Numerical modeling of SiC–CVD in a horizontal hot-wall reactor

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Abstract

A numerical simulation was carried out on SiC–CVD in a horizontal hot-wall reactor. In order to explain the effect of surface polarity, Si-face and C-face, the surface reaction model was improved. Then, the growth processes and doping features of both Si-face and C-face were analyzed. The role of conditions at growing surface, such as surface mass flux of both Si-containing and C-containing species, surface concentration of Si-containing and C-containing species and their ratio, is investigated. Then, the deposition and etching rates, and doping concentration are analyzed as the function of those parameters. In addition, surface morphology of growing epitaxial layer is also investigated in connection with growing surface condition.

Keywords: Chemical vapor deposition; Simulation; Deposition; Etching; Doping; Surface reaction

1. Introduction

There are lots of experimental reports on SiC–CVD [1–6]. Each report states that the result depends on the experimental condition and reactor design. In addition, the discussion of inlet conditions such as source gas C/Si ratio, and not the conditions at the surface where the deposition occurs is leading to the confusion. There are several reports on numerical simulations that attempt to explain the mechanism of SiC–CVD [2–6], however, there are problems remaining to be solved, such as doping incorporation. Silicon carbide is a polar material, i.e. the surfaces are terminated either with silicon (Si-face) or carbon (C-face) in the *c*-axis direction. The doping incorporation features of C-face appear to be different from those of the Si-face [7].

In this study, a surface reaction model [8] is improved to explain the effect of surface polarity, Si-face and C-face. Using this model, a numerical simulation was carried out on SiC–CVD in a horizontal hot-wall reactor.

The roles of growth surface conditions, especially the mass flux of Si- and C-containing species to the growing surface and its concentration in the gas phase, are discussed.

2. Numerical modeling

Fig. 1 shows the schematic model applied in this study. The horizontal hot-wall CVD reactor has been simplified in the 2D model. Only the gas phase region with the susceptor surfaces is regarded as a numerical domain. In this study, CFD-ACE+ commercially available software was used [9].

Shown in Tables 1 and 2 shows the model proposed by Meziere et al. [8] for SiC–CVD reactions in gas phase and on the surface. They showed a good agreement in etching and deposition distribution between the model and the experiment for the Si-face [8]. In this study, to explain the effect of surface polarity, Si-face and C-face, their surface reaction model was improved by changing the rate constant of surface reactions. The concept was deduced from the SiC crystal structure. In the Si-face, each surface silicon has three bonds with the next carbon layer, and each surface carbon has only one bond with the next silicon

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Fig. 1. Schematic model of numerical simulation (bold line: measurement temperature distribution was settled as boundary condition).

Table 1
Gas phase reaction model [8]

SiH_4	=	$\text{SiH}_2 + \text{H}_2$	(1)
Si_2H_6	=	$\text{SiH}_2 + \text{SiH}_4$	(2)
SiH_2	=	$\text{Si} + \text{H}_2$	(3)
$2\text{H} + \text{H}_2$	=	2H_2	(4)
C_3H_8	=	$\text{CH}_3 + \text{C}_2\text{H}_5$	(5)
$\text{CH}_4 + \text{H}$	=	$\text{CH}_3 + \text{H}_2$	(6)
$\text{C}_2\text{H}_5 + \text{H}$	=	2CH_3	(7)
2CH_3	=	C_2H_6	(8)
$\text{C}_2\text{H}_4 + \text{H}$	=	C_2H_5	(9)
C_2H_4	=	$\text{C}_2\text{H}_2 + \text{H}_2$	(10)
H_3SiCH_3	=	$\text{HSiCH}_3 + \text{H}_2$	(11)
H_3SiCH_3	=	$\text{SiH}_2 + \text{CH}_4$	(12)
Si_2	=	2Si	(13)
$\text{Si}_2 + \text{CH}_4$	=	$\text{Si}_2\text{C} + 2\text{H}_2$	(14)

Table 2
Surface reaction model [8]

$\text{C} + \text{Si}_\text{s} + \text{H}_2$	→	$\text{SiH}_2 + \text{C}_\text{s}$	(1)
$2\text{Si} + 2\text{C}_\text{s} + \text{H}_2$	→	$\text{C}_2\text{H}_2 + 2\text{Si}_\text{s}$	(2)
$\text{SiH}_4 + \text{C}_\text{s}$	→	$\text{SiH}_2\text{s} + \text{H}_2 + \text{C}$	(3)
SiH_2s	→	$\text{H}_2 + \text{Si}_\text{s}$	(4)
$\text{SiH}_2 + \text{C}_\text{s}$	→	$\text{SiH}_2\text{s} + \text{C}$	(5)
$\text{Si} + \text{C}_\text{s}$	→	$\text{Si}_\text{s} + \text{C}$	(6)
$\text{C}_2\text{H}_2 + 2\text{Si}_\text{s}$	→	$2\text{C}_\text{s} + \text{H}_2 + 2\text{Si}$	(7)
$\text{C}_2\text{H}_4 + 2\text{Si}_\text{s}$	→	$2\text{C}_\text{s} + 2\text{H}_2 + 2\text{Si}$	(8)
$\text{CH}_4 + \text{Si}_\text{s}$	→	$\text{C}_\text{s} + 2\text{H}_2 + \text{Si}$	(9)
$\text{HSiCH}_3 + \text{C}_\text{s}$	→	$\text{C} + \text{Si}_\text{s} + \text{H} + \text{CH}_3$	(10)
$\text{CH}_3 + \text{Si}_\text{s}$	→	$\text{Si} + \text{C}_\text{s} + 1.5\text{H}_2$	(11)
$\text{Si}_2 + 2\text{C}_\text{s}$	→	$2\text{C} + 2\text{Si}_\text{s}$	(12)
$\text{Si}_2\text{C} + \text{Si}_\text{s}$	→	$\text{Si}_2 + \text{Si} + \text{C}_\text{s}$	(13)
$\text{SiCH}_2 + \text{C}_\text{s}$	→	$\text{C} + \text{Si}_\text{s} + \text{CH}_2$	(14)
$\text{CH}_2 + \text{Si}_\text{s}$	→	$\text{C}_\text{s} + \text{Si} + \text{H}_2$	(15)

* s means the surface species in solid phase.

layer. It can therefore be assumed that removal of carbon is much easier than that of silicon, and the deposited silicon is much more stable than the deposited carbon. In the case of the C-face, the opposite features can be expected because each surface carbon has three bonds with the next silicon layer, and each surface silicon has only one bond with the next carbon layer. Based on this concept, the reaction rate constants in Table 2 were modified in this study as follows. In the case of Si-face, during both the removal and deposition processes, the surface of the solid phase must be terminated by surface silicon (Si_s), and the surface

reactions that produce surface carbon (C_s) are the rate determining step with small reaction rate constant. On the other hand, in the case of C-face, during both the removal and deposition processes, the surface of the solid phase must be terminated by surface carbon (C_s), and the surface reactions that produce surface silicon (Si_s) are the rate determining step with small reaction rate constant.

3. Results and discussion

3.1. Growth process

Fig. 2 shows the calculated growth rate at the center of the wafer with Si-face. From Fig. 2(a), it can be seen that when C_3H_8 flow rate is small, the growth rate increases with C_3H_8 flow rate. And the C_3H_8 flow rate dependencies vary with the SiH_4 flow rate. Above the certain C_3H_8 flow rate, the growth rate increases only slightly, even though the C_3H_8 flow rate increases. This critical C_3H_8 flow rate also depends on the SiH_4 flow rate. Fig. 2(b) shows the relationship between the surface C flux and the growth rate at the center of the wafer of the Si-face. From Fig. 2(b), it can be seen that when the surface C flux is small, the growth rate increases proportionally to the surface C flux regardless of the inlet source gas flow rate. However, above

Fig. 2. Growth rate obtained by numerical modeling. ($P = 250$ mbar, $\text{H}_2 = 40$ slm constant.) (a) Effect of inlet C_3H_8 flow rate and (b) effect of surface C flux.

a certain surface C flux, the growth rate increases only slightly. In this region, the growth rate depends on a surface Si flux. This means that under and above the certain surface C flux condition, surface C flux and surface Si flux determine the growth rate, respectively. At the critical condition, the surface C flux is equal to the surface Si flux. From Fig. 2(b), growth rate is explained as a simple function of surface C and Si fluxes regardless of inlet condition. The surface flux appears to be the universal parameter that explains the SiC-CVD process independently of the inlet condition. Numerical results of the C-face are the same as Fig. 2.

Fig. 3 shows the effect of source gas flow rate on both the growth rate and C/Si ratio in the gas phase at the center of the wafer of the Si-face. From Fig. 3(a), as the source gas flow rate increases, the growth rate also increases. However, the expected surface morphology is different with C/S ratio at the inlet as shown in Fig. 3(a). From Fig. 3(b), it can be seen that when the inlet C/Si is equal to 1.5, with increasing the source gas flow rate, the surface C/Si ratio increases. Then, the excess carbon might result in an increases surface roughness. On the other hand, when the C/Si ratio at the inlet is 0.5, the surface C/Si ratio

decreases with increasing the source gas flow rate. A decreased C/Si ratio on the growing surface leads to a decreased surface energy. Then the micropipe closing can be expected from Frank's rule [10]. According to the Frank's rule, with decreased the surface energy, the magnitude of the Burgers vector also decreases. Similar phenomena could be expected when growth pressure decreases. [11] However, when the surface C/Si is too small, the excess silicon vapor composes silicon droplet, and leads to the rough surface.

As shown in Table 2, the surface reaction model used in this study contains both removal and deposition steps. Recently, this surface reaction model has been also applied to etching process. [12,13] Then, it was numerically suggested that the good surface morphology could be kept during the H_2 etching process with additional SiH_4 . It was because of small C/Si ratio on the wafer surface that leads to the small surface energy.

3.2. Doping

Recently, Kojima et al. [7] experimentally investigated the doping incorporation features on both the Si-face and the C-face [7]. In their experiments, to change the C/Si ratio at the inlet, the SiH_4 flow rate was fixed and the C_3H_8 flow rate was varied. Concerning N doping, increasing the C_3H_8 flow rate leads to decreased doping concentration. This can be explained in terms of the site competition model [14,15]. If nitrogen replaces carbon, increasing the amount of carbon, while keeping the nitrogen amount constant leads to a decreased replacement ratio. With respect to Al doping, increasing the C_3H_8 flow rate increases the doping concentration. However, in their experiment, the SiH_4 and $Al(CH_3)_3$ flow rates were constant. According to the site competition model, aluminum replaces silicon. It appears that the site competition model can not explain why the replacement ratio changes in spite of the silicon and aluminum flow rates remaining constant.

In this study, the amounts of surface silicon and surface carbon in the gas phase were also calculated. Fig. 4 shows the relationship between the calculated molar fraction of the surface carbon and the surface silicon at the center of the wafer and the experimentally obtained nitrogen and aluminum doping concentration, respectively. In the experiment, nitrogen was doped unintentionally, and aluminum was doped with a small TMA flow rate. In this study, the nitrogen and aluminum amounts were assumed to be very low and constant. Then only the surface carbon and surface silicon amounts were considered for the replacement ratio. Fig. 4 shows that as the molar fractions of surface carbon and surface silicon increase, nitrogen and aluminum doping concentration decreases, respectively. The surface silicon amount changes with C_3H_8 flow rate even though the inlet SiH_4 flow rate is constant, and from Fig. 4, the doping incorporations of both nitrogen and aluminum could be explained by the site competition model while taking account of the molar fractions of the surface

Fig. 3. Effect of source gas flow rate on growth rate and expected surface morphology. ($P = 250$ mbar, $H_2 = 40$ slm, and C/Si at inlet constant.) (a) Growth rate obtained by numerical modeling and surface morphology obtained by experiment and (b) surface C/Si ratio obtained by numerical modeling and surface morphology obtained by experiment.

Fig. 4. Relationship between calculated surface molar fraction and doping concentration obtained experimentally. ($P = 250$ mbar, $\text{SiH}_4 = 6.67$ sccm, C_3H_8 flow rate was varied, $\text{H}_2 = 40$ slm.) (a) Nitrogen doping (N was doped unintentionally.) (b) Aluminum doping ($\text{Al}(\text{CH}_3)_3 = 0.1$ sccm in experiments.)

carbon and the surface silicon. Fig. 4(a) shows that nitrogen concentration on C-face is higher than that on Si-face. It might be because the nitrogen can easier replace the surface carbon in the first layer on the C-face than replacing the second layer of C-atoms in growth on the Si-face. On the other hand, Fig. 4(b) shows that aluminum concentration on Si-face is higher than that of C-face, since aluminum can easier replace surface silicon on the Si-face than replacing the second layer of Si-atoms in growth on the C-face. However, the molar fraction dependences of the Si-face and C-face are different, suggesting that the doping

mechanisms on the Si-face and C-face, and of nitrogen and aluminum, are different.

4. Conclusion

In this study, the surface reaction model was improved to explain the effect of surface polarity. The improved model was able to explain the growth processes precisely, and showed that the growing surface condition is a good parameter to explain the growth rate and surface morphology. Concerning doping incorporation, the improved model shows that the site competition model can explain the doping features of nitrogen and aluminum while taking account of the molar fractions of the surface silicon and the surface carbon, respectively.

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