

NON-AQUEOUS SOL-GEL ROUTES APPLIED TO ATOMIC LAYER DEPOSITION

E. Rauwel¹, G. Clavel¹, M.-G. Willinger¹, P. Rauwel², F. Ducroquet³, N. Pinna¹

1 - Department of Chemistry and CICECO, University of Aveiro, 3810-193 Aveiro

2 - Department of Ceramics and CICECO, University of Aveiro, 3810-193 Aveiro

3 - Minatec-IMEP, 3 Parvis Louis Néel, BP 257, 38016 Grenoble

Usually traditional Atomic Layer Deposition (ALD) processes use aqueous sol-gel routes for oxide thin film growth. Typically, transition metal precursors (halides, alkoxide or amide) are reacted with an oxidizing agent (e.g. water, radical oxygen or ozone). More specifically the reaction of such metal complexes with water leads, upon hydrolysis and condensation, to the formation of a metal oxide thin film. The films grown by this traditional way are amorphous; hence a post-synthetic heat treatment is generally required to induce the desired crystallization in order to improve the quality of the film. They also contain large amounts of undesired impurities ranging from unreacted carbon species to halides. Furthermore, as water is a strong oxidizing agent at the typical ALD range of deposition temperatures (200-400 °C) some substrates (e.g. Silicon) are rapidly oxidized. In fact, metal oxide thin films grown on silicon always present a non-negligibly thick oxidized interface layer (silica or silicates) in between the silicon and the deposited metal oxide which usually hinders microelectronic applications.

Many solutions are presently proposed to overcome these problems, like using new metal organic precursors [1,2] or by the utilization of plasma during the deposition process.

Recently various non-aqueous sol-gel routes were proposed for the formation of metal oxide nanoparticles [3,4] and hybrid materials [5] in solution. They proved to be powerful alternatives, especially because they have the capacity to overcome the main drawbacks of traditional sol-gel routes. However, only a few non-aqueous routes were applied to ALD. The most successful were the ones reported on the reaction of metal alkoxides with metal halides [6] and the formation of silica and silicates [7, 8].

In this work we present a novel non-aqueous approach applied to ALD [9] leading to the formation of high quality metal oxide thin films. Moreover, this approach demonstrates a real ability to reduce the oxide interlayer in the case of deposition on silicon substrates. This process enables to grow metal oxides coating at temperatures as low as 50 °C on various supports including monocrystalline substrates, carbon nanotubes, organic fibers, etc. The characterization of these films will be presented together with their possible formation mechanism.

References:

- [1] A. C. Jones, et al. *Chem. Vap. Dep.* **2006**, 12, 83.
- [2] J. Niinistö, et al. *Chem. Mater.* **2007**, 19, 3319.
- [3] N. Pinna, M. Niederberger, *Angew. Chem. Int. Ed.* **2008**, DOI: 10.1002/anie.200704541
- [4] M. Niederberger, G. Garnweitner, N. Pinna, G. Neri, *Prog. Solid State Chem.* **2005**, 33, 59.
- [5] N. Pinna, *J. Mater. Chem.* **2007**, 17, 2769.
- [6] M. Ritala, K. Kukli, A. Rahtu, P. I. Räsänen, M. Leskela, T. Sajavaara, J. Keinonen, *Science* **2000**, 288, 319.
- [7] R. G. Gordon, J. Becker, D. Hausmann, S. Suh, *Chem. Mater.* **2001**, 13, 2463.
- [8] D. Hausmann, J. Becker, S. L. Wang, R. G. Gordon, *Science* **2002**, 298, 402.
- [9] E. Rauwel, G. Clavel, M.-G. Willinger, P. Rauwel, N. Pinna, *Angew. Chem. Int. Ed.* **2008**, DOI: 10.1002/anie.200705550