

**PHASE CHANGE ANALYSIS OF CRYSTALLINE SILICON THIN FILM
GROWN BY VERY HIGH FREQUENCY – PLASMA ENHANCED
CHEMICAL VAPOUR DEPOSITION AND RADIO FREQUENCY –
MAGNETRON SPUTTERING**

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UNIVERSITI TEKNOLOGI MALAYSIA

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requirements for the award of the degree of
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DEDICATION

IN THE NAME OF ALLAH, ALMIGHTY GOD

To my lovely father and mother, Kadir Rosman Bin Nordin and Suraya Binti Kamaruddin who always give me unconditional support, love, motivation and prayers for over the years. To my family and my dearest Khairunnisya, who gives me inspirations and relentlessly to remind me things are possible to complete and achievable. Thank you for all your love and support. This thesis is dedicated to all of you.

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ABSTRACT

In this study, silicon thin films had been successfully produced by using Very High Frequency-Plasma Enhanced Chemical Vapour Deposition (VHF-PECVD) technique. The phase transition from amorphous to crystalline silicon along with crystallite types remains unknown, especially at VHF region up to 200 MHz. In this work, very high frequencies ranging from 35 MHz until 200 MHz were investigated. The deposition time were fixed for 3 minutes and 15 minutes, while Radio Frequency (RF) power were fixed at 20 W and 30 W. For comparison purpose, RF-Magnetron Sputtering technique was used to deposit silicon thin films with the same RF power at 20 W and 30 W. Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy and Raman spectroscopy were used to determine the phase transition of film structure from amorphous to crystal, while X-Ray Diffraction (XRD) technique was used to determine the crystallites in the samples for both deposition techniques. Morphology study was carried out using Field Emission Scanning Electron Microscope (FESEM) and Atomic Force Microscope (AFM). The transition from hydrogenated amorphous silicon (a-Si:H) to hydrogenated crystalline silicon (c-Si:H) in the thin film samples was observed as deposition frequency increased from 35 MHz to 200 MHz. Typical Si (111) and Si (311) crystalline were formed in VHF-PECVD samples while only Si (311) was formed in RF-Magnetron Sputtering. VHF-PECVD produced 248 nm and 250 nm film thicknesses compared to RF-Magnetron Sputtering at only 34 nm. Rougher films were produced by VHF-PECVD with maximum average surface roughness of 3.64 nm compared to RF-Magnetron sputtering at 0.38 nm. Therefore, it can be concluded that the transition of silicon film from amorphous to crystal occurred at high deposition frequency using VHF-PECVD technique, but were hardly seen for RF-Magnetron Sputtering samples as the deposited thin films were too thin.

ABSTRAK

Dalam kajian ini, filem tipis silikon telah berjaya dihasilkan melalui teknik pemendapan wap kimia peneguhan plasma-berfrekuensi sangat tinggi (VHF-PECVD). Perubahan fasa daripada amorf ke hablur silikon dengan jenis kristalit terhasil masih tidak diketahui, terutamanya pada frekuensi sangat tinggi sehingga 200 MHz. Dalam kerja ini, frekuensi sangat tinggi dalam julat 35 MHz sehingga 200 MHz telah dikaji. Tempoh masa pemendapan ditetapkan pada 3 minit dan 15 minit, manakala kuasa frekuensi radio (RF) pula ditetapkan pada 20 W dan 30 W. Bagi tujuan perbandingan, teknik percikan magnetron berfrekuensi radio diguna pakai untuk memendap filem tipis silikon dengan menggunakan kuasa RF yang sama, iaitu pada 20 W dan 30 W. Spektroskopi pantulan keseluruhan dikesilkan – infra merah transformasi Fourier (ATR-FTIR) dan spektroskopi Raman telah digunakan untuk menentukan perubahan fasa struktur filem daripada amorf kepada hablur, manakala teknik pembelauan sinar-X (XRD) digunakan untuk menentukan kristalit dalam sampel-sampel untuk kedua-dua teknik pemendapan. Kajian morfologi pula telah dijalankan menggunakan mikroskop elektron pengimbasan pancaran medan (FESEM) dan mikroskop daya atom (AFM). Transisi daripada amorf silikon berhidrogen (a-Si:H) kepada hablur silikon berhidrogen (c-Si:H) dalam sampel filem tipis telah dicerap apabila frekuensi pemendapan meningkat dari 35 MHz ke 200 MHz. Kristalit lazim Si (111) dan Si (311) telah terbentuk dalam kesemua sampel VHF-PECVD, manakala hanya kristalit Si (311) yang terhasil pada filem melalui teknik percikan magnetron berfrekuensi radio. VHF-PECVD menghasilkan filem berketebalan 248 nm dan 250 nm berbanding dengan teknik percikan magnetron berfrekuensi radio hanya pada 34 nm. Filem yang lebih kasar dihasilkan oleh VHF-PECVD dengan purata maksimum kekasaran permukaan mencecah 3.64 nm, berbanding percikan magnetron pada 0.38 nm. Oleh itu, kajian ini telah menyimpulkan bahawa berlakunya transisi filem silikon daripada amorf kepada hablur pada frekuensi pemendapan yang tinggi menggunakan teknik VHF-PECVD, namun perkara ini tidak dapat dilihat dengan jelas pada filem yang dihasilkan melalui teknik percikan magnetron kerana filem tipis termendap adalah terlalu nipis.

TABLE OF CONTENTS

| | TITLE | PAGE |
|------------------|--|--------------|
| | DECLARATION | iii |
| | DEDICATION | iv |
| | ACKNOWLEDGEMENT | v |
| | ABSTRACT | vi |
| | ABSTRAK | vii |
| | TABLE OF CONTENTS | viii |
| | LIST OF TABLES | xi |
| | LIST OF FIGURES | xii |
| | LIST OF ABBREVIATIONS | xvi |
| | LIST OF SYMBOLS | xviii |
| | LIST OF APPENDICES | xxi |
| CHAPTER 1 | INTRODUCTION | 1 |
| | 1.1 Research Background | 1 |
| | 1.2 Problem Statement | 4 |
| | 1.3 Objectives | 6 |
| | 1.4 Scope of the Study | 6 |
| | 1.5 Significant of the Study | 7 |
| CHAPTER 2 | LITERATURE REVIEW | 9 |
| | 2.1 Introduction | 9 |
| | 2.2 Silicon | 9 |
| | 2.3 Silicon Thin Film Deposition | 11 |
| | 2.3.1 Models of Epitaxy Film Grown | 11 |
| | 2.3.2 Plasma Enhanced Chemical Vapour Deposition (PECVD) | 12 |
| | 2.3.3 Radio Frequency Magnetron Sputtering | 18 |
| | 2.4 Hydrogenated Silicon Thin Film in Plasma Enhanced Chemical Vapour Deposition | 21 |

| | | |
|------------------|---|-----------|
| 2.4.1 | Crystalline Hydrogenated Silicon Thin Film (c-Si:H) | 23 |
| 2.4.2 | Amorphous Hydrogenated Silicon Thin Film | 25 |
| 2.5 | Application of Microstructure and Morphology Study in Si Thin Film Technologies | 26 |
| 2.6 | Characterisation Method | 26 |
| 2.6.1 | Raman Scattering In Raman Spectroscopy | 27 |
| 2.6.2 | Role of X-Ray in X-Ray Diffractometer | 31 |
| 2.6.3 | X-Ray Reflectivity In X-Ray Diffractometer | 34 |
| 2.6.4 | Atomic Force Microscopy | 35 |
| 2.6.5 | Attenuated Transmission Reflectance in Fourier Transform Infra-Red Spectroscopy | 37 |
| 2.6.6 | Electron Imaging in Field Emission Scanning Electron Microscopy (FESEM) | 39 |
| CHAPTER 3 | METHODOLOGY | 43 |
| 3.1 | Introduction | 43 |
| 3.2 | Research Flowchart | 43 |
| 3.3 | Sample Preparation | 45 |
| 3.4 | Deposition of Silicon Thin Film | 45 |
| 3.4.1 | Procedure for Thin Film Deposition | 50 |
| 3.5 | Sample Characterisation | 54 |
| 3.5.1 | X-Ray Diffractometer (XRD) | 54 |
| 3.5.2 | Raman Spectrometer | 57 |
| 3.5.3 | Atomic Force Microscopy (AFM) | 57 |
| 3.5.4 | Attenuated Total Reflectance-Fourier Transform Infra-Red (ATR-FTIR) | 58 |
| 3.5.5 | Field Emission Scanning Electron Microscope (FESEM) | 59 |
| CHAPTER 4 | RESULTS AND DISCUSSIONS | 61 |
| 4.1 | Introduction | 61 |
| 4.2 | Raman Analysis | 61 |
| 4.3 | X-Ray Diffraction (XRD) Analysis | 66 |

| | | |
|------------------|---|------------|
| 4.4 | Attenuated Transmission Fourier Transform Infra-Red (ATR-FTIR) Spectroscopy Analysis and Discussion | 69 |
| 4.5 | Atomic Force Microscopy Results and Analysis | 72 |
| 4.6 | Field Emission Scanning Electron Microscopy (FESEM) Analysis | 76 |
| CHAPTER 5 | CONCLUSIONS | 81 |
| 5.1 | Introduction | 81 |
| 5.2 | Conclusion | 81 |
| 5.3 | Future Works | 83 |
| | REFERENCES | 85 |
| | LIST OF PUBLICATIONS | 121 |

LIST OF TABLES

| TABLE NO. | TITLE | PAGE |
|-----------|---|------|
| 2.1 | Possible reactions in chamber for VHF-PECVD. | 15 |
| 2.2 | Summary of findings for VHF-PECVD from previous researchers. | 17 |
| 2.3 | Summary of findings for RF-Magnetron Sputtering from previous researchers. | 20 |
| 3.1 | Subsystem and components in PECVD. | 47 |
| 3.2 | Parameters setting for all samples. | 52 |
| 4.1 | Presence of peak position (cm^{-1}) for VHF-PECVD samples. | 64 |
| 4.2 | Raman crystallinity ratio, X_c . | 65 |
| 4.3 | FWHM and grain size from XRD deconvolution data. | 69 |
| 4.4 | Hydrogen content, C_H with according to corresponding deposition frequency. | 71 |
| 4.5 | Average surface roughness and grain size for all samples. | 74 |

LIST OF FIGURES

| FIGURE NO. | TITLE | PAGE |
|------------|--|------|
| 2.1 | Si bonded with another Si with covalent bond. | 9 |
| 2.2 | Si crystal structure: a) the upper half; b) the bottom half, c) full Si crystal. | 10 |
| 2.3 | Models of Film Growth: a) Frank and van de Merwe; b) Volmer and Weber island growth; c) Stranski and Krastanov growth island on layer. | 12 |
| 2.4 | Silicon thin film deposition by using VHF-PECVD. | 13 |
| 2.5 | Silicon thin film deposition by RF-magnetron sputtering. | 18 |
| 2.6 | The possible reactions on substrate's surface. | 22 |
| 2.7 | Analogy formation of amorphous silicon thin film: a) SiH_3 land on bonded Si:H to form a bond with H; b) successfully bonded SiH_3 with H atom to form SiH_4 ; c) another SiH_3 land on dangling bond of Si; d) formation of Si- SiH_3 bond. | 25 |
| 2.8 | The virtual energy level: (a) Rayleigh scattering; (b) Stokes Raman Raman scattering; (c) Anti-Stokes Raman scattering. | 27 |
| 2.9 | Raman spectrometer schematic diagram experimental set-up. | 28 |
| 2.10 | Example of Si peaks of Raman spectroscopy with different value of R . | 29 |
| 2.11 | Different path between beam 1 and 2. | 31 |

| | | |
|------|--|----|
| 2.12 | Detector angle scanning the crystal plane: a) first crystal plane reflect the X-ray at lower angle, θ_i ; b) second crystal plane reflect the X-ray at higher angle, θ_{ii} . | 32 |
| 2.13 | Example of Si peaks in XRD result. | 32 |
| 2.14 | X-ray interaction with film and substrate: a) Incident angle less than critical angle; b) Incident angle equal to critical angle; c) Incident angle bigger than critical angle. | 34 |
| 2.15 | XRR dropping reflectivity as incident angle exceeding the critical angle. | 35 |
| 2.16 | AFM working principle with main parts connecting to signal processing unit. | 36 |
| 2.17 | FTIR working principle: a) Michelson interferometer; b) phase difference in relation with moving mirror. | 37 |
| 2.18 | The pathway IR beam from source to detector. | 38 |
| 2.19 | Example of Si FTIR results Si-H stretching band. | 39 |
| 2.20 | FESEM schematic diagram. | 40 |
| 2.21 | Type of electrons produced in FESEM. | 41 |
| 3.1 | Flowchart throughout the study. | 44 |
| 3.2 | Systems in PECVD. | 46 |
| 3.3 | PECVD machine components; a) VHF generator with pressure indicator panel; b) sample stage without chamber lid; c) fully closed chamber with impedance matching box in red; d) variable capacitor and inductor as tuner for impedance matching box; e) RF amplifier; f) chamber with glowing Ar plasma during deposition. | 48 |

| | | |
|------|--|----|
| 3.4 | RF-Magnetron Sputtering machine; a) full machine with components, b) glowing of Ar plasma in the chamber during deposition. | 49 |
| 3.5 | Vacuum system in RF-Magnetron Sputtering | 50 |
| 3.6 | Samples deposited by VHF-PECVD and RF-Magnetron Sputtering. | 54 |
| 3.7 | Minimum incident angle determination in XRR graph. | 55 |
| 3.8 | XRD spectrometer by Rigaku; a) XRD spectrometer from the outside; b) XRD spectrometer components during measurement; c) XRD with GI 2 θ mode measurement. | 56 |
| 3.9 | Raman spectrometer by Horiba Rigaku. | 57 |
| 3.10 | AFM model by SII environmental SPM SPA-300HV. | 58 |
| 3.11 | ATR-FTIR model by Perkin Elmer | 59 |
| 3.12 | (a) FESEM by Hitachi SU8020; (b) Ion cleaner JOEL EC-52000IC. | 60 |
| 4.1 | Raman spectroscopy results; a) VHF-PECVD; b) RF-Magnetron Sputtering | 62 |
| 4.2 | XRD results for; a) VHF-PECVD; b) RF-Magnetron Sputtering | 67 |
| 4.3 | FTIR Results for VHF-PECVD; a) sample 2 (100 MHz); b) sample 3 (160 MHz); c) sample 5 (200MHz). | 70 |
| 4.4 | AFM for all samples; a) sample 1 (35 MHz Preliminary); b) sample 4 (200 MHz Preliminary); c) sample 2 (100 MHz); d) sample 3 (160 MHz); e) sample 5 (200 MHz); f) sample 6 (20 W); | |

| | | |
|-----|--|----|
| | g) sample 7 (30 W); h) sample 8 (200 W); h) 200W (sample 8). | 75 |
| 4.5 | Comparison for AFM: a) VHF-PECVD sample 3 (160 MHz); b) RF-Magnetron Sputtering sample 8 (200 W). | 76 |
| 4.6 | FESEM cross-section; a) sample 3 (160MHz); b) sample 5 (200 MHz), c) sample 8 (200 W) with 500 nm and d) sample 8 (200 W) with 300 nm scale. | 78 |
| 4.7 | FESEM Morphology; a) sample 3 (160MHz); b) sample 5 (200 MHz); c) sample 8 (200 W); d) sample 8 (200 W) in scale 300 nm. | 79 |

LIST OF ABBREVIATIONS

| | | |
|--------|---|---|
| PECVD | - | Plasma Enhanced Chemical Vapour Deposition |
| PVD | - | Physical Vapour Deposition |
| VHF | - | Very High Frequency |
| RF | - | Radio Frequency |
| MEMS | - | Micro Electro Mechanical System |
| Si:H | - | Hydrogenated Silicon |
| c-Si:H | - | Crystalline Hydrogenated Silicon |
| a-Si:H | - | Amorphous Hydrogenated Silicon |
| Cz | - | Czochralski |
| VW | - | Volmer and Weber |
| SK | - | Stranski and Krastanov |
| FCC | - | Face Centered Cubic |
| TO | - | Transverse Optical |
| AFM | - | Atomic Force microscopy |
| FTIR | - | Fourier Transform Infrared |
| IR | - | Infra Red |
| ATR | - | Attenuated Total Reflectance |
| XRD | - | X-ray Diffraction |
| XRR | - | X-ray Reflectivity |
| FWHM | - | Full Width Half Maximum |
| FESEM | - | Field Emission Scanning Electron Microscope |
| SE | - | Secondary Electron |
| BSE | - | Back Scattered Electron |

RMS - Root Mean Square

LIST OF SYMBOLS

| | | |
|------------------|---|-------------------|
| Si | - | Silicon |
| SiO ₂ | - | Silicon Dioxide |
| P | - | Phosphorus |
| B | - | Boron |
| SiH ₄ | - | Silane |
| H | - | Hydrogen |
| Ar | - | Argon |
| O ₂ | - | Oxygen |
| N ₂ | - | Nitrogen |
| CH ₄ | - | Methane |
| HF | - | Hydrofluoric Acid |
| MHz | - | Megahertz |
| eV | - | Electronvolt |
| W | - | Watt |
| mW | - | Milliwatt |
| cm | - | Centimeter |
| μm | - | Micrometer |
| nm | - | Nanometer |
| Å | - | Angstrom |
| mTorr | - | Millitorr |
| Pa | - | Pascal |
| k | - | 1000 |
| °C | - | Degree Celcius |

| | | |
|--------------------|---|---|
| cm^3 | - | Centimeter Cubic |
| a | - | Amorphous |
| c | - | Crystal |
| X_c | - | Raman Crystallinity |
| C_H | - | Hydrogen Content |
| R | - | Hydrogen Dilution Ratio |
| δ | - | Skin Depth |
| ρ | - | Bulk Resistivity |
| μ_0 | - | Permeability of Vacuum |
| μ_r | - | Relative Permeability of Sample |
| f | - | Frequency |
| d | - | Spacing Between Atomic Planes |
| τ | - | Grain Size |
| D | - | FWHM XRD peak |
| λ | - | Wavelength |
| k | - | Constant for XRD measurement |
| θ | - | Angle |
| ω_0 | - | Free Resonance Frequency |
| k | - | Spring Constant |
| m | - | Mass of Cantilever |
| z | - | Distance Between Tip of Cantilever and Sample |
| F_{Total} | - | Total Force Between Tip and Sample |
| E_1 | - | Original IR Signal |
| E_2 | - | Shift of IR Signal |
| Z | - | Atomic Number |

R_a - Average Surface Roughness

LIST OF APPENDICES

| APPENDIX | TITLE | PAGE |
|----------|--|------|
| A | Raman Crystallinity, X_c Calculation | 95 |
| B | Raman Report from UIRL, UTM | 96 |
| C | XRR Intensity for XRD Analysis | 104 |
| D | XRD Grain Size, τ Calculation | 108 |
| E | XRD Fitting using OriginPro | 110 |
| F | Hydrogen Content, C_H Calculation | 116 |
| G | ATR - FTIR Fitting using OriginPro | 119 |

CHAPTER 1

INTRODUCTION

1.1 Research Background

Silicon (Si) thin film has been in the semiconductor and solar cell industries since decades. Silicon plays an important role in these industries as it has metalloid properties, which not all elements have. In addition, silicon really perform effectively in its optical properties and electrical properties, making it become one of the famous elements to be used in these industries (1–7).

Atomic arrangement of Si thin film has always been part of the main course of the research. This is due to the fact that difference in atomic arrangement may possess different characteristics and therefore can be used for different applications. For example, in heterojunction type solar cell, thin film of hydrogenated amorphous silicon (a-Si:H) has been used due to increase the efficiency of solar cell, while for Micro-Electro Mechanical System (MEMS), its best application is its crystalline structure (c-Si:H) as crystal can withstand more pressure and better strength distribution (3,8,9). In term of surface morphology study, rougher film is needed for solar cell fabrication, which will increase the efficiency as the capabilities of rougher film to trap the incident light (10). The morphology condition also has been developed and doped with other materials to improve the capabilities of light trapping mechanism in related with the morphology condition of the film (11).

There are many ways to deposit silicon thin film, such as by using Radio Frequency (RF) Magnetron Sputtering, Plasma Enhanced Chemical Vapour Deposition (PECVD), spin coating and others (12). All these techniques have their own advantages and drawbacks. Typically, in conventional PECVD, silane (SiH_4) and hydrogen (H_2) gases are used as precursor while argon gas (Ar) is used as plasma source. These gases will produce the deposition of hydrogenated silicon (Si:H) thin

film (13). In contrast, sputtering technique uses a solid target as main source of Si film since sputtering is a type of Physical Vapour Deposition (PVD), with only Ar is involved for plasma generation process.

The transition from a-Si:H to c-Si:H thin film depends on several PECVD parameters such as temperature, working pressure, power density and plasma excitation frequency. In 2004, C. Das et al. have shown in their studies that the transition from amorphous to crystal occurred along with the increment of crystal size as the temperature of substrate increased from 180°C to 370°C (1). For sputtering, usually post annealing is needed to provide the transition from amorphous to crystalline if the film deposited at low temperature with low RF power, otherwise, higher temperature is needed during deposition compare to PECVD (14–16). Apart of temperature, pressure also plays important role. Different working pressure can provide significant change to the sample. W. Li et al. (2009), found that the working pressure of PECVD above 300 Pa with hydrogen to silane flow rate ratio, or also known as hydrogen dilution ratio, R , ranging from 300 to 500 led to better crystallinity of the silicon thin film compared to below 300 Pa, with no trace of silicon crystal in the analysis (17). It has also been shown in a study by G. Lihui et al. (1998), at 13.56 MHz, deposition rate improved from 0 Torr until 4 Torr, then decreased when the pressure set increased to 8 Torr (18). Meanwhile, for Magnetron Sputtering, deposition pressure also affects the film deposition rate, as chamber pressure will affect the mean free path of adatoms. According to S. B. Hashim et al., (2012), Si film deposited by RF sputtering shown decrement of deposition rate as the deposition pressure increased from 5 mTorr to 8 mTorr (19).

In correlation of RF power and crystallinity of the sample, P. Pratim et al. (2002) have shown that the transition of hydrogenated Si (Si:H) thin film from a-Si:H to c-Si:H exists as RF power up to 285 mW/cm² in PECVD (20). Furthermore, S. Q. Xiao et al. (2010) also shown the same transition of Si by varying the power densities from 16.7 mW/cm² to 20.8 mW/cm² (21). This also provide similarities with the results from Magnetron Sputtering deposition technique. According to Y. Bouizem et al. (2013), the transition can be seen into crystalline silicon film when RF power increased from 180 W to 200 W (22).

On the other hand, excitation frequency for both PECVD and Magnetron Sputtering may affect the atomic structure Si thin film. H. Haijie et al. (2014) stated that the driving frequency may affect the state of Si film in Magnetron Sputtering. In their study, 2 MHz and 60 MHz excitation frequency set caused increased in crystal compared to conventional RF excitation frequency (23). Meanwhile in PECVD, according to M. Fukawa et al. (2001), frequency does affect the atomic structure of the thin film. The frequencies used were ranging from 13.56 MHz to 40 MHz. The results shown that the crystallinity increased as the excitation frequency increased to 40 MHz (24). In 2001, J. Takuya Matsui et al. did study the performance of solar cell in polycrystalline Si thin film, which grown by PECVD at 100 MHz. From the results, it clearly shown that polycrystal can be existing at that particular frequency (6). Correlation of the deposition of thin film using Very High Frequency (VHF) PECVD and crystallinity of the thin film can be shown in these previous studies (1,7,25–28). This strengthen the theory that higher frequency can affect the structure of the thin film. Typical Si crystallites grown at VHF frequencies are Si (111), Si (220) and Si (311) (1,26,28).

Conventionally, the RF excitation frequency in PECVD is around 13.56 MHz. Therefore, many studies had been carried out at this frequency. However, until now, there are still lacking in studies related with structural and morphology properties in frequency range until 200 MHz. Hence, phase change analysis from amorphous to crystalline in VHF deposition technique will be fundamental for this research with the effect of the phase change towards film structure and morphology. In this research, conventional RF-Magnetron Sputtering also will be included and discussed together with VHF-PECVD in Chapter 4.

1.2 Problem Statement

As mentioned earlier, there are many possible parameters that can be altered to obtain crystalline Si deposition. Even in conventional RF frequency, crystalline Si still can be produced at higher substrate temperature, which is higher than 100°C and above; high hydrogen dilution ratio, optimum deposition pressure and deposition power (2,29–31). However, the crystallinity remain unknown if the deposition frequency is increased up to 200 MHz. Perhaps, VHF can produce higher Si crystallinity, at much lower temperature. Meanwhile, RF-Magnetron Sputtering usually needs either higher than 200°C or post annealing process to produce crystalline Si with chamber pressure more than 4 Torr. Therefore, the deposition of Si film by RF-Magnetron Sputtering with similar temperature and deposition pressure as VHF-PECVD will provide information in term of film crystallinity along with phase change from amorphous to crystalline state (32)(33).

On the other hand, another significant consequence that can relate is hydrogen content, C_H . According to the previous studies, crystallinity of the Si film will affect the amount of C_H in the film (1,34,35). The reduction of C_H in the film may give high purity of Si film. Consequently, this study may give a knowledge regarding the effect of VHF toward C_H in the Si thin film.

Typical polycrystalline usually produced in Si film are Si (220), Si (111) and Si (311). Among of these three crystallites, the possibilities and transition from one crystallite to another still remain unclear. There were several studies shown that disappearing certain XRD peaks as the substrate temperature increased at VHF-PECVD deposition (1,29). Therefore, this study is an opportunity to investigate the effect of VHF plasma excitation towards the crystallite types in the Si film. For RF-Magnetron Sputtering, type of crystallite form at low temperature remained unknown, as majority of previous study need high temperature. This eventually can support information with related to crystallinity regarding types of crystallite which can be formed at low temperature.

The unknown film morphology condition and deposition rate at VHF plasma excitation ranging to 200 MHz may rise questions. These two things are significantly important especially in the solar cell performance (10,36,37). C. Das et al. stated that, the surface roughness is related with the crystallinity in the sample. Nevertheless, it will reduce as the deposition temperature increase (1). Regardless with the statement, it is an opportunity to determine the effect of VHF plasma excitation toward surface roughness. On the other hand, deposition rate and morphology condition for film grown by RF-Magnetron Sputtering without involvement of high temperature could be known.

1.3 Objectives

The objectives of the research are:

- (a) To determine the effect of VHF plasma excitation in PECVD to the transition of a-Si:H to c-Si:H, and the amount of hydrogen content in the Si film by using Raman spectroscopy and ATR.
- (b) To analyse the crystallite types of silicon thin film deposited using VHF-PECVD and RF-Magnetron Sputtering, using XRD.
- (c) To characterise the surface morphology of the Si thin film deposited using VHF-PECVD and Magnetron Sputtering by using AFM and FESEM.

1.4 Scope of the Study

In this study, only two types of film deposition techniques were used; VHF-PECVD and RF-Magnetron Sputtering. The deposition temperature was set to 180°C in order to have minimal defect densities at the samples (2,38). The frequencies were varied and increased gradually from 35 MHz to 200 MHz for VHF-PECVD, while for RF-Magnetron Sputtering, fixed at 13.56 MHz. All samples were deposited on Si (100) wafer, doped with boron. This is to provide a study that can be benefits to MEMS and solar cell application whereby film usually deposited on Si substrate or another Si film (16,39). For characterisation, XRD, Raman spectroscopy and FTIR were used to determine the transition of film structure from a-Si:H to c-Si:H along with the C_H for selected PECVD films. While for deposition rate and morphology study, FESEM and AFM analysis had been done. All data then were compared with RF-Magnetron Sputtering samples.

1.5 Significant of the Study

To date, there is still no study related with crystallite types and Raman crystallinity, X_c of VHF-PECVD deposition of silicon thin film carried out at higher frequency up to 200 MHz. As a consequence, the results can be used as reference for other researcher to grow specific crystal orientation. The amount of hydrogen content, C_H also significant in this study as researcher may keep updating on the way to produce high purity of Si thin film, with less amount of hydrogen bonded silicon. On the other hand, fixed at 180°C will give set of results with low defect density. Consequently this will be beneficial for those researchers who want to study the effect of high frequency deposition with low defect densities (38). All the data also will be discussed along with RF-Magnetron Sputtering. This definitely will give extra information regarding Si thin film fabrication by these two techniques, thus enlightens not only the academia, but also the semiconductor and solar cell industries.

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