Origin of Pseudo Second Order Reaction in a-Si:H Growth

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It is generally accepted that a pair of SiH₃ radicals are responsible for the film growth reactions of hydrogenated amorphous silicon, namely a first SiH₃ radical to pick up surface-terminating H leaving active site on the growing surface, and a second SiH₃ to stick there. Since the first reaction step is rate determining, the film growth rate is proportional (1st order) to the SiH₃ density. However, in some cases, 2nd order dependence on SiH₃ density is reported, especially when the film growth rate (and thus the SiH₃ density) is quite low. This funny behavior contradicts the general concept that a higher order reaction will take place when the number density of the concerning species is high. In this report, a detailed analysis of these growth reactions based on the method of steady state is given to reveal that the origin of such a pseudo 2nd order dependence is clearly explained by introducing the reverse reaction to the first step that determines the growth rate. In addition, discussion is presented to show that such a reverse reaction is plausible. [DOI: 10.1380/ejssnt.2017.93]

Keywords: Growth; Surface Chemical Reaction; Amorphous Thin Films; SiH₃; 2nd Order Reaction; Method of Steady State

I. INTRODUCTION

Evidenced by the direct detection of SiH₃ number density and its linear relationship to the film growth rate [1], it is generally accepted that SiH₃ radical is the dominant growth precursor in the PECVD (plasma enhanced chemical vapor deposition) grown a-Si:H (hydrogenated amorphous silicon) films with SiH₃ source gas. The film growing surface reactions by SiH₃ radicals are explained by the following sequence: a first SiH₃ to pick up the surface terminating hydrogen leaving active site (dangling bond) at growing surface, and a second SiH₃ to stick there [2]. Since two radicals are taking part in this sequence, a 2nd order reaction feature might be expected instead of 1st order on this growth precursor density, as mentioned in Ref. [2]. However, as presented in the following section, the film growth rate dependence on this radical density should be 1st order according to a detailed reaction analysis based on the method of steady state. In addition, the 2nd order dependence reported in Ref. [2] has appeared only in the lower density side of this growth precursor. This behavior clearly contradicts the general concept that a higher order reaction should appear when the number density of the particle that concerns (SiH₃ radicals, here in this case) is high. In order to identify the origin of this funny behavior, the surface reaction scheme is examined to show that this reported 2nd order behavior is reasonably explained by introducing the reverse reaction that annihilates the surface dangling bonds.

II. REACTION MODELS

At first, the above-mentioned growth reaction sequence is described as following:

\[
\begin{align*}
\text{SiH}_3 + \text{H-Surf} & \xrightarrow{k_1} \text{SiH}_4 + \text{Surf} \\
\text{SiH}_3 + \text{Surf} & \xrightarrow{k_2} \text{H}_3\text{Si-Surf}
\end{align*}
\]

[I]

Here, SiH₃ represents the SiH₃ radical. H-Surf, Surf and H₃Si-Surf represent the surface site of hydrogen terminated, bare (dangling bond) and radical-stuck, respectively, while k₁ and k₂ are the reaction rate constant for each reaction step. By applying the method of steady state, namely assuming the density of intermediate species (Surf) to be constant (zero setting to its time derivative), the rate equation of entire sequence is expressed in the following:

\[
\frac{d}{dt} \left[ \text{Surf} \right] = k_1 \left[ \text{SiH}_3 \right] \left[ \text{H-Surf} \right] - k_2 \left[ \text{SiH}_3 \right] \left[ \text{Surf} \right] = 0
\]

(1)

The square brackets denote the number density of each species. Since the growth rate RG is proportional to the radical sticking rate, using equation (1), RG can be simply written as follows:

\[
R_G \propto \frac{d}{dt} \left[ \text{H}_3\text{Si-Surf} \right] = k_2 \left[ \text{SiH}_3 \right] \left[ \text{Surf} \right]
\]

(2)

The almost fully hydrogen-terminated nature of a-Si:H growing surface is reported [3–10], so [H-Surf] can be assumed to be constant. As a result, it is concluded that the growth rate must show 1st order dependence on the SiH₃ density, as mentioned earlier. This alternatively means that step [I] is the rate determining process. This seems quite natural since step [I] is Si-H bond transfer from surface to gas phase molecule and thus the energy gain is not so large, while step [II], simply forming a Si-Si bond, is energetically quite favored and thus expected to proceed more quickly.

Then, the next step to investigate is to identify the origin of this 2nd order behavior reported in Ref. [2], which appears in quite slow growth rate of below 0.05 Å/s. Since this behavior is observed as the sub-linear decrease of the RG with lowering the SiH₃ radical density, it seems that some kind of reaction is disturbing the growth. As described above, since the rate determining reaction is the first step [I], one may assume that once-formed surface active site (Surf) would be annihilated by some reasons. To include such assumption, it is useful to introduce the reverse reaction to reaction step [I] with reverse rate constant of kᵣ, resulting the modification of the step [I] into
following:

\[ \text{SiH}_3 + \text{H-Surf} \xrightarrow{k_1/k_r} \text{SiH}_4 + \text{Surf} \quad \text{[III]} \]

Then, Eq. (1) should be revised as well:

\[
\frac{d}{dt} \left[ \text{Surf} \right] = k_1 [\text{SiH}_3][\text{H-Surf}] - k_r \left[ \text{SiH}_4 \right][\text{Surf}] - k_2 [\text{SiH}_3][\text{Surf}] = 0 \quad (3)
\]

From this Eq. (3), \([\text{Surf}]\) is explicitly obtained:

\[
[\text{Surf}] = \frac{k_1 [\text{H-Surf}][\text{SiH}_3]}{k_r[\text{SiH}_4] + k_2 [\text{SiH}_3]} \quad (4)
\]

Using this Eq. (4), the equation for growth rate \(R_C\) can be expressed in a little bit complicated way as follows:

\[
R_C \propto \frac{d}{dt} [\text{H}_3\text{Si-Surf}] = k_2 [\text{SiH}_3][\text{Surf}]
\]

\[
= \frac{k_1 k_2 [\text{H-Surf}]^2 [\text{SiH}_3]}{k_r[\text{SiH}_4] + k_2 [\text{SiH}_3]}
\]

\[
= \begin{cases} 
  k_1 [\text{H-Surf}][\text{SiH}_3] & \text{1st order} \\
  k_1 k_2 [\text{H-Surf}]^2 / k_r \text{[SiH}_4] & \text{2nd order}
\end{cases} \quad (5)
\]

The situation of \(R_C\) can be categorized into two cases depending on the density of \(\text{SiH}_3\), as shown above. The 1st order dependence is obtained in the case of higher \(\text{SiH}_3\) density, as is the previous derivation without considering the reverse reaction. Meanwhile, when the \(\text{SiH}_3\) density is quite low, 2nd order dependence will appear with the reverse reaction assumed. So it is concluded that the reported 2nd order behavior can be explained by this way of introducing the reverse reaction to the first step.

### III. DISCUSSION

It should be discussed that such a kind of reverse reaction is really taking place. It is already known that at a bare (unterminated) Si surface under high temperature, \(\text{SiH}_4\) will decompose and leave surface-terminating hydrogen atoms, along with Si-containing species on the surface as well. With that occasion, Si growth would take place, resulting an increase of growth rate, which will contradict the discussing situation of lower \(R_C\).

According to the report by Gates and coworkers (Fig. 9 in Ref. [11]), the Si-H bonding energy of surface-terminating \(\text{H}\) is 83 kcal/mol, and is smaller than that in \(\text{SiH}_4\) of 90 kcal/mol. This means the reverse reaction of [III] is energetically disfavored, although the energy difference is only 7 kcal/mol.

We have an experimental observation that may suggest an occurrence of surface annihilation similar to the reverse reaction of [III]. As shown in Fig. 1, in-situ IR monitoring of surface \(\text{H}\) [3–10] on PECVD-grown a-Si:H films at 430°C revealed that, under vacuum of \(2 \times 10^{-8}\) Torr, the surface \(\text{H}\) gradually disappears with time, while under \(\text{SiH}_4\) ambient of 20 mTorr, it stays almost unchanged.

This means that at this temperature, surface \(\text{H}\) will thermally desorbs gradually, leaving dangling bonds at surface. This also suggests that under \(\text{SiH}_4\) ambient, they can be cured by the \(\text{H}\) transfer from \(\text{SiH}_4\). It should be noted that there is almost no film growth judging from the flat baseline of these spectra (otherwise the baseline begins to incline as a part of interference fringes, as seen in Fig. 4 in Ref. [4]).

However, the situation of thermally-induced surface hydrogen desorption shown in Fig. 1 is somewhat different from the above formulation of \(\text{SiH}_3\)-induced. It is generally accepted that thermal desorption of hydrogen will occur in molecular form [12], leaving two dangling bonds at surface. (They seem to form some kind of weak bonding so that the hydrogen desorption is energetically favored.) Such a situation is good for \(\text{SiH}_4\) molecule to stick on surface in a dissociative manner (most likely into \(\text{H}\) and \(\text{SiH}_3\) [13, 14]), since two active sites of very close to each other are available at surface. When it comes to the situation of \(\text{SiH}_3\)-induced, only a single active site alone will be produced by the first reaction step. This situation seems not good for \(\text{SiH}_4\) molecule to react with such an isolated active site alone, without a cooperation of a secondary active site or a radical point. The only possibility for such a second point candidate is \(\text{SiH}_3\) radical that comes on to the surface similar to the case of the reaction step [II]. All these considerations lead us to assume the overall...
annihilation reaction (with no film growth) as following:

\[ \cdot \text{Surf} + \text{SiH}_4 + \cdot \text{SiH}_3 \rightarrow \text{H-Surf} + \text{Si}_2\text{H}_6 \quad \text{[IV]} \]

This reaction scheme has two advantageous features, when it is compared to simply assuming the reverse reaction of [III]. First, this scheme is energetically favored since it includes the Si-Si bond formation that has far larger energy gain (74 kcal/mol [11]) compared to the energy loss in the H transfer from SiH\textsubscript{4} to \cdot\text{Surf}. Second, it ends up in the stable species formation and thus no need to assume any further reactions (including the reverse reaction of [IV] itself). Although its details are still open question, this overall reaction scheme [IV] should be the most possible candidate to cause the pseudo 2nd order behavior in a-Si:H film growth.

It would be worth to comment on the similar quasi 2nd order growth feature reported for PECVD-grown a-Ge:H (hydrogenated amorphous germanium) from GeH\textsubscript{4} [15], where explanation similar to Ref. [2] is given (but the growth precursor is GeH\textsubscript{3} instead of SiH\textsubscript{3}). In that case, however, 2nd order dependence is appeared not only at the lower side but in entire region of growth rate investigated. This can be easily explained by the similar way of introducing the reverse reaction into the first step as well, with a consideration that the Ge-H bonding is much weaker than Si-H and thus easier to transfer H from GeH\textsubscript{4} to surface dangling bond.

Finally, it should be noted that, although a minor correction to introduce the reverse reaction into step [I] is necessary (only at a very low growth rate), the reaction set of steps [I] and [II] is quite good to explain the established linear relationship between the growth rate and SiH\textsubscript{3} density in a-Si:H film growth.

### IV. CONCLUSIONS

By introducing the reverse reaction into the first step of film growing reactions, the pseudo 2nd order feature is clearly explained. Discussion is presented to show that such a reverse (annihilation) reaction of transferring H from gas phase SiH\textsubscript{4} to surface dangling bond that is created by SiH\textsubscript{3} is plausible.

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