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Group IV Semiconductor Growth

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Atomic layer epitaxy (ALE) is a method for epitaxial growth of semiconductor thin films that utilizes the adsorption kinetics of source gases for external control of the film growth process. [1] ALE takes advantage of the self-limiting nature of the chemisorption process for achieving layer-by-layer growth of semiconductors with uniform film thickness, ideally, 1 ML per each adsorption cycle. The 1 ML/cycle film growth is a uniquely distinguishing feature, that makes ALE highly attractive for preparation of ultrathin films of precisely controlled thickness. Other unique characteristics of ALE growth are that the spatial homogeneity of thin films, and the film thickness per cycle are insensitive to small variations in the external process parameters. The parameter space in which ALE is independent of external conditions is known as the ALE window. [2]

The existence of the ALE window in II-VI, and III-V compound semiconductor ALE is intuitive and fairly straightforward to realize in practice. [2,3] The polar nature of the chemical bonding between successive layers in these materials assures that each chemisorption cycle terminates after formation of a monolayer. Multilayer adsorption characterized by much weaker interactions is easily eliminated by elevating the substrate temperature above the range where physisorption occurs. A film of finite thickness is deposited by alternating exposure to the constituent source gases in a sequential fashion.

Because bonding in group IV materials is covalent (non-polar), group IV ALE cannot be realized simply based on the difference in the interaction strength between chemisorption and physisorption. Instead, an alternative strategy that is based on utilizing bonding with peripheral atoms of different electronegativity has been proposed. [4] For example, several processes using the H/Cl exchange reaction for realizing silicon ALE have been reported. [5] Silicon ALE by the H/Cl exchange reaction is perceived to occur between a saturated layer of either surface hydride, or surface chloride with the appropriate silicon source gas to release HCl and to deposit a silicon film. However, formation of an ALE window with either silicon hydride, or silicon chloride source gases is not well understood. [6] In this paper, the role of a fundamental kinetic parameter, the kinetic order of the elementary reaction steps, in formation of the ALE window in group IV semiconductors is explored by modeling the overall film growth reaction in terms of its elementary reaction steps. To facilitate meaningful comparison with experiments, the formation, and evolution of a hydridic layer, for which a wealth of data exist will be used as an example. [7] However, the conclusions that are reached have a general significance, and are applicable in other chemisorption systems.

The surface hydride coverage in epitaxial growth of silicon from silanes is the consequence of the dynamic equilibrium between silane chemisorption and molecular hydrogen desorption. However, instead of the absolute hydride coverage, the description of the thin film growth process is more meaningful in terms of the depletion and the regeneration of active film growth sites. [7,8] In group IV thin film growth, the dangling bonds represent the active sites. The depletion of the active surface sites is described by the following rate equation:

$$\frac{d\theta}{dt} = k_1(1 - \theta)^n - k_2\theta^m, \quad (1)$$

where θ is the fraction of depleted active sites, k_1 is the depletion rate constant, k_2 is the regeneration rate constant, and n , and m , are the reaction orders of the depletion, and the regeneration steps, respectively.

Hydrogen desorption from the Si(100) has received a great deal of attention in recent years because it was found to be first order, rather than second order as expected for recombinative desorption. [9] Additionally, first order molecular hydrogen desorption was found following chemisorption of disilane on the Si(100) surface. [7] According to experimental data, first order behavior of hydrogen desorption from the Si(100) surface is quite general and is independent of whether the hydride coverage is produced by atomic hydrogen adsorption, or by chemisorption of silanes. [10] Similarly, first order hydrogen desorption was found from the Ge(100) surface following chemisorption of digermane. [11] Therefore, governed by the experimental data, the solution to the above rate equation will only be sought for a first order ($m = 1$) regeneration step.

In contrast with molecular hydrogen desorption, a consensus has not been reached on the reaction order of the chemisorption step. The results of mechanistic studies of fragments produced by annealing of adsorption layers of silanes formed below room temperature, suggest that the elementary reaction step of source gas chemisorption is second order. [12] On the other hand, the reaction order in kinetic studies of thin film growth processes was found to be first order. [7] Since the reaction order of the chemisorption step is not clearly established by experiment, both first ($n = 1$), and second ($n = 2$) order depletion of active sites need to be considered in modeling of the film growth process.

The solutions to the rate equation describe the time dependence of the active site coverage. The solution for $n = m = 1$ is given by:

$$\theta(t) = \theta_0 \exp[-(k_1 + k_2)t] + \frac{k_1}{(k_1 + k_2)} \{1 - \exp[-(k_1 + k_2)t]\}. \quad (2)$$

where θ_0 is the fraction of the depleted active sites at $t = 0$. For $n = 2$ and $m = 1$ the solution is given by:

$$\theta(t) = \frac{1}{2k_1} \left[2k_1 + k_2 + r \left(\frac{1 + C \exp(rt)}{1 - C \exp(rt)} \right) \right], \quad (3)$$

where $r = \sqrt{k_2^2 + 4k_1k_2}$, and $C = (2k_1\theta_0 - 2k_1 - k_2 - r)/(2k_1\theta_0 - 2k_1 - k_2 + r)$. In terms of the absolute hydrogen coverage, the above solutions represent pure monohydride coverage.

Since the thin film growth rate is directly proportional to the rate of the active site depletion, the total film thickness $\mathcal{T}$ at time t is obtained by integrating the active site depletion rate from Eq. (1) between 0 and t .

$$\mathcal{T}(\text{ML}) = \int_0^t k_1(1 - \theta(t))^n dt. \quad (4)$$

The integral in Eq. (4) for $n = 1$ is given by:

$$\mathcal{T}(\text{ML}) = -\frac{k_1(\theta_0(k_1 + k_2) - k_1)}{(k_1 + k_2)^2} + \frac{k_1k_2}{(k_1 + k_2)}t + \frac{k_1(\theta_0(k_1 + k_2) - k_1)}{(k_1 + k_2)^2} \exp[-(k_1 + k_2)t]. \quad (5)$$

and for $n = 2$ the integral is given by:

$$\mathcal{T}(\text{ML}) = \frac{1}{4k_1} \left[k_2^2 + 2k_2r \left(\frac{1 + C \exp(rt)}{1 - C \exp(rt)} \right) + r^2 \left(\frac{1 + C \exp(rt)}{1 - C \exp(rt)} \right)^2 \right] t. \quad (6)$$

Assuming that one original active site is regenerated per each atom that is incorporated into the film. Eq. (5) and Eq. (6) describe the evolution of film thickness for first, and second order depletion of active sites, respectively.

The significance of Eq. (5) and Eq. (6) is that these equations identify time as an important variable in the ALE of group IV semiconductors. The time-dependence in group IV semiconductor growth comes from the fact that the active sites regenerated by desorption of molecular hydrogen are immediately depleted by chemisorption of new source gas molecules, resulting in continuous film growth. However, the first term in Eq. (5) is independent of time, and suggests that a self-limiting mechanism could be achieved if the contributions from the time-dependent terms are made negligible. Assuming that $\theta_0 = 0$, Eq. (5) shows that ideal ALE, i.e. 1 ML/cycle growth requires that $k_1 \gg k_2$,

$$\mathcal{T}(\text{ML}) = 1 + k_2t - \exp(-k_1t). \quad (7)$$

The exponential term in the above equation is associated with reaching steady-state, and the k_2t term describes continuous film growth, characteristic of gas source MBE. Eq. (5) and Eq. (7) illustrate that thin film growth from a first order depletion step occurs by two kinetically different stages. The initial stage corresponding to growth of the first monolayer can be thought to occur in a discrete fashion. After the first monolayer is grown, the rest of the film grows continuously. Consequently, a strategy for achieving ALE requires separation of the two film growth stages, and assuring that upon completion of the first monolayer, continuous film growth is cut off as quickly as possible. The parameter space for achieving ALE type behavior

is illustrated by the three-dimensional plot in Fig. 1. The ALE window corresponds to the plateau region in which monolayer-thick adsorption layer formation is maintained.

In comparison, the expression for film growth from a second order chemisorption step given by Eq. (6), contains only time-dependent terms. The time-dependence implies continuous film growth, and more importantly, indicates that no self-limiting mechanism can be generated based on the kinetic parameters considered by the model. Thus, if depletion of the active sites occurs by a second order process, ALE cannot be realized because no mechanism for turning off continuous film growth exists. A three-dimensional plot of the film thickness given by Eq. (6) is shown in Fig. 2. The film thickness shows a linear dependence on the growth parameters, except in the very early stages of growth where a transient peak is predicted. The transient peak scales with the fraction of initially covered active sites (θ_0). The transient peak has a maximum height for ($\theta_0 = 0$) and disappears for ($\theta_0 = 1$). Therefore, second order depletion of active sites could be confirmed by observation of the transient film growth peak.

FIG.1. Three-dimensional plot of the film thickness for $n = m = 1$ and a fixed $k_1 = 100s^{-1}$. The plateau in the 1 ML region represents the ALE window.

FIG.2. Three-dimensional plot of the film thickness for $n = 2$, $m = 1$ and $k_1 = 100s^{-1}$. Note the transient peak at 0.2 ML, and the absence of self-limiting behavior.

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