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Modeling of Silicon Nanodots Nucleation and Growth Deposited by LPCVD on SiO₂ : From Molecule/Surface Interactions to Reactor Scale Simulations

Ilyes Zahi^{1,2}, Hugues Vergnes², Brigitte Caussat², Alain Esteve¹, Mehdi Djafari Rouhani¹, Pierre Mur³, Philippe Blaise³, and Emmanuel Scheid¹

¹Laboratoire d'Analyse et d'Architecture des Systèmes, UPR-CNRS 8011, 7, av du Colonel Roche, Toulouse, 31077, France

²Laboratoire de Génie Chimique, ENSIACET, Institut National Polytechnique de Toulouse, UMR-CNRS 5503, 5 rue Paulin Talabot, Toulouse, 31106, France

³CEA-LETI-MINATEC, 17 avenue des Martyrs, Grenoble, 38054, France

ABSTRACT

We present first results combining models at continuum and atomistic (DFT, Density Functional Theory) levels to improve understanding of key mechanisms involved in silicon nanodots (NDs) synthesis on SiO₂ silicon dioxide surface, by Low Pressure Chemical Vapor Deposition (LPCVD) from silane SiH₄. In particular, by simulating an industrial LPCVD reactor using the CFD (Computational Fluid Dynamics) code Fluent, we find that deposition time could be increased and then reproducibility and uniformity of NDs deposition could be improved by highly diluting silane in a carrier gas. A consequence of this high dilution seems to be that the contribution to deposition of unsaturated species such as silylene SiH₂ highly increases. This result is important since our first DFT calculations have shown that silicon chemisorption on silanol Si-OH or siloxane Si-O-Si bonds present on SiO₂ substrates could only proceed from silylene (and probably from other unsaturated species). The silane saturated molecule could only contribute to NDs growth, i.e. silicon chemisorption on already deposited silicon bonds. Increasing silylene contribution to deposition in highly diluting silane could then also exalt silicon nucleation on SiO₂ substrates and then increase NDs density.

INTRODUCTION

The need of high integrated systems (PC, car, MP3, mobile ...) of the everyday life involves a permanent evolution of the microelectronic industry. Non volatile Flash memory is a good example of these trends. The poly-silicon floating gate technology of the Flash memories could be replaced, in a near future, by a discrete trap floating gate technology in which discrete traps are made up of silicon nanodots (NDs)^{1,2}. The deposition of NDs by Low Pressure Chemical Vapor Deposition (LPCVD) from silane SiH₄ on SiO₂ surfaces remains one of the most promising ways of synthesis. Nevertheless, it is mandatory to reach an area density of at least 10¹² NDs/cm² and NDs radii lower than 5 nm to industrialize convenient and reliable Flash memories. Despite a huge experimental effort to reach such density and size targets, fundamental understanding of the key mechanisms of NDs nucleation and growth remains elusive.

In particular, NDs deposition in industrial LPCVD reactors involves run durations as low as 10 s. In such conditions, it has been observed that this step has not a convenient reproducibility and in addition NDs are not deposited uniformly from wafer to wafer on an

industrial load involving more than 150 wafers³. Moreover, it has been shown⁴ that the kinetic laws established for conventional thick silicon films, (i.e. >50 nm), for instance that of Wilke et al. (1986)⁵, largely overestimate the deposition rate of NDs. The reason is that the chemical bonds present on a thermally grown SiO₂ surface (silanol Si-OH and siloxane Si-O-Si bonds, according to Vansant and al. (1997)⁶) are much less reactive than fresh silicon dangling bonds. Some authors⁷, express this phenomenon by the existence of an incubation time, delaying the onset of deposition. Of course, kinetics of these first deposition steps dominates kinetics of NDs formation, which is not the case for thicker films. As a consequence, it seems logical that the classical heterogeneous laws established for conventional thick layers are no more valid in the case of ultrathin films like silicon NDs.

To overcome these various problems, we have decided to model existing physical and chemical mechanisms from the scale of precursor molecules and surface bonds toward that of industrial reactor, operating in two steps. On one hand, at the reactor scale, we have investigated by CFD (using the Fluent software) how the addition of a carrier gas can improve reproducibility and uniformity of deposition in a tubular reactor by decreasing deposition rate and increasing run durations. Influences of the nature of the carrier gas (hydrogen or nitrogen) and of the dilution ratio of silane will be presented. On the other hand, in order to develop new intrinsic heterogeneous kinetic laws valid for NDs deposition, we have investigated the fundamental heterogeneous chemical reactions taking place at the initial stages of deposition via first principles calculations (DFT). Chemical pathways and associated activation barriers for SiH₂/SiH₄ reactions onto oxide surface species will be detailed. We will also describe interactions of SiH₄/SiH₂ species on two different SiO₂ surface bonds: hydroxylated {SiO₂}-OH and siloxane bridged bond {SiO₂}-Si(H)-O-Si(H). The final objective of this work is at mid-term, to implement in the CFD code simulating the industrial reactor, intrinsic kinetics of these first steps reactions from DFT results so as to reach a better mastery of the NDs features, i.e. density and size, deposited in such industrial equipments.

FLUENT SIMULATION OF THE INDUSTRIAL PROCESS

Si NDs are synthesized in a Tokyo Electronic Limited (TEL) industrial vertical tubular hot wall LPCVD reactor which contains 170 silicon wafers 8' in diameter as detailed elsewhere³. We use the CFD Fluent software (Fluent 6.1.18) to solve the governing equations of mass, momentum, and reactive species transport and predict gas flow and species concentration versus position in the reactor. Fluid physical properties are calculated using the Fluent data base. The main assumptions are steady state conditions, isothermal reactor, axial symmetry, ideal gas. As the Reynolds number is very small, the gas flow is considered as laminar. Homogeneous and heterogeneous chemical reactions have been considered. We have retained for our temperature and pressure conditions the homogeneous chemical path and kinetic laws of Cordier et al.⁸ involving only silane SiH₄ and silylene SiH₂ as silicon precursors:



Such a simplification of the chemical scheme of silane pyrolysis does not limit the interest of our results because it is well known that in LPCVD conditions, the contribution to deposition of polysilanes of order higher than 2 is negligible and that silylene is among the most concentrated unsaturated species^{8,9}. For the heterogeneous reactions, we have considered a Langmuir-Hinshelwood formulation⁵ for silane decomposition onto surface and kinetic theory

for unsaturated species (here silylene) with a sticking coefficient of 1. The corresponding heterogeneous reactions are the following:



Of course we are aware that with these conventional heterogeneous kinetic laws, an over-estimation of NDs deposition rates will be obtained as explained in introduction. But we wish here to analyse from one simulation to another the influences of the carrier gas and dilution ratio on the deposition rates obtained along the load. Clearly, the objective here is to sharply decrease the total deposition rate in maintaining a uniform value along the load, so as to increase the deposition duration to values greater than 60 s. With such run durations, the unsteady regime corresponding to the filling-in of the reactor and to establishment of reactive mass transfers will become negligible in comparison with the steady state regime³. Silane dilution ratios comprised between 75 and 95 vol. % in either H₂ or N₂ have been studied. A uniform temperature of 580°C has been assumed into the reactor for a total inlet flow rate of 500 sccm. In conventional NDs deposition conditions, pure silane is used.

Figure 1a gives the evolution of the deposition rate from silane for different carrier gases and dilution ratios. From this figure, it appears that for 95% of silane dilution, deposition rates are decreased by a factor of almost 7. But due to different molar weights, these carrier gases affect more or less diffusion coefficients and then uniformity of deposition rates along the load. Indeed, adding H₂ in the initial mixture involves an important increase of diffusion coefficients thus improving deposition uniformity. Using nitrogen, the slope of the deposition rate along the load is higher, due to the low coefficients of diffusion involved. But due to safety reasons, inert gas such as N₂ will be preferred to H₂. For 90% of silane dilution, the difference in total deposition rate between the first and the last wafers of the load is less than 15 % and the time duration is increased by a factor 3.5 to 4 in comparison with the nominal run performed with pure silane.

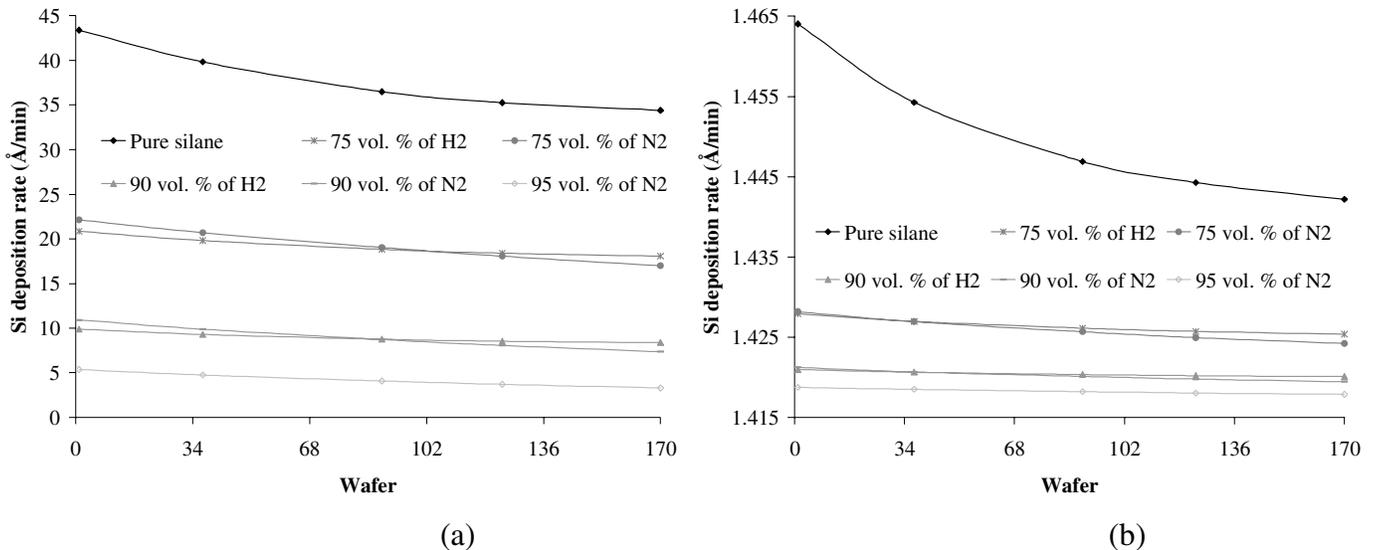


Figure 1. Silicon deposition rate (Å/min) along the load: 75-90 vol. % of H₂, N₂ and 95 vol. % of N₂ (a) from silane decomposition on surface and (b) from silylene decomposition on surface.

Figure 1b gives evolution of the deposition rates from silylene for different carrier gases and dilution ratios. Contrarily to the deposition rate from silane, the deposition rate from silylene remains quasi constant whatever the nature of the carrier gas and the dilution ratio. This insensitive effect is assumed to be linked to the far away equilibrium of the process. For cases tested, silylene concentration is connected to the balance between its volumic production and its surface consumption. As these phenomena are always the same, the concentration of this molecule is nearly the same, and as a consequence the deposition rate from SiH_2 is constant. When using pure silane, silylene contribution to deposition is around 4%, silane contributing to the remaining 96%. When using a silane dilution ratio of 90-95%, this contribution reaches 20 to 30%. This result is important since a higher SiH_2 contribution to deposition could favor nucleation and then increase NDs density as explained below. To the best of our knowledge, these results are original. Deposition experiments of thick Si films (i.e. 100 nm) in these conditions of high dilution are in progress in CEA/Leti to validate these simulation results.

DFT CALCULATIONS ON THE SiO_2 SURFACE

As for ultrathin Si layers conventional heterogeneous kinetic laws over-estimate deposition rates, it has been decided to evaluate initial sticking coefficients on a SiO_2 surface by ab-initio calculations. To study the influence of the nature of surface bonds, we focus on DFT calculations. Parameters such as activation barriers and sticking coefficients are being estimated and will be implemented in the CFD reactor model as soon as their validity will be ascertained. We present results dealing with SiH_2 and SiH_4 interactions on surface bonds such as simple silanol Si-OH groups and siloxane Si-O-Si bridged sites. Configurations thus modelled correspond to the very first step of nucleation on a SiO_2 substrate.

This study has been performed within the framework of Kohn-Sham (KS) density functional theory (DFT), especially with the gradient corrected hybrid Becke three parameters exchange functional¹⁰ and the Lee-Yang-Parr correlation functional¹¹ (B3-LYP). All the atoms are described by 6-31+G** basis set; more details can be found elsewhere¹².

We present results for reactions whose chemical pathways are shown in Figure 2, from chemisorption of the precursor molecules up to the final structure.

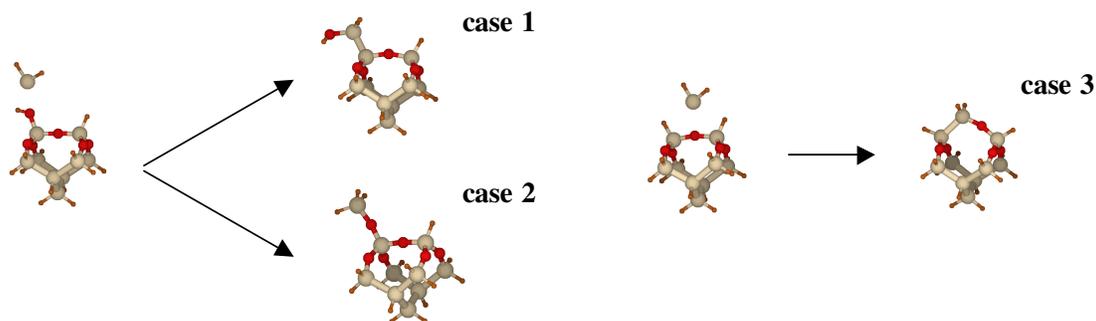


Figure 2. Structures of the modeled clusters from the initial stage of the reaction to a final stable structure state for decomposition of SiH_2 on SiO_2 , onto SiO_2 hydroxyl, case 1 and 2, and onto siloxane bridge, case 3.

The first results indicate that the unsaturated species SiH_2 contributes to NDs nucleation with activation energies of 0.58/0.88 eV for insertion onto the hydroxyl group, case 1 and 2 respectively and 0.65 eV for SiH_2 insertion into the siloxane bridge. The energetics of $\text{SiH}_4/\text{SiO}_2$ surface exhibits very low adsorption energy (\sim no gain in energy) and activation barriers for decomposition around 3 eV. Therefore it can be concluded that SiH_4 precursor could only contribute to NDs growth, i.e. to silicon chemisorption on already deposited silicon atoms. Further calculations are required to complete the nucleation process. Anyway, at this preliminary stage, sticking coefficients C can be derived from these DFT results. For a typical temperature of 580°C , we can consider:

-for silylene, i.e. low partial pressure conditions, no accumulation:

$$C = \frac{\text{Reaction flux}}{\text{Desorption flux} + \text{Reaction Flux}}$$

where the flux depends on the associated energy, temperature and vibration frequency $\nu = 10^{14} \text{ s}^{-1}$

Reaction/Desorption flux = $\nu \times e^{-\frac{E}{kT}}$. We found very interesting results:

$$C(\text{SiH}_2/\text{hydroxyl, case 1}) = 0.025$$

$$C(\text{SiH}_2/\text{hydroxyl, case 2}) = 0.6$$

$$C(\text{SiH}_2/\text{siloxane bridge, case 3}) = 0.005$$

-for silane, i.e. accumulation (physisorption), high activation: $C = \frac{\text{Reaction flux}}{\text{Incident flux}}$

where the incident flux is given as follows: Incident flux = $\frac{P \times S \times N_A}{\sqrt{2\pi \times M_{\text{SiH}_4}} \times R \times T}$, where P

corresponds to pressure and S to the incident surface.¹³⁻²⁰ For silane we obtain result very similar to its interaction onto silicon surface¹³⁻²⁰:

$$C(\text{SiH}_4/\text{SiO}_2) = 10^{-6} \text{ to } 10^{-7}$$

These results are very important in two ways. First they indicate that silylene (and probably other unsaturated species) will be the most important species to nucleate on SiO_2 surface and thus act on NDs density. Second differences between sticking coefficients onto hydroxyl and siloxane bridges consolidate studies showing that a surface pre-treatment forming hydroxyl Si-OH groups to the detriment of siloxane Si-O-Si bonds increases the nucleation rate²¹⁻²⁴.

CONCLUSIONS

CFD simulations at industrial reactor scale have been performed using the CFD code Fluent. They show that deposition time could be increased from almost 10s to more than 1 min. Then reproducibility and uniformity of NDs deposition could be improved by highly diluting silane in a carrier gas such as H_2 or N_2 . Indeed total deposition rate can be divided by factor as high as 7 for a silane dilution ratio of 95% whatever the carrier gas. Nitrogen seems to be the most adapted gas to increase deposition time thanks to its inertness. In addition, silylene contribution to deposition could reach 20 to 30 % in highly diluted conditions, instead of 4 % when using pure silane. This result is important since first DFT calculations have shown that silicon chemisorption on silanol or siloxane bonds present on SiO_2 substrates could only proceed

from silylene (and probably from other unsaturated species). The silane saturated species could only contribute to NDs growth, i.e. silicon chemisorption on already deposited silicon bonds. Increasing silylene contribution to deposition in highly diluting silane could then exalt silicon nucleation on SiO₂ substrates and then increase Si NDs density probably in lowering their size. Further works are in progress to (i) experimentally confirm the deposition rates calculated by Fluent in conditions of high dilution, (ii) analyze by DFT interactions of silane and silylene with silicon bonds and (iii) complete our chemical mechanism for silane pyrolysis by considering gaseous species such as disilane Si₂H₆ or silylsilylene Si₂H₄.

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