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Growth and Characterization of SiC Films by Hot-Wire Chemical Vapor Deposition at Low Substrate Temperature Using $SiF_4/CH_4/H_2$ Mixture

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Microcrystalline SiC films were grown by hot-wire chemical vapor deposition (HW-CVD) at a low substrate temperature using a $SiF_4/CH_4/H_2$ mixture, and their structural properties were characterized. Low growth pressure resulted in a narrow full width at half maximum (FWHM) of the Si-C peak in Fourier transform infrared absorption spectroscopy (FT-IR) spectra. The deposition rate and the FWHM value increased with increasing filament temperature. This seemed to be caused by change of the concentration ratio of precursors on the growth surface with increasing filament temperature. Also, the film crystallinity depended on the CH_4/SiF_4 flow rate ratio, and μc-3C-SiC(111) films were successfully obtained at low substrate temperature of 250°C.

KEYWORDS: hot wire, CVD, 3C-SiC, SiF_4 ,H_2 dilution, low-temperature film growth

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1. Introduction

Silicon carbide (SiC) is a promising material for a wide variety of device applications and for replacing conventional semiconductor materials such as silicon and gallium arsenide (GaAs) in certain critical applications. In particular, SiC has attracted recent attention for use in high-power and high-temperature devices because of its superior properties such as a wide band gap, a high breakdown field, and a high thermal conductivity.[1)] It is widely recognized that high temperatures above 1200°C are required for the preparation of crystalline SiC films by thermal chemical vapor deposition (CVD). This high growth temperature prevents flexibility in the design of electronic devices.

Amorphous SiC and microcrystalline SiC films can be prepared at substrate temperatures lower than 300°C by plasma-enhanced (PE) CVD and hot-wire (HW) CVD. Recently the low-temperature epitaxial growth of 3C-SiC has also been reported.[2)] In the SiC growth by PECVD, various Si sources, such as SiH_4,[3)] methylsilanes,[4)] and silicon halide,[5)] have been used. SiH_4 and methylsilane have also been applied to HW-CVD.[6,7)] Here, atomic hydrogen plays a key role.

It is expected that fluorosilane gases can be used in Si film growth for the removal of the surface oxide from the substrate without cleaning procedures because of their etching capability,[8)] which is advantageous for producing SiC films with favorable crystallinity[9,10)] and electrical properties.[11)] Silicon tetrafluoride (SiF_4) has been used as a Si source for preparing SiC film by plasma CVD.[12)] However, SiC film growth by HW-CVD using silicon halide sources has not been reported.

In this study, microcrystalline SiC films were grown by HW-CVD at a low substrate temperature using a $SiF_4/CH_4/H_2$ mixture, and their structural properties were characterized.

2. Experimental Procedure

The SiC films were grown on Si(001) and Si(111) substrates using a HW-CVD system with an "S"-shaped tungsten filament as a hot wire. The filament diameter and length were 0.5 and 150 mm, respectively. The filament-substrate distance was maintained at 40 mm. The growth chamber was evacuated to 2×10^{-6} Torr using a turbo-molecular

pump. The source gases were SiF_4 (>99.999%) and CH_4 (>99.999%). H_2 (>99.99999%) was used as a dilution gas. The substrates were cleaned by an ultrasonic treatment in acetone, etched by 5% hydrofluoric acid, and rinsed in deionized water prior to loading into the CVD system. The growth pressure (P_G) and wire temperature (T_W) were varied from 0.5 to 4.5 Torr and from 1500 to 2000°C, respectively. The SiF_4, CH_4, and H_2 gas flow rates were varied from 3.5 to 5.0 sccm, 1.0 to 5.0 sccm, and 70 to 150 sccm, respectively. The substrate temperature (T_S) was varied from 250 to 500°C.

The structural properties and bonding configuration of the SiC films were characterized by X-ray diffractometry (XRD), Fourier transform infrared absorption spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS).

3. Results and Discussion

Figures 1 and 2 show the dependence of FT-IR spectra and the concentration of elements in the film on the growth pressure, respectively. Low growth pressure resulted in a narrow full width at half maximum (FWHM) of the Si-C bond at 800 cm^{-1}. The narrow FWHM suggested that crystalline SiC films were obtained. From the XPS measurements, F was found to be incorporated in the film and its concentration increased with increasing growth pressure. Therefore, at a higher growth pressure, the film might be amorphous SiC. Because the mean free path is shorter at a higher pressure, the flux of atomic hydrogens generated on the wire might decrease in number on the growth surface by a gas-phase reaction. Thus, the extraction reaction of F on the growth surface by H^* may be suppressed with decreasing H^* concentration.

The temperature of the W wire was varied to increase the flux of precursors (SiF_x^* and CH_x^*) and H^* on the growth surface. Figures 3 and 4 show the dependence of deposition rate and FT-IR spectra on the wire temperature T_W, respectively. A higher wire temperature resulted in a higher deposition rate. Thus, the flux of the precursors seemed to increase with increasing wire temperature. However, the FWHM of the Si-C peak in the FT-IR spectra became wider at the higher wire temperature. This result suggests that the ratio of SiF_x^* to CH_x^* on the growth surface changes because of the difference of the gas decomposition temperature on the W wire between SiF_4 and CH_4.

The SiC films were grown with various CH_4/SiF_4 flow rate ratios. Figures 5 and 6 show the dependence of the XRD pattern and the SiC grain size on the CH_4/SiF_4 ratio, respectively. From the XRD pattern, μc-3C-SiC films were successfully obtained by controlling the CH_4/SiF_4 ratio. The SiC grain size was calculated by the Scherrer equation from the FWHM values of the 3C-SiC peak. The grain size became maximum at a CH_4/SiF_4 ratio of around 0.6. Thus, it is suggested that the most suitable CH_4/SiF_4 flow rate ratio changes when the W wire temperature changes.

Figure 7 shows the dependence of the XRD pattern on the CH_4/SiF_4 ratio and the substrate temperature. At the CH_4/SiF_4 ratio of 1, crystalline SiC could not be obtained at 300°C. On the other hand, at the ratio of 0.4, we succeeded in growing μc-SiC films at the low substrate temperature of 250°C. Generally, it is well known that the role of atomic hydrogens, such as in the hydrogen termination at the surface, is very important in the crystal growth of Si and SiC films at low substrate temperatures.[13,14] In this study, the effect of the F radicals is also important in SiC crystal growth. Therefore, it is considered that the flux ratio of precursors, atomic hydrogens, and F radicals are a key factor in determining film crystallinity. The results of this study are in agreement with this consideration.

In the SiC films grown in this study, the Si-H configuration was not detected in the FT-IR spectra, although the substrate temperature decreased to 250°C. Figure 8 shows the dependence of the FT-IR spectra on the substrate temperature. No peak at around 2000 to 2100 cm^{-1}, originating from Si-H bonds, was detected. Generally, a-Si and μc-Si films grown by HW-CVD contain comparatively little hydrogen, less than that of films grown by PECVD.[15,16] However, in this study, the H concentration in the film was almost 0%. This result suggests that the F radicals generated from SiF_4 prevent the incorporation of H in the film. Therefore, controlling the concentration ratio of atomic hydrogens and F radicals on the growth surface is also important for improving crystallinity.

4. Conclusions

SiC films were grown by HW-CVD using a $SiF_4/CH_4/H_2$ mixture at a low substrate temperature, and their structural properties were characterized. Microcrystalline 3C-

SiC(111) films were successfully obtained at 250°C. The film crystallinity is improved by controlling the growth pressure and the CH_4/SiF_4 flow rate ratio. No Si-H bonds were detected, although the substrate temperature decreased to 250°C. The results suggest the importance of the ratio of atomic hydrogens to F radicals on the growth surface.

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Figure captions

Fig. 1. FT-IR spectra as a function of the growth pressure. The films were grown at T_W of 1800°C, T_S of 500°C, and CH_4/SiF_4 flow rate ratio (R) of 1.0.

Fig. 2. Dependence of film composition obtained from XPS on the growth pressure. The films were grown at T_W of 1800°C, T_S of 500°C, and R of 1.0.

Fig. 3. Dependence of deposition rate on the W wire temperature. The films were grown at T_S of 500°C, R of 1.0, and P_G of 1.0 Torr.

Fig. 4. FT-IR spectra as a function of the W wire temperature. The films were grown at T_S of 500°C, R of 1.0, and P_G of 1.0 Torr.

Fig. 5. XRD pattern as a function of the ratio of CH_4/SiH_4 flow rate. The films were grown at T_W of 2000°C, T_S of 500°C, and P_G of 1.0 Torr.

Fig. 6. Dependence of SiC grain size on the CH_4/SiH_4 ratio. The films were grown at T_W of 2000°C, T_S of 500°C, and P_G of 1.0 Torr.

Fig. 7. XRD pattern as a function of the substrate temperature and the CH_4/SiF_4 ratio at T_W of 2000°C and P_G of 1.0 Torr. (a) CH_4/SiF_4 ratio is 1.0. (b) CH_4/SiF_4 ratio is 0.4.

Fig. 8. FT-IR spectra as a function of the substrate temperature. The films were grown at T_W of 2000°C, R of 1.0, and P_G of 1.0 Torr.

Fig. 1

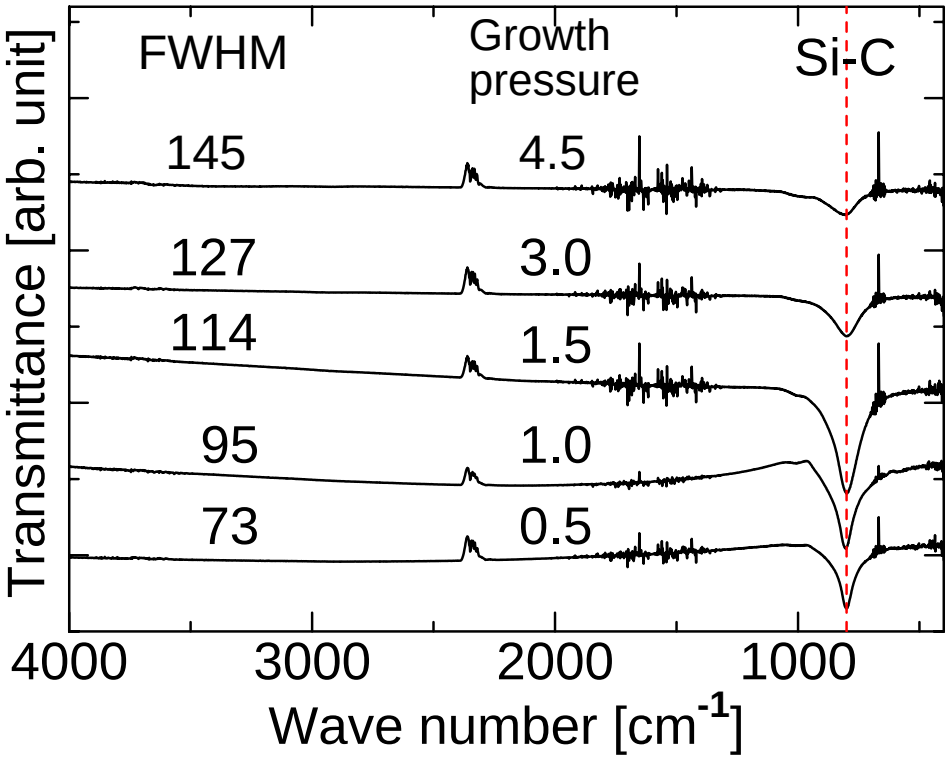

FWHM
Growth pressure
Si-C
145
4.5
127
3.0
114
1.5
95
1.0
73
0.5
Transmittance [arb. unit]
4000
3000
2000
1000
Wave number [cm-1]

Fig. 2

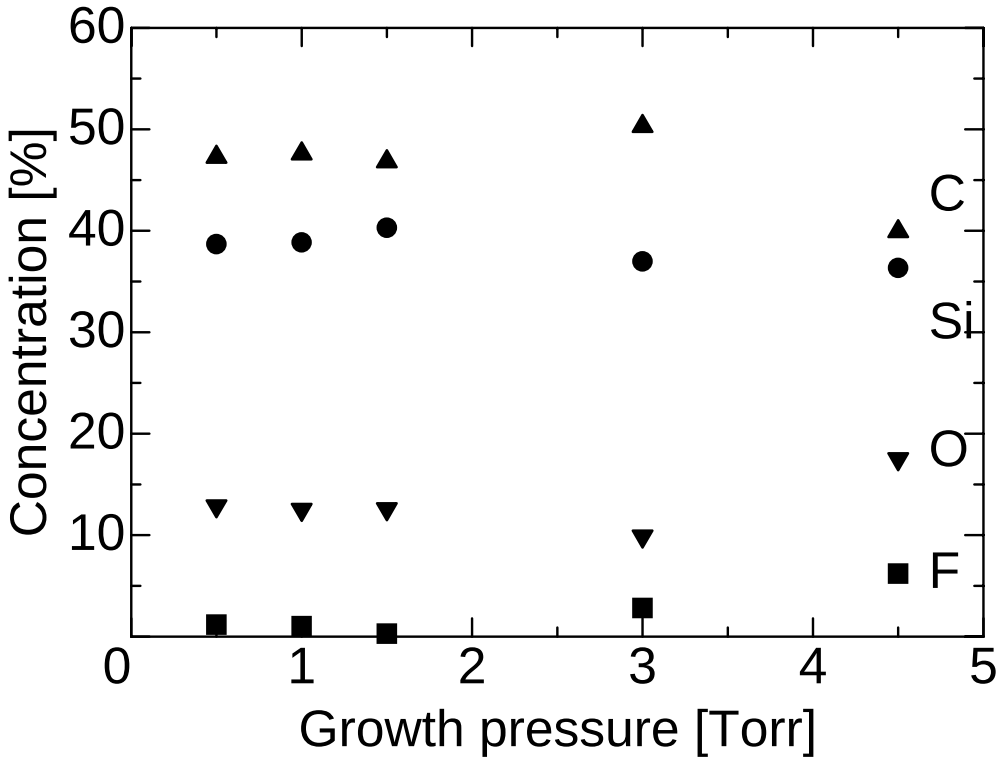

60
50
40
30
20
10
0
1
2
3
4
5
Concentration [%]
Growth pressure [Torr]
C
Si
O
F

Fig. 3

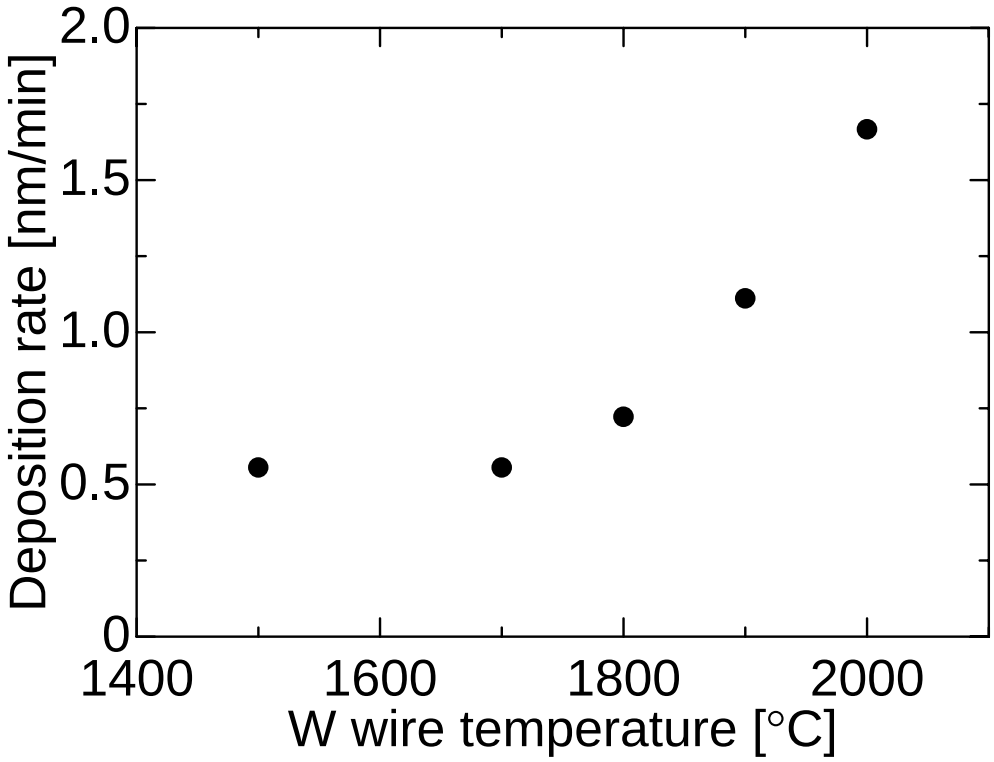

Deposition rate [nm/min]
2.0
1.5
1.0
0.5
0
1400
1600
1800
2000
W wire temperature [°C]

Fig. 4

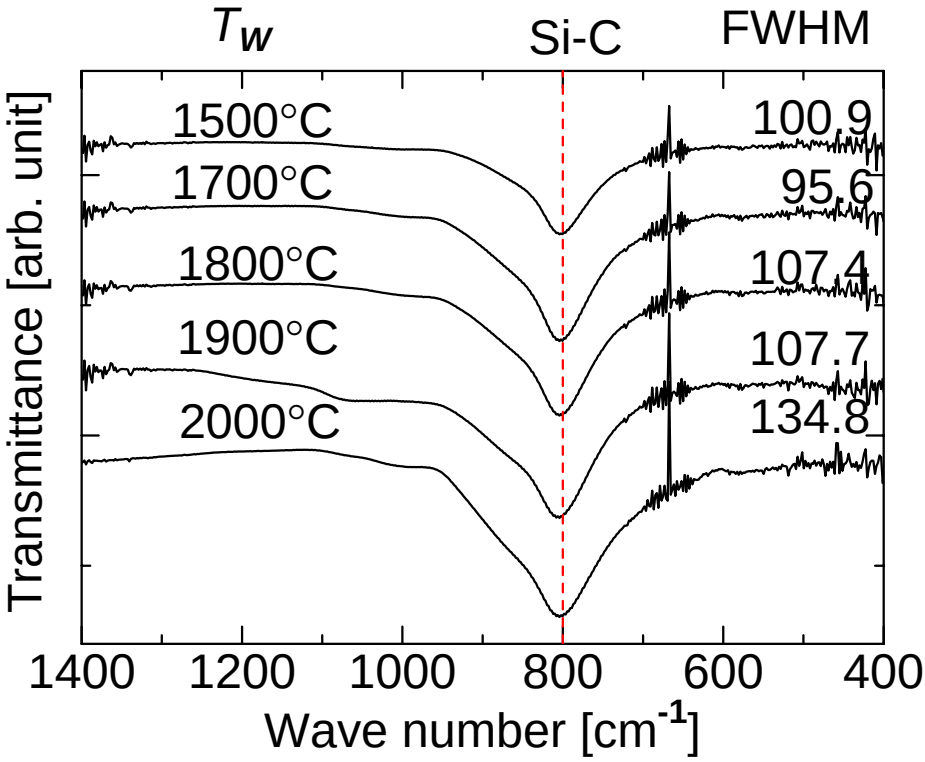

T_W
Si-C
FWHM
1500°C
1700°C
1800°C
1900°C
2000°C
100.9
95.6
107.4
107.7
134.8
Transmittance [arb. unit]
1400
1200
1000
800
600
400
Wave number [cm^{-1}]

Fig. 5

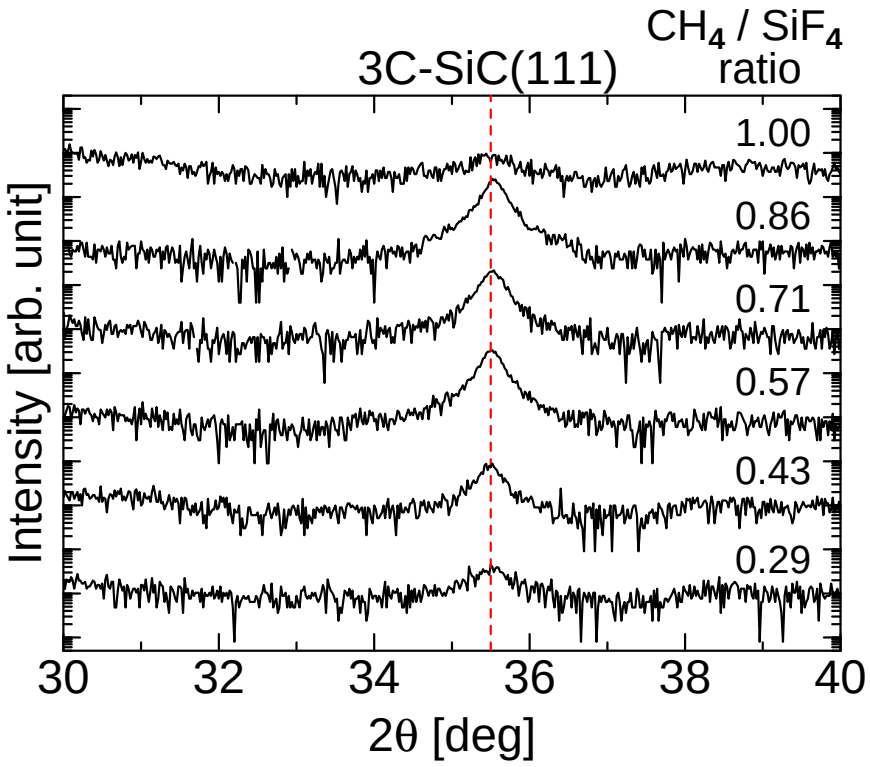

3C-SiC(111)
CH4 / SiF4 ratio
1.00
0.86
0.71
0.57
0.43
0.29
Intensity [arb. unit]
30
32
34
36
38
40
2θ [deg]

Fig. 6

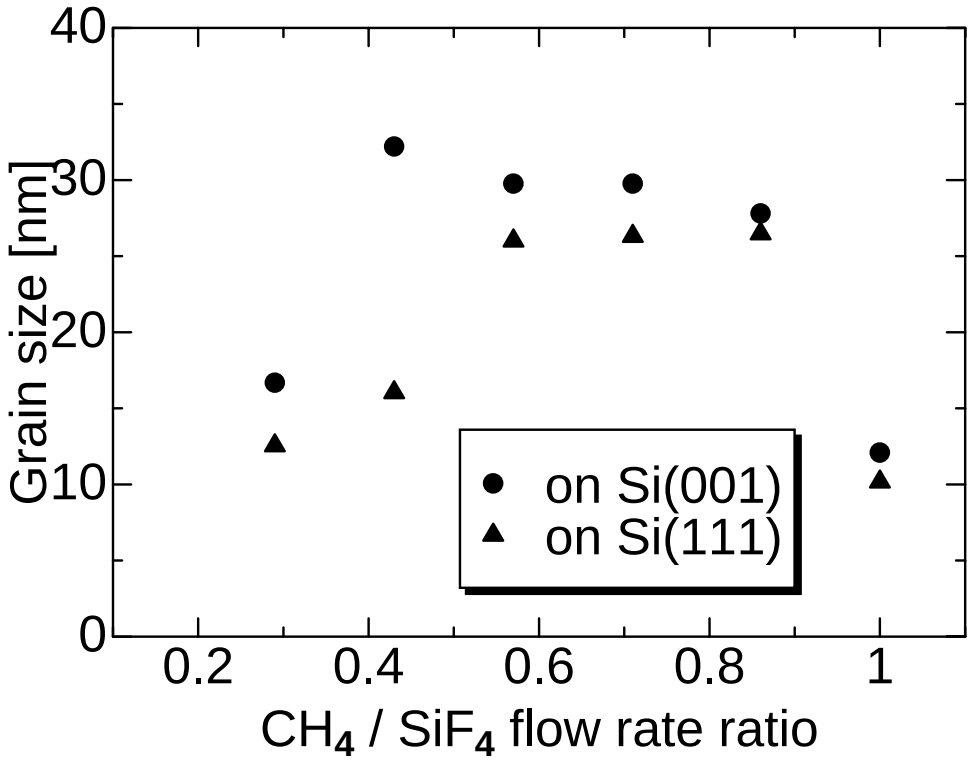

40
30
20
10
0
Grain size [nm]
0.2
0.4
0.6
0.8
1
CH4 / SiF4 flow rate ratio
on Si(001)
on Si(111)

Fig. 7

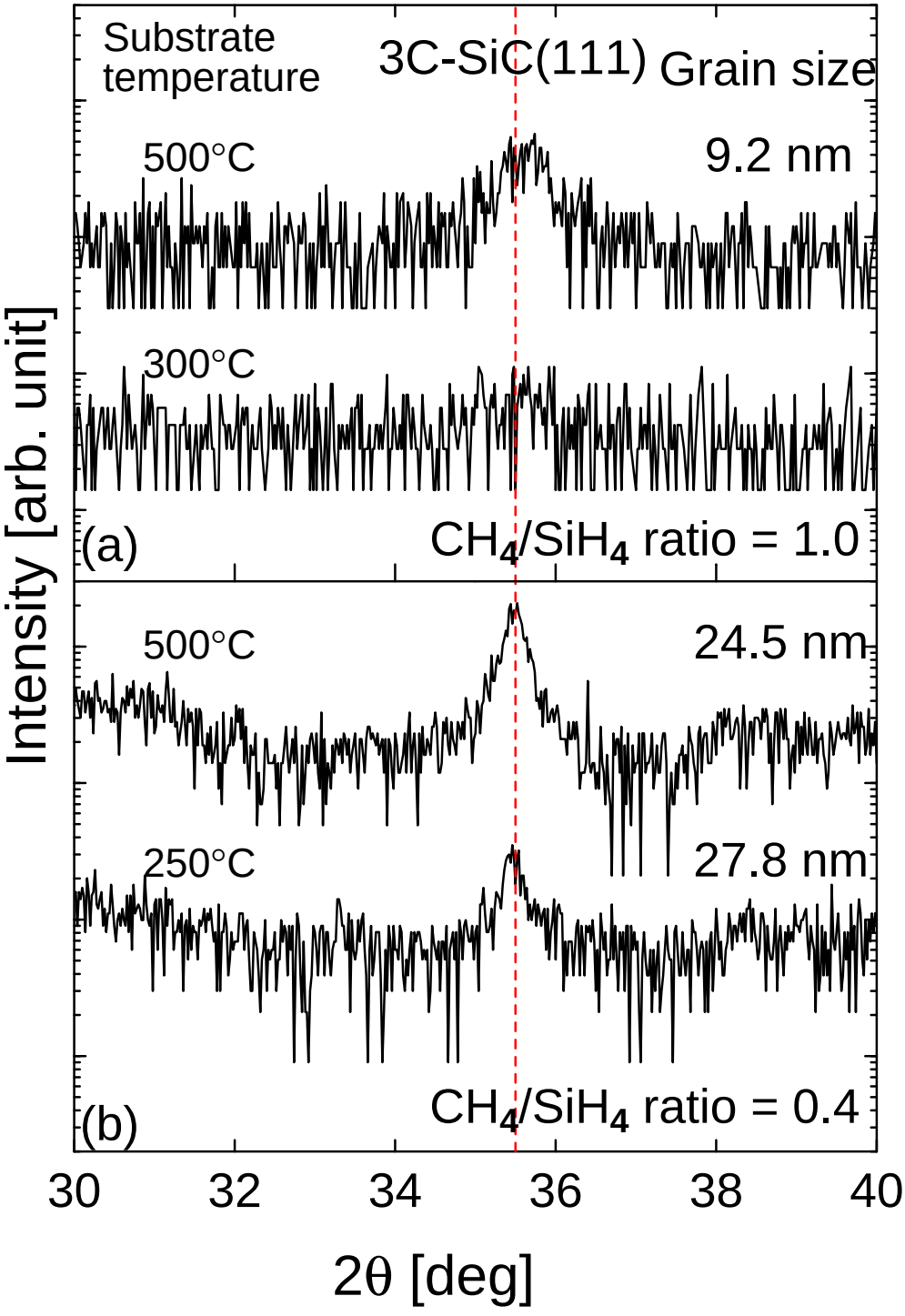
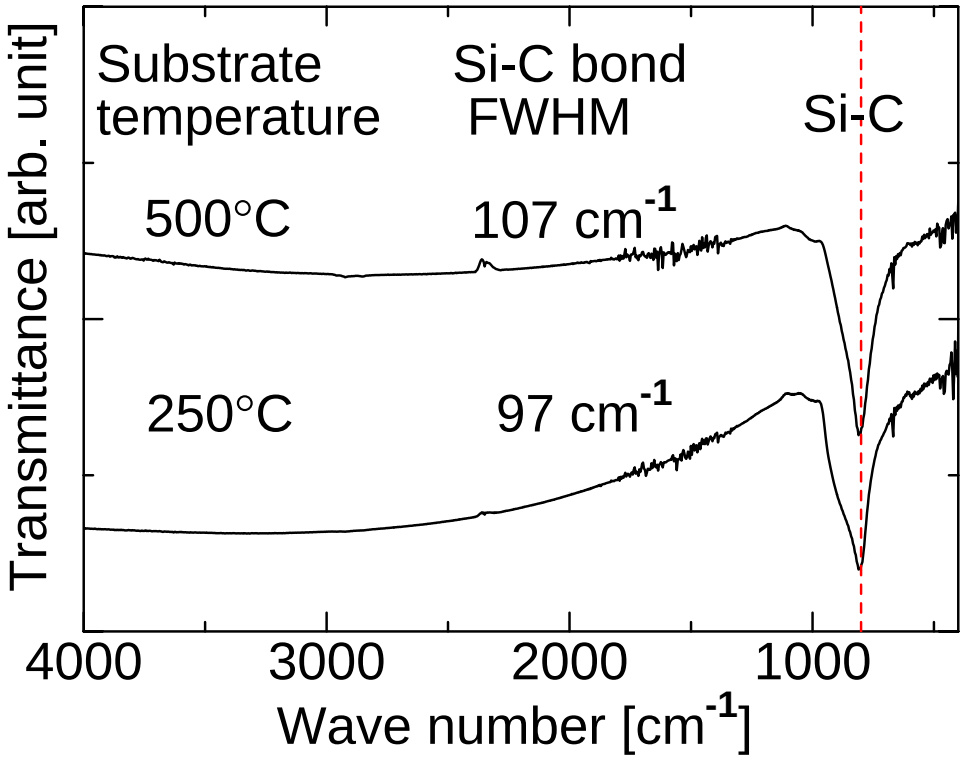

Substrate temperature
3C-SiC(111) Grain size
500°C
9.2 nm
300°C
(a)
CH4/SiH4 ratio = 1.0
500°C
24.5 nm
250°C
27.8 nm
(b)
CH4/SiH4 ratio = 0.4
Intensity [arb. unit]
30
32
34
36
38
40
2θ [deg]

Fig. 8


Substrate temperature
Si-C bond FWHM
Si-C
500°C
107 cm-1
250°C
97 cm-1
Transmittance [arb. unit]
4000
3000
2000
1000
Wave number [cm-1]