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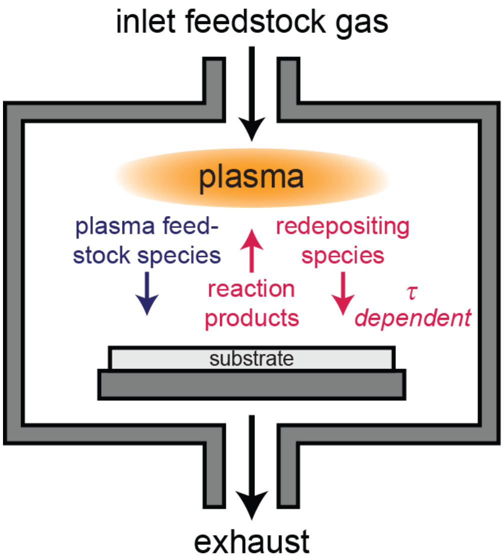
ALD of nitrides: opportunities for plasmas?

Summary

Films of nitrides are of great interest to the ALD community mainly due to their importance in the semiconductor industry. For thermal ALD of nitrides, NH_3 is the most popular co-reactant. Unfortunately, the reactivity of the processes using NH_3 is (or seems to be) lower compared to oxide processes using H_2O. Therefore, achieving high material quality for nitrides can be challenging, especially when applications demand moderate or low substrate temperatures. Because of the limited reactivity of the thermal nitride processes, plasmas are often considered as a co-reactant where NH_3, N_2 and H_2 can be used as feedstock gasses. Which gasses or gas mixtures should be used to obtain the best process results, and the role of different plasma species, is often unclear. Furthermore, the surface chemistry and the nature of the surface before and after plasma is generally unknown.



Schematic illustration of general processes in plasma ALD. During the plasma exposure step, precursor ligands are liberated from the surface and enter the gas phase. These reaction products can dissociate in the plasma (e.g., by electron impact) leading to reactive species which can redeposit on the surface. The extent of the redeposition and its effect on the ALD process will depend on the gas residence time τ, the used gasses, and the chemistry.

In this session, we will try to identify key processes responsible for (i) growth and (ii) material quality of nitrides deposited using ALD. Several nitride ALD processes, both thermal and plasma, will be reviewed. We will focus on the opportunities for plasmas in ALD of nitrides with an emphasis on ALD of SiN_x. The overview presentation will be followed by a case study illustrating the use of density functional theory (DFT) calculations in understanding ALD FUN*damentals*.

Outline of the overview presentation

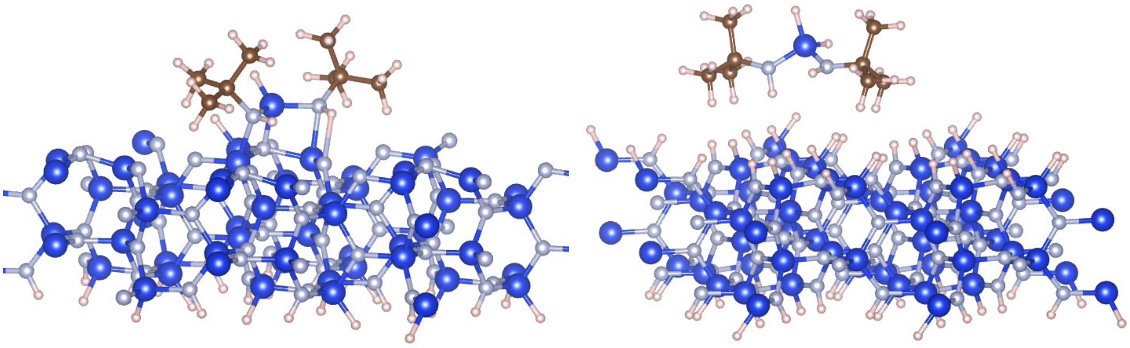
The following topics will be addressed during the overview presentation:

- Chemistry(ies) during nitride ALD
- Material properties and effect of plasma conditions and time

- Role of plasma species
- ALD of silicon nitride
- Dissociation in the plasma studied by optical emission and mass spectrometry
- Redeposition and its effect on material quality and growth
- Hydrogen, friend or foe?
- Surface-precursor interactions

Case study

While experiments, undeniably, are the mainstay of knowledge about ALD, atomistic modeling can provide deeper insights into the FUN*damentals* of ALD. In the case study, we will take the case of SiN_x ALD and see what we can learn from atomistic modeling. It is well known that thermal ALD of SiN_x is challenging, especially at modest or low temperatures. However, the usage of N_2 plasma provides a route towards low temperature SiN_x ALD. In this case study, we will show how surface termination (passivation of the surface) can explain both why SiN_x deposition is challenging at low temperatures and how using N_2 plasma can enable deposition at low temperatures. We use density functional theory (DFT) calculations to study the adsorption of a Si precursor on a variety of model surfaces with different surface terminations (passivation models). It will be shown how surface passivation affects precursor adsorption, and how this can explain why low temperature thermal ALD of SiN_x is energetically unfavorable. Furthermore, we will also motivate how an N_2 plasma is capable of regenerating reactive surface sites making precursor adsorption more favorable and thereby, low temperature SiN_x ALD feasible.



BTBAS interacting with an under-coordinated bare Si_3N_4(0001) surface (left) and a H passivated Si_3N_4(0001) surface (right). While there is a strong interaction with the under-coordinated surface, the interaction with the passivated surface is very weak.

How to participate?

You can participate actively in the session about low-temperature ALD by giving a short presentation or a pitch after the two presentations that are already scheduled. Please submit a short presentation clearly describing the **observation, issue or open question** that you would like to discuss to contact@nanomanufacturing.nl. We would like to receive your presentation **before the 29th of May**, which will allow sufficient time for us to evaluate your contribution. You might receive suggestions from the session coordinators to fit it in the session.

If your short-talk is accepted, you can chose to bring a poster in addition to giving the short talk. The poster will receive attention during the breaks and during lunch. The poster will allow you to present more background information and interesting findings which cannot be discussed during the sessions due to time constraints.

[not shown to participants beforehand]

Statements/Theses/Propositions

- Hydrogen and hydrogen containing co-reactants should be avoided in plasma ALD of silicon nitride.
- Maximizing GPC is not a good strategy for high-quality nitrides.
- Ions help the reactions and are needed to obtain reasonable cycle times.
- Lowest impurity level does not necessarily provide lowest resistivity value; carbon can be a welcome impurity.
- Poisoning and redeposition are the same.
- Precursor saturation should be studied over orders of magnitude in exposure to separate slow from fast reactions. What is the real GPC of a process?