

Comment on “Analysis of hydroxyl group controlled atomic layer deposition of hafnium oxide from hafnium tetrachloride and water” [J. Appl. Phys.95, 4777 (2004)]

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Comment on “Analysis of hydroxyl group controlled atomic layer deposition of hafnium oxide from hafnium tetrachloride and water” [J. Appl. Phys. 95, 4777 (2004)]

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In this comment we address issues raised by Puurunen in a paper comparing our model of atomic layer deposition (ALD) growth to Puurunen's. The main conclusion is that our models are fundamentally different. In our model, we employ two differential equations, describing the deposition of HfO_2 per cycle, and the creation rate of new OH groups per cycle. These two equations enable us to explain all observed ALD growth behaviors related to the concentration of OH nucleation sites. Puurunen's model is essentially geometry based, and takes into account the concentration of nucleation sites, but contains no equation analogous to our second differential equation describing the evolution of OH groups from cycle to cycle. We then go on to address several specific points that Puurunen raised. © 2005 American Institute of Physics.

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After reviewing our model of atomic layer deposition (ALD) growth¹ and comparing it to her own,^{2,3} Puurunen concludes⁴ that some aspects of our model are both physically and mathematically inconsistent. We are gratified that our model had a thought provoking effect, but we believe the review⁴ to be based on a misreading of our model.

Puurunen's model and ours differ in a fundamental way. In our model,¹ we employ two differential equations: the first describes the deposition of HfO_2 per cycle, and the second the creation rate of new OH groups (nucleation sites) per cycle. We can thus arrive at exact (numerical) or asymptotic (analytical) solutions that can explain all of the relevant experimental data.⁵ Puurunen's model,^{2,3} on the other hand, contains no equation describing the evolution of OH groups from cycle to cycle. Whereas, for example, the observed parabolic growth behavior of HfO_2 on H-terminated $\text{Si}^{1,4,5}$ (very few OH groups to begin with) is correctly predicted by our model, the Puurunen model can only explain the observed parabolic behavior if a parabolic dependence of nucleation sites is assumed to begin with.² We need make no such assumption.

In essence, both the Puurunen model^{2,3} and the earlier model of Ylilammi⁶ (which is cited in the review⁴), are geometry-based models that take into account the concentration of absorption (nucleation) sites. Neither model predicts or attempts to treat the evolution of these sites as growth proceeds. Puurunen⁴ goes to great lengths to demonstrate that her model is equivalent to ours¹ (see, for example, Sec. III A).⁴ However, it is only shown that the Puurunen model will arrive at the same first differential equation as ours;

neither the Puurunen model, nor any other, has anything equivalent to our second differential equation describing OH group evolution.

Now we address the most important of the issues raised by Puurunen. (The section numbers refer to her paper⁴.)

- (1) *Comment*: “Because of the many parameters, there is freedom in modeling the OH surface concentration” (Sec. III B 2).

Response. We assume that Puurunen is implying that due to the large number of parameters in our model, we could fit any curve with such parametrization, and therefore our model is not predictive. We disagree. There are four physically meaningful parameters in our model: maximum number of OH sites, N_0 ; OH site-generation efficiency per cycle, k_2 ; steric hindrance factor, K_{cov} ; and branching efficiency per cycle, α_{cov} . Among them, N_0 is fixed by HfO_2 film density and cannot be adjusted, and the other three parameters have restricted ranges: $k_2 < 1$, $1/7 < K_{\text{cov}} < 1$, and $1 < \alpha_{\text{cov}} < 3$. Further, both K_{cov} and α_{cov} are continuous functions of the number of ALD cycles, C . Given these restrictions, we claim that one has very little freedom to fit data sets that contain, for example, 12 data points (see Fig. 9 of Ref. 1). The ability of the same set of parameters to predict other curves (Fig. 9 of Ref. 1) would indicate that the parameters are physically meaningful and predictive.

- (2) *Comment*: “...and assuming an analogy between t and C seems scientifically not well founded...” (Ref. 53 of Puurunen paper⁴).

Response. Let us explain: discrete systems are described by difference equations and continuous systems are described by differential equations. However, for large val-

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ues of the discrete variable (e.g., cycles > 10) it is mathematically convenient to convert the difference equation into a differential equation, solve the system using techniques borrowed from the field of continuous functions, and then evaluate the resulting function at discrete values ($C=1, 2, 3, \dots$, but not $C=1.5$, for example). This amounts to no more than a simple mathematical mapping to solve a problem, and one should not be confused into searching for any deeper physical analogy between time (t) and cycle number (C).

- (3) *Comment*: “Recently, ‘substrate-inhibited’ ALD growth has been observed.... The growth curve is then strongly nonlinear and the growth per cycle is not constant, suggesting complex interaction between the substrate and the reactants used in ALD growth” (Sec. I).

Response. One of the outcomes of our model is that using relatively simple assumptions, all features (except in the first one or two cycles of growth, where some of our assumptions break down) of the data⁵ can be explained, and physically meaningful growth parameters may be extracted. Detailed knowledge of the complexities of the surface chemistry is not necessary for the construction of our model. The atomic level chemistry of interaction between OH groups and HfCl_4 molecules may indeed be complex, but the macroscopic growth behavior that ensues is not; in fact, as we show, it is quite predictable. We do not concern ourselves with *a priori* knowledge of OH/ HfCl_4 reaction mechanisms; such information is derived experimentally, applying our data to our model, as exemplified by our interpretation of the observed steric hindrance factor of $\sim 1/7$.

- (4) *Comment*: “Fundamentally different equations are obtained for random deposition in ALD and in continuous deposition.... In the random deposition model, assuming the number of cycles to be a continuous instead of a discrete variable would cause considerable error. The error in model B (i.e., the Alam–Green model), caused by assuming a continuous number of ALD reaction cycles C remains to be analyzed” (Sec. IV C).

Response. Our paper developed a simple model that focused on cycle dependence of the growth process by integrating over its spatial dependence. Many areas of physics use such integral formulation [e.g., charge control theory for metal-oxide-semiconductor field-effect transistor (MOSFET) devices, rather than solving the Boltzmann equation,⁷ or the mean-field or effective-media theory for approximating composite systems⁸]. As with any simplification, some details must be left out. The question is if such an approach is appropriate for the problem being studied. Our interest was to understand the integrated number of HfO_2 molecules deposited during ALD growth. Therefore we believe that when averaged over a few cycles, our model provides meaningful predictions with small errors. Future work will quantify the errors.

- (5) *Comment*: “...because the numerical solution has been derived with assumption $\alpha_{\text{cov}}=1$ which is not valid for the HfO_2 process” (Sec. III B 2).

Response. $\alpha_{\text{cov}}=1$ must be interpreted in an average

manner, as we clearly stated in our paper. From our definition of α_{cov} one can see that it is a measure of how many OH sites are created from one cycle to another. In the very earliest stages of growth, α_{cov} cannot be exactly equal to 1, but it reaches the value of 1 within the first few cycles (because of islanding effect) and continues to be close to 1 (when averaged over a few cycles) throughout the simulation.

- (6) *Comment*: “Clearly, the OH surface concentrations assumed by model B (i.e., the Alam–Green model) are systematically higher than the real values” (Sec. III B 2).

Response. While Puurunen goes to great lengths on this point, we feel that it completely ignores one of the messages of our model. Since it is the amount of HfO_2 , and not OH sites, that is the goal of our calculation, the question of how many OH sites are present is only part of the issue. Our model clearly points out that in the presence of large numbers of OH sites ($N_{\text{OH}} \geq 1/7 N_0$), growth is controlled by steric hindrance of the incoming HfCl_4 molecules, and any concentration of OH sites greater than $(1/7)N_0$ will not be utilized in any event. Since the OH site concentrations shown in her table are all approximately greater than $(1/7)N_0$, knowledge of the exact OH concentration, if it is high, is not critical to the correct prediction of linear growth behavior. Our calculation of N_{OH} for the parabolic stage of growth, when N_{OH} can be zero or very small initially, is correct and accurately describes the data.^{1,5}

- (7) *Comment*: “No physical significance has been assigned to this specific form of K_{cov} ” (Sec. III B 2).

Response. We used one of many possible parametrizations of K_{cov} that is consistent with the physical restrictions on that function, i.e., that the value of K_{cov} must remain between 1 and $1/7$, and the transition between these upper and lower limits must be continuous. Moreover, K_{cov} must be approximately equal to 1 until at least $1/7$ of the surface is covered by random sites and K_{cov} must approach $1/7$ when more than $6/7$ of the sites are covered. Apart from these physical requirements and the simplicity of the function chosen, we believe that further justification of the actual form of K_{cov} can only come from more detailed Monte Carlo simulation and space-resolved experimental studies.

- (8) *Comment*: “According to model B (i.e., the Alam–Green model), in contrast, the OH surface concentration does not go through a maximum, but the maximum in growth per cycle is caused by a sudden decrease in the fraction K_{cov} of OH groups reacted” (Sec. IV A).

Response. The decrease in the fraction of K_{cov} is physically motivated and it reflects the fact that as the number of OH sites grows, a large molecule can shadow many reaction sites. As a result, the reactivity per cycle will be reduced from the maximum as the ALD film begins to coalesce.

- (9) *Comment*: “...has a reported packing density of $1/9$ (Ref. 35) or $1/8$ (Ref. 22) Why two different p values have been obtained by applying the same model is not clear” (Sec. II A).

Response. We have gone over Ylilammi’s calculation⁶ of

the packing factor for HfCl_4 many times, but we do not fully understand the reason for the difference between our two values, as we point out in our paper.¹ In any case, the difference is inconsequential to our model.

¹M. A. Alam and M. L. Green, J. Appl. Phys. **94**, 3403 (2003).

²R. L. Puurunen, Chem. Vap. Deposition **9**, 249 (2003).

³R. L. Puurunen, Chem. Vap. Deposition **9**, 327 (2003).

⁴R. L. Puurunen, J. Appl. Phys. **95**, 4777 (2004).

⁵M. L. Green *et al.*, J. Appl. Phys. **92**, 7168 (2002).

⁶M. Ylilammi, Thin Solid Films **279**, 124 (1996).

⁷R. Pierret, *Semiconductor Device Fundamentals* (Addison-Wesley, Reading, MA, 1996).

⁸R. Zallen, *Physics of Amorphous Solids* (Wiley, New York, 1983).