Explanation of the limiting thickness observed in low-temperature silicon epitaxy

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Solution of the partial differential equation for diffusion of mobile atoms during solid film growth demonstrates that the observed phase transition in low-temperature silicon epitaxy is triggered by supersaturation of the growing layer with hydrogen. The limiting thickness of the epitaxial layer, \( h_{\text{epi}} \), is completely determined by measurable quantities: the flux of hydrogen, the hydrogen diffusion coefficient, and the layer growth rate. Our model accounts for the observed Arrhenius and growth rate dependence of \( h_{\text{epi}} \).

The literature is replete with examples of abrupt phase transitions that disrupt homogeneous thin-film growth. Many of these are of considerable technological importance. A sudden phase transition frequently limits the overall thickness to which a layer can be grown for a given set of conditions, and uncontrolled transients during growth often create interfaces that dominate device performance. Examples of such phase transitions include: the remarkable discovery of a critical Si epitaxial thickness, \( h_{\text{epi}} \), by Eaglesham et al.\(^1\) and Jorke et al.,\(^2\) the well-known transition from amorphous to microcrystalline thin-film Si during plasma-enhanced chemical vapor deposition (PECVD), and gradual changes in morphology observed in many amorphous layers. These transitions have been studied by a variety of authors.\(^1\)–\(^14\) Aspects of our more detailed analysis\(^15\) apply to many of these phase transitions. In this letter, we explain the temperature and growth-rate dependence of the limiting-thickness observed in low-temperature epitaxial Si growth\(^1\)–\(^2\),\(^8\)–\(^12\),\(^14\) based on the supersaturation of the growing layer with diffusing hydrogen.

Low-temperature Si epitaxy is of broad scientific and technological interest. It is required for fabrication of nanoscale junctions, useful in making delta-doped layers and buried channel devices, and shows promise for producing high-speed electronic devices. Here we explain the long standing scientific puzzle of temperature dependent limits to epitaxial layer thickness before the layer undergoes a phase transition to amorphous growth.\(^1\)–\(^2\),\(^8\)–\(^12\),\(^14\) The limiting thickness has an increasing Arrhenius dependence on substrate temperature, \( T \). Prior to this important discovery,\(^1\) it was believed that there was a simple critical temperature, \( T_{\text{epi}} \), below which epitaxy could not be sustained.

The Jorke model\(^2\) is the only previous quantitative explanation of \( h_{\text{epi}} \). This model is based on the kinetics of defect formation and provides a temperature and growth-rate dependent probability of forming crystallographic imperfections. However, it does not have the observed Arrhenius temperature dependence.\(^1\)–\(^8\),\(^11\),\(^14\) Figure 1 is a plot of the growth temperature dependence of experimental values for \( h_{\text{epi}} \) along with the theoretical curve for the Jorke model\(^2\) (solid line). The data points clearly show the Arrhenius dependence of \( h_{\text{epi}} \). The Jorke model does not reproduce this temperature dependence, and because of the model’s functional form, even adjusting parameters cannot bring it into agreement with experiment.

In the case of low-temperature molecular-beam epitaxial (MBE) Si, there are numerous examples of hydrogen affecting growth and there is strong empirical evidence linking the breakdown in epitaxy to hydrogen.\(^8\)–\(^13\) Although \( h_{\text{epi}} \) exhibits a dependence on hydrogen dose, it is not a simple function of surface coverage; this has impeded the understanding of hydrogen’s effects.\(^1\) Positron-annihilation defect-spectroscopy (PAS) gave the best evidence that atomic H is connected to the breakdown of epitaxy.\(^1\)–\(^12\) The authors showed that for MBE Si, a critical concentration of hydrogen in the silicon bulk is associated with a catastrophic breakdown in epitaxy. Thus, one can speculate that hydrogen could be the source of the breakdown of epitaxy, perhaps by bond disruption once a critical concentration is reached. It is suggested that the slope of the Arrhenius plots in Fig. 1 is about 0.48 eV, the same activation energy as for hydrogen diffusion in c-Si.\(^16\)

Based on the preceding observations we assume that H causes the breakdown of low temperature epitaxy and develop the first quantitative theory able to explain the experi-

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FIG. 1. Limiting-thickness data from various sources at growth rates shown in the legend. The solid superlinear curve is the prediction of Jorke et al. (Ref. 2). The solid circles are from Eaglesham et al. (Ref. 1). The winged data points are from Murty et al. (Refs. 11 and 12) and the triangular data points are from Varhue et al. (Ref. 14). Dashed curves from our theoretical fits to the reported data are as indicated in legend.
mental data. The model is based on the idea that a supersaturation of hydrogen at the growth surface to a critical concentration, \( C_s \), will trigger an abrupt transition from crystalline to amorphous growth. The limiting thickness therefore depends on the film growth rate, \( V_G \), the flux of atomic hydrogen at the growth surface, \( F_0 \), and the hydrogen diffusion coefficient, \( D_H \). Figure 1 compares this model, described below, with limiting-thickness data. The theory contains three parameters: \( V_G \), \( F_0 \), and \( C_s \), all of which can be measured. As can be seen in Fig. 1, our theory gives excellent agreement with a variety of data.

Using the Laplace transform, we derived a new closed form solution of the time-dependent partial differential equation representing diffusion of a mobile species during film growth. Here we are especially interested in the time evolution of the hydrogen concentration, \( C_H(x,t) \) at the growth surface, \( x = 0 \). The exact solution is:

\[
C(0,t) = \frac{C_s}{2} \left[ \text{erfc} \left( -\sqrt{\frac{t}{\tau}} \right) - \left( \frac{\alpha}{1 - \alpha} \right) \text{erfc} \left( \sqrt{\frac{t}{\tau}} \right) \right] \\
- \left( 1 - \frac{\alpha}{1 - \alpha} \exp \left( \frac{4(\alpha^2 - \alpha)t}{\tau} \right) \right) \times \text{erfc} \left( (2\alpha - 1) \sqrt{\frac{t}{\tau}} \right).
\]

(1)

To make the Laplace transformation tractable, the front surface coordinate is fixed at \( x = 0 \) as the film grows. Therefore Eq. (1) is valid on a homogeneous semi-infinite interval, implying that the film and the substrate have the same diffusion coefficient. It is useful to introduce a “flux velocity”, \( V_F = F_0/C_s \). For a given initial flux of H, \( V_F \) is proportional to the rate that hydrogen atoms are impinging on the surface. During growth \( V_F \) and \( V_G \) have opposite effects on the H concentration. High \( V_F \) tends to increase the concentration and high \( V_G \) tends to decrease the H concentration. The ratio of these velocities, \( \alpha = V_F/V_G \), determines the relative importance of the arrival rate of H at the surface and film volume expansion due to growth. Consequently, \( \alpha \) is a key parameter describing how rapidly the impinging H will bring the surface to a saturated concentration.

When \( C_H(O,t) = C_S \) the phase transition and breakdown of epitaxy occurs. Equation (1) is strictly valid if and only if \( D_H \) is constant. This assumption certainly breaks down right at the phase transition since \( D_H \) for c-Si is orders of magnitude greater than in a-Si or hydrogen saturated c-Si. We use Eq. (1) because we expect that the significant changes in \( D_H \) occur as \( C_H(O,t) \rightarrow C_S \) only in a small region just near the growing surface and very shortly before epitaxy breaks down.

Figure 2 shows the evolution of the fractional hydrogen concentration, \( C_H \), near \( C_S \), \( D_H \) decreases and hydrogen diffusion away from the surface slows. This positive feedback causes \( C_H \) to build up superlinearly. Thus, we expect the phase transition to occur at some value of \( C_H/C_S \) close to be less than unity, for example 0.9. Using this criterion for epitaxial breakdown, we have studied solutions of Eq. (1) for various values of \( \alpha \) and determined that the time at which breakdown occurs is inversely proportional to \( \alpha^2 \). This allows us to reach a simple relation between \( h_{\text{epi}} \) and measurable parameters:

\[
h_{\text{epi}} = 0.1 V_G \tau \alpha^{-2} = 0.4 D_H V_G V_F^{-1} = 0.4 \frac{V_G}{V_F} D_O \exp \left( E_a/kT \right),
\]

(2)

where \( k \) is Boltzmann’s constant and \( T \) the absolute temperature. \( D_O \) and \( E_a \) are, respectively, the preexponential factor and the activation energy for hydrogen diffusion. Equation (2) is the main result of this letter. For a given \( \alpha \) and \( V_G \), the thickness at which a film experiences a hydrogen driven phase transition, will be linearly proportional to the hydrogen diffusion coefficient. Equation (2) clarifies that the Arrhenius dependence of \( h_{\text{epi}} \) simply reflects the Arrhenius dependence of \( D_H \). Unfortunately, the hydrogen diffusion coefficients for the data in Fig. 1 were not measured. Therefore, we have used the literature value of the activated form for \( D_H \). For our values of \( \alpha \) and \( V_G \), the following MBE \( D_O = 0.000094 \text{ cm}^2/\text{s} \) and \( E_a = 0.48 \text{ eV} \) and determined \( \alpha \) from the fit of Eq. (2) to the data in Fig. 1. We find that this

![FIG. 2. Fractional hydrogen concentration at the growth surface vs scaled time for the case \( \alpha = 0.02 \). The intercept at \( C_H/C_S = 0.09 \) and \( \tau = 0.416 \text{s} \) defines breakdown of epitaxial growth.](image)

### Table I. Expressions for \( h_{\text{epi}} \) from Arrhenius fits to the reported limiting thickness data, and the derived values of \( \alpha \). The values for \( F_0 \) were derived using \( C_s = 2 \times 10^{15} \text{ cm}^{-3} \).

<table>
<thead>
<tr>
<th>Method/rate</th>
<th>Parameters</th>
<th>MBE 0.07 nm/s</th>
<th>PECVD 0.05 nm/s</th>
<th>MBE 0.09 nm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fit to data</td>
<td>( h_{\text{epi}} ) (nm)</td>
<td>2 \times 10^2 \exp(0.48/kT)</td>
<td>1 \times 10^7 \exp(-0.48/kT)</td>
<td>7.6 \times 10^6 \exp(-0.48/kT)</td>
</tr>
<tr>
<td>derived</td>
<td>( \alpha )</td>
<td>104</td>
<td>87</td>
<td>58</td>
</tr>
<tr>
<td>derived</td>
<td>( F_0 ) (cm(^{-2}) s(^{-1}))</td>
<td>1.7 \times 10^{13}</td>
<td>9 \times 10^{12}</td>
<td>1 \times 10^{13}</td>
</tr>
</tbody>
</table>

1. The values for \( \alpha \) were derived using \( C_s = 2 \times 10^{15} \text{ cm}^{-3} \).
approach then provides excellent fits to the data in Fig. 1. The reported H flux\textsuperscript{10,12} in the reactor of Ref. 1 is virtually identical to the flux we derive in this way. Thus, we have fit the data of Ref. 1 \textit{without any free parameters.}

Table I lists the values of $\alpha$ and $F_0$ found from fits to each data set. From $\alpha$ we can determine $V_F$, since $V_G$ is known. However, to estimate $F_0$ requires knowledge of $C_S$. The best estimate of $C_S$ comes from the work of Asoka-Kumar et al.\textsuperscript{10,12} In this work nuclear reaction analysis coupled with positron annihilation spectroscopy was used to show that a lower bound for the critical concentration of hydrogen is the Si layer at which a phase transition occurs is about $C_S=2\times10^{19}$ cm$^{-3}$. As stated above, their samples were prepared under conditions similar to those used by Eaglesham et al.\textsuperscript{1} Using this value for $C_S$ we calculate the values of $F_0$ in Table I. The values of $F_0$ are close to the value of $1.5\times10^{13}$ cm$^{-2}$/s reported\textsuperscript{11,13} for sample used in the determination of $C_s$ and in the Eaglesham \textit{et al.}\textsuperscript{1} determination of $h_{\text{epi}}$.

One reported set of limiting thickness data is not reproduced in Fig. 1. In this case, Eaglesham \textit{et al.}\textsuperscript{1} reported an activation energy of 1.5 eV at the high growth rate of 1.1 nm/s. This value appears high for an activation energy of hydrogen diffusion in c-Si, but may actually represent the diffusion coefficient of hydrogen in highly defective c-Si. Diffusion coefficients for hydrogen saturated c-Si have been shown to have an activation energy of $\sim1.5$ eV, similar to that of hydrogenated amorphous Si.\textsuperscript{17} But since our analysis assumes a constant $D_H$, we are reluctant to apply it to an experiment where $D_H$ is likely to depend on strongly on time.

In conclusion, we have developed a model for the limiting thickness seen during a low-temperature epitaxial Si growth. This model is based on the observation that hydrogen incorporation in a growing film limits $h_{\text{epi}}$. The key temperature-dependent process determining $h_{\text{epi}}$ arises from hydrogen diffusion in the growing layer. Equation (2) is the quantitative expression for our model; and nearly all the available limiting thickness data fit well. Even though we have studied Si as a model epitaxial growth system, our analysis is likely applicable to temperature-dependent limiting thickness data for other low-temperature epitaxial processes: for example, GaAs and Si/Ge heteroepitaxy.\textsuperscript{1}

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