Aluminum doping of epitaxial silicon carbide

U. Forsberg[a,*], Ö. Danielsson[a], A. Henry[a], M.K. Linnarsson[b], E. Janzén[a]

[a] Department of physics and measurement technology, Linköping University, SE-581 83 Linköping, Sweden
[b] Solid State Electronics, Royal Institute of Technology, SE-164 40 Kista, Sweden

Abstract

Intentional doping of aluminum in 4H and 6H SiC has been performed using a hot-wall CVD reactor. The dependence of aluminum incorporation on temperature, pressure, C/Si ratio, growth rate, and TMA flow has been investigated. The aluminum incorporation showed to be polarity dependent. The high aluminum incorporation on the Si-face is closely related to the carbon coverage on the SiC surface. Changes in process parameters changes the effective C/Si ratio close to the SiC surface. Increased growth rate and C/Si ratio increases the aluminum incorporation on the Si-face. Diffusion limited incorporation occurs at high growth rate. Reduced pressure increases the effective C/Si ratio, and at low growth rate, the aluminum incorporation increases initially, levels off at a critical pressure, and continues to decrease below the critical pressure. The aluminum incorporation showed to be constant in a temperature range of 50°C. The highest atomic concentration of aluminum observed in this study was 3×10^{17} and 8×10^{18} cm^{-3} in Si and C-face, respectively.
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1. Introduction

With the introduction of the step-controlled growth [1] and the understanding of the different process parameters involved during chemical vapor deposition (CVD) of SiC, the ability to grow high quality device structures, such as thick drift layers for high power and thin multilayers for microwave devices, have become possible. Depending on the device structure, the growth condition is different for different devices. A power device requires a thick ($\sim 50\,\mu$m) drift layer, which should be low doped and preferably grown with high growth rate. A microwave device should be grown with relatively low growth rate to obtain abrupt doping profiles between the different epitaxial layers [2]. Most devices need a highly doped cap layer to form an ohmic contact. The

*Corresponding author. Okmetic AB, Hans Meijers väg 2, SE-583 30 Linköping, Sweden. Tel.: +46-13-282-699; fax: +46-13-142-337.
E-mail address: urban.forsberg@okmetic.com (U. Forsberg).

doping should, in the case of p-type material, be at least in the high 10^{18} cm^{-3} range. All the epitaxial layers should also be grown without any defects and with a good morphology.

In SiC, aluminum is the most important p-type dopant. To our knowledge, no thorough investigation has been made on aluminum incorporation in SiC in a horizontal hot-wall CVD reactor. In this paper we present how the aluminum incorporation in a hot-wall CVD reactor is influenced by several important process parameters, such as C/Si ratio, growth rate, pressure, and temperature. First thermodynamical calculations will be presented, and then results from simultaneous growth on 6H and 4H polytypes, as well as on C- and Si-face. A comparison with previously published results will be made.

2. Experimental procedure

The reactor used in the experiment is a commercial hot-wall CVD reactor. The reactor has been modified to fulfill our demands on intentional aluminum doping in the range of 10^{14}–10^{20} cm^{-3}. The SiC-coated susceptor has previously been described [3]. The precursors were silane (5% in H$_2$ (purity 99.9999%)) and propane (5% in H$_2$ (purity 99.9999%)). Palladium diffused hydrogen was used as carrier gas and trimethylaluminum (TMA) was used as dopant gas. The SiC coated graphite susceptor was inductively heated by an RF generator. The temperature was measured by a two-color pyrometer. Silicon melting was performed to calibrate the temperature inside the susceptor to an accuracy better than $\pm 5^\circ$C. A throttle valve was used to vary the pressure from atmospheric pressure down to 50 mbar during the same run. The base pressure in the reactor chamber before growth was always lower than 1×10^{-6} mbar. Commercially available 4H- and 6H-SiC Si-face and 6H-SiC C-face substrates were used. The 4H- and 6H-SiC substrates were off-oriented 8° and 3.5° towards the $\langle 1\,1\,\bar{2}\,0 \rangle$ direction, respectively. All samples were cut and then cleaned using (H$_2$O, NH$_3$ (25% in H$_2$O), H$_2$O$_2$; 5:1:1), (H$_2$O, HCl, H$_2$O$_2$; 5:1:1), and a final HF dip for 1 min.

Secondary ion mass spectrometry (SIMS) measurements were performed on all samples. An intentional doping with aluminum was performed during these runs to provide an aluminum atomic concentration higher than 1×10^{14} cm^{-3}, which is the lowest detection limit for SIMS.

3. Aluminum incorporation model

In the case of aluminum doping of SiC the main aluminum-containing species are found in the AlH$_2$, AlCH$_3$ Al, AlH$_3$ and AlH. The SiC "building" block is a tetrahedral where the silicon atom is placed in the middle, see Fig. 1. Since aluminum substitutes the silicon atom in the SiC lattice, its bonding to the surface may be different for different faces. Aluminum, which has a high vapor pressure, may easily desorb. The degree of desorption is dependent on not only the chosen growth parameters, but also whether the substrate surface is terminated by silicon (Si-face) or carbon (C-face). On the Si-face terrace the aluminum atom, at a Si surface site, will form three bonds to the three different carbon atoms, assuming ideal bulk terminated surface. This assumption is valid due to the high growth temperature used for SiC growth. On the C-face, the aluminum atom can only form one bond with one carbon atom, and therefore the aluminum atom may easily desorb. The adsorption energy of an aluminum atom on a Si- and C-face are calculated to 578 and 1349 kJ/mol, respectively [4], indicating a more than two times stronger bonding on the Si-face.
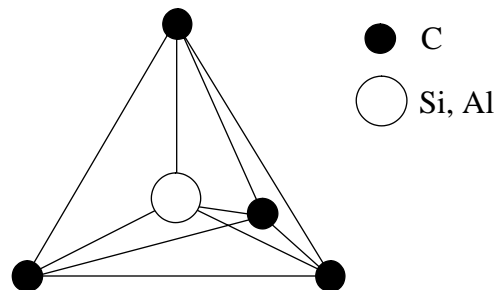

Fig. 1. The tetrahedral building block of SiC and the position for a substituted silicon atom.
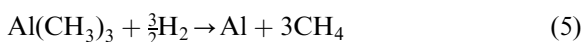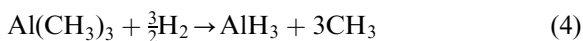
4. Thermodynamic calculations

In order to get an insight on the process of aluminum incorporation into the SiC lattice we have applied equilibrium thermodynamic calculations. The analysis was performed on the H_2–SiH_4–C_3H_8–$Al(CH_3)_3$ system using the commercially available code CFD-ACE+[1]. The calculations were performed under the assumption that the gas is ideal. In a CVD system the vapor phase is commonly considered to be ideal since the precursors are highly diluted in the hydrogen carrier gas [5]. Since the SiC growth and aluminum incorporation occur on the surface where there is no equilibrium condition, our theoretical analysis could only guide us but not give a full understanding of the aluminum incorporation. The silicon, carbon, and aluminum-containing species taken into account in the analysis are presented in Table 1.

The calculations showed that the main aluminum-containing species are AlH_2, $AlCH_3$, Al, AlH_3 and AlH. Aluminum is believed to form the highly stable aluminum carbide species (Al_4C_3) [5]. However in our equilibrium thermodynamical calculations we obtained concentrations that were 10^{-10} times less than for the main aluminum-containing species. Several reaction models of TMA with hydrogen have been proposed [6–8]. The main decomposition process is believed to be the following process:

$$Al(CH_3)_3 \rightarrow Al(CH_3)_2 + CH_3 \qquad (1)$$
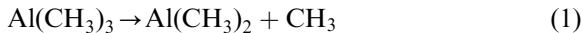
The release of a methyl group is very efficient. In the presence of hydrogen the methyl group(s) are easily replaced by hydrogen(s) according to
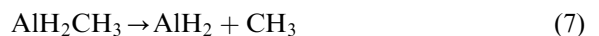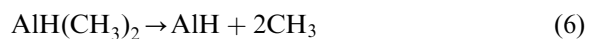
$$Al(CH_3)_3 + \tfrac{1}{2}H_2 \rightarrow AlH(CH_3)_2 + CH_3 \qquad (2)$$

$$Al(CH_3)_3 + H_2 \rightarrow AlH_2CH_3 + 2CH_3 \qquad (3)$$

$$Al(CH_3)_3 + \tfrac{3}{2}H_2 \rightarrow AlH_3 + 3CH_3 \qquad (4)$$

$$Al(CH_3)_3 + \tfrac{3}{2}H_2 \rightarrow Al + 3CH_4 \qquad (5)$$
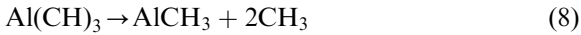
Table 1
Different species taken into account in the thermodynamical calculations

24 Carbon species	35 Silicon + Carbon species	8 Carbon + Aluminum species
C	SiC	AlC
CH	SiCH	$AlCH_3$
CH_2	HSiC	H_2AlCH_3
CH_3	$SiCH_2$	$HAlCH_3$
CH_4	H_2SiC	$Al(CH_3)_2$
C_2	H_2SiCH	$HAl(CH_3)_2$
C_2H	$HSiCH_2$	$Al(CH_3)_3$
C_2H_2	H_3SiC	$Al_2(CH_3)_6$
C_2H_3	$SiCH_3$	**2 Condensed phases**
C_2H_4	$HSiCH_3$	SiC(s)
C_2H_5	H_2SiCH_2	Al_4C_3(s)
C_2H_6	H_3SiCH	**5 Included condensed**
C_3	H_2SiCH_3	**phases giving zero**
C_3H_2	H_3SiCH_2	**concentration in all**
H_2CCCH	H_3SiCH_3	**calculations**
CH_3CC	SiC_2	C(s)
C_3H_4	SiCCH	Si(s)
CH_2CHCH_2	HSiCCH	Si(l)
CH_3CCH_2	H_2SiCCH	Al(s)
CH_3CHCH	H_2CCHSi	Al(l)
C_3H_6	$H_2CCHSiH$	
i-C_3H_7	H_3SiCCH	
n-C_3H_7	$H_2CCHSiH_2$	
C_3H_8	$Si(CH_3)_2$	
2 Pure Hydrogen species	$H(CH_3)SiCH_2$	
H	$H_2CCHSiH_3$	
H_2	$HSi(CH_3)_2$	
14 Silicon species	$H_2Si(CH_3)CH_2$	
Si	$H_2Si(CH_3)_2$	
SiH	$(CH_3)_2SiCH_2$	
SiH_2	$Si(CH_3)_3$	
SiH_3	$HSi(CH_3)_2CH_2$	
SiH_4	$HSi(CH_3)_3$	
Si_2	Si_2C	
Si_2H_2	$CH_3SiH_2SiH_2CH_3$	
Si_2H_3	**6 Aluminum species**	
H_2SiSiH_2	Al	
H_3SiSiH	AlH	
Si_2H_5	AlH_2	
Si_2H_6	AlH_3	
Si_3	Al_2	
Si_3H_8	Al_2H_6	

Eqs. (2) and (3) is involved in the following reaction:

$$AlH(CH_3)_2 \rightarrow AlH + 2CH_3 \qquad (6)$$

$$AlH_2CH_3 \rightarrow AlH_2 + CH_3 \qquad (7)$$

Eq. (1) can be taken one step further and we obtain

$$Al(CH)_3 \rightarrow AlCH_3 + 2CH_3 \qquad (8)$$

Eqs. (4)–(8) gives the five most dominant aluminum-containing species as obtained from the thermodynamical calculations, i.e. Al, AlH, AlH_2, AlH_3 and $AlCH_3$. There are other reaction paths, for example

$$AlH_2CH_3 + \tfrac{1}{2}H_2 \rightarrow AlH_2 + CH_4 \qquad (9)$$
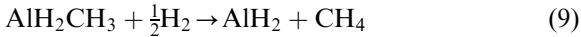
where more methane is produced. The true reaction path(s) are difficult to determine and the above reaction paths should be considered as a good model.

The decomposition of the TMA molecule starts slowly already at temperatures slightly above $100°C$ (see, for example, Ref. [9]) and we can assume that all the TMA molecules are decomposed when they reach the hot zone inside the susceptor. The aluminum incorporation will be controlled by the vapor pressure of the aluminum-containing species. It is difficult to say which of the main aluminum-containing species contributes the most to the incorporation and also if hydrogen is incorporated at the same time.

Two different sets of equilibrium calculations have been performed. One that allowed formation of solid phases and another that prohibited formation of solid phases. The calculation where the solid phase is prohibited, known as partial equilibrium, is a more realistic simulation of the gas phase [10]. The calculation where the solid phases are allowed is a simple model of the situation close to the SiC surface. It should be noted that in this first model surface reactions, like dissociation of molecules, are not taken into account. In Fig. 2a and b the mole fractions of the different silicon, carbon, and aluminum-containing species for the two different calculations are presented as a function of the temperature.

In the case of aluminum doping, almost all aluminum species are found in the hydrogen-containing molecules. The only aluminum species,
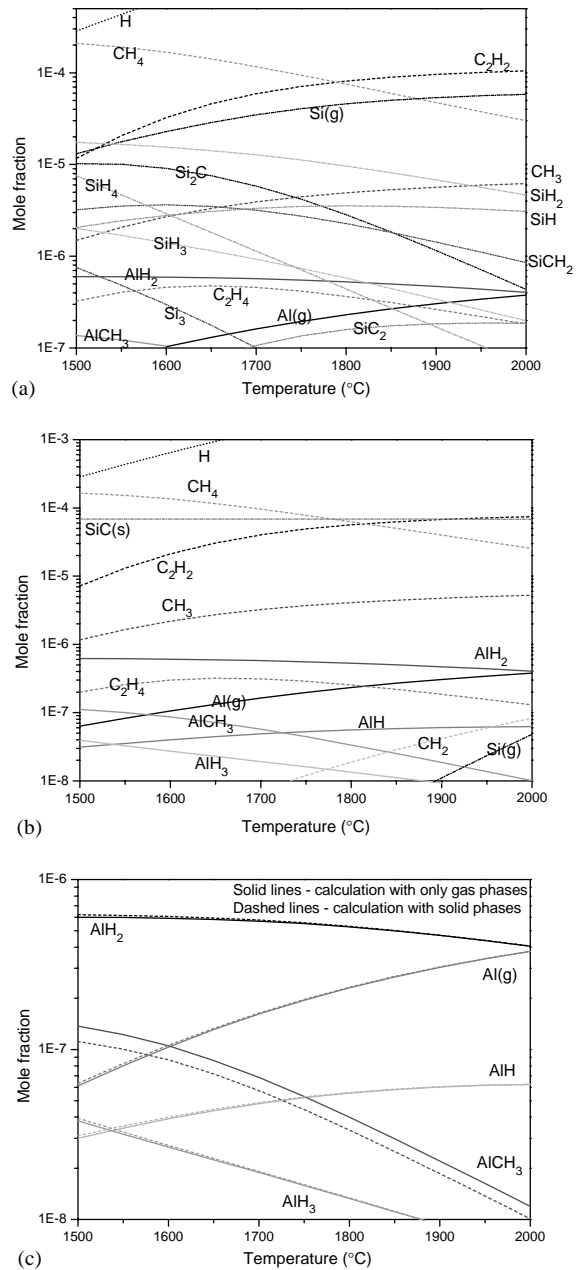

Fig. 2. Equilibrium thermodynamical calculations on an H_2–SiH_4–C_3H_8–$Al(CH_3)_3$ system. The calculations were performed with a total pressure of 1000 mbar, $T = 1600°C$, 13 l/min of H_2, 0.9 ml/min of SiH_4, 1.05 ml/min of C_3H_8 and 0.0114 ml/min of TMA: (a) Formation of solid SiC was not allowed, (b) formation of solid phases were allowed, and (c) the difference in mole fraction for the five most dominant aluminum-containing species between the two different calculations.

with a relatively large gas phase concentration, which contains carbon or silicon is the $AlCH_3$ molecule. The changes in the aluminum concentration between the different simulations are presented in Fig. 2c. As can be seen, there are no significant changes in the concentration of the aluminum-hydrogen molecules. The $AlCH_3$ molecule decreases slightly in concentration, which is probably due to the contribution of carbon to the SiC growth. These results are very different from the nitrogen incorporation in SiC, where the most dominant nitrogen-containing species is different for the two calculations [11]. Nitrogen can form molecules with both carbon and silicon atoms, with high concentrations, and consequently the results are more difficult to interpret. The temperature dependence of the partial pressures for four of the aluminum-containing species is found to follow an Arrhenius relationship, $P \propto \exp(-\Delta E / RT)$ with an apparent activation energy ΔE. The activation energy for the four most dominant aluminum-containing species are presented in Table 2.

Equilibrium thermodynamic calculations have previously been performed on a SiH_4–C_3H_8–H_2 system [10]. These calculations showed that the main carbon-containing species contributing to the growth is the C_2H_2 molecule. Although there is a large concentration of CH_4 in the calculations, this molecule is believed not to contribute to the SiC growth due to its high stability and low sticking coefficient. In the present model, the assumption that C_2H_2 is the dominant carbon-containing species for the SiC growth will be made.

5. Results

The only technique suited for epitaxial growth of SiC, where a controlled doping incorporation is available, is the CVD technique. Several different growth parameters must be precisely controlled to obtain the necessary uniformity and reproducibility. In a CVD reactor, the main process parameters influencing the aluminum incorporation are the aluminum (TMA) flow rate, reactor pressure, C/Si ratio, temperature, and growth rate. A study of the dependence on these process parameters has been made for 4H- and 6H-polytype and for both polarities.

5.1. TMA flow rate dependence

We have investigated the aluminum incorporation by varying the input TMA flow rate. The growth temperature was $1600°C$ and a C/Si ratio of 3.5 was used. The growth rate was kept unchanged at $3.2\,\mu m/h$. In Fig. 3 the aluminum doping dependence on the input TMA flow rate is presented.

As the TMA flow rate is increased the doping increases for both polytypes and faces. The aluminum incorporation on the Si-face is approximately 10 times higher than on the C-face. On the Si-face the aluminum atoms will bond to the
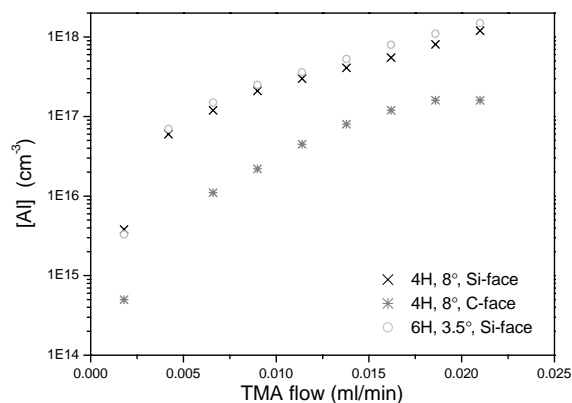
Table 2
Apparent activation energies (ΔE) for the four most dominant aluminum-containing species

Species	Al	AlH	AlH_2	AlH_3
ΔE	32	14	−4	−26

The calculations are made between $1500°C$ and $1800°C$ for two different restrictions on the simulations. The values are given in kcal/mol.

Fig. 3. The aluminum incorporation as a function of the TMA flow rate. The growth was performed at $T = 1600°C$, $p = 1000\,mbar$, C/Si $= 3.5$ and a constant growth rate of $3.2\,\mu m/h$.

surface with all its three available bonds (to three different carbon atoms), whereas on the C-face it will only form one relatively loose bond to the C-atom. Consequently, aluminum atoms on C-face are more loosely bonded compared to the Si-face and more aluminum species will desorb from the C-face, explaining the lower incorporation on the C-face. The aluminum incorporation on the C-face show a tendency to saturate at a concentration of $2 \times 10^{17} \, cm^{-3}$ and it seems difficult to obtain high p-type doping on C-face material, as previously reported [12].

5.2. Growth rate dependence

The aluminum incorporation as a function of the growth rate has been investigated. By increasing both the silane and the propane flow rates the growth rate was increased from 1.5 to 5.6 μm/h. The C/Si ratio was maintained constant at 3.5, the growth temperature was 1600°C and the pressure was one atmosphere. In Figs. 4a and b the aluminum incorporation and the growth rate versus the silane input flow rate are presented, respectively.

The amount of aluminum on the surface is in equilibrium with the gas phase and is not influenced by the increased precursor flow rate. As the growth rate is increased, the aluminum incorporation increases on the Si-face, which is due to the increased propane flow rate. The increased carbon coverage on the surface creates more available sites for the aluminum species to bond to, resulting in an increased aluminum incorporation with increasing growth rate. At very high growth rate the aluminum incorporation saturates, and a further increase is limited by diffusion of aluminum-containing species from the gas-phase to the surface. The incorporation could be increased further by increasing the TMA flow rate at the same silane flow rate. For C-face material the incorporation follows the same tendency, with the exception that the growth rate does not have as much influence as on the Si-face. The aluminum incorporation is almost constant for low growth rates but it seems to increase at very high growth rates. The lower incorporation on the C-face was explained in Section 5.1.
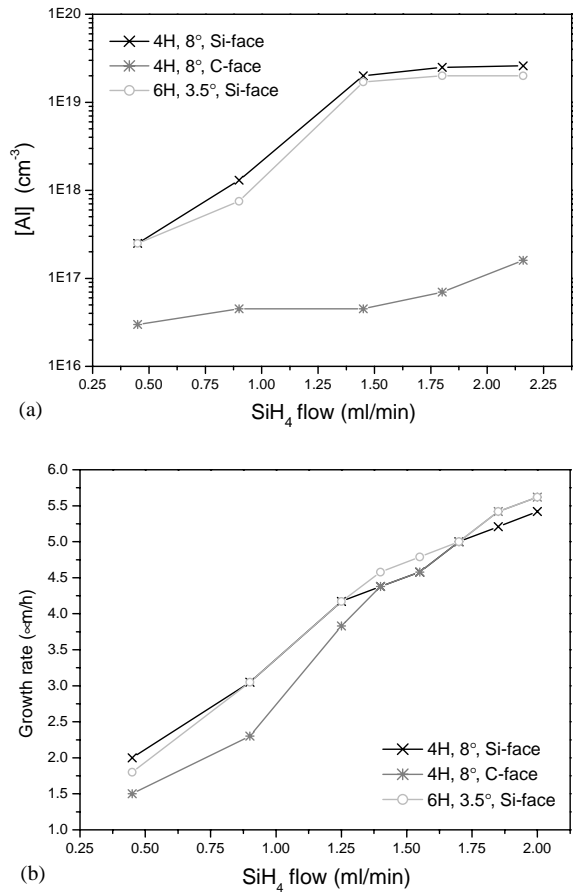

Fig. 4. (a) The aluminum incorporation versus the silane input flow, and (b) the growth rate versus the silane input flow. The growth was performed at $p = 1000 \, mbar$, TMA $= 9 \times 10^{-3} \, ml/min$, $T = 1600°C$ and C/Si $= 3.5$.

An interesting observation is that at silane flow rates of 0.45 ml/min (growth rate = 2 μm/h) and 2.0 ml/min (growth rate = 5.5 μm/h) the aluminum doping is $2 \times 10^{17} \, cm^{-3}$ and $3 \times 10^{19} \, cm^{-3}$, respectively, for the 4H Si-face, i.e. more than two orders of magnitude difference. The diffusion of aluminum species through the boundary layer is believed to be independent of the diffusion of silicon and carbon-containing species, i.e. independent of silane and propane concentration, due to the very high dilution of hydrogen. Therefore, we believe that at the low growth rate, the surface is covered with 100 times more aluminum atoms than what is incorporated. The majority of the

aluminum atoms on the surface will be desorbed due to absence of available free lattice sites. Although the decomposition of TMA is highly efficient, the aluminum incorporation on the SiC surface is in fact quite inefficient at low growth rates and at low carbon coverage.

5.3. C/Si ratio dependence

The ratio between propane and silane flow is denoted as the C/Si ratio. Aluminum atoms is believed to compete with silicon atoms for the Si-sites in the SiC lattice. At each silicon site the aluminum atom will bond to carbon atoms. As the C/Si ratio is increased, by an increase in the propane flow, the aluminum incorporation increases on the Si-face. The C-face is independent on C/Si ratio changes, as can be seen in Fig. 5.

Kimoto et al. [13] suggested a model where the C-face surface is terminated with carbon atoms during both silicon- and carbon-rich growth conditions. However, the Si-face is terminated with silicon atoms during silicon-rich growth conditions, and with carbon atoms under carbon-rich growth conditions. In this model, an aluminum atom could bond to the C-face surface with only one bond for all C/Si ratios, making aluminum incorporation on the C-face insensitive to C/Si ratio changes. The increase on the Si-face is explained by the "site competition theory" stating
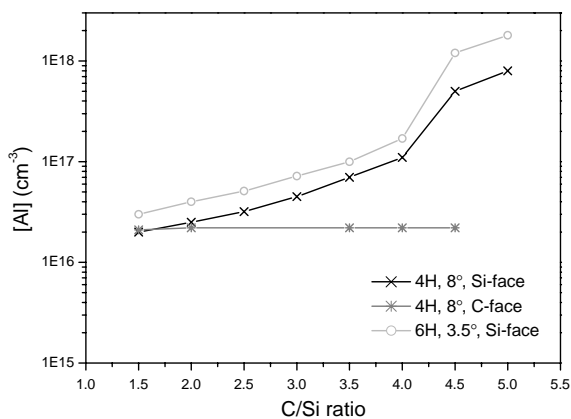
that an increase of the C/Si ratio reduces the relative amount of Si competing with aluminum on the Si-sites, and as a result, the aluminum incorporation increases.

As the C/Si ratio is increased, by increasing the propane flow rate, the amount of carbon-containing species impinging on the surface is relatively larger compared to the silicon-containing species, that are maintained constant. On the Si-face surface there will be more available sites for the aluminum to bond to, due to the higher surface coverage of carbon, resulting in an increase of the aluminum incorporation.

5.4. Pressure dependence

One important process parameter is the total pressure in the reactor. It is well known that thickness and doping uniformities are improved at reduced pressure. The depletion of reactants along the gas flow is reduced as mass transport becomes more rapid with reduced pressure [5]. We have investigated the aluminum incorporation in the pressure range of 50–1000 mbar. The growth temperature was $1600°C$ and the C/Si ratio 3.5. During growth, the total pressure in the growth chamber was reduced from atmospheric pressure to 50 mbar. Two different growth rates were used, 3.6 and $5.6 \mu m/h$. The growth rate increases slightly (5–10%) as the total pressure is reduced from 1000 to 50 mbar. This would lead to an increased aluminum incorporation, according to the arguments in Section 5.2. However, the effect is very small, and cannot explain the change in aluminum incorporation with pressure. Therefore, in the following, the effect of the higher growth rate at lower pressure will be neglected.

In Fig. 6a the aluminum incorporation is plotted versus the total pressure at a growth rate of $3.6 \mu m/h$. The incorporation of aluminum on the Si-face shows quite a remarkable behavior. When the total pressure is reduced from atmospheric pressure the aluminum incorporation starts to increase. At a total pressure of around 300 mbar, the aluminum incorporation reaches its maximum and a further decrease in pressure results in a decrease of the aluminum incorporation. Two major changes occur on the SiC surface when the
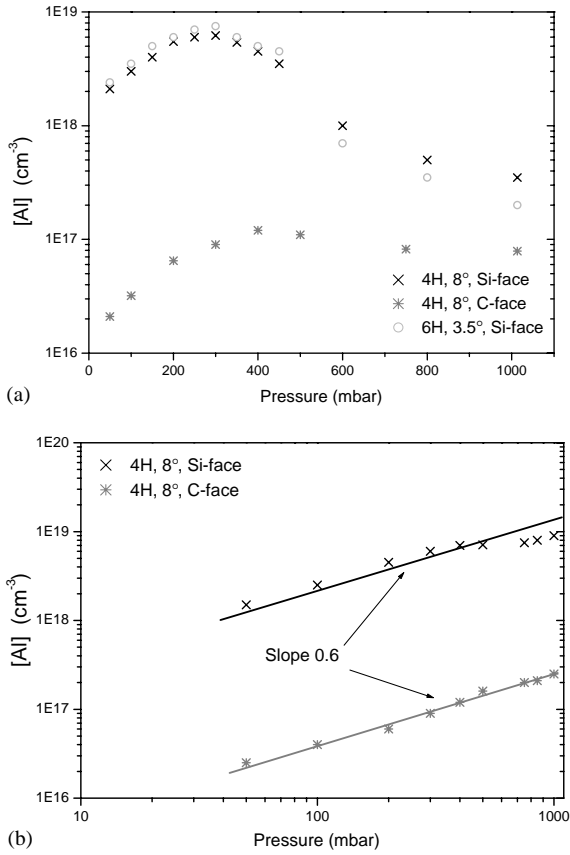

Fig. 5. The Aluminum incorporation as a function of C/Si ratio. The growth was performed at $T = 1600°C$, $p = 1000$ mbar, TMA $= 3.6 \times 10^{-3}$ ml/min and a constant growth rate of $3.2 \mu m/h$.

(a)

(b)

Fig. 6. The aluminum incorporation versus the total pressure in the reactor: (a) the growth rate was $3.6\,\mu m/h$, and (b) the growth rate was $5.6\,\mu m/h$. The growth was performed at $T = 1600^\circ C$ and with C/Si = 3.5.

(a)

(b)

Fig. 7. (a) Equilibrium thermodynamical calculations on an H_2–SiH_4–C_3H_8–$Al(CH_3)_3$ system where solid SiC was allowed form. The calculations were performed at $T = 1600^\circ C$, $13\,l/min$ of H_2, $0.9\,ml/min$ of SiH_4, $1.05\,ml/min$ of C_3H_8 and $0.0114\,ml/min$ of TMA. (b) The highest concentration of carbon, silicon and aluminum-containing species. The C_2H_2 molecule increases with decreased total pressure whereas the Si concentration is maintained constant (not shown due to very low concentration). The hydrogen concentration is too high to be shown in the graphs.

total pressure is decreased. Firstly, the partial pressures of the aluminum-containing species are reduced, which leads to a lower surface coverage of aluminum-containing species. Secondly, the *effective* C/Si ratio is increased. The increase in C/Si ratio is not only due to a reduced concentration of silicon species, resulting in a lower growth rate, but also to a relative increase of the main carbon-containing species.

In Fig. 7a the concentration of different silicon-, carbon-, and aluminum-containing species, obtained from equilibrium thermodynamical calculations, are presented as a function of the total pressure. The calculations have been performed allowing formation of solid phases, and with a gas mixture composition corresponding to the same
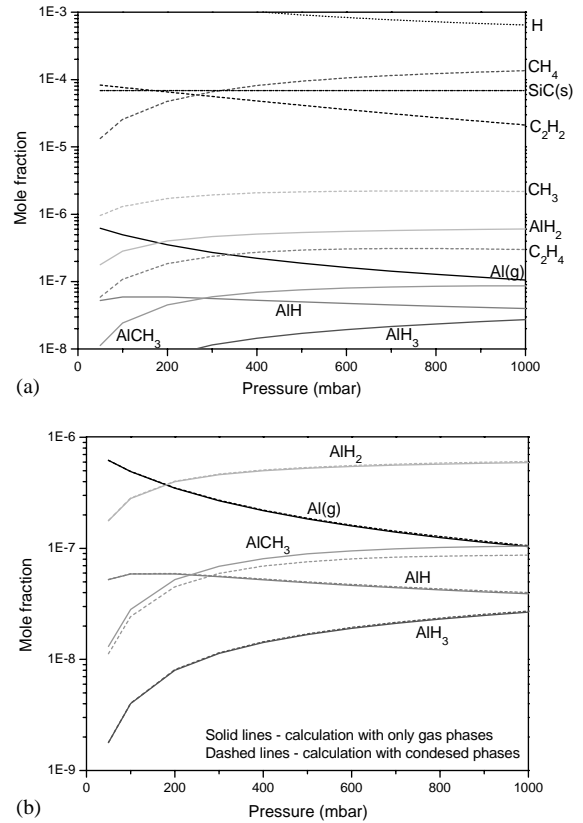
gas flow rates (and TMA flow rate) as used to obtain a growth rate of $3.6\,\mu m/h$. As can be seen in the figure, the molar fraction of the C_2H_2 molecule increases as the total pressure is reduced. This molecule is believed to be the main carbon-containing species in the SiC growth, and consequently the *effective* C/Si ratio will increase with decreased total pressure. The increased carbon pressure (mainly C_2H_2) will enhance the aluminum incorporation as explained in Section 5.3. When the total pressure is reduced from 1000 to 300 mbar, the mole fraction of C_2H_2 is increased

by a factor of 3. According to what was presented for the C/Si dependence (presented with a maximum C/Si ratio of 5.0), this would indicate an increased aluminum incorporation of more than 100%. The aluminum species, and their mole fractions, are presented in Fig. 7b as a function of the total pressure.

As has been observed, the growth rate drops slightly when the pressure is reduced, which is explained by a higher desorption of silicon-containing species. Although we can verify a desorption of silicon-containing species, there might as well be an increased desorption of carbon-containing species at lower pressure. However, we believe that although *some* carbon-containing species may be desorbed, the *net result* will be an increased C/Si ratio with reduced total pressure.

At low growth rate (3.6 µm/h) the Si-face surface is covered with more aluminum-containing species than what is incorporated, as explained in Section 5.2. It is possible to incorporate more aluminum if more suitable lattice sites are *available* for the aluminum atoms occupy. As the pressure is reduced, more carbon atoms arrive at the surface, giving rise to more available sites for the aluminum atoms to occupy, resulting in a very fast increase of the aluminum incorporation, as can be seen in Fig. 6a. At a *critical* total pressure of $P_{crit} = 300$ mbar the aluminum incorporation saturates and a further decrease of the total pressure reduces the incorporation due to reduced partial pressures of the aluminum-containing species. The highest aluminum incorporation occurs at the *critical* pressure, where the incorporation is limited by diffusion of aluminum-containing species from the gas phase to the surface. Although the carbon concentration continues to increase at pressures below 300 mbar the aluminum incorporation is limited by the partial pressures of aluminum-containing species, which are reduced with reduced total pressure.

The second investigation was performed with a higher growth rate, 5.6 µm/h, presented in Fig. 6b. According to the results presented in Section 5.2, all aluminum-containing species are incorporated at atmospheric pressure. As the total pressure is reduced the partial pressures of the aluminum species are reduced and consequently the aluminum incorporation decreases. The increased C/Si ratio does not influence the aluminum incorporation since all aluminum-containing species are already incorporated. The incorporation is now limited by diffusion of aluminum species from the gas phase to the surface. A slope of $0.6 \, cm^{-3}$/mbar is observed for both Si- and C-face material. The Si-face material shows a small saturation at the highest pressure. A slightly higher growth rate would remove it, and the slope would follow that of C-face material.

5.5. Temperature dependence

Simulations of the temperature distribution inside the susceptor [14] have shown that there is a large temperature gradient over the substrate. In order to determine whether this temperature gradient influences the aluminum incorporation process, an investigation was made changing the growth temperature in the range 1500–1600°C. The C/Si was equal to 3.5 and the growth was performed at atmospheric pressure at a constant growth rate of 3.6 µm/h. At the lowest temperature the growth rate decreased approximately 5%.

In Fig. 8 the aluminum doping for 4H Si-face is presented for the temperature interval 1500–1600°C. As the temperature is increased from 1500°C to 1550°C, the aluminum doping decreases, which could be due to an increased desorption of aluminum-containing species. Between 1550°C and 1600°C, the aluminum incorporation is almost constant, which indicates the presence of a mass transport limited process. On C-face the aluminum incorporation is almost constant over a temperature range 100°C. The insensitivity of the aluminum incorporation on C-face could be explained by the single weak bond between the aluminum and the carbon atom resulting in a high desorption of aluminum species in the investigated temperature interval.

6. Discussion

An understanding of the incorporation mechanisms of aluminum in SiC and its dependence on growth parameters is important when device
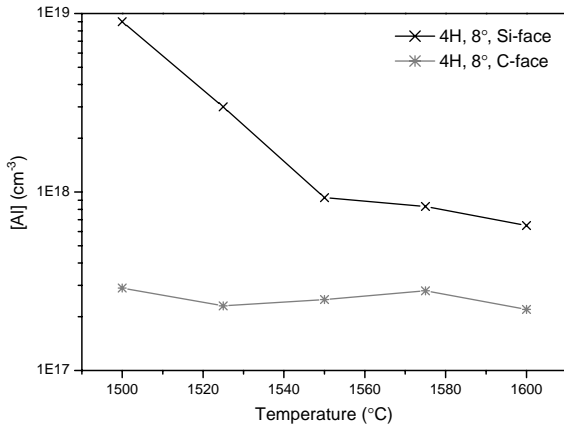
Fig. 8. The aluminum incorporation versus the temperature for 4H material. The growth was performed at $p = 1000\,\text{mbar}$, TMA $= 9 \times 10^{-3}\,\text{ml/min}$ and C/Si $= 3.5$. The constant doping temperature range for Si- and C-face is approximately $50°C$ and $100°C$, respectively.

structures are grown and in the design of new reactors. Equilibrium thermodynamic calculations indicate five different aluminum-containing molecules; Al, AlH, AlH_2, AlH_3, and $AlCH_3$, in the gas phase. Since single aluminum atoms are found in large concentrations, the incorporation of aluminum may to a large extent be governed by the concentrations of these atoms.

Our results indicate that aluminum incorporation on Si-face material is governed by available lattice sites on the terraces, where the aluminum atoms will bond to the underlying carbon atoms. Our model states that the aluminum atoms are relatively immobile on the surface due to the strong bonding, and the aluminum is incorporated as the growth step buries the bonded aluminum atoms. The creation of available lattice sites is controlled by the carbon coverage on the terrace. This is referred to as the *effective* C/Si ratio on the SiC surface. As different process parameters are changed, the *effective* C/Si ratio is changed, although the *input* C/Si ratio is maintained constant.

Increased growth rate or input C/Si ratio will increase the effective C/Si ratio, and as a result the aluminum incorporation will increase on the Si-face. The aluminum incorporation can also be diffusion limited, which is observed at very high growth rates, and as a result, the aluminum

incorporation saturates. The pressure dependence on the aluminum incorporation is also related to the effective C/Si ratio, and a reduced total pressure increases the effective C/Si ratio. To describe the effective C/Si ratio, only the C_2H_2 molecule is taken into account, since it is the dominating carbon-containing specie in the gas-phase.

The initial growth rate will determine the aluminum incorporation behavior. High growth rate will result in a decreased aluminum incorporation with reduced pressure, which is due to reduced partial pressures of the aluminum-containing species. The increased effective C/Si ratio will in this case not influence the incorporation, since all aluminum species are already incorporated. At low growth rate, the effective C/Si ratio will be very important. The reduced reactor pressure will increase the effective C/Si ratio, and the aluminum incorporation increases with reduced reactor pressure. This is possible since the surface is covered with more aluminum than what is incorporated. A critical pressure is observed where the aluminum incorporation has its maximum, and a further reduction in the reactor pressure results in reduced aluminum incorporation. Below the critical pressure, the aluminum incorporation behavior (and concentration) is the same for both low and high growth rates. The aluminum incorporation on the C-face follows that of the Si-face, except that the incorporation is much lower. The single bond between the aluminum and carbon atoms is very weak. Consequently, there is a greater rate of desorption of aluminum at the C-face. The only indication of increased incorporation that has been seen occurs only at very high growth rates. The highest aluminum incorporation observed in this systematic study are 3×10^{17} and $8 \times 10^{18}\,\text{cm}^{-3}$ for the Si- and C-face, respectively. We have, however, grown epitaxial layers with an atomic aluminum concentration of $8 \times 10^{20}\,\text{cm}^{-3}$ [15] on Si-face 4H-SiC, but the solubility of aluminum in SiC has not been investigated in the present study. High aluminum incorporation $(> 3 \times 10^{20}\,\text{cm}^{-3})$ has shown to create aluminum precipitates [16] with a size of $300 \times 300\,\text{Å}$.

The model is fairly simple with a close connection between the carbon coverage on the surface

and the aluminum incorporation. It is assumed that on the Si-face, the aluminum atoms are rather immobile. The different off-axis angle of the different polytypes indicates that an increased step density does not influence the aluminum incorporation. This supports the model stating that most aluminum atoms are bonded to the terraces and not at steps.

The aluminum incorporation is very different from what is observed for nitrogen incorporation [11]. Due to large concentrations of aluminum atoms, the dissociation of larger molecules are not needed, and the bonding of aluminum atoms to the SiC surface becomes more important.

7. Summary

Intentional aluminum doping in 4H and 6H SiC has been investigated in a hot-wall CVD reactor by changing several process parameters. The investigations show that the aluminum incorporation is closely related to the carbon coverage on the SiC surface. Changes in process parameters alter the carbon coverage on the surface, i.e. the effective C/Si ratio, close to the SiC surface. The carbon coverage is related to the amount of stable lattice sites for the aluminum atoms to bond to. Increased carbon coverage increases the amount of bonded aluminum atoms, unless the aluminum incorporation is limited by diffusion of aluminum species from the gas-phase to the SiC surface. This is the case at very high growth rates, when the aluminum incorporation saturates. Increased growth rate, increased C/Si ratio, or reduced pressure results in an increased effective C/Si ratio at the surface. The aluminum incorporation is always higher on the Si-face, than on the C-face. This is probably due to the stronger bonding of the aluminum atoms to the Si-face, whereas the C-face suffers from a greater desorption rate of aluminum-containing species, due to weaker bonding.

Acknowledgements

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