Surface Analysis of Cubic SiC Thin Films Prepared by High Vacuum Chemical Vapor Deposition Using 1,3-Disilabutane

K.-S. Yu*'***, J. W. Lee**, M. M. Sung***, S.-B. Lee* and Y. Kim***

*Department of Chemistry, Sung Kyun Kwan Univ. Suwon ,Kyunggi-Do, 440-745, Korea
**Korea Material Analysis Corp., 590-5 Guam-Dong, Yusong-Gu, Taejon 305-311, Korea
***Advanced Materials Division, Korea Research Institute of Chemical Technology, Yusong P.O. Box 107, Taejon 305-600, Korea

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Thin films of cubic SiC have been prepared on Si(001) by high vacuum CVD using 1,3-disilabutane at various temperatures (450-1150 °C). A series of cubic SiC/Si(001) film surfaces were characterized by *in situ* X-ray photoelectron spectroscopy (XPS). As-deposited films were examined by Rutherford backscattering spectrocopy (RBS), scanning electron microscopy (SEM), and X-ray diffraction (XRD). *In situ* XPS study evidently shows that stoichiometric SiC films are grown on Si(001) surfaces over the temperature range 600-1000 °C. However, the optimum temperatures for the formation of epitaxial 3C-SiC films were found to be between 800 and 1000 °C on the basis of XRD analyses.

1. INTRODUCTION

Cubic silicon carbide (3C-SiC) is a compound semiconductor highly suitable for electronic devices in high temperature, high power, high frequency and strong radiation environments[1], due to its excellent thermal and chemical stability at high temperatures, wide band gap[2], and other good electronic properties. More recently, SiC is being considered for high temperature microsensor and microactuator [MicroElectroMechanical Systems (MEMS)] applications[3,4], since similar devices based on Si lack high-temperature capabilities with respect to both electrical and mechanical properties.

Up to the present, it is common to grow 3C-SiC films heteroepitaxially on carbonized Si substrates by chemical vapor deposition using separate Si and C source gases, such as SiH_3Cl(or $SiHCl_3$, SiH_4) and C_3H_8(or CH_4, CH_3Cl) with a carrier gas (H_2), usually at temperatures higher than 1200 °C[5-7]. The process requires independent flow control of each source and the use of dangerous source chemicals. This situation has spurred the investigation of alternative precursors for SiC deposition. In general, a precursor designed for this purpose[8] would contain directly bonded Si and C atoms and would decompose at relatively low temperatures into a film of stoichiometric SiC. Examples of such alkylsilane precursors reported to date include methylsilane (CH_3SiH_3)[9,10], methyltrichlorosilane (CH_3SiCl_3)[11], tetramethylsilane $\{(CH_3)_4Si\}$ [12], diethylsilane $\{(C_2H_5)_2SiH_2\}$ [12], tripropylsilane $\{(C_3H_7)_3SiH\}$ [12], hexamethyldisilane $\{(CH_3)_6Si_2\}$ [13], dimethyldichlorosilane $\{(CH_3)_2SiCl_2\}$ [14], dimethylisopropylsilane $\{(CH_3)_2CHSiH(CH_3)_2\}$ [15] and silacyclobutane (c-$C_3H_6SiH_2$) [16]. Recently, epitaxial cubic SiC films were grown on Si(001) surfaces with and without carbonization at relatively low temperatures (900-1000 °C) by high-vacuum CVD using only 1,3-disilabutane ($H_3SiCH_2SiH_2CH_3$)[17, 18]. In this research, we have studied the temperature effect on the initial growth of SiC films using 1,3-disilabutane.

In this study, we report on the heteroepitaxial growth of 3C-SiC on Si(001) without carbonization by high vacuum chemical vapor deposition using 1,3-disilabutane over the temperature range 450-1150 °C. In addition to lowering of growth temperature, this method has the advantage of a much simpler deposition process and system in comparison with other CVD and MBE techniques, since only a single source is employed to

deposit SiC films on Si(001) without using any carrier gas. The grown 3C-SiC films were characterized by *in situ* X-ray photoelectron spectroscopy (XPS). The deposited films were examined by Rutherford backscattering spectrocopy (RBS), scanning electron microscopy(SEM), and X-ray diffraction (XRD).

2. EXPERIMENTAL

The deposition experiments were performed in an ultrahigh vacuum chamber (preparation chamber of ESCALAB MK II, VG Scientific Ltd.) designed for high vacuum CVD.

The preparation chamber was modified for substrate heating using an e-beam heater. A substrate holder was placed on the analytical sample probe. The reactor was equipped with a quadrupole mass analyzer for acquisition of mass spectra of source gas, residual gas, and decomposed species, and was connected to the precursor dosing line and handling system through a variable leak valve and metal bellows valves. The substrate used in this study was Si(001), cut into a square of 12 $\times$ 12 mm^2. The substrate needs to be properly cleaned and prepared for the deposition to avoid residual surface impurities that can create defects in the growing films. Therefore, prior to introducing the Si substrate into the reactor, it was initially treated by a chemical cleaning process, which involves degreasing, alkali treatment, acid treatment, rinsing in deionized water, similar to the method proposed by Ishizaka and Shiraki[19] to remove contamination and form a thin oxide layer on the surface. This initial treatment of the substrate enables us to obtain clean surfaces by annealing at relatively low temperatures (below 900 °C) in the reactor. The control of substrate temperature was made by the filament current of the e-beam heater. The temperature of the substrate was measured with an optical pyrometer.

The single precursor 1,3-disilabutane is a colorless liquid at room temperature and its vapor pressure was measured to be 400 Torr at 26.6 °C. It was transferred into a glass bulb attached to the gas handling system under high vacuum condition(< 3.0×10^{-7} mbar) and was further purified by freeze-pump-thaw cycles using liquid nitrogen. The vapor of 1,3-disilabutane was dosed from a nozzle located about 16 mm above the Si substrate. Before deposition, the e-beam and sample holder assembly (made of Mo and Ta) was degassed at 1200-1300 °C for more than 1 h to minimize outgassing from the surface of the holder and the filament. The substrate was heated up to 850 °C and kept at this temperature for about 20 min to remove the protective oxide layer. It was then allowed to cool to below 100 °C. Then, its temperature was raised to the growth temperature over a period of 20 min. After such annealing, clean Si substrates could always be observed by *in situ* XPS examination. SiC films were deposited directly on the clean Si surface without the carbonization process at varying temperatures (450-1150 °C) under high vacuum conditions (2.0×10^{-6} mbar). The duration of deposition was about 2 h, and the growth rate changed depending on the experimental conditions. The film surfaces were characterized by *in situ* XPS, SEM, and XRD, RBS.

3. RESULTS AND DISCUSSIONS

The X-ray photoceletron spectroscopy (XPS) investigation was carried out with Al Kα radiation as excitation source ($h\nu$ = 1486.6 eV). The electron energy analyzer was operated in fixed analyzer transmission (FAT) mode with a constant pass energy of 50 eV.

Table 1. Ratios of C/Si of interest obtained from the *in situ* XPS data (take-off angles 90° and 20°).

Growth	C/Si ratio		Sensitivity
Temp.(°C)	90°	20°	factor
1150	0.60	0.75	C1s(0.25) Si2p(0.27) O1s(0.66)
1000	0.87	0.85	
900	0.87	0.73	
800	1.03	0.92	
700	0.93	1.04	
450	0.07	0.27	

All measurements were performed at pressures lower than 5.0×10^{-10} mbar in the

analysis chamber. Corrections of the binding energy shift due to steady-state charging of the samples were made by taking the C1s in SiC as reference at 282.7 eV [20].

Quantification of the XPS data was performed by normalizing the area of each peak using the atomic sensitivity factors. High resolution XPS spectra for Si2p, C1s and O1s (< 1 atomic %) were obtained for all the SiC films. The O1s spectra, which are not shown here, are composed mainly of a single peak with a binding energy corresponding to SiO_2 (532.0 eV). No other elements were detected in significant amounts by XPS. This result indicates that the Si2p peak at 100.6 eV and the C1s peaks at 282.7 eV correspond to the SiC phase. It is shown in Table 1 that the Si:C ratio for the SiC films is 1.0 ± 0.2 for the SiC films obtained in the growth temperature range 700-1000 °C.

In order to increase the surface sensitivity of XPS, the take-off angle was changed. When the angle is decreased from 90° to 20°, the C/Si ratio is seen to increase for the films obtained in the range 450-700 °C. The ratio decreases for the films prepared above this range. The ratio at 90° take-off angle has about the same trend, with the maximum at 800 °C. At higher temperatures the film surfaces have less carbon than the bulk of the films. It was reported in literature that Si overlayers exist on CVD-grown SiC films at temperatures above 940 °C[21].

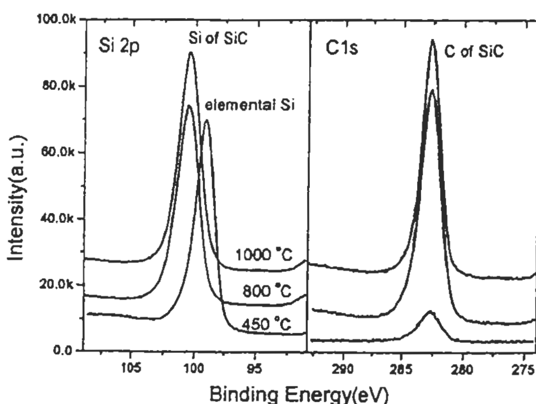

Figure 1. Si2p and C1s XPS spectra for the films deposited at 450, 800, 1000 °C (take-off angle 90°).

The Si2p and C1s spectra for the films are presented in Fig. 1. The Si2p peaks can be assigned to elemental Si (99.0 eV, at 450 °C) and the Si (100.6 eV) in SiC (at 800, 1000 °C). The C1s peaks were all assigned to the carbidic carbons (282.7 eV, C in SiC). It is observed from Fig. 1 that at 450 °C the deposition does not proceed appreciably. The Si2p peak is clearly due to elemental Si of the substrate.

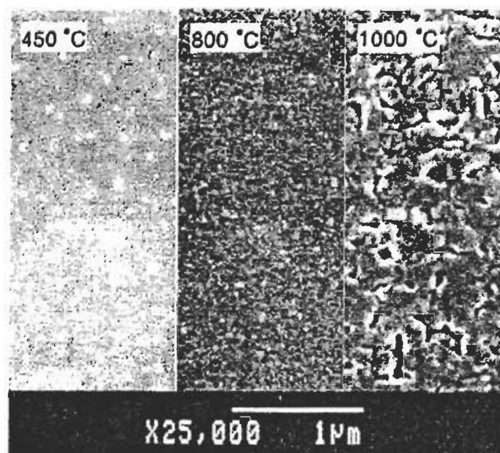

Figure 2. SEM micrographs of the surfaces of 3C-SiC films grown at different temperatures (450, 800, 1000 °C).

Fig. 2 shows changes in the surface morphology of the 3C-SiC films grown at various temperatures. The surface morphology of the film grown at 800 °C is better than that of the film grown at 1000 °C. The small white forms on the

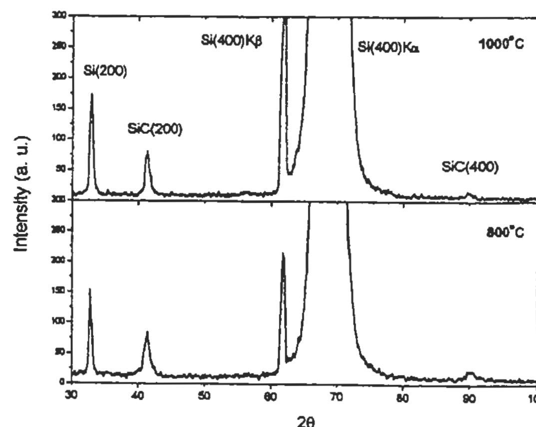

Figure 3. X-ray diffraction patterns of the 3C-SiC films grown on Si(001) at 1000 °C (top), and 800 °C (bottom). Their thicknesses are about 0.1 μm(RBS).

film grown at 450 °C are thought to be islands of SiC. Fig. 3 shows the XRD patterns (θ-2θ scan) for the SiC films deposited at 800 and 1000 °C for 2 h. In addition to the Si peaks due to the substrate, we can see that only a single sharp peak due to the cubic structure of the SiC film appears at 2θ = 41.4° for (200) and 2θ = 90.0° for (400) reflections. This signifies that the SiC films were grown epitaxially.

4. CONCLUSIONS

Thin films of cubic SiC have been prepared on Si(001) by HVCVD using 1,3-disilabutane at various temperatures. The surfaces of as-grown films were characterized by *in situ* XPS, SEM, and XRD. The *in situ* XPS results indicated that the Si2p peak at 100.6 eV and the C1s peak at 282.7 eV correspond to the SiC phase. The Si:C ratio for SiC is 1.0 ±0.2 for the SiC films grown at 700-1000 °C range. The surface morphology of the film grown at 800 °C is better than that of the film grown at 1000 °C. The XRD analysis shows only a single sharp peak due to the cubic structure of the SiC film. These results demonstrate that the growth technique of using the single source 1,3-disilabutane is suitable and effective for epitaxial growth of SiC on Si substrates at temperatures below 1000 °C.

5. REFERENCES

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