

## Selective chemical vapor deposition of $\beta$ -SiC on Si substrate using hexamethyldisilane/HCl/H<sub>2</sub> gas system

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## Hexamethyldisilane/HCl/H<sub>2</sub> gas system을 이용한 Si 기판에서 $\beta$ -SiC의 선택적 화학기상증착

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**Abstract** Using a single precursor of hexamethyldisilane ( $\text{Si}_2(\text{CH}_3)_6$ ),  $\beta$ -SiC film was successfully deposited on a Si substrate at 1100°C by a chemical vapor deposition method. Selectivity of SiC deposition on a Si substrate partially covered with a masking material was investigated by introducing HCl gas into hexamethyldisilane/H<sub>2</sub> gas system during the deposition. The schedule of the precursor and HCl gas flows was modified so that the selectivity of SiC deposition between a Si substrate and a mask material should be improved. It was confirmed that the selectivity of SiC deposition was improved by introducing HCl gas. Also, the pulse gas flow technique was effective to enhance the selectivity.

**요 약** Hexamethyldisilane( $\text{Si}_2(\text{CH}_3)_6$ )의 single precursor를 사용하여 화학기상증착법으로 1100°C에서 Si 기판위에  $\beta$ -SiC 막을 증착시켰다. 증착과정 중 hexamethyldisilane/H<sub>2</sub> gas system에 HCl gas를 도입하여 mask 재료에 의해 부분적으로 덮여져 있는 Si 기판에서 SiC 증착의 선택성을 조사하였다. Si 기판과 mask 재료에서 SiC 증착의 선택성을 증진시키기 위해 출발물질과 HCl gas의 공급 방법을 변화시켰다. 결국, HCl gas를 도입함으로써 SiC 증착의 선택성은 증진되었고 펄스 형태로의 gas 공급 방법은 선택성을 향상시키는데 효율적이었다.

### 1. Introduction

Cubic SiC has a wide band gap energy (2.2 eV at 300 K), a high saturated electron velocity ( $2.7 \times 10^7$  cm/s), a high electron mobility ( $1000 \text{ cm}^2/\text{V} \cdot \text{s}$ ) and a high thermal conductivity (3.5 W/cm°C at 300 K) [1-3]. Therefore, it is a favorable semiconductor material for high temperature, high power and high speed electronic devices. In case of Si-based devices, they should be kept below 150°C for its normal operation because it has the narrower band gap energy of 1.1 eV, whereas SiC device can be used

at higher temperature range than that of Si device, due to its wide band gap energy more than 2.0 eV [4, 5].

However, it is very difficult to use a conventional wet etching technique for the SiC patterning that is necessary for device fabrication, because of chemical and thermal stabilities of SiC. Although new etching methods like as ion-beam etching [6] and ECR plasma etching [7] can be used, the etched surface becomes unsuitable for a microelectronic device application. In spite of these attractive properties, SiC does not have wide applications as a useful

semiconductor material. Therefore, the selective deposition technique of SiC becomes one of the promising ways to achieve the patterning. It is often necessary to deposit smooth, uniform layers of materials such as metals or semiconductors on a microelectronic substrate and such depositions must sometimes be made through patterned openings in a masking layer applied to the substrate [8]. Using this deposition technique, it will be able to use SiC as a semiconductor material for the high temperature devices.

In order to enhance the selectivity, modified two-stage deposition and etching processes have been required. In the modified processes, the film deposition and the film etching should be preferentially occurred in the unmasked area during the deposition process and in the masked area during the etching process, respectively.

In this study, effects of deposition condition on SiC film were investigated. Also, the selectivity of SiC deposition was investigated between a Si substrate and a mask material using the pulse gas flows of precursor gas. Especially, the selectivity of SiC deposition on a Si substrate and SiO<sub>2</sub> mask area was compared by controlling the precursor flow time.

## 2. Experimental procedures

The low pressure chemical vapor deposition system was used to deposit SiC films. CVD system consisted of the hot-wall type horizontal reaction tube with SiC heater. Figure 1 shows the schematic diagram of the hot-wall type CVD system.

Hexamethyldisilane (HMDS, Si<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>) was used as a single precursor for SiC deposition. <100> oriented p-type Si wafer patterned with SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> mask materials was used as a substrate. Dimensions of patterned openings in a masking layer were 1.61 mm

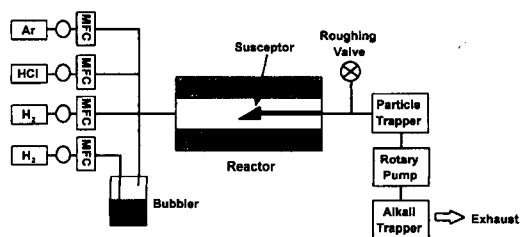


Fig. 1. Schematic diagram of the hot-wall type CVD apparatus.

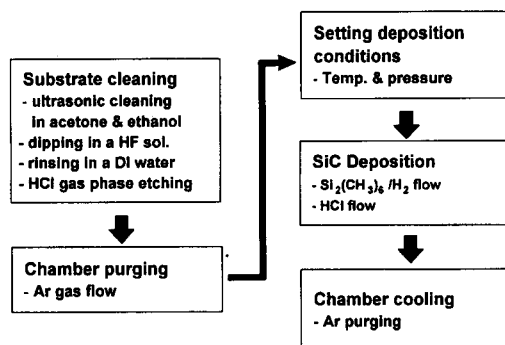


Fig. 2. Typical experimental procedure of the SiC deposition in CVD system.

×0.510 mm. Substrates patterned with mask materials were prepared using a conventional photolithography [9] and wet or dry etching technique [10]. Before being loaded into the reaction tube, substrates were rinsed by an ultrasonic cleaner in the baths of acetone and ethanol, and then dipped in a buffered HF solution to remove a native oxide. Finally, they were rinsed in a deionized water.

The flow rate of the source gas was determined by the flow rate of carrier H<sub>2</sub> gas, the vapor pressure of liquid source or the temperature of bubbler containing liquid HMDS precursor. Bubbler temperature was held at 3~4°C using ice water bath. The vapor pressure of liquid source at this temperature was about 9 torr [11]. The flow rate of carrier H<sub>2</sub> gas through a bubbler was varied from 1 to 5 sccm. The flow rate of atmosphere H<sub>2</sub> gas directed to a reactor was kept at 1,000 sccm. In order to etch the Si nuclei and enhance the selectivity of SiC deposition, hydrogen chloride (HCl) gas was introduced to HMDS/H<sub>2</sub> gas system during the  $\beta$ -SiC deposition. The flow rate of HCl gas was varied from 20 to 200 sccm.  $\beta$ -SiC deposition was carried out at the substrate temperature of 1100~1200°C and the reactor pressure of 30~50 torr. Figure 2 shows typical experimental procedure.

The deposited films were analyzed by X-ray Diffractometer, Scanning Electron Microscope, Wavelength Dispersive Spectrometer, X-ray mapping, Auger Electron Spectrometer and Atomic Force Microscope.

## 3. Results and discussions

A typical deposition process, especially the

chamber pressure, was modified. In the modified process, heating and cooling procedures were carried out at the atmospheric pressure with a flow of Ar gas and the deposition was carried out at the reduced pressure. The stable interface relationship was observed between the deposited film and the Si substrate. The film deposited with the growth rate of about  $1.9 \mu\text{m/hr}$  showed a mirror-like surface. Also, by WDS analysis, it was confirmed that SiC film of the stoichiometric composition was grown on the Si substrate. The cross-sectional view of the film deposited on unpatterned Si substrate at  $1100^\circ\text{C}$  was shown in Fig. 3.

However, a few of the defects of fiber-like growth were appeared on the surface of the film deposited at the substrate temperature above  $1150^\circ\text{C}$ . Therefore, optimum substrate temperature was chosen at  $1100^\circ\text{C}$ . By the X-ray diffraction patterns, the deposited films were identified as  $\beta$ -SiC phase and preferentially

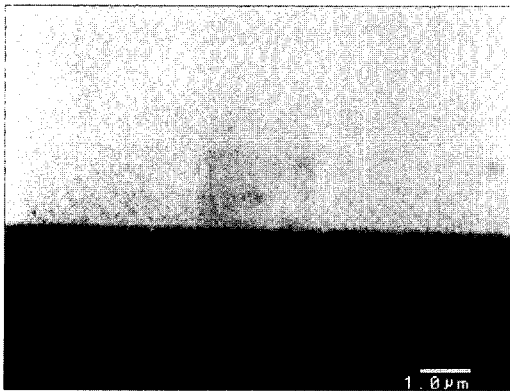


Fig. 3. SEM micrograph showing the cross-sectional view of  $\beta$ -SiC film deposited at  $1100^\circ\text{C}$ .

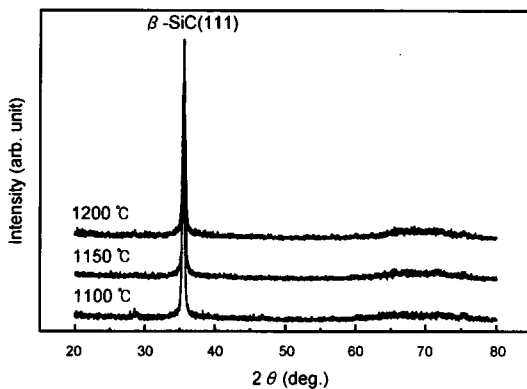


Fig. 4. XRD patterns of the films deposited at various substrate temperatures.

grown along the  $\langle 111 \rangle$  direction. Figure 4 show XRD patterns of the films deposited on unpatterned Si substrate.

In order to enhance the selectivity of SiC deposition, it was necessary to introduce the etching process to be able to suppress the initial nucleation on a mask area. HCl gas that could etch the Si nuclei was

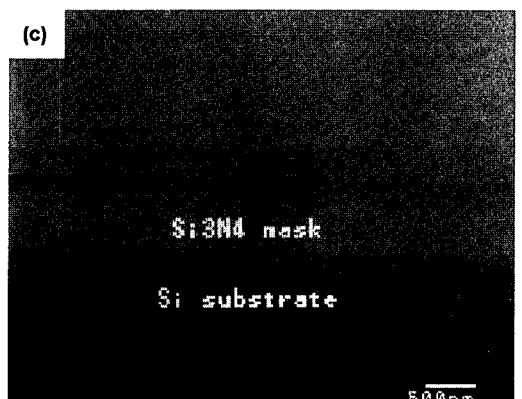
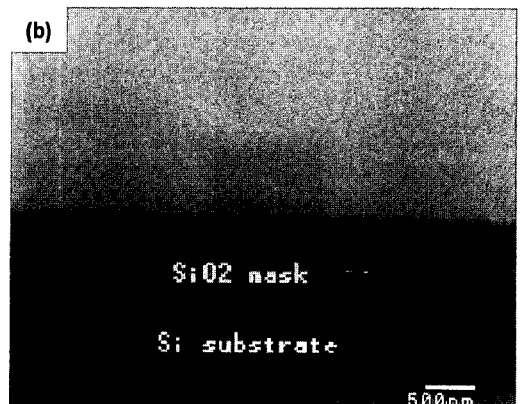
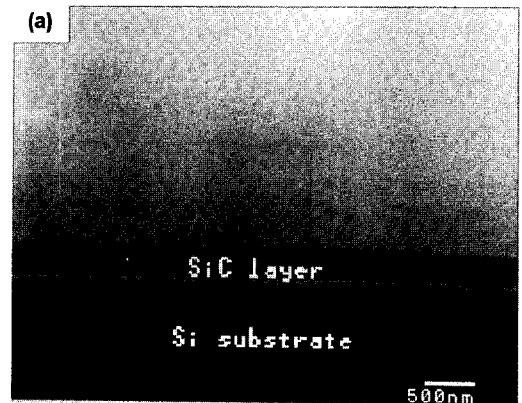


Fig. 5. SEM micrographs showing the SiC film deposited on (a) Si substrate, (b)  $\text{SiO}_2$  mask and (c)  $\text{Si}_3\text{N}_4$  mask at HCl gas of 200 sccm.

introduced to HMDS/H<sub>2</sub> gas mixture.

First, the precursor and HCl gases were introduced simultaneously. The flow rate of HCl gas was varied from 20 to 50 and 100 sccm. However, in this case, the deposition rate of SiC film on a substrate and a mask area was the same, regardless of the HCl gas flow rate. It was considered that the effect of the HCl gas etching was limited by the continuous precursor flow.

To improve the selectivity of SiC deposition, the schedule of precursor flows was modified. HCl gas flow was continuous, whereas the precursor flow into the reactor was maintained for 30 sec, and then stopped for 120 sec, as a pulse type flow. As the HCl gas flow rate increased, both the thicknesses of SiC films on a Si substrate and a mask area decreased. But, the deposition rate on a Si substrate was faster than that on a mask area. Also, the effect of mask materials (SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>) on the selectivity in SiC deposition was not observed. Figure 5 show the SEM micrographs of the SiC films deposited at HCl gas of 200 sccm. It was observed that the film of about 0.23  $\mu$ m thick was deposited on a Si substrate and film of less than 0.1  $\mu$ m was deposited on a SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> mask.

In order to enhance the selectivity of SiC deposition and differentiate the nucleation rates on a substrate and mask areas, the precursor flow time was decreased to 20 and 10 sec. Figure 6 shows SEM micrograph of the SiC film deposited between the Si substrate and the SiO<sub>2</sub> mask at the precursor flow of 10 sec and HCl gas of 200 sccm. The film of about 0.2  $\mu$ m thick was deposited on the Si substrate.

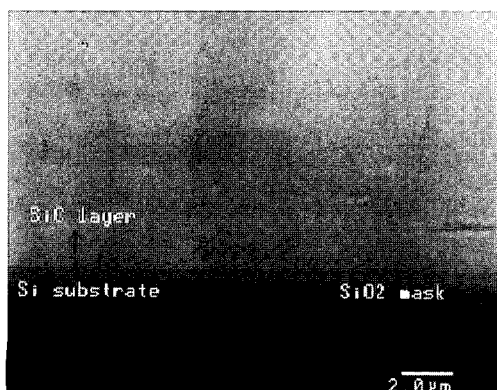


Fig. 6. SEM micrograph showing the SiC film deposited between a Si substrate and SiO<sub>2</sub> mask at the precursor flow of 10 sec and HCl gas of 200 sccm.

However, it was impossible to observe SiC film on the SiO<sub>2</sub> mask by SEM. Therefore, in order to investigate the selectivity of SiC deposition, X-ray mapping of SiC film at the interface between Si substrate and SiO<sub>2</sub> mask was carried out. As shown in Fig. 7, the intensities of silicon and carbon on the Si substrate were uniformly distributed and were

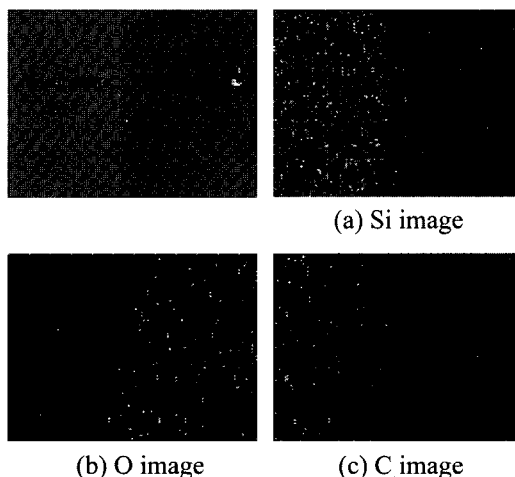


Fig. 7. X-ray mapping image of SiC film at the interface between Si substrate and SiO<sub>2</sub> mask: (a) Si image, (b) O image and (c) C image were shown.

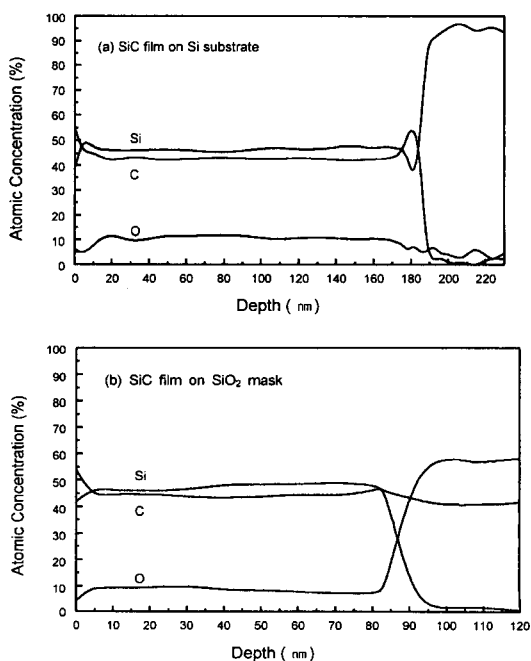


Fig. 8. AES depth profiles of the films deposited on (a) the Si substrate area and (b) the SiO<sub>2</sub> mask area.

higher than those on the SiO<sub>2</sub> mask. Therefore, the preference of SiC deposition on a Si substrate could be observed.

Figure 8 show AES depth profiles of the films deposited on the Si substrate and the SiO<sub>2</sub> mask. It was observed that the SiC film of about 0.08  $\mu\text{m}$  thick was deposited on a SiO<sub>2</sub> mask. Accumulation of carbon was observed in the interface between the SiC film and Si substrate. It was expected that higher accumulation of carbon in the interface between the SiC film and Si substrate rather than that between the SiC film and SiO<sub>2</sub> mask resulted in the preference of carbonization reaction on a Si substrate by excess carbon in the HMDS precursor. Also, it was revealed that chlorine was not incorporated in the film. It was expected that relatively high atomic concentration of oxygen in SiC film resulted from unintentionally introducing of oxygen gas.

Figure 9 show the AFM images of  $\beta$ -SiC films deposited without HCl gas and with HCl gas. Both film thicknesses were about 0.4  $\mu\text{m}$ . Average roughnesses of the film surfaces (Figs. 9 (a) and (b)) were 25.8  $\text{\AA}$  and 27.6  $\text{\AA}$ , respectively. There was no apparent difference between the roughness of these two films. Therefore, it was concluded that HCl gas did not affect the surface roughness seriously and the surface of the film was smooth enough for the microelectronic device application. Figure 10 show the

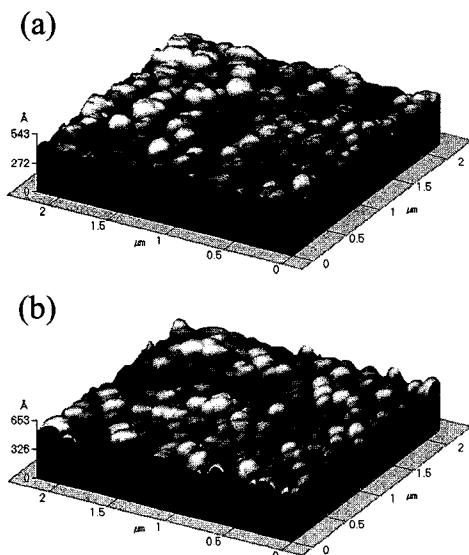


Fig. 9. AFM images of  $\beta$ -SiC films deposited (a) without HCl gas and (b) with HCl gas.

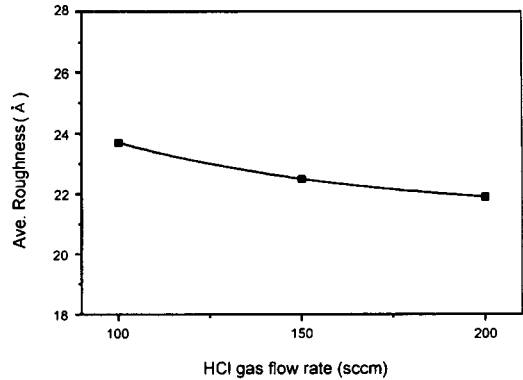


Fig. 10. Average roughness of SiC films obtained at various HCl gas flow rate.

average roughnesses of SiC films obtained at various HCl gas flow rate. Significant change in the average roughness was not observed for the varieties of the HCl gas flows. It was confirmed that the selectivity of SiC deposition was improved by introducing HCl gas. Also, the pulse flow technique of the precursor gas was effective to enhance the selectivity.

#### 4. Conclusions

The optimum condition of the substrate temperature for SiC deposition using HMDS/H<sub>2</sub> gas system was determined as 1100°C. The film was preferentially grown along the <111> direction with a mirror-like surface.

As the HCl gas flow rate increased, both the thicknesses of SiC films on a Si substrate and a mask area decreased. However, the deposition rate on a Si substrate was faster than that on a mask area. X-ray mapping and AES depth profile of SiC film proved the preference of SiC deposition on a Si substrate rather than SiO<sub>2</sub> mask. Introduction of the HCl gas did not affect the surface roughness seriously and the surface of the film was suitable for microelectronic device application. HCl gas and the pulse flow technique of the precursor gas were effective to enhance the selectivity.

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