ALD HfO_2 Gate Dielectric: Growth Behavior and Scaling Limits

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The international roadmap calls for gate dielectrics with EOT < 1.0 nm at about 2007. Therefore, it seems appropriate to understand how far one of the most promising high-κ candidate materials, HfO_2, can be scaled. To achieve minimum EOT, it is also important to understand the growth behavior of HfO_2.

We have developed an extensive body of nucleation and growth data for HfO_2 that reproducibly exhibits either linear or exponential–linear kinetics, depending upon the underlayer (or lack thereof) onto which the film is deposited. We are able to describe the growth behavior with a novel mathematical model. Further, we studied the capacitor characteristics of many samples grown on various substrates. In the capacitor study, the major parameters studied were type of underlayer (RTO, RTON, ChemOx), HfO_2 layer thickness (3 – 6 nm) and post-deposition anneal (PDA) (temperature, 600 – 1000°C; time, spike anneal – 600 seconds; and ambient, N_2, O_2 or NO). Chemical oxide underlayers were favored in this study, as they gave rise to the smoothest and most two-dimensional films; therefore, continuous films could be achieved at the thinnest possible physical thickness.

Regardless of the PDA ambient, we find that high temperature anneals are required to lower ΔV_{fb}. Further, some interfacial regrowth is required to achieve low ΔV_{fb}. Fig. 1 shows EOT as a function of the extent of regrowth during PDA. It can be seen that for 3 nm HfO_2, about the thinnest practical film, even if PDA occurred with zero regrowth, the minimum achievable EOT would be 1.23 nm. Therefore, to achieve subnanometer gates, the underlayer should be eliminated entirely (unless a higher dielectric constant material than HfO_2 is introduced). However, growth on H-terminated Si(100) is three dimensional and rough. Chemical functionalization of this surface is required, which must result in as high-quality a film as can be produced on a chemical oxide underlayer.

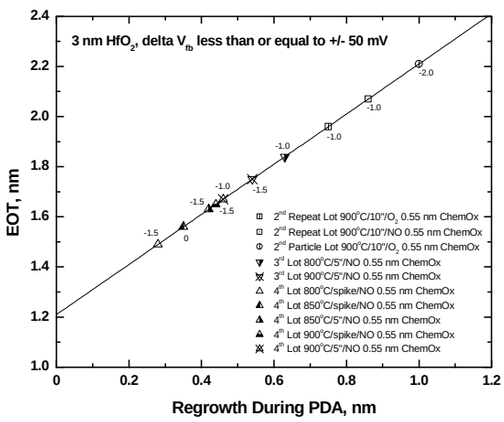

Figure 1. EOT as a function of the extent of regrowth during PDA, for 3 nm HfO_2 films.

Atomic layer deposition (ALD) is a leading candidate for the deposition of such films. Our phenomenological mathematical model fits the growth data very well. We know of no other such model for ALD growth in the literature.

Our model assumes that either Si-OH or Hf-OH groups are the nuclei for ALD growth. The model is based on classical chemical kinetic theory, from which one can derive and solve two differential equations. One describes the deposition rate of HfO_2, including the effects of steric hindrance; the second describes the creation and interaction of new Si-OH or Hf-OH sites that result from the HfO_2 deposition, as the film grows.

The assumption that there are ample OH sites for the case of the chemical oxide, applied to the solution of the differential equation for HfO_2 growth, leads to the prediction of linear growth behavior, as is experimentally observed, Fig. 1. The slope in Fig. 1 indicates that 1/7 of a monolayer of HfO_2 is deposited per cycle. A 1/9 steric hindrance factor can be theoretically calculated to result from a tetrahedral $HfCl_4$ molecule attaching itself by one of its four apices to a surface OH group. Attachment to two OH groups via the edge of the tetrahedron would result in a 1/3 steric hindrance factor. A combination of both attachments could explain the experimentally determined 1/7 factor.

On the other hand, assuming there is a very small OH concentration on the H-terminated (HF-last) surface, and further assuming that initially there will be no steric hindrance due to the spacing of the Hf-OH groups that eventually nucleate, one can explain the experimentally observed growth kinetics by an exponential-linear fit. Both growth behaviors are shown with their fits, according to our model, in Fig. 2.

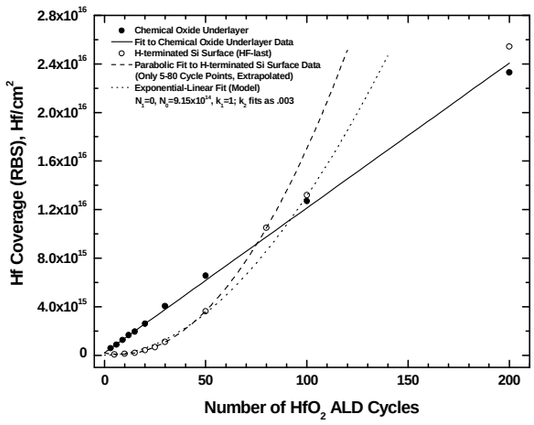

Figure 2. Growth data and model fits for linear (chemical oxide) and exponential-linear (H-terminated Si) growth modes.