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Effects of CH_4/SiH_4 flow ratio and microwave power on the growth of β-SiC on Si by ECR-CVD using $CH_4/SiH_4/Ar$ at 200 °C

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Abstract

The effects of CH_4/SiH_4 flow ratio and microwave power on the formation of SiC at 200 °C by electron cyclotron resonance chemical vapor deposition is investigated. When the CH_4/SiH_4 flow ratio is varied from 0.5 to 10, crystalline phase of films vary from polycrystalline silicon to polycrystalline β-SiC, and finally to amorphous silicon carbide. However, as the microwave power increases from 300 to 1500 W, the film microstructure changes from polycrystalline Si to amorphous SiC, and finally to polycrystalline β-SiC. The deposition mechanism which controls the film characteristics is also presented. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chemical vapor deposition; Cyclotron resonance studies; Silicon carbide; Transmission electron microscopy

1. Introduction

Silicon carbide (SiC) is a promising semiconductor material for electronic and optical devices, owing to its superior properties such as high thermal conductivity, high-melting point, high breakdown field, high saturated drift velocity, small dielectric constant, and wide band gap [1–3]. However, due to its physical stableness, chemical inertness, and hardness, it can be used as optical filter antireflection hard coatings, X-ray masks, and corrosion-resistant materials. Furthermore, SiC can also be used as a thin buffer layer for the growth of diamond films on silicon [4] and GaN films on α-Al_2O_3 [5].

With rapid miniaturization of devices and circuits, significantly lower growth and processing temperatures are being sought. However, conventional ways of depositing SiC films by CVD methods were carried out in a high temperature environment. A high-temperature CVD process of depositing SiC films is not suitable for device fabrication, because it may lead to autodoping and causing non-abrupt heterojunctions between SiC and silicon. A relatively new technique, known as electron cyclotron resonance chemical vapor deposition (ECR-CVD) has the ability to deposit β-SiC (3C-SiC) at low temperatures [6,7].

In this study, we examine effects of CH_4/SiH_4 flow ratio and microwave power on the properties of SiC films.

2. Experimental

Silicon carbide (SiC) films were deposited in a commercial Plasma-Quest Model-357 ECR-CVD reactor using $CH_4/SiH_4/Ar$ gas mixtures. The ECR-CVD system configuration has been described elsewhere [8].

The substrates used were (100) oriented, p-type silicon wafers with a resistivity of 5–15 Ωcm, and in size of 15×30 mm^2. The substrates were ex situ cleaned by a modified spin-etching method [9] to provide a hydrogen-terminated silicon surface and prevent surface oxidation during air exposure [10]. The substrate was then loaded into the reactor within a few minutes after cleaning.

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The deposition conditions of SiC films were as follows. Ar was used as the plasma excitation gas, and CH_4 and SiH_4 were used as reaction gases. The total pressure, substrate temperature, Ar flow rate, and SiH_4 flow rate were kept constant at 20 mtorr, 200 °C, 100 sccm, and 5 sccm, respectively. The change of CH_4 flow rate varied the CH_4/SiH_4 flow ratio. The effect of microwave power was investigated by keeping the CH_4 and SiH_4 flow rates at 5 and 2.5 sccm, respectively. The deposition time was 30 min in all cases. Since the microwave power can lead to quite different self-induced temperatures without any compensation, the substrate was maintained at 200 ± 2 °C by a resistive heater intentionally.

Crystalline structure of the deposited SiC film was examined in a JEOL 2000FX STEM. The samples used for both plan-view and cross-sectional transmission electron microscopy (XTEM) inspection were cut into a size of 2×5 mm^2. The XTEM is a destructive analysis technique to observe the deposited film with electron beams perpendicular to the sample surface, providing the information of crystalline phase and lattice constant of the deposited films.

Fourier transform infrared spectroscopy (FTIR) spectra were obtained with a BIO-RAD FTS-40 spectrometer from 400 to 4000 cm^{-1}, with a resolution of 4 cm^{-1} and 16 scan times. XPS analyses were performed in a VG Microtech MT-500 spectrometer. The spectrometer was equipped with a hemispherical analyzer and all X-ray photoelectron spectroscopy (XPS) data presented here were acquired using the MgKα X-rays (1253.6 eV). Peak positions were calibrated with respect to the C1s peak at 284.6 eV from the adventitious hydrocarbon contamination. The composition X of the deposited film (SiC_X) can be evaluated from the ratio of the C1s to Si2p peak areas corrected by suitable sensitivity factors of $S_{Si}=0.27$ and $S_C=0.25$ [11]. Rutherford backscattering spectroscopy (RBS) was performed in a Canberra Series 35 Plus spectrometer using 2.0 MeV helium ions, and a backscattering angle of 170°.

3. Results and discussion

An appropriate CH_4/SiH_4 flow ratio is crucial for crystalline SiC formation according to our results. Fig. 1 shows the XTEM dark-field and bright-field micrographs with electron diffraction patterns of the films grown at 200 °C, 1200 W, and various CH_4/SiH_4 flow ratios from 0.5 to 5. Fig. 1a shows that at a CH_4/SiH_4 flow ratio of 0.5, the deposited film on Si is of polycrystalline-Si (poly-Si) determined by the ring spacing of the electron diffraction pattern. When the CH_4/SiH_4 flow ratio was increased to 1 (the same as in the cases of flow ratios of 1.5, 2 and 4), Fig. 1b shows that the films grown are of polycrystalline structure. Using the spot diffraction pattern of the Si⟨100⟩ zone in Fig. 1b as a reference, the structure and lattice constant of the film can be determined by measuring the ring spacing of the same electron diffraction pattern in Fig. 1b. The film was identified to be a zinc-blende structure with a lattice constant of 0.436 ± 0.005 nm, which is identical to that of bulk β-SiC [12]. A plan-view TEM micrograph of the $CH_4/SiH_4=2$ film is shown in Fig. 2. The grain size of β-SiC is approximately 0.20 μm. However, amorphous SiC (a-SiC) is obtained when the CH_4/SiH_4 flow ratio is 5 (the same as in case of flow ratio of 10), as shown in Fig. 1c.

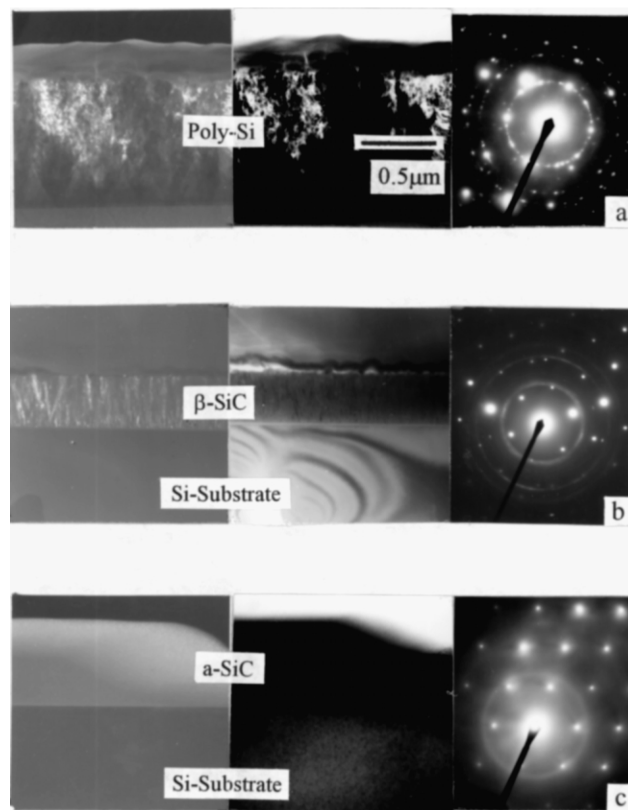

Fig. 1. XTEM dark-field and bright-field micrographs with selected-area electron diffraction patterns of the films grown at 200 °C, 1200 W, with (a) $CH_4/SiH_4=0.5$, (b) $CH_4/SiH_4=1$, and (c) $CH_4/SiH_4=5$.

According to the XTEM results, it is interesting to find that at 200 °C and 1200 W, polycrystalline β-SiC film can be grown as the CH_4/SiH_4 flow ratio is from 1 to 4. Polycrystalline-Si is obtained when the CH_4/SiH_4 flow ratio is approximately 0.5, while amorphous-SiC is deposited as the CH_4/SiH_4 ratio is approximately 5 or higher. The above results were also confirmed by Fourier transform infrared (FTIR), X-ray photoelectron spectrometry (XPS), and RBS analyzes.

Fig. 3 shows FTIR spectra of the films deposited at various CH_4/SiH_4 flow ratios. The stretching mode of SiC appears at 800 cm^{-1} [13]. The weak peaks at approximately 1100 and 600 cm^{-1} are due to SiO_2 and

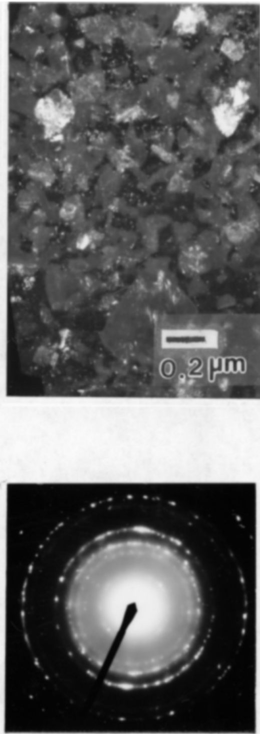

Fig. 2. Plan-view TEM micrograph of the microcrystalline β-SiC layer grown at 200 °C, 1200 W, and $CH_4/SiH_4=2$.

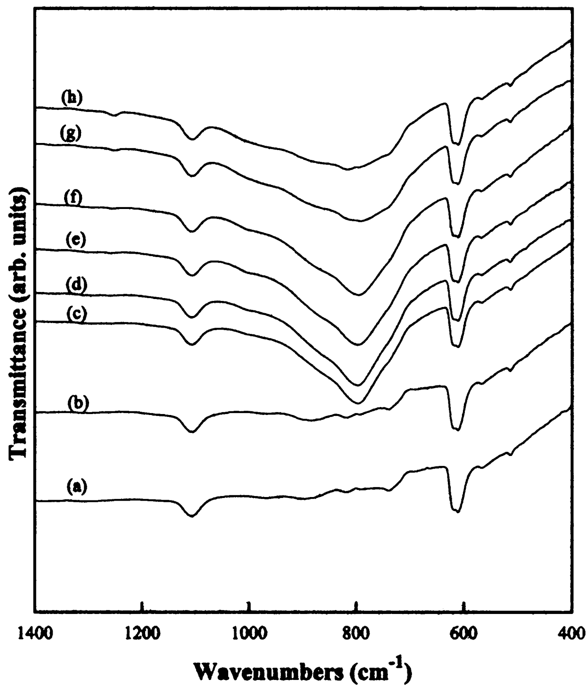

Fig. 3. FTIR transmission spectra of the Si substrate and the films deposited at various CH_4/SiH_4 flow ratios. (a) Si substrate, (b) $CH_4/SiH_4=0.5$, (c) $CH_4/SiH_4=1$, (d) $CH_4/SiH_4=1.5$, (e) $CH_4/SiH_4=2$, (f) $CH_4/SiH_4=4$, (g) $CH_4/SiH_4=5$, and (h) $CH_4/SiH_4=10$.

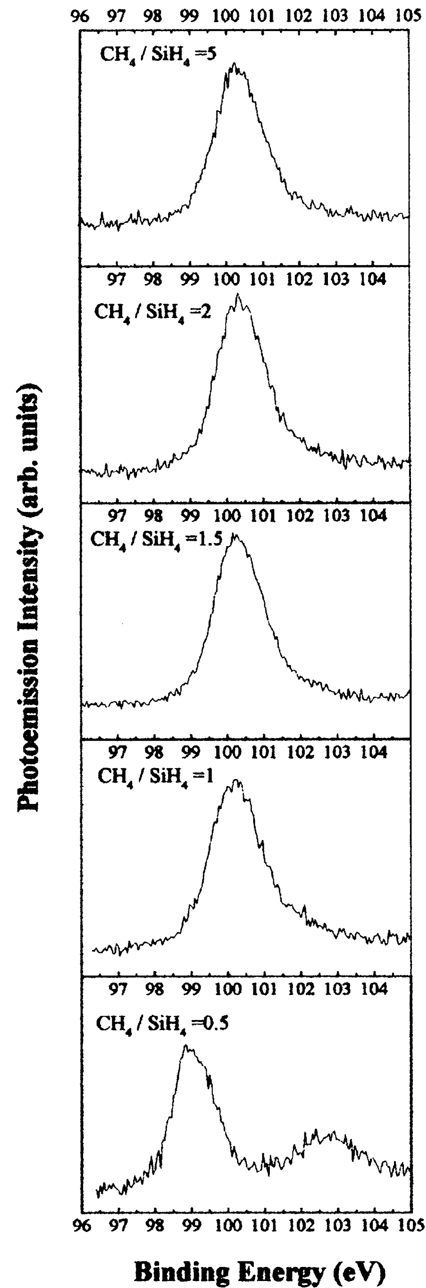

Fig. 4. XPS core level peaks of Si2p for the films deposited at various CH_4/SiH_4 flow ratios.

Si, respectively. In Fig. 3 we can clearly observe from Fig. 3 that when the CH_4/SiH_4 flow ratio is 0.5, the spectrum only exhibits peaks of Si and SiO_2, which are the same as those of the bare Si substrate. When the CH_4/SiH_4 flow ratios are of 1 and higher, the peak which appears at 800 cm^{-1} indicates the formation of SiC. The above results are consistent with those obtained by XTEM.

Fig. 4 shows the high resolution XPS spectra of the films deposited at various CH_4/SiH_4 flow ratios. The Si2p spectra exhibit two peaks which are assigned to

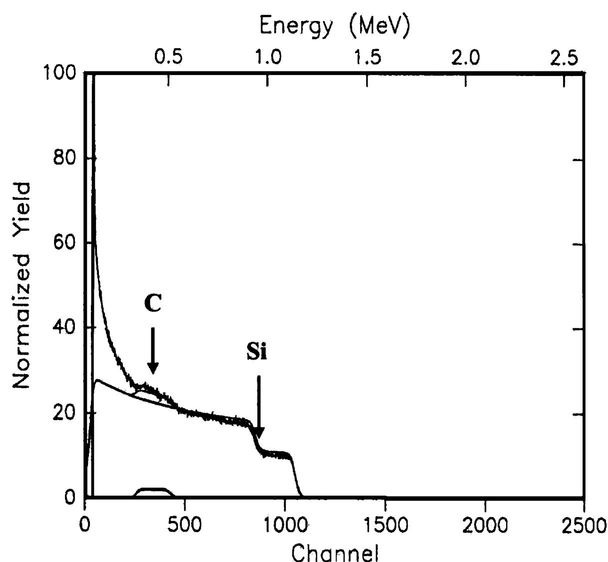

Fig. 5. Rutherford backscattering spectrum for a β-SiC layer deposited at a CH_4/SiH_4 flow ratio of 1.

elemental Si (99 eV) and SiC (100.4 eV), respectively. The binding energies measured here are slightly deviated from those obtained by other researchers [14], but an energy difference ΔSiC (C1s–Si2p) of 182.2 eV is in agreement with those reported [14]. Fig. 4a shows that only Si is formed at a CH_4/SiH_4 flow ratio of 0.5. When the CH_4/SiH_4 flow ratio is increased to 1 (Fig. 4b), the Si2p peak shifts from the binding energy of elemental Si to that of the SiC. From Fig. 4, it can be found that as the CH_4/SiH_4 flow ratio is increased to 1 and higher, only SiC is formed.

Fig. 5 presents the typical RBS spectrum of the $CH_4/SiH_4=1$ sample. The scattered points indicate the experimental data and the smooth line represents the simulated fit to the data. The channel numbers, at which steps occur, correspond to those of carbon and silicon. Similar data measured on the other samples deposited at different CH_4/SiH_4 flow ratios show only small variations from Fig. 5. Table 1 shows the ratio of C/Si obtained from XPS and RBS analyses. It was found that both XPS and RBS analyzes show the same results on the composition of deposited films.

According to XTEM, FTIR, XPS and RBS analyses of this study, we observe that at 200 °C and 1200 W, polycrystalline-SiC film can be grown as the CH_4/SiH_4 flow ratio is from 1 to 4. Polycrystalline-Si is obtained when the CH_4/SiH_4 flow ratio is 0.5. We expect that the mixed films of Si and SiC, or Si*CX* are possibly grown when the ratio is between 0.5 and 1 because in a previous study [15], we reported that a mixed film of poly-Si and a-SiC was obtained when the CH_4/SiH_4 flow ratio is less than 2, using H_2 as the carrier gas. Therefore, we believe that the transmission region maybe too narrow to be observed in this study when Ar is used as the carrier gas. Also, according to FTIR, XPS and RBS analyses, we find that at 200 °C and 1200 W, stoichiometric SiC films can be grown as the CH_4/SiH_4 flow ratio is as high as 5 and no amorphous carbon is observed. The deposition of amorphous SiC (a-SiC) is confirmed by the XTEM dark-field and bright-field micrographs with electron diffraction patterns in Fig. 1.

The bonding energy of a Si–H bond is 70.4 kcal mol^{-1}, while that for a C–H bond it is 98.8 kcal mol^{-1} [16]. Compared with CH_4, SiH_4 is easier to decompose. This is why the CH_4/SiH_4 flow ratio is one of the key factors in SiC growth. Deviated from utilizing the high microwave power (1200 W) which supplies sufficient energy to dissociate CH_4 efficiently and form SiC in this work, other experiments in our group which employ a microwave power of 300 W or lower show that no SiC is deposited at all the above CH_4/SiH_4 flow ratios under similar growth conditions. At the same time, since only poly-crystalline Si films are obtained, it suggests that the sticking coefficient of CH_x radicals is lower than that of SiH_x radicals. Therefore, when the CH_4/SiH_4 flow ratio is 0.5, the amount of adsorbed CH_x radicals is insufficient to react with SiH_x for SiC formation and consequently the loosely adsorbed CH_x radicals desorb from the surface. The major species adsorbed on substrate surface are SiH_x radicals so that polycrystalline Si is deposited. As the CH_4/SiH_4 flow ratio is increased to 1 by increasing CH_4, i.e. the concentration of adsorbed CH_x on the substrate is comparable with that of SiH_x, the adsorbed SiH_x and CH_x radicals react and form polycrystalline β-SiC. However, when the CH_4/SiH_4 flow ratio is increased to 5 or higher by further increasing CH_4 flow, i.e. in a condition that the amount of CH_x is much higher than that of SiH_x, the rate of SiC formation becomes so high that the SiC molecules on the substrate surface do not have enough time to migrate to suitable sites for crystalline SiC formation, resulting in the deposition of amorphous SiC.

Experiments with varied microwave powers were conducted at a total pressure of 20 mtorr and a temperature of 200 °C. The CH_4/SiH_4 flow ratio was kept constant at 2. Microstructures of the films grown at

Table 1
SiC composition in the films deposited at various CH_4/SiH_4 flow ratios obtained from RBS and XPS analyses

CH_4/SiH_4 flow ratio	C/Si ratio (RBS)	C/Si ratio (XPS)	Error
0.5	–[a]	–[a]	–[a]
1	1.0	0.99	±0.01
1.5	1.0	0.99	±0.01
2	1.02	1.00	±0.02
5	1.08	1.05	±0.03

[a] There are no data for the film grown at $CH_4/SiH_4=0.5$ because no Si–C bonds formed under this condition.

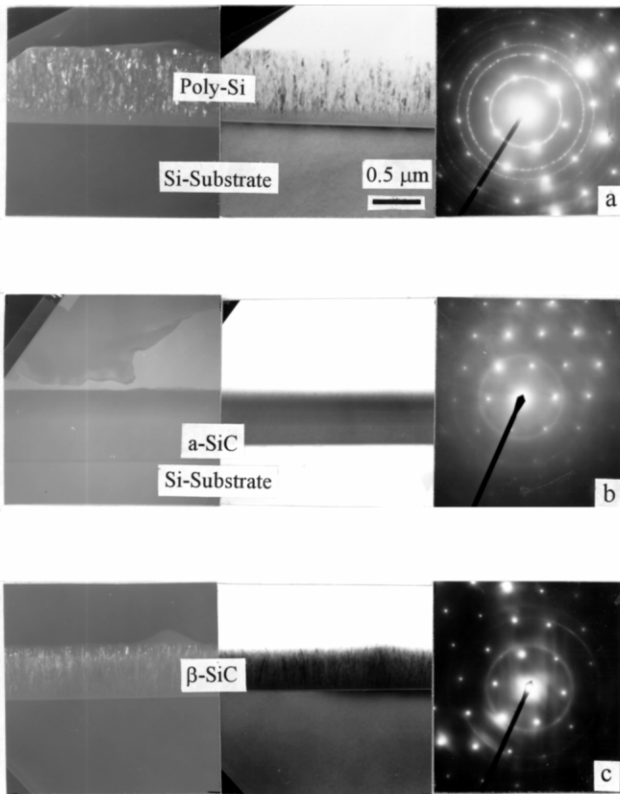

Fig. 6. XTEM dark-field and bright-field micrographs with selected-area electron diffraction patterns of the films grown at 200 °C, $CH_4/SiH_4=2$, and a microwave power of (a) 300, (b) 500, and (c) 1500 W.

different microwave powers were investigated and the results are shown in Fig. 6. When the microwave power is 300 W, Fig. 6a indicates that only polycrystalline Si is deposited. The XTEM micrograph of amorphous SiC is shown in Fig. 6b which is deposited at 500 W. However, when the microwave power is increased to 1200 W and higher, polycrystalline β-SiC films are deposited as shown in Fig. 6c.

Fig. 7 shows FTIR spectra of the bare silicon wafer and the films deposited at different microwave powers. The films grown at 300 W have a characteristic curve identical to that of the bare silicon, indicating that no SiC bonds were formed. An absorption peak at 800 cm^{-1}, due to the stretching mode of SiC, can be found in the other four curves measured from the 500, 800, 1200 and 1500 W samples. The full width at half-maximum (FWHM) of this peak becomes narrower with increasing microwave power, which indicates that film crystallinity is improved at higher microwave powers. Therefore, a sufficient microwave power is required to deposit polycrystalline β-SiC.

When the microwave power is as low as 300 W, the deposited film is still poly-Si (Fig. 6a) even at a CH_4/SiH_4 flow ratio of 2. That is still because the energy needed for SH_x formation is lower than that of CH_4 decomposition and the energy is enough for the subsequent decomposition of SiH_x to occur. However, at 500 W microwave power, the energy supplied by plasma may be enough for the dissociation of CH_4 so that most SiH_x radicals can react with CH_x radicals to form SiC, which may not have enough energy for surface rearrangement. Therefore, amorphous SiC could be observed in the film (Fig. 6b). As the microwave power is increased to 1200 W and higher, the supplied energy is sufficient for both the formation of radicals and the crystallization of amorphous SiC into polycrystalline β-SiC (Fig. 6c). The FTIR data (Fig. 7) also show the change of film type from poly-Si to SiC.

The self-induced bias voltage observed during the film deposition is between 0 and 10 V and varies within a narrow range. We believe that there should be no significant influence of self-induced bias voltage on the SiC formation due to such a small value of self-induced bias voltage.

4. Conclusion

β-SiC films were deposited on silicon substrates by ECR-CVD from $SiH_4/CH_4/Ar$ mixtures at 200 °C. Crystalline structure and chemical composition of the deposited film were influenced by CH_4/SiH_4 flow ratio and microwave power. With a sufficient energy supply from microwave power of 1200 W and a CH_4/SiH_4 flow ratio of 1 and higher, stoichiometric SiC could be deposited on Si substrates. For the case of microwave power 1200 W, polycrystalline β-SiC was grown at

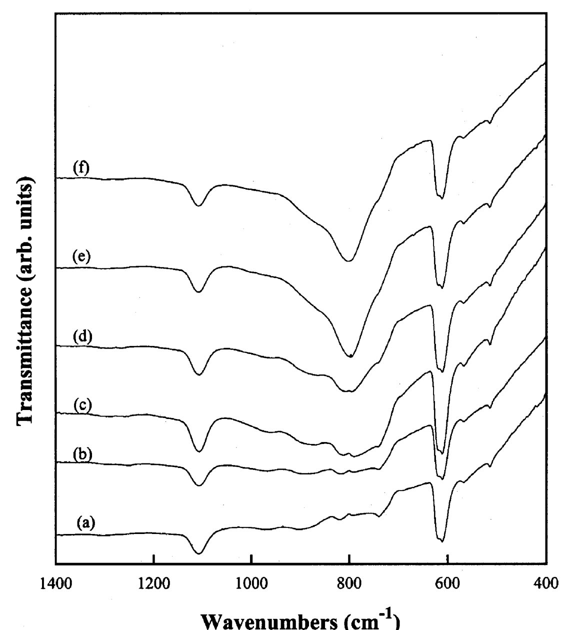

Fig. 7. FTIR transmission spectra of the Si substrate and the films deposited at various microwave powers. (a) Si substrate, (b) 300, (c) 500, (d) 800, (e) 1200, and (f) 1500 W.

CH_4/SiH_4 flow ratios between 1 and 4, whereas amorphous SiC was obtained at the CH_4/SiH_4 flow ratios higher than 4. Under CH_4/SiH_4 flow ratio and temperature of 2 and 200 °C, respectively, when the CH_4/SiH_4 flow ratio was 0.5, only polycrystalline Si could be deposited. When the microwave power was 300 W, polycrystalline Si was deposited. At a microwave power of 500 W, amorphous SiC film was deposited. However, when the microwave power was increased to 1200 W and higher, polycrystalline β-SiC films were deposited.

Acknowledgments

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