A model for Al_2O_3 ALD conformity and deposition rate from oxygen precursor reactivity

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Abstract

The atomic layer deposition of alumina using TMA (Trimethyl-aluminum) and O_3, O (atomic oxygen), or H_2O into high aspect ratio trenches is investigated. We determine the activation energy of the initial adsorption step by ab initio calculations and derive an effective sticking coefficient. We show that this quantity essentially determines the film conformity and deposition rate of self limiting ALD processes. Implementing this effective model into a custom feature scale simulator, coupled to a fluid dynamical reactor simulator, a consistent description of ALD on atomistic, feature, and reactor scale is obtained. With this multi scale approach it is possible for the first time to simulate film profile evolution during dielectric ALD into high aspect ratio trenches for future DRAM generations.

Introduction

Increasing aspect ratios in DRAM cells lead to aggressive requirements with respect to step coverage and film homogeneity of high-k dielectrics. Even for ALD it is not trivial to fulfil the above specifications. To support this task by simulation we introduce a novel ALD model for the wide range of available precursors, process conditions, and the large variety of tools. The overall goal is to identify the most important kinetic property and predict the desired film profile as well as the minimal process time, both of which are crucial criteria for future technology generations (1).

Ab initio calculation of ALD mechanism

The adsorption mechanism of ozone and O precursors on a methylated alumina surface is investigated by ab initio calculations. For these calculations we have used the B3LYP gradient corrected DFT functional, a numerical basis set, and full relaxation (2). The transition state is searched by a synchronous transit method. We have identified the mechanisms and calculated the activation energies to insert oxygen into the $OHAl(CH_3)_2$ cluster from O_3 and O precursor, as summarized in Eq. (1)/(2) and Fig. 1(a)/(b), respectively. Both result in a hydroxylated surface. For comparison also the H_2O and TMA adsorption steps as proposed in (3) are presented in Eqn. (3)/(4) and Fig. 1(c)/(d). The major results are the activation energies for the investigated precursors in Table I and the derived sticking coefficients s in the relevant temperature range. The general behaviour is as follows: O_3 has a significant barrier and therefore the smallest s with a strong temperature dependence. H_2O has an intermediate value of s with only moderate temperature dependence. O and TMA both have a sticking coefficient close to unity.

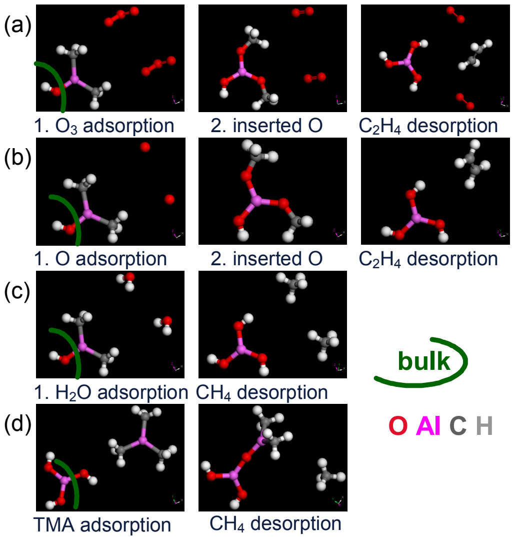

Figure 1: (a), (b) and (c) show the summarized O_3, O and H_2O adsorption on $OHAl(CH_3)_2$ with the corresponding by-products, respectively. (d) TMA adsorption on OH terminated surface.

Summary of mechanisms:
(1) $2O_3 + OAl(CH_3)_2(s) \rightarrow AlO(b) + 2OH(s) + C_2H_4 + 2O_2$
(2) $2O + OAl(CH_3)_2(s) \rightarrow AlO(b) + 2OH(s) + C_2H_4$
(3) $2H_2O + OAl(CH_3)_2(s) \rightarrow AlO(b) + 2OH(s) + 2CH_4$
(4) $TMA + OH(s) \rightarrow OAl(CH_3)_2(s) + CH_4$

The mechanisms 1, 3 and 4 are confirmed by mass spectroscopy measurements during the ALD cycles as shown in Figure 2(a)-(b).

TABLE I: energy gain and activation energies for oxygen insertion/adsorption for the precursors under investigation. The corresponding sticking coefficients are also given for the relevant temperature regime. For comparison, the values for TMA adsorption are also given.

precursor	ΔE(eV)	E_A(eV)	Sticking coefficient
O_3	-3.1	0.4	0.01-0.001
O	-6.5	-0.1	0.9-0.1
H_2O (2)	-1.5	0.1	0.1-0.01
TMA (2)	-1.7	-0.1	0.9-0.1

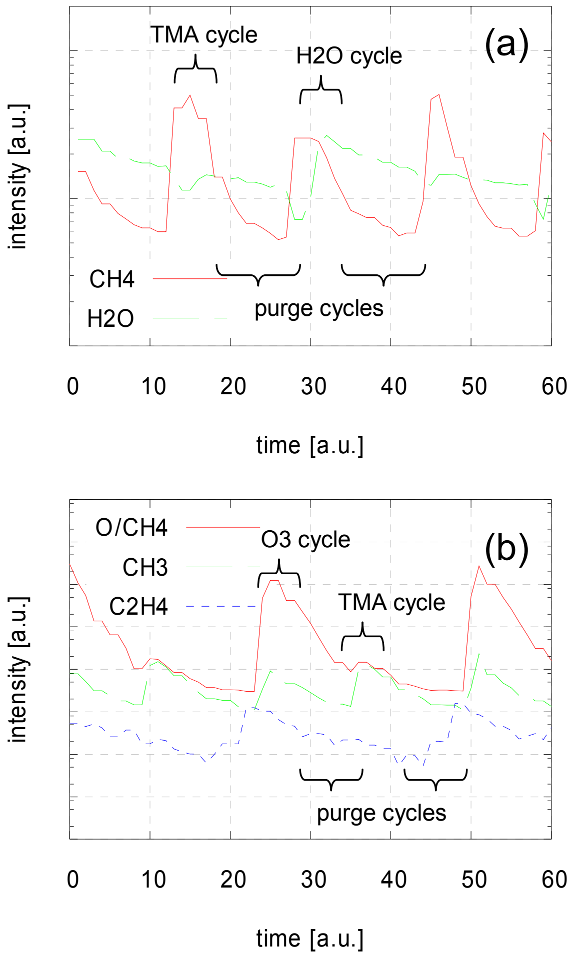

Figure 2: mass spectra for CH_4 and H_2O during TMA/H_2O (a) deposition. (b) Due to the mass overlap between O and CH_4, also CH_3 data are presented to indicate the cycle sequence for TMA/O_3 ALD. The data clearly demonstrates the C_2H_4 formation during the Ozone cycle. No significant C_2H_6 signal could be detected.

Feature scale model

We have developed a feature scale simulator capable of treating high aspect ratios as well as arbitrary particle transport and chemical kinetics models (4). 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 versus grid size, 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.

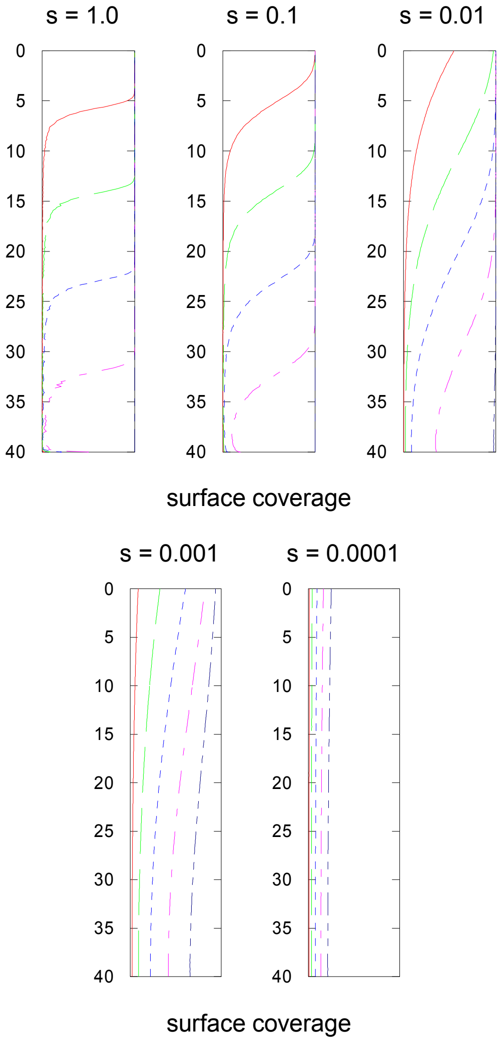

Figure 3: Profile evolution in a DT with an aspect ratio of 40 depending on effective sticking coefficient and pulse time. For small s and insufficient pulse times the film profile is similar to CVD film with < 100% step coverage.

We calculated the time dependence of the surface coverage in a trench for s=1, 0.1, 0.01, 10^{-3}, and 10^{-4} as shown in Fig. 3. The coverage directly corresponds to the film profile of the investigated precursor if the pulse time of the other precursor is large enough for complete saturation. The simulations show a film profile reaching a depth depending on pulse time and s and a front which becomes smoother with smaller s. For very small s ($<10^{-3}$) the film profile is similar to a CVD film with <100% step coverage.

To translate the coverage into a pulse time needed to cover the trench surface we have integrated the surface coverage (Fig. 4). For high sticking coefficients (0.1 - 1) the front position is equivalent to the saturated trench depth. The main observation is that for high sticking coefficients and large AR (> 20) the front movement is nearly independent on s. However for small sticking coefficients ($< 10^{-3}$) the surface saturation time scales with 1/s as expected.

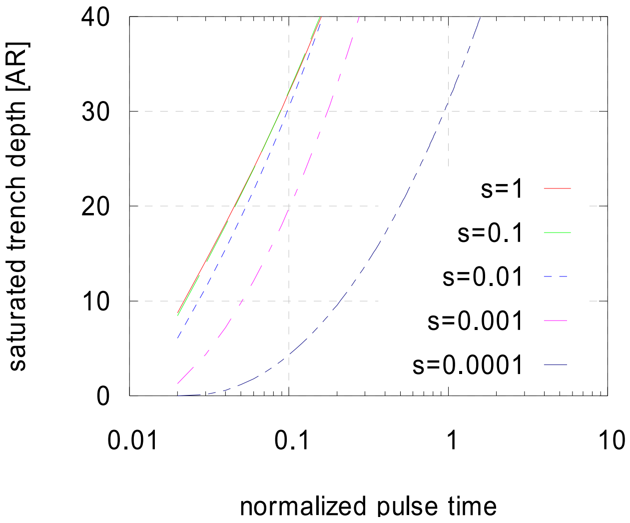

Figure 4: saturation depth in deep trench (measured in aspect ratio) as a function of pulse time and sticking coefficient for constant precursor flux.

Coupling to reactor model

The determination of the effective sticking coefficient of an ALD precursor from saturation vs. cycle time measurements is generally obscured by gas phase depletion in the reactor. Additionally the presence of deep trenches introduces a further time scale for transport, depending on aspect ratio and surface area. To resolve this difficulty we have coupled the feature scale simulator bi-directionally to a commercial fluid flow simulator (5) (see Fig. 5).

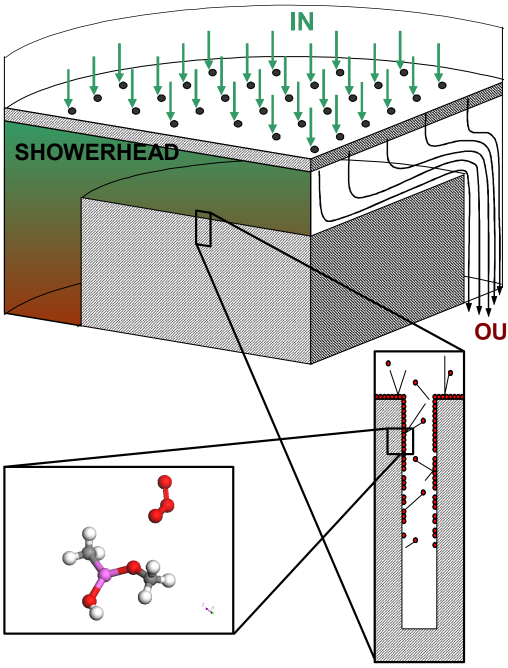

Figure 5: schematic sketch of the model hierarchy for deep trench ALD process simulations.

The substrate surface is divided into regions to monitor reactor scale concentration differences. Each region is represented in the feature scale simulation by a symmetry element – a single trench geometry - with appropriate multiplicity. In Fig. 6 a time snapshot after several milliseconds is presented for the TMA precursor evolution in a typical axisymmetric single wafer reactor. Fig. 7 shows the time evolution of the precursor concentration in the reactor at the (idealized) inlet, in the middle of the reactor, and at the trench opening of a product wafer for a precursor with s = 0.1. The depletion on reactor scale leads to a significant reduction of the precursor partial pressure at the trench opening. Consequently, the rate of planar surface coverage is not proportional to the sticking coefficient s (Fig. 8). Fig. 9 finally resolves the relation between s and the depth of complete saturation in the trench. For very low sticking coefficients ($<10^{-4}$) depletion on reactor scale is small and the filling time scales with 1/s. For medium and high sticking coefficients an essentially sticking coefficient independent trench filling time is obtained. Additionally the depletion on reactor scale modifies the filling time. Depending on open area, AR, diffusion coefficient, etc. precursors with medium sticking coefficients may even lead to slightly shorter filling time as compered to a precursor with higher sticking coefficient (see Fig. 9).

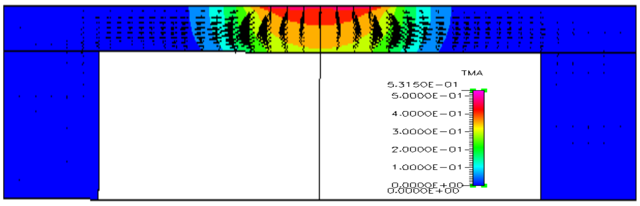

Figure 6: The TMA dispersion after some milliseconds is shown for a typical axisymmetric reactor. The legend indicates the mass fraction of TMA within the carrier gas.

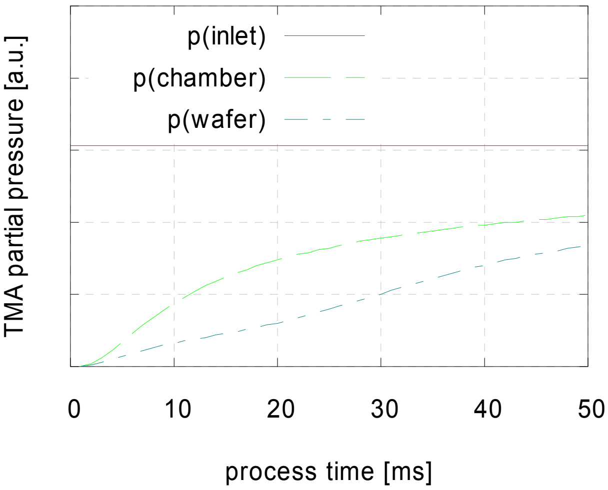

Figure 7: TMA partial pressure at an ideal inlet, at the chamber center and immediately above the wafer surface with s = 0.1. The strong depletion leads to a drastic drop in the TMA partial pressure at the wafer surface.

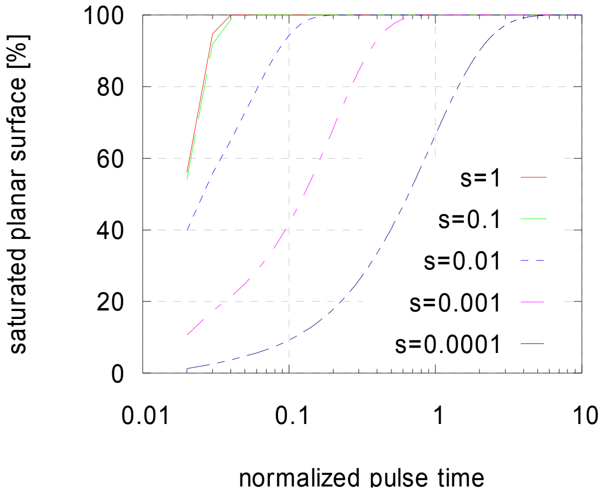

Figure 8: pulse time dependent planar coverage for several effective sticking coefficients. Due to the strong precursor depletion in the reactor (for large s) at the wafer surface, the time to saturation is not proportional to the sticking coefficient s.

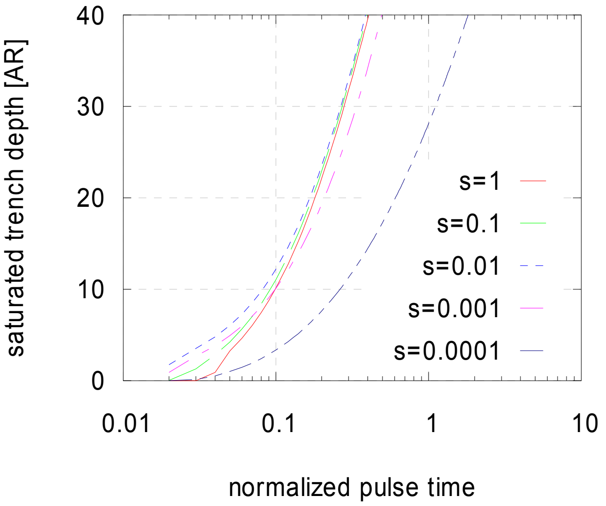

Figure 9: saturation depth in deep trench (measured in aspect ratio) as a function of pulse time and sticking coefficient in the single wafer reactor under investigation.

Comparison with data

We have confirmed the model with film thickness data in trenches from Al_2O_3-ALD processes in a conventional single wafer reactor. The standard cycle time for TMA and oxygen precursors are chosen such that 100% conformity is reached, as shown in Fig. 10 (a) for TMA/H_2O. If the pulse time for TMA is reduced, the film does not cover the whole depth (Fig. 10 (b)). The sharpness of the transition region corresponds to 1>s(TMA)>0.1 which is in excellent agreement with our simulations. For an O_3 precursor the standard pulse time is not sufficient for full conformity. Fig. 10 (c) shows about 75% conformity as expected for a small effective sticking coefficient. Increasing temperature improves the conformity to 100%, corresponding to the calculated strong T dependence of s for ozone.

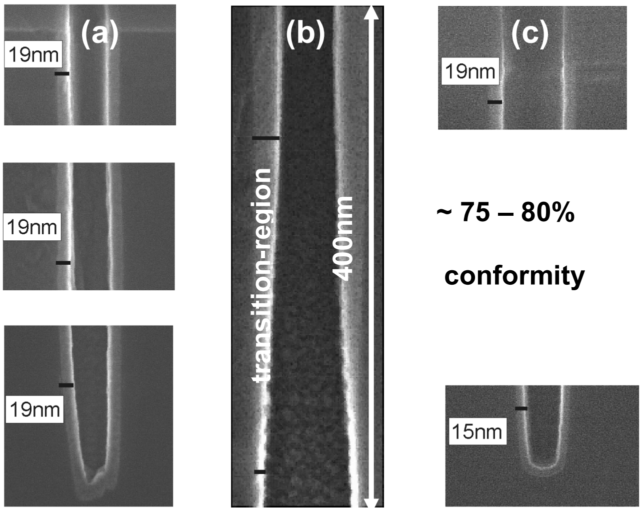

Figure 10: (a) conformally filled deep trench using TMA/H_2O as precursor and standard process conditions. (b) transition region of a partially filled deep trench with reduced TMA pulse. The sharpness of the film front corresponds to s(TMA)>0.1. (c) With standard pulse time and O_3 instead of H_2O only about 75% conformity is obtained.

Conclusion

With the introduction of an effective sticking coefficient as kinetic parameter from ab initio we are able to model and simulate the observation of Al_2O_3-ALD conformity in the deep trench. The performed multi scale approach allows the prediction of the step coverage and the minimal pulse time depending on oxygen precursor, temperature, used ALD tool, and trench geometry. Furthermore, using the presented general modelling strategy we are able to support quantitatively the selection of ALD precursors and process conditions for high aspect ratio capacitor dielectrics. For the manufacturing of DRAMS with high AR it turns out that the variety of potential precursors is hardly limited by required minimal process time.

We acknowledge discussions with M.Gutsche, H.Seidl.

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