

Crystallinity And Morphology Of Silicon Carbide Thin Films Deposited Using Very High Frequency Plasma Enhanced Chemical Vapor Deposition

Muhamad Muizzudin Azali^{1, a}, Abd Khamim Ismail^{1, b}, Muhammad Firdaus Omar^{1, c}

¹Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.
(*mzzdn2193@gmail.com)

Physics Department, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.

*Corresponding author E-mail: ^bkhamim@utm.my, ^cfirdausomar@utm.my

Abstract

Conventional plasma enhanced chemical vapor deposition (PECVD) has been widely used since decades to deposit silicon carbide (SiC) thin film. However, lower RF frequency tends to produce hydrogenated amorphous silicon carbide (a-SiC:H) and polycrystalline (p-SiC) type of films. This work aims to investigate the crystallinity, morphology and deposition temperature of SiC thin films at higher RF frequency. SiC thin films have been prepared on silicon substrates by using very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD). The utilisation of plasma at higher frequency is predicted to give a great impact to allow the chemical reaction at lower temperature with better crystallinity and morphology compared to conventional PECVD method. In this work, the substrate temperature and deposition time were kept constant at 400°C and 15 minutes respectively, while the RF frequency was varied between 100 MHz to 200 MHz. The crystallinity of SiC thin film samples was observed using Raman Spectroscopy while the morphology was examined under the atomic force microscopy (AFM) and scanning electron microscopes (SEM). The results shown that the crystallinity and morphology of the samples were slightly improved as frequency increases. It was observed that the surface roughness of SiC thin films is improves from 5.43 nm at 100 MHz to 13.91 nm at 200 MHz.

Keywords: Silicon carbide; Plasma Enhanced Chemical Vapor Deposition; X-ray Diffraction; Raman Spectroscopy

1. Introduction

Silicon carbide (SiC) is one of a well-known semiconductor material which get high interest among the researcher due to its stand-out mechanical properties, great electrical properties with wide band gap, chemical inertness, thermal stability and high resistance to shock in harsh environment. Its outstanding properties are important for several applications in the optoelectronics devices such as light emitting diode (LED), nanoelectromechanical system (NEMS) sensors, macroelectromechanical system (MEMS) sensors and thermoelectric cooling (TEC) devices [1][2][3].

The nanostructure silicon carbide (ns-SiC) thin films can be grown by conventional plasma enhanced chemical vapor deposition PECVD technique at 13.56 MHz. In most cases, high temperature deposition is required in order to improve the thin films crystallinity. However, high deposition temperature could induce thermal stress in the deposited samples. Moreover, this conventional technique generally produces amorphous (a-SiC) and poly-crystalline (ps-SiC) type of films which are less competitive to a ns-SiC [3][4]. Thus, the very high frequency PECVD (VHF-PECVD) has been used and developed in this work in order to deposit the ns-SiC thin films at lower temperature compared to conventional PECVD. The effect of frequency to the crystallinity and morphology of SiC thin films will be investigated in this work. VHF-

PECVD could give a great impact to allow the chemical reaction at lower temperature with better crystallinity and morphology compared to conventional PECVD method. The existence of plasma has been proven to produce a good quality of thin film with unique composition and properties [5].

2. Methodology

2.1. Sample Preparation

The SiC thin films were prepared by using VHF-PECVD with specified precursor gases. Silane (SiH₄) was used as silicon source, Methane (CH₄) as the carbon source while Argon (Ar) and Hydrogen (H₂) were used as the enhancer for the nucleation of the SiC formation. The quality of thin films will critically depends on the quality and clarity of the substrate and therefore a high quality of Si (100) wafer with low resistivity and thickness was chosen for this work. The substrate was cut into small pieces and degreased with acetone in an ultrasonic bath. The substrate was then immersed into isopropyl solution to remove microorganism from the surface. This was followed by 2% of Hydrofluoric acid (HF) etch and followed by drying with Nitrogen in order to remove native oxide on the surface. Finally, the substrate was placed into VHF-PECVD chamber for SiC thin films deposition. The parameter

such as chamber pressure, RF power and substrate temperature (400°C) were kept constant but RF frequency was varied; 100MHz, 160MHz and 200MHz.

2.2. Characterization

The characterization was performed to study the crystallinity and the morphology of the samples. Various techniques were employed in this work such as AFM, SEM and Raman Spectroscopy. The morphology and crystallinity of the samples with various RF frequencies were obtained.

Scanning electron microscope (SEM) is the technique have been used to observe the condition of sample surface. In addition, SEM also observable technique for measuring the thickness of the sample by cross section [6], while Raman spectroscopy was used to gain information on molecular vibrations and crystal structures by using laser light source directed to the samples. This technique also can measure the amount of crystallinity of the samples.

AFM is the one kind of scanning probe microscope (SPM). It is the powerful method to study the surface morphology of the sample. There are consists of three modes which is contact mode, tapping mode and non-contact mode. The contact mode is suitable for hard surface while the non-contact mode most useful for imaging soft surface but sensitive to the external vibrations. The tapping mode is probably for imaging soft biological specimen or poor surface adhesion (carbon nanotubes) [7].

The AFM produces a 3D images on a nanoscale by scanning and measure the forces of interactions between a sharp probe and surface with short distance. In this study, the probe is hang by the flexible cantilever and non-contact mode tip is used to the surface. The sample was mounted on a piezoelectric scanner with three-dimension piezo-movements. The deflection of the cantilever is measured by optical method. In non-contact mode, the cantilever do not contact but oscillates near the surface of the sample. The oscillation slightly above resonant frequency.

3. Results and Findings

3.1. Atomic Force Microscopy

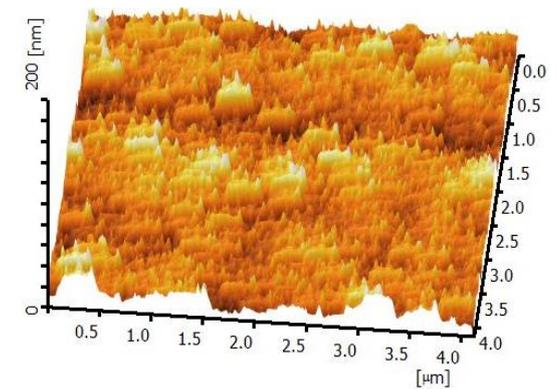
The effect of frequency on deposition of SiC thin films were observed through AFM. Figure 1 shows the AFM images of deposited SiC with different frequency; 100MHz, 160MHz and 200MHz. The AFM images was observed via SPIWin software. The calculated parameters such as surface roughness, mean size and mean diameter values were obtained from the installed AFM software.

The mean size (S_v) is determined by using equation below.

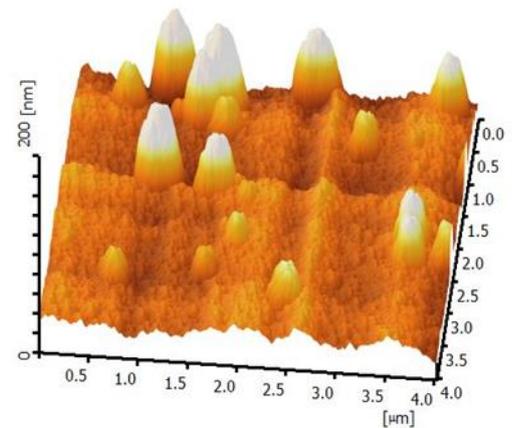
$$\text{Mean Size, } S_v = \frac{S_T}{N},$$

where S_T is a grain area and N is a grain count, while the mean diameter (D_v) is determined as follows;

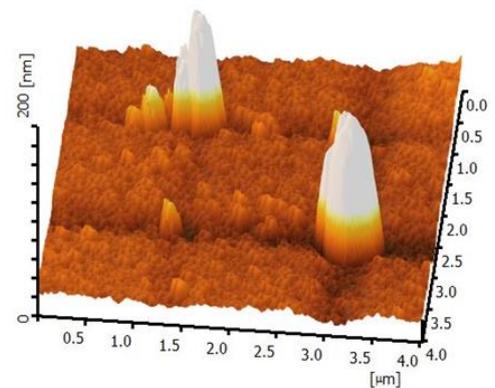
$$\text{Mean Diameter, } D_v = 2 \sqrt{\frac{S_T}{N}} \quad (c)$$



(a)



(b)



(c)

Figure 1: 3D images of SiC thin films for frequency at (a) 100MHz (b) 160MHz (c) 200MHz

The surface of SiC films on Si substrate becomes rougher as the number of SiC granules has increases. The surface roughness also depends on the thickness of the nanocrystalline Si-C (nc-SiC) films produced. The surface morphology changed depends on the rate of formation of films whereby more particles packed with each other and covered with nanosized grains to produce nc-SiC. Table 1 shows the physical properties of the samples with different frequency.

Table 1: Physical properties of SiC thin films

	100MHz	160MHz	200MHz
Roughness, RMS (nm)	5.43	11.94	13.91
Mean Size (nm²)	9.18x10 ³	6.45x10 ⁴	7.27x10 ⁴
Mean Diameter (nm)	1.08x10 ²	2.87x10 ²	3.04x10 ²

Figure 1 shows a dense films with continuous morphologies of crystalline nano-structures were observed where z-dimension determined the particle heights. The grown of nanostructures of the films are noticeably affected by the frequency. As the frequency increases, bigger energy was imparted to electron via stochastic heating or called collision less heating which helps the dissociation of SiH₄ and CH₄ and reduces the energetic ion impact on the growth surface of the thin films [8][9]. Thus, the higher growth rate with dense film were produced. In addition, most researcher got that the higher frequency would also result in a reduced sheath thickness and a lower voltage potential across the electrodes that makes the deposition growth of films greater and provide better uniformity of films thickness [8]. Thus, the roughness of the SiC thin films is 5.43nm, 11.94nm and 13.91nm obtained at 100MHz, 160MHz and 200MHz respectively which is greatly become more compact as the frequency increased.

3.2. Atomic Force Microscopy

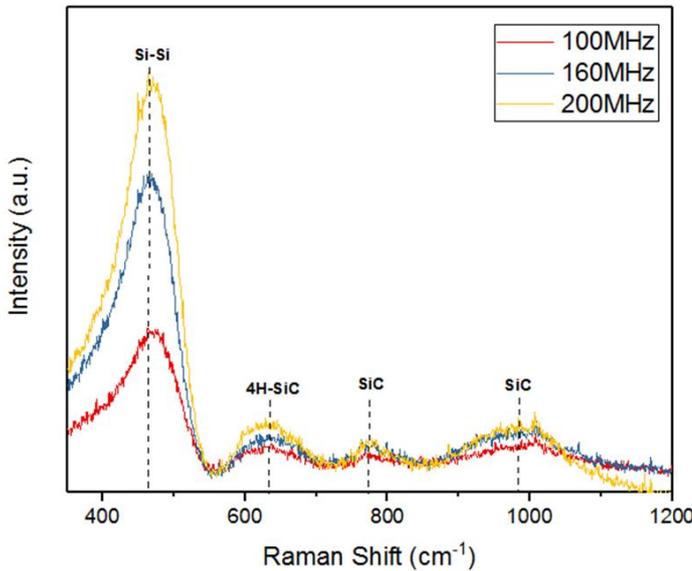


Figure 2: Raman spectra for all samples

Figure 2 above shows the Raman spectra of the samples with different frequency; 100MHz, 160MHz and 200MHz after the baseline correction. The range are set from 350 cm⁻¹ until 1200 cm⁻¹ as the peaks appeared around this specified range. The intensity is slightly increases as the frequency increases.

All samples appeared four identical peak bands. The spectra was divided into two regions which are 400 cm⁻¹ to 600 cm⁻¹ and 600 cm⁻¹ to 1000 cm⁻¹. The first region was clearly shown the broad peak around 480 cm⁻¹ indicated that Si-Si bonds of amorphous Si clusters existed in the samples. In the second region, the peaks exist around 600 cm⁻¹ to 650 cm⁻¹ which corresponding to longitudinal acoustic (LA) modes of 4H-SiC while the peaks around 780⁻¹ to 800 cm⁻¹ and 970 cm⁻¹ to 980 cm⁻¹ are attributed to SiC longitudinal optical (LO) and SiC transverse optical (TO) respectively [10][11][12]. A bit shift occurred may lead by the stress of the films due to high lattice and thermal mismatch [13]. This confirms the amount of Si-C bonding are present in our samples. The spectra from all samples were fitted with lorentzian-gaussian approximation with installed Origin Software. This can be explained that the peak and amount of crystallinty increases as the frequency increases. It agreed with the AFM result which is the roughness of the surface directly proportional to the amount of crystallinty.

Table 2 shows the percentage of crystallinity of all samples. The percentage of crystallinity can be obtained by equation below [14].

$$\% \text{ of crystallinity} = \frac{A_L}{A_L + A_G} \times 100$$

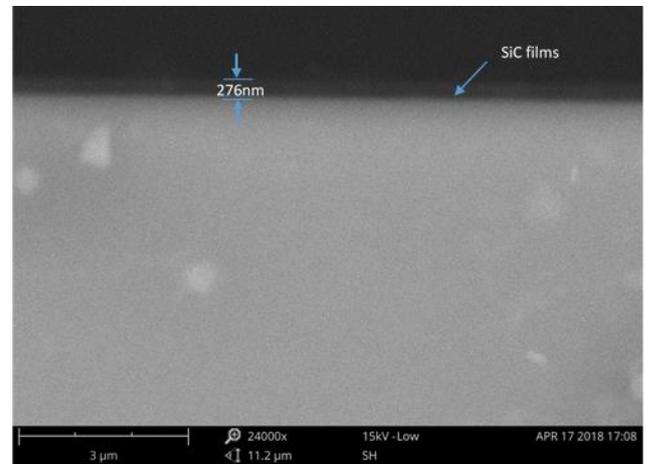
where the A_L is the area under Laurentzian approximation while A_G is the area under Gaussian approximation

Table 2: Amount of crystallinity

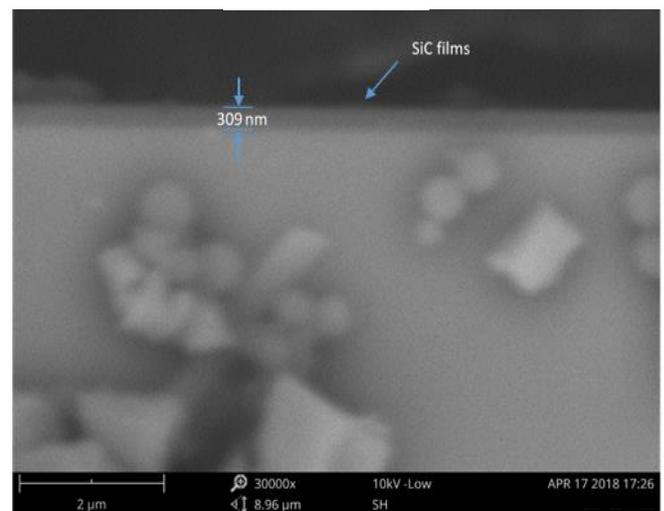
	100MHz	160MHz	200MHz
% Crystallinity	50.89	52.37	53.32

3.3 Scanning Electron Microscopy

Figure 3 shows the cross sectional of the samples observed by SEM technique. The thickness increases from 276nm to 309nm when the frequency increases from 160MHz to 200MHz. It shows that the thickness of the samples are depend on the frequency. As the higher frequency was used, the growth rate of Si-C increases, thus the thickness of the samples increases [15].



(a)



(b)

Figure 3: Cross sectional of SiC thin films for frequency at (a) 160MHz and (b) 200MHz

4 Conclusion

In summary, the SiC thin films were successfully prepared using VHF-PECVD system. The effect of frequency on the crystallinity and morphology were investigated. The surface roughness, film thickness, intensity and amount of crystallinity of the samples increases with frequency. The crystallinity measured by Raman spectra were slightly increases from 50.89% to 53.32% when the frequency increases as it enhanced the growth rate of Si-C on the substrate. Higher frequency gives strong effect which helps the dissociation of SiH₄ and CH₄ and reduces the energetic ion impact on the growth surface of the thin films.

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References

- [1] J. Palmour, J. Edmond, ... H. K.-W.-B.-G., and undefined 1993, "6H-silicon carbide devices and applications," *Elsevier*.
- [2] S. Sheng, M. Spencer, X. Tang, ... P. Z.-M. S. and, and undefined 1997, "An investigation of 3C-SiC photoconductive power switching devices," *Elsevier*.
- [3] C. A. Zorman and R. J. Parro, "Micro- and nanomechanical structures for silicon carbide MEMS and NEMS," *Phys. Status Solidi Basic Res.*, vol. 245, no. 7, pp. 1404–1424, 2008.
- [4] C. Jung, D. Lim, H. Jee, M. Park, ... S. K.-S. and C., and undefined 2003, "Hydrogenated amorphous and crystalline SiC thin films grown by RF-PECVD and thermal MOCVD; comparative study of structural and optical properties," *Elsevier*.
- [5] C. Summonte, R. Rizzoli, M. Bianconi, A. Desalvo, D. Iencinella, and F. Giorgis, "Wide band-gap silicon-carbon alloys deposited by very high frequency plasma enhanced chemical vapor deposition," *J. Appl. Phys.*, vol. 96, no. 7, pp. 3987–3997, Oct. 2004.
- [6] J. L. M. Shibata, "Cross Section Specimen Preparation Device Using Argon Ion Beam for SEM," 2004.
- [7] R. De Oliveira, D. A.-... -Imaging, undefined Measuring, and undefined 2012, "Measurement of the nanoscale roughness by atomic force microscopy: basic principles and applications," *intechopen.com*.
- [8] H.-L. Chen, Y.-C. Tu, C.-C. Hsieh, D.-L. Lin, and K.-C. Leou, "Generation of uniform large-area very high frequency plasmas by launching two specific standing waves simultaneously," *J. Appl. Phys.*, vol. 116, no. 10, p. 103307, Sep. 2014.
- [9] S. Zhang, L. Raniero, E. Fortunato, ... L. P.-J. of non, and undefined 2004, "Characterization of silicon carbide thin films prepared by VHF-PECVD technology," *Elsevier*.
- [10] H. Zhang, Z. X.-O. Materials, and undefined 2002, "Microstructure of nanocrystalline SiC films deposited by modified plasma-enhanced chemical vapor deposition," *Elsevier*.
- [11] Z. An *et al.*, "Fabrication of silicon carbide thin films by plasma immersion ion implantation with self-ignited glow discharge," *Elsevier*.
- [12] R. Tu *et al.*, "Effect of CH₄/SiCl₄ ratio on the composition and microstructure of 110-oriented β-SiC bulks by halide CVD," *Elsevier*.
- [13] M. Bosi *et al.*, "Growth and Characterization of 3C-SiC Films for Micro Electro Mechanical Systems (MEMS) Applications," *Cryst. Growth Des.*, vol. 9, no. 11, pp. 4852–4859, Nov. 2009.
- [14] Sabu Thomas, Mohammed Arif P, E. Bhoje, *Cyrstallization in Multiphase Polymer System*. 2017.
- [15] E. Chen *et al.*, "RF-PECVD deposition and optical properties of hydrogenated amorphous silicon carbide thin films," *Elsevier*.