



Dr. Angel Yanguas-Gil  
Argonne National Lab

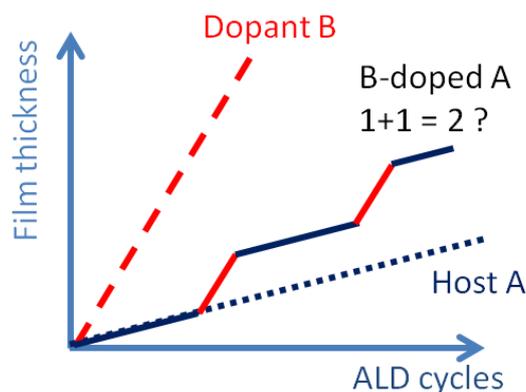


Yizhi Wu  
Eindhoven Univ. of Technology

## ALD of multi-element oxides: Is 1 + 1 equal to 2?

### Summary

Multi-element oxides can be synthesized by ALD by carrying out supercycles in which cycles of material A are alternated with cycles of material B. By selecting the ratio of cycles of process A and process B, the material composition can generally be controlled quite accurately while the films also benefit from the other key merits offered by ALD. However, the synthesis of multi-element oxides by ALD is one of the areas in which 1+1 does not necessarily equal two: the growth-per-cycle, stoichiometry and film properties depend on the interaction between the two different ALD processes. These two processes can interact in ways that are hard to predict based solely on the behavior of process A and process B.



*The material “B-doped A” can be obtained by ALD by supercycles in which  $x$  cycles of host material A are alternated by one cycle of dopant material B. The film thickness might not just be a linear superposition of the growth-per-cycles for the two materials as the two processes can interact with each other in particular ways.*

In this session we will address the fundamentals, challenges, and opportunities of the synthesis of multi-element oxides. The session will concentrate on the preparation of doped oxides, materials that play an important role in many different applications, from semiconductor manufacturing to solar energy and from solid state lighting to catalysis. The case study will address the synthesis of Al-doped ZnO by ALD and highlight all kinds of effects which deviate from  $1 + 1 = 2$  behavior.

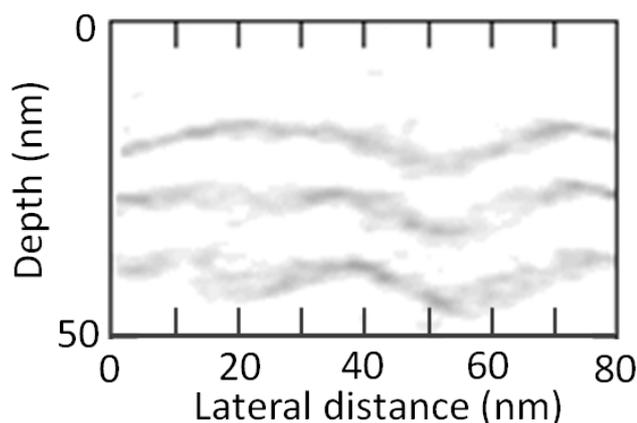
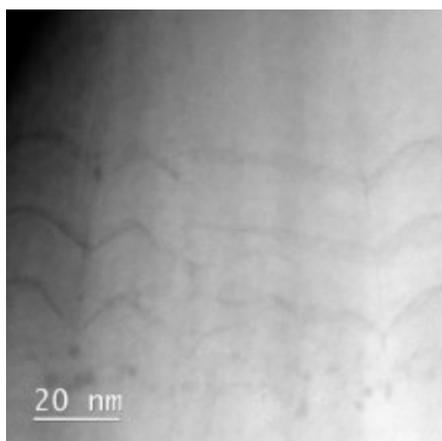
### Outline of the overview presentation

The following topics will be addressed during the introduction:

- Introduction to the synthesis and application of doped materials
- When 1+1 equals 2: the ideal ALD doped material
- When 1+1 is not 2: factors contributing to the departure from the ideal behavior
- The blurred line between doped materials and nanolaminates, and the impact on materials properties
- When 1+1 leads to completely new materials
- From lab to manufacturing: advantages and challenges of ALD of doped materials

## Case Study

In this study case, ALD of Al-doped ZnO will be taken as an example. The ZnO has been deposited by  $\text{Zn}(\text{C}_2\text{H}_5)_2$  and  $\text{H}_2\text{O}$  while the Al doping has been achieved by ALD cycles from  $\text{Al}(\text{CH}_3)_3$  and  $\text{H}_2\text{O}$  and by ALD cycles from  $\text{Al}(\text{CH}_3)_2(\text{O}^i\text{Pr})$  and  $\text{H}_2\text{O}$ . Studies were carried out by *in situ* spectroscopic ellipsometry as well as by Rutherford backscattering, transmission electron microscopy and atom probe tomography. Several reasons for deviation from linear growth after the  $\text{Al}_2\text{O}_3$  cycle will be addressed. The effects include enhanced growth, delayed growth and etching by the dopant cycle. Also the influence of such effects on the film properties will be addressed and it will be presented how some of the effects can be mitigated, e.g. by selecting a different precursor for the dopant.



*High-resolution high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image for an Al-doped ZnO film prepared by 85 cycles of ZnO with 1 cycle of  $\text{Al}_2\text{O}_3$ . The 2D depth profile of the Al-fraction as measured by atom probe tomography is also given. This figure shows the Al-distribution in the multilayer stack.*

## How to participate?

You can participate actively in the session about ALD of multi-element oxides 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](mailto:contact@nanomanufacturing.nl). We would like to receive your presentation **before the 29<sup>th</sup> 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 better in the session.

If your short-talk is accepted, you can choose 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.