Effects of CH$_4$/SiH$_4$ flow ratio and microwave power on the growth of $\beta$-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 $\beta$-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 $\beta$-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 $\alpha$-Al$_2$O$_3$ [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 $\beta$-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 $\Omega$cm, 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.
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 BIORAD 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 (SiCx) can be evaluated from the ratio of the C1s to Si2p peak areas corrected by suitable sensitivity factors of $S_{c}$ = 0.27 and $S_{x}$ = 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, 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 spectroscopy (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 CH₄/SiH₄ = 2.

Fig. 3. FTIR transmission spectra of the Si substrate and the films deposited at various CH₄/SiH₄ flow ratios. (a) Si substrate, (b) CH₄/SiH₄ = 0.5, (c) CH₄/SiH₄ = 1, (d) CH₄/SiH₄ = 1.5, (e) CH₄/SiH₄ = 2, (f) CH₄/SiH₄ = 4, (g) CH₄/SiH₄ = 5, and (h) CH₄/SiH₄ = 10.

Fig. 4. XPS core level peaks of Si2p for the films deposited at various CH₄/SiH₄ flow ratios. Si, respectively. In Fig. 3 we can clearly observe from Fig. 3 that when the CH₄/SiH₄ flow ratio is 0.5, the spectrum only exhibits peaks of Si and SiO₂, which are the same as those of the bare Si substrate. When the CH₄/SiH₄ 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 CH₄/SiH₄ flow ratios. The Si2p spectra exhibit two peaks which are assigned to
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 ASiC (C1s–Si2p) of 182.2 eV is in agreement with those reported [14]. Fig. 4a shows that only Si is formed at a CHy/SiH flow ratio of 0.5. When the CHy/SiH 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 CHy/SiH flow ratio is increased to 1 and higher, only SiC is formed.

Fig. 5 presents the typical RBS spectrum of the CH4/SiH flow ratio = 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 CHy/SiH 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 CH4/SiH flow ratio is from 1 to 4. Polycrystalline-Si is obtained when the CH4/SiH flow ratio is 0.5. We expect that the mixed films of Si and SiC, or SiCx 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 CH4/SiH flow ratio is less than 2, using H2 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 CH4/SiH 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 CH4, SiH4 is easier to decompose. This is why the CHy/SiH 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 CH4 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 CH4/SiH flow ratios under similar growth conditions. At the same time, since only polycrystalline Si films are obtained, it suggests that the sticking coefficient of CH radicals is lower than that of SiH4 radicals. Therefore, when the CHy/SiH flow ratio is 0.5, the amount of adsorbed CH radicals is insufficient to react with SiH4 for SiC formation and consequently the loosely adsorbed CH radicals desorb from the surface. The major species adsorbed on substrate surface are SiH4 radicals so that polycrystalline Si is deposited. As the CHy/SiH flow ratio is increased to 1 by increasing CH4, i.e., the concentration of adsorbed CH4 on the substrate is comparable with that of SiH4, the adsorbed SiH4 and CH radicals react and form polycrystalline β-SiC. However, when the CHy/SiH flow ratio is increased to 5 or higher by further increasing CH4 flow, i.e., in a condition that the amount of CH4 is much higher than that of SiH4, 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 CH4/SiH flow ratio was kept constant at 2. Microstructures of the films grown at

![Fig. 5. Rutherford backscattering spectrum for a β-SiC layer deposited at a CH4/SiH flow ratio of 1.](image-url)

### Table 1

<table>
<thead>
<tr>
<th>CH4/SiH flow ratio</th>
<th>C/Si ratio (RBS)</th>
<th>C/Si ratio (XPS)</th>
<th>Error</th>
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<td>~</td>
<td>~</td>
</tr>
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<td>5</td>
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<td>1.05</td>
<td>±0.03</td>
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</table>

*There are no data for the film grown at CH4/SiH = 0.5 because no Si–C bonds formed under this condition.
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$_4$ formation is lower than that of CH$_4$ decomposition and the energy is enough for the subsequent decomposition of SiH$_4$ 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$_4$ radicals can react with CH$_4$ 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
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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References