

## ***Chapter 5***

*Results, Analysis and Discussions  
(Part II):  
Silicon Carbide Thin Films from  
HW-PECVD Technique*

## **5.1 Introduction**

This chapter presents the results and analysis of the silicon carbide thin films prepared by combined HW-CVD and DC-PECVD techniques which are later referred to as HW-PECVD technique. Upon analysis and discussions in the previous chapter, it is decided that for this deposition technique, the highest methane to silane gas flow rate ratio ( $R=14$ ) be used as one of the deposition parameters. This is due to its promising results such as high incorporation of carbon and existence of crystalline structures. The role of hydrogen in producing high quality silicon carbide films such as that done by other researchers is taken into consideration in this study. Therefore, hydrogen is utilized to further investigate its effects on the production of silicon carbide thin films by HW-PECVD technique. However, since direct current is utilized in this hybrid deposition technique, the effects of applied DC voltage on the silicon carbide thin films prepared without hydrogen dilution is first discussed. Then the next part of this chapter discusses the results and analysis of the silicon carbide thin films prepared by HW-PECVD with hydrogen dilution. This is followed by discussions on the results and analysis of the silicon carbide thin films prepared by HW-PECVD with hydrogen being utilized as a surface treatment agent.

## **5.2 The Effects of Applied DC Voltage on the Silicon Carbide Thin Films Prepared by Hot-Wire Plasma Enhanced Chemical Vapour Deposition Technique without Hydrogen Dilution**

The effects of DC voltage have not been studied extensively by other research groups. However, one research group (Soum-Glaude *et al.*, 2005) have reported significant change in Si-C and Si-CH<sub>n</sub> absorptions in variation of DC bias in the deposition of hydrogenated silicon carbide (SiC:H) thin films. In this work, studies the on the effects of applied DC voltage on the film deposition of silicon carbide thin films

prepared by HW-PECVD technique is inevitable. For this purpose, the applied DC voltage is varied across the deposition chamber at 1000 V, 1300 V, 1400 V and 1800 V. These values were chosen starting from 1000 V based on the highest value of optical energy band gap produced at 1000 V from DC-PECVD deposition.

### 5.2.1 Deposition Rate and Optical Energy Gap

The optical transmission spectra for the silicon carbide thin films prepared by HW-PECVD technique at elevated applied DC voltages is presented in Figure 5.1. All the films show minimum number of interference fringes indicating that the films are relatively thin as compared to the silicon carbide films prepared by other techniques. However, all the films prepared in this work show high energy absorptions that occur in the wavelength range of 250 to 300 nm.

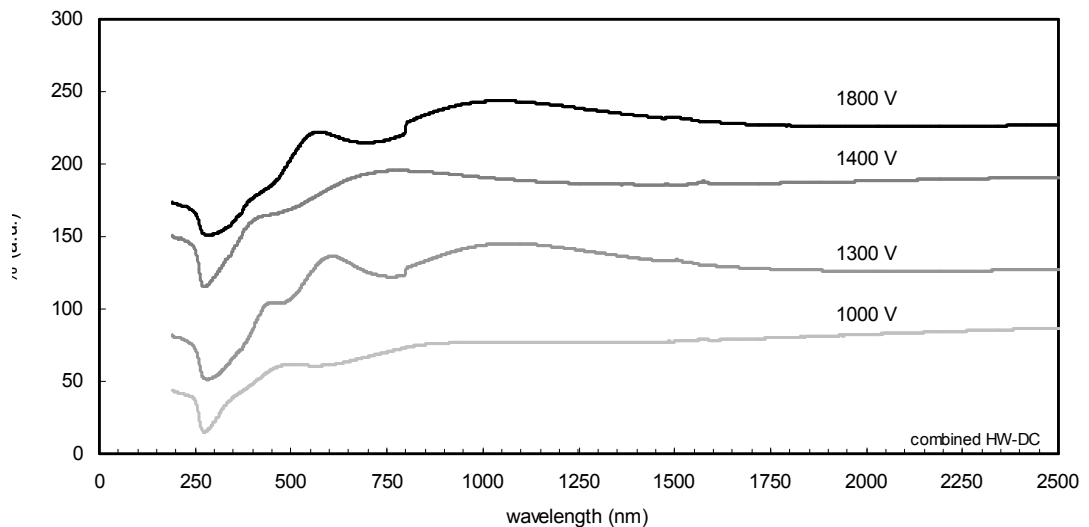


Figure 5.1: Optical transmission spectra of SiC thin films prepared by HW-PECVD technique.

The deposition rate of silicon carbide thin films is affected by voltage when prepared using HW-PECVD technique as shown in Figure 5.2. Silicon carbide thin films prepared at lower voltage (1000 V) have lower deposition rate as compared to the films prepared at higher voltages. Generally, an increased trend is observed with values

between 1.2 nm/s and 2.4 nm/s as the voltage is increased from 1000 V to 1800 V. This result shows that higher growth rate could be achieved by increasing the applied DC voltage in this preparation technique. It also indicates that high DC voltage has increased the dissociation rate of methane molecules in the plasma. At the same time, the presence of hot-wire has resulted in dissociation of silane molecules. Therefore the film growth is encouraged by the primary and secondary reactions that occur vigorously in the plasma. Increased number of interference fringes observed in Figure 5.1 as the applied DC voltage is increased could be explained by the increased thickness of the deposited film.

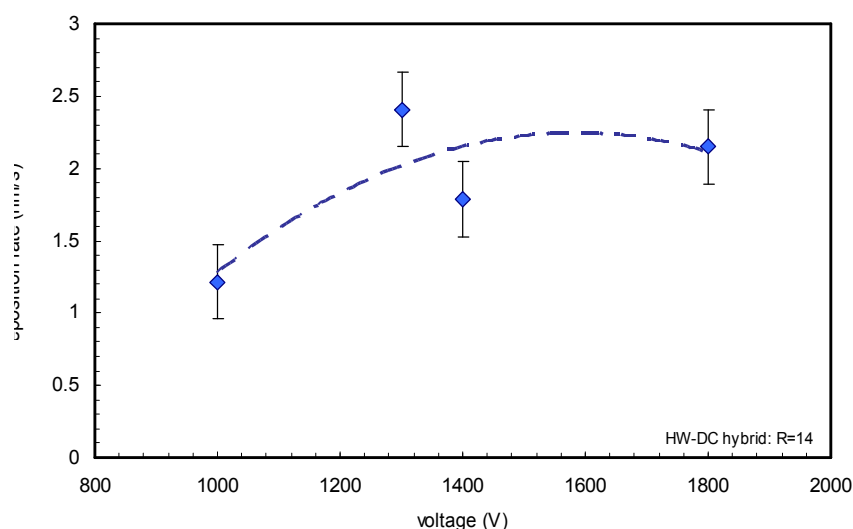


Figure 5.2: Deposition rate of SiC thin films prepared by HW-PECVD technique at various applied DC voltage.

The optical energy gap for the silicon carbide thin films prepared by HW-PECVD technique, without hydrogen dilution at various applied DC voltages is shown in Figure 5.3. The values of optical energy gap prepared by this technique are in the highest range as compared to other deposition techniques. Silicon carbide thin films deposited at the lowest voltage (1000 V) show the highest value of energy gap (3.26 eV). The value decreases as the voltage increase and a minimum of 2.48 eV is produced for the silicon carbide film deposited at 1800 V. Comparing Figure 5.2 to Figure 5.3, it

is concluded that silicon carbide thin films with high energy band gap could be produced by HW-PECVD technique with low applied DC voltages while the rate of film deposition is in the range of 1.0-2.0 nm/s.

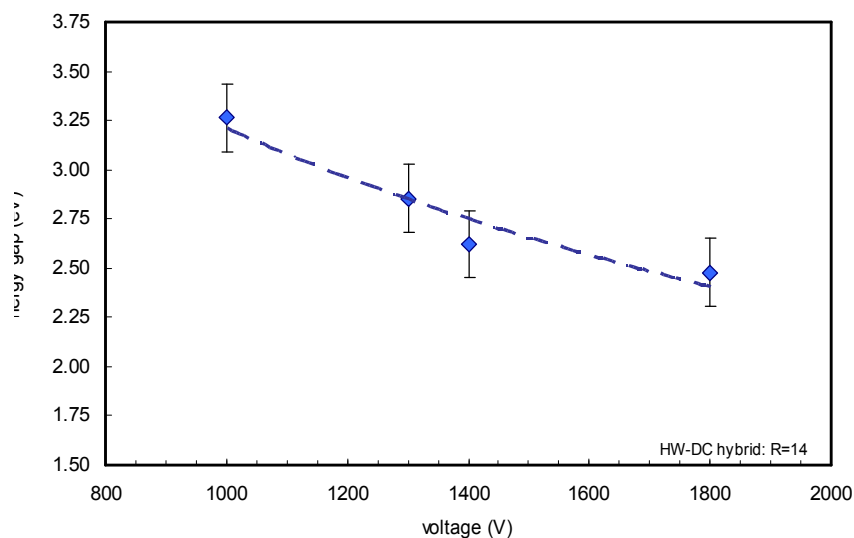


Figure 5.3: Optical energy gap of SiC thin films prepared by HW-PECVD technique at various applied DC voltage.

### 5.2.2 Si-C and Si-H Bonding Configuration

FTIR spectra for silicon carbide thin films prepared using HW-CVD technique at elevated applied DC voltages is shown in Figure 5.4. The films prepared by this deposition technique show absorption only in the wave number region where the vibration bands signify the existence of Si-H<sub>n</sub> wagging mode, a combination of the Si-C stretching mode and Si-(CH<sub>3</sub>)<sub>n</sub> wagging mode are concerned.

For the silicon carbide thin films prepared by this technique, the intensities of the vibration modes are generally low. The film composition does not differ much as the applied DC voltage is varied from 1000 V to 1800 V. The silicon carbide thin films prepared at low voltage (1000 V) show individual vibration bands in the wave number region between 400 cm<sup>-1</sup> and 1200 cm<sup>-1</sup>. For this film, a prominent vibration mode at 600 cm<sup>-1</sup> which outstand the vibration mode at 750 cm<sup>-1</sup> was found. The signatures of Si-H<sub>n</sub>

wagging mode at  $600\text{ cm}^{-1}$  is weak and  $\text{Si-H}_n$  stretching mode at  $2100\text{ cm}^{-1}$  did not appear in this spectrum.

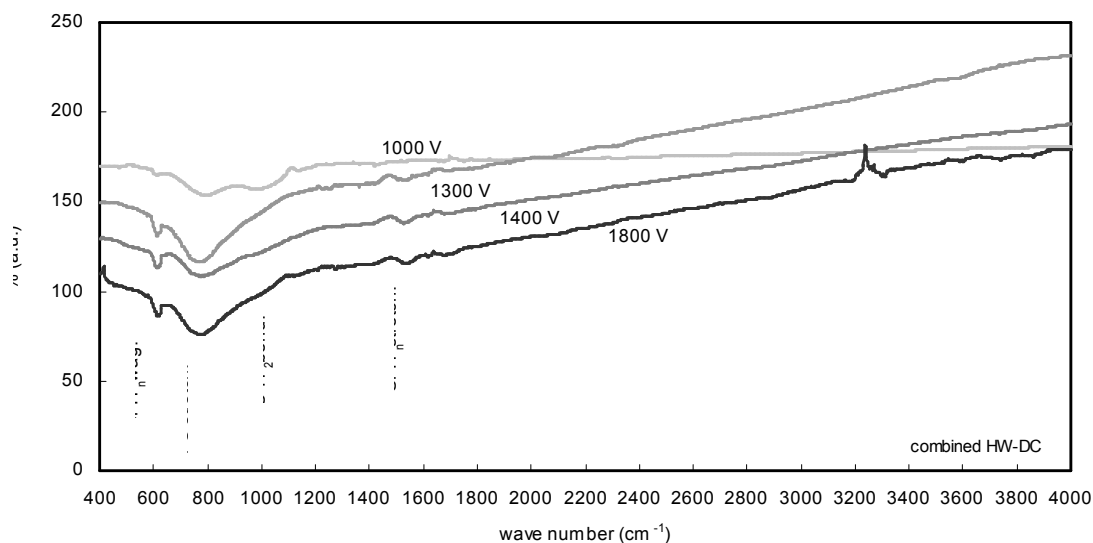


Figure 5.4: FTIR spectra for SiC thin films prepared using HW-CVD technique at elevated values of applied DC voltage.

On the other hand, the silicon carbide films prepared at higher applied DC voltages (1300 V, 1400 V and 1800 V) show broad vibration bands in the wave number region between  $400\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$ . These films show sharp vibration band at  $600\text{ cm}^{-1}$  to signify the existence of  $\text{Si-H}_n$  wagging mode (Wang, Yue and Liu, 2002), a broad vibration band centered at  $750\text{ cm}^{-1}$  which signifies a combination of the Si-C stretching mode (Wang, Yue and Liu, 2002) and  $\text{Si-(CH}_3)_n$  wagging mode (Tabata *et al.*, 2004), and a rather significant vibration peak at  $1500\text{ cm}^{-1}$  which signify the existence of  $\text{Si-CH}_3$  bending or asymmetric deformation (Das, Chattopadhyay and Barua, 1998). The vibration peak at  $2100\text{ cm}^{-1}$  also appears in the existence of  $\text{Si-H}_n$  stretching mode. For these films, the intensity of vibration mode at  $600\text{ cm}^{-1}$  is reduced and a better vibration mode at  $750\text{ cm}^{-1}$  is produced.

At low applied DC voltage (1000 V), dissociation of methane molecule is incomplete. Only hydrogen atom is dissociated from the  $\text{CH}_4$  molecule thus the plasma

is still rich of C-H<sub>2</sub> radicals. At this voltage, association of carbon to silicon based precursor is also very low although the silane molecules are already dissociated by the hot-wire filament. At higher applied DC voltages (1300 V, 1400 V and 1800 V), dissociation rate of methane molecules become more rapid and the formation of Si-C structure is encouraged as depicted from the FTIR spectra in Figure 5.4. Decreased intensity of the C-H<sub>2</sub> bending vibration is explained by the limited supply of C atoms from the fixed methane to silane gas flow rate ratio.

### **5.2.3 Film Structure**

The XRD spectra for silicon carbide thin films prepared by HW-PECVD technique at various voltages, without the presence of hydrogen dilution are shown in Figure 5.5. Diffraction peak at  $2\theta=35.6^\circ$  is attributed to (111) oriented crystallites of 3C-SiC (Tabata and Komura, 2007). Regardless of voltage, all the films prepared show a small diffraction peak at  $57^\circ$  that could be due the existence of face-centered cubic-Si crystals (Tabata and Komura, 2007). This result confirmed that the hybrid system comprising of DC-PECVD and HW-CVD techniques had successfully produced silicon carbide thin films with embedded Si-nanocrystallites as in the silicon carbide films prepared by DC-PECVD technique but with higher deposition rate which is in the range of the films prepared by HW-CVD technique.

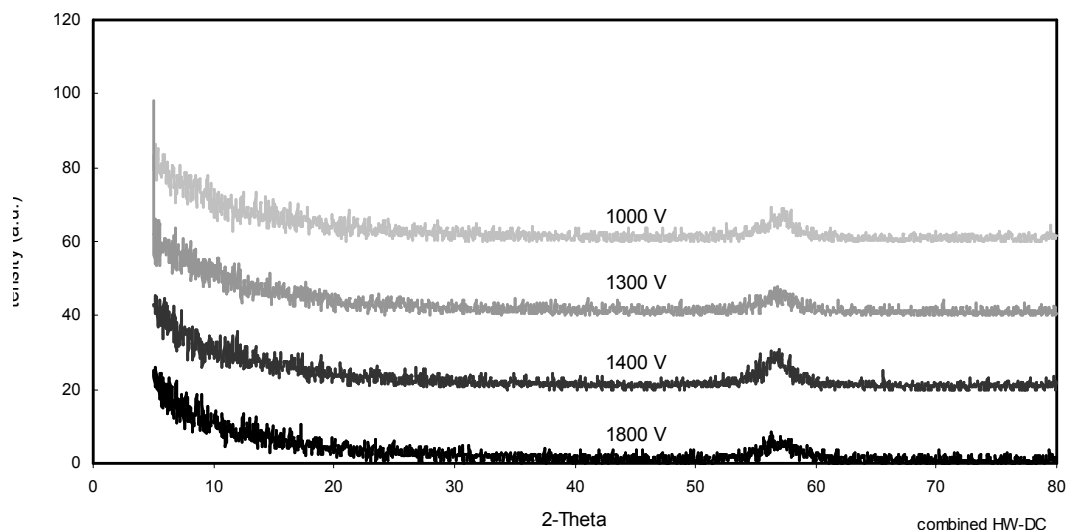


Figure 5.5: XRD spectra for SiC thin films prepared using HW-PECVD technique at various applied DC voltages.

### 5.3 The Effects of Hydrogen Dilution on the Silicon Carbide Thin Films Prepared by Hot-Wire Plasma Enhanced Chemical Vapour Deposition Technique

In this work, preparation of silicon carbide thin films by HW-CVD technique is first advanced by introduction of hydrogen dilution. In the purpose of this study, the methane to silane gas flow rate ratio is fixed at high ( $R=14$ ) and low ( $R=2$ ) while hydrogen gas is flown into the deposition chamber at 30 sccm. The applied DC voltage used in this work was 1000 V. Analysis in this section were carried out to investigate the effects of hydrogen dilution on the optical energy band gap, bonding configurations especially of Si-C and Si-H bonds and the crystal formation in the silicon carbide thin films.

#### 5.3.1 Deposition Rate and Optical Energy Gap

Figure 5.6 shows the optical transmission spectra for silicon carbide thin films prepared by HW-PECVD technique with high ( $R=14$ ) and low ( $R=2$ ) methane to silane gas flow rate ratios. There is an obvious difference in the absorption wavelength as the films were prepared at high and low methane to silane gas flow rate ratios. It indicates



that ultra violet light absorption for the silicon carbide film prepared at  $R=14$  occurs at higher energy as compared to the silicon carbide film prepared at  $R=2$ .

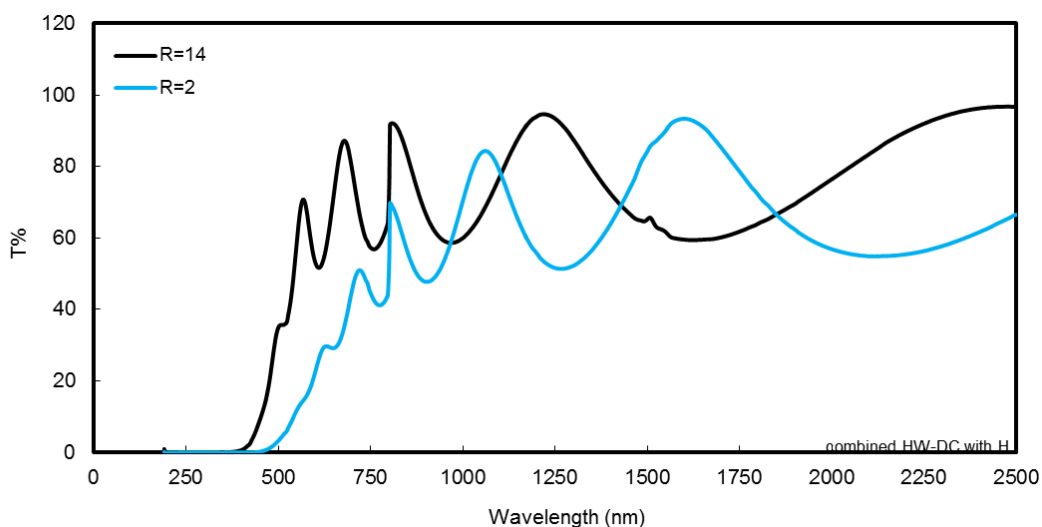


Figure 5.6: Optical transmission spectra for SiC thin films prepared using HW-PECVD technique with hydrogen dilution.

Table 5.1 shows the deposition rate and optical energy gap for the silicon carbide thin films prepared by HW-PECVD technique with hydrogen dilution. The deposition rate of the film is less than 1.0 nm/s and is reduced when prepared at high methane to silane gas flow rate ratio. On the other hand, the optical energy gap is larger for the silicon carbide film prepared at high methane to silane gas flow rate ratio. The optical energy gap for the silicon carbide thin films prepared by HW-PECVD technique with hydrogen dilution is 1.71 eV for the film prepared at  $R=2$  and 2.22 eV for the film prepared at  $R=14$ . Both values are intermediate between the values of optical energy gap gained for the silicon carbide thin film prepared by DC-PECVD and the silicon carbide thin film prepared by HW-CVD without hydrogen dilution. The results are consistent that the value of optical energy gap is increased by reduced rate of film deposition.

Table 5.1: Deposition rate and optical energy gap of SiC thin films prepared by HW-CVD technique with hydrogen dilution.

<b>Methane to Silane Gas Flow Rate Ratio (<i>R</i>)</b>	<b>Deposition Rate (nm/s) ± 0.10 nm/s</b>	<b>Optical Energy Gap (eV) ± 0.01 eV</b>	<b>Si-C/Si-H integrated Intensity ratio ± 0.01</b>
2	0.90	1.71	6.16
14	0.80	2.22	8.53

### **5.3.2 Si-C and Si-H Bonding Configurations**

The FTIR spectra for the silicon carbide thin films prepared at  $R=2$  and  $R=14$  using HW-PECVD technique with hydrogen dilution is shown in Figure 5.7. The silicon carbide thin film prepared at  $R=2$  shows three vibration bands in the wave number region between  $400\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$  where the Si-H<sub>n</sub>, Si-C and Si-CH<sub>n</sub> bonds are concerned. On the other hand, the silicon carbide thin film prepared at  $R=14$  shows only one broad peak consisting of these three vibration bands. It is noted that for both gas flow rate ratios, the  $600\text{ cm}^{-1}$  vibration peak which identify the Si-H<sub>n</sub> wagging mode is still significant in the spectra. However, the vibration peak for Si-H<sub>n</sub> stretching mode at  $2100\text{ cm}^{-1}$  is not present for the film prepared at  $R=2$  but can be seen rather clearly for the film prepared at  $R=14$ .

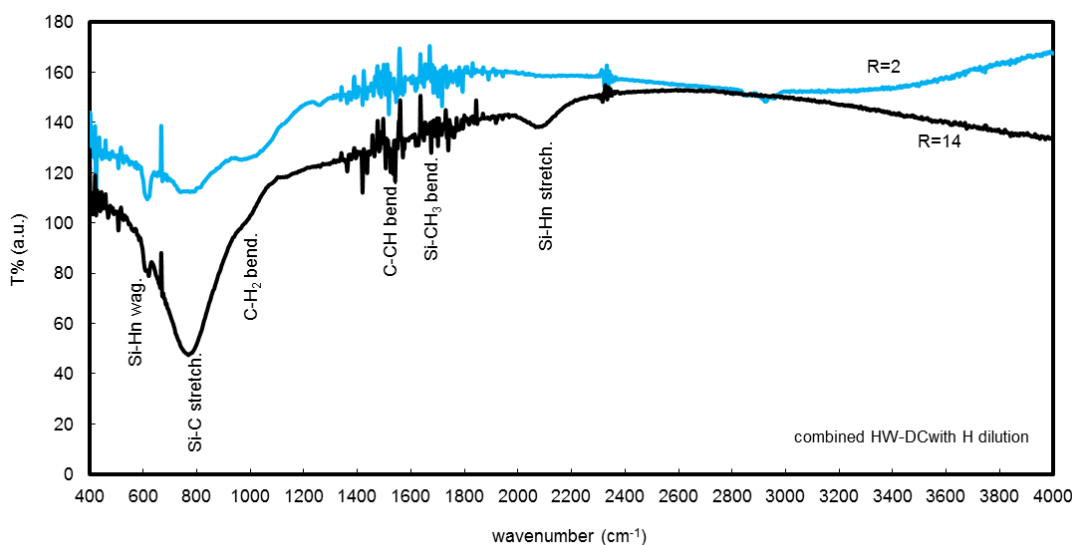


Figure 5.7: FTIR spectra for SiC thin films prepared using HW-PECVD technique with hydrogen dilution.

Figure 5.8(a) and Figure 5.8(b) are absorption coefficients in the wavenumber region  $450\text{--}1250\text{ cm}^{-1}$  and  $1990\text{--}2250\text{ cm}^{-1}$  respectively. Silicon carbide film prepared at  $R=14$  contains higher concentration of Si-H bonds as compared to Si-C bonds and the ratio of Si-C to Si-H integrated intensity is shown in Table 5.1.

At low methane to silane gas flow rate ratio ( $R=2$ ) where the ratio of  $\text{CH}_4:\text{SiH}_4:\text{H}_2$  is 2:1:6, the concentration of hydrogen molecule is high as compared to those of methane or silane. Therefore, the presence of hydrogen has encouraged the primary reaction between the molecules by providing extra pressure in the deposition chamber. Fair amount of Si- and C- precursors were produced and have attracted the H atoms to form a lot of Si- $\text{H}_n$  and C- $\text{H}_n$  bonds in the plasma. Secondary reaction is hindered due to shortage of Si- precursor which has mostly been consumed in the primary reaction. Thus, fairly equal absorptions in the wavenumber region  $450\text{--}1250\text{ cm}^{-1}$  is observed for these bonds, as could be seen in Figure 5.8(a) for  $R=2$ .

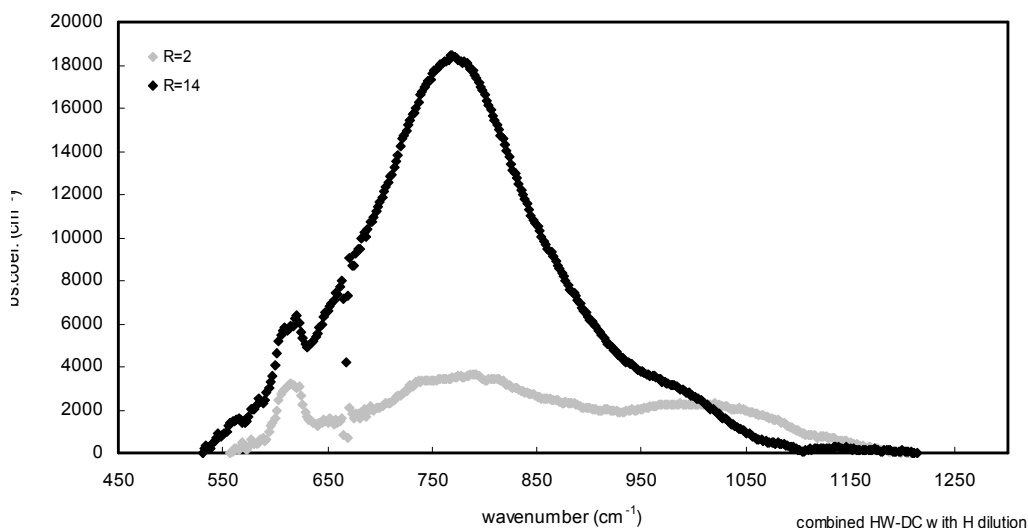


Figure 5.8(a): Absorption coefficient of vibration modes in the 450-1250  $\text{cm}^{-1}$  wavenumber region for SiC thin films prepared using HW-PECVD technique with hydrogen dilution.

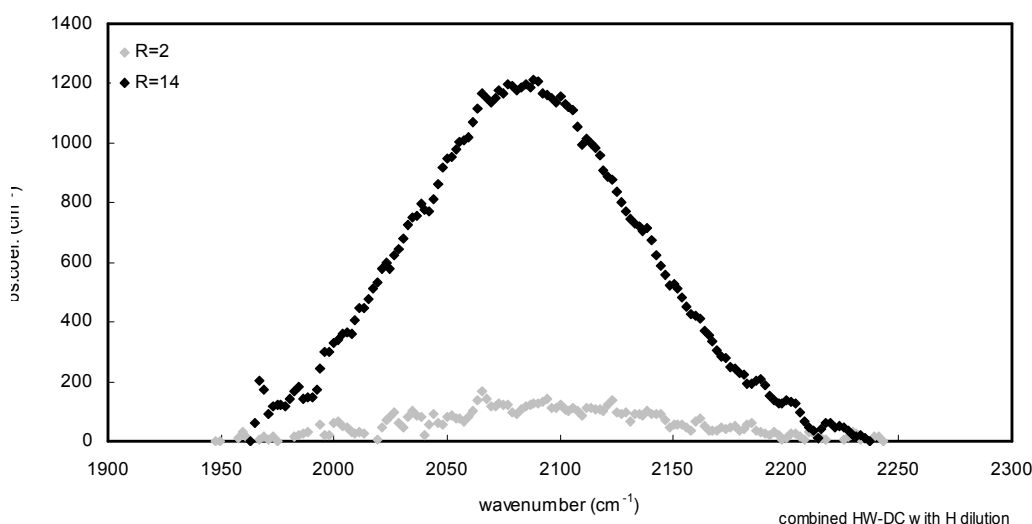


Figure 5.8(b): Absorption coefficient of Si-H<sub>n</sub> stretching mode for SiC thin films prepared using HW-PECVD technique with hydrogen dilution.

On the other hand, when silicon carbide thin film is prepared at high methane to silane gas flow rate ratio ( $R=14$ ), the ratio of  $\text{CH}_4:\text{SiH}_4:\text{H}_2$  becomes 14:1:6. For this preparation, methane gas is dominant and has the highest concentration in the plasma. Therefore, although the formation of Si-H<sub>n</sub> and C-H<sub>n</sub> bonds still occur almost as much as in the low ratio deposition, excess methane in the high ratio deposition has enabled the secondary reaction where Si-C bonds were formed. The presence of hydrogen atoms

and molecules has also encouraged the reaction by reducing the mean free path in the deposition chamber. As a result, high intensity Si-C absorption is detected as seen in Figure 5.8(a) for  $R=14$ .

The high absorption of the Si-H<sub>n</sub> stretching mode for the deposition at high methane to silane gas flow rate ratio ( $R=14$ ) as seen in Figure 5.8(b) is due to increased concentration of H atoms in the hydrogen diluted, methane rich plasma. However, data in Table 5.1 shows that in spite of the increased concentration of Si-H bonds, Si-C bonding configuration is still favourable in this high energy plasma. Therefore, for silicon carbide thin film prepared at  $R=14$  with H dilution by HW-PECVD technique, the high carbon incorporation had resulted in increased optical energy band gap for the film. Lower deposition rate too may have contributed to these results.

### **5.3.3 Film Structure**

The Micro-Raman spectra for silicon carbide thin films prepared at low  $R$  ( $R=2$ ) and high  $R$  ( $R=14$ ) by HW-PECVD technique with H dilution is compared in Figure 5.9. The films show sharp vibration peak at 517 cm<sup>-1</sup> which is attributed to TO mode of Si nanocrystals (Xu *et al.*, 2003). The SiC thin film prepared at  $R=14$  shows an obviously higher intensity for this peak indicating higher crystalline fraction as compared to the silicon carbide thin film prepared at  $R=2$ . A weak and broad band could also be observed at 900-1000 cm<sup>-1</sup> for the silicon carbide thin film prepared with  $R=14$  which is suspected to home the 960 cm<sup>-1</sup> second order TO mode of Si-Si vibration (Yu *et al.*, 2004) and the 986.4 cm<sup>-1</sup> band corresponding to TO mode of crystalline SiC (Yu *et al.*, 2000).

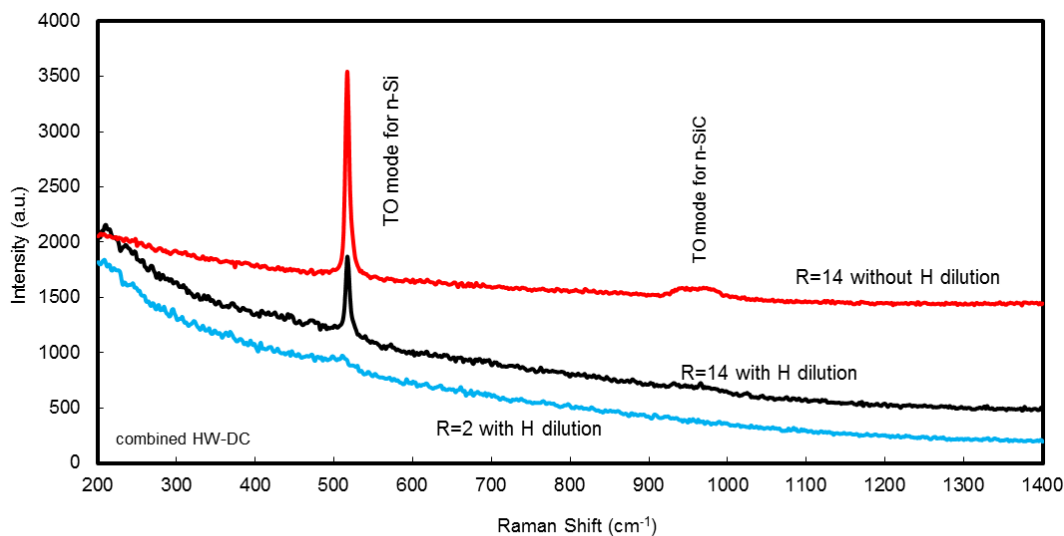


Figure 5.9: Micro-Raman spectra for SiC thin films prepared using HW-PECVD technique with H dilution and without H dilution.

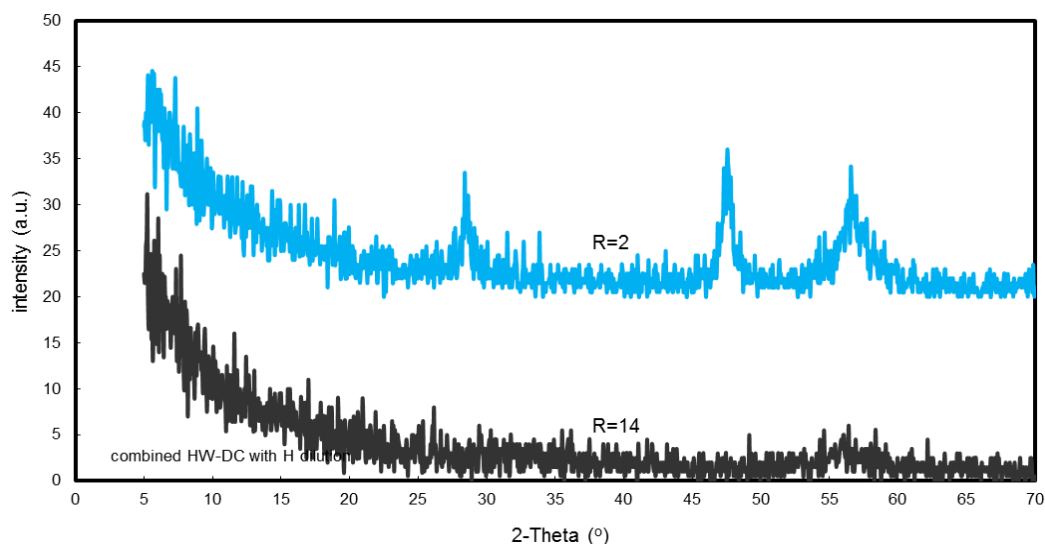


Figure 5.10: XRD spectra for SiC thin films prepared using HW-PECVD technique with H dilution.

Silicon carbide thin films prepared with hydrogen dilution were also investigated using the XRD spectra and shown in Figure 5.10. The film prepared at  $R=2$  shows three diffraction peaks at  $28.5^\circ$ ,  $47.5^\circ$  and  $56.0^\circ$  which is identified to be face-centered cubic Si-crystals. Similar pattern was observed in literature (Komura *et al.*, 2008) where the films were indicated to contain Si nanocrystals due to mean crystallite size between 18-26 nm. On the other hand, the film prepared at  $R=14$  shows no sign of

crystallization except for a weak diffraction centered at approximately  $57^\circ$  as could be seen in Figure 5.10 which is close to the orientations of Si(100) assigned diffraction peaks at  $2\theta=60.0^\circ$  and  $2\theta=71.7^\circ$  to (220) and (311) oriented crystallites of 3C-SiC respectively (Mandracci *et al.*, 2001, Tabata and Komura, 2007). For this film, the SiC crystallites are suggested to be embedded in the amorphous SiC film matrix.

#### **5.4 The Effects of Hydrogen Surface Treatment on the Silicon Carbide Thin Films Prepared by Hot-Wire Plasma Enhanced Chemical Vapour Deposition Technique**

Further investigations on the properties of the silicon carbide in this work were carried out by applying hydrogen surface treatment in the deposition of silicon carbide thin films prepared by HW-PECVD technique. In this work, the HW-PECVD deposition system was utilized in a way that hydrogen gas was exposed to the silicon carbide film for limited time intervals during the film deposition. The objective of this technique is to provide hydrogen surface treatment on the depositing silicon carbide thin film. At this point, the surface treatment time is brought in as the affecting parameter. The effects of direct current and hot-wire on the molecular reactions were also taken into consideration. The details of the experiment are explained in Chapter 3. This section discusses the results and analysis according to the effects of the various treatment times.

##### **5.4.1 Deposition Rate and Optical Energy Gap**

Figure 5.11 shows the optical transmission spectra for the silicon carbide thin films prepared by HW-PECVD technique with hydrogen surface treatment. It was observed that for the prepared silicon carbide thin films, absorption edges were observed at wavelengths in the range between 380 nm and 410 nm.

The deposition rate of the silicon carbide thin films prepared by this technique is not applicable due to the deposition technique itself where hydrogen treatment was applied at several stages during deposition. In this case, only the final thickness of each film is measured and displayed in Table 5.2. In spite of the increased hydrogen treatment time, it was found that thicker films were produced. The film thickness increased from 559 nm for the films prepared with 1 minute hydrogen treatment to 721 nm for the film prepared with 3 minutes hydrogen treatment.

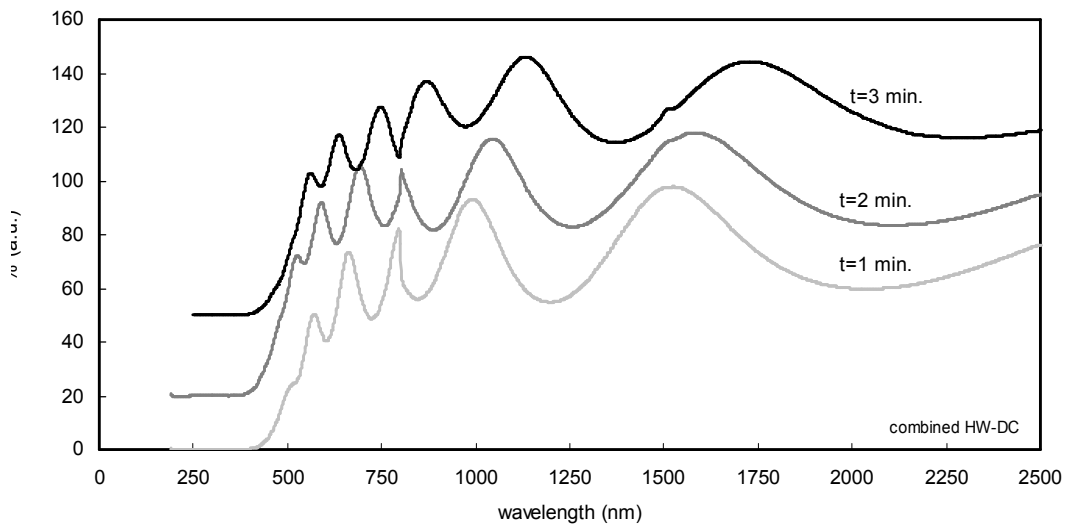


Figure 5.11: Optical transmission spectra of SiC thin films prepared using HW-PECVD technique with hydrogen surface treatment at various treatment times.

Deposition rate is considered constant throughout the whole deposition process and total deposition time is considered accountable for the final film thickness, then average deposition rate can be taken as the final thickness of the produced film divided by the total deposition time. The average deposition rate at several hydrogen surface treatment time is displayed in Table 5.2. Interestingly, it is found that although the longest surface treatment time (3 min.) has produced the thickest silicon carbide film, its average deposition rate is at the lowest. However, this contrasting manner is not surprising since the total deposition time for this silicon carbide film is far beyond the



other films. The low deposition rate for this film is explained by the bombardment effects caused by the hydrogen molecules that are believed to have retarded the growth process. The parameters for the silicon carbide thin films prepared by this technique are shown in Table 5.2.

Table 5.2: Parameters of SiC thin films prepared by HW-PECVD technique with hydrogen surface treatment.

<b>Hydrogen Surface Treatment Time</b>	<b>1.0 min.</b>	<b>2.0 min.</b>	<b>3.0 min.</b>
Final Film Thickness (nm) ± 10 nm	560	630	720
Total Deposition Time (min.) ± 1 min.	16.0	20.0	24.0
Average Deposition Rate (nm/s) ± 0.10 nm/s	0.60	0.50	0.50
Optical Energy Gap (eV) ± 0.01 eV	2.10	2.22	2.05
Si-C/Si-H integrated intensity ratio ± 0.01	4.56	2.83	2.12

As shown in Table 5.2, the optical energy gaps for the silicon carbide thin films prepared by HW-CVD technique with hydrogen surface treatment are 2.10 eV (1 min.), 2.22 eV (2 min.), and 2.05 eV (3 min.). Although the silicon carbide film prepared with 2 minutes hydrogen surface treatment shows the highest value of optical energy gap, relatively the optical energy gap values for other films are not much differed. This result shows that for this film deposition technique, the optical energy gap is not influenced by the growth rate of the film.

#### **5.4.2 Si-C and Si-H Bonding Configurations**

Study on the effects of hydrogen on the silicon carbide thin film is continued by allowing hydrogen atoms to act as surface treatment factor. Various surface treatment times has resulted in different bonding configurations in the film. It is shown in Figure 5.12 that longer treatment time produces higher intensity of the vibration band in the wave number region between 400  $\text{cm}^{-1}$  and 1200  $\text{cm}^{-1}$ . The signs of Si-H<sub>n</sub> wagging mode at 600  $\text{cm}^{-1}$  start to appear as the films were prepared with longer hydrogen surface treatment time. This effect can be seen in the absorption spectra as in Figure 5.13(a) and Figure 5.13(b).

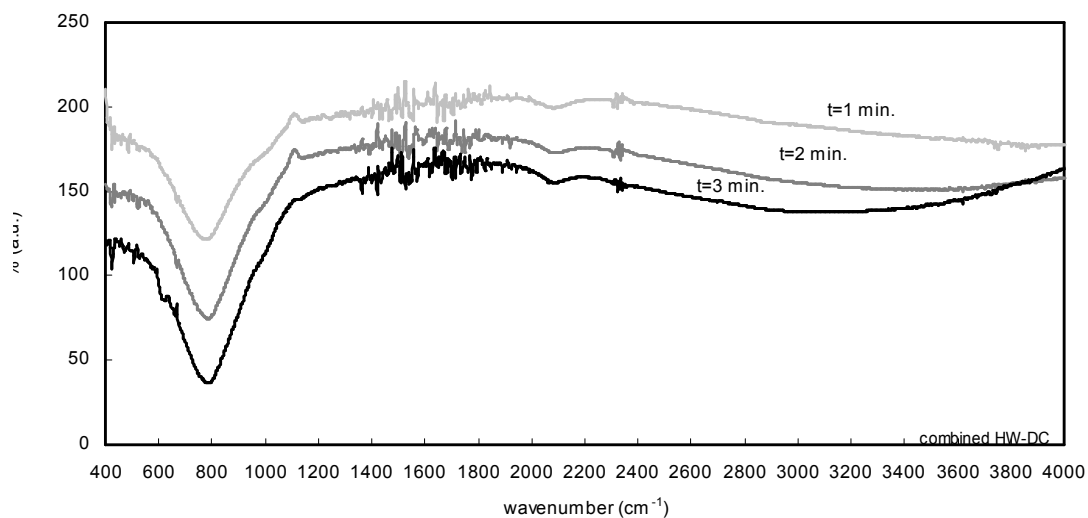
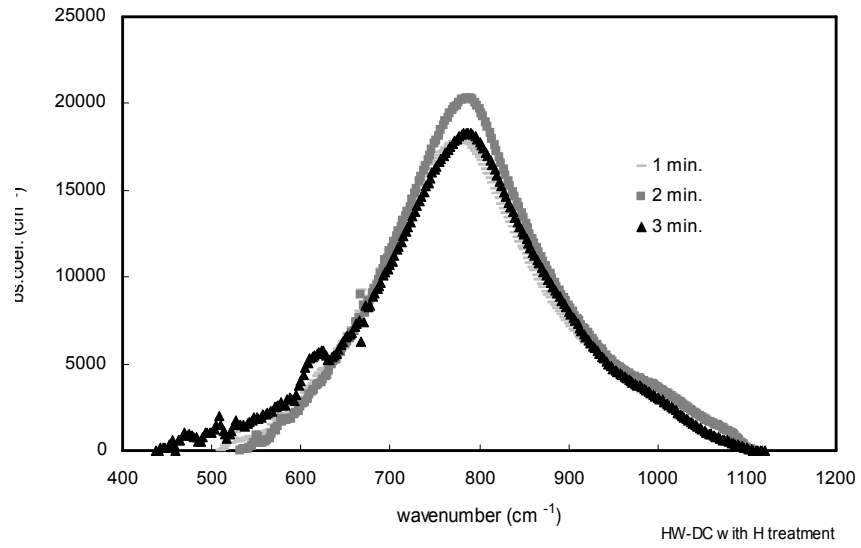
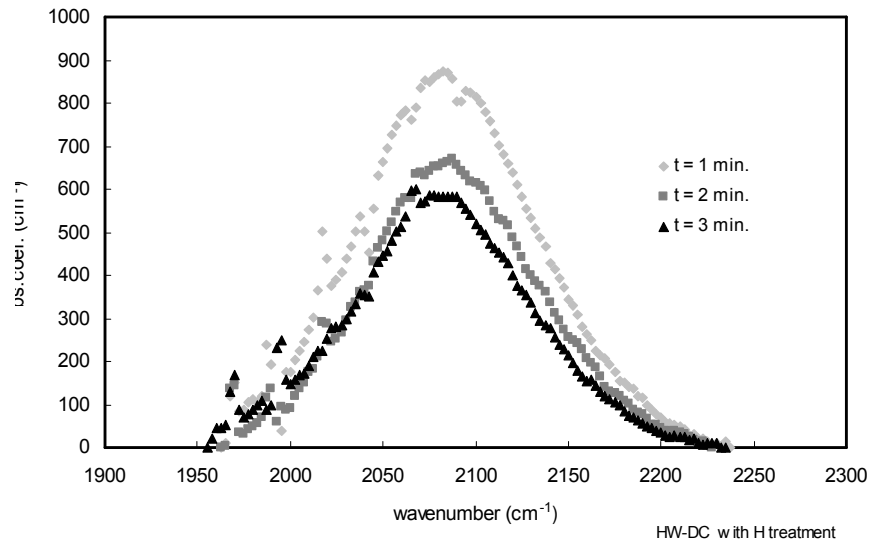


Figure 5.12: FTIR Spectra of the SiC thin films prepared using HW-PECVD technique with hydrogen surface treatment.



(a)

Figure 5.13(a): Effects of hydrogen treatment time on the absorption coefficient of vibration modes in 500-1500  $\text{cm}^{-1}$  region for SiC thin films prepared by HW-PECVD technique.



(b)

Figure 5.13(b): Effects of hydrogen treatment time on the absorption coefficient of  $\text{Si-H}_n$  stretching mode for SiC thin films prepared by HW-PECVD technique.

Table 5.2 also shows the effects of H surface treatment on integrated intensity of Si-C bands as compared to the Si-H<sub>n</sub> bands for the silicon carbide thin films prepared using HW-PECVD technique. This results show that the bonding reaction between silicon atoms and other radicals are affected by the time duration of the surface treatment. Longer exposure to hydrogen plasma has resulted in higher concentration of Si-H bond in the film although the film is dominated by Si-C bond.

In this experiment, before the hydrogen gas is introduced into the deposition chamber, the film is allowed to grow in the HW-PECVD environment for three (3) minutes. This provides enough time for primary chemical reaction to occur thus producing radicals and precursors such as Si-, Si-H<sub>2</sub>, Si-H<sub>3</sub>, Si<sub>2</sub>-H<sub>2</sub>, C-, C-H<sub>2</sub>, C-H<sub>3</sub>, Si-C and even H<sub>2</sub> molecules. Later, when hydrogen gas is allowed to flow into the deposition chamber, hydrogen molecules and atoms are easily attracted to the dangling bonds that are readily available. Longer time exposure results in higher concentration of Si-H<sub>n</sub> species which is identified in the increased absorption as seen in Figure 5.13(b). Due to the fixed ratio of methane to silane gas flow rate ( $R=14$ ), the concentration of Si-C bond is limited by the amount of methane molecules that existed in the plasma. Therefore, for longer duration of hydrogen surface treatment, a decrease in the Si-C to Si-H ratio is expected as could be seen in Table 5.2.

### **5.4.3 Film Structure**

The Micro-Raman spectra for silicon carbide thin films prepared at  $R=14$  using HW-PECVD technique with hydrogen surface treatment is shown in Figure 5.14. Generally, sharp peak at 520 cm<sup>-1</sup> indicates formation of microcrystalline film (Nakamura and Koshi, 2006). In this work, as seen in the figure (Figure 5.14), there are crystalline-Si peak at 517 cm<sup>-1</sup> for all samples regardless of treatment time which is

attributed to TO mode of Si nanocrystals. Any vibration band at  $500\text{ cm}^{-1}$  is attributed to the vibration mode related to the interfaces of Si nanocrystals with a-Si matrix (Xu *et al.*, 2003).

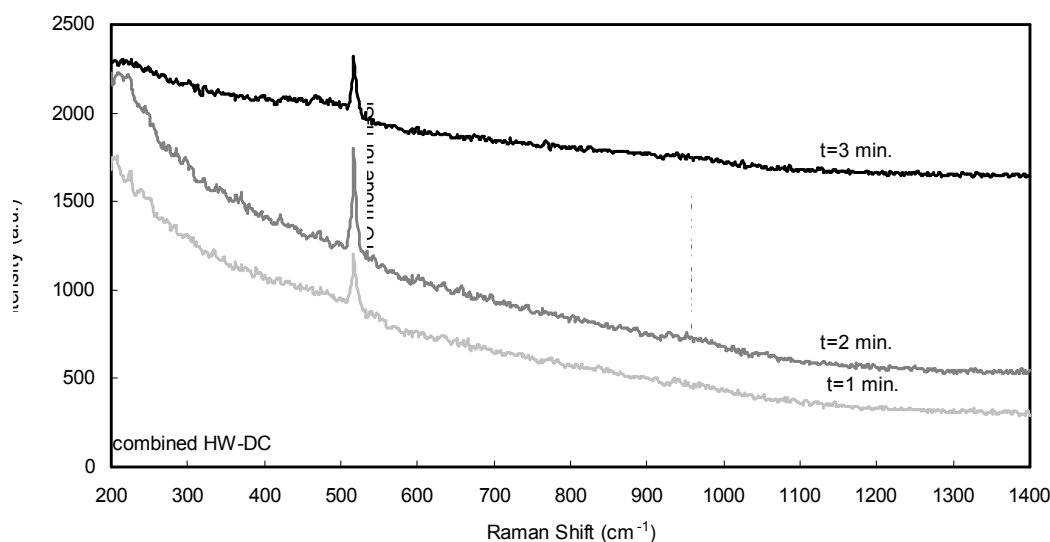


Figure 5.14: Micro-Raman spectra for SiC thin films prepared using HW-PECVD technique with hydrogen surface treatment.

The silicon carbide thin film prepared with the longest hydrogen surface treatment time ( $t=3\text{ min.}$ ) show a broad shoulder peak in the range of  $400\text{-}500\text{ cm}^{-1}$  which is contributed by the existence of  $480\text{ cm}^{-1}$  band and are due to either first-order scattering of Si-Si vibrations in the transverse optical (TO) mode (Yu *et al.*, 2004) or amorphous Si-Si mode at  $475\text{ cm}^{-1}$  and crystalline-Si vibration mode at  $521\text{ cm}^{-1}$  (Swain and Dusane, 2006). Also identified in these films is a weak vibration band in the  $900\text{-}1000\text{ cm}^{-1}$  region which signify traces of  $960\text{ cm}^{-1}$  second order TO mode of Si-Si vibration (Yu *et al.*, 2004), and the  $986.4\text{ cm}^{-1}$  vibration band which corresponds to TO mode of crystalline SiC (Yu *et al.*, 2000).

Silicon carbide thin films prepared using HW-PECVD technique with hydrogen surface treatment show similar XRD spectra as that observed for films prepared by

other techniques. The spectra for these film prepared by HW-PECVD technique is shown in Figure 5.15. The silicon carbide thin films prepared at extended treatment time ( $t=3$  min.) shows a shifted peak where the  $2\theta=57^\circ$  is slightly shifted to smaller angle  $56.1^\circ$ , along with a broad diffraction peak at  $2\theta=35^\circ$ . This is suspected to belong to SiC(101) as assigned by Cobalt (Cobalt *et al.*, 2006) whom assigned a peak at  $2\theta=33.6^\circ$  to SiC(101).

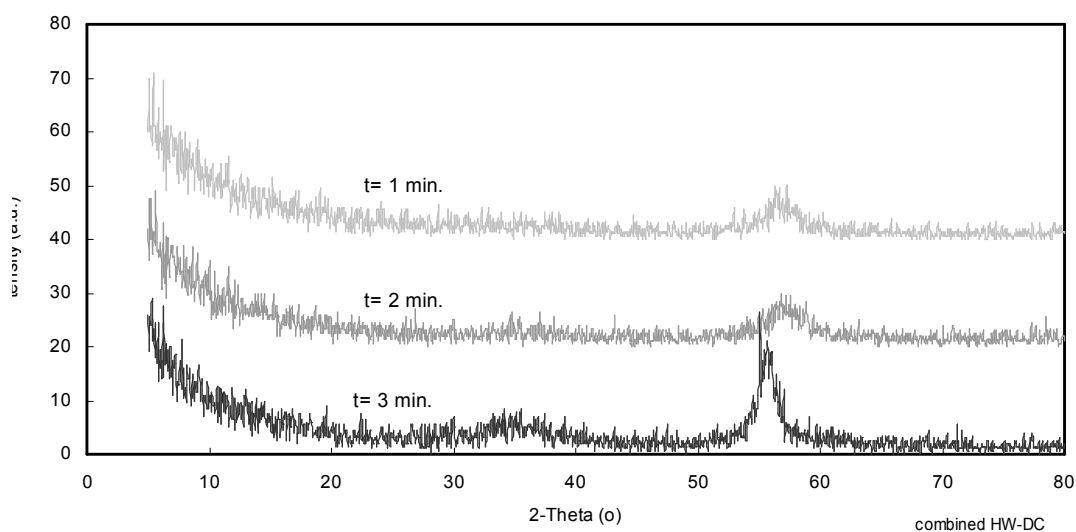


Figure 5.15: XRD spectra for SiC thin films prepared using HW-PECVD technique with hydrogen surface treatment.

Results in this work depicted existence of silicon nanocrystallites in all the silicon carbide thin films prepared by HW-PECVD technique with hydrogen surface treatment and is clearest for the film prepared with the longest treatment time of 3 minutes as supported by the appearance of crystalline-Si vibration mode at  $521\text{ cm}^{-1}$  in Figure 5.14. The XRD results for this film shown in Figure 5.15 shows that the film also consists of SiC crystallites. It concludes that when the hydrogen surface treatment time is extended to 3 minutes, the Si-C compound has transformed into SiC crystallites and is embedded in amorphous Si matrix.

## **5.5 Summary**

A hybrid deposition system comprising of HW-CVD technique and DC-PECVD technique have been developed in this work using exactly the same deposition system built and discussed in Chapter 4. The system had successfully produced silicon carbide thin films as depicted by its FTIR spectra. Beside methane to silane gas flow rate ratio, the applied DC voltage can also be manipulated to produce silicon carbide thin films with tuneable value of optical energy band gap. This technique has produced silicon carbide thin films with the highest optical energy band gap range as compared to other techniques in this work even without the advantage of hydrogen existence.

However, seeing the high potential of hydrogen as an important substance used in the production of nanocrystallites in thin films, the deposition system built in this work is extended to be flexible to hydrogen applications. This chapter has showed that hydrogen gas can be either diluted into the precursor gases or let to flow individually as surface treatment agent during the deposition process. By using the HW-PECVD system built in this work, both methods have proven to be successful in producing amorphous silicon carbide thin films with embedded nanocrystallites. The optical energy band gap of the produced films is also enhanced to higher range as compared to individual methods.