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MODELING OF THIN-FILM GaAs GROWTH

By
John H. Heinbockel, Principal Investigator

Progress Report
For the period January 30, 1981 to June 16, 1982

Prepared for the
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23665

Under
Research Grant NAG1-148
Ronald A. Outlaw, Technical Monitor
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INTRODUCTION

The Solid-on-Solid (SOS) model of crystal growth (ref. 1) is represented by a rectangular array of integers where each integer represents the number of adatoms in a column perpendicular to some reference frame. The adatoms can represent atoms or molecules that are being stacked. Figure 1 illustrates the surface adatoms that are at the tops of their columns. It is assumed that an adatom event of adsorption or desorption can only occur at the top of a column.

We are concerned with constructing a model of crystal growth that takes into account the processes of nucleation on the growing surface as well as considering the processes of surface migration and desorption of adatoms.

In the SOS model the columns are constructed upon an $M \times M$-square array by randomly placing adatoms upon the array and allowing these randomly deposited adatoms to either condense, evaporate, or migrate. The SOS model can be described as an array of interacting columns of varying integer heights. The surface adatoms, being at the tops of columns, are allowed to migrate, remain stationary, or evaporate as is dictated by a set of rules which will be described presently.

The term "epitaxy" means "an arrangement" and is used to denote the growth of one substance upon the crystal surface of a foreign substance. The term "autoepitaxy" is the oriented growth of a substance onto itself and "heteroepitaxy" is used for the growth of one material upon the surface of a different material. Obviously, heteroepitaxy becomes autoepitaxy after one layer of adatoms has been deposited over the growing surface. We use the SOS method to simulate epitaxial growth of crystals.

*Professor, Department of Mathematical Sciences, Old Dominion University, Norfolk, Virginia 23508.
## LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>i, j</td>
<td>site numbers</td>
</tr>
<tr>
<td>M</td>
<td>size of square array</td>
</tr>
<tr>
<td>$U_0 = U_o(i, j)$</td>
<td>potential at site (i, j)</td>
</tr>
<tr>
<td>$\phi_0, \phi_1, \phi_2, \phi_3$</td>
<td>potential energy changes</td>
</tr>
<tr>
<td>$w_i, i = 1, ..., 8$</td>
<td>potential energy changes</td>
</tr>
<tr>
<td>$E(i, j)$</td>
<td>random energy</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>time interval</td>
</tr>
<tr>
<td>$U = U(i, j)$</td>
<td>total energy at site (i, j)</td>
</tr>
<tr>
<td>$U_e$</td>
<td>evaporation potential</td>
</tr>
<tr>
<td>$U_m$</td>
<td>migration potential</td>
</tr>
<tr>
<td>$E$</td>
<td>energy</td>
</tr>
<tr>
<td>$K$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$f(E)$</td>
<td>Boltzmann distribution</td>
</tr>
<tr>
<td>(100), (110), (111)</td>
<td>crystal orientations</td>
</tr>
<tr>
<td>$\alpha_2, \alpha_3$</td>
<td>scale factors</td>
</tr>
<tr>
<td>$\xi$</td>
<td>crystal orientation factor</td>
</tr>
<tr>
<td>$u^{(1)}<em>{ks}, u^{(2)}</em>{ks}$</td>
<td>kink site potentials</td>
</tr>
<tr>
<td>$\Delta\text{Hevap}$</td>
<td>heat of evaporation</td>
</tr>
<tr>
<td>$N_e, N_m, N_e$</td>
<td>fraction of adatoms evaporating, migrating or remaining localized</td>
</tr>
<tr>
<td>$\Gamma_{ij}$</td>
<td>position factor</td>
</tr>
</tbody>
</table>

### POTENTIAL ENERGY OF ADATOMS

The rules by which the columns of the SOS model interacted were governed by the following ideas relating to the potential energy and potential energy changes associated with the adsorption, migration, or desorption of...
adatoms from an arbitrary row $i$ and column $j$ of an $M \times M$ array. Energies associated with an arbitrary site $(i,j)$ were defined as follows: $U_0 = U_0(i,j)$—the potential energy at a site because of surface bonding and crystal structure; $\Phi_0$—the potential energy change at site $(i,j)$ because of the deposition of an adatom (assumed the same for all sites); $-W_l(i = 1, ..., 8)$—the potential energy changes at neighboring sites when an adatom is deposited at site $(i,j)$; $E(i,j)$—the random surface energy associated with site $(i,j)$ and time interval $\Delta t$; $U(i,j) = U_0(i,j) + E(i,j)$—the total energy associated with site $(i,j)$ during the time interval $\Delta t$; $U_e$—the evaporation potential; and $U_m$—the migration potential. All of the above energies were measured in electron volts.

We developed a Monte Carlo computer simulation of crystal growth (refs. 2, 3, 4, and 5) by developing rules that determined the SOS kinetics of condensation evaporation or surface migration of adatoms. These rules led to a consistent and physically reasonable description of the fundamentals associated with crystal growth. We first considered the adsorption of a thermally accommodated adatom onto the surface at some general site where the potential at this site was changed and, simultaneously, potential energy changes at all of the neighboring sites occurred. In Table 1 the potential energy changes are depicted by the mnemonic mask. The center of this mask is placed over the site $(i,j)$ to illustrate the changes to be made in the potential at the central site as well as the potential changes in the surrounding neighboring sites.

The potential changes in the case of desorption of an adatom from the central site are again depicted with the mask of Table 1, with the opposite signs on the potential changes. The case of surface migration was treated as a desorption from a site $(i,j)$ followed by an adsorption at a nearest neighbor location, together with the correct potential mask changes associated with each process. The nearest neighbor migration site was determined by a random walk to one of the unoccupied nearest neighbor sites.
Table 1. Potential energy changes associated with central site \((i,j)\) and neighbor sites due to deposition of an adatom.

| \(-w_7\) | \(-w_8\) | \(-w_1\) |
| \(-w_2\) | \(-w_3\) | \(-w_4\) |

\(-w_7 = -w_7(i-1,j-1)\)
\(-w_8 = -w_8(i,j)\)
\(-w_1 = -w_1(i-1,j+1)\)
\(-w_2 = -w_2(i,j+1)\)
\(-w_3 = -w_3(i+1,j+1)\)
\(-w_4 = -w_4(i+1,j)\)

The Monte Carlo simulation of crystal growth involved a random deposition of thermally accommodated surface adatoms during a time interval \(\Delta t\). These deposited adatoms changed the potential energies at the random surface sites under consideration. The values assigned to the central potential change \(\phi_0\) and neighboring potential changes \(-w_i\), \(i = 1, \ldots, 8\) dictated the new potential energy values when an adatom was deposited or removed from a site. In this way each surface site had an energy barrier to translation or evaporation, represented by a potential well. We assumed that the thermally accommodated adatoms had a surface energy distribution described by the Boltzmann distribution

\[ f(E) = \frac{1}{KT} \exp \left( \frac{-E}{KT} \right), \, E > 0 \]  

which has a mean energy of \(KT\).

During each time interval \(\Delta t\), the Boltzmann distribution was used to assign a random energy \(E(i,j)\) to each of the surface adatoms. We let

\[ U(i,j) = U_o(i,j) + E(i,j) \]  

denote the total energy possessed by a surface adatom at a site \((i,j)\) during this time interval. This total energy is the sum of the potential energy \(U_o\) due to the lattice structure and a random energy \(E\) from the Boltzmann distribution which characterizes the random surface energy. When \(U\) was less than some material-dependent migration level \(U_m\), the adatom remained stationary at the surface site. If \(U_m < U < U_e\), surface
migration by random walk was allowed to occur. If $U$ was greater than the evaporation potential $U_e$, the adatom was removed from the site.

The rate of impingement of adatoms upon the surface was independent of the surface configuration. The rates associated with the evaporation and migration of adatoms depended upon the potential barriers $U_e$ and $U_m$ and also upon the values assigned to the potential changes $\Phi_0$ and $-\Phi_1$, $(1 = 1, ..., 8)$. These later potential changes had to take into account the type of crystal structure and orientation of the growth we were trying to simulate with the SOS model. In Figure 2(a), for growth on the (100) face, we set up a correspondence between the central site, the nearest neighbor potentials $\Phi$, second nearest neighbor potentials $\Phi_2$, and the adatom potential changes for the mask in Table 1 (e.g., $\Phi_1 = \Phi_2$, $\Phi_2 = \Phi_1$). In a similar manner we were able to set up the correspondences illustrated in Figure 2(b) and (c) for the (111) and (110) orientations. In Table 2, we selected the relation between the neighbor potentials $\Phi_0$, $\Phi_1$, $\Phi_2$, $\Phi_3$ in such a way that when the first level of adatoms covered the surface, the potential distribution returned to its original value. By simply adding adatoms to the surface it was readily verified that the potential changes, assigned to the mask, had to adhere to the rules given in Table 2. In these rules, a negative sign denotes an attractive potential and after one complete layer of adatoms is deposited, the potential energy values at each site will return to their initial values.

We let $\Phi_1$ denote the change in the nearest neighbor potentials due to the addition of an adatom to the surface and let $\Phi_2$, $\Phi_3$ denote the second and third nearest neighbor potential changes. We assumed that $\Phi_2 = a_2\Phi_1$ and $\Phi_3 = a_3\Phi_1$ where $a_2$, $a_3$ are scale factors which are less than one. This allowed us to define the crystal orientation factor $\xi$ as

$$\xi = \begin{cases} 2 + 2a_2, & (100) \\ 3 + a_2, & (111) \\ 1 + a_2 + 2a_3, & (110) \end{cases}$$

which takes into account the different crystal orientations. We also defined the kink site potentials before $U_{ks}^{(1)}$ and after $U_{ks}^{(2)}$ and the capture of an adatom as $U_{ks}^{(1)} = U_0 - \xi\Phi_1$, $U_{ks}^{(2)} = U_0 + \xi\Phi_1$. (Note that $\Phi_0 = 2\xi\Phi_1$.)

5
Table 2. Potential changes for addition of an adatom to an arbitrary site.

<table>
<thead>
<tr>
<th>Crystal Face</th>
<th>Relation Between Neighbor Potentials</th>
<th>Potential Changes for Addition to Arbitrary Site I</th>
<th>Distances to Neighboring Sites</th>
</tr>
</thead>
</table>
| (100)        | $\phi_0 = 4\phi_1 + 4\phi_2$        | \[
\begin{bmatrix}
-\phi_2 & -\phi_1 & -\phi_2 \\
-\phi_1 & -\phi_0 & -\phi_1 \\
-\phi_2 & -\phi_1 & -\phi_2
\end{bmatrix}
\] | \[
\frac{\sqrt{2}a_0}{c}
\] |
| (111)        | $\phi_0 = 6\phi_1 + 2\phi_2$        | \[
\begin{bmatrix}
-\phi_1 & -\phi_1 & -\phi_2 \\
-\phi_1 & -\phi_0 & -\phi_1 \\
-\phi_2 & -\phi_1 & -\phi_2
\end{bmatrix}
\] | \[
\frac{\sqrt{2}a_0}{c}
\] |
| (110)        | $\phi_0 = 2\phi_1 + 2\phi_2 + 4\phi_3$ | \[
\begin{bmatrix}
-\phi_3 & -\phi_2 & -\phi_3 \\
-\phi_1 & -\phi_0 & -\phi_1 \\
-\phi_3 & -\phi_2 & -\phi_3
\end{bmatrix}
\] | \[
\frac{\sqrt{3}a_0}{c}
\] |

ORIGINAL PAGE IS OF POOR QUALITY
THE SIMULATION MODEL AND PARAMETERS

A flow chart of the simulation model is illustrated in Figure 3. The model is simple and presents an alternative viewpoint for the interaction of surface molecules: An assumed impingement rate dictates the number of adatoms arriving on the surface during a time interval $\Delta t$. Each of these adatoms are added to the surface at random sites and the potentials at each of these sites and neighboring sites are adjusted. If the $\Delta t$ time interval is so small that no adatoms arrive on the surface, then every surface adatom can still be assigned a random energy from the Boltzmann distribution and surface interactions can be taken into account. We continued scanning the surface each $\Delta t$ time interval until enough time accumulated for the addition of another adatom.

The model allows for various assumptions to be made about the interaction of potentials and assignment of potential values. We let $U_e = 0$ denote the evaporation level, then $\Delta U_e = U_e - U_0$ represented the desorption energy $\Delta \text{Hevap}$. The activation energy for migration of adatoms in a flat surface was $\Delta U_m = U_m - U_0$. The various potentials are illustrated in the Figure 4. The values assigned to $U_m$ and $U_0$ greatly affected the model behavior. For example, the Boltzmann distribution is illustrated in Figure 5, where nominal values of $\Delta U_m$ and $\Delta U_e$ are illustrated. The number of surface adatoms with a statistical surface energy less than $\Delta U_m$ is proportional to the area under the probability density curve which is given by $N_x = 1 - \exp(-\Delta U_m/\kappa T)$.

The number of adatoms that escaped from the surface is proportional to $N_e = \exp(-\Delta U_e/\kappa T)$ and the number of adatoms that migrated is proportional to the area $N_m = 1 - N_x - N_e$. Letting $\alpha = \Delta U_m/\Delta U_e$, Figure 6 was constructed which illustrates the migration effect as $\alpha$ decreases.

The values of $\phi_0$, $\phi_1$, $\phi_2$, $\phi_3$ which denote the potential energy changes at a central site $(i,j)$ and nearest neighbor sites can be different for the substrate and the growing material. For the substrate material we could use the depth of the surface potentials and migration levels to stimulate a variety of surface morphologies. In this model we envisioned a flat substrate as a periodic lattice structure 20-x-20 square where each
lattice is a potential well. The substrate can vary from flat to rough and
the potentials adjusted to reflect various surface preparations. For an
ideally flat substrate we assumed that the depths of the potential wells
were uniform, given by $U_{0s}$. After one layer of growing material
covered the surface, the potentials at each site were assumed to convert to
the autoepitaxy potentials $U_i$. In order to make this transition we
assumed that $\phi_{0} = \sum_{i=1}^{8} w_i + (U_{0} - U_{0s})\Gamma_{ij}$ where $\Gamma_{ij}$ is zero if the
height $h_{ij}$ at position (ij) is greater than or equal to one and
$\Gamma_{ij}$ is one in the case where $h_{ij}$ is zero. Thus, if an adatom was
deposited at a first layer site (i,j) we adjusted the potential at this site
by the relation by $U_{0} - U_{0s}$ in addition to the mask potential changes as
this produced the desired change that heteroepitaxy produces in the potential
at the surface site.

Nucleation on the substrate was controlled by the values assigned to
$\Delta U_e$, $\Delta U_m$, and $\phi_0$. For large values of $\Delta U_m$ there were deep potential
wells that captured all thermally accommodated adatoms. For small $\Delta U_m$
values there was an increase in surface migration and a decrease in the
number of adatoms that remained localized. This increased the probability
of an adatom combining with other adatoms to form a critical cluster. Then
growth was characterized by the lateral motion of adatoms and their addition
to the steps of clusters that produced the lateral growth.

Various potentials were proposed for the addition of an adatom to the
surface (refs. 6 and 7):

- **Buckingham Potential** $E = \frac{\lambda_0}{r^6} - \frac{\lambda_1}{r^4}$
- **Modified Buckingham Potential** $E = \left[ \frac{6}{g} \sum \frac{\alpha l - r_{ij}}{r_{mj}} - \frac{r_{mj}}{r} \right] \frac{e}{1 - \theta}$
- **Lennard-Jones (Mie Potential)** $E = \frac{\lambda_n}{r^n} - \frac{\lambda_m}{r^m}$
- **Morse Potential** $E = D e^{-2\alpha(r - r_0)} - D e^{-(r - r_0)}$
- **Born-Mayer Potential** $E = Ae^{-Br}$
These potentials reflect the vertical effect of potential change. For the lateral interaction between potentials and resultant changes (ref. 8), we find:

Kiselev Potential \[ E = E_0 - NCGF(r) \]

where \( E_0 \) is interaction at zero coverage, \( C \) is dispersion constant, \( N \) is the number of nearest neighbors at half a monolayer coverage and \( r \) is mean distance between molecules.

Output from the computer program can be graphic as illustrated in the Figure 7 or quantitative.
### Quantitative Measures of Crystal Growth and Parameters of Model

<table>
<thead>
<tr>
<th>Measures of Crystal Growth</th>
<th>Parameters of Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Growth rate of crystal</td>
<td>1. Deposition rate of adatoms</td>
</tr>
<tr>
<td>2. Critical clusters</td>
<td>2. Potential changes $\phi_0, \phi_1, \phi_2, \phi_3$</td>
</tr>
<tr>
<td>a. size</td>
<td>3. Mean $U_0$ and standard deviation $\sigma_0$ associated with normal distribution $N(U_0, \sigma_0)$ of surface potentials (initially $U_0 = 0$)</td>
</tr>
<tr>
<td>b. shape</td>
<td>4. Traps in surface</td>
</tr>
<tr>
<td>c. density</td>
<td>5. Temperature of substrate</td>
</tr>
<tr>
<td>vs. time or deposition rate</td>
<td>6. Number of migration scans (time $\Delta t$)</td>
</tr>
<tr>
<td>3. Surface diffusion (mobility)</td>
<td>7. Crystal orientation</td>
</tr>
<tr>
<td>4. Condensation rate</td>
<td>8. Substrate and growing potentials can be different</td>
</tr>
<tr>
<td>5. Evaporation rate</td>
<td>9. Mean $U_m$ and standard deviation $\sigma_m$ of migration levels associated with normal distribution $N(U_m, \sigma_m)$</td>
</tr>
<tr>
<td>6. Rate of nucleation</td>
<td>10. Initial substrate geometry and potentials</td>
</tr>
<tr>
<td>7. Other characteristics</td>
<td>11. Assumptions in regard to retention of incident energy</td>
</tr>
</tbody>
</table>

\[
E_{\text{random}} = E_{\text{Boltzmann}} + E_{\text{Retention}}
\]

(Surface Kinetic Energy) Energy of Incident Adatom

### Nominal Values for Potential Energies for Germanium in eV (1 eV = 23 KCAL/MOLE) *

- $\Delta_{\text{Hevap}} = 3.87$ eV
- $\Delta_{\text{Hads}} = 0.86$ eV Ge on CaF$_2$
- $\Delta_{\text{Hads}} = 0.55$ eV Ge on graphite
- $\Delta_{\text{Hads}} = 0.60$ eV Ge on carbon
- $\Delta_{\text{Hads}} = 1.6$ eV Ge on W

- $\text{Qd} = 0.52$ eV Ge on CaF$_2$
- $\text{Qd} = 0.32$ eV Ge on graphite
- $\text{Qd} = 0.35$ eV Ge on carbon
- $\text{Qd} = 0.75$ eV Ge on W

* See ref. 9.
REFERENCES


Figure 1. SOS model for crystal growth.
Figure 2. FCC model and potential changes associated with different crystal orientations.
Figure 3. Flow chart of simulation model.
\[ \Delta H_{ads} = \text{HEAT OF ADSORPTION FOR SINGLE ADATOM} \]
\[ \Delta H_{evap} = \text{HEAT OF EVAPORATION} \]
\[ U_e = \text{EVAPORATION BARRIER} \]
\[ U_m = \text{MIGRATION BARRIER} \]
\[ U_0 = -\Delta H_{evap} = \text{NOMINAL VALUE FOR POTENTIAL UNIFORM SURFACE} \]
\[ \phi_0 = \Delta H_{evap} - \Delta H_{ads} = \text{POTENTIAL CHANGE DUE TO ADDITION OF ADATOM AT SITE (i,j)} \]
\[ \phi_1 = \text{NEAREST NEIGHBOR POTENTIAL CHANGE} \]
\[ \phi_2 = \text{SECOND NEAREST NEIGHBOR POTENTIAL CHANGE} \]
\[ Q_d = \text{DIFFUSION ACTIVATION ENERGY} \]

Figure 4. Potential for uniform flat surface (solid line) and potential after adatom has been added to site (i,j) (dashed line) together with energy barrier nomenclature.
Figure 5. Boltzmann distribution.
\[ \alpha = \frac{\Delta U_m}{\Delta U_e}, \quad N_e = 1 - N_r, \quad N_m = N_r - N_e, \quad \bar{N}_m + N_r + N_e = 1 \]

- \( N_m \) = FRACTION MIGRATING
- \( N_r \) = FRACTION REMAINING LOCALIZED

\( N_e \) = FRACTION OF ADATOMS EVAPORATING

Figure 6. Evaporation, migration, and localization of adatoms for various values of \( \Delta U_m / \Delta U_e \).
Figure 7. Graphic display of crystal growth (100) orientation.