Selective Chemical Vapor Deposition of β-SiC on Si Substrate Using Hexamethyldisilane/HCl/H_2 Gas System

Won Jae Yang, Seong Jin Kim*, Yong Sun Chung and Keun Ho Auh****

Department of Ceramic Engineering, Hanyang University,

Seoul 133-791, Korea

***Samsung Advanced Institute of Technology, P. O. Box 111,**

Suwon 440-600, Kyunggi-do, Korea

****Ceramic Processing Research Center, Hanyang University,**

Seoul 133-791, Korea

Abstract

Selectivity of SiC deposition on a Si substrate partially covered with a masking material was investigated by introducing HCl gas into hexamethyldisilane/H_2 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.

I. Introduction

Cubic SiC is a favorable semiconductor material for high temperature, high power and high speed electronic devices, because of a wide band gap energy (2.2 eV at 300K), a high saturated electron velocity (2.7×10^7cm/s), a high electron mobility (1000 $cm^2/V\cdot s$) and a high thermal conductivity (3.5 W/cm℃ at 300K)[1-2]. In case of Si-based devices, they should be kept below 150℃ 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[3,4].

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[5] and ECR plasma etching[6] can be used, the etched surface becomes unsuitable for a microelectronic device application. Therefore, the selective deposition technique of SiC

becomes one of the promising ways to achieve the patterning.

In this study, the relation between the SiC film and the deposition conditions was 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.

Ⅱ. Experimental Procedures

Hexamethyldisilane ($Si_2(CH_3)_6$) was used as a single precursor for SiC deposition. <100> oriented p-type Si wafer patterned with SiO_2 and Si_3N_4 mask materials was used as a substrate. Dimensions of patterned openings in a masking layer were 1.615 ㎜ × 0.510㎜. 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_2 gas, the vapor pressure of liquid source or the temperature of bubbler containing liquid HMDS precursor. Bubbler temperature was held at 3~4℃ using ice water bath. The vapor pressure of liquid source at this temperature was about 9 torr[7]. The flow rate of carrier H_2 gas through a bubbler was varied from 1 to 5 sccm. In order to etch the Si nuclei and enhance the selectivity of SiC deposition, hydrogen chloride (HCl) gas was introduced to HMDS/H_2 gas system during the β-SiC deposition. The flow rate of HCl gas was varied from 20 to 200 sccm. β-SiC deposition was carried out at the substrate temperature of 1100 ~ 1200℃ and the reactor pressure of 30 ~ 50 torr.

Ⅲ. Results and Discussions

The film deposited on unpatterned Si substrate with the growth rate of about 1.9 ㎛/hr showed a mirror-like surface. 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℃. Therefore, optimum substrate temperature was chosen at 1100℃. By the X-ray diffraction patterns, the deposited films were identified as β-SiC phase and preferentially grown along the <111> direction.

The schedule of precursor flows was modified to investigate the selectivity of SiC deposition. 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. 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_2 and Si_3N_4) on the selectivity in SiC deposition was not observed.

In order to enhance the selectivity of SiC deposition and differentiate the nucleation rates on a substrate and mask areas, the precursor flow time decreased to 20 and 10 sec. Fig. 1 shows SEM micrograph of the SiC film deposited between the Si substrate and the SiO_2 mask at the precursor flow of 10 sec and HCl gas of 200 sccm. The film of about 0.2 ㎛ thick was deposited on the Si substrate. However, it was impossible to observe SiC film on the SiO_2 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_2 mask was carried out. As shown in Fig. 2, the intensities of Si and C on the Si substrate were uniformly distributed and were higher than those on the SiO_2 mask. Therefore, the preference of SiC deposition on a Si substrate could be observed.

Fig. 3 show AES depth profiles of the films deposited on the Si substrate and the SiO_2 mask. It was observed that the SiC film of about 0.08 ㎛ thick was deposited on a SiO_2 mask. Accumulation of C was observed in the interface between the SiC film and Si substrate as well as the SiC film and SiO_2 mask. It was expected that higher accumulation of C in the interface between the SiC film and Si substrate rather than that between the SiC film and SiO_2 mask resulted in the preference of carbonization reaction on a Si substrate. It was expected that relatively high atomic concentration of O resulted from unintentionally introducing of oxygen gas.

Fig. 4 show the AFM images of β-SiC films deposited without HCl gas and with HCl gas. Both film thicknesses were about 0.4 ㎛. Average roughnesses of the film surfaces (Fig. 4 (a) and (b)) were 25.8 Å and 27.6 Å, 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. Also, significant change in the average roughness was not observed during 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.

Ⅳ. Conclusions

The optimum condition of the substrate temperature for SiC deposition using HMDS/H_2 gas system was determined as 1100℃. 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. 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 was effective to enhance the selectivity.

Acknowledgments

This work was supported by the Korean Science and Engineering Foundation (KOSEF) under the project No. 971-0802-024-2.

References

1. S. Nishino, H. Suhara, H. Ono and H. Matsunami, "Epitaxial Growth and Electric Characteristics of Cubic SiC on Silicon," *Journal of the Applied Physics*, **61** [10] 4889-4893 (1987).

2. G. Krotz, W. Legner, G. Muller, H. W. Grueninger, L. Smith, B. Leese, A. Jones and S. Rushworth, "Structural and Electronic Characterization of β-SiC Films on Si Grown from Mono-methylsilane Precursors," *Materials Science and Engineering B*, **29** 154-159 (1995).

3. J. A. Powell, L. G. Matus and M. A. Kuczmarski, "Growth and Characterization of Cubic SiC Single-Crystal Films on Si," *Journal of the Electrochemical Society,* **134** [6] 1558-1565 (1987).

4. K. Shibahara, S. Nishino and H. Matsunami, "Surface Morphology of Cubic SiC(100) Grown on Si(100) by Chemical Vapor Deposition," *Journal of Crystal Growth*, **61** 538-544 (1986).

5. S. Matsui, S. Mizuki, T. Yamoto, H. Aritone and S. Namba, "Reactive Ion-beam Etching of Silicon Carbide," *Japanese Journal of the Applied Physics*, **20** L38-L40 (1981).

6. S. Dohmae, K. Shibahara, S. Nishino and H. Matsunami, "Plasma Etching of CVD Grown Cubic SiC Single Crystals," *Japanese Journal of the Applied Physics*, **24** L873-L875 (1985).

7. K. Takahashi, S. Nishino and J. Saraie, "Low-Temperature Growth of 3C-SiC on Si substrate by Chemical Vapor Deposition Using Hexamethyldisilane as a Source Material," *Journal of the Electrochemical Society*, **139**(12) 3565-3571 (1992).

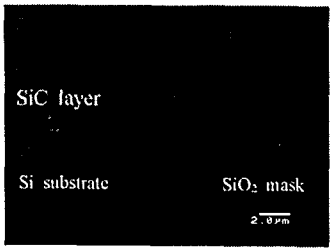

Fig. 1. SEM micrograph showing the SiC film deposited between a Si substrate and SiO_2 mask at the precursor flow of 10 sec and HCl gas of 200 sccm..

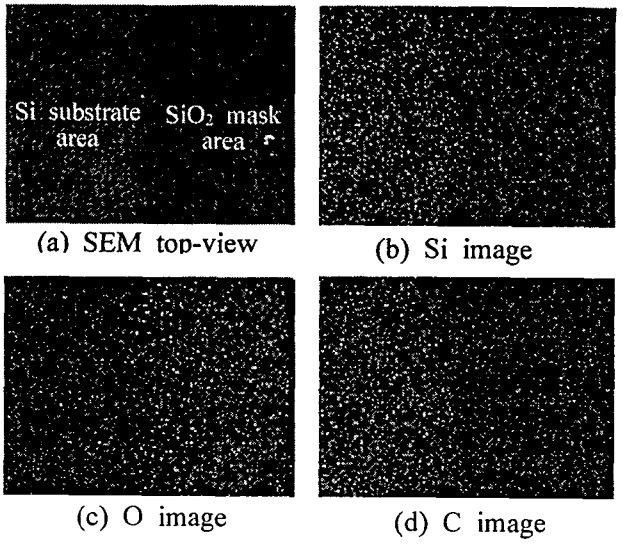

Fig. 2. X-ray mapping image of SiC film at the interface between Si substrate and SiO_2 mask

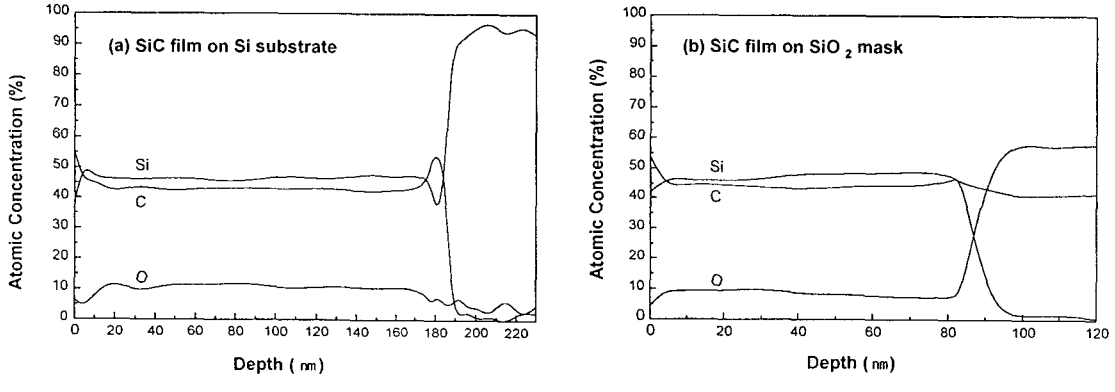

Fig. 3. AES depth profiles of the films deposited on (a) the Si substrate area and (b) the SiO_2 mask area.

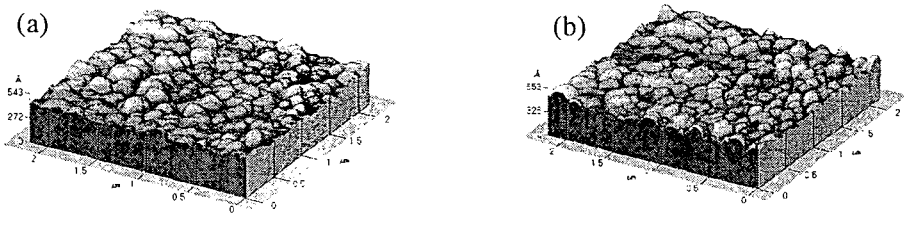

Fig. 4. AFM images of β-SiC films deposited (a) without HCl gas and (b) with HCl gas.