Surface processes during growth of GaAs by MOCVD

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A discussion is given of the electronic properties of the (111)Ga and (001)As-stabilized surfaces of GaAs and of the electronic nature of the gas phase species present during the growth by metalorganic chemical vapour deposition (MOCVD). The reconstruction of the (001)As-stabilized surface is taken into account, allowing only for the formation of $\sigma$ bonds. In connection with the adsorbates attention especially is given to those situations where more or less electrons are present than the two required to form the chemical bond. As an example we have calculated the coverages on both surfaces under near equilibrium growth conditions.

1. Introduction

The understanding of the CVD process in general can be called rather advanced on the point of gas phase transport and to a somewhat lesser degree in the matter of gas phase chemistry, but altogether this part of the growth process can be considered as well understood. This in contrast to our knowledge of the processes that occur at the surface, which consist of adsorption and desorption at the surface, diffusion over the surface to the steps, adsorption desorption and incorporation at the steps, whereby all these processes are subject to chemical reactions. Here our knowledge is very limited, except for the generally accepted idea that the main chemical interactions occur at the step. In addition there is quite a lot of experimental and theoretical evidence that at high temperatures desorption of the growth species becomes rate limiting, although it is not clear whether the desorption takes place from the surface or from the steps.

In this paper we will address the issue of adsorption of radicals on the (001) and (111)Ga surfaces of GaAs during the growth by MOCVD at 1 bar, especially focussing on the maximum values for the coverages for the growth species under near equilibrium conditions.

2. Definitions of electronic structures

2.1. The (111)Ga and (001)As-stabilized surfaces

The electronic structure of the (111)Ga surface is simple: all available bonding electrons of the Ga atoms are needed for the three bondings directed towards the bulk, i.e. the surface orbitals of the Ga atoms are all empty (fig. 1a).

For the (001) surface we will only consider the arsenic stabilized situation, because this structure is most likely to be present under the arsenic rich growth conditions during MOCVD where the growth rate is only a function of the TMG partial pressure. In the truncated case (fig. 1b), two of the five electrons are in surface orbitals, the other three are needed to form the bondings with the Ga atoms in bulk. When no adsorbates are present, these surface electrons will form $\sigma$ and/or $\pi$ bonds leading to the well-known dimer reconstructed surface. Recently a $p(2 \times 4)$ reconstruction of the (001) GaAs surface was observed at temperatures up to 585°C in the presence of 100 Torr of hydrogen even in the absence of arsine [1]. In fig. 1b, the cases for $\sigma$ bond only and $\pi + \sigma$ bond formation are depicted.

In the similar case of the (001) surface of silicon the energy for the $\pi$ bond $E_{\pi} = 14$
Fig. 2. Energy diagrams for adsorption of AsH₃ (a) on (111)Ga surface and (b) on a (001)As-stabilized surface.

we assume that the π bonds are completely broken, so we will base our calculations on the structure where only the σ bond is present, i.e. during adsorption no π bonds have to be broken up.

2.2. Electronic properties of molecules and radicals in the gas phase

In table 1 the species which — according to chemical calculations — are of interest for the adsorption are given with their electronic config-

Table 1
Species of interest for adsorption and their electronic configuration

<table>
<thead>
<tr>
<th>As species</th>
<th>Electronic configuration</th>
<th>Ga species</th>
<th>Electronic configuration</th>
<th>Other species</th>
<th>Electronic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsH₃(4s)²</td>
<td>Singlet</td>
<td>Ga(CH₃)₃</td>
<td>Singlet</td>
<td>H(1s)¹</td>
<td>Doublet</td>
</tr>
<tr>
<td>AsH₂(4s)²(4p)¹</td>
<td>Doublet</td>
<td>Ga(CH₃)₂(4s)¹</td>
<td>Doublet</td>
<td>CH₃(2s)¹</td>
<td>Doublet</td>
</tr>
<tr>
<td>AsH(4s)²(4p)²</td>
<td>Triplet</td>
<td>GaH(4s)¹</td>
<td>Singlet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As(4s)²(4p)³</td>
<td>Quartet</td>
<td>GaH(4s)²</td>
<td>Singlet</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In order to be able to make a chemical bond with a surface atom which has one electron in a surface orbital, each species must have at least one electron in an unpaired state, i.e. their electronic configuration must consist of a doublet, triplet or quartet. Several species have singlet ground states, however, where the two electrons are paired in one orbital. In principle such a singlet state should be excited to the antibonding state in order to make adsorption possible. The electron pairing energy for the arsenic and gallium atoms are not really known. From the formation energy and heat of dissociation of trimethyl gallium (TMG), dimethyl gallium (DMG) and monomethyl gallium (MMG), a value of 20 kcal/mol can be deduced for the transition from the single ground state to the lowest lying excited state of Ga(4s)\(^2\), quite close to the pairing energy for Si(3s)\(^2\) which is 17.2 kcal/mol [3]. A literature search for As(4s)\(^2\) did not give evidence for a pairing energy, so a value of 0 kcal/mol is likely, but this is not at all sure; a depairing energy of 20 kcal/mol close to that of Ga(4s)\(^2\) is also possible. It must be questioned whether depairing to an excited state must be considered at all when the receiving orbital is completely empty, as e.g. for the (111)Ga surface. As is evident from fig. 2, the necessary depairing energy – whether existing or not – cancels out in the formation of the two bonds with the surface, because the electronic bonds are formed from the excited levels. However, in case the receiving orbital already contains one electron – as for the (001) surface – the end situation is a radical with still one electron in an excited state, the amount of energy involved then is anything between 0 and 10 kcal. As the latter situation from an energetic point of view certainly is less stable than the bond which is formed between AsH\(_3\) and (111)Ga, we have chosen for an energy correction of 10 kcal/mol in those cases where one 4s electron remains unbonded. Indeed, some examples exist where only one electron is available to form a bond (-CH\(_3\) on (111)Ga, etc). Here the adsorption energy is certainly much lower than for the normal bond. When the partial pressures of these species also are very low (<10\(^{-9}\) bar), these adsorptions will become negligible.

Table 3
Standard adsorption entropies on (001)As-stabilized and on (111)Ga \(^{a)}\)

<table>
<thead>
<tr>
<th>Species</th>
<th>(\Delta S^\circ) (e.u.)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsH(_3)</td>
<td>-35.1</td>
<td>-35.1</td>
</tr>
<tr>
<td>AsH(_2)</td>
<td>-33.2</td>
<td>-32.4 Non-linear (g) (\rightarrow) non-linear (a)</td>
</tr>
<tr>
<td>AsH</td>
<td>-28.2</td>
<td>-27.6 Linear (g) (\rightarrow) non-linear (a)</td>
</tr>
<tr>
<td>As</td>
<td>-23.7</td>
<td>-23.0</td>
</tr>
<tr>
<td>DMG</td>
<td>-41.0</td>
<td>-40.0 Non-linear (g) (\rightarrow) non-linear (a)</td>
</tr>
<tr>
<td>MMG</td>
<td>-28.6</td>
<td>-27.6 Linear (g) (\rightarrow) non-linear (a)</td>
</tr>
<tr>
<td>GaH(_2)</td>
<td>-28.8</td>
<td>-27.8 Non-linear (g) (\rightarrow) non-linear (a)</td>
</tr>
<tr>
<td>GaH</td>
<td>-28.1</td>
<td>-27.0 Linear (g) (\rightarrow) non-linear (a)</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>-33.8</td>
<td>-33.8</td>
</tr>
<tr>
<td>H</td>
<td>-27.0</td>
<td>-26.5</td>
</tr>
</tbody>
</table>

\(^{a)}\) Smallest values, rotations on surfaces are still allowed; standard state \(p = 1\) bar, \(T = 1000\) K, \(\theta = \frac{1}{2}\).
3. Adsorption calculations under near equilibrium growth

For the calculation of the coverages, we assume Langmuir adsorption as governed by the expression
\[ \Theta_i = \frac{p_i K_i}{1 + \sum_j p_j K_j} \]

The equilibrium constants \( K_i \) were calculated from the expression
\[ RT \ln K_i = -\Delta G_i^\circ = -(\Delta H_i^\circ - T \Delta S_i^\circ) \]
for \( T = 1000 \) K. It should be kept in mind that the given expression for the coverages leads to maximum values for the growth species. The reason is that the Langmuir expression neglects the effects due to what can be called the chemical reactions at the surface, or more complete creation and annihilation processes of the adsorbed surfaces species, in short sources and sinks such as formation of species by surface reactions, incorporation at steps, etc. For instance, when these effects are combined in one constant \( k_r \), the actual expression for a two-component system A, B where only component A reacts, whereas B serves as an inert impurity, should be:
\[ \Theta_A = \frac{K_A P_A}{1 + \sum_{i=A,B} K_i p_i + (k_r/k_{dA})(1 + K_B P_B)} \]
\[ \Theta_B = \frac{K_B P_B (1 + k_r/k_{dA})}{1 + \sum_{i=A,B} K_i p_i + (k_r/k_{dA})(1 + K_B P_B)} \]
where \( k_{dA} \) = desorption constant of species A.

The activation energy of the desorption of A always will be larger than the activation energy for reaction, so for high temperatures \( k_{dA} \) will increase very sharply and \( k_r/k_{dA} \) will become small. In that case near equilibrium values for \( \Theta_A \) and \( \Theta_B \) will be reached. From this intermezzo it will be clear that when we apply the simpler Langmuir expression as given in the beginning of this section also for lower temperatures, we will be sure to obtain the maximum values for the coverages for the growth species.

For the case of near equilibrium growth, the partial pressures were calculated for a growth mixture of 1% \( \text{AsH}_3 \) in \( \text{H}_2 \) and a V/III ratio of 20. The total pressure of the gas mixture was 1 bar. The calculation was performed for the homogeneous case which yields the highest supersaturation for all As and Ga species in the gaseous phase. The formation of solid GaAs was not allowed; also, the formation of the gaseous species \( \text{As}_2 \) and \( \text{As}_4 \) was not taken into account since these species never have been reported in actual growth situations. In this way all partial pressures of the \( \text{AsH}_x \) molecules will be exaggerated. In fig. 3 the partial pressures are given as a function of temperature for the temperature interval 800 to 1100 K.

The resulting coverages for \( T = 1000 \) K are given in fig. 4. For the (001)As-stabilized surface, the non-growth species \( \text{AsH}_3 \) and \( \text{H} \) lead to cover-
ages of 0.1% and 39%, respectively. The coverage by the growth species is mainly due to GaH₂ at a value of 1% and to MMG with value of \(5 \times 10^{-2}\%\). The coverage by CH₃ is lower than \(10^{-3}\%\). Of the arsenic radicals AsH and As are equally covering the surface for 0.3%.

On the (111)Ga surface, the main species is AsH₃ with a coverage of 8%; the coverage by atomic hydrogen has decreased to zero due to the single electron in the Ga–H bond. The most important adsorbed Ga species is MMG with a coverage of 0.8%. Of the arsenic species atomic As and AsH both have a coverage of 0.2%.

The above calculation describes the situation when growth occurs under near-equilibrium conditions, as may be realized in a furnace during closed tube transport. The method can also be applied to the halide process when chlorine adsorption is accounted for. It must be remembered that the above calculated coverages have been maximized in several respects: (a) the most favourable entropy chance has been applied, (b) the maximum supersaturation in the gas phase has been used, (c) the formation of As₂ and As₄ has been suppressed and (d) all other paths on the surface which lead to reduction of the adsorbed growth species have been neglected. Still only small values for the coverages of the radical species containing Ga or As are found, in contrast to the high coverages by atomic H on (001) and by AsH₁ on (111)Ga. Especially the coverage by H seems to be controversial for MOCVD conditions which are far from equilibrium. In addition, the presence of GaH₂ should be questioned for real MOCVD growth situations. Another problem is how the growth rates of both surfaces can be equal in the diffusion transport limited regime although their coverages of Ga species are quite different.

4. Conclusion

Maximum adsorption coverages have been calculated for the GaAs surface under conditions of MOCVD growth. It is shown that for near equilibrium calculations:
(a) a high surface coverage (39%) with H is expected for (001), but not for (111)Ga;
(b) the coverage by CH₃ is negligible on both surfaces;
(c) on (001) the coverage by MMG is very small, while GaH₂ covers the (001) surface by 1%; on the (111)Ga surface only MMG is present for 0.8%;
(d) AsH₃ covers the (001) surface by 0.1% and the (111)Ga surface by 8%.

It must be understood that this case is not representative for a description of real growth. In a forthcoming paper, the kinetic approach as used by Tirtowidjojo and Pollard will be taken to calculate the coverages under more realistic conditions.

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\[
\begin{array}{cccccccccc}
\text{AsH}_3 & \text{AsH}_2 & \text{AsH} & \text{As} & \text{TMG} & \text{DMG} & \text{MMG} & \text{GaH}_3 & \text{GaH}_2 & \text{GaH} & \text{CH}_3 & \text{H} \\
0 & \times 10^{-2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}
\]

(001)As-stabilized

\[
\begin{array}{cccccccccc}
\text{AsH}_3 & \text{AsH}_2 & \text{AsH} & \text{As} & \text{TMG} & \text{DMG} & \text{MMG} & \text{GaH}_3 & \text{GaH}_2 & \text{GaH} & \text{CH}_3 & \text{H} \\
0 & \times 10^{-2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}
\]

(111)Ga

Fig. 4. Calculated near-equilibrium coverages for the (001)As-stabilized and for the (111)Ga surface.
References