

Modeling CVD effects in Atomic Layer Deposition on the Feature Scale

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Abstract

Simulation of atomic layer deposition requires the coupling of complex surface chemistry to ballistic transport in geometrical structures. The calculation furthermore has to be transient with chemical process models which have transients on different time scales. The paper shows a solution of this problem with a Monte Carlo based model implemented in the general purpose feature scale simulator TOPSI 3D. The chosen example is HfO_2 deposition with $\text{HfCl}_4 / \text{H}_2\text{O}$ in a trench which may show a nonconformal film profile.

1 CVD Effects in Atomic Layer Deposition

Conformal deposition into high aspect ratio structures is an important technological achievement enabled by atomic layer deposition (ALD). For example the suitability of ALD Al_2O_3 as node dielectric for trench capacitors with excellent conformality and thermal stability was demonstrated [1]. For HfO_2 ALD, however, CVD effects have been reported [2,3] which may lead to nonconformal deposition in trenches and nonuniformity over the wafer. In this paper we present a feature scale model which is able to explore a sophisticated, well calibrated chemistry model [4] on the feature scale and to identify the root cause for such effects.

2 Feature Scale Model

We have developed a 3D feature scale simulator capable of treating high aspect ratios as well as arbitrary particle transport and chemical kinetics models [5]. The level set front propagation module achieves high accuracy and efficiency by using a narrow band discretization and a fast marching algorithm. The local velocity is calculated on the extracted front segments from the particle fluxes and is extended to the level set grid nodes. The physical fluxes at the front are calculated using ballistic transport from user-defined particle sources. Thermally and kinetically activated surface reactions of arbitrary order are consistently calculated as a function of sampled flux and surface coverages.

A new algorithm developed for proper description of ALD processes allows the calculation of transient surface coverages with the ballistic Monte-Carlo based flux model. While in conventional film growth the time discretization is determined by the maximum speed, in ALD simulations it is controlled by the rate of change of the surface coverages. After temporal evolution of the chemistry over a time step, the

ballistic particle transport is repeated using the newly calculated surface reactivity. With this approach essentially arbitrary surface reaction mechanisms can be coupled to the particle transport. In a previous work, the propagation of the film front in a trench has been calculated with a reactive sticking coefficient chemistry model [6].

3 ALD Chemistry Model

In this paper we demonstrate the capability of the feature scale model to solve the coupled reaction-transport problem with a highly complex chemistry model in the geometry of an axisymmetric trench of aspect ratio 40. We choose the $\text{HfCl}_4 / \text{H}_2\text{O}$ ALD model developed in the HIKE project [4]. The kinetic mechanism proposed for the growth of HfO_2 was developed using *ab initio* calculation. Key elements in the model are the thermally activated processes forming hydroxylated, partially dehydroxylated, and entirely dehydroxylated surfaces. The activation energy of the recombination reaction of surface sites was matched to experimental data and was shown to be a function of the degree of surface dehydroxylation.

4 Film Conformity in the Feature

In the feature scale simulation of the process we have chosen $\text{HfCl}_4 / \text{purge} / \text{H}_2\text{O} / \text{purge}$ times of 1s / 1s / 1s / 1s respectively for each cycle with a HfCl_4 partial pressures of 1 mTorr and a H_2O partial pressure of 200 mTorr. We consider wafer temperatures of 300°C, 220°C and 180°C and 50°C. The cycle was repeated several times after initializing with 100% hydroxylation. The resulting film profiles are shown in Figure 1.

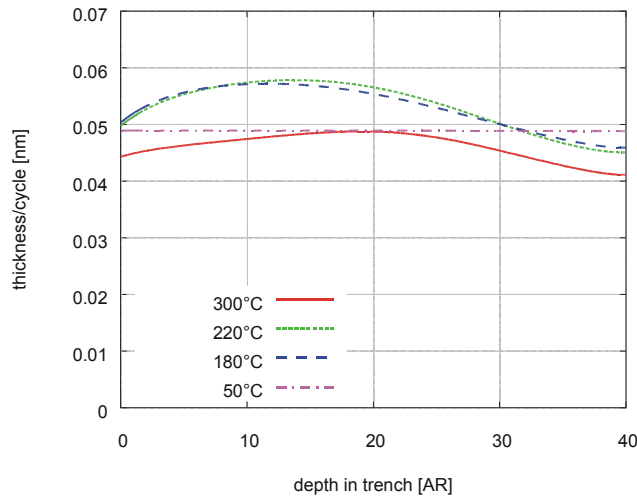


Figure 1: Deposition of HfO_2 into a trench of AR 40 with the $\text{HfCl}_4/\text{H}_2\text{O}$ model for an idealized ALD process and temperatures of 300°C, 220°C, 180°C and 50°C. Except at 50°C, the film is not conformal for the chosen process times.

Except for the lowest temperature the film thickness is not conform, although the precursor dose is saturating. The reason are temperature dependent transients in the surface reactions coupled to the transport in the feature. Figure 2 shows the mass increment in different positions inside the trench. In the HfCl_4 deposition step the mass coverage increases, in the H_2O deposition step the mass coverage decreases after oxygen incorporation and removal of the chlorine as HCl . The net mass gain is positive, decreases with temperature and matches the experimental growth rate. The delay time for the mass change increases with depth because the precursor is first consumed in the upper parts of the trench until the surface is saturated and diffuses to the lower parts.

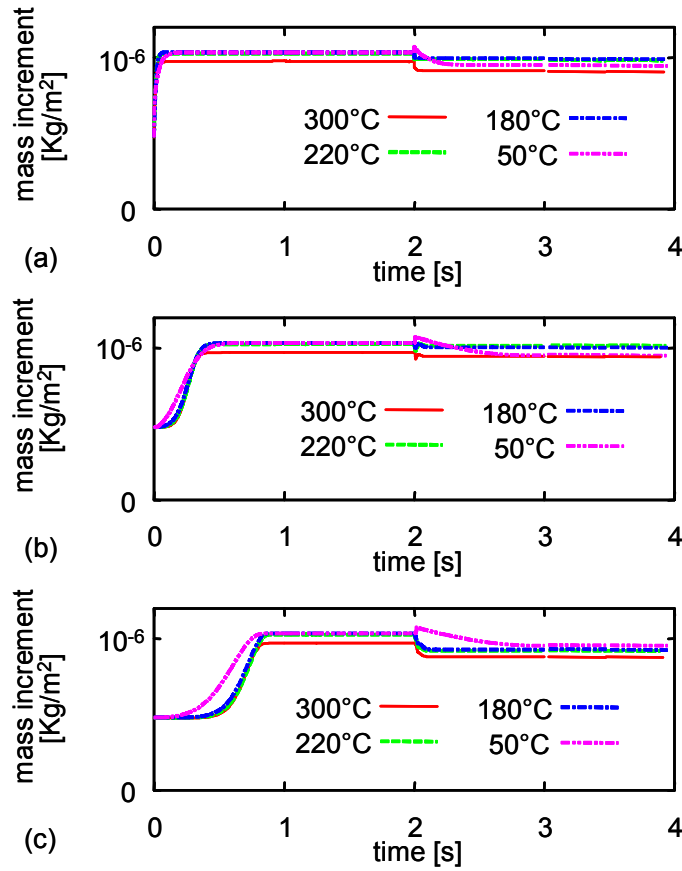


Figure 2: Mass increment of a surface element on the trench side wall in a position close to the trench top, in the middle of the trench and close to the bottom.

Not visible on the scale of Figure 2 is a further mass loss mechanism from surface dehydroxilation which has a small rate but persists on a long time scale. Hydroxyl groups recombine and desorb as H_2O with a coverage dependent rate [4]

$$\text{flux}(\text{H}_2\text{O}) = A \exp(-E([\text{OH}])/kT). \quad (1)$$

The water is subject to diffusive transport until it becomes readsorbed. The time scale of this effect can be made visible with a further simulation corresponding to an increased purge time experiment. The results in Figure 3 show that the hydroxyl group coverage and hence film thickness decreases significantly with excessive purge time, which corresponds to the experimental observation of T.Kawahara [3].

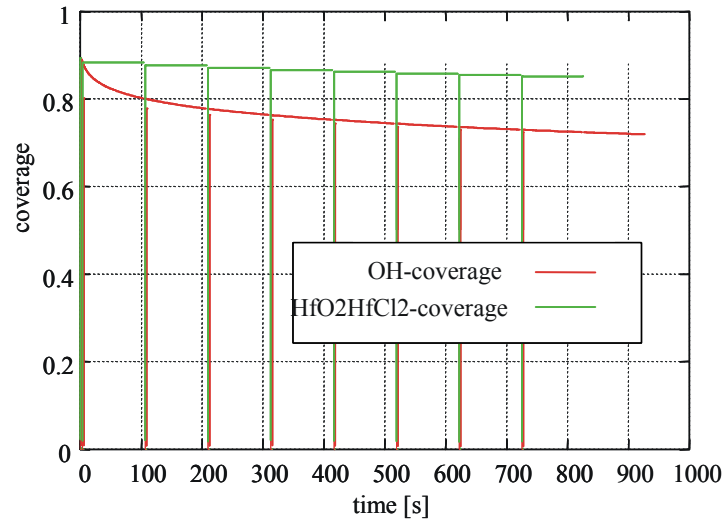


Figure 3: OH-coverage after three initial cycles of HfCl_4 /purge/ H_2O /purge of 1s/1s/1s/1s followed by 1s /1s/1s/100s cycles with the excessive H_2O purge. The overall coverage decreases from 90% to 70%. Also shown is $\text{HfO}_2\text{HfCl}_2$ surface coverage for 1s/100s/1s/1s cycles with excessive HfCl_4 purge. The desorption effects are here negligible. The results are compatible with the data in [3].

On the feature scale, the precursor adsorption, desorption, transport and readsorption finally lead to a nonconformal film to a degree which depends on the chosen process time and temperature. Neglected in this simulation are the transport effects on the reactor scale, which will lead to further effects on the film profile from water which leaves the trench and reenters again..

To conclude, we have developed a feature scale simulator which is able to solve the transient transport-reaction problem which is posed by ALD.

This work was partially funded by EU project HIKE under IST-2000-29295.

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