



METHANE FLOW RATE TUNE THE OPTICAL AND MICROSTRUCTURE PROPERTIES OF HYDROGENATED AMORPHOUS SILICON CARBIDE FILMS DEPOSITED BY PECVD.

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ABSTRACT

Hydrogenated amorphous silicon carbide ($a\text{-Si}_{1-x}\text{C}_x\text{:H}$) thin films were prepared by plasma-enhanced chemical vapor deposition rf-PECVD technique from the gas mixture of $\text{CH}_4/\text{SiH}_4/\text{H}_2$. The effect of methane flow rate $[\text{CH}_4]$ on microstructure and optical properties of the films have been investigated using infrared IR spectroscopy, Raman spectroscopy, and optical transmission measurements. A multiphase structure of grown materials is showed by Raman analyses. IR spectra show an increase in the peak intensity of Si-H_n , Si-C , C-H_n modes with increasing $[\text{CH}_4]$ from 20-60 sccm, revealed the increase in total hydrogen and carbon content in the films. The optical band gap shows increasing trend due to carbon incorporation. High $[\text{CH}_4]$ caused inhomogeneity in the material as reflected by the decrease in disorder parameter, and low refractive index. Methane flow rate has a strong influence on the structure of the films and tunes their optical parameters.

Keywords: Amorphous silicon carbide (SiC), thin-films, PECVD, Hydrogen, Gap.

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1. INTRODUCTION

Amorphous silicon carbide ($a\text{-Si}_{1-x}\text{C}_x\text{:H}$) thin films are recognized by interesting physical, chemical and mechanical properties, thanks to this, it has many industrial applications, as semi-conducting materials at high temperature [1], in transistors [2], for photonic and Optic [3], optoelectronic materials and in third-generation solar cells [4]. The significance of this material is that its electrical and optical properties can be controlled by the carbon, silicon and hydrogen compositions of the film [5]. Amorphous silicon carbide $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ thin films were prepared by RF-PECVD, which has become the main technique for semiconductor film deposition due high uniformity [6]. During the last decade, considerable work has been done on the electrical, optical, mechanical, chemical and stress properties of $a\text{-SiC:H}$ thin films [7,8,9]. While, the main purpose to vary the methane flow rate is to adjust the optoelectronic properties of the films by alloying silicon with carbon. Few experimental studies have been carried out on the influence of PECVD deposition conditions (especially methane flow rate) on the growth mechanism, chemical bonding configuration, and composition of $a\text{-SiC:H}$ thin films. In this study we have investigated the influence of the CH_4 flow rate on structural and optical properties of the films. The results show that the chemical bonding configuration and optical parameters of the films can be tuned by the methane flow rate.

2. EXPERIMENTAL DETAILS

The $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films were deposited on Corning glass by the RF-PECVD technique, using $\text{SiH}_4\text{-CH}_4\text{-H}_2$ gaz mixture. The RF power, the deposition pressure, the silane and hydrogen flow rate and inter electrodes distance are fixed at: 20 W (113mW/cm^2), 2.3 torr, 13 sccm, 500 sccm, 1.2 cm respectively. The methane gas flow rates [CH_4] for the samples studied in this work were 20, 40, 60 and 100 sccm. The substrate temperature (T_s) was kept constant at 285°C , and with deposition time of 20 min. The vibrational modes were analyzed by a Bruker FTIR spectrometer (ALPHA FTIR Spectrometer) in the range of $400\text{-}4000\text{ cm}^{-1}$ using the reflection mode and single beam configuration, with a resolution of 4 cm^{-1} . Correlations between the microstructure of the films and the deposition parameters were investigated by Raman spectroscopy using a laser beam ($\lambda=633\text{ nm}$). The thickness, the refractive index and the optical energy gap were determined from the optical transmission spectra of the films using Standard optical transmission (OT) measurements performed on a CHIMADZU UV 3600-double beam spectrophotometer over the wavelength range $0.5\text{--}2.5\mu\text{m}$.

3. RESULTS AND DISCUSSION

3. 1 RAMAN ANALYSIS:

Figure 1 shows the Raman scattering spectra of films deposited with different [CH_4]. We can see that the Raman scattering of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films is similar to that of $a\text{-Si:H}$ in the range of

100–600 cm^{-1} .

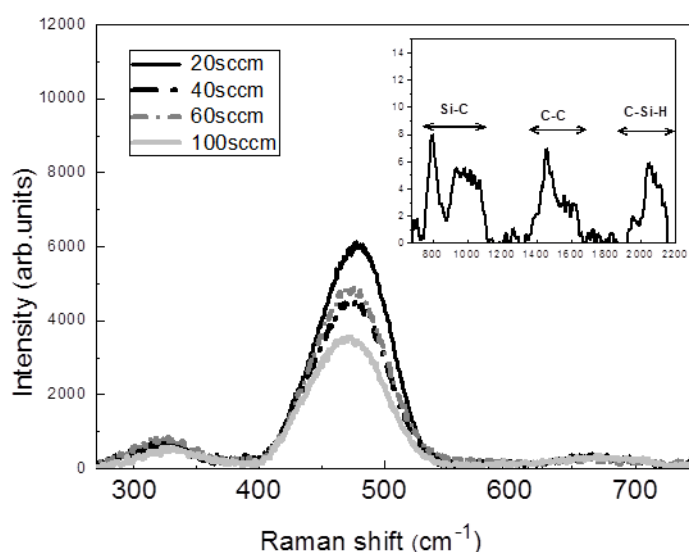


Figure 1: Raman spectra of $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ films as function as $[\text{CH}_4]$ in the region 200–750 cm^{-1} . The inset is Raman spectrum in the region 750–2200 cm^{-1} for the sample deposited at 20 sccm of $[\text{CH}_4]$.

The peaks at about 310 cm^{-1} and 480 cm^{-1} are due to first-order scattering of Si–Si vibrations in the Longitudinal acoustical (LA) and transverse optical (TO) modes respectively [10]. It is generally thought that the TO mode mainly reflects short distance order of the material and its peak width is directly proportional to the mean bond angle distortion [11]. While the increasing in CH_4 flow rate can result in lower Raman scattering intensity. The weak vibration band near 620 cm^{-1} corresponds to the second-order LA mode of Si–Si vibration.

In the inset, the Raman spectrum for a sample deposited at 20 sccm in the range 750–2200 cm^{-1} is illustrated as example, we can observe a weak peak at around 850 cm^{-1} [12], can be assigned to the Si–C vibration mode, which is consistent with the IR result, a broad shoulder centered at 960 cm^{-1} and can be assigned to SiC longitudinal optic (LO) phonon vibrations [13]. The presence of the broad band in the range of 1350 and 1600 cm^{-1} , attributed to the vibration modes of the C–C bonds and suggesting the presence of amorphous carbon [14]. Also, the Si–H vibrations are present around 2000 cm^{-1} . A multiphase structure of the grown $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ thin films is suggested, which possess the amorphous Si–C network, amorphous carbon and amorphous silicon network.

3. 2 INFRARED ATTENUATED REFLECTION (ATR) ANALYSIS:

The bonding configurations of the deposited thin films were investigated by infrared attenuated reflection (ATR) spectroscopy. Figure 2 shows the thickness normalized IR absorption spectra in the wave number region of 500–3000 cm^{-1} , of deposited $\text{a-Si}_{1-x}\text{C}_x\text{:H}$

films for different $[\text{CH}_4]$.

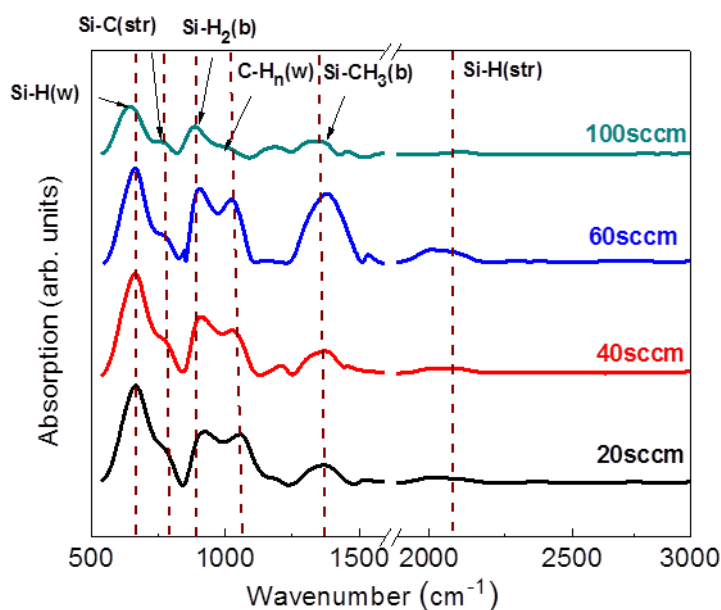


Figure 2: IR spectra of $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ films deposited at 20, 40, 60, 100 sccm of $[\text{CH}_4]$.

For all spectra we can observe the same absorption bands regions. The peak at 668 cm^{-1} corresponds to the Si-H_n wagging mode or Si-C stretching mode (str) [15]. The band at 780 cm^{-1} can be assigned to the Si-C stretching mode (str) or Si-CH_3 wagging mode (w) [15]. The peak at 900 cm^{-1} is associated to the Si=H_2 bending mode (b). The shoulder at $(990\text{--}1030)\text{ cm}^{-1}$ can be attributed to the rocking and wagging (w) mode of C-H_n in Si-CH_n bonds [15, 16]. The band between $1200\text{--}1400\text{ cm}^{-1}$ is related to Si-CH_3 bending mode [17]. The band at $2080\text{--}2100\text{ cm}^{-1}$ is related to Si-H_n stretching modes. A dominance of Si-CH_3 bonding is observed and can confirm the incorporation of carbon in the films in methyl groups [18].

Figure 3 shows the evolution of Si-C(str) , $\text{Si-CH}_3(\text{w})$, $\text{C-H}_n(\text{w})$ and $\text{Si-CH}_3(\text{b})$, $\text{Si-H}_n(\text{str})$ absorption modes with varying $[\text{CH}_4]$, we can observe the increase of Si-C bond intensities in the range 20-60 sccm of $[\text{CH}_4]$. This result suggests increase in Si-C bond density and hence carbon content in the film with increasing $[\text{CH}_4]$. A significantly decrease in peaks intensities for the sample deposited at 100 sccm of $[\text{CH}_4]$, can be related to a decrease in Si-C bond density.

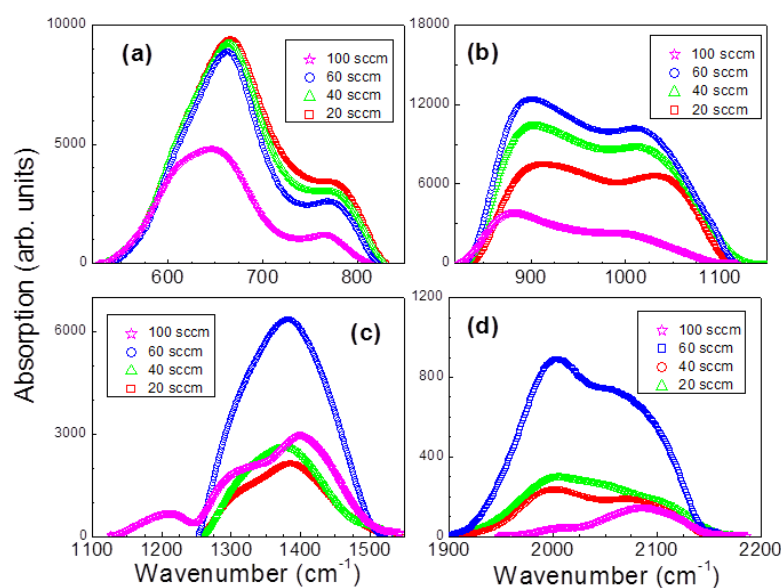


Figure 3: Evolution of the different absorption peaks in regions (a):500-850 cm^{-1} , (b):850-1100 cm^{-1} , (c):1100-1600 cm^{-1} , (d):1900-2200 cm^{-1} as function as $[\text{CH}_4]$.

With increasing $[\text{CH}_4]$ more CH_n and SiH_n radicals will be generated, which may be the main reason why the intensities of vibration bands of the Si-C(str), Si- CH_3 (w), C- H_n (w) and Si- CH_3 (b), Si- H_n (str)) reach a maximum value at $[\text{CH}_4]$ of 60 sccm. At 100 sccm of $[\text{CH}_4]$, the SiH_n radicals can be decrease due to the reduction of percentages of SiH_4 content in PECVD chamber [17]. Therefore, less SiH_n radicals can be bonded to CH_n radicals to form more related Si-C bonds, thus, the intensities of vibration bands of the peaks decrease at 100 sccm of $[\text{CH}_4]$. Since, a shift of Si-C stretching mode at 780 cm^{-1} to 750 cm^{-1} at 100 sccm of $[\text{CH}_4]$ is also observed (figure 3(a)), it is reasonable to believe that the number of carbon atoms bonded to one silicon atom in the a-SiC:H thin films did changed.

The evolution of the 1900-2200 cm^{-1} absorption region with variation of $[\text{CH}_4]$ was studied and is shown in figures 4. The presence of two bands can distinguished with increasing $[\text{CH}_4]$: Si-H monohydride bonding around 2000 cm^{-1} , and $(\text{Si-H}_2)_n$ polyhydride bonding around 2090-2100 cm^{-1} . While, a shift of the peaks to higher wave number with increasing $[\text{CH}_4]$ is observed. Indeed, it is known from the literature that the 2000 cm^{-1} Si-H stretching band can shift towards 2090 cm^{-1} due to carbon back-bonding [19, 20].

The increase of the peak intensity of Si-H (str) modes in the range of 20-60 sccm of $[\text{CH}_4]$ (figure 3(d)), as a consequence, we can suggest the increase in total hydrogen in the films. While, at 100 sccm of $[\text{CH}_4]$ an impotent decrease in Si-H (str) peak can be interpreted by a reduce in total hydrogen in the film.

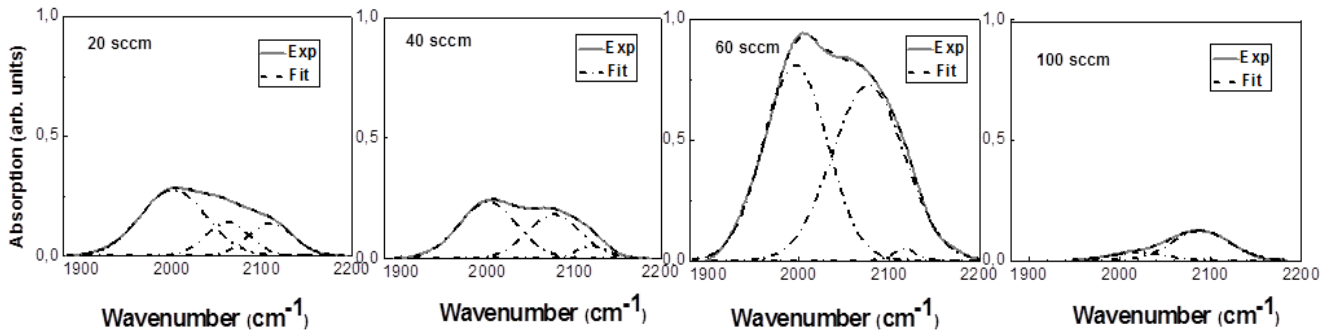


Figure 4: Déconvolution of the absorption peak in the region 1900-2200 cm^{-1} as a function of $[\text{CH}_4]$.

The microstructure parameter R is often proposed [21]:

$$R = \frac{I_{2090}}{I_{2090} + I_{2000}} \quad (1)$$

where I_{2000} , I_{2090} are the integrated areas under the absorption bands corresponding to Si-H n stretching modes at frequency 2000, 2090 cm^{-1} respectively. A low microstructure parameter is often a sign of low void density material. The microstructure parameter is plotted on figure 5.

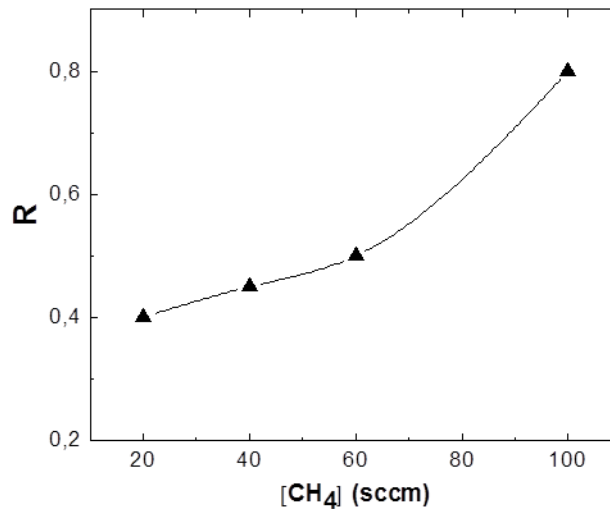


Figure 5: Microstructure parameter as a function of $[\text{CH}_4]$.

From these figures it is seen clearly that:

- In the range 20-60 sccm of $[\text{CH}_4]$, the stretch mode at 2000 cm^{-1} , associated with Si-H groups, remains dominant, revealed a low microstructure parameter. This means that hydrogen is mainly incorporated in the bulk of the material as monohydride groups strongly

bonded, corresponding to a dense structure.

- The spectrum corresponding to the sample deposited at 100 sccm of $[\text{CH}_4]$ presents a dominance of the contribution at 2100 cm^{-1} associated with Si-H₂ bonds related to high microstructure parameter, this means that hydrogen is incorporated in polyhydrides groups weakly bonded. The trends observed as $[\text{CH}_4]$ is varied must be correlated to significant changes in the microstructure and in the properties of the material.

3. 3 OPTICAL TRANSMISSION:

The optical constants (the refractive index n , the extinction coefficient k or the absorption coefficient $\alpha = 4\pi k/\lambda$; λ is the wavelength) and the thicknesses of the films were carefully determined from the OT spectra, using the envelope method proposed by R. Swanpoel [22]. Figure 6 shows a shift of optical absorption spectra to high energies with increasing of $[\text{CH}_4]$ which is due to the increase of the band gap [23]. In the visible region, the optical absorption is lower with increasing $[\text{CH}_4]$ and the films transparency is higher.

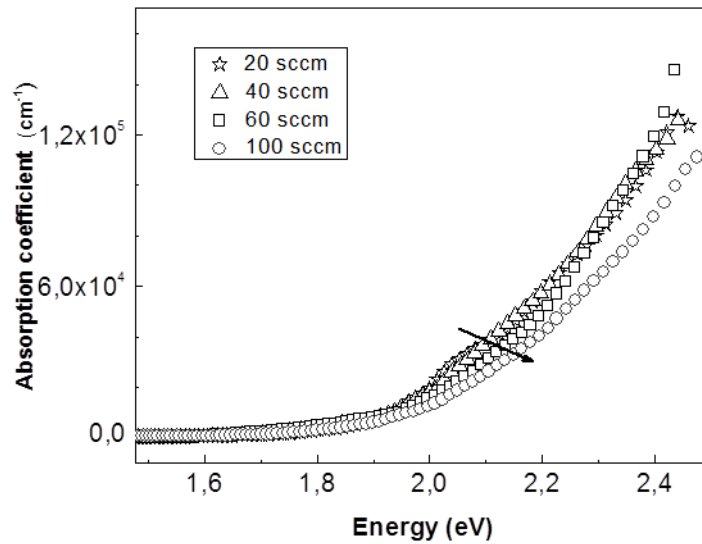


Figure 6: The effect of $[\text{CH}_4]$ on absorption coefficient of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films

The Wemple–Didomenico one-oscillator model [24] for the energies lower than the optical gap is used to determine the static refractive index n_0 , the average gap E_m , and the dispersion energy E_w :

$$n^2(\hbar\omega) = 1 + \frac{E_m E_w}{E^2 (\hbar\omega)^2} \quad (2)$$

by considering the variation of $[n^2(\hbar\omega) - 1]^{-1}$ as function of $(\hbar\omega)^2$. The values of the optical band gap E_T , have been also determined according to the non-direct transition model proposed by Tauc [25]: $(\alpha(\hbar\omega))^{1/2} = B(\hbar\omega - E_T)$, where B denotes the so-called Tauc slope.

In order to examine the effect of the hydrogen-bonding configurations on the microstructure of the material, we determine the static refractive index n_0 , which is often related to the optical gap, to the material density, or to both of them.

The disorder-induced localization of states near the band edges leads to tail states extending into the gap. It can be characterized by the Tauc slope parameter B. A higher value of B represents a smaller degree of structural disorder [26, 27]. The optical parameter values deduced from this analysis are summarized in table 1.

Table 1: Values of the film thickness d , the static refractive index n_0 , the average energy E_m , the optical gap E_T and the dispersion energy E_w , E_{04} and the factor B. The microstructure parameter R deduced from infrared absorption spectra for samples at various $[CH_4]$.

Samples	$[CH_4]$ (sccm)	d (nm)	n_0	E_m (eV)	E_T (eV)	E_w (eV)	E_{04} (eV)	B ($cm^{-1/2}$. $eV^{-1/2}$)	R
E1	20	458	3.37	3.32	1.8	34.56	1.939	818	0.4
E2	40	384	3.62	3.55	1.82	43.10	1.937	897	0.45
E3	60	304	3.36	3.34	1.9	34.44	1.946	1039	0.5
E5	100	462	3.08	3.32	1.8	28.25	1.952	800	0.8

As seen in table1, the band gap E_T increases from 1.8 eV to 1.9 eV when $[CH_4]$ varied from 20 to 60 sccm. The main factors that affect the band gap of SiC:H films are the C to Si ratio, the amount of hydrogen, and crystalline fraction [28]. Increase in band gap may be due to increase in total hydrogen and carbon content in the film with increase in $[CH_4]$. Our IR spectroscopy analysis shows increase Si-H and Si-C bond densities; reveal an increase in total hydrogen and carbon content in the films in the range 20-60 sccm of $[CH_4]$. For the sample deposited at 100 sccm of $[CH_4]$, a decrease in the band gap is observed, can be due to a decrease in and carbon content in the film, related to a reduce in Si-H and Si-C bond densities.

The dispersion energy values E_w reflects the coordination number in the films, follow the same trend as n_0 in the range 20-60 sccm of $[CH_4]$, suggesting an increase in the coordination number, corresponding to a dense structure, refracted by high disorder parameter. This trend is linked to hydrogen incorporation in monohydride groups strongly bonded (low structural parameter). At 100 sccm of $[CH_4]$, a decrease in both n_0 and E_w is observed, corresponding to a decrease in the films density. These suggest that the inhomogeneous structure which appears in the material, which must be attributed to the incorporation of the hydrogen as polyhydride $(Si-H_2)$ and $(Si-H_2)_n$ groups weakly bonded in the bulk of the material (high structural parameter). Since, a high structural parameter was founded.

The band-edge width factor B, was deduced from Tauc's relationship for an amorphous semiconductor, by applying it to the optical absorption spectra is plotted in figure 7. The

factor B increases with increasing the CH₄ in the range 20-60 sccm. While, the widest band gap showing maximum order due to homogeneous amorphous silicon carbon alloy. At 100 sccm the B-parameter dramatically dropped indicating that the films were highly disordered.

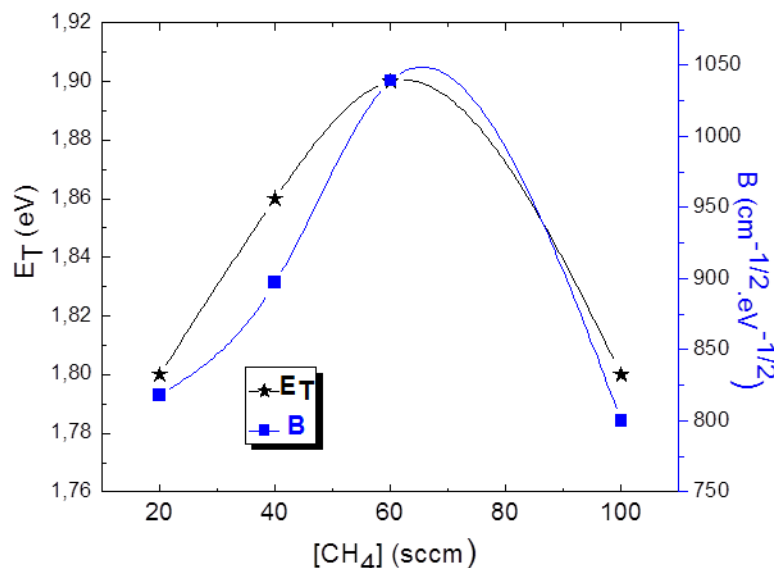


Figure 7: Dependence of band gap and disorder parameter on [CH₄].

4. CONCLUSIONS

In this work, a-Si_{1-x}C_x:H films have been deposited by RF-PECVD using the mixture of SiH₄ and CH₄ at substrate temperature (285°C), with varying the methane flow rate from 20-100 sccm. The structural and optical properties of the deposited films are investigated by IR, Raman spectroscopy, and optical transmission measurements. Formation of SiC:H films has been confirmed by IR and Raman analysis. Raman analysis revealed a multiphase structure of the grown a-SiC:H thin films, which possess the Si-C network, amorphous carbon and amorphous silicon network. IR spectra show an increase in the peak intensity of Si-H_n, Si-C, C-H_n modes with increasing [CH₄] from 20-60 sccm, revealed the increase in total hydrogen and carbon content in the films. The band gap shows increasing trend with increase in [CH₄] due to carbon incorporation in the films. In the range 20-60 sccm of [CH₄], the static refractive index n_0 increased, as reflected by an increase in disorder parameter. Thus, related to a dense structure, mainly attributed to hydrogen incorporation in monohydrides groups strongly bonded. High methane flow rate produced inhomogeneity in the film as reflected by the decrease in disorder parameter and low refractive index. Thus, related to a small density loss in the material, mainly attributed to hydrogen configuration in Si-H₂ polyhydrides groups weakly bonded. It turns out that methane gas flow rate is key parameter to tune the film structure and optical constants.

5. ACKNOWLEDGEMENTS

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