THE INFLUENCE OF THE CHLORINE–HYDROGEN RATIO IN THE GAS PHASE ON THE STABILITY OF THE (113) FACES OF SILICON IN Si–H–Cl CVD


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The orientation dependence of silicon crystal growth in the Si–H–Cl CVD system has been studied as a function of the chlorine–hydrogen ratio of the gas phase. This was done by the use of hemispherical single crystal substrates. As was reported before, the stability of faces with the indices \( \{ h k l \}_{h \times k} \) is dependent on temperature: above a certain critical temperature flat \( \{ 113 \} \) and \( \{ 337 \} \) faces are found on the hemispheres, while below this temperature only macroscopic steps appear in positions corresponding to these faces. In this study it is found that the above-mentioned critical temperature is strongly dependent on the chlorine–hydrogen ratio in the gas phase. It will be demonstrated that this “chemical roughening” effect is caused by the competitive adsorption of chlorine and hydrogen. From the experimental dependencies values for the heat of chemisorption of chlorine and hydrogen can be derived of \(-370 \pm 70 \text{ kJ mol}^{-1}\) and \(-316 \pm 5 \text{ kJ mol}^{-1}\), respectively. These values are in good agreement with literature values of Si–Cl and Si–H bond strengths.

1. Introduction

In a previous paper [1] we reported on the orientation dependence of the crystal growth of silicon as a function of temperature in the Si–H–Cl system. Among other things it was found that the stability of faces with indices \( \{ h k k \}_{h 	imes k} \) \((h \neq 0)\) increases at higher temperatures, an effect which was explained by the dependence of the surface tension on the adsorption of hydrogen, as demonstrated by a plot of surface tension versus the angle \( \phi \) in the [110] zone [2]. From this plot it was derived that the step free energy on the \( \{ 113 \} \) faces decreases with increasing hydrogen coverage. A certain critical coverage exists, at which this step free energy becomes zero, which means that at and above this critical coverage the \( \{ 113 \} \) faces no longer have the tendency to grow flat. In view of the fact that the surface coverage increases at lower temperatures, it could thus be concluded that the \( \{ 113 \} \) faces will not grow flat below a certain critical temperature. In the following we shall call this temperature the “chemical roughening” temperature of the \( \{ 113 \} \) faces, to distinguish it from the well-known “thermal roughening” temperature (see, e.g., ref. [3]) of a crystal face.

In ref. [2] it was calculated that the adsorption of hydrogen might explain the observed trend as a function of temperature, however, the absolute temperature below which the \( \{ 113 \} \) faces no longer grow flat, was calculated to be approximately 400 K below the observed value. In order to study the adsorption effects in more detail, in this paper the influence of variations in the chlorine–hydrogen ratio of the gas phase on the stability of the \( \{ h k k \}_{h 	imes k} \) faces will be investigated.

As was demonstrated in ref. [2], the effect of fundamental gas phase parameters on the stability of crystal faces in the chemical vapour deposition (CVD) of silicon can be studied very nicely by the use of hemispherical substrates (see also ref. [4]) in an experimental system where crystal growth is carried out at near-equilibrium conditions, as was described by Bloem et al. [5]. It was shown before that equilibrium calculations can be used to describe the processes that take place in this system [5–9]. The gas phase composition which follows from these equilibrium calculations will be the

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basis of our discussion of the adsorption effects. It will be shown that the above-mentioned temperature effect on the stability of {113} most probably is caused by the competitive adsorption of chlorine and hydrogen.

2. Experimental

The experimental procedure was essentially the same as described before [1]. In this study we will concentrate on the changes in crystal habit as a consequence of variations in the chlorine–hydrogen ratio of the gas phase, together with variations in growth temperature. As a definition of the chlorine–hydrogen ratio \((\text{Cl/H})\) of the gas phase we will use:

\[
\frac{\sum_{i=1}^{m} z_i p(Si_{x_i}H_{y_i}Cl_{z_i})}{\sum_{i=1}^{m} y_i p(Si_{x_i}H_{y_i}Cl_{z_i})} = (\text{Cl/H})
\]  

In this expression \(m\) stands for the total number of gas phase species present in the system, and \(p(Si_{x_i}H_{y_i}Cl_{z_i})\) for the partial pressure of the gaseous species \(Si_{x_i}H_{y_i}Cl_{z_i}\), obtained from equilibrium calculations [5,10].

In the experiments the chlorine hydrogen ratio of the gas phase was varied from 0.005 to 0.12 by a change in the relative amounts of mass flow of the input gases \(SiH_2Cl_2\), \(HCl\) and \(H_2\). The supersaturation (see ref. [1] for a definition) in these experiments was always 0.1 or lower, except for the experiments at a \((\text{Cl/H})\) ratio of 0.005, where in order to obtain mean thicknesses of several microns on the hemispheres, it was necessary to use supersaturations of up to 1.0; it was noticed that in order to have decisive information on the stability of faces, epitaxial layers of at least several microns are required. The thicknesses of the grown layers, averaged over the surface of the hemispheres, normally varied from approximately 3 \(\mu m\) to approximately 50 \(\mu m\).

The total mass flow of the gases was always 400 SCCM, leading to a gas velocity of approximately 15 cm s\(^{-1}\) at the growth temperature. The duration of all growth experiments was 2 h. The radius of the hemispheres was 3.00 ± 0.05 mm.

It was found that the growth rate on the planar (001) substrates (2°-off in one of the \(\langle 110 \rangle\) directions), which were used to obtain near-equilibrium conditions at the position of the hemispheres [1], was in good correspondence with the “solubility” curves [5] taken from equilibrium calculations, which confirmed that these calculations had given a good description of the near-equilibrium crystal growth process.

3. Results

At a constant \((\text{Cl/H})\) ratio the morphology of the hemispheres at angles from approximately \(20^\circ\) to \(35^\circ\) from the (111) face in the \(\{hhk\}_{h<k}\) part of the [110] zone was different for different temperatures. This is shown in figs. 1a–1c. Three different morphologies can be distinguished. At low temperatures morphology I is observed: only macroscopic steps appear (fig. 1a). These steps reach from the (111) faces to the nearest \(\{001\}\) faces. No \{113\} or \{337\} faces can be distinguished. The positions where they should occur are indicated in the figure.

On the other hand, at high temperatures in these regions at approximately \(23.5^\circ\) and \(29.5^\circ\) from the \{111\} faces the flat faces \{337\} and \{113\} appear, respectively. This will be called morphology III (fig. 1c). When this morphology occurs, in the part of the \(\{hhk\}_{h<k}\) region between the \{113\} faces and the nearest \{001\} face macroscopic steps either are only slightly visible or do not appear at all.

Morphology II is an intermediate case between morphologies I and III (see the discussion section). It is observed either when the amount of silicon deposited on the hemisphere is relatively low (e.g. for very short growth experiments or very low supersaturations), or at conditions where the \{337\} and \{113\} faces obviously are not very stable. In fig. 1b these faces can be seen as very small bands. Their position, which can be derived from the narrowing of the range of macroscopic steps, is indicated by arrows (the two thin white lines are artefacts due to the photo composition).
In a following series of experiments the stability of these two faces has been studied as a function of the (Cl/H) ratio between 0.005 and 0.15 and as a function of temperature between 1190 and 1480 K. The temperature regions where morphologies I, II and III are present turn out to be dependent on the (Cl/H) ratio, as is shown in fig. 2. The dotted line is used to indicate the transition from morphology I to morphology II. A more detailed analysis reveals that for experiments with conditions close to the dotted line in fig. 2, the transition from morphology I to morphology II takes place at a somewhat higher temperature (10 K at most) for the {337} faces than for the {113} faces.

In fig. 2 the experimental data of Van den Brekel and Nishizawa are indicated. These authors have investigated the orientation dependence of silicon CVD, using cylindrical [11] or hemispherical [12] substrates. They report the presence of flat {113} and {112} faces. Except for the indices of the latter faces (in our opinion these are not correct, the faces should be indexed {337}, see ref. [1]), their findings fit well with our observations.

Fig. 1. Morphology of the parts of the hemisphere which can be described with the crystallographic indices \(\langle hkl \rangle_{\alpha, \beta, \gamma}\). (a) Morphology I: macroscopic steps, at low temperatures; (b) morphology II: very small (113) and (337) faces, at intermediate temperatures; (c) morphology III: large (113) and (337) faces, at high temperatures. Note: in (a) and (b), the surface is curved in the vertical direction of the pictures, so the indicated length scale is only valid for the horizontal direction in these two cases.
Unfortunately, as indicated in fig. 2, they have not examined growth temperatures below 1400 K, and for that reason have not observed the same temperature effects as we have.

4. Discussion

4.1. General aspects of growth forms

Very generally it can be said that after crystal growth on hemispheres three different categories of morphological features may show up:

1. flat faces, i.e. surfaces which are not curved in any direction (see fig. 1c, morphology III);
2. ranges of macroscopic steps, i.e. surfaces which are curved in one direction (see fig. 1a, morphology I);
3. surfaces which are curved in all directions.

A way to interpret these morphologies is to consider the variation of surface tension, \( \gamma \), as a...
A very low surface tension \[13\]. In our case the crystallographic direction of the terrace edges is [110], which is the direction of the strongest periodic bond chain (PBC) in the crystal bulk structure of silicon \[14\].

Similar reasoning as above can be used to interpret the other morphologies in fig. 1. Morphology III is thus the result of cusped minima in both \(\gamma(\alpha)\) and \(\gamma(\beta)\) for both the (113) and (337) orientations. In our opinion this is also the case in morphology II, however, for one of the two functions the minima are only very shallow, leading to only very small flat regions with orientation (113) and (337). Thus morphology II can be considered an intermediate case between I and III, where in the sequence III–II–I the minima in one of the functions \(\gamma(\alpha)\) or \(\gamma(\beta)\) disappear.

In a previous paper \[2\] we have given a possible explanation for the disappearance of cusped minima in the \(\gamma\)-plot. In this discussion we will use the theoretical results of that paper to explain the effect of the \((\text{Cl}/\text{H})\) ratio on the stability of the \(\{hhk\}\) faces. To do this we will first investigate the changes that occur in the gas phase equilibrium composition as a result of a change in the \((\text{Cl}/\text{H})\) ratio.

### 4.2. Gas phase equilibrium composition as a function of the chlorine–hydrogen ratio

In fig. 4 the result of a gas phase equilibrium calculation \[5–10,15\] is presented. In the calculation the following gaseous species are included: \(\text{Si}, \text{Si}_2, \text{Si}_3, \text{SiH}, \text{SiH}_2, \text{SiH}_3, \text{SiH}_4, \text{Si}_2\text{H}_6, \text{SiCl}, \text{SiCl}_2, \text{SiCl}_3, \text{SiCl}_4, \text{SiHCl}, \text{SiHCl}_3, \text{SiH}_2\text{Cl}_3, \text{SiH}_3\text{Cl}, \text{H}, \text{H}_2, \text{HCl}, \text{Cl}, \text{and Cl}_2\). The gas phase is in equilibrium with solid silicon. Thermochemical data were taken from refs. \[16–19\]. The figure shows the partial pressures of the main gas phase species in the \(\text{Si–H–Cl}\) system as a function of \((\text{Cl}/\text{H})\), at atmospheric pressure and 1350 K.

As can be seen in this figure, the main consequence of an increase in \((\text{Cl}/\text{H})\) is that chlorine-containing species become more important with respect to species which do not contain chlorine. This also implies that the total amount of silicon in the gas phase (the "solubility", see e.g. ref. \[5\]) increases with an increase in \((\text{Cl}/\text{H})\).
The gas phase compositions extracted from equilibrium calculations, as e.g. presented in fig. 4, will be used in the following discussion on the influence of adsorption on the stability of the \( \{ hkk \}_{h<k} \) faces. In ref. [2] it was derived that when the crystal surface is free from adsorbates, flat \( \{113\} \) faces are expected, because in the Wulff plot cusped minima are present for these orientations. Unfortunately, with the aid of the structural models in ref. [2], no cusped minima could be found for the \( \{337\} \) faces, so we are not able to discuss the stability of the latter faces quantitatively, but the rules derived for the \( \{113\} \) faces qualitatively also apply for \( \{337\} \).

4.3. The influence of adsorption on the occurrence of the \( \{hkk\}_{h<k} \) faces

In ref [2] the influence of temperature on the appearance of the \( \{113\} \) faces was explained by the effect of adsorption on the \( \gamma \)-plot versus the angle \( \phi \) in the \([110]\) zone: below a critical coverage \( \theta_{cr} \) in this plot an inward pointing cusp exists at the angle \( \phi_{113} \) corresponding to the \( \{113\} \) face, above this \( \theta_{cr} \) an outward pointing cusp at \( \phi_{113} \) appears. Or, in other words: at low coverages a positive step free energy (see, e.g., ref. [3]) exists on the \( \{113\} \) face, while at high coverages the step free energy becomes negative [2]. It is well known that the surface coverage will increase at lower temperatures, so that the above is consistent with the observation that due to the high coverage, the \( \{113\} \) faces are absent from the (near-)equilibrium growth from the silicon crystal below a certain critical temperature \( T_{cr} \), the "chemical roughening" temperature of the \( \{113\} \) faces.

In ref. [2] the above described phenomenon was explained by the adsorption of hydrogen. However, with the use of reasonable values of the heat and entropy of hydrogen adsorption, the chemical roughening temperature of the \( \{113\} \) faces was calculated to be 920 K. This is much lower than the experimentally observed value of 1340 K at the \( \text{(Cl/H)} \) ratio of 0.06, which was used in ref. [1]. Although the thermochemical data for H adsorption are not known very accurately, this discrepancy led us to the opinion that in addition to H other species in the gas phase might be responsible for the destabilizing effect on \( \{113\} \). This idea can now be supported by the experimental data in fig. 2: it can be seen that the chemical roughening temperature depends on the \( \text{(Cl/H)} \) ratio. From fig. 4 it is also clear that in the range of experimental \( \text{(Cl/H)} \) values the partial pressure of atomic hydrogen does not depend on the \( \text{(Cl/H)} \) ratio, so the observed changes in morphology as discussed in this paper for the \( \{hkk\}_{h<k} \) faces can not be caused by the adsorption of hydrogen alone. It is therefore plausible to assume that a chlorine-containing adsorbate is involved in the shift of \( T_{cr} \) of these faces.

To examine this in more detail the following strategy will be pursued: first it will be assumed that only chlorine atoms are present on the surface of the silicon crystal. It will be investigated whether this assumption can explain the observed effects and whether the adsorption parameters that can be derived from the experimental dependencies are in reasonable correspondence with known...
thermochemical data for silicon-chlorides and estimated adsorption data. Next the case will be considered where both chlorine and hydrogen atoms are chemisorbed on the silicon crystal surfaces, and it will be examined whether or not this gives a satisfactory description of the data in fig. 2. Finally the importance of the adsorption of silicon-containing species will be investigated.

4.3.1. Chlorine adsorption

Suppose that chlorine atoms are the only adsorbates present on the silicon surface. An adsorption equilibrium to describe this case would be:

$$\text{Cl}_{\text{gas}} + \text{surface site} \rightleftharpoons \text{Cl}_{\text{adsorbed}}$$  \hspace{1cm} (2)

with equilibrium constant $K_{\text{Cl}}$, which is defined in the conventional way. For Langmuir adsorption the chlorine coverage of the silicon surface, $\theta_{\text{Cl}}$, is given by the equation:

$$\theta_{\text{Cl}} = K_{\text{Cl}} p_{\text{Cl,eq}} / (1 + K_{\text{Cl}} p_{\text{Cl,eq}}),$$  \hspace{1cm} (3)

where $\theta_{\text{Cl}}$ is the fraction of surface sites covered by chlorine atoms, and $p_{\text{Cl,eq}}$ the equilibrium partial pressure of chlorine atoms, as e.g. given in fig. 4. When the equilibrium constant $K_{\text{Cl}}$ in eq. (3) is written in a form that contains the thermodynamic parameters $\Delta H^0_{\text{Cl}}$ and $\Delta S^0_{\text{Cl}}$, which are the change in standard enthalpy and entropy for equilibrium reaction (2), respectively, the following equation is obtained:

$$\ln \left( \frac{\theta_{\text{Cl}}}{p_{\text{Cl,eq}} (1 - \theta_{\text{Cl}})} \right) = - \frac{\Delta H^0_{\text{Cl}}}{RT} + \frac{\Delta S^0_{\text{Cl}}}{R},$$  \hspace{1cm} (4)

where $R$ is the gas constant.

It is possible to use the data in fig. 2 to fit the thermodynamical parameters in eq. (4) in the following way: in ref. [2] an equation was derived to describe the effect of adsorption on surface tension $\gamma[\phi]$:

$$\gamma[\phi] = \gamma_\ast[\phi] - k T q[\phi] \ln(1/\theta_\ast),$$  \hspace{1cm} (5)

where $\gamma_\ast[\phi]$ is the surface tension of the adsorbate-free surface, $q[\phi]$ the adsorption site density, $\theta_\ast$ the fraction of free sites and $\phi$ the angle of the surface with a predefined reference plane; $[\phi]$ is used to indicate the orientation dependent parameters in eq. (5).

The surface tension of a crystal face which is only slightly misoriented from a flat face at angle $\phi_0$ can be calculated with the aid of:

$$\gamma[\phi] = \gamma[\phi_0] + (\gamma_{\text{step}} / d) |\phi - \phi_0|,$$  \hspace{1cm} (6)

where $\gamma_{\text{step}}$ is the free energy of a step on the face at $\phi_0$ and $d$ the height of this step.

Eq. (6) can be rewritten in the following form:

$$\frac{\gamma_{\text{step}}}{d} = \frac{\gamma[\phi] - \gamma[\phi_0]}{|\phi - \phi_0|}.$$  \hspace{1cm} (7)

For $\phi$ larger than but very close to $\phi_0$, the term on the right of the equality sign can be replaced by $d \gamma / d \phi$.

Application of the foregoing to eq. (5) leads to:

$$\frac{\gamma_{\text{step}}}[d] = \frac{\gamma_{\text{step}}}[d] - \frac{d q[\phi]}{d \phi} k T \ln(1/\theta_\ast).$$  \hspace{1cm} (8)

In words: at a certain coverage of adsorbates the step free energy on a surface at an angle $\phi$ is equal to the step free energy on this surface, when no adsorption takes place, minus a term proportional to the variation of the adsorption site density with orientation and proportional to the parameter $T \ln(1/\theta_\ast)$.

$\theta_\ast$ will always be positive and less than one, which leads to a positive term $T \ln(1/\theta_\ast)$. Adsorption will therefore either lower or raise the step free energy on a particular face, dependent on whether the term $d q[\phi]/d \phi$ is positive or negative, respectively. In ref. [2] it was shown that $d q[\phi]/d \phi$ is positive for steps on the (113) face which are parallel to the [110] direction, which is the direction of the most stable PBC in the silicon crystal, and inclined in, e.g., the [332] or in the [332] direction. Therefore for these steps the step free energy will decrease with an increase in $T \ln(1/\theta_\ast)$. Most probably the same will hold for steps on the (337) face which are parallel to the [110] PBC direction. For steps on the (113) face inclined in the [110] or in the [110] direction and parallel to e.g. the [332] direction (i.e. steps perpendicular to the stable PBC directions) the term $d q[\phi]/d \phi$ is also positive, so for these steps also
the step free energy will decrease with increasing \( T \ln(1/\theta_*) \).

In ref. [2] it was derived that if for steps on the (113) face which are parallel to the [110] direction the term \( T \ln(1/\theta_*) \) becomes larger than 2250 K, the step free energy on this face will no longer be positive, and these faces will no longer grow flat, i.e. the faces have become "chemically roughened". Although in ref. [2] this was only discussed for the case of hydrogen adsorption, the above requirement for the term \( T \ln(1/\theta_*) \) on the (113) faces applies for every species which adsorbs in adsorption sites similar to those for H.

If the transition from morphology II to morphology I in fig. 2 is interpreted as a chemical roughening phenomenon, it thus follows that at the dotted line in this figure the following relation should hold:

\[
T_c \ln(1/\theta_*) = 2250 \text{ K.} \quad (9)
\]

Considering that in the case of Cl adsorption \( \theta_* = 1 - \theta_{Cl} \), we can thus calculate \( \theta_{Cl} \) as a function of \( T \) from the data in fig. 2. To obtain the parameters \( \Delta H^{0}_{Cl} \) and \( \Delta S^{0}_{Cl} \), we have to plot the term on the left-hand side of the quality sign in eq. (4) versus \( T_c^{-1} \). The slope of the resulting straight line will then correspond to the value of \(-\Delta H^{0}_{Cl}/R\) and the intercept of the line with the vertical axis to \( \Delta S^{0}_{Cl}/R \). Such a plot is shown in fig. 5, where values of \( P_{Cl eq} \) from equilibrium calculations as, e.g., shown in fig. 4 are used.

Two different linear least-squares fits of the points in fig. 5 were made:

(i) the dashed line in the figure is a fit through the five points without further assumptions. This leads to the values:

\[
\Delta H^{0}_{Cl} = -440 \pm 20 \text{ kJ mol}^{-1},
\]
\[
\Delta S^{0}_{Cl} = -180 \pm 30 \text{ J K}^{-1} \text{ mol}^{-1}.
\]

(ii) With the use of statistical-thermodynamical arguments (see, e.g., ref. [15]) it is possible to estimate the entropy change for the adsorption of chloride atoms. This is shown in table 1. If the calculated value of \( \Delta S^{0}_{Cl} \) at 1300 K, \(-133 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1} \), divided by \( R \), is used as a fixed point in a linear least-squares fit of fig. 5 (this value should occur for \( T^{-1}_c = 0 \)), the solid line results. From the slope of this line we obtain:

\[
\Delta H^{0}_{Cl} = -380 \pm 20 \text{ kJ mol}^{-1}.
\]

This value which is valid for temperatures from 1210 to 1350 K. According to equilibrium reaction (2), \( \Delta H^{0}_{Cl} \) should be approximately equal to the strength of a Si–Cl bond on the silicon surface. In table 2, literature values of Si–Cl bond dissociation energies are given for several silicon-chloride compounds. With statistical thermodynamical

**Table 1**

<table>
<thead>
<tr>
<th>Entropy contribution</th>
<th>Entropy changes at 298 K (J K(^{-1}) mol(^{-1}))</th>
<th>Entropy changes at 1300 K (J K(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss</td>
<td>Gain</td>
<td>Loss</td>
</tr>
<tr>
<td>Translation</td>
<td>153</td>
<td>0</td>
</tr>
<tr>
<td>Rotation</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Vibration a)</td>
<td>0</td>
<td>20–35</td>
</tr>
<tr>
<td>Electronic b)</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>Nett</td>
<td>137 ± 8</td>
<td>133 ± 9</td>
</tr>
</tbody>
</table>

\(a)\) Estimated vibrations (see refs. [15,20–23]): a stretch mode with a frequency of 300–550 cm\(^{-1}\), and two bend modes with frequencies of 100–200 cm\(^{-1}\) (550 cm\(^{-1}\) is the value of the Si–Cl stretch frequency in the SiH\(_4\)Cl molecule according to ref. [24]).

\(b)\) The adsorbate-free silicon surface site and the adsorbed chloride atom are assumed to be electronically doubly degenerate.
Table 2
Silicon–chloride bond strengths at 298 K

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond strength (kJ mol⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂Si–Cl</td>
<td>464 ± 8</td>
<td>[25]</td>
</tr>
<tr>
<td>Cl₂Si–Cl</td>
<td>448 ± 8</td>
<td>[26]</td>
</tr>
<tr>
<td>Cl₃Si–Cl</td>
<td>276</td>
<td>[25]</td>
</tr>
<tr>
<td>Cl₃Si–Cl</td>
<td>289 ± 8</td>
<td>[26]</td>
</tr>
<tr>
<td>ClSi–Cl</td>
<td>477</td>
<td>[25,27]</td>
</tr>
<tr>
<td>Si–Cl</td>
<td>381</td>
<td>[25,27]</td>
</tr>
<tr>
<td>(CH₃)₂Si–Cl</td>
<td>473</td>
<td>[25]</td>
</tr>
<tr>
<td>H₂Si–Cl</td>
<td>527</td>
<td>[28]</td>
</tr>
<tr>
<td>H₂ClSi–Cl</td>
<td>463</td>
<td>[29]</td>
</tr>
<tr>
<td>HCl₂Si–Cl</td>
<td>438</td>
<td>[29]</td>
</tr>
<tr>
<td>(CH₃)H₂Si–Cl</td>
<td>479</td>
<td>[29]</td>
</tr>
</tbody>
</table>

methods it is possible to calculate that $\Delta H^0_{\text{Cl}}$ will only be approximately 5 kJ mol⁻¹ higher for the temperatures examined in our experiments. Therefore it can be concluded that both values of $\Delta H^0_{\text{Cl,298}}$ as deduced from fig. 5 are in agreement with the literature values of Si–Cl bond strengths as given in table 2.

It can be calculated that for steps on the (113) face parallel to the [332] direction (i.e., perpendicular to the PBCs), the step free energy will become negative when the term $T \ln(1/\theta_*)$ exceeds 31500 K. This value is much larger than the above-mentioned value for steps parallel to the [110] direction, which is understandable because in order to form these steps, the stable PBCs should be broken up, which requires high amounts of energy. The high value of the term $T \ln(1/\theta_*)$ implies that on the {113} faces, most probably for all the growth conditions used in this study, the step free energy in the {332} directions will be larger than zero. This is consistent with the observation that in all our growth experiments either macroscopic steps parallel to the stable PBC directions or flat faces are observed at the positions of {113} on the hemispheres.

4.3.2. Competitive adsorption of hydrogen and chlorine

It may be expected that next to chlorine, also hydrogen will be present on the surface of the silicon crystal, which means that next to the equilibrium reaction (2), also the following adsorption equilibrium has to be considered:

$$ \text{H}_{\text{gas}} + \text{surface site} \rightleftharpoons \text{H}_{\text{adsorbed}} $$

with equilibrium constant $K_{\text{H}}$. The coverage of the silicon surface with species X (i.e., H or Cl) is now given by the equation:

$$ \theta_X = \frac{K_X P_{X,\text{eq}}}{1 + K_X P_{X,\text{eq}} + K_{\text{Cl}} P_{\text{Cl,eq}}}. $$

Again at the critical temperatures $T \ln(1/\theta_*)$ will be equal to 2250 K (see the previous section); however, in this case $\theta_\star = 1 - \theta_\text{Cl} - \theta_\text{H} = 1 - \theta_\text{total}$. From this relation and equation (11) it then follows that:

$$ K_{\text{Cl}} P_{\text{Cl,eq}} = \frac{\theta_\text{total}}{1 - \theta_\text{total}} - K_{\text{H}} P_{\text{H,eq}}. $$

This equation can be rewritten in a form that resembles equation (4):

$$ \ln \left( \frac{\theta_\text{total}}{1 - \theta_\text{total}} - K_{\text{H}} P_{\text{H,eq}} \right) - \ln P_{\text{Cl,eq}} = - \frac{\Delta H^0_{\text{Cl}}}{RT_\star} + \frac{\Delta S^0_{\text{Cl}}}{R}. $$

To study whether the assumption of competitive adsorption of chlorine and hydrogen adsorption can explain the experimental results, we evaluated this equation in the following way: $P_{\text{H,eq}}$ was obtained from equilibrium calculations (see above), and several different values of the adsorption heat of hydrogen, $\Delta H^0_{\text{H}}$, were considered; in this evaluation the adsorption entropy of hydrogen, $\Delta S^0_{\text{H}}$, was assumed to be $-125$ J K⁻¹ mol⁻¹ [15] in the temperature range considered, i.e. from 1210 to 1350 K. After the calculation of the term $K_{\text{H}} P_{\text{H,eq}}$ in eq. (13) with these data, we fitted the resulting parameters in the same way as was done in the previous section for eq. (4). The values of $\Delta H^0_{\text{Cl}}$ and $\Delta S^0_{\text{Cl}}$ obtained from these linear least-squares fits of eq. (13) are shown in figs. 6 and 7, respectively.

It is assumed that the values of $\Delta H^0_{\text{Cl}}$ and $\Delta H^0_{\text{H}}$ that best fit the data of fig. 2 are those which agree with the theoretical value of $\Delta S^0_{\text{Cl}}$ of $-133$
Table 3
Silicon–hydrogen bond strengths at 298 K

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond strength (kJ mol(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{Si–H})</td>
<td>378</td>
<td>[27]</td>
</tr>
<tr>
<td>(\text{H}_2\text{Si–H})</td>
<td>268</td>
<td>[27]</td>
</tr>
<tr>
<td>(\text{HSi–H})</td>
<td>351</td>
<td>[27]</td>
</tr>
<tr>
<td>(\text{Si–H})</td>
<td>293</td>
<td>[27]</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{Si–H})</td>
<td>382</td>
<td>[27]</td>
</tr>
<tr>
<td>(\text{Cl}_2\text{Si–H})</td>
<td>378</td>
<td>[27]</td>
</tr>
<tr>
<td>(\text{Si(111)})–(\text{H})</td>
<td>300–340</td>
<td>[30]</td>
</tr>
<tr>
<td>(\text{Poly-Si–H})</td>
<td>318</td>
<td>[31]</td>
</tr>
<tr>
<td>Amorphous-Si–H</td>
<td>270–360</td>
<td>[33]</td>
</tr>
</tbody>
</table>

The corresponding value of \(\Delta H_\text{Cl}^0\) follows from fig. 6:
\[
\Delta H_\text{Cl}^0 = -370 \pm 70 \text{ kJ mol}^{-1}.
\]

If it is assumed that \(\Delta H_\text{Cl}^0\) does not change more than a few percent over the temperature range 298–1400 K (see above), it can be seen that the values of \(\Delta H_\text{Cl,298}^0\) and \(\Delta H_\text{H,298}^0\) are in agreement with the literature values of Si–Cl and Si–H bond strengths in tables 2 and 3, respectively.

4.3.3. Adsorption of silicon compounds

To obtain a complete view of the influence of gas phase composition on the stability of the \(\{hkk\}_{h<k}\) faces, in addition to the adsorption equilibria (2) and (10), the following series of equilibria has to be included:

\[
\text{Si}_2\text{H}_n\text{Cl}_{2-n}\text{gas} + \text{surface site} \rightleftharpoons \text{Si}_2\text{H}_n\text{Cl}_{2-n}\text{adsorbed}. \tag{14}
\]

Of all the silicon compounds which are present in the gas phase at equilibrium, we will assume that only radicals are able to chemisorb on the silicon surface; of these SiCl\(_2\), SiCl\(_3\), SiHCl, and SiH\(_2\) are the most abundant in the equilibrium gas phase mixtures (see fig. 4). As a very rough estimate of the heat of adsorption of these species, we take \(\Delta H_{298}^0 \approx -226 \text{ kJ mol}^{-1}\) (see, e.g., ref. [15]).
which is minus half the sublimation enthalpy of silicon, and \( \Delta S_{298}^0 \approx -170 \text{ J K}^{-1} \text{ mol}^{-1} \). To have some idea of the surface coverage, we summarized the equilibrium partial pressures of these species and used the before-mentioned thermodynamic data and the Langmuir isotherm. The resulting coverages as a function of the \((\text{Cl}/\text{H})\) ratio, together with those of hydrogen and chlorine, are shown in fig. 8 for three different temperatures.

As can be seen, the surface coverage of growth species is always much less than that of chlorine and hydrogen, even at extremely high chlorine–hydrogen ratios of, e.g., 0.3 (i.e. log(\(\text{Cl}/\text{H}) = -0.5\)). Therefore we conclude that in above discussion on the effect of adsorption on the stability of the \{113\} faces, the contribution of silicon species can be neglected.

4.3.4. Concluding remarks

It was shown in this section that the shift of the “chemical roughening” temperature of the \{113\} faces with the \((\text{Cl}/\text{H})\) ratio is caused by the competitive adsorption of \text{Cl} and \text{H}. As it was derived that chemical roughening of these faces occurs when the term \( T \ln(1/\theta_*) \) exceeds the value of 2250 K, it can be calculated that in the temperature range examined in the experiments (1200–1450 K) the \{113\} faces become rough if \( \theta_* \) becomes lower than approximately 0.2. It can be seen from fig. 8 that at low (\text{Cl}/\text{H}) ratios the coverage of the silicon surface with \text{Cl} is low, so that the chemical roughening temperature in this case is almost completely determined by \text{H} adsorption. At higher (\text{Cl}/\text{H}) ratios the coverage of \text{Cl} increases, while the \text{H} coverage remains the same or decreases somewhat because of the competition with \text{Cl}. So at the higher (\text{Cl}/\text{H}) ratios the chemical roughening temperature will be determined by the adsorption of both \text{Cl} and \text{H}. As the total coverage \( \theta_{\text{total}} \) at higher (\text{Cl}/\text{H}) ratios becomes higher, chemical roughening will start to occur for \( \theta_{\text{total}} = 1 - \theta_* \geq 0.8 \). At still higher (\text{Cl}/\text{H}) ratios the growth temperature has to be raised in order to ensure the stability of the \{113\} faces. This is exactly the trend observed in fig. 2.

Finally we want to make some remarks on the derived heats of adsorption of \text{Cl} and \text{H}. Comparison of the derived values with those in tables 2 and 3 shows that although the agreement is satisfactory, the value of \( \Delta H_{\text{Cl}}^0 \) is somewhat lower than most values in table 2. A reason for this may be that at the relatively high coverages which we are dealing with (see above), adsorbate interactions will become substantial. More specifically, it may be expected that the large electronegativity of the \text{Cl} atoms with respect to \text{Si} will lead to a small negative charge on the adsorbed \text{Cl}, leading to a repulsive interaction between these adsorbates. This repulsion will lower the heat of adsorption, which might explain the observed difference.

5. Summary

In this paper the orientation dependence of silicon crystal growth in the \text{Si–H–Cl} CVD system was studied as a function of the chlorine–hydrogen ratio of the gas phase. This was done by the use of hemispherical single crystal substrates.

As was reported before [1], above a certain critical temperature flat \{113\} and \{337\} faces are found on the hemispheres, while below this temperature only macroscopic steps appear in posi-
tions corresponding to these faces. This critical temperature is strongly dependent on the chlorine–hydrogen ratio of the gas phase. It was demonstrated that this so-called “chemical roughening” effect is caused by the competitive adsorption of chlorine and hydrogen. From the experimental dependencies, values for the heat and entropy changes for chemisorption of chlorine and hydrogen can be derived. These values are in good agreement with literature values of Si–Cl and Si–H bond strengths and entropy values derived with the use of statistical-thermodynamical methods.

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References