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EFFECT OF METHANE FLOW RATE ON THE PROPERTIES OF HWCVD SILICON CARBIDE THIN FILMS

F. Shariatmadar Tehrani*, R. Ritikos, B. T. Goh, M. R. Muhamad and S. A. Rahman

Solid State Research Laboratory, Physics Department, University of Malaya,
50603 Kuala Lumpur, Malaysia

ABSTRACT

Silicon carbide (SiC) thin films were prepared by Hot Wire Chemical Vapor Deposition (HWCVD) from SiH_4/CH_4 gases on glass and crystalline silicon substrates. The SiH_4 gas flow rate was 1 sccm and influences of CH_4 gas flow rate, [CH_4], on structural properties of SiC thin films were investigated. The mean crystallite size was increased with decreasing [CH_4] from 100 to 10 sccm. Infrared absorption spectra showed that the Si–C bonds increased with decreasing the methane gas flow rate.

Keywords: SiC; thin film; optical bond gap;

INTRODUCTION

Crystalline (nano-, micro- and poly-) silicon carbide (SiC) films have emerged as semiconductor materials of great technological importance because of wide tunable refractive index, wide tunable optical band gap, high hardness, high thermal conductivity, high stability, good chemical resistance, high breakdown field and high saturated drift velocity [1–3]. Consequently, these materials are finding applications in solar cells, light emitting devices and in thin film transistors [1,4] and also have been proposed for the realization of power electronics and high frequency devices [5].

In the thin film form, truly crystalline SiC has been difficult to prepare by many of the established chemical vapour deposition (CVD) techniques. In most cases, microcrystalline SiC was reported to form as a phase mixture of Si crystallites and amorphous SiC [6]. In some recent works, successful growth of thin films containing SiC crystallites by HWCVD using monomethyl-silane (MMS, SiH_3CH_3) precursor have been demonstrated [7,8]. However, the cost of SiH_3CH_3 is much higher compared with that of methane (CH_4) and silane (SiH_4). Therefore, using CH_4 and SiH_4 as the carbon and silicon sources respectively is important from the view point of cost reduction. In this study we have investigated the influence of CH_4 flow rate ([CH_4]) on the structural and optical properties of thin films.

EXPERIMENTAL METHOD

SiC films were deposited on both Corning 1737 glass and p-type (111) crystal silicon (c-Si) wafers using the HWCVD technique. A tungsten wire of 0.5 mm in diameter was coiled into a 25 mm helix and was placed 26 mm above the substrates. The deposition pressure was fixed at 0.8 mbar. The methane gas flow rates [CH_4] for the five samples studied in this work were 100, 70, 40, 20, and 10 sccm. The substrate temperature (T_s) was kept constant at 320 ^oC. The filament temperature (T_f) measured by optical pyrometer, was kept at 1950^{o}C. A new tungsten wire was replaced for every film deposition. Before every deposition, the filament was pre-heated at 2000^{o}C in H_2 atmosphere for 10 min.

The film thickness was measured using a P-16+/P-6 KLA-TENCOR mechanical profilometer. The crystallinity of the films was studied using SIEMENS D2000 X-ray diffractometer (XRD) while Fourier transform infrared (FTIR) spectroscopy was used to investigate the chemical bonding properties of the films. The refractive index and the optical energy gap were determined from the optical transmission spectra of the films by JASCO V-570 UV/Vis/NIR spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the deposition rate of the films on both glass and c-Si substrates as a function of CH_4 flow rate. The variation of deposition rate of the SiC film on c-Si and glass substrates with [CH_4] produces two similar trends with the highest deposition rate observed for the film on glass substrate deposited at methane flow rate of 100 sccm. Our samples show high deposition rate comparing to the other works in similar conditions [9-11].

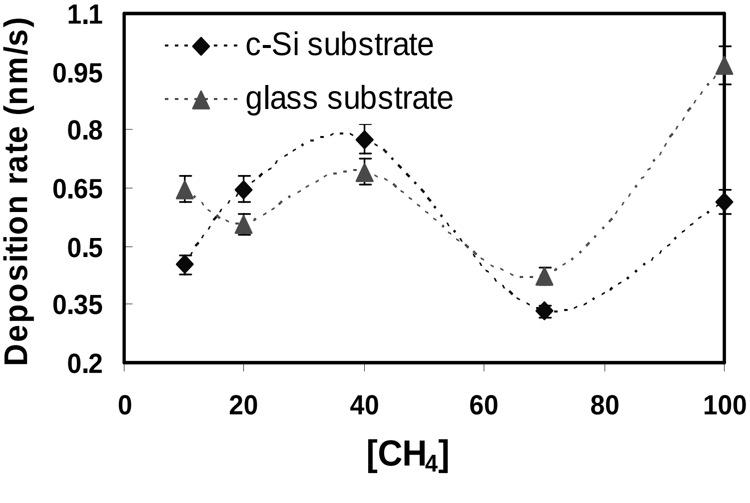

Figure 1: Variation of deposition rate of SiC films versus [CH_4] for samples on glass and c-Si substrates

The dependence of the optical band gap (E_{04}) and refractive index (n) of the films that have obtained from optical transmission spectra on the methane flow rate are shown in Figure 2. At low [CH_4], the refractive index decreases to a minimum at [CH_4]=20 sccm while the optical energy gap increases to a maximum at [CH_4]=20 sccm and increases again to a higher value at [CH_4]=70 sccm. The optical energy gap and the refractive index decrease with increase in methane flow rate from 70 to 100 sccm.

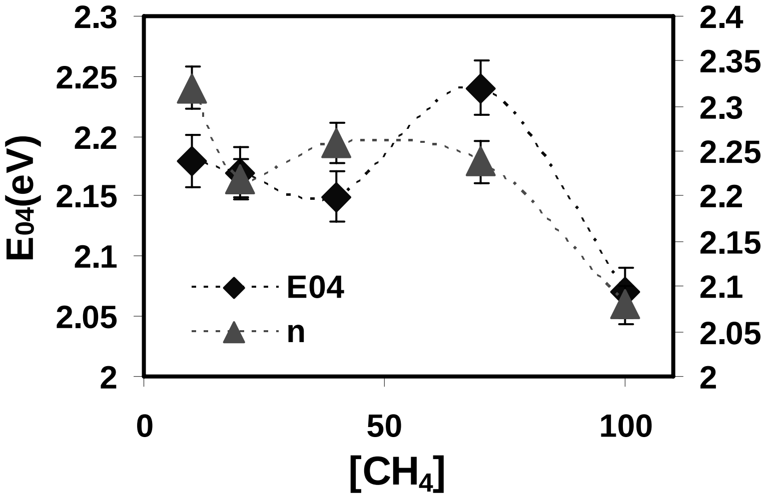

Figure 2: Optical energy gap and refractive index of SiC film as a function of [CH_4] for samples on glass substrates

The IR transmission spectra for all samples are shown in Figure 3. In the wavenumber region of 400–1400 cm^{-1}, several peaks can be observed: Si–H_n wagging (640 cm^{-1}), Si–C stretching (780 cm^{-1}), C–H wagging (~1000 cm^{-1}) and Si–H stretching (2100 cm^{-1}) modes. The films prepared at high methane gas flow rates of 100 and 70 sccm showed a clear peak of Si–H_n (w) mode, indicating that these were silicon-rich films. However, the Si–H_n (w) peak decreased with decreasing the. On the other hand, the Si–C (str) peak predominated at lower [CH_4].

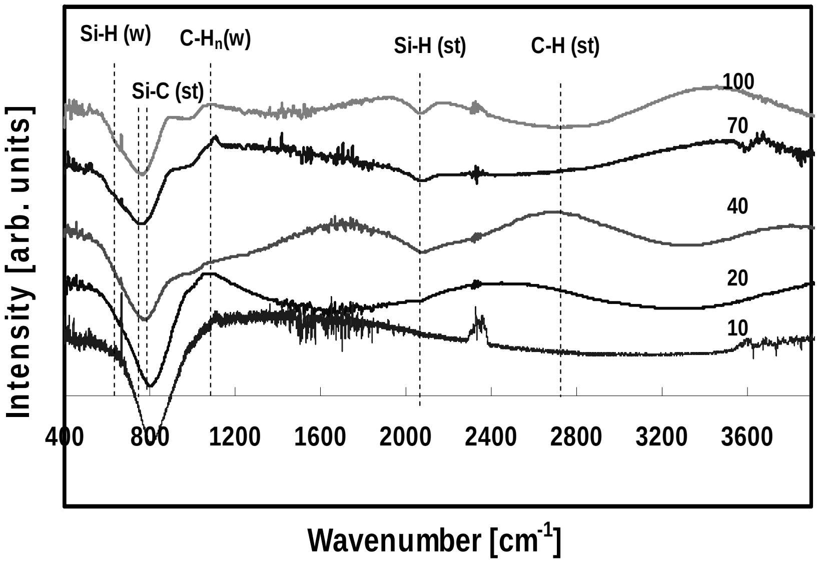

Figure 3: FTIR spectra transmission of SiC films on c-Si substrates prepared at different methane flow-rates [CH_4]

The variations of the integrated intensities of the Si-H and Si-C stretching bands and the ratio of the integrated intensity of Si-C to Si-H stretching band (Si-C/Si-H) are plotted in Figure 4. Si-C/Si-H is high at lowest [CH_4] and decreases to a minimum at [CH_4] =40 sccm and increases slowly to a saturation value with further increase in methane gas flow rate.

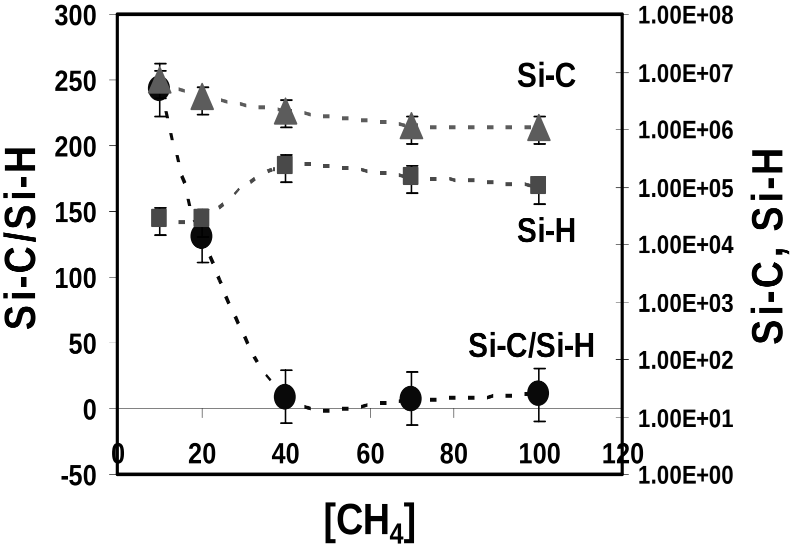

Figure 4: Variations of integrated intensity of Si-H and Si-C stretching band and the ratio of the integrated intensity of Si-C to Si-H (Si-C/Si-H) with [CH_4]

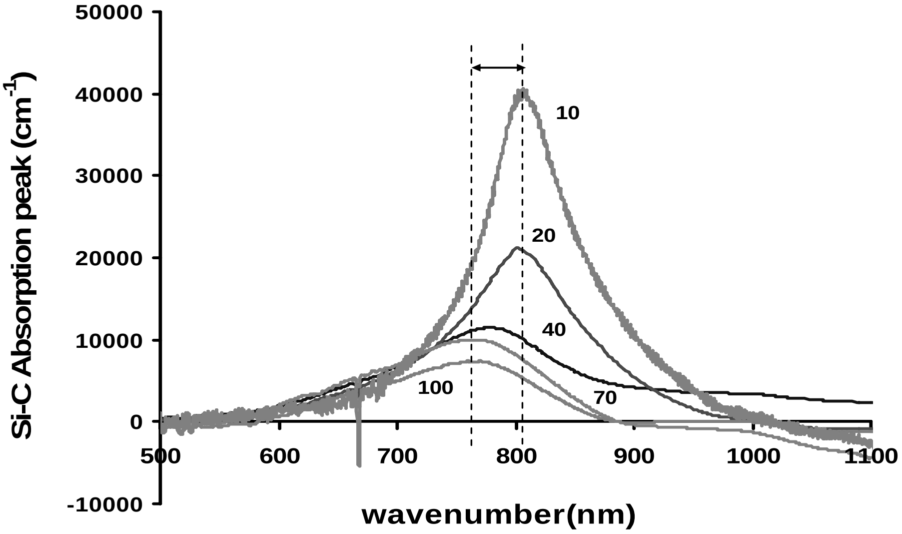

Figure 5: Si-C absorption peaks for all samples with different [CH_4]

The absorption peaks of Si-C for al samples are shown in Figure 5. The lineshape of the IR absorption bonds can provide information on the structural order of the silicon carbon network. At lower methane flow rate the IR absorption peak is in Gaussian shape and it changes to Lorentzian shape with decreasing the [CH_4]. This indicates a transition from the amorphous to micro-crystalline phase. In addition Si-C peak is shifted to higher wavelength and lower energy with decreasing the [CH_4] from 100 to 10 sccm. This shift also confirmed the transition from amorphous phase to crystalline (3C-SiC).

Figure 6 shows XRD spectra of films prepared at different [CH_4]. The Si-C (111) orientation peak is observed only for the film prepared at the lowest methane flow rate [CH_4] =10, 20 sccm. This result confirm that the crystalline structure has obtain for [CH_4] =10, 20 sccm and [SiH_4] =1 sccm. The films at [CH_4] =10, 20 sccm shows three diffraction peaks at $2\theta = 35.6^{o}$, $60\ ^{o}$ and 72^{o} which correspond to (111), (220) and (311) of 3C–SiC, respectively. But the other samples are in amorphous form and the peaks in their graphs are due to silicon substrate. This indicates that films at [CH_4] =10, 20 sccm included 3C–SiC nanocrystallites. This result is consistent with IR transmission that shows crystallinity at low [CH_4].

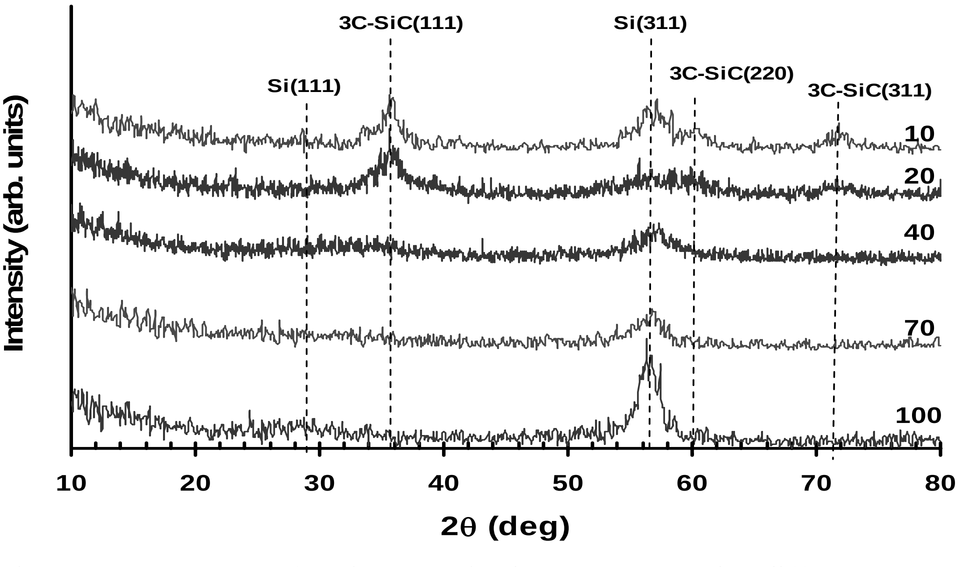

Figure 6: XRD spectra for SiC on c-Si substrates prepared at different [CH_4]

The XRD peak intensity increased with decreasing methane flow rate. Mean crystallite size, estimated from Scherrer's formula, increased monotonously from 1.4 nm to 4.25 nm with decreasing methane flow rate from 40 to 10 sccm.

CONCLUSION

The high deposition rate (0.33-0.96 nm/s) SiC thin films were prepared by HWCVD technique and the influence of methane gas flow rate on optical and structural properties of SiC thin films was investigated. For the methane flow rates below 20 sccm the structural order increased. XRD peaks related to 3C-SiC and high intensity of Si-C bonds with lorentzian lineshape in IR spectra have been detected. It was found that methane gas flow rates were important parameter for controlling film structure.

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