In-situ study on thermal decomposition of 1,3-disilabutane to silicon carbide on Si(1 0 0) surface

Hae-geun Jee, Sang-Hun Nam, Jin-Hyo Boo*, Seong Kyu Kim, Soon-Bo Lee*

Department of Chemistry and Institute of Basic Science, Sungkyunkwan University, Suwon, 440-746, Republic of Korea

A R T I C L E   I N F O

Article history:
Available online 15 February 2011

Keywords:
1,3-Disilabutane
Thermal decomposition
RIS and TPRIS
TPD
AES

A B S T R A C T

The intermediates of thermal decomposition of 1,3-disilabutane (SiH₅CH₂SiH₂CH₃, DSB) to form SiC on Si(1 0 0) surface were in situ investigated by reactive ion scattering (RIS), temperature programmed reactive ion scattering (TPRIS), temperature programmed desorption (TPD), and auger electron spectroscopy (AES). DSB as a single molecular precursor was exposed on Si(1 0 0) surface at a low temperature less than 100 K, and then the substrate was heated up to 1000 K. TPD, AES investigations showed that DSB adsorbed molecularly and decomposed to SiC via some intermediates on Si(1 0 0) surface as substrate temperature increasing. Between 117 and 150 K molecularly adsorbed DSB desorbed partially and decomposed to CH₄SiH₂, which is the first observation on Si(1 0 0) surface, and further decomposed to CH₄Si between 150 and 900 K. CH₄Si lost hydrogen and formed SiC over 900 K.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Silicon carbide is the only compound that exists in the solid state among the Si-C systems, and has many polytype structures [1]. Among these structures, cubic silicon carbide (3C- or β-SiC) has desirable properties as a semiconducting material [2,3]. Due to this reason, many researchers have been studying the deposition of SiC on Si substrate for semiconductor device applications [4]. In the early studies, single crystalline SiC films were grown on a buffer-layered Si substrate by chemical vapor deposition (CVD) using separate sources for carbon and silicon, such as hydrocarbon and silane, and hydrogen as a carrier gas [5–8]. Although the grown films satisfied the stoichiometric C:Si ratio, high temperatures around 1700 K and buffer layers were needed for the high quality film growth conditions. But, the high growth temperature may cause serious problems in the 3C-SiC/Si structure, i.e., high tensile stresses and crystalline lattice defects such as misfit dislocations and stacking faults due to the difference in lattice constants and thermal expansion coefficients between SiC and Si. Furthermore, the use of silane requires safety precautions. To overcome these problems, organosilanes which contain carbon and silicon atoms in the same molecule namely single molecular precursor have been used as a single molecular precursor for the SiC film growth [9–14]. The grown films with single molecular precursors showed single crystalline properties, satisfied stoichiometric ratio of silicon and carbon, and were formed at relatively low temperatures around 1300 K. Among these precursors, some precursors such as 1,3-disilabutane (DSB, SiH₅CH₂SiH₂CH₃) produced good single crystalline 3C-SiC films at the temperatures around 900 K lower than other precursors did [11–13,15,16]. Although many researchers studied depositions and applications of SiC using single molecule precursors, there are only few works on details about adsorption and decomposition of DSB [17–19]. In this study, the intermediates of thermal decomposition of DSB on the Si(1 0 0) surface were investigated by reactive ion scattering (RIS) and auger electron spectroscopy (AES). RIS as well as TPRIS is an effective surface analysis tool for detecting molecular adsorbate, which developed and established by Kang and co-workers [18,20–25].

2. Experimental

Experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 1 × 10⁻¹⁰ Torr. It was equipped with a quadrupole mass spectrometer (QMS, Hiden, EPIC500N), a cesium ion gun (Cs⁺-gun, Kimball Physics, ILG-4), and an electron gun for low energy electron diffraction and Auger electron spectroscopy (LEED/AES, Omicron, Spectraleed). The Si samples were p-type Si(1 0 0) wafers with 10–20 Ω cm resistivity. For linear heating in the temperature range between 80 K and 1000 K, tantalum was coated on the backside of the wafer by RF-magnetron sputtering with argon gas. The thickness of coated Ta was 510–540 μm, as measured by scanning electron microscopy (SEM). After coating, the Ta coated wafer was cut by a diamond saw to the size of 8 × 23 mm². But the exposed area to vacuum was 8 × 13 mm².

* Corresponding authors.
E-mail addresses: jhboo@skku.edu (J.-H. Boo), xpslee@skku.edu (S.-B. Lee).
(1.04 cm²) in the UHV chamber, because of the two cover plates at the both ends of samples.

The sample was chemically cleaned before mounting on the holder. The wafer was rinsed with distilled water, methanol, acetone, and trichloroethylene in a sonicator for 10 min in the order named. The rinsed sample was dipped in 353 K piranha solution for 10 min and the oxides layer of the sample was removed by 10 V% HF solution within 10 s.

To mount it on the sample holder, two samples were piled up. The one was Ta coated sample and the other was a Si(100) sample without Ta coating. The Ta coated side faced with the backside of non-coated sample. The both ends of sample were covered by Ta clip (8 × 10 × 0.05 mm²). The sample temperature was monitored by K-type thermocouple contacted to the sample side. Ta tip (1.2 × 3 × 0.1 mm²) was spot welded to the end of K-type thermocouple and was inserted to the gap of piled samples. So, the end of thermocouple contacted to the side of the Ta coated sample and it could read the correct sample temperature. Once placed inside the UHV chamber, the sample was degassed at a temperature of 850 K for overnight, and cleaned by flashing over 1300 K. The surface cleanness was confirmed by the LEED/AES and RIS. The sample was cooled down less than 100 K and maintained by a helium cryogenic cooler.

DSB [pre-silicone, 98%] was introduced into the chamber through a variable leak valve and guided by a stainless tube doser to 1 cm above the sample surface. Before the DSB dosing, it was purified by several freeze-pump-thaw cycles in a pyrex bulb immersed in liquid nitrogen.

RIS was consisted of QMS and Cs⁺ ion gun with 10–150 eV kinetic energy. The angle between an incident beam and a QMS was fixed at 90°, and the incident beam direction was 45° to the surface normal. AES was performed with 3 keV beam energy. Sample was heated by resistively up to 800 K before every DSB dosing and TPD was performed by resistively heating from the temperature less than 100 K up to 1000 K with 5 K/s temperature increasing rate.

3. Results and discussion

Si(100) surface was exposed to DSB vapor at a temperature less than 100 K and analyzed by the RIS technique with various cesium beam energies. In Fig. 1, mass spectra (a)–(c) show RIS products with 100, 80, 50 eV, respectively. Each spectrum shows two peaks. One is an elastically scattered Cs⁺ peak at 133 amu, and the other peak at mass of 223 amu is produced by RIS process. The mass at 223 amu is assigned to Cs[SiH₃CH₂SiH₂CH₃]⁺.

This product results from the molecularly physisorption of DSB (SiH₃CH₂H₂CH₃, mass = 90 amu) on the Si(100) surface. The condensation of residual H₂O vapor on cooled silicon substrate is natural phenomena. But, there is no peak about water at 151 amu, because H₂O molecules were removed by resistive sample heating before every DSB dosing. Removing of water from surface is very important, because it is not clear whether DSB reacts with H₂O and, derive and/or leave side product on a Si(100) surface or not.

In the energy range between 10 and 150 eV, Cs⁺ beam did not occurred fragmentation by increasing impact energy for physisorbed DSB. But, intensity and shape of peak at 223 amu are dependent on impact energy and dosing amounts. For example, peak intensity of CsDSB⁺ decreased by increasing impact energy and peak width was broadened by decreasing impact energy. For this reason, 80 eV beam energy was mainly used for RIS experiments.

Silicon surface was exposed to DSB vapor at a temperature less than 100 K followed by annealing at 117–1000 K for 10 s or shorter in order to examine the decomposition behavior of DSB. Fig. 2 shows the RIS spectrum of a surface that was exposed to DSB and annealed at 117 K. New peak appeared at 205 amu but the peak at 223 amu didn’t disappear completely. Peak at 205 amu is assigned to CH₄Si₂. When the sample was annealed at 130 and 150 K, the peak at 223 amu disappeared clearly and only 205 amu peak remained in RIS mass spectra as shown in Fig. 3(a) and (b). One more peak was also observed at 161 amu and can be assigned to CsSi⁺ suggesting that this signal was originated from the sputtered surface silicon atom due to relatively high Cs⁺ impact energy (80 eV). The RIS spectrum of clean Si(100) surface shows the peak from elastically scattered Cs⁺ ions and the peak at 161 amu (CsSi⁺).

Since the peak at 161 amu was not observed either right after DSB was dosed on the Si surface or after the dosed DSB/Si was subsequently annealed at 117 K, therefore, this peak must have not been produced by collisional fragmentation of CH₄Si₂ adspecies. This indicates that the formation and desorption of CH₄ and H₂ species decomposed from molecularly adsorbed DSB, considering on the mass difference (18 amu) between DSB and CH₄Si₂ adspecies. CsSi⁺ peak at 161 amu was observed from the clean surface but its signal disappeared after DSB dosing because the sputtering of surface silicon atoms was disturbed by adsorbed DSB. As shown in the Fig. 3(f), the CsSi⁺ peak could originate either from a deposited SiC layer or from unreacted surface regions. But the CsSi⁺ peak without CsC⁺ peak implies that Si atoms are from unreacted surface.

As the sample temperature increasing above 150 K up to 900 K, the peak at 205 amu disappeared clearly and new peak at 177 amu appeared in Fig. 3(c)–(e); the new peak is assignable to Cs(CH₄Si)⁺.
It means that CH₄Si₂ aspecies further decomposed to CH₄Si at above 150 K by losing Si atom. In the temperature range between 300 and 700 K, the intensity ratio of Cs(CH₄Si)⁺ to Cs⁺ was not changed much [see Fig. 3(c) and (d)] but the intensity of the 177 amu peak decreased almost to the noise level when the sample was heated to 900 K [see Fig. 3(e)]. And when the sample was annealed at 1000 K, Cs(CH₄Si)⁺ signal disappeared completely leaving only CsSi⁺ signal [see Fig. 3(f)]. This result indicates that with increasing the temperature from 700 K to 900 K as shown in the Fig. 3(e), further decomposition of CH₄Si to SiC was occurred by losing two hydrogen molecules, resulting in SiC formation. The CsSi⁺ peak as shown in the Fig. 3(f) could originate either from a deposited SiC layer or from unreacted surface regions. But the CsSi⁺ peak without Cs⁺ peak implies that Si atoms are from unreacted surface. At 1000 K, Cs(CH₄Si)⁺ signal disappeared completely leaving only CsSi⁺ signal in Fig. 3(f). At this temperature, all the molecular aspecies decomposed to SiC on the surface.

Based on the residual gas analysis (RGA) and RIS spectrum, 2 and 89 amu masses were used in temperature programmed desorption for hydrogen and DSB, respectively. The molecular mass of DSB is 90 amu, but 89 amu is the major peak in the RGA pattern. Figs. 4 and 5(a) are the TPD spectra for 89 and 2 amu obtained from the Si(100) surface exposed by 1.2 L DSB from 83 K up to 972 K with 5 K/s temperature increasing rate. In Fig. 4(a), molecular desorption peaks of DSB were observed at 114 and 126 K. In the RIS results, molecular DSB and first decomposition intermediate co-exist on the surface after annealing at 117 K. So, the first desorption peak at 114 K originated from desorption of physisorbed DSB above second layer and the second peak at 126 K originated from the surface adsorbed DSB layer. At this stage, we propose that the second layer of molecularly adsorbed multilayer of DSBs can desorb at 114 K and the surface monolayer of DSB starts decomposition to the first intermediate, CH₄Si₂, with formation of chemical bonds between the adsorbate and the surface dangling bonds at temperature range between 114 and 150 K, respectively. Thus the surface adsorbed layer of DSB partially desorbed and decomposed on the surface at 114 and 126 K, respectively. To clarify this, the temperature programmed reactive ion scattering (TPRIS) analysis as well as RIS measurement was also carried out after 0.7 L DSB was dosed to the surface at 80 K observing masses of Cs⁺-ion clusters of 223, 205, and 177 amu, respectively. During the TPRIS measurements, the sample heating rate was 5 K/s and the sample holder was translated linearly up or down by a stepper motor with the speed of 30–36 μm/s to maintain the cesium expose less than 0.01 monolayer at the focused spot of the sample. Based on TPRIS results [see Fig. 4(b)] taken with an Cs⁺ ion impact energy of 80 eV, we could obtain an information that the intensity of CsDB⁺ peak (223 amu), which was originated from molecularly adsorbed DSB, decreased and disappeared completely above 120 K. The Cs(CH₄Si₂)⁺ peak (205 amu) appeared around 125 K and disappeared around 170 K. As the temperature was further increased, only the Cs(CH₄Si)⁺ peak (177 amu) was detected until the temperature reached 900 K.

In Fig. 5, hydrogen desorption was observed at four temperatures. Two desorption peaks under 300 K originate from the fragment of desorbed molecular DSB. Above 300 K, two desorption peaks were observed at 650 K (α-state) and 855 K (β-state). To follow the results of RIS experiments, surface adsorbate at 650 K is only CH₄Si. And this desorption temperature is similar with the hydrogen desorption from the silicon surface covered by atomic hydrogen [26]. So, TPD peak of 2 amu at 650 K originate from the surface hydrogen. At 700 K, RIS results showed that the second intermediate (CH₄Si) present on the surface and it disappear at 900 K. The other peak appeared in a high temperature region at 855 K originates from the dehydrogenation of CH₄Si on the surface.

The formation of SiC was also identified by AES. AES experiments were performed with 3 keV electron beam in the temperature range between 85 and 1300 K after 10 L DSB was exposed on a Si(100) surface at 85 K. Fig. 6 shows AES spectra obtained from the surface annealed at 85 K, 150 K, 500 K, 700 K, 900 K, and 1000 K. AES results show that carbon atoms remain on the surface up to 1000 K.
AES measurements showed carbon peaks at 276 eV up to 700 K. And carbon peak shifted to 272.9 and 272 eV at 900 and 1000 K, respectively. It is remarkable shift, because the peak at 272 eV is corresponded to 3C-SiC [27]. Each carbon peaks were deconvoluted with three species of molecular DSB, graphitic, and carbidic carbon. Relative area ratio changes are displayed in the Fig. 7. These relative area changes mean that molecular DSB decomposed to SiC via intermediates.

Based on adspecies identified by RIS and TPRIS at various temperatures, we can suggest the decomposition reaction path from DSB to SiC. Fig. 8 shows summary for the reaction path. Comparing with previous works of the decomposition path of DSB on Si(111) [17,18], the decomposition of DSB on Si(100) has different pathway. In the previous work, it is suggested that DSB chemisorbed on a Si(111) losing two hydrogen atoms and the breakdown of the center of backbone of DSB, Si–C–Si–C, made and leave two CH$_4$Si adspecies on the surface by thermal decomposition. The reaction intermediate, CH$_4$Si, converted to SiC layer above 900 K.

But, in this study the physisorbed DSB on a Si(100) surface at a temperature less than 100 K produces chemisorbed CH$_4$Si$_2$ by losing six hydrogen atoms and one carbon atom in the temperature...
range between 117 and 150 K. And this result is the first observation of CH$_4$Si$_2$ on Si(1 0 0) surface. Above 150 K, all adspecies on the surface convert to CH$_4$Si by further decomposition of CH$_4$Si$_2$ on the surface, most likely via breakage of the C–Si bond. The first intermediate, CH$_4$Si$_2$, is probably bonded to the two dangling bonds of a Si dimer forming five-membered ring. When silicon atoms of CH$_4$Si$_2$ at 1 and 3 position bond to the dangling bonds, it has low angle stress. And the second intermediate, CH$_4$Si, is probably lying down on the surface with $\text{H}_2\text{C} = \text{SiH}_2$ formation, as the same reason like CH$_4$Si$_2$ on a surface dimer.

All results of RIS, TPD, and AES are consistent with the CVD studies using DSB by Kim and co-workers [15,16], who reported that SiC formation starts at 900 K. Schematic decomposition process is shown in Fig. 8.

4. Conclusions

DSB was exposed to a Si(1 0 0) surface at a temperature less than 100 K and the decomposition of DSB to SiC on the surface was investigated by RIS, TPD, and AES increasing the temperature up to 1000 K. RIS and TPD experiments showed that DSB molecularly physisorbed on the surface at a temperature less than 100 K and DSB desorbed molecularly and partially decomposed at 114 and 126 K, respectively. Physisorbed DSB was decomposed to SiC via two intermediates steps. The first intermediate (CH$_4$Si$_2$), which is the first observation on Si(1 0 0) surface, was detected from the DSB adsorbed surface between 117 and 150 K by RIS and TPRIS. CH$_4$Si was only molecular intermediate by further decomposition of CH$_4$Si$_2$ above 150 K. At 900 K, CH$_4$Si disappeared in the RIS and TPRIS spectra and hydrogen desorption was observed 855 K in the TPD experiments. Desorption of hydrogen originated from the dehydrogenation of CH$_4$Si on surface, but the formation of SiC was confirmed by AES spectra and the SiC formation temperature agrees well with previous SiC film growth works.

Acknowledgements

Special thanks to Prof. H. Kang for his advice about RIS. This work was supported by the National Research Foundation of Korea (NRF) under the grants NRF-20100025481 (Basic Science Research Program) and R11-2001-091-00000-0 (SRC program of the Center for Nanotubes and Nanosstructured Composites at the Sungkyunkwan university).

References