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**STRUCTURAL PROPERTIES OF SI:H THIN FILM GROWN BY
VHF- PECVD**

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Abstract

Hydrogenated silicon (Si:H) thin film is one of the most promising technology that has been developed throughout the years. The film structure possess a variety of traits, especially in semiconductor and solar cell industry; depends on its molecule condition either in crystal or amorphous state. Plasma Enhanced Chemical Vapour Deposition (PECVD) technique is chosen in this work as it may give high quality of silicon thin film at lower temperature compared to conventional Chemical Vapour Deposition (CVD) technique. This work aims to study the transition of silicon thin film from amorphous to crystal as the effect of very high RF frequency (VHF) deposition. Three frequencies were used throughout the experiment; 100 MHz, 160MHz and 200 MHz. The films were deposited for 15 minutes on Boron doped Si (100) substrate while the temperature, power density and gaseous flowrate were kept constant. Raman spectroscopy, Fourier Transform Infrared (FTIR) and Atomic Force Microscopy (AFM) were used as characterization techniques. The results shown that significant dependence of Si:H film with VHF as the transition occurs from amorphous to crystalline along with rough surface as deposition frequency increases while from FTIR results, the amount of Si:H shown an increment with the increased in frequency.

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Keywords: VHF-PECVD, hydrogenated silicon thin film, Raman spectroscopy, FTIR.



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1. Introduction

Hydrogenated Silicon (Si:H) thin film is a well-known technology that has been developed throughout the years. High performance of Si:H has benefits many industries especially for solar cell industries, semiconductor industries and even for Micro-Electro Mechanical System (MEMS) (Martinu, Zabeida, & Klemberg-Sapieha, 2010; Iliescu et al., 2011; Kondo & Matsuda, 2001; Lien et al., 2010). The nano-structure and morphology study becoming the centre of attention in this study since these information may give better understanding in film fabrication and its affect from Very High Frequency (VHF) deposition.

Plasma Enhanced Chemical Vapour Deposition (PECVD) is chosen due to its capability to grow Si:H film at much lower temperature, compared to conventional CVD (Kondo & Matsuda, 2001). As plasma discharge from coupled capacitor in the chamber, the gas reactants will be dissociated and formed and undergo several chemical reactions before finally deposit onto the substrate. At higher RF frequency, the deposition rate is higher and better deposition could be achieved due to high amount of electron density compared to conventional plasma excitation frequency, 13.56 MHz (Matsuda, 2004; Heintze, Zedlitz, & Bauer, 1993; Das, Jana, & Ray, 2004). As a result, by varying the excitation frequency, different type of Si:H will be deposited. According to Fukawa, Suzuki, Guo, and Kondo, the transition from amorphous hydrogenated silicon (a-Si:H) to crystalline hydrogenated silicon (c-Si:H) will occur as the deposition frequency increased (2001). As time pass by, the continuation of much higher frequency is needed in order to give better information in term of crystallinity, chemical bonding of Si:H and its morphology for further references.

2. Problem Statement

Si thin film can be existing in both crystalline and amorphous state, depending on the parameters set for the deposition. There are many possible parameters that can be altered to obtain Si crystal deposition. Even in low deposition frequency, crystalline Si still can be produced by having higher substrate temperature, which is around 200 °C and above; high hydrogen dilution ratio and high deposition pressure (Kondo & Matsuda, 2001; Guo, Ding, Yang, Ling, & Cheng, 2011 ; Johnson, Kroely, & Roca I Cabarrocas, 2009; Kondo et al., 2000). However, the crystallinity still become unknown if the deposition frequency that will be used is around 200 MHz. The surface roughness also can be related with the crystallinity of the sample, as it can affect the solar cell performance (Brinza, Rath, & Schropp, 2009; Isabella, Krč, & Zeman, 2010; Scholtz, Ladanyi, & Mullerova, 2014). The amount of Hydrogen content in Si:H also remain unclear in the VHF deposition..

3. Research Questions

The PECVD deposition technique is a well-known technique to grow a thin film, especially at conventional frequency (13.56 MHz). However, at the range of VHF, there are still little studies that have been done especially at 200 MHz. Therefore, this experiment is done based on the main question regarding on what type of Si:H film will be grown at this particular frequency. This included the morphology study, the amount of hydrogen in the film and the crystallinity of the film.

4. Purpose of the Study

The main objective for this study is to relate the VHF-PECVD deposition of silicon thin film and the crystallinity of the Si:H film. The next objective is to find the surface roughness for each film by having morphology study and the last objective is to have the amount of hydrogen in the Si:H film for each deposition frequency.

5. Research Methods

Boron doped silicon substrate with (100) orientation was used as substrate, with 1 cm x 1 cm dimension. First, the substrates were cleaned with standard cleaning process. Three deposition frequencies were chosen which were 100 MHz, 160 MHz and 200 MHz with Argon (Ar) as source of plasma. The silicon film then was deposited for 15 minutes, with constant stage temperature, 180 °C. Hydrogen dilution ratio (H₂/SiH₄) was maintained with 10 throughout the experiment for sample 160 MHz and 200 MHz, with 100 sscm and 10 sscm; while for 100 MHz sample, 80 sscm and 8 sscm was chosen. The deposition pressure ranged between 2×10^{-2} torr to $6 \cdot 10^{-1}$ torr.

Characterizations and analysis were performed to give better understanding on the effect of frequencies to Si:H film. First, Raman spectroscopy analysis was carried out to represent the transition of Si:H film from a-Si:H to c-Si:H. The sample was excited by using 532 nm laser in order to get Raman spectra shift. The morphology study was performed by Atomic Force Microscopy (AFM) with 1 μm resolution. This analysis provides data regarding surface roughness alongside with the grain size for each sample. Finally, the chemical bonding analysis was carried out using Attenuated Total Reflectance Fourier-Transform Infrared spectroscopy (ATR-FTIR) which focus only for Si:H bond

6. Findings

In this section, all data will be discussed and reviewed to match the objectives of this experiment.

6.1. Raman Spectra Analysis

In Raman spectra analysis, the significant peaks for Si:H film are located around 480 cm⁻¹, 500 cm⁻¹ and 520 cm⁻¹. Generally, broad Gaussian peak at 480 cm⁻¹ represents to a-Si:H, while 500 cm⁻¹ refers to the combination of a-Si:H and c-Si:H and the sharp peak at 520 cm⁻¹ as c-Si:H (Mukhopadhyay, Das, & Ray, 2004; Lyon & Nemanich, 1983). Figure 1 shows the Raman shift for all samples and with its comparison.

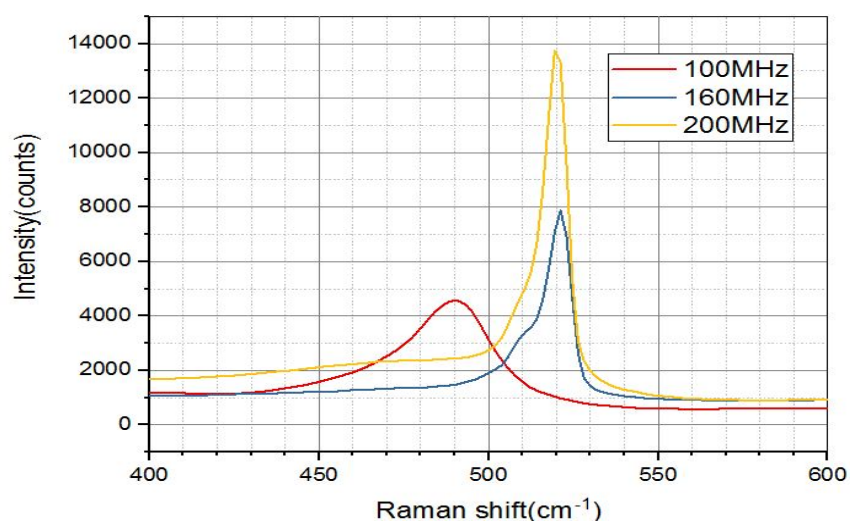


Figure 01. Raman Spectra for different RF frequencies; 100 MHz, 160 MHz and 200 MHz.

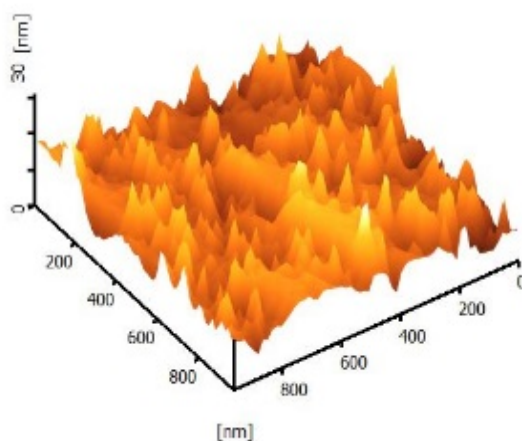
For Si:H film grown by 100 MHz, the results clearly shown that only a-Si:H existed on the substrate. As the deposition frequency increased to 160 MHz and 200 MHz, the 480 cm^{-1} peak disappeared and significant peaks were found at 500 cm^{-1} and 520 cm^{-1} . This clearly states that film grown at 160 MHz and 200 MHz are in crystal state compared to 480 cm^{-1} . Raman crystallinity, X_c have been calculated for both 160 MHz and 200 MHz samples by using Eq. (1):

$$X_c = (I_{520}) / (I_{520} + I_{500} + I_{480}) \quad (1)$$

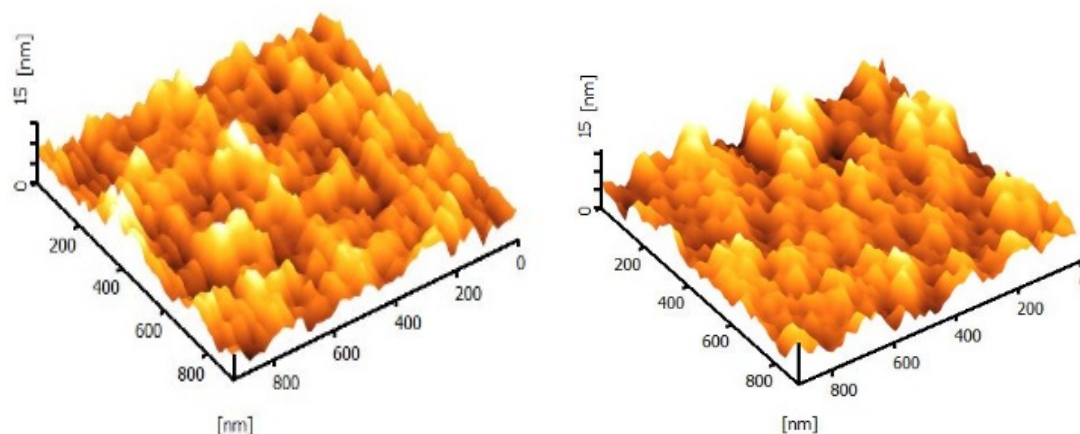
whereby, I represents as intensity for corresponding peak. From the calculation, the film with 200 MHz deposition frequency has higher ratio of crystal compared to 160 MHz, which $X_{c200} = 0.71$ while, $X_{c160} = 0.65$.

6.2. AFM Analysis

The morphology study has been carried out for all the samples in order to provide better information regarding surface roughness and grain size. Figure 2 shows images from AFM.



a) 100 MHz



b) 160 MHz

c) 200 MHz.

Figure 02. AFM Images a) 100 MHz; b) 160 MHz; c) 200 MHz.

Ideally, crystalline film has rougher surface compare to amorphous as the grain size increased. Therefore, the morphology study from Table 1 shown that 200 MHz has rougher surface and larger grain size compare to 160 MHz. This eventually in agreement with other studies related with crystallinity, surface roughness and the grain size (Altmannshofer et al., 2018; Mossad & Kobayashi, 2014). However, rougher surface for 100 MHz may due to its amorphous state. According to C. Das et al. (2004), as the crystallinity increased, the molecule becomes denser and packed to form smoother surface (Das et al., 2004). Table 1 shows the surface roughness and grain size for all samples.

Table 01. Surface Roughness and Grain Size.

	100 MHz	160 MHz	200 MHz
Root Mean Square Surface Roughness, R_{rms} (nm)	3.46	2.21	2.44
Average Surface Roughness A_v (nm)	2.67	1.76	1.96
Mean Grain Size (nm)	3.918×10^3	8.19×10^3	8.98×10^3
Mean Grain Diameter (nm)	7.063×10^1	1.02×10^2	1.069×10^2

6.3. ATR-FTIR Analysis

Deposition of Si:H on the substrate may varied from one to another sample. This is due to the dissociation of precursor gas SiH_4 and H_2 in the chamber at different frequency of plasma and different amount of hydrogen flowrate for 100 MHz sample, compared to 160 MHz and 200 MHz. Figure 3 shows the results for ATR-FTIR.

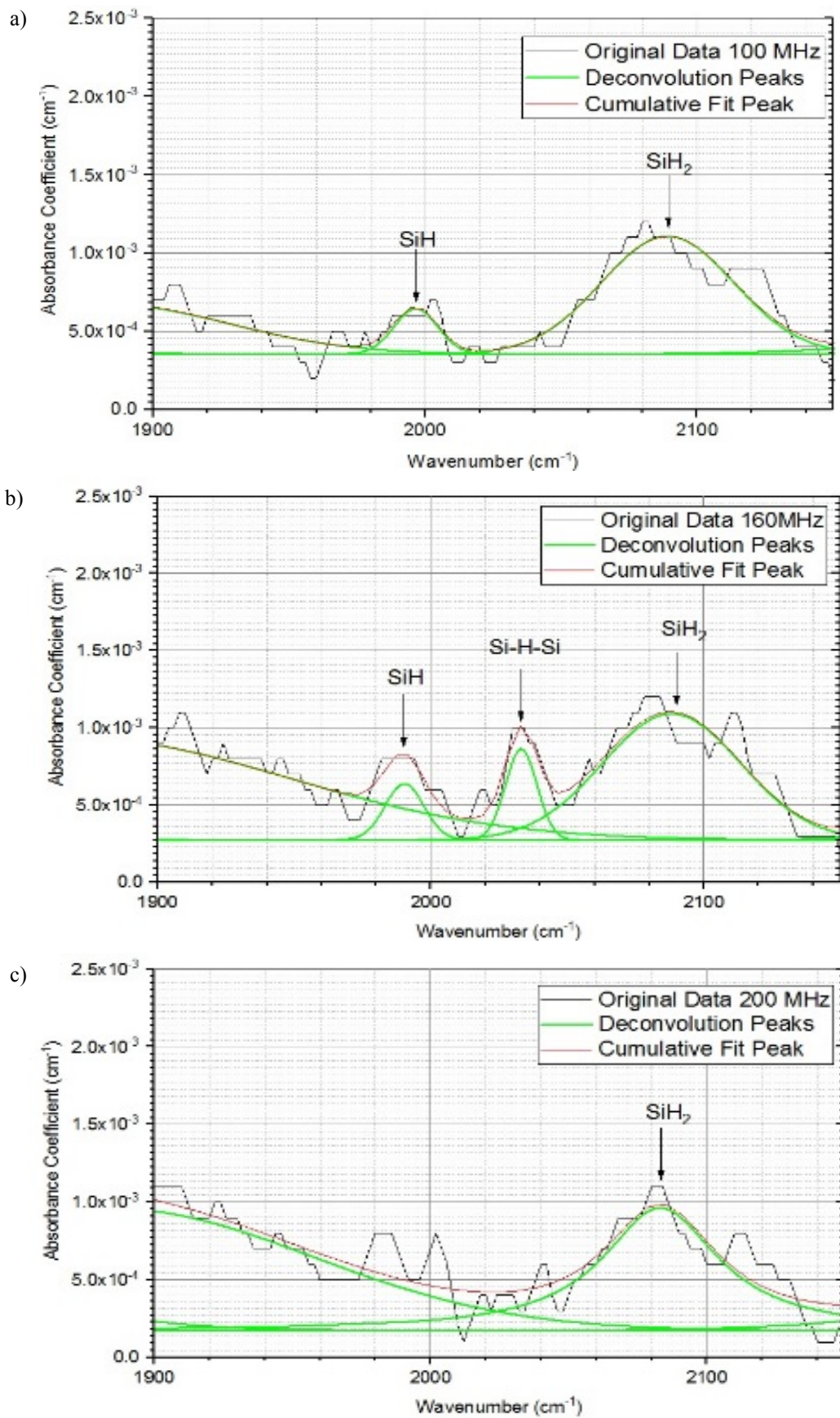


Figure 03. ATR-FTIR Analysis a) 100 MHz; b) 160 MHz; c) 200 MHz.

The Peaks ranging from 1950 cm⁻¹ to 2100 cm⁻¹ were analysed to study the bonding of Si:H. This range of frequency is chosen due to its capability to determine the amount of Hydrogen content (Langford, Fleet, Nelson, Lanford, & Maley, 1992). The results agreed with Raman results, as the crystallinity increased, the amount of monohydride Si:H decreased (Langford et al., 1992; Samanta & Das, 2017). By referring to Figure 3, there is a presence of peak 2000 cm⁻¹ for 100 MHz sample, but decreasing in 160 MHz, until it disappeared at 200 MHz. This may suggest possibilities of shifting from monohydride species to dihydride of SiH₂ and bond centred Hydrogen Si-H-Si (Jadhavar et al., 2017). In order to calculate the amount of Hydrogen for all samples, N_H, Eq. (2) is used:

$$N_H = A_{2100SiH}I_{2100SiH} + A_{2000}I_{2000} \quad (2)$$

whereby $A_{2000} = 9.0 \times 10^{19} \text{ cm}^{-2}$ and $A_{2100SiH} = 2.2 \times 10^{20} \text{ cm}^{-2}$; the proportional factor for IR stretching modes while I_{2000} and $I_{2100SiH}$ are the intensity at the respective spectra (Langford et al., 1992). Table 2 shows the results for Hydrogen content for all three samples.

Table 02. Hydrogen content

	100 MHz	160 MHz	200 MHz
Hydrogen Content, N _H (x10 ¹⁷ cm ⁻³)	3.014	3.196	2.121

As stated in Table 2, the amount of Hydrogen Content, N_H significantly shows declining as the deposition frequency increased from 160 MHz to 200 MHz. However, the superiority of N_H for 160 MHz over 100 MHz can be related with the amount of Hydrogen flowrate in 100 MHz lower compared to 160 MHz at the earlier experiment.

7. Conclusion

Three sets of samples consist of a-Si:H and c-Si:H have been successfully deposited using VHF-PECVD. The VHF plasma excitation frequency significantly affects the crystallinity of the Si:H film. As the frequency increases, tendency to form c-Si:H is much greater compared to a-Si:H. This has been proven by analysis in Raman spectroscopy by shifting peak from I_{480} towards I_{500} and I_{520} . On the other hand, surface study also gives the rougher surface for 200 MHz compared to 160 MHz. Nevertheless, 100 MHz has the rougher surface among all of them due to its amorphous state. In the ATR-FTIR analysis, the results shown that, the decreased in Si:H bonded at peak 2000 cm⁻¹ which can be verified as possible of shifted peaks from monohydride to dihydride and bond centred hydrogen. The hydrogen content also reduced as crystallinity increased

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