of 25 mg as shown in Figure 4.2 (e). Furthermore, the nanowires demonstrated a notable increment in the size and length of 221 ± 28 nm and 12.1 ± 4.5 µm, respectively. The estimated aspect ratio for the SiNWs growth is 54.6. The as-grown sample also revealed a non-uniform distribution of Si nanorods with only octahedron facets (Figure 4.2 (f)). The estimated growth of these Si nanorods followed the aspect ratio of 4 where the nanorods size and length are 174 ± 29 nm and $0.7 \pm 0.1 \mu$ m, respectively.

Significantly, the sample prepared at SiO₂ source mass of 100 mg exhibited only SiNWs with greatly decrease in their diameter around 31.8 ± 3.0 nm and a length of 1.6 \pm 0.3 µm (the estimated aspect ratio of 51.8). It is well noticeable that these nanowires exhibited superior alignment compared to the samples prepared at lower SiO₂ source masses, as depicted in Figure 4.1 (d). Furthermore, the nanowires presented a relatively higher density and length indicating high growth rate of the nanowires and was attributed to high diffusion rate of SiO vapors during the growth process (Shih et al., 2017). On the other hand, no coalescence of the catalyst particles was observed (as depicted in Figure 4.2 (g)). The hindering of Si micro-grains (~51 nm) formation at high SiO₂ mass could be explained by the adequate diffusion of SiO vapors into the catalyst droplets for sustaining the nucleation and nanowire growth processes (Zhang et al., 2003).

An increased in the SiO₂ source mass provided sufficient amounts of oxide which in returns resulted in higher rate of surface diffusion. Hence, the nanowires growth could be enhanced. Figure 4.1 (e) shows a high density but non-uniform distribution of SiNWs prepared at SiO₂ (125 mg) with an average size of 48 ± 4 nm and $1.7 \pm 0.2 \mu$ m in length (estimated aspect ratio of 34.5). The various morphologies of wires formations as presented in Figure 4.2 (h) may be due to the varying local concentrations of SiO_x vapors (Zhu et al., 2009). SiO_x vapors are produced at high temperature during the deposition process. These vapors accumulated with time, resulted in rise in vapor pressure and SiO_x vapor concentration. The adequate amount of SiO_x vapor concentration will yield a high density of nanowires. On top of that, the relatively higher amount of oxide in SiO₂ source

mass of greater than 50 mg could play an essential role in facilitating the growth of SiNWs, eventually.

An increase of SiO₂ source mass to 150 mg led to a decrease in the density of SiNWs as shown in Figure 4.1 (f). The SiNWs have an average wider diameter of 82 ± 17 nm and length of $2.8 \pm 1.6 \mu$ m (estimated aspect ratio of 33.7). Kinked structures of SiNWs were observed showing large diameter and non-uniform sizes, clearly shown in Figure 4.2 (i). The change in diameter could be due to formation of large Si solid nanoparticles which results in the growth of larger SiNWs. However, it can be deduced that the increase in SiO₂ source masses produced significant changes in the size and diameter of the nanostructures. SiO₂ source acted as nucleation sites to provide oxygen and Si source for the nanowires growth. In sum, this has revealed that the morphology of Si nanostructures is highly dependent with the source mass.



Figure 4.1: FESEM images of as-grown Si nanostructures at (a) 15, (b) 25, (c) 50, (d) 100, (e) 125 and (f) 150 mg of SiO₂ source masses.



Figure 4.2: High magnification FESEM images of as-grown Si nanostructures at (a & b) 15, (c & d) 25, (e & f) 50, (g) 100, (h) 125 and (i) 150 mg of SiO₂ source masses.

The microstructure of the as-grown Si nanostructures was investigated by TEM and HRTEM imaging, as depicted in Figure 4.3. The nanostructures prepared at SiO₂ source mass of 100 mg was selected for the TEM measurement due to its high density of nanowires. Figure 4.3 (a) illustrates that the stem of a single nanowire is mainly straight with an average diameter of 40 nm along the length. Small kinks formed near to the root due to the change of growth direction as influenced by variation in temperature and pressure during the nanowire growth (Lugstein et al, 2008). The kinking in nanowires usually occurs at both thin area (tips of the nanowires) and thick area (nanowires root). The formation of kinks in nanowires are strongly correlated with the stability of the triple boundary line, where the liquid droplet, the solid nanowires and the gas phase coexist (He et al., 2015). The SiNWs are forced to kink kinetically in which the frequency of kinking is proportional to the degree of kinetic forcing (Madras et al., 2009). The nanowires are consider kinetically forced when the growth rates are faster than other thermally activated process such as surface diffusion that may contribute to its growth. Indeed, studies have also reported that the thermal conductivity of nanowires is correlated with the surface roughness or kinking of the nanowires (Zhao et al., 2019). Furthermore, the TEM image also clearly illustrated a significant catalyst droplet located on the tip. It is notable that this catalyst droplet exhibited flower bud-shape morphology, which is obviously different as compared to spherical metallic catalyst droplet that was generally reported in literature (Kibria et al., 2015). The HRTEM images obtained at the tip and stem are depicted in Figures 4.3 (b & c) respectively. Interestingly, the results show no significant metallic catalyst impurities which suggested that the conventional metal assisted growth vaporliquid-solid (VLS) mechanism was not playing the role. The HRTEM image scanned on the sidewall of the tip revealed only crystal structure of Si, mainly in crystal plane of (111) orientation and its lattice spacing of approximately 0.30 nm (JCPDS Card No. 01-089-2749) (Liu et al., 2005). Moreover, the crystal growth direction in (111) plane was

also clearly revealed (inset of Figure 4.3 (b)). The HRTEM scanned on the sidewall of the stem (Fig. 4.3 (c)) also presented similar lattice spacing of Si (111) crystal plane (about 0.30 nm). The growth direction of (111) plane was also confirmed for the tip (inset of Figure 4.3 (c)). The similar crystal lattice spacing of the nanowire and its catalyst particle suggested a self-catalyzed growth of these Si nanowires. The HRTEM image showed a perfect crystal structure with their shape crystal lattices indicating the single crystal structure of these as-grown Si nanowires. These nanowires were surrounded by a very thin amorphous layer (approximately 1-2 nm thickness) as depicted in Figure 4.3 (c) and could be due to the oxidation of the nanowires forming amorphous SiO_x layer as generally reported by CVD-grown nanowires (Gao et al., 2019; Sen et al., 2014; Shakthivel et al., 2019; Xu et al., 2018). The amorphous SiO_x is the essential element in encouraging the nucleation and 1D growth of SiNWs.

TEM image near the base of the nanowires is depicted in Figure 4.3 (d) showing large diameter of nanorods (around 166 nm) with octahedron facet and semi spherical grain structures on their tips. We believed that these structures could be the seeds, which acted as the diffusion sites of Si for the growth of Si nanowires. Figures 4.3 (e & f) depict the HRTEM images obtained at positions below and above the boundary of the octahedron/nanorod interface, respectively. The two images revealed similar crystalline lattice fringes of Si (111) plane and their lattice spacing of approximately 0.30 nm. The crystal structure above the boundary (in octahedron structure) depicts a relatively better crystal orientation than the structure below the boundary (nanorods) suggesting the solidification effect of Si crystal due to its low surface energy (Lan et al., 2012; Shah et al., 2014; Yuan et al., 2018). The thin amorphous layer in the images indicates the oxidation effect on the octahedron crystal surface. The Fast Fourier Transform (FFT) patterns are depicted in each HRTEM images to support the single crystalline structure

of SiNWs and grains. On the other hand, the semi spherical-grain tip's nanorod is expected to have a similar growth mechanism as the flower-bud tip's nanowires.



Figure 4.3: (a & d) TEM images of typical single Si nanowire and Si nanorod grown at SiO₂ source mass of 100 mg respectively. (b, c, e & f) HRTEM images represent their respective lattice fringes of Si nanowires and Si nanorods at different spots. Insets represent their FFT images of the respective HRTEM images.

4.3 The Structural Studies of Si nanostructures

To verify the self-catalyzed growth of Si nanowires, the EDX elemental maps on the single nanowire and nanorod prepared at 100 mg were collected using STEM with a HAADF detector in the TEM and the results are shown in Figure 4.4. Figure 4.4 (a) depicts the high magnification of dark-field STEM image scanned at near the tip of Si nanowire on a carbon film supported by copper grid. The dark-field image was overlapped with elemental maps which mainly consisted of carbon (C), oxygen (O), and silicon (Si). The single element of each elemental maps was presented in the insets. Clearly, the Si was dominant along the length of the nanowire. The mapping also revealed the corresponding distribution of C indicating SiC formation. It was obvious that the relatively high concentration of O was observed at the tip of the nanowire as compared to the length. This revealed that the O could play an important role in facilitating the growth of these high crystalline Si nanowires. The adsorption and formation of amorphous SiO_x layer on the catalyst droplets at the initial stage of the nucleation creates a diffusion barrier on the top surface thus leading to high diffusion rate at the bottom edge interfaces (Aharonovich et al., 2008; Lee et al., 2004). As a result, this phenomena leads to the 1D vertical growth mechanism which similar to the conventional nanowires growth as reported (Jiraborvornpongsa et al., 2014; Wu et al., 2014). The high content of O in the catalyst droplet as shown in Table 4.1 supports the oxide-assisted growth mechanism of these Si nanowires.

Figure 4.4 (b) shows the high magnification of dark-field STEM image for the selected octahedron structure located near to the supported copper grid. This image was scanned exactly on the top areas of the structure. The overlapped elemental maps consisted similar elements of C, O, and Si. The Al and Cu were the impurities and were ignored in the maps. In addition, the inset figures presented the single element of each elemental maps. It can be seen that the structure mainly consisted of Si and nearly no O content is observed

in the mapping (see Table 4.1). This indicates that these large octahedron crystal grains were formed due to the excessive diffusion of Si into the catalyst droplet without any SiO_x diffusion barrier, which eventually leading to the formation of crystalline Si grains. We believed that the similar diffusion effect happened to the large spherical Si grains as shown in Figure 4.4 (b). The excessive diffusion of Si into the catalyst droplet could greatly inhibits the growth of crystalline Si nanowires following the oxide-assisted growth mechanism (Hutagalung et al., 2007). Based on Table 4.1, the O amounts in Si nanowires was approximately 7 times higher than in the Si nanorods, indicated that the highly crystalline growth of Si nanowires were significantly assisted by the oxide.



Figure 4.4: Dark field STEM images with its elemental RGB images of (a) typical single Si nanowire and (b) Si nanorod grown at SiO₂ source mass of 100 mg. Insets represent the respective EDX elemental maps of the single Si nanowire and nanorod.

Sample	Nanostructure	Elements				
	-	Cu	Si	С	Ο	Others
100 mg	Si nanowire	62.3	10.6	4.8	6.2	16.0
100 mg	Si nanorod	40.8	49.5	7.6	0.9	1.2

Table 4.1: Element contents of the typical single Si nanowire and Si nanorod grown at SiO₂ source mass of 100 mg.

The Raman analysis of the Si nanostructures prepared at different SiO₂ source masses are depicted in Figure 4.5 with Raman scattering spectra within the range of 100 to 1200 cm⁻¹, respectively. Figure 4.5 (a) represents the full-scale spectra of the Si nanostructures. The sharp typical Si excitation band at 520 cm⁻¹ is clearly observed for all samples and corresponds to first-order crystalline Si (c-Si) transverse optic (TO) phonon mode (Al-Masoodi et al., 2016; Hamzan et al., 2015; Krause et al., 2019). The formation of c-Si band represented the characteristics band of Si-Si vibration (Shen et al., 2019). Furthermore, Figure 4.5 (b) demonstrates minor peaks at 150, 300 and 420 cm⁻¹ and were associated with transverse acoustic (TA), longitudinal acoustic (LA) and longitudinal optic (LO) modes of the crystalline Si, respectively (Chong et al., 2012; Nazarudin et al., 2014; Yang et al., 2010). The appearance of broad second-order Si TO mode (2TO) observed at 980 cm⁻¹ corresponded to the stretching mode of amorphous Si-Si band. The presence of small Raman excitation band at 780 cm⁻¹ was associated to crystalline cubic SiC TO mode observed for all samples which indicated the formation of SiC in the nanostructures (shown in Figure 4.5 (b)). This is due to the used of organic carbon powder for the growth of these Si nanostructures. During the heating process, SiO₂ and C atoms are continuously evaporated from the Si substrate. The Si and C vapors are then adsorbed on the surface by the assistance of O₂ and form a SiC nuclei. The SiC nuclei will then individually grow SiC nanostructures.

The full-width at half-maximum (FWHM) of the crystalline Si peak located at 520 cm⁻¹ was also calculated for all samples. The estimated FWHM for Si nanostructures prepared at SiO₂ source masses of 15, 25, 50, 100, 125 and 150 mg are 9.98, 10.23, 8.96, 10.09, 8.96 and 9.83, respectively. The small FWHM values suggest that all samples have high crystallinities of Si nanorods and nanowires as reported (Droz et al., 2004). The Raman results are in good agreement with the HRTEM images of the single crystalline Si nanostructures.



Figure 4.5: (a) Full scale and (b) narrow scale Raman scattering spectra for Si nanostructures grown at different SiO₂ source masses respectively.

XRD patterns of the Si nanostructures grown at different SiO₂ source masses are depicted in Figure 4.6. Figure 4.6 (a-c) represent the Si nanostructures prepared at SiO₂ source masses of 15, 25 and 50 mg which showed prominent diffraction peaks at 28.44°, 47.33° , and 56.13° . These peaks were corresponding to crystalline Si planes of (111), (220), and (311) orientations (Hamzan et al., 2015), respectively (JCPDS card No. 01-089-2749). The nanostructures grown at 100 mg demonstrated similar crystal orientations but with highest peak intensity correlating to high crystallinity as compared to other samples (Figure 4.6 (d)). In addition, as the SiO₂ source masses were increased to 100, 125 and 150 mg, a small diffraction peak appeared at 35.7° which belonged to 3C-SiC (111) crystalline plane according to the JCPDS card number 00-002-1050 as shown in Figure 4.6 (d-f). The SiC nanowires peak demonstrated an increase in intensity as the SiO₂ source masses were increased, respectively. The crystallites sizes of the nanostructures can be estimated by Scherrer's equation using the relation of D = $k\lambda/\beta cos\theta$, where k, λ , β and θ are the Scherrer's constant, the wavelength of X-ray (1.5406 Å), the full-width at half-maximum (FWHM) and Bragg angle of the diffraction peak (Goh et al., 2012). The estimated Si and SiC crystallites sizes, D values for samples prepared at SiO₂ source masses of 15, 25, 50, 100, 125 and 150 mg are measured and tabulated in Table 4.2. The small crystallites size generate broadening of the diffraction peaks (Wani et al., 2011).

SiO₂ diffraction peak was also observed in the patterns for all samples at 45.61° which was associated to orthorhombic structure in (202) orientation (JCPDS card No. 01-082-1570), respectively. However, nanostructures grown at 25 and 50 mg of SiO₂ source masses displayed an additional minor diffraction peak of SiO₂ detected at 37.68°. The peak is corresponded to cubic structure in (002) orientation (JCPDS card No. 01-082-1553). The appearance of SiO₂ peaks indicated the involvement of SiO vapor in the growth of these Si nanostructures. The higher amount of SiO₂ source masses (100-150





Figure 4.6: XRD patterns of the Si nanostructures grown at SiO₂ source masses of (a) 15, (b) 25, (c) 50, (d) 100, (e) 125 and (f) 150 mg, respectively. The standard XRD patterns of single crystalline Si, SiO₂, and SiC are inserted as red lines in (c & d).

Sample (mg)	Crystallite sizes, D (nm)			
	Si	SiC		
15	37.22	-		
25	34.55	-		
50	42.89	-		
100	36.05	28.48		
125	35.97	27.85		
150	37.39	29.82		

Table 4.2: Crystallites sizes, *D* for samples prepared at different SiO₂ source masses.

The density and growth rate of Si nanorods and nanowires are plotted in Figure 4.7. The Si nanorods grown at SiO₂ source mass of 15 mg have an estimated density of 0.31 rods μ m⁻². Meanwhile, the estimated nanowires densities prepared at 25, 50, 100, 125 and 150 mg are 2.6, 2.8, 18.6, 12.0 and 6.6 wires μ m⁻², respectively. The Si nanowires densities increased from low source masses up to 100 mg and significantly dropped at higher source masses of 125 and 150 mg. The highest nanowires density demonstrated by the sample prepared at SiO₂ source mass of 100 mg coincides with the FESEM image discussed earlier. In terms of growth rate, Si nanorods showed the highest growth rate of 1.62 nm s⁻¹ prepared at the SiO₂ source mass of 15 mg. On the other hand, the Si nanowires showed a similar growth rate of 0.16 nm s⁻¹ for samples prepared at high source masses of 100 to 150 mg, as formerly shown.



Figure 4.7: Variations of density and growth rate of nanowires at respected SiO₂ source masses.

4.4 Chemical Composition and Binding Energy

The chemical states of the as-grown Si nanorods and nanowires were investigated by XPS using synchrotron X-ray sources. The chemical compositions of the Si nanostructures were clearly shown by wide scan spectra in Figure 4.8 which consist of Si 2p, Si 2s, C 1s and O 1s. The samples prepared at 15 and 100 mg were chose to compare the chemical composition of Si nanorods and nanowires. The high-resolution spectra of Si 2p peak for the Si samples are shown in Figures 4.9 (a & b), respectively. These Si 2p peaks were deconvoluted into four main components of Si-Si, Si-C, Si-O_x, and Si-SiO₂ bonds, which located at binding energies of 98.8, 101.3, 102.8 and 103.2 eV, respectively. It is well noted that the Si component had relatively higher intensity for the Si nanowires as compared to the Si nanorods. This agrees with the Raman and XRD results that indicated the higher crystallinity of as-grown Si nanowires with high yield of nanowires (according to their density as discussed). Moreover, the oxide related components were significantly suppressed for the Si nanowires prepared at high SiO₂ source mass of 100 mg. The calculated Si-Si to Si-O_x integrated intensity ratios were approximately 1:1.5 and 2:1 for the samples prepared at 15 and 100 mg respectively. This reveal that the oxideassisted growth of Si nanostructures, either nanorods or nanowires requires certain range of thickness for the SiO_x layer to act as a diffusion barrier in sustaining the self-catalyzed growth of these nanostructures (Bernasconi et al., 2019; Pehkonen et al., 2018). The thinner the film, the faster it takes for the O to diffuse through interstitial lattice sites. In addition, the formation of SiC bonds is also clearly revealed in the Si 2p peak. These SiC bands are basically related to Si-C bonds. The presence of SiC bonds is in good agreement with the XRD results and showed that the oxide-assisted growth mechanism of SiC nanowires involved the SiO and CO vapors in forming homogenous crystal structure. This can be correlated by the relatively high contents of C-related bonds for the Si nanowires grown at 100 mg as compared to the Si nanorods grown at 15 mg. The

deconvolution of C 1s peak comprised of three main components at 283.2, 284.6 and 285.9 eV, corresponding to C-Si, C=C and C-C bonds respectively (Figures 4.9 (c & d)). In Figures 4.9 (e & f), the O 1s peak shows three main components of O-O, O=C and O=Si located at 531.2, 531.8 and 532.9 eV respectively. Furthermore, the oxide components in the O 1s peak for the Si nanowires grown at 100 mg are significantly higher than the similar components in the Si nanorods grown at 15 mg. This indicates that more oxides are involved in the growth of Si nanowires via oxide-assisted growth mechanism.



Figure 4.8: Wide scan XPS spectra of Si nanostructures prepared at different SiO₂ source masses.


Figure 4.9: Typical narrow scans of XPS spectra at (a & b) Si 2p, (c & d) C 1s, and (e & f) O 1s for the Si nanostructures grown at SiO₂ source masses of 15 and 100 mg respectively. The empty circles and solid black curves represent the experimental and the fitted spectra respectively. The colour curves (green, blue, and pink) represent the deconvoluted components of each narrow scan spectra.

4.5 The Optical Studies of Si nanostructures

The optical transmission spectra of the as-grown Si nanostructures prepared at different SiO₂ source masses of 15 and 100 mg are investigated by UV-Vis-NIR spectroscopy. The transmittance spectra were plotted over the range of 200-800 nm as depicted in Figure 4.10 (a). Obviously, the Si nanowires exhibited lower transmittance values (~70%) as compared to the Si nanorod (T > 80%), mainly in the range of the visible light regions. This is due to the fact that high density of Si nanowires absorbed more light in the visible and near-infrared regions. The large surface area of nanowires are beneficial for an optimal light absorption and fast charge carriers transportation (Hassan et al., 2020). Moreover, nanowires have high re-scattering ability thus able to enhance the photo absorption and re-absorption coefficient in the visible regions as compared to the nanorods.

The band gap calculation of the absorption coefficient of the as-grown Si nanostructures, $(\alpha h\nu)^2$ was plotted against photon energy, $h\nu$ as shown in Figure 4.10 (b). Meanwhile, the optical energy gap, E_g of the nanostructures are obtained from the Tauc's plot. The estimated band gaps energy, E_g of Si nanorods and Si nanowires were approximately 1.8 and 1.9 eV. These E_g values are proportional to 688 and 652 nm for the Si nanowires and Si nanorods, respectively. The high band gap value of Si nanorods may be due to the outer layers of amorphous SiO₂ on the Si core nanowires (Chong et al., 2012). An increase in the SiO₂ source mass at 100 mg significantly induced the growth of core Si nanowires with the presence of SiO₂/SiC shell. This accompanied with a slight increase of the band gap related to the additional amorphous SiC outer layer and highly crystalline structure. These results agree well with the sharp absorption edges of the optical spectrum at a photon wavelength below 400 nm. Significant multiple adsorption edges reflect the core-shell structures of Si nanowires and Si core si nanowires with different

band gap energies. Considering the presence of SiO₂ and SiC outer layers, the band gap energies of these Si nanostructures have successfully been tuned, larger than the band gap of bulk crystal silicon (1.12 eV) (Goh et al., 2014). This revealed that the optical properties of the Si nanostructures is highly influenced by the quantum size effects in which the size of the crystals were shrink (Kurokawa et al., 2012). These crystallites get photoexcited from the valence band of Si cluster and results in the increment of excitation energy accountable for the shifting of the bands (Hasan et al., 2013; Ray et al., 2009).

The light absorption ability of a material is not only affected by the band gap energy. Electronic states failure or distortions may also occurred, resulting in the modifications of band gap due to the defect levels (Kumar et al., 2020). These band defects level extending like a tail within the band gap region erecting the metallic behaviour of the samples (Kumar et al., 2019). Generally, these defect energy level usually occurred from the top edge of valence band and deep into mid band gap, similarly from the bottom edge of conduction band and deep into the band gap of a semiconductor or insulator materials (Kumar et al., 2020). The width of the band-tail was determined by the types of defects or disorders found in the sample. The linear absorption would be affected since the optical characteristics of the materials are mostly impacted by their electronic band structure. The spread of energy levels near the band edge is known as Urbach energy, E_u . Figures 4.10 (c & d) represents the Urbach plots of the Si nanostructures. The calculated E_u observed for both Si nanorods and Si nanowires are 0.7 and 0.26 eV, respectively.



Figure 4.10: (a) Optical transmission spectra of the Si nanostructures grown at SiO₂ source masses of 15 and 100 mg. (b) The Tauc plots as a function of photon energy for Si nanostructures. (c & d) Urbach plots of Si nanostructures grown at SiO₂ source masses of 15 and 100 mg.

Photoluminescence (PL) spectroscopy analysis was carried out to further determine the optical properties of the nanostructures. The origin of PL is elucidated since it is crucial for altering the optical properties of nanostructures. Basically, there are two key points of view regarding this topic. First is the quantum confinement model, which relates the PL to quantum size effect of Si nanocrystalline core (Harun et al., 2014) and the surface defect model which assigned the PL to oxygen-related defects at the interface between Si and native oxides (Bonu et al., 2015). The PL spectra of the samples prepared at different SiO₂ source masses of 15 and 100 mg are depicted in Figure 4.11. A broad PL band was clearly observed at wavelength from 300 to 900 nm which covered the whole visible region and a lower wavelength region of NIR. The broad PL spectrum for both samples were also noticed to be asymmetric and contained apparent shoulder. An intense PL band at approximately 600 nm, as referred to orange emission (Yu et al., 2015), has been observed. The appearance of this peak may be attributed to oxide defects such as oxygen deficiency and proxy linkage (Chong et al., 2013). This visible orange PL emission was caused by the defect structures as a result of nonstoichiometric (oxygen vacancy) structure which occurred due to an incomplete oxidization on Si surface. These results were in consistent with the presence of significant number of kinking structures as observed from FESEM image earlier. Indeed, the oxide defects or oxide interface defects initiate intermediate states in between the bandgap energy levels due to localized state at the interface of Si nanostructures with the surrounding SiO₂ matrix (Hadjisavvas et al., 2004). Hence, it is noted that the oxide defects in material does greatly affecting the PL recombination process (Leontis et al., 2013).



Figure 4.11: PL spectra of the Si nanostructures prepared at SiO₂ source masses of 15 and 100 mg.

4.6 Proposed Growth Model of Si nanostructures

After extensive research on the surface morphologies, structural and chemical compositions of the as-grown Si nanostructures, a simplified growth model is proposed. The growth mechanism of the Si nanostructures followed a self-catalyzed growth mechanism which was essentially facilitated by the SiO_x layer. Figure 4.12 depicts the schematic diagram of the oxide-assisted growth mechanisms (OAG) of Si nanorods and Si nanowires according to the morphologies as observed in Figures 4.1, 4.2 and 4.3. These nanostructures were grown by OAG without involving metal catalytic nanoparticles, as a substitution of the conventional VLS mechanism to avoid metal contaminations in the growth of Si nanostructures (Hasan et al., 2013; Shin et al., 2014; Zhang et al., 2003). The high temperature oxides served as a driving force for the nanostructure's growth. In this growth process, three phenomena could happen according to the presence of oxide and without oxide. For the growth mechanism in the presence of oxide, thickness of oxide layer formation is a critical factor to determine the morphology of Si nanostructures either in nanorod or nanowires as the end products assigned as A, B or C (as shown in Figure 4.12). The formation of octahedron micro-grains as presented by A is likely related to its lack of native oxides. A thin SiO_x shell produced Si nanorods as shown by B while highly crystalline Si nanowires are formed due to the presence of thick SiO_x sheath (denoted as C).

At the initial stage, oxygen atoms were desorbed from SiO₂ and C powders and decomposed to highly reactive SiO and CO vapors at high reactor temperature of 1410 °C. This temperature is very close to the melting temperature of crystal Si in solid form as the Si melting temperature was approximately 1414 °C. In this study, the graphite powder was used as a reducing agent for the decomposition of SiO₂ (Lee et al., 2010; Ryabchikov et al., 2014).

Basically, the decomposition of SiO₂ powder is followed as below:

$$2\mathrm{SiO}_2(\mathrm{s}) \to 2\mathrm{SiO}(\mathrm{v}) + \mathrm{O}_2(\mathrm{v}) \tag{4.1}$$

At the substrate temperature of 1410 °C which is similar with the reactor temperature, the adsorbed SiO could easily find a nucleation site on the substrate surface to form Si nuclei. The Si nanorods or nanowires are then produced and covered with an oxide sheath of SiO₂ (Lee et al., 2004). According to Mohammad et al. (2020), the formation of Si core and SiO₂ shell of heterostructure nanomaterials are highly dependent on the surface energy of the materials constituting the core and shell. Lower surface energy material formed the shell, while the higher surface energy material formed the core. The surface energy of SiO₂ is comparatively lower (320 mJ m⁻²) than the corresponding Si (1140 mJ m⁻²). Hence, the nanostructures grown by OAG has an oxide sheath with an oxide made up of the same semiconductor/metal materials. On the other hand, the formation of SiC was insufficient during the initial stage since the process was not thermodynamic favourable and there was no direct contact of SiO₂ and C powders. Thus, the production of SiO and CO vapors are the dominant growth species through the gas-phase transport process as below:

$$2\text{SiO}(v) \rightarrow \text{Si}(s) + \text{SiO}_2(s) \tag{4.2}$$

$$\operatorname{SiO}_2(s) + C(s) \rightarrow \operatorname{SiO}(v) + \operatorname{CO}(v)$$
 (4.3)

In this work, the SiO₂ atoms played two crucial roles as nucleation sites to provide oxide and silicon source for the growth of Si nanostructures. SiO_x layer acted as the diffusion barrier for the diffusion of SiO and CO vapors into the seed of nanostructures (nanorods or nanowires). The SiO_x diffusion barrier are observed on top of Si catalyst droplet surface thus causing increase in the diffusion rate at the bottom edge. As a result, the Si nanowires tend to grow in an upward direction. Higher SiO₂ source masses of 100150 mg led to the production of thick SiO_x layer due to the high diffusion of SiO and CO vapors. Besides, the high SiO_2 source masses also leads to the formation of SiC (as observed from XRD and XPS analysis) following the chemical reaction as below (Hu et al., 2016):

$$SiO(v) + 3CO(v) \rightarrow SiC(s) + 2CO_2(v)$$

$$(4.4)$$

On the other hand, low SiO₂ source mass of 15, 25 and 50 mg does not provide sufficient amount of SiO vapors (low diffusion of SiO and CO vapors) to form SiO_x layer or just thin SiO_x layer. The direct continuous diffusion of SiO vapors onto Si catalyst droplets hindered the growth of Si nanowires however contributed to the formation of Si nanorods. The accesses of SiO and CO vapors could lead to the formation of SiO₂ and SiC nanocrystals mainly at the base of the nanostructures (Dai et al., 2015; Meng et al., 2011). For the case of no SiO_x layer, the diffusion barrier was absence and the continuous diffusion of SiO and CO vapors lead to the formation of large crystalline grains without the 1D structure.



Figure 4.12: Oxide-assisted growth mechanism of the Si nanostructures grown via the CVD processes.

4.7 Photoelectrochemical behaviour of Si nanostructures

The photoelectrochemical (PEC) behaviours of Si nanorods and nanowires prepared by CVD technique are investigated. The measurements including the charge transfer resistance, capacitance-voltage and flat band potential are evaluated by the linear sweep voltammetry (LSV), chronoamperometry, EIS-Nyquist plot and Mott-Schottky.

The LSV was conducted to measure the PEC performance for both Si nanorods and nanowires prepared at SiO₂ source masses of 15 and 100 mg under dark and visible light conditions as shown in Figure 4.13. The current density curves against potential were scanned from -0.6 to 0.6 V. In the dark condition, Si nanostructures electrodes exhibited low current density of 0.15 mA at 1 $V_{Ag/AgCl}$. These non-zero dark current was observed due to the sweeping voltage to the negative direction (Wheeler et al., 2017). Meanwhile, the Si nanostructures electrodes showed notable enhancement in the photocurrent density values under visible light illumination. It is worth noted that the Si nanowires produced a photocurrent density of 0.7 mA, relatively higher than Si nanorods with a photocurrent density of 0.2 mA respectively at 0.6 V. The high photocurrent density of Si nanowires was also attributed to smaller crystallite size or smaller average diameter of the nanowires, leads to larger surface area which absorbed a large number of photons and resulted in more photoelectrons generated (Rashid et al., 2019).



Figure 4.13: Linear sweep voltammetry (LSV) curves of Si nanostructures electrodes prepared at SiO₂ source masses of 15 and 100 mg.

The durability of Si photoanode to light on/off cycling under stepped voltage was measured by current-time plot as shown in Figure 4.14. The chronoamperometry waveform at 0 V of the sample prepared at SiO₂ source mass of 100 mg presented higher current as compared to that 15 mg. Upon illumination, a rapid rise in the current density of the Si nanowires was detected, revealing fast photo response and good stability of photoanodes thus leading to rapid charge transportation and low electron/hole recombination (Rasouli et al., 2018). The saturation time of the current density is 0.5-1s which was likely attributed to slow diffusion of charge carriers in electrolyte near the nanostructure/electrolyte interface and/or related to surface changes as a result of oxidation and corrosion (Alizadeh et al., 2018; Alizadeh et al., 2020). The prepared photoanode possessed significant chemical stability as the height of the cycles is not considerably decreased at the end of the measurement. However, the chronoamperometry experiments were conducted in less than 60 min, further evaluations would be required to study the long-time stability.



Figure 4.14: Chronoamperometry plots of Si nanostructures electrodes prepared at different SiO₂ source masses of 15 and 100 mg.

The EIS-Nyquist plots of Si nanostructures electrodes prepared at 15 and 100 mg of SiO₂ source masses were shown in Figure 4.15. The plots displayed circular radii of different diameters. The EIS-Nyquist data were fitted to an equivalent circuit consists of electrolyte solution resistance, R_s and charge transfer resistance, R_{ct} . Obviously, the sample prepared at SiO₂ source mass of 100 mg exhibited a notable smaller arc diameter. The calculated arc diameter for SiO₂ source masses of 15 and 100 mg were 3.0 k Ω and 2.7 k Ω respectively. Smaller arc diameter indicates longer charge carrier lifetime, efficient charge separation and lower charge transfer resistance, R_{ct} (Dong et al., 2018; Jani et al., 2017; Zhang et al., 2015). From the corresponding EIS-Nyquist plot, it can be seen that the R_{ct} value is larger at low SiO₂ source mass. Larger R_{ct} indicated its poor conductivity for water splitting. Conversely, lower R_{ct} shown by Si nanowires signified less holes engaged in the water oxidation reaction. The lower density of holes is efficient for good electron recombination resulted in high separation efficiency across the interface between the photoanode and the electrolyte (Liu et al., 2015).



Figure 4.15: EIS-Nyquist plots of Si nanostructures electrodes prepared at SiO₂ source masses of 15 and 100 mg with its equivalent circuit, respectively.

The Mott-Schottky plots of Si nanostructures photoelectrodes are shown in Figures 4.16 (a & b). In general, Mott-Schottky plots were used to determine the doping type and the flat band potential of a material. Both Si nanorods and nanowires demonstrated a linear curves with positive slopes as observed in the figure which suggest the n-type semiconductor characteristics (Bera et al., 2017). The flat band potential, V_{fb} of the Si photoelectrodes was examined by extrapolating the voltage axis of Mott-Schottky plots, respectively. The flat band potential of Si nanowires was found to be -0.7 V vs Ag/AgCl, slightly lower than Si nanorods with V_{fb} of -0.6 V vs Ag/AgCl. The substantial change in the V_{fb} towards more negative value indicated that Si nanowires photoelectrodes have greater electron donor densities. It is worth noting that the semiconductor materials having a lower V_{fb} are superior in facilitating charge transfer in PEC mechanism (Yang et al., 2017). The calculated R_s , R_{ct} , diameter of semicircle and V_{fb} were tabulated in Table 4.3.



Figure 4.16: Mott-Schottky plots of (a) Si nanorods and (b) Si nanowires prepared at different SiO₂ source masses of 15 and 100 mg, respectively.

Table 4.3: The values of R_s , R_{ct} , Diameter of semicircle and V_{fb} of Si nanostructures prepared at different SiO₂ source masses of 15 and 100 mg.

Nanostructure	$R_s(k\Omega)$	R_{ct} (k Ω)	Diameter (kΩ)	$V_{fb}(V)$
Si nanowire	2.8	2.4	2.7	-0.7
Si nanorod	3.8	2.9	3.0	-0.6

Briefly, the PEC mechanism of Si nanostructures photoelectrodes prepared by different SiO₂ source masses has been explained. These as grown Si nanostructures acted as a visible light driven photocatalyst to generate hydrogen. Si nanowires prepared at SiO₂ source masses of 100 mg exhibited low charge transfer resistance, R_{ct} (2.4 k Ω) compared to Si nanorods in which contributes to rapid separation of photoexcited electrons and photogenerated holes thus slowing the recombination process. The photoelectrons transferred to counter electrode and reduced water, producing H₂. Meanwhile, the photogenerated holes transferred to semiconductor electrode and undergo oxidation process and release O₂. The excellent performance of Si nanowires photoelectrodes was attributed to the extremely large surface area and suitable E_g (1.9 eV) within the visible light region. In fact, the electrochemical contact areas between the electrodes and electrolytes were greatly enhanced due to the large surface area of the nanostructures.

4.8 Summary

In this chapter, the morphology, structure, chemical compositions and optical properties of Si nanostructures at different SiO_2 and C source masses have been extensively investigated and studied in detail. A growth model was proposed as in accordance with the formation of Si nanostructures and was reviewed in this chapter.

Si nanostructures were grown with two different kinds of structures, mainly nanorods and nanowires. Needle-like Si nanorods were observed at low SiO₂ source mass of 15 mg. Contributed by the sufficient amount of oxide presence at high SiO₂ source masses of 100, 125 and 150 mg, the samples demonstrated the growth of SiNWs facilitated by the high diffusion rate of SiO vapors during the deposition process. Small kinks were detected near to the root as observed in SiNWs prepared at SiO₂ source mass of 100 mg, which resulted from the change in growth direction as the effect of variation in temperature and pressure. A thin amorphous SiO_x layer was observed surrounding the nanowires which helped in the nucleation and growth of SiNWs.

The structural properties of Si nanostructures demonstrated by Raman spectra clearly indicates the highly crystalline Si peak suggested by the small estimated FWHM reported by all samples. On the other hand, the Si nanowires grown at 100-150 mg presents the appearance of SiC diffraction peak corresponds to 3C-SiC with small crystallites sizes. The morphology and structure properties of the Si nanostructures were highly influenced by the source masses. Additionally, the band gap energy of Si nanorods and Si nanowires have been successfully tailored. The band gap energy alteration within the UV and visible light range was relatively essential to represent the light absorption capability of the nanostructures. The electronic states failure or distortions might also affect in the band gap tuning of materials.

The oxide-assisted growth (OAG) mechanism of Si nanostructures based on the morphologies, structures and chemical compositions of the as-grown sample has been proposed and well discussed. Last but not least, the PEC properties of Si nanostructures as photoelectrodes are also presented in the last part of the chapter.

CHAPTER 5: CONCLUSION AND SUGGESTIONS FOR FUTURE WORKS

5.1 Conclusion

This last chapter highlights the significant results achieved from the works and the future works suggestions. Basically, this work was divided into two parts which includes the synthesis of Si nanostructures, namely Si nanowires and Si nanorods by CVD method. The as-grown samples were prepared from waste biomass using natural carbon from palm kernel shell as the source material. The influence of SiO₂ and C source masses during the nanostructures growth were investigated. The source masses were kept varied throughout the experiment following the SiO₂:C ratio of 4:3. The low source mass of SiO₂ produced octahedron Si micro-grains and Si nanorods. The morphology of the nanostructures transformed to Si nanowires as the source masses are increased. The nanowires grown at SiO₂ source mass of 100 mg exhibited superior alignment and highest nanowire density approximately 18.6 wires μm^{-2} , revealed the high growth rate of the nanowires. Furthermore, these nanowires demonstrated a remarkable small diameter around 30 nm respectively. It is also noted that the higher amount of oxide produced from high SiO₂ source masses could play a crucial role in facilitating the Si nanowires growth. High resolution transmission electron microscope (TEM) images revealed the kinking of Si nanowires. Small kinks formed near the root due to the change of growth directions which implied that the variation in temperature and pressure are contributed to the kinking. A thin amorphous SiO_x layer (approximately 1-2 nm) was also observed surrounding the Si core, indicated the oxidation effect of Si nanostructures. This SiO_x layer acted as a diffusion barrier in sustaining the self-catalyzed growth of nanostructures. On the other hand, the appearance of 3C-SiC layer was successfully detected by the Raman, XRD and XPS analysis. The SiC peak intensity increased for nanowires as the SiO₂ source masses are increased. The accesses of SiO and CO vapors at high temperature could lead to the formation of SiO₂ and SiC nanocrystals. From the morphology,

structural and chemical composition properties of the Si nanostructures, it can be deduced that the Si nanostructures were grown by the oxide-assisted growth (OAG) mechanism. Meanwhile, the optical energy gap of Si has successfully been tuned from 1.12 eV to a wide range of 1.8-1.9 eV mainly within the visible light region. Small crystallites sizes of Si nanowires reported resulted in the widening of the optical energy gap, E_g . The light absorption of a materials is also influenced by the Urbach energy, E_u which is referred to electronic states failure that were able to alter the band gap due to the defect in energy levels.

The second part of the work included the investigation of Si nanorods and nanowires performance in PEC water splitting devices. The improved PEC performance of the asprepared Si nanostructures was figured by LSV curves, which showed high photocurrent density of Si nanowires (~0.7 mA), indicating large number of photons absorbed by the sample. The Si nanowires photoanodes also possessed good chemical stability revealing fast photo response upon illumination during the light on/off cycles. Furthermore, Si nanowires exhibited R_{ct} value of 2.4 k Ω , comparably lower than Si nanorods (2.9 k Ω), revealing their superior conductivity for PEC water splitting. The significant properties of Si nanowires as a promising PEC device were contributed to its small crystallites size which provide optimal light absorption owing to the rapid diffusion of photo-excited electrons and photo-generated holes.

The important results obtained from this work validated the completion of the research objectives as proposed previously in the introduction part. The low-cost and environmentally friendly natural material using biomass as well as the simple CVD production method have made this present approach feasible towards the fabrication of Si-based photoelectrodes for hydrogen generation via solar driven water splitting process.

5.2 Suggestions for Future Works

The accomplishment of the self-catalytic growth of Si nanostructures from waste biomass has struck the interest in adapting a green synthesis of photoelectrodes for PEC device. As discussed in chapter 4, the band gap of Si nanowires has been effectively tuned within the UV and visible range by controlling the crystallites size grown at different source masses. However, the influence of deposition pressure in controlling the crystallite sizes of Si nanowires required further investigation. The controlled morphology of Si nanowires is highly desirable to benefit from optimal light trapping effects. Besides, the comprehensive studies on the quantum confinement model are recommended to obtain detail knowledge on the electronic configuration to the particle's physical dimensions. On the other hand, the integration of Si nanowires as core and SiC structure as shell is also proposed for future work to provide greater enhancement in PEC performance benefited from the advantages given by both Si and SiC. Finally, with regards to the PEC properties, further analysis on the volumetric measurement of H₂ gas generation and the hydrogen evolution profile can be carried out to fortify the overall water splitting process.

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