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CARBONIZATION LAYER GROWN BY ACETYLENE REACTION ON Si(100) AND (111) SURFACE USING LOW PRESSURE CHEMICAL VAPOR DEPOSITION

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Abstract. Surface carbonization on Si(100) and Si(111) using acetylene as single carbon source was performed in a low-pressure chemical vapor deposition chamber using rapid thermal technique. The dependences of crystallinity, crystal orientation and bonding state of carbonization layer on acetylene flow rates, pressures, temperatures and times were evaluated using X-ray diffractometry and electron probe microanalysis analytical techniques. The stoichiometric carbonization layer with good crystallinity, crystal orientation and bonding state was successfully formed at 1100 °C with C_2H_2 flow rate of 2 sccm and reaction pressure of 0.3 Torr.

Keywords: X-ray diffraction; chemical vapor deposition; semiconducting silicon compounds

Abstrak. Permukaan karbonisasi pada Si(100) dan Si(111) menggunakan acetylene (C_2H_2) sebagai sumber karbon tunggal dibuat di dalam ruang endapan wap kimia (CVD) bertekanan rendah menggunakan teknik cepat panas. Kebergantungan kristaliniti, orientasi kristal dan keadaan ikatan lapisan karbonisasi ke atas kadar aliran acetylene, tekanan, suhu dan masa telah dievaluasi dengan menggunakan teknik pembelauan X-Ray dan analisis 'electron probe microanalysis'. Lapisan karbonisasi stoikiometri dengan kristaliniti, orientasi kristal dan keadaan ikatan yang baik dapat dibentuk pada 1100 °C dengan kadar aliran C_2H_2 sebanyak 2 sccm dan tekanan tindak balas pada 0.3 Torr.

Kata kunci: Pembelauan X-ray; endapan wap kimia; campuran silikon separa-pengalir

1.0 INTRODUCTION

Silicon carbide (SiC) is a wide band-gap semiconductor with large saturation electron drift velocity, large breakdown electric field and large thermal conductivity. Therefore, this material is of great interest for high-temperature and high-power applications [1, 2]. Recently, SiC has also been expected as the substrates of gallium nitride (GaN) epitaxial growth [3]. The progress in development of SiC-based devices, however, has been slow due to the unavailability of large-area SiC substrate. The technique of SiC

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heteroepitaxy on Si substrates is an alternative way to produce large-area SiC substrates for device applications. Cubic-SiC (3C-SiC) is of particular interest, because of the possibility to grow its heteroepitaxial films on single crystalline silicon (Si) substrates by chemical vapor deposition (CVD) at lower temperature (below 1300 °C). Usually, SiC films are grown on Si substrate by CVD using silane (SiH_4) and hydrocarbon gases such as propane (C_3H_8) [4, 5]. However, this method requires high growth temperature (~1300 °C), which may induce high tensile stress because of the difference in thermal expansion coefficient between Si and SiC and the formation of the voids in Si substrates [6]. In order to overcome these problems, the use of single precursor gases such as organosilicon compounds instead of SiH_4 and C_3H_8 are useful, because they contain Si-C bonds in their molecules and are decompose at low temperature. In addition, simplified chemical vapor deposition (CVD) can be utilized because they are non-pyrophoric gases.

In the previous report, we presented the experimental results of low-temperature epitaxial growth of 3C-SiC on Si(100) and Si(111) substrates by rapid thermal triode plasma CVD and thermal CVD using dimethylsilane (DMS) and hydrogen radicals without carbonization process [7, 8]. To be specific, the effects of hydrogen dilution rate, reaction pressure and temperature on the quality of SiC films were reported.

In the present study, we have investigated the crystallinity and crystal orientation of carbonization layer obtained by acetylene (C_2H_2) reaction with Si(100) and (111) substrates for subsequent epitaxial growth of 3C-SiC. The effects of C_2H_2 flow rate, carbonization pressure, carbonization temperature and carbonization times on the quality of carbonization layer are reported.

2.0 EXPERIMENTAL STUDY

The schematic of the low-pressure chemical vapor deposition (LPCVD) apparatus is shown in Figure 1. C_2H_2 was used as a single carbon source and hydrogen (H_2) as a carrier gas. Experimental conditions are as follows: H_2 flow rate 112 sccm, C_2H_2 flow rate 1 ~ 10 sccm, substrate H_2 terminated Si(100), Si(111), total gas pressure during carbonization 0.1 ~ 1.4 Torr, substrate temperature 1000 ~ 1100 °C, carbonization time 10 ~ 90 minutes. The time chart for carbonization process is schematically shown in Figure 2 and is summarized as follows. After degreasing, dipping in buffered HF and rinsing in deionized water, Si(100) and (111) substrates were immersed in boiling ultrapure water. After evacuating the growth chamber to 10^{-7} Torr, the substrate temperature was raised to 350 °C. Substrates were heated on a carbon heater and the substrate temperature was measured using an optical pyrometer. With the supply of source gas, C_2H_2, substrate temperature was rapidly raised from 350 °C to carbonization temperature in hydrogen flows as shown in Figure 2. Their crystallinity and crystal orientation was evaluated using an X-ray diffractometer (RIGAKU, RAD-IIIA) equipped with a graphite monochromator. The composition of carbonization layer or the bonding state was evaluated using electron probe microanalysis (EPMA).

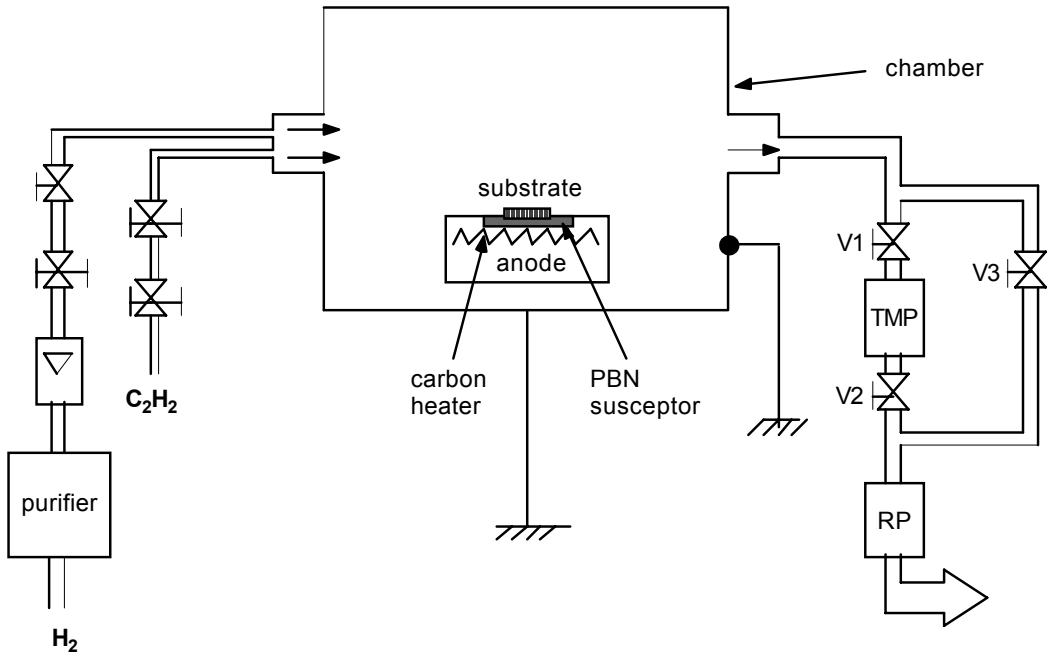


Figure 1 Schematic of low pressure chemical vapor deposition

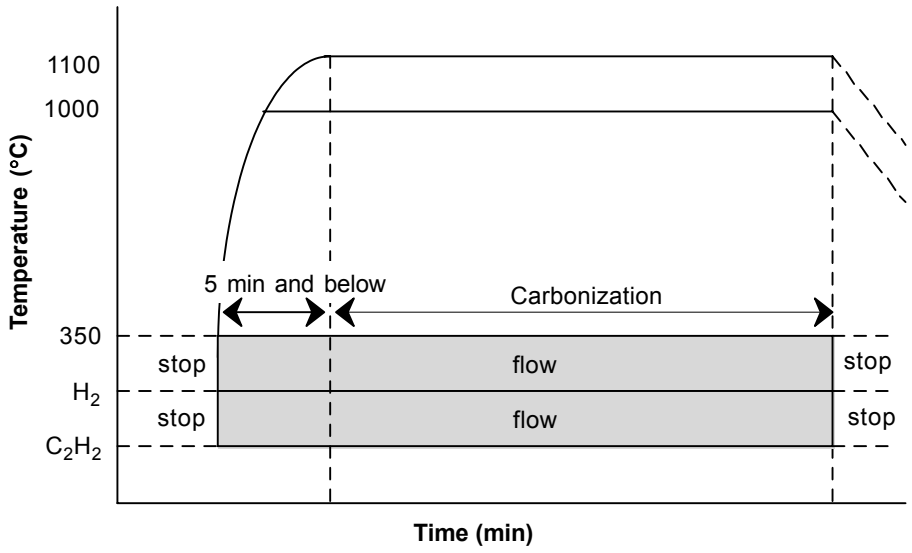


Figure 2 The time chart for carbonization process by low pressure chemical vapor deposition

3.0 RESULTS AND DISCUSSION

3.1 Variation of Crystallinity and Crystal Orientation at Various C_2H_2 Flow Rate, Carbonization Pressure, Carbonization Temperature and Carbonization Times

The typical ω-rocking curve of SiC(200) and SiC(111) peak of SiC thin film on Si(100) substrate is shown in Figure 3(a) and (b), respectively. From both figures, it can be concluded that 3C-SiC thin film with good orientation were obtained. However, as shown in Figure 3(b), two peaks were observed at the location of ±15° from the center peak. These two peaks show that there are two (111) plane which have ±15° slope referred to the substrate plane. The same results were also obtained and discussed in ref. [6]. Figure 4(a) and (b) shows the variations in full width at half maximum (FWHM) of X-ray diffraction (θ-2θ) and ω-rocking curve of SiC(111) and SiC(200) as a function of the C_2H_2 flow rate, respectively. It is shown in both figures that SiC(111) diffraction peak shows very small FWHM value at the C_2H_2 flow rate below 5 sccm and large FWHM value at 10 sccm. In this experiment, we do not observe any SiC(200) diffraction peak at 5 sccm and 10 sccm of C_2H_2 flow rate. From these results, the crystallinity and crystal orientation of carbonization layer degrades with the decrease of hydrogen dilution rate of C_2H_2 (H_2/C_2H_2). In other word, carbonization layer with good cystallinity and crystal orientation can be obtained at hydrogen dilution rate of C_2H_2 above 20. It was found that the intensity of Si(111) diffraction peak is larger than any

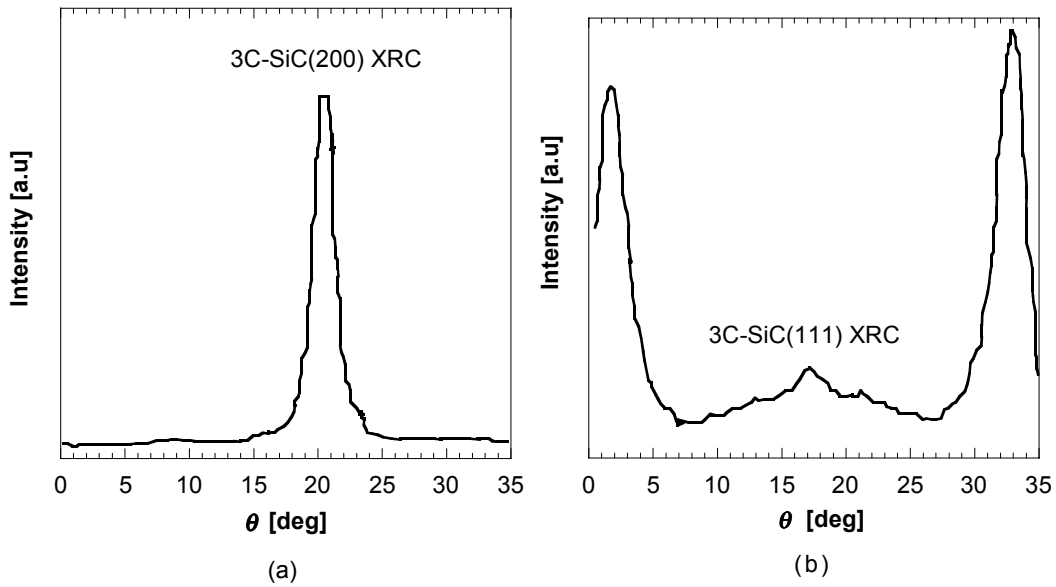
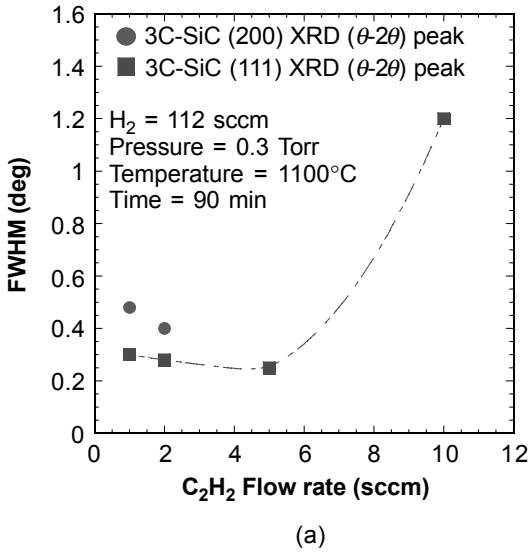
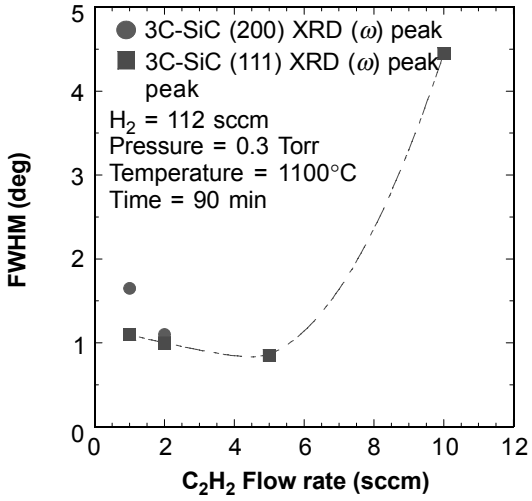


Figure 3 Typical ω-rocking curve of SiC(200) and SiC(111) peak of SiC thin film on Si(100) substrate



(a)

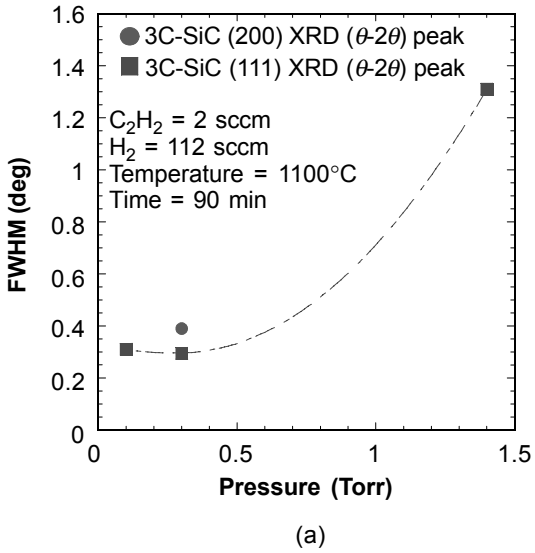


(b)

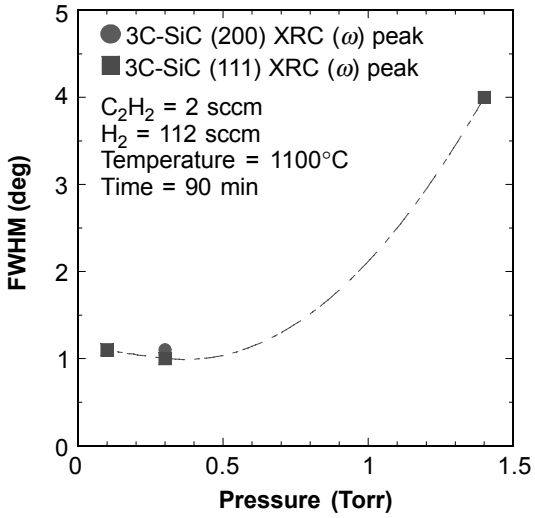
Figure 4 Variations in FWHM of (a) θ-2θ scan and (b) ω-rocking curve of SiC(111) and SiC(200) diffraction peak as a function of C_2H_2 flow rates

Si(200) diffraction peak. Thus, it can be simply concluded that the formation rate of carbonization layer on Si(111) substrate is faster than Si(100) substrate.

Figure 5(a) and (b) show the variations in FWHM of θ-2θ scan and ω-rocking curve of SiC(111) and SiC(200) diffraction peak as a function of growth pressure, respectively. It is clearly seen in Figures 5(a) and 5(b) that SiC(111) diffraction peak on Si(111) shows very small FWHM value at growth pressure of 0.1 and 0.3 Torr and large value



(a)



(b)

Figure 5 Variations in FWHM of (a) θ-2θ scan and (b) ω-rocking curve of SiC(111) and SiC(200) diffraction peak as a function of growth pressures

at 1.4 Torr. However, SiC(200) diffraction peak on Si(100) substrate was not observed at 1.4 Torr. From these results, we can conclude that the crystallinity and crystal orientation of carbonization layer degrades with the increase of growth pressure and the growth rate of carbonization layer on Si(111) is faster than Si(100). The results in this experiment show the similar dependence of crystallinity and crystal orientation on

hydrogen dilution rate and growth pressure with the epitaxial growth of SiC film without pre-carbonization process presented in reference [8]. It is speculated that under large hydrogen dilution rate, excessive methyl groups were effectively extracted by large amount of hydrogen radicals. It is also speculated that under low growth pressure, Si atoms from substrate are adequately supplied for carbonization process.

The dependences of FWHM value of θ-2θ scan and ω-rocking curve of SiC(111) and SiC(200) diffraction peak on the carbonization temperatures are shown in Figure 6(a) and (b), respectively. It is shown that the carbonization process is well promoted with the increase of temperature as predicted.

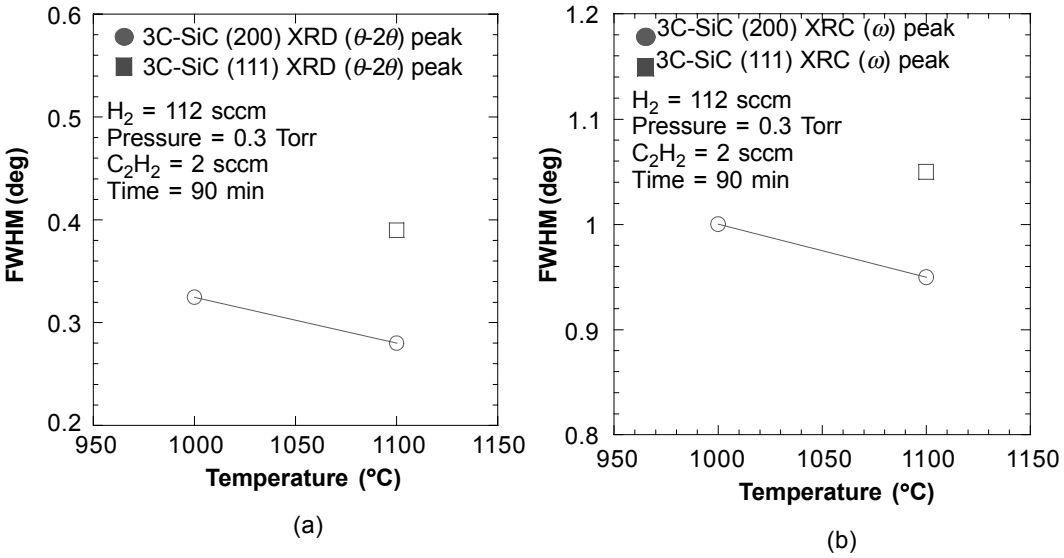


Figure 6 The dependences of FWHM of (a) θ-2θ scan and (b) ω-rocking curve of SiC(111) and SiC(200) diffraction peak on the carbonization temperatures

Figure 7(a) and (b) show the variation in the FWHM of θ-2θ scan and ω-rocking curve of SiC(111) and SiC(200) diffraction peak as a function of the carbonization times, respectively. The drastic change of FWHM of SiC(111) diffraction peak on Si(111) substrate was not observed for carbonization times above 30 minutes. It is shown that the crystallinity and crystal orientation of carbonization layer on Si(100) substrate are worse compared to Si(111) for carbonization time less than 30 minutes. However, the FWHM values of both diffraction peaks show almost the same value at 90 minutes. From the results presented so far, we might say that the values of FWHM are not only reflected by the crystallinity and crystal orientation but also the thickness of carbonization layer. It is known that the maximum thickness of carbonization layer formed by single carbon sources is around several tens nanometers. In other words, the large values of FWHM might be resulted from the thickness below several tens nanometer although the crystallinity of carbonization layer is perfect. From these results,

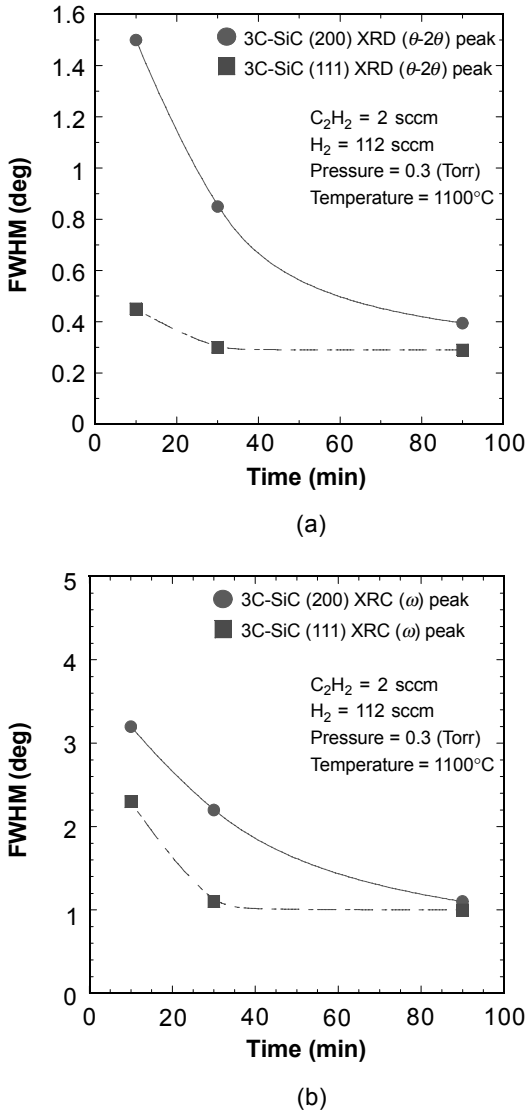


Figure 7 Variation in FWHM of (a) θ-2θ scan and (b) ω-rocking curve of SiC(111) and SiC(200) diffraction peak as a function of carbonization times

carbonization layer with good crystallinity and crystal orientation can be accomplished in 30 minutes for Si(111) but in more than 30 minutes for Si(100).

3.2 Variation of Bonding States at Various C_2H_2 Flow Rates and Carbonization Pressures

The comparison between the FWHM of C-Kα line of carbonization layer and SiC single crystal film using EPMA measurement was performed. From this measurement,

it can be estimated the bonding state of carbon because the bonding state of carbon is reflected by the value of FWHW. Figure 8(a) shows the FWHM of C-Kα line as a function of C_2H_2 flow rate. It is clearly shown that the FWHM of carbonization layer under C_2H_2 flow rate of 2 sccm shows almost the same value with the SiC single crystal, meaning that the bonding state of carbonization layer is similar to SiC single crystal. These results show good agreement with the crystallinity data measured by X-ray diffraction. As the flow rate of C_2H_2 increase, the FWHM become wide which is near to the value of diamond and graphite. Thus, it can be speculated that the C-C bonding increase with the C_2H_2 flow rate.

Figure 8(b) shows the dependence of the FWHM of C-Kα line on the carbonization pressure. The FWHM value at 0.3 Torr is very close to the value of SiC single crystal. Again, this data show good agreement with the crystallinity data determined by XRD. The FWHM values of C-Kα line at other pressures give large values which are near to the values given by diamond and graphite, representing the increase of C-C bonding at those pressures. In summary, we conclude that the high quality carbonization layer can be obtained under the following conditions; (i) C_2H_2 flow rate 2 sccm, (ii) carbonization pressure 0.3 Torr, (iii) carbonization time 90 minutes and (iv) carbonization temperature ~1100 °C.

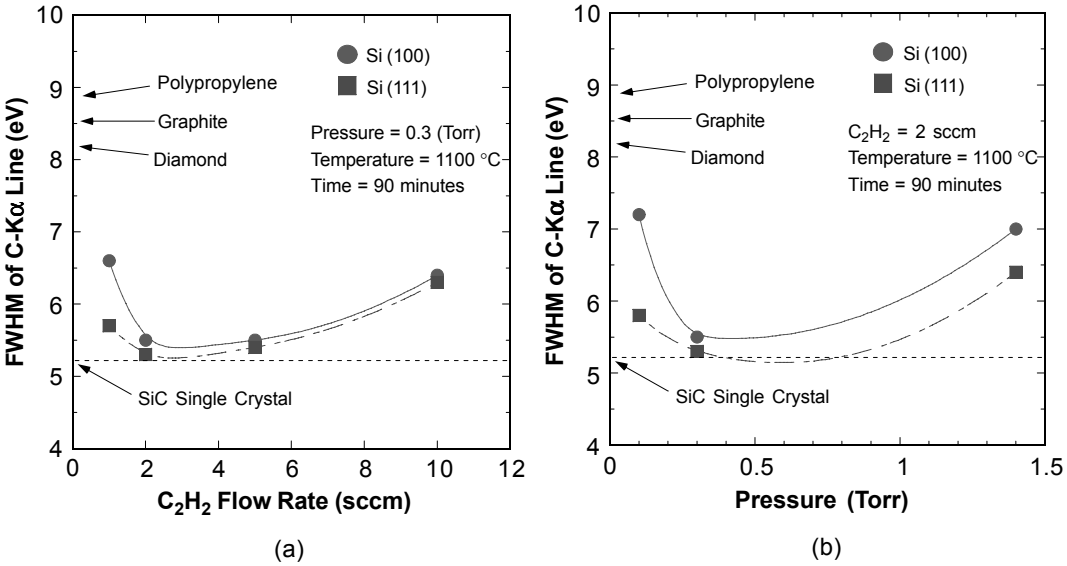


Figure 8 FWHM of C-Kα line as a function of (a) C_2H_2 flow rates and (b) dependence of the FWHM of C-Kα line on the carbonization pressures

4.0 CONCLUSION

The carbonization process using C_2H_2 as carbon source on Si(100) and Si(111) substrates was investigated using XRD and EPMA techniques. The stoichiometric

carbonization layer with good crystallinity, crystal orientation and bonding state was successfully formed at 1100 °C with C_2H_2 flow rate of 2 sccm and reaction pressure of 0.3 Torr. The subsequent epitaxial growth of SiC thin films is now underway. It is believed that the organosilicon compounds such as monomethylsilane (MMS) is more suitable for the subsequent epitaxial growth of SiC films compared to dimethylsilane (DMS) because the ratio of Si atom and C atom in DMS is 1:2. The excess C atom may promote the reaction of C-C bonding instead of Si-C bonding.

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REFERENCES

[1] Munch, W. V. and P. Hoeck. 1978. *Solid State Electron*. 21: 479.
[2] Fuma, H., M. Kodama, H. Tadano, S. Sugimoto and M. Takigawa. 1990. Technical Report of IEICE CPM90-20 (in Japanese).
[3] Takeuchi, T., H. Amano, K. Hiramatsu and I. Akasaki. 1991. *J. Non-Cryst. Solids.* 115: 634.
[4] Nishino, S., Y. Hazuki, H. Matsunami and T. Tanaka. 1980. *J. Electrochem. Soc*. 127: 2674.
[5] Ishida, Y., T. Takahashi, H.Okumura, S.Yoshida and T. Sekigawa. 1997. *Jpn. J. Appl. Phys*. 36: 6633.
[6] Sano, S., S. Nishino and J. Saraie. 1995. In Proc. 6th Int. Conf. Silicon Carbide and Related Materials, Kyoto, Japan. 209.
[7] Yasui, K., M. Kimura, K. Sanada and T. Akahane. 1999. *Appl. Surf. Science.* 142: 381.
[8] Hashim, A. M. and K. Yasui. 2006. In 2006 IEEE Int. Conf. Semiconductor Electronics, Kuala Lumpur, Malaysia. 646-650.