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SR-ALD Workshop

12 – 15 June 2016

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Welcome!

Dear participant,

We have the great pleasure to welcome you to the first SR-ALD workshop, which is held in Barcelona from June 12 to 15, 2016. SR-ALD is organized by the **ALBA synchrotron** and the COST action **HERALD**. It brings together scientists interested or involved in the use of synchrotron radiation (SR) for probing atomic layer deposition (ALD) processes. The goal is to share experiences, to discuss how to answer fundamental research questions about ALD with SR-based experiments, to find solutions for technical obstacles and to develop new ideas for SR-based ALD experiments.

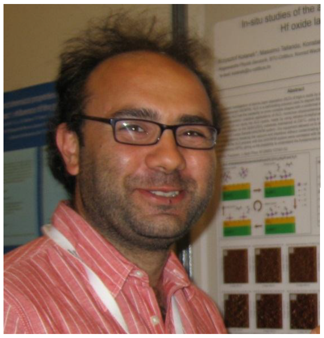
We would like to thank, in particular, all invited speakers for accepting our invitation to deliver a talk or tutorial, which undoubtedly will promote fruitful discussions during this workshop. We also want to acknowledge ALBA, HERALD and our industrial sponsors for their kind support. We also would like to express our gratitude to the members of the scientific committee, who have kindly advised us in preparing the program conference.

The program of the workshop is divided in two parts. On the first two days, there will be invited lectures and contributed talks, and one poster session. On the third day, there will be an open session to allow for a profound discussion among the participants and tutorial sessions on the treatment and analysis of SR-data. Additionally, we will offer a visit to the beamlines of ALBA.

This meeting would not be possible without your participation and we are really grateful to all of you for coming to Barcelona. We hope that this SR-ALD workshop will stimulate many fruitful discussions. We wish you an enjoyable workshop and a pleasant stay in Barcelona.

Massimo Tallarida, ALBA Synchrotron

Jolien Dendooven, Ghent University



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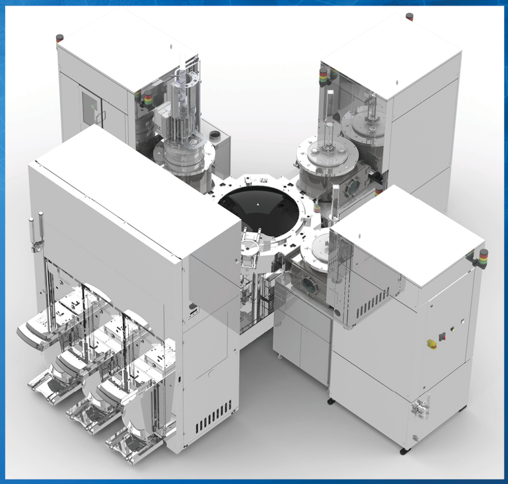

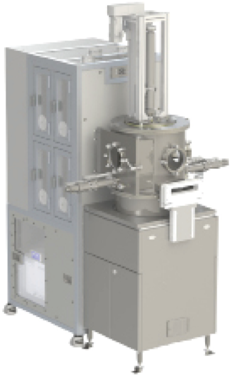

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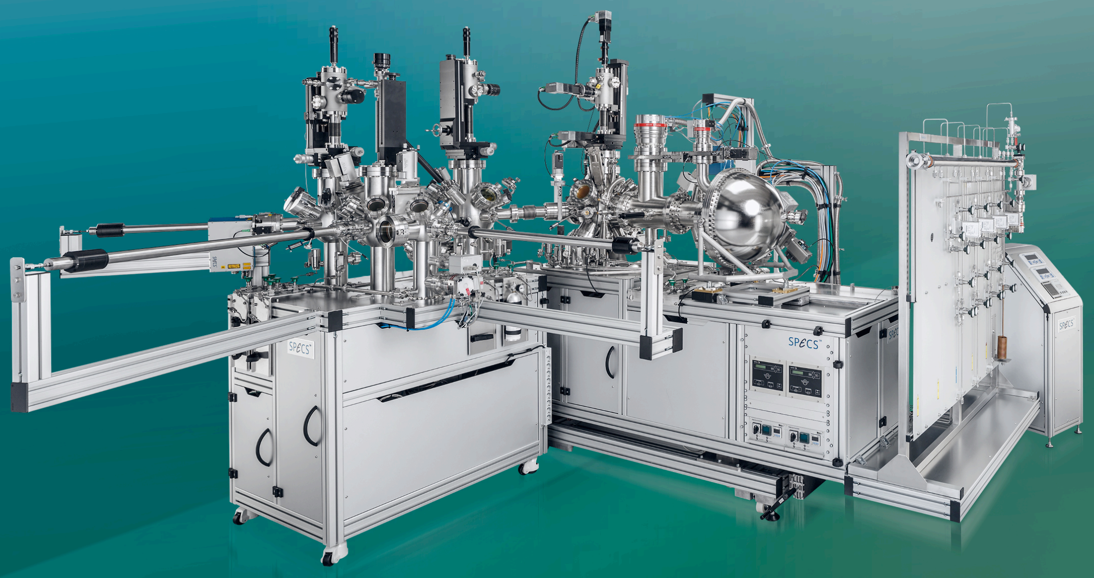

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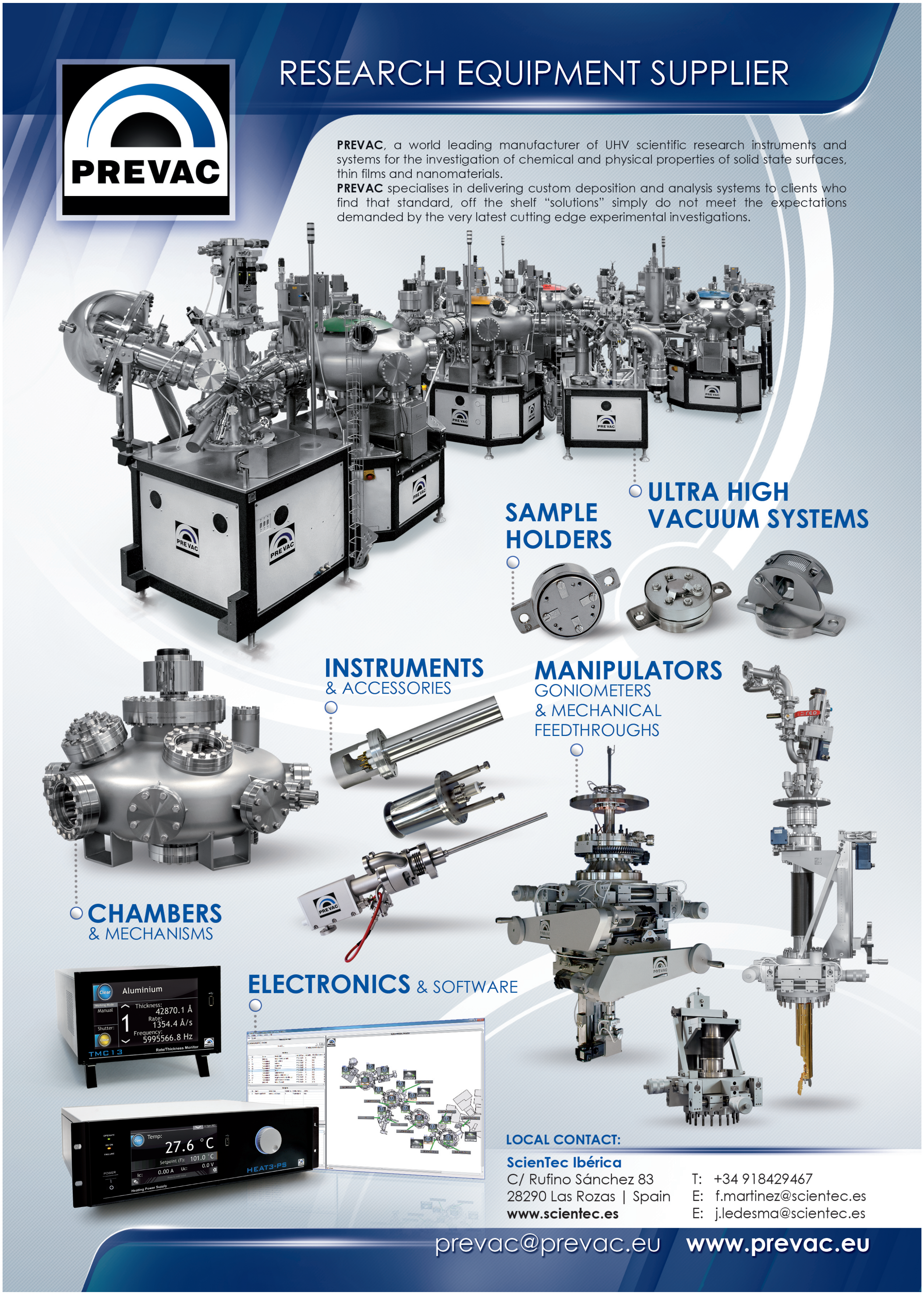

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PROGRAM

Sunday, June 12th		
20:00 22:00	**Welcome Reception & Registration**	
Monday, June 13th		
09:00 09:15	**Arrival & Registration**	
09:15 09:30	**Welcome messages**	
09:30 10:15	**Invited talk**	**Ola Nilsen, University of Oslo, Norway** ***ALD - From Ideal to Real***
10:15 10:35	Contributed talk	Mariona Coll, Institut de Ciencia de Materials de Barcelona, Spain *Epitaxial Complex Oxide Thin Films by Atomic Layer Deposition*
10:35 10:55	**Coffee break & Registration**	
10:55 11:15	Contributed talk	Yael Etinger-Geller, Technion, Israel *Controlling the Short-range Order of Amorphous Oxides by Nanometer size*
11:15 11:35	Contributed talk	Ville Miikkulainen, University of Helsinki, Finland *Straightforward Conversion of MnO_2 to $Li_xMn_2O_4$ by Gas-solid Reactions*
11:35 11:55	Contributed talk	Laura Evangelio, Institut de Ciencia de Materials de Barcelona, Spain *Use of Atomic Layer Deposition for Improving Pattern Transfer in Directed Self-assembly of PS-b-PMMA*
11:55 12:40	**Invited talk**	**Salvador Ferrer, ALBA Synchrotron, Spain** ***Synchrotron Radiation and Thin Film Growth Phenomena***
12:40 13:00	Contributed talk	Klaus Attenkofer, Brookhaven National Laboratory, USA *Characterization Capabilities of Atomic Layer Deposition at the NSLS II*
13:00 14:30	**Lunch**	
14:30 16:00	**Poster session**	
16:00 16:20	Contributed talk	James Engstrom, Cornell University, USA *Gas-source MBE Growth of 2D Materials Examined Using Synchrotron Radiation*
16:20 16:40	Contributed talk	Beatrix Pollakowski, Physikalisch-Technische Bundesanstalt, Germany *Speciation Depth-profiling of Nano-structured Specimen by combined GIXRF-NEXAFS*
16:40 17:00	Contributed talk	Mercedes Carrillo Solano, GSI Helmholtz Zentrum, Germany *Production and Tailoring of Etched Ion-track Nanopores and Nanotubes by ALD*
17:00 17:20	**Coffee break**	
17:20 17:40	Contributed talk	Alfonso Monreal, IMDEA Materials Institute, Spain *Bulk Heterojunction Electrodes Based on CNT fibre/ZnO Hybrids Produced by ALD*
17:40 18:00	Contributed talk	Tony Schenk, NaMLab Dresden, Germany *Investigation of Si-doped HfO_2 ALD Films by means of EXAFS and XANES*
18:00 18:20	Contributed talk	Andrea Hadley, The Australian National University, Australia *SAXS Investigation of Nano-Pore Membranes Coated by Atomic Layer Deposition*

Tuesday, June 14th		
09:00 09:45	**Invited talk**	**Christophe Detavernier, Ghent University, Belgium** ***In-situ Characterization during ALD***
09:45 10:05	Contributed talk	Simon Elliott, Tyndall National Institute, Ireland *The Need for Validation of ALD Mechanisms Predicted from First Principles*
10:05 10:25	Contributed talk	Aafke Bronneberg, Helmholtz-Zentrum Berlin für Materialen und Energie,Germany *Controlling the Ti Oxidation State in TiO2 – An In-Line XPS Study*
10:25 10:45	Contributed talk	Eduardo Solano, Ghent University, Belgium *In Situ Study of the Morphological Stability of ALD-Grown Pt Nanoparticles During Thermal Annealing*
10:45 11:05	**Coffee break**	
11:05 11:25	Contributed talk	Claudia Wiemer, Institute for Microelectronics and Microsystems, Italy *SR X-ray Diffraction and X-ray Absorption Fluorescence Spectroscopy Study of Er-doped HfO_2 Deposited by Atomic Layer Deposition*
11:25 11:45	Contributed talk	Paul Plate, Helmholtz-Zentrum Berlin für Materialen und Energie, Germany *On the Oxidation State of MnO_x – An In-Line XPS Study*
11:45 12:05	Contributed talk	Philipp Hönicke, Physikalisch-Technische Bundesanstalt, Germany *Quantitative and Chemical Characterization Capabilities for Atomic Layer Depositions using Synchrotron-based Reference-free X-ray Spectrometry*
12:05 12:25	Contributed talk	Alessio Lamperti, Institute for Microelectronics and Microsystems, Italy *XANES and XMCD of Pure and Fe-doped ZrO_2 Thin Films Grown by ALD*
12:25 12:45	Contributed talk	Christoph Wiegand, Universität Hamburg, Germany *Interfacial and Surface Effects during the Growth of Sb_2Te_3/Sb_2Se_3 Ternary Films and Multilayer Structures studied by QCM in situ Analysis*
12:45 13:05	Contributed talk	Mikko Heikkilä, University of Helsinki, Finland In Situ High Temperature X-Ray Scattering Studies of some Atomic Layer Deposited Layers of Metals and Metal Oxides
13:05 14:30	**Lunch**	
14:30 15:15	**Invited talk**	**Joachim Schnadt, Lund University, Sweden** ***Live Monitoring of ALD by Ambient Pressure X-ray Photoelectron Spectroscopy***
15:15 16:00	**Invited talk**	**Hubert Renevier, Grenoble Institute of Technology, France** ***In Situ X-ray Studies of Crystalline Texture and Strain During the Initial Stages of ZnO Atomic Layer Deposition***
16:00 16:20	Contributed talk	Virginia Anderson, US Naval Research Laboratory, USA *Aluminum Nitride Grown by Atomic Layer Epitaxy Characterized with Real-Time Grazing Incidence Small Angle X-ray Scattering*
16:20 16:40	Contributed talk	Christelle Yeromonahos, Université de Lyon, France *Near-Ambient Pressure X-ray Photoelectron Spectroscopy Study of the Atomic Layer Deposition of HfO_2 on SiO_2/Si*
16:40 17:00	**Coffee break**	
17:00 17:20	Contributed talk	Matthias Minjauw, Ghent University, Belgium *Thin, Low Roughness Ru Films Deposited by Thermal and Plasma-enhanced Atomic Layer Deposition using RuO_4 and H_2 at Low Temperatures*
17:20 17:40	Contributed talk	Gianluca Ciatto, Synchrotron SOLEIL – Beamline SIRIUS, France *An Atomistic View of the Incipient Growth of Zinc Oxide by in-situ X-ray Absorption Spectroscopy*
17:40 18:00	Contributed talk	Jolien Dendooven, Ghent University, Belgium *In Situ Synchrotron-based XRF and GISAXS Study of ALD Encapsulation of Supported Nanocrystals*

18:00 18:15	**Open Session proposals**	
20:30 23:00	**Social dinner**	
Wednesday, June 15th		
09:30 11:00	Visit to ALBA	
11:00 11:30	**Coffee break**	
11:30 13:00	Open discussion	
13:00 14:30	**Lunch**	
14:30 15:30	**Invited tutorial**	Andris Anspoks, University of Latvia, Latvia *EXAFS*
15:30 16:30	**Invited tutorial**	Jolien Dendooven, Ghent University, Belgium Marina Ganeva, Forschungszentrum Jülich, Germany *GISAXS*
16:30 17:00	**Coffee break**	
17:00 18:00	**Invited tutorial**	Elzbieta Guziewicz, Polish Academy of Sciences, Poland *XPS*

ALD – From Ideal to Real

O. Nilsen and H. Sønsteby

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Atomic layer deposition (ALD) is mostly known as a technique that produces perfect films with atomic resolution on large substrates with complex geometries, even under fluctuating production conditions. This is also true for several processes, but not all.

ALD is a chemical process that relies on available active sites on a substrate, and has proven capable to grow on surfaces one initially would assume to be inert, such as Teflon and gold. The initial stages of such growth deviates from the ideology of a layered growth, what happens then with the evolution in growth?

ALD can produce materials with textures varying from completely amorphous to well crystalline, and their growth dynamics can lead to film evolution that seemingly disobeys the linear growth process most related to ALD. The crystal growth dynamics known from PVD processes does not apply in the ALD regime. What are the factors that determine the evolution in texture?

ALD relies on self-terminating surface reactions to secure robust growth. What happens to the robustness if the bulk of the material is capable of absorbing some of the precursor and act as a reservoir?

ALD is most suited for deposition of binary compounds, and has proven well capable of production of ternary and quaternary compounds. However, control of stoichiometry is not as straight forward as simple combination of several binary processes. What controls the deposited stoichiometry?

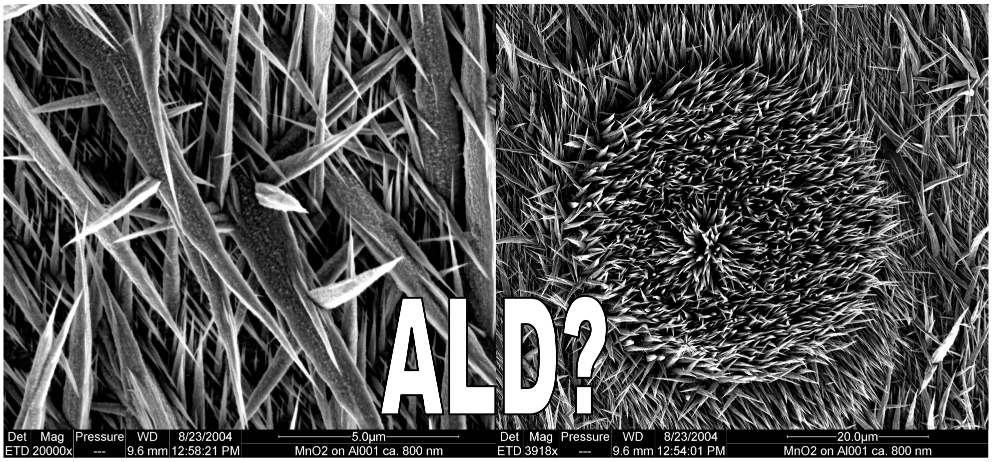

Figure 1: Needles of MnO_2 made by ALD [1].

[1] O. Nilsen et al. *J. Nanosci. Nanotechnol.* 2007, 8, 1–9, DOI: 10.1166/jnn.2007.037

Epitaxial Complex Oxide Thin Films by Atomic Layer Deposition

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Preparation of complex oxide thin films at very low temperatures, over large areas and compatible with low-cost and flexible substrates offers great industrial potential. The degree of crystal perfection required for these materials varies according to specific application. However, in general, high temperature thermal treatments and textured growth are required for improved functional properties. This adds complexity in the materials processing in device integration. Perovskites, ABO_3, and spinels, AB_2O_4, are very rich families of complex oxides where A- and B- site engineering can strongly modify their properties offering many possibilities to design future applications including sensors, microelectronics, spintronics and photovoltaics. Here we will present the study of ALD for two case examples: $BiFeO_3$ and Co_2FeO_4.

We demonstrate that nanocrystalline $BiFeO_3$ (BFO) thin films (15-30 nm) can be prepared on $SrTiO_3$ single crystal substrates by ALD at 250ºC, using $Bi(thd)_3$ and $Fe(Cp)_2$ for the metal precursors and ozone as oxygen source. Post annealing at 650 °C converts the sample to a full crystalline film with improved ferroelectric behavior. [1]

On the other hand, we demonstrate that ALD is also a powerful deposition method to stabilize metastable phases at 250ºC such as the magnetic Co_2FeO_4 thin films (5-25 nm) at 250ºC using $Co(Cp)_2$, $Fe(Cp)_2$ and ozone. High coervice fields, 15 kOe, and high saturation of magnetization, 3.3 μB per formula unit, (at 10K) are preserved down to 10 nm.[2]

A combination of x-ray diffraction, reflection high energy electron diffraction, scanning transmission electron microscopy and x-ray photoelectron spectroscopy complete a thorough study of the structural, morphological and composition analysis of these films.

These results show promising prospects for the use of atomic layer deposition over the existing thin-film deposition techniques to stabilize ultrathin multicomponent materials with nanoscale control on a wide variety of substrates for which processing temperature is a major drawback.

[1] M.Coll et al. *Chem. Mater.* **2015**, 27, 6322–6328 DOI: 10.1021/acs.chemmater.5b02093
[2] M.Coll et al. *Adv. Funct. Mater*. **2014**, 24, 5368–5374 DOI: 10.1002/adfm.201400517

Controlling the Short-Range Order of Amorphous Oxides by Nanometer Size

Y. Etinger-Geller, A. Katsman and B. Pokroy

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Amorphous materials, in contrast to crystalline ones, lack long-range order. Its order decays rapidly with the distance; yet, the local environment for a particular type of atom is quite similar - though not identical. These fine changes in the atomistic structure of the materials lead to new and very interesting phenomena which are unique for amorphous materials. Although many aspects of science and technology rely on amorphous materials, much less research is conducted about their structure than on their crystalline counterparts.

In nature there are many organisms that use crystallization via an amorphous phase in order to achieve controlled mineralization. One of the main advantages of this method is that it enables the organism to exert control over the resulting polymorph which is not necessarily the thermodynamic stable one, by first controlling the short-range order in the amorphous phase.

In this research we draw inspiration from nature and study the ability to control various structural aspects of amorphous materials via nanometer size effects. We chose atomic layer deposition (ALD) as our material deposition method, since it is a technique that can provide extremely precise, sub-nanometric, thickness control and can deposit conformal and pinhole-free amorphous films of various materials.

It was shown lately in our group that indeed the short-range ordering changes as a function of nanometer size in amorphous aluminium-oxide. The results indicate that the surface of the amorphous alumina possesses a different short-range order than the average in its bulk, so the thinner the amorphous solid is, the more its short-range order resembles that near the surface [1].

In this research we continue the study on how size affects the short-range order of different amorphous systems and correlate these changes to different properties. We believe that this novel strategy if adopted for man-made materials could revolutionize many technological applications.

[1] L. Bloch, Y. Kauffmann and B. Pokroy, *Crystal Growth & Design* **2014**, 14, 3983-3989.

Straightforward Conversion of MnO_2 to $Li_xMn_2O_4$ by Gas-Solid Reactions

V. Miikkulainen,[1] M. J. Heikkilä,[1] P. John,[1,2] M. Ritala[1] and M. Leskelä[1]

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[2]Ruhr University Bochum, Germany

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Lithium manganese oxide spinel ($Li_xMn_2O_4$) is an important cathode material for lithium-ion batteries. It has high specific capacity, it is non-toxic and also cheap material owing to high abundance of Mn. Moreover, it undergoes only minor volumetric changes upon charge-discharge cycling.[1] That is an important property for all-solid-state thin-film batteries, where the constituting films form a rigid stack. $Li_xMn_2O_4$ has been deposited by physical vapor deposition (PVD) for thin-film lithium-ion batteries.[2] PVD limits the film stack into a planar design. Atomic layer deposition (ALD) by contrast would allow conformal film deposition onto more complex substrates enabling much higher capacity per area than by PVD.

Deposition of $Li_xMn_2O_4$ by ALD can be realized by combining $Mn(thd)_3$-O_3 cycles with Li(thd)-O_3 or LiO^tBu-H_2O cycles. Alternatively, this material can be made by first depositing MnO_2 and then exposing the film to aforementioned lithium subcycles. In both methods, lithium insertion takes place notably easily transforming the rutile MnO_2 to spinel $Li_xMn_2O_4$ suggesting that the gas-solid reactions during the lithium precursor pulse are not limited by the surface only but there is a film bulk component as well. Active redox chemistry of manganese combined with the high mobility of lithium ions most likely are the driving forces for the process.[3]

In the present study we have focused on lithiation of predeposited MnO_2 films by LiO^tBu-H_2O cycles. Ex situ X-ray diffraction was utilized for studying the phase transformations as a function of number of lithiation cycles. Phase content during post-deposition annealing was analyzed by high-temperature XRD. Results on these studies as well as open questions of the process, potentially solvable with synchrotron methods, will be discussed in the presentation.

[1] M.M. Thackeray et al. *Mater. Res. Bull.* 1984, 19, 179–187, DOI: 10.1016/0025-5408(84)90088-6
[2] N.J. Dudney et al. *J. Electrochem. Soc.* 1999, 146, 2455–2464, DOI: 10.1149/1.1391955
[3] V. Miikkulainen et al. *J. Phys. Chem. C* 2014, 118, 1258–1268, DOI: 10.1021/jp409399y

Use of Atomic Layer Deposition for improving Pattern Transfer in directed Self-assembly of PS-b-PMMA

L. Evangelio, M. Lorenzoni, M. Fernández-Regúlez, S. Gottlieb and F. Pérez-Murano

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Block copolymer (BCP) nanolithography is emerging as a very promising technique in the semiconductor industry, since it allows achieving very high resolutions [1]. Combining their intrinsic property to self-assemble into periodic arrays of nanostructures, with classical lithographic techniques, they can be oriented by following chemical or topographical patterns [2]. A requirement for their use on nanolithography relies on the possibility of selectively remove one of the two blocks. In order to realize the pattern transfer with high fidelity it is necessary to have sufficient etching contrast. PS-*b*-PMMA is one of the most common used BCPs due to several technical and practical reasons. However, despite having a high etching contrast with O_2 plasma, the PS remaining mask is not resistant enough to transfer the pattern into the substrate. Therefore, there is a need to enhance the pattern transfer process by means of introducing materials that could improve the etching resistance of one of the blocks, thus avoiding the use of intermediate hard-masks.

In this contribution, we propose the use of Atomic Layer Deposition (ALD) technique to selectively deposit a metal oxide layer on the top of the PMMA domains by sequential exposure to vapours of trimethylaluminum (TMA). This organometallic precursor is chosen due to its ability to perfuse the film and bind only with the PMMA through an attractive interaction with the carbonyl groups. The whole process for ALD selectively deposition after block copolymer self-assembly is shown in figure 1a. As it is seen in figure 1b, the ALD is selective to PMMA domains and it is also demonstrated by an increase of the Young's modulus in peak force experiments [3]. Figure 1c shows the PS blocks removal by using different etching times. It can be observed that after longer times, the PMMA + alumina mask starts to degrade due to under-etching effects. In order to avoid this problem, we are currently working on the full PMMA infiltration.

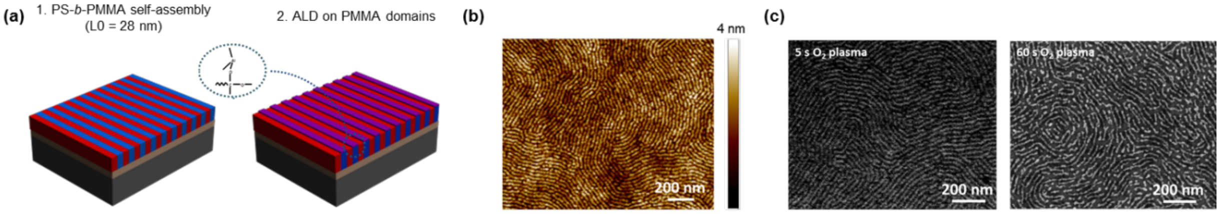

Figure 1: (a) Overall ALD process (b) AFM topography image after selective ALD process and (c) SEM images after different PS etching times

[1] R. Ruiz, H. Kang, F. A. Detcheverry, E. Dobisz, D. S. Kercher, T. R. Albrecht, J. J. De Pablo, and P. F. Nealey, "Density Multiplication and Improved Copolymer Assembly," *Science (80).*, vol. 321, pp. 936–940, 2008.
[2] M. Fernández-Regúlez, L. Evangelio, M. Lorenzoni, J. Fraxedas, and F. Pérez-Murano, "Sub-10 nm Resistless Nanolithography for Directed Self-Assembly of Block Copolymers," *ACS Appl. Mater. Interfaces*, vol. 6, pp. 21596–21602, 2014.
[3] M. Lorenzoni, L. Evangelio, S. Verhaeghe, C. Navarro, and F. Pérez-Murano, "Assessing the Local Nanomechanical Properties of Self-Assembled Block Copolymer Thin Films by Peak Force Tapping," 2015.

Synchrotron Radiation and Thin Film Growth Phenomena

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The talk will describe different applications of synchrotron radiation to study thin film growth. To start, the X ray reflectivity measured in antiphase Bragg scattering will be described and several examples on metal epitaxy involving the effect of imperfections and surfactants will be shown. The evolution of the specular and diffuse scattering will be discussed. Recent pioneering experiments using transversally coherent beams will be presented as an example of possible future applications.

Lattice strain and relaxations during growth will be described and examples of the use of GISAXS to visualize the shape of metallic islands in metal growth on oxide substrates will be presented.

Characterization Capabilities for Atomic Layer Deposition at the National Synchrotron Light Source II

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Driven by the needs of sub-15nm integrated chip design, power electronics, and energy conversion devices, a wide range of coating and etching processes are in development which allow single layer growth or removal controlled by complex chemical processes on the substrate and/or in the gas phase resulting in self-limiting growth/etching approaches. The invention of new processes for conventional and spatial Atomic Layer Deposition (ALD) is one of the most prominent applications; even if it has a potentially high impact on the technology, used by everybody in future, it faces the challenge of an enormously large parameter space and costly and lengthy experiments developing the various precursor compounds. A theory inspired approach, combining combinatorial methods with computational modeling, may significantly reduce the risks and costs of the development process; however, to connect both approaches, an in-situ characterization tool will be required characterizing structure, and chemistry of the surface compounds, the gas and the film itself. X-ray spectroscopic may be this technique which provides chemical and structural sensitivity under complex reaction conditions.

The Inner Shell Spectroscopy (ISS) beamline at NSLS-II at Brookhaven National Laboratory is a high flux hard x-ray spectroscopy beamline, which is optimized for in-situ and operando experiments in the area of catalysis and materials growth. A high flux, fast scanning spectroscopy beamline is combined with a sophisticated gas handling system (GSH) which allow fast switching rates of gas streams in the second and sub-second range. The integration of the GSH into the safety and controls system of the beamline allows to operate with a wide range of toxic, flammable, oxidizing, and pyrophoric materials including four liquid sources. In future, corrosive gases can be implemented.

A wide range of detection systems, like silicon drift diodes combined with soller slits, von Hamos, and spherical backscattering analyzers can be simultaneously used and combined either with a double, or four-crystal monochromator system. With scan rates of up to 20Hz and the capability to cross the full energy range from 4.9-36keV in less than 10s, all modern spectroscopic tools, like XAFS, EXAFS, RIXS, energy loss spectroscopy, and valence band emission spectroscopy can be applied on time scales relevant to the ALD community.

The provided sample handling system allows preparation of the substrate in a glove box and the transport of the system in a sample transfer system (vacuum suitcase). A sample robot will load one of ten samples into the sample chamber. During the processing of the sample inside the probe chamber 8 electric connections and 3 gas lines (2 feed lines and one vent-line) will ensure the processing and monitoring.

In the talk we will present an overview and discuss the capabilities on selected thought-experiments.

Gas-Source MBE Growth of 2D Materials Examined using Synchrotron Radiation

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Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. A number of these TMDs are semiconductors in their native (bulk) state, and they possess many of the beneficial attributes of graphene, while not retaining many of the potential challenges. Some of the most important challenges concerning TMDs involve exploring the potential composition and microstructural phase spaces. Graphene was "invented" or "discovered" by exfoliation, which was sufficient initially for numerous fundamental investigations. For true technological impact to occur, however, the material needs to be grown via some thin film technique, modified (e.g., doped) and patterned. These challenges are significant in the case of graphene. TMDs need to overcome these same challenges, both to investigate new fundamental phenomena associated with new compositions and microstructures, as well as solve issues with growth, modification, and patterning that will be essential for nearly all technological applications.

Recently, we have demonstrated the gas-source MBE growth of thin films of WSe_2 using $W(CO)_6$ and elemental Se, and monitored the process in situ and in real time with X-ray synchrotron radiation. We use an ultrahigh vacuum chamber that is fitted with Be windows at G-line at the Cornell High Energy Synchrotron Source (CHESS). At present, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of $W(CO)_6$ in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence. In this initial work, we examined growth for a variety of conditions: growth with coincident fluxes of $W(CO)_6$ and Se, and growth in which one of the two reactant fluxes was gated. These experiments were conducted at different substrate temperatures on graphite (HOPG) and on so-called epitaxial graphene (on SiC). For continuous exposure to $W(CO)_6$ and Se we observe, after a short incubation period, continuous growth of both the W and Se intensities. Analysis of this data indicates a stoichiometry consistent with WSe_2. We also find diffraction features consistent with the crystalline phase of WSe_2, where the basal plane is in the plane of the substrate. Particularly interesting is what we see when one of the reactants is gated: growth is halted by gating the incident flux of $W(CO)_6$, while the film is stable in the presence of a flux of Se. The physical properties of these thin films are essentially the same as those grown using continuous exposure to both reactants. We find a different result if the flux of Se is gated: the absence of Se, but the presence of $W(CO)_6$, leads to loss of Se, and an increase of W. Since the termination of both fluxes does not lead to the loss of either element, it must be that $W(CO)_6$ is providing the species that leads to the loss of Se. The most likely scenario is that a ligand exchange reaction occurs producing the gas phase species, SeCO(g). Perhaps our most exciting result involves the growth of WSe_2 on epitaxial graphene. There, in addition to measuring the X-ray fluorescence, we also measured in situ and in real time the intensity at the anti-Bragg condition, which we have shown to be are very effective way to monitor thin film crystal growth [1]. We observe strong and sustained oscillations, indicating layer-by-layer growth of WSe_2 of up to at least 5 monolayers. This is a very exciting result, and it indicates that we can employ synchrotron radiation effectively to examine the growth of TMD thin films.

[1] See, e.g., A. R. Woll, T. V. Desai and J. R. Engstrom, Quantitative modeling of in situ x-ray reflectivity during organic molecule thin film growth, Phys. Rev. B 84, 075479/1-14 (2011).

Speciation Depth-profiling of Nano-structured Specimen by combined GIXRF-NEXAFS

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An important challenge of modern material science is the depth-sensitive and nondestructive analysis of the chemical binding state of complex structures consisting of multiple thin layers. In general, the correlation of the material functionality and underlying chemical and physical properties is the key question in view of directed device development, performance, and quality control.

Here, we would like to demonstrate that the combined method grazing incidence X-ray fluorescence analysis (GIXRF) and near edge X-ray absorption fine structure spectroscopy (NEXAFS) can significantly contribute to the nondestructive chemical analysis of buried thin films, interface structures [1], and multilayered nanoscaled thin film structures [2] regarding chemical speciation. Measurement strategies adapted to nanoscaled samples enable a depth-resolved analysis of multilayered nanoscaled thin film structures. Additionally, the use of calibrated instrumentation and the reference-free XRF approach strongly support the development of such complex measurements strategies.

By means of appropriate model systems, the methodology has been developed and successfully validated. The first model systems consist of a carbon cap layer, two titanium layers differing in their oxidation states and separated by a thin carbon layer, and a silicon substrate covered with molybdenum and a carbon layer. The other one consists of a silicon substrate, a physically vapor deposited Ni metal layer, and, on top, a chemically vapor deposited $B_xC_yN_z$ light element layer.

One may expect that the procedure has to be adapted for every class of samples in view to use this technique as a reference measurement technique for validation.

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[2] B. Pollakowski et al. *Anal. Chem.* 2015, 87, 10117-10124

Production and Tailoring of Etched Ion-Track Nanopores and Nanotubes by ALD

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Synthetic nanopores and nanotubes attract wide attention due to possible applications in the fields of nanofluidics, filtration, catalysis, and sensorics. Tailoring of single nanopores with nanometric diameters enables the mimicking of ion channels in biological cell membranes. Also, synthetic single-pore membranes have great potential as single-molecule sensors and devices for molecular recognition.

At the GSI Helmholtz Center in Darmstadt, polymer foils are irradiated with MeV - GeV heavy ions. The irradiation conditions can be adjusted to vary the ion density between one single ion per sample up to ~10^{10} ions/cm^2 [1]. By chemical etching each ion track is selectively dissolved and enlarged into a nanopore with well-controlled diameter. Atomic layer deposition (ALD) is applied for conformal modification of the pore surface and tailored decrease of the pore diameter to a few nanometers.

In this work, 30 µm thick polycarbonate membranes were employed to produce series of single- and multi-pore membranes with various pore diameters between 18 and 55 nm. After surface modification by ALD, homogeneity, conformity, and composition of the coatings (SiO_2, Al_2O_3 and TiO_2) inside the nanopores were investigated. Small angle x-ray scattering before and after ALD showed conformal coating along the full pore length. X-ray photoelectron spectroscopy evidenced nearly stoichiometric composition of the different coatings. By wet-chemical methods, the ALD-deposited films were released from the supporting polymer templates providing 30 µm long self-supporting nanotubes with walls as thin as 5 nm. Electrolytic ion-conductance measurements provided proof-of-concept that combining ALD coating with ion-track nanotechnology offers promising perspectives for single-pore applications by controlled shrinking of an oversized pore to a preferred smaller diameter and fine-tuning of the chemical and physical nature of the inner channel surface [2].

[1] M.E. Toimil-Molares, *Beilstein J Nanotechnol* 2012**,** *3*, 860-83, DOI:10.3762/bjnano.3.97
[2] A. Spende et al. *Nanotechnology* 2015, *26*(33), 335301, DOI:10.1088/0957-4484/26/33/335301

Bulk Heterojunction Electrodes Based on CNT fibre/ZnO Hybrids Produced by ALD

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This work shows the production and structure of bulk heterojunctions of macroscopic fibres of CNTs and semiconducting metal oxides. The macroscopic CNT fibre is produced by drawing an aerogel of CNTs directly from the gas-phased during their growth by catalyst floating CVD. Around 500m of fibre are collected as a unidirectional non-woven array. This fibre structure, shown in Figure 1 a), is similar to that of a yarn but unprecedented in a high-performance fibre. It consists of a network of nanotubes aggregated in bundles (crystals) but leading to a large porosity (250m2/g [2]) spanning from the meso to macro-range. This porous materials has high electrical conductivity [2] and high tensile strength [2] and modulus [2], and is this an ideal current collectors for a variety of multifunctional electrodes [3], such as in light-weight energy harvesting and storage applications.

The hybridisation process is carried out by ALD of ZnO onto the conductive CNT fibre array [4]. The resulting structure consists of a bulk heterojunction as a result of the conformal growth of ZnO, as shown in Figure 1 b). The growth mechanism and preferential orientation of the oxide have been studied by SAXS/WAXS at BL11-NCD ALBA synchrotron. Moreover, preliminary in-situ synchrotron electrochemistry results are presented showing the important changes of the structure during electrochemical processes (i.e. energy storage applications).

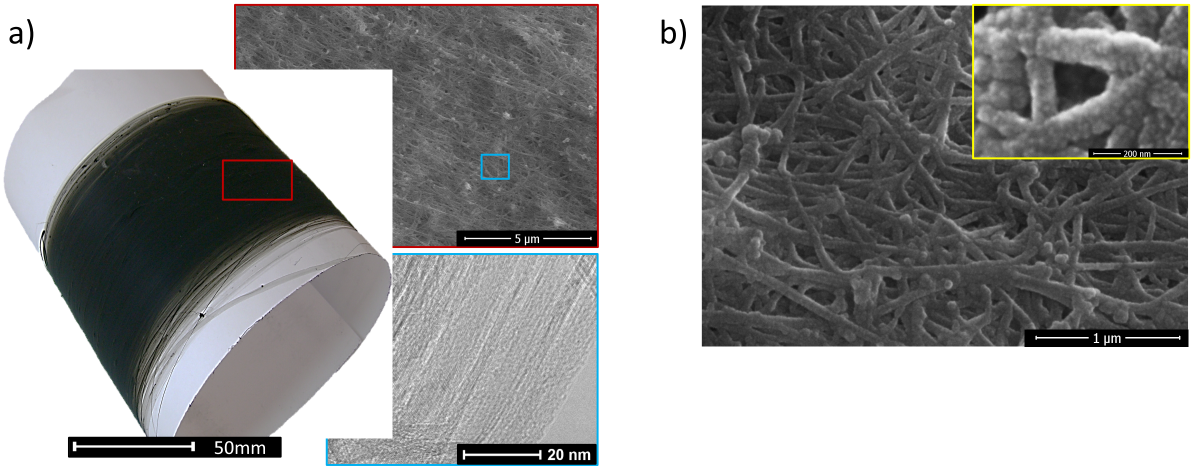

Figure 1: CNT fibre hierarchized structure before a) and after b) ZnO ALD.

[1] V. Reguero et al. *Chem. Mater.* 2014, 26, 3550-3557, DOI: 10.1021/cm501187x
[2] E. Senokos et al. *Nanoscale,* 2016, 8, 3620-3628, DOI: 10.1039/c5nr07697h
[3] J.J. Vilatela, et al. *Chem. Mater.* 2015, 27(20), 6901-6917, DOI: 10.1021/acs.chemmater.5b02783
[4] N. Kemnade et al. *Nanoscale.* 2015, 7, 3028-3034, DOI: 10.1039/C4NR04615C

Investigation of Si-doped HfO_2 ALD films by means of EXAFS and XANES

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In this contribution, we show the characterization of Si-doped HfO_2 films by means of Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Spectroscopy (XANES). Following the first reports of ferroelectric properties in HfO_2 in 2011 [1], this new class of ferroelectrics has been attracting considerable interest in both fundamental and application oriented research. As recently recognized by the International Technology Roadmap for Semiconductors, ferroelectric hafnia is also a promising candidate to overcome integration and scaling issues associated with conventional ferroelectrics [2].

Metal-insulator-metal (MIM) capacitors were fabricated on Si substrates. TiN top and bottom electrodes were reactively sputtered at 250 °C. The 30 nm thick Si:HfO_2 films were deposited by atomic layer deposition (ALD) at 280 °C. Their Si content was determined by varying the ratio of SiO_2 (silanediamine, N,N,N',N'-tetraethyl / O_2 plasma) and HfO_2 subcycles (tetrakis-(ethylmethylamino)hafnium / H_2O) within the supercycles. After a crystallization anneal of 10 min in N_2 ambient, a 10 nm thick Ti adhesion layer and about 50 nm Pt were evaporated through a shadow mask to form circular contact pads for subsequent electrical characterization. These pads also served as hard mask during wet chemical removal of the exposed TiN by a solution of NH_4OH and H_2O_2.

Two series of samples were studied: Series 1 consisted of samples with fixed Si content of 4 cat% subjected to different annealing temperature from 550 °C to 800 °C. For series 2, the Si content was varied between 2 cat% and 7.3 cat% with fixed anneal conditions of 800 °C.

The XAS measurements were performed at the CLÆSS beamline of the ALBA CELLS synchrotron at room temperature. The white radiation beam obtained from a wiggler was monochromatized using a double crystal Si(111) monochromator. Higher harmonic contributions to the selected energies were rejected by the incidence angles and by the coatings of the collimating and focusing mirrors. The results were analyzed in order to determine the distinct roles of annealing temperature and Si content. The change of Si doping was found to have a strong influence on the structural and electronic properties of the samples. The spectroscopic differences correlate with the different electrical behavior. The derived structural changes of the crystal phase correspond to the anticipated evolution of the dielectric behavior from paraelectric via ferroelectric and antiferroelectric to, again, paraelectric.

[1] T.S. Böscke et al. *Appl. Phys. Lett.* 2011, 99, 102903, DOI: 10.1063/1.3634052
[2] International Technology Roadmap for Semiconductors − Emerging Research Devices, http://www.itrs.net/Links/2013ITRS/2013Chapters/2013ERD.pdf (accessed Sept. 28, 2014)

SAXS Investigation of Nano-Pore Membranes Coated By Atomic Layer Deposition

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Irradiation with high energy heavy ions and subsequent chemical etching can be used to form highly uniform nano-porous membranes in a variety of materials, including polymers like polycarbonate, PET and polyimide, and in solid state materials such as silicon dioxide (SiO_2) and silicon nitride (Si_3N_4). The pore radius can vary from several nanometres to around one hundred nanometres, with pore lengths up to 30µm or more. The ion track etching technique is a highly controllable and industrially compatible process that can be further tailored to functionalize the pores for specific applications using atomic layer deposition (ALD). ALD is the most desirable deposition technique for these high aspect ratio structures, as very thin and uniform coatings can be achieved along the length of the pores [1].

Synchrotron based small angle x-ray scattering (SAXS), in combination with advanced Monte-Carlo (MC) simulation techniques, provides an ideal method for characterisation of these complex pore structures. The etched pores can exhibit cylindrical, conical or double conical shapes, depending on the etching conditions and supporting membrane matrix material. Compared to cross-sectional transmission and scanning electron microscopy, SAXS in combination with MC simulations enables a more accurate reconstruction of the size and shape of the pores as well as providing the opportunity to leverage superior statistics, since a large number of pores may be measured simultaneously. SAXS also allows us to extract information on the morphology of the entire length of the pores. This is essential information for the development and application of the membrane technology.

We are currently developing the technology for controlled fabrication of nano-pore membranes in 0.5-2 µm thin SiO_2 and Si_3N_4 layers, however the ion track etching technique has been more extensively used to fabricate porous membranes in polymers such as polycarbonate, PET and polyimide [2]. SAXS analysis of several ALD coating materials in polycarbonate membranes will be presented, along with initial SAXS results of ALD coated pores in SiO_2 and Si_3N_4 membranes.

[1] A. Spende et al., TiO_2, SiO_2, and Al_2O_3 coated nanopores and nanotubes produced by ALD in etched ion-track membranes for transport measurements. *Nanotechnology* **2015,** *26* (33), 335301.
[2] M. E. Toimil-Molares, Characterization and properties of micro- and nanowires of controlled size, composition, and geometry fabricated by electrodeposition and ion-track technology. *Beilstein J Nanotechnol* **2012,** *3*, 860-83

In-situ Characterization during ALD

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To explore ALD processes, in situ techniques offer the advantage that the ALD process is no longer occurring in a 'black box', but that the surface chemistry and the properties of the growing film can be monitored in real time. Over the past decade, a variety of in situ techniques have been developed and several have even become available on commercial ALD reactors. Optical techniques have proven the easiest to use in practice, as they can remotely probe the sample surface and only require an entry and exit window to pass light into and out of the reactor.

Lab-based in situ setups with spectroscopic ellipsometry and Fourier-transform infrared spectroscopy exploit the UV/Vis (using quartz windows) and IR part (using KBr windows) of the spectrum to monitor layer thickness and the presence of specific surface groups. Recently, several groups have explored expanding the spectral range towards x-rays (using Be windows), thus opening up an even wider variety of characterization possibilities [1]. The high photon flux at synchrotron facilities enables the study of layer growth from the very first ALD cycle onward, and the use of synchrotron based x-rays has broadened the available tool box of in situ methods to x-ray fluorescence (XRF, measuring film composition), x-ray absorption spectroscopy (XAS/EXAFS, measuring the local atomic environment), x-ray photoelectron spectroscopy (XPS, measuring surface composition and oxidation state), x-ray diffraction (XRD, measuring film crystallinity, grainsize), x-ray reflectivity (XRR, measuring film thickness, roughness and density), and grazing incidence small angle x-ray scattering (GISAXS, measuring surface morphology).

In this presentation, we will first briefly discuss the advantages and limitations of lab-based in situ spectroscopic ellipsometry and infrared spectroscopy during ALD. This will be followed by case studies where we have used in situ XRF and GISAXS to study the initial growth of gate oxides on Si and Ge substrates [2], to study conformal ALD growth into mesoporous films [3, 4], and to study the initial nucleation of ALD Pt layers on oxide substrates [5].

[1] K. Devloo-Casier et al. *J. Vac. Sci. Technol. A* 2014, 32, 010801, DOI: 10.1116/1.4851716
[2] K. Devloo-Casier et al. *Appl. Phys. Lett.* 2011, 98, 231905, DOI: 10.1063/1.3598433
[3] J. Dendooven et al. *J. Phys. Chem. C* 2011, 115, 6605–6610, DOI: 10.1021/jp111314b
[4] J. Dendooven et al. *Nanoscale* 2014, 6, 14991-14998, DOI: 10.1039/c4nr05049e
[5] J. Dendooven et al., presentation at the AVS-ALD conference in Kyoto, 2014

The Need for Validation of ALD Mechanisms Predicted from First Principles

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First principles calculations (such as density functional theory, DFT) are an accurate way to investigate the nature of chemical bonding at the atomic scale. Applying such calculations to the gas-surface reactions of atomic layer deposition (ALD) can give information about surface intermediates and reaction pathways, quantifying the electronic state and atomic structure of likely surface species at each stage of the ALD cycle without any fitted parameters [1].

Of course, most real systems are too complex to allow all details to be simulated at this level and so simplified models must be built to focus in on the properties of interest. Validation of the models is difficult, because few experimental techniques have sufficient resolution to directly measure these quantities at this scale. This gap in experimental validation and feedback means that model-building still relies on intuition and guesswork, and the potential power of the first principles approach is not being fully realised. There is therefore an opportunity for fruitful exchange of information between first principles simulations and high-resolution characterisation of surfaces during ALD using synchrotron radiation.

In this presentation, I give some examples of the type of atomic-scale information that can be computed from first principles, focussing in particular on the oxidation state of metal cations during adsorption/desorption and how important this is for understanding ALD mechanism. Examples of such redox reactions include 'clean-up' of native oxide from GaAs [2] surfaces and deposition of Cu metal by transmetallation. On the other hand, I will also present cases where our calculations predict weak adsorption of ALD precursors, with no change in chemical bonding at the surface layer. For all these examples, the aim is to see whether these results could be validated by high-resolution X-ray experiments.

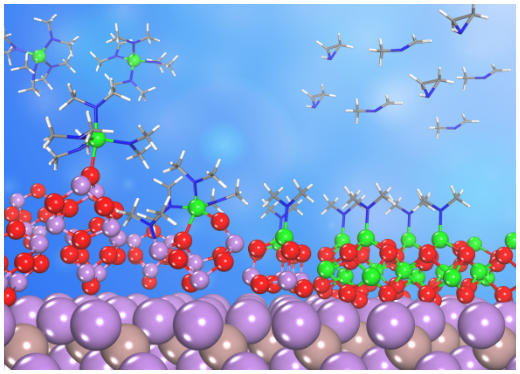

Figure 1: The mechanism of 'clean-up' by metal amides of a III-V native oxide, followed by deposition of the metal oxide.

[1] S. Elliott et al. *Adv. Mater.* 2015, DOI: 10.1002/adma.201504043
[2] S. Klejna et al. *J. Phys. Chem. C* 2012, 116, 643-654, DOI: 10.1021/jp206566y

Controlling the Ti Oxidation State in TiO_2 – An In-Line XPS Study

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Recently, TiO_2 received renewed attention in the field of photoelectrochemical (PEC) water splitting as corrosion protection layer for unstable, small-bandgap photoelectrodes [1–4]. Two approaches are being pursued for protecting photoanodes with TiO_2: (1) using thin layers (~2 nm) to enable hole transport via a tunnelling mechanism or (2) preparing TiO_2 with hole-conducting properties. In particular the hole-conducting properties of TiO_2 (also referred to as 'leaky' TiO_2) proved key towards a stable PEC device [4].

For the thin-film approach, it is of particular importance to study the nucleation behaviour on specific substrates. Although the ALD process of TiO_2 is one of the most widely studied deposition processes, only a few papers report on the initial growth [5, 6]. In this work we studied the nucleation mechanism of ALD-grown TiO_2 from $TiCl_4$ and H_2O on silicon with a 2 nm native surface oxide (which should not affect the charge transport [3]).

The film deposition and analysis are carried out in our in-line ALD reactor/ultrahigh vacuum (UHV) chamber that allows for X-ray photoelectron spectroscopy (XPS) measurements after each precursor pulse, without breaking the vacuum. This enables us to analyze the elemental composition and chemical state of each species during nucleation and subsequent film growth. While our TiO_2 process exhibited no nucleation delay, we found that especially during the nucleation phase longer precursor exposure times are necessary to reach saturated growth than the exposure times typically found from growth-per-cycle (GPC) saturation curves. Furthermore, prolonged water exposure times were found to reduce the amount of Cl impurities built in at the interface.

The resulting thin films did not provide significant protection for the Si anodes, probably due to the presence of pinholes. In addition, the thicker films (~10 nm) were found not to be hole-conducting and are therefore not suited to protect photoanodes. The origin for the hole-conducting properties of TiO_2 is not yet fully understood. A likely cause are defect states present in the bandgap formed by the presence of Ti^{3+} species [7, 8], presumably in the form of interstitial ions. We found that we can control the amount of incorporated Ti^{3+} with the deposition temperature and the purge time after the Ti-precursor step. The implications of these findings for the fabrication of TiO_2 protection layers on photoelectrodes will be discussed.

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[2] B. Seger et al., *RSC Adv.* 2013, 3, 25902, DOI: 10.1039/c3ra45966g
[3] Y. W. Chen et al., *Nat. Mater.* 2011, 10, 539–544, DOI: 10.1038/nmat3047
[4] S. Hu et al., *Science* 2014, 344, 1005–9, DOI: 10.1126/science.1251428
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[7] G. D. Wilk et al., *J. Appl. Phys.* 2001, 89, 5243–5275, DOI: 10.1063/1.1361065
[8] M. T. Mcdowell et al., *ACS Appl. Mater. Interfaces* 2015, 7, 15189–15199, DOI: 10.1021/acsami.5b00379

In Situ Study of the Morphological Stability of ALD-Grown Pt Nanoparticles During Thermal Annealing

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Atomic Layer Deposition (ALD) was used to fabricate supported noble metal nanoparticles on different surfaces with high conformality and precise control over the particle size, spacing and composition [1,2]. These supported nanoparticles are of interest for catalysis since they present a high active area. However, the harsh conditions generally required for these catalytic applications may induce particle sintering. Undesirably, the active surface area is then diminished, leading to a reduction in the catalyst activity. Multiple mechanisms including atom diffusion and particle mobility have been suggested to play a key role during the sintering process, depending on the reaction conditions and material system [3,4].

In situ studies concerning particle sintering are a matter of interest for understanding and preventing particle coarsening. Synchrotron based *in situ* Grazing Incidence Small Angle Scattering (GISAXS) was applied to study the particle morphology evolution during the thermal sintering up to 1000ºC in reducing (H_2) and oxidizing (O_2) atmospheres. ALD-grown Pt nanoparticles on different substrates, i.e. SiO_2, Al_2O_3 and MgO, were annealed and GISAXS patterns were continuously acquired. The obtained images allowed to describe the particle coarsening behavior, defining their thermal stability and sintering evolution. The “fast analysis” developed to extract particle information was corroborated by using GISAXS simulations and *ex situ* SEM, confirming the validity of the extracted data and providing valuable morphological information.

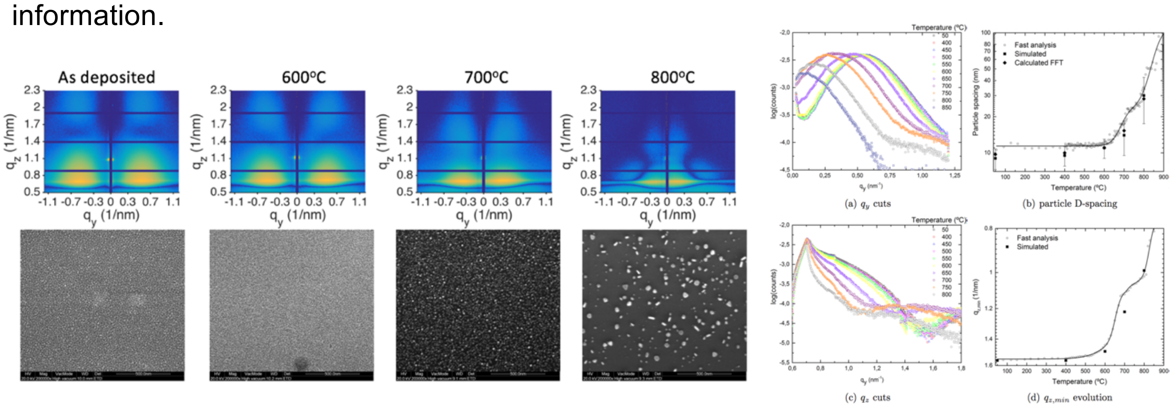

Fig. 1. A selection of in situ GISAXS images acquired during the continuous heating of ALD-Pt nanoparticles on SiO_2 annealed under O_2 20% in He atmosphere. Vertical and horizontal cuts on the GISAXS patterns were used to extract continuous information concerning the particle center-to-center (D) spacing and particle height trend during the particle annealing. Simulated GISAXS patterns and FFT images support the extracted data.

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[4] Schneider, S. et al. *Micron* **2014**, *63*, 52–56.

SR X-ray Diffraction and X-ray Absorption Fluorescence Spectroscopy Study of Er-doped HfO_2 Deposited by Atomic Layer Deposition

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Doped transition metal oxides thin films deposited by atomic layer deposition are advanced solutions that spread the properties of currently used high-*k* materials for logics to novel field of applications like capacitors for dynamic random access memories, 3D architectures based on charge trapping for NAND, ferroelectric memories, metal-insulator-metal structures for resistive memories and neuromorphic applications.

An opportune choice of the dopant and of its chemical content actually favors the stabilization of metastable polymorphs which are associated to different values of the dielectric constant and can also show different electrical behavior in term of leakage current, breakdown voltage, defect density and interfacial properties. In particular, the thermodynamic stable monoclinic structure has the lowest dielectric constant (16) which is estimated by theoretical calculation to be higher for the cubic fluorite (29) and indeed significantly higher (70) for the tetragonal polymorph [X. Zhao, D. Vanderbilt, PRB 65, 233106 (2002)].

In order to discern among the different crystallographic structures, laboratory X-ray diffraction experiment are often not sufficient. In this work, we present a systematic analysis of the effect of doping on as-deposited and 900°C annealed 5-20 nm thick Er-HfO_2. Samples were deposited by atomic layer deposition on Si(001) covered with 1 nm thick chemical oxide using $(iPrCp)_3Er$ and $(MeCp)_2HfMe(OMe)$ and O_3 at 300°C. Er percentage was within the 1.5-15% range, as evaluated by TXRF and EDS during TEM analysis. Grazing incidence X-ray diffraction and X-ray absorption fluorescence spectroscopy at the Er^{3+} edge were conducted at beamlines BM02 and BM08, respectively, at ESRF. From fitting of the experimental data, lattice parameters and interatomic distances of the first (Er-O) and second (Er-Hf) shell are extracted. Results are compared with theoretical modeling of the different crystallographic structures based on DFT.

For thickness below 5 nm this analysis evidences how crystallographic amorphous Er-HfO_2 (Er 15%) has interatomic distances compatible with those simulated for the cubic HfO_2 polymorph, and is therefore expected to show higher dielectric constant than monoclinic HfO_2. Cubic and tetragonal polymorphs are stabilized in our samples due to precise Er doping. Their structures are found to be more similar to each one than what is expected for the corresponding high temperature metastable phases.

The dielectric constants of the films have been extracted as a function of the Er% by means of capacitance-voltage measurements. Results are compared to theoretical evaluations. For samples where the cubic and tetragonal polymorphs are stabilized, the *k* value is discussed in terms of the low tetragonal distortion found in our samples.

On the Oxidation State of MnO_x – An In-Line XPS Study

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MnO_x is an interesting candidate as a catalyst for electrochemical water oxidation [1,2]. Mn is an earth abundant element, cheap and environmentally benign [3]. The catalytic activity is known from the photosystem II, where the Mn_4CaO_5 cluster plays an important role in the water oxidation process [4]. The ability of manganese to appear in different oxidation states, predominantly +3/+4, is crucial for the catalytic activity. However, up till now it remains unclear how the Mn oxidation state is changing during catalytic water splitting, and how this relates to the local environment of the manganese ions.

A promising strategy for photoelectrochemical water oxidation is to deposit MnO_x as a thin film on a semiconducting photoelectrode. This film must be thin enough to minimize parasitic optical absorption, but also thick enough to provide an adequate amount of catalytic material. To investigate the relation between film thickness and catalytic activity, we utilize atomic layer deposition (ALD) to deposit thin films of MnO_x with monolayer-precision [3,5]. Our in-line X-ray photoelectron spectroscopy (XPS) system allows us to study the oxidation state of Mn after each successive ALD half-cycle, without exposing the samples to air.

In this work we present the ALD process on our custom-built thermal ALD system using $Mn(EtCp)_2$ and H_2O as precursors. Monolayer growth control is realized, as shown by *in situ* spectroscopic ellipsometry. XPS spectra showed the as-deposited films to consist of a MnO/Mn_2O_3 mixed phase. Post-deposition heat treatment allows us to control the Mn oxidation state. The effect of the oxidation state on the catalytic activity will be discussed.

[1] A. Ramiréz et al. *J. Phys. Chem. C*, 2014, 118, 14073-14081, DOI: 0.1021/jp500939d

[2] P. Hillebrand et al. *ECS Trans.*, 2014, 61, 9-20, DOI: 0.1149/06114.0009ecst

[3] K. L. Pickrahn et al. *Adv. Energy Mater.,* 2012*,* 2, 1269-1277, DOI: 10.1002/aenm.201200230

[4] J. Yano et al *Science*, 2006, 314, 821-825, DOI: 10.1126/science.1128186

[5] B. B. Burton et al. *J. Phys. Chem. C,* 2009*,* 113, 1939-1946, **DOI:** 10.1021/jp806088m

Quantitative and Chemical Characterization Capabilities for Atomic Layer Depositions using Synchrotron-based Reference-free X-Ray Spectrometry

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Atomic layer deposition (ALD) is a widely used deposition technique, being able to deposit layers with atomic scale precision. Synchrotron-based X-ray spectrometry can contribute to the characterization of both ALD deposited layers and layer stacks or the characterization of the deposition process itself, e.g. by studying growth inhibition or island growth during the initial cycles.

At the BESSY II synchrotron laboratory of the Physikalisch-Technische Bundesanstalt, Germany’s national metrology institute, in-house built and radiometrically calibrated instrumentation [1] are employed for reference-free X-ray spectroscopy experiments.

In addition to X-ray reflectometry experiments, this allows for a reference-free quantitative analysis using the X-ray fluorescence technique. By tuning the angle between the incident X-ray beam and the sample surface to the grazing incidence regime, excellent sensitivity also for sub-monolayers or single cycle ALD can be achieved [2,3,4]. By varying the incident angle around the critical angle for total external reflection, also depth dependent information can be derived [5].

In addition, X-ray absorption fine structure analysis in the near edge (NEXAFS) and extended edge regions (EXAFS) can be conducted in order to derive chemical and structural information about ALD induced changes, e.g. to passivation layers [4] or the deposition itself.

[1] J. Lubeck et al., Rev. Sci. Instrum. 84, (2013), 045106.
[2] M. Müller et al., Materials 7(4), (2014), 3147.
[3] P. Hönicke et al., Phys. Stat. Solidi A (2015) 212(3), 523.
[4] A. Delabie et al., J. Vac. Sci. Technol. A (2012) 30, 01A127
[5] M. Müller et al., Solid State Phenomena (2013) 195, 95.

XANES and XMCD of Pure and Fe-doped ZrO_2 Thin Films grown by ALD

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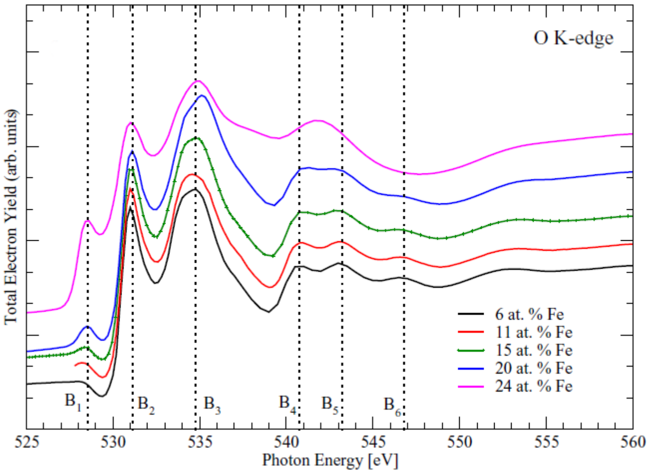
Pure ZrO_2 and ZrO_2:Fe films, with nominal thickness 20 nm, were grown from $Zr(TMHD)_4$, $Fe(THD)_3$ and O_3 in an ASM F120 reactor on SiO_2/Si substrates [1] at 350°C. Preliminary spectroscopic ellipsometry, X-ray reflectivity and X-ray diffraction at grazing incidence were performed in laboratory to check film thickness, roughness, density and crystallinity.



Further, ZrO_2:Fe system was studied with x-ray absorption near edge structure (XANES) at $L_{2,3}$, $M_{2,3}$, and K edges of, respectively, Fe, Zr, and O for different Fe dopant concentrations x (from x ~ 6% to x ~ 25% at.). Fe is uniformly distributed in the sample, as proved by TEM measurements. Experimental data were also compared with ab initio simulations at the O K-edge [2]. Substituting Zr with Fe atoms leads to a radical change in the O K-edge XANES spectrum (see Figure), especially in the pre-edge region, where a pre-edge peak appears. This pre-edge peak is ascribed to dipole transitions from O(1s) to O(2p) states that are hybridized with the unoccupied Fe(3d) states. Both theory and experiment reveal an increase of the intensity of the pre-edge peak with Fe concentration, suggesting the increase of unoccupied Fe 3d states. The increase of Fe concentration increases oxygen vacancies as required for charge neutrality. According to first-principles calculations, the effect of one Fe atom is mostly localized in the first oxygen shell and vanishes as one moves far from it.

Thus the increase of the O K-pre-edge peak with increasing Fe concentration is due to the increase of percentage of oxygen atoms that are near neighbors to Fe atoms. The x-ray magnetic circular dichroism (XMCD) measurements show no evidence of ferromagnetic (FM) order for all the analyzed samples, in agreement with ab initio simulations suggesting an antiferromagnetic (AFM) order. The increase of oxygen vacancy with Fe concentration improves AFM ordering [2,3]. Experiments using x-ray magnetic linear dichroism (XMLD) are planned to confirm ab initio predictions. Exploring the evolution of XANES structure with in-situ ALD to unravel the dynamics of Oxygen vacancies as a function of Fe concentration is foreseen.

[1] A. Lamperti at al., Thin Solid Films **533** 83 (2013)
[2] D.H. Douma et al., Phys. Rev. B **90** 205201 (2014)
[3] A. Debernardi et al., J. Appl. Phys. **115** 17D718 (2014)

Interfacial and Surface Effects during the Growth of Sb_2Te_3/Sb_2Se_3 Ternary Films and Multilayer Structures Studied by QCM *In Situ* Analysis

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The development of new synthesis techniques has led to nanostructured materials with high purity and crystallinity enabling the discovery of highly conductive topological surface states in 3D topological insulators (TI). Recently, it has been shown, that with adding a thin layer of a certain material onto the surface of a TI, the electrical properties of the topological insulating materials can be drastically modified.[1],[2] Due to its self-limiting nature and conformal coating complex even on high aspect ratio nanostructures, ALD is the method of choice especially for complex structures such as nanowires and nanotubes.

The combination of ALD growth with a quartz crystal microbalance (QCM) enables the *in situ* observation of the precursor interaction with the surface. Since ALD is based on chemical reaction of surface species with the precursor, the growth might differ significantly in the first cycles compared to the steady-state growth leading to alternated properties of the interface.

Herein, we show QCM results for interplay of Sb-, Te- and Se-precursors with Sb_2Se_3 and Sb_2Te_3 surfaces focusing on the exchange interactions at the material interfaces. We deposit a thin film on the surface of our QCM-crystal and study the evolution of sfrequency/film thickness when the QCM is exposed to different precursors. One exemplary result is shown in figure 1, in which the frequency change of the QCM is displayed whilst pulsing only $Te(SiEt_3)_2$ onto a Sb_2Se_3 surface. Since tellurium is heavier than selenium, the change in frequency can be interpreted as an exchange reaction between Se and the tellurium precursor on the solid state surface. This exchange reaction is limited by the diffusion of selenium atoms from the bulk to the surface to act there as a reaction partner with the exposing Te-precursor. Hence the slope of the frequency change per time - corresponding to pulses - decreases because of the limited diffusion speed in the solid state.

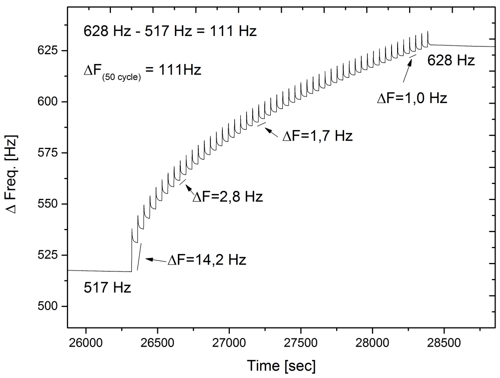

Figure 1: Change in frequency through the interactions of the tellurium precursor $Te(SiEt_3)_2$ with the Sb_2Se_3 surface.

[1] T. M. Menshchikova et al. *Nano Lett.* 2013, 13, 6064–6069, DOI: 10.1021/nl403312y
[2] Y. Zhao et al. *Scientific Reports* 2013, 3, 3060, DOI: 10.1038/srep03060

In Situ High Temperature X-Ray Scattering Studies of some Atomic Layer Deposited Layers of Metals and Metal Oxides

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Post-deposition thermal annealing is often required to achieve the final performance of the atomic layer deposited (ALD) films. As the acquired properties depend *e.g.* on the temperature and atmosphere, the possibilities for different conditions are numerous. *In situ* methods like high temperature x-ray diffraction (HTXRD) and reflectivity (HTXRR) are useful for screening suitable conditions and observing changes during the annealing. Here we present a few examples on high temperature x-ray scattering measurements conducted on ALD materials with a conventional laboratory instrument.

Noble metals and their oxides are used *e.g.* as electrical contacts or diffusion barriers in film stacks, and knowing their oxidation behaviour is essential. When heated in oxygen, structural changes in Pt, Ir, Ru and Rh films were observed in HTXRR data clearly below the oxidation temperatures obtained from the HTXRD data [1].

$LiNbO_3$ is an interesting material due to its piezoelectric, pyroelectric and photoelastic properties. It has been grown previously by first laminating lithium oxide and niobium oxide and then forming the final structure by annealing [2]. Here we have studied a bilayer of Li_2CO_3 and Nb_2O_5. According to the HTXRD, the $LiNbO_3$ phase is formed at 475 °C when heated in air. HTXRR data shows that the topmost Li_2CO_3 layer is changing already above 330 °C and a single layer is formed above 420 °C. Roughening of the surface coincides with the crystallization temperature.

Nanolaminates are an interesting group of thin film materials due to the possibility of tailoring their physical properties. Ho_2O_3-TiO_2 laminate is one example [3]. The as-deposited laminate was x-ray amorphous and crystallized above 800 °C to form $Ho_2Ti_2O_7$. However, according to HTXRR the mixing of the layers started already above 425 °C and was complete around 725 °C. This intermixing is bound to have effects on electrical and magnetic properties making HTXRR a very useful method in probing possible changes like that. Another example is a multilayer of Al_2O_3 and TiO_2. Upon heating TiO_2 starts to crystallize to anatase at 700 °C and then transforms to rutile above 780 °C. Around 900 °C Al_2O_3 crystallizes to corundum. Only rutile and corundum remain when heated to 1050 °C, and no stable aluminium titanates were formed in this case. As above, mixing of the layers starts at much lower temperature than the crystallization, in this case around 550 °C.

All these examples would benefit from smaller temperature intervals, larger angular ranges, simultaneous gathering of HTXRD and HTXRR data, and better signal to noise ratio. Synchrotrons are therefore a very attractive option.

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[2] E. Østreng et al., *J. Mater. Chem. C*, 2013, 1, 4283–4290, DOI: 10.1039/c3tc30271g
[3] K. Kukli et al., *Thin Solid Films*, 565 (2014) 165–171, DOI: 10.1016/j.tsf.2014.06.039

Live Monitoring of ALD by Ambient Pressure X-ray Photoelectron Spectroscopy

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X-ray photoelectron spectroscopy (XPS) has been used for the characterisation of thin films grown by ALD at least since the beginning of the 1980s, if not longer. With its surface sensitivity and chemical specificity the method can contribute greatly not only to providing information about surface stoichiometry, but also to identifying surface chemical species. Normally, XPS is limited to vacuum conditions and cannot contribute to the real-time monitoring of growth processes. Important information on intermediate surface species, reaction mechanisms, and growth kinetics remain hidden. Ambient pressure x-ray photoelectron spectroscopy (APXPS) is an instrumental adaptation of XPS to elevated pressures in the mbar range and higher, which allows the real-time monitoring of ALD at relevant processing pressures. While originating in the 1970s, it is only the advent of third-generation synchrotron light sources and improvement of electron energy analyser technology, which during the past 10 to 15 years have made APXPS truly viable.

In my talk I will report on the application of APXPS to the ALD (and CVD) of several oxides (TiO_2, SiO_2, and HfO_2) on semiconductor (InAs, Si) and oxide surfaces (TiO_2, RuO_2) from a metal precursor and water. The experiments allow the identification not only of expected surface species, but also of pressure-dependent side reactions and reaction intermediates [1-3] (see Fig. 1). The measurements also provide insight into growth kinetics. Hence, APXPS results in detailed information on the ALD mechanism, and the observed pressure dependence highlight the utility of APXPS in studying growth processes *in situ*. Future developments in APXPS instrumentation can be expected to further improve e.g. the proximity of the experimental to ALD/CVD reactor conditions and the time resolution, which will lead to further deepened insight in the nature of the ALD mechanism.

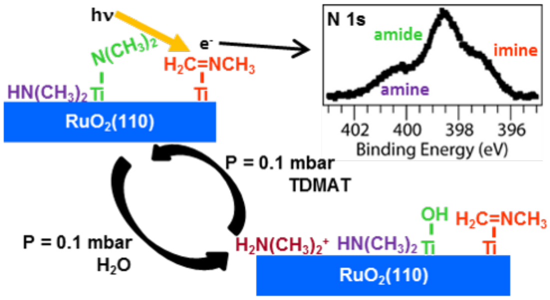

Figure 1: Illustration of the APXPS identification of side reaction products in the ALD of TiO_2 on $RuO_2(110)$ from tetrakis(dimethylamido) titanium and water.

[1] S. Chaudhary et al. *J. Phys. Chem. C* 2015, 119, 19149–19161, DOI: 10.1021/acs.jpcc.5b04985
[2] A. R. Head et al. *J. Phys. Chem. C* 2016, 120, 243–251, DOI: 10.1021/acs.jpcc.5b08699
[3] R. Timm et al., unpublished.

In Situ X-ray Studies of Crystalline Texture and Strain During the Initial Stages of ZnO Atomic Layer Deposition

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Atomic layer deposition (ALD) is unmatched in its ability to produce conformal films. Metal Organic Chemical Vapor Deposition (MOCVD) is the industry standard for producing stoichiometric compounds over large areas. A key consideration in many modern devices is the atomic structure of the heterointerface, which often ultimately governs the electronic or chemical process of interest. The structure of the deposit and its interface naturally depends on the atomic mechanisms that take place during growth, which for ALD and MOCVD, have been difficult to study due to the near-atmospheric pressure, and for MOCVD, high temperature deposition conditions.

In LMGP laboratory we optimize and use ZnO thin films and nanostructures (nanowires, nanoparticles) as building blocks for micro-electronics, optoelectronics and photovoltaic devices. We aim to understand the growth and doping mechanisms of ZnO nanostructures grown by chemical deposition techniques. For obtaining *in situ* structural and chemical information during ZnO ALD [1-3], we have built an ALD/MOCVD chamber that mounts onto the diffractometer at the beamlines SIRIUS (SOLEIL) and ID3 (ESRF).

Here, we report on the chemical and structural evolutions during the initial ZnO ALD by using a complementary suite of *in situ* synchrotron X-ray techniques: grazing-incidence diffraction, absorption, fluorescence and small angle scattering. We compare ZnO growth behavior on three different types of substrate, Si(001) with its native oxide (a-SiO_2), c-Al_2O_3 and $In_{0.47}Ga_{0.53}As$, focusing our studies on the first cycles of deposition [4]. We find that the growth behavior and crystalline texture depend strongly on the choice of substrate. More generally, we aim to stress on the combination of *in situ* characterization techniques, i.e., synchrotron x-ray scattering and absorption, optical substrate curvature measurements and others, being a powerful approach with unique potential for obtaining real-time structural and chemical information during ALD.

[1] M. Tallarida et *al*., J. Appl. Phys. *104*, 064116 (2008)
[2] D.D. Fong et *al*., Appl. Phys. Lett. 97, 191904 (2010)
[3] J.A. Klug et *al*., Rev. Sci. Instrum. 86, 113901 (2015)
[4] R. Boichot et *al*., Chem. Mater. 28, 592 (2016)

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Aluminum Nitride Grown by Atomic Layer Epitaxy Characterized with Real-Time Grazing Incidence Small Angle X-ray Scattering

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J.K. Hite, K.F. Ludwig, and C.R. Eddy, Jr.

US Naval Research Laboratory

Aluminum nitride, gallium nitride, and indium nitride and their ternaries are used for light emitting diodes, and under continued investigation for applications in optoelectronics and efficient power switching technologies [1]. Currently, III-nitride films are primarily deposited by metalorganic chemical vapor deposition and molecular beam epitaxy. Temperatures of 900°C and higher are required to deposit high quality AlN. Research into depositing III-nitrides with atomic layer epitaxy (ALE) is ongoing because it is a fabrication friendly technique allowing lower growth temperatures [2].

AlN grown by ALE using alternating trimethylaluminum and nitrogen/hydrogen plasma pulses at 500°C has shown relatively high crystal quality, but unacceptable carbon and oxygen levels for an electronic material, so understanding film deposition mechanism is the focus of ongoing research [3]. Real-time grazing incidence small angle x-ray scattering (GISAXS) is sensitive to the change of surface features, and has been used to obtain information on the film nucleation and development for atomic layer deposited films under various growth parameters [4]. The ALE of AlN on a-plane sapphire was examined with real-time GISAXS using custom reactors designed for use at the Brookhaven National Synchrotron Light Source and the Cornell High Energy Synchrotron Source. GISAXS data of AlN grown by ALE from 350°C to 500°C was complemented with *ex situ* characterization with x-ray photoelectron spectroscopy and atomic force microscopy. The real time monitoring data provides insight into film evolution during growth (example below). Details of developing the experimental apparatus and methods as well as highlights of related work on InN growth using ALE will also be discussed.

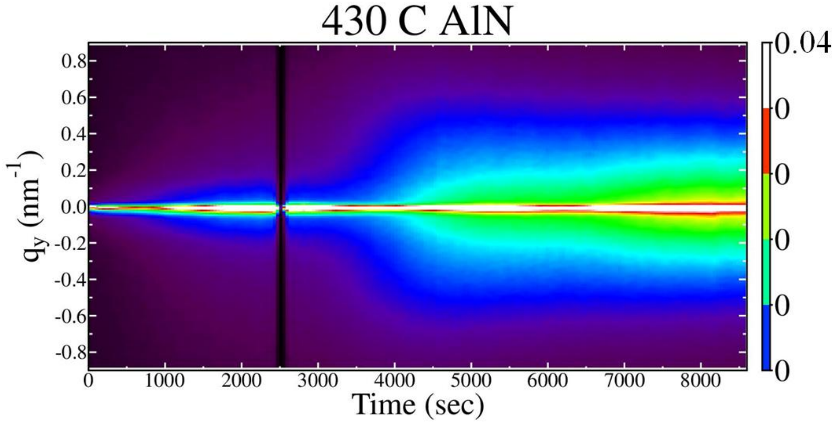

Figure: GISAXS of AlN on sapphire with 60 sec cycle times showing normalized intensity.

[1] M. Mori et al., *Appl. Phys. Express* **5** 082301 (2012)
[2] M. Bosund et al., *Appl. Surf. Sci.* **17** 7827 (2011)
[3] N. Nepal et al., *Appl. Phys. Lett.* **103** 082110 (2013)
[4] K. Devloo-Casier et al., *Appl Phys. Lett.* **98** 231905 (2011)

Near-Ambient Pressure X-ray Photoelectron Spectroscopy Study of the Atomic Layer Deposition of HfO_2 on SiO_2 / Si

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Hafnium dioxide (HfO_2)-based dielectrics are integrated as a gate oxide in field-effect transistors in current complementary metal-oxide-semiconductor technology. HfO_2 is also extensively studied as a resistive switching oxide for non-volatile memories and memristive devices. Moreover, it was recently shown that it can exhibit ferroelectric properties under peculiar processing conditions. Atomic Layer Deposition (ALD) offers unique advantages for high-k growth: conformal coverage, sub-nanometer thickness control, selectivity via substrate functionalization, etc. Previous studies have shown the key role of the starting surface and of the precursor chemistry on the ALD growth of HfO_2. Due to the relatively high working pressure during ALD growth, surface analysis techniques such as conventional XPS cannot be used to study the ongoing ALD process. Therefore, in most cases the grown films are characterized *ex situ* with no information on the very first stages of the growth.

In this work, the initial stages of the ALD growth of HfO_2 are investigated. Advantage is taken of the real-time monitoring capabilities of near-ambient pressure x-ray photoelectron spectroscopy (NAP-XPS, TEMPO, SOLEIL). Here NAP-XPS was used to follow the growth of HfO_2 on a SiO_2/Si(100) substrate from $Hf(EtMeN)_4$ and H_2O.

A delivery system was connected to the XPS chamber in order to evaporate the precursors and to introduce them in the chamber. $Hf(EtMeN)_4$ was kept at 70°C in a bubbler. High-speed diaphragm valves, capable of opening or closing time of less than 5 ms, were used. Reactive species introduced in the chamber were identified and monitored by mass spectrometry using a spectrometer mounted in the lens of the analyzer. The substrate temperature was tuned from room temperature to 750 K. For each study, we monitored the Si2p, Hf4f, O1s, N1s, and C1s core level spectra.

The measured binding energies are consistent with the growth of a HfO_2 film. Evidence for additional reactions is found. C-carboxyles appear on the surface during the H_2O introduction and purge and desorb during the $Hf(EtMeN)_4$ introduction and purge. The Hf:O ratio is close to the stoichiometric ratio after each cycle, while N contamination is found to amount to around 1-3%. C is not detected in the HfO_2 film. The effects of process conditions (chamber pressure, substrate temperature from room temperature to 750 K, and in situ post-baking) on the film growth will be discussed.

Thin, Low Roughness Ru Films Deposited by Thermal and Plasma Enhanced Atomic Layer Deposition using RuO_4 and H_2 at Low Temperatures

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Though ALD is traditionally perceived as a layer-by-layer technique, and this is true for ALD of metal oxides, a nucleation controlled growth mode is generally observed for noble metal ALD. After a certain incubation period, during which the actual nucleation takes place, growth is initiated in localized islands spread across the surface. Only in a later growth stage, the islands coalesce into a continuous layer which, depending on the density of nuclei, may have a rough surface morphology. This prevents the application of noble metal ALD in nanoelectronics as very thin, continuous and smooth metal films are required. [1]

In this work, a thermal and a plasma enhanced Ru ALD process [2, 3] were monitored by in situ grazing incidence small angle x-ray scattering (GISAXS) and x-ray fluorescence (XRF) to obtain in-depth information about the morphological evolution during the nucleation and growth. [4] In Fig 1, in situ XRF and GISAXS data are shown for experiments conducted at the SIXS beamline of the Soleil synchrotron. One can see from the XRF data that the thermal process has a large incubation period on oxide surfaces, and this period can be reduced by using the plasma enhanced process. From the GISAXS data it was derived that for PEALD Ru on oxides a nucleation controlled growth mode was observed. For thermal ALD growth on Si-H the film starts to grow as a flat layer.

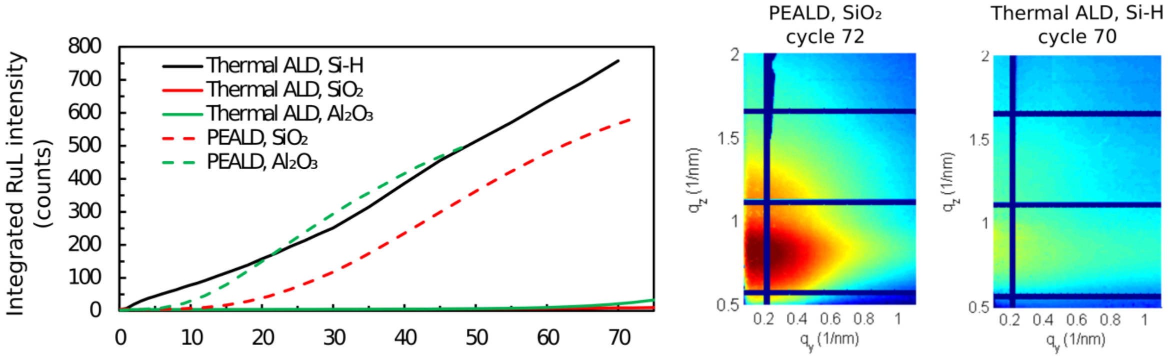

Figure 1: (Left) In situ XRF data for the thermal and plasma enhanced process on different substrates. The abbreviation Si-H stands for H-terminated Si. (Right) Selected GISAXS patterns for PEALD on SiO_2 and thermal ALD on Si-H (both have the same intensity scale).

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[3] M. M. Minjauw et. al. J. Mater. Chem. C (2015) 3, 4848. DOI: 10.1039/c5tc00751h
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An Atomistic View of the Incipient Growth of Zinc Oxide by *in-situ* X-ray Absorption Spectroscopy

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The growth of zinc oxide thin films by atomic layer deposition is believed to proceed through an embryonic step in which 3D nano-islands form and then coalesce to trigger a layer-by-layer growth mode [1]. This transient initial state is characterized by a poorly ordered atomic structure, which may be inaccessible by x-ray diffraction techniques. X-ray absorption spectroscopy is sensitive to short-range order and can probe atomic bonding and local site symmetry even in absence of a crystal structure.

In this work, we apply x-ray absorption spectroscopy *in situ* to address the local structure of Zn in ZnO after each atomic layer deposition cycle, using a custom-built reactor mounted at the SIRIUS beamline of synchrotron SOLEIL, and we shed light on the atomistic mechanisms taking place during the first stages of the growth. We find that such mechanisms are surprisingly different comparing the growth on amorphous (silica) and crystalline (sapphire) substrate. *Ab initio* simulations of x-ray absorption near-edge structure spectroscopy (XANES) and quantitative analysis of extended x-ray absorption fine structure spectroscopy (EXAFS) data allow the formulation of a comprehensive growth model, based on the different effects of surface atoms and grain boundaries in the nanoscale islands, and the consequent induced local disorder [2]. Other models, based on oxygen vacancies, bonding to substrate atoms or local strain have been tested and discarded via a comparison between experimental data and calculations.

From a comparison of these spectroscopy results with the x-ray diffraction ones taken on the same samples and reported very recently [3], we observe that the final structure of the zinc oxide nano-layers depends strongly on the mechanisms taking place during the initial stages of growth. The approach followed here for the case of zinc oxide will be of general interest for characterizing and optimizing the growth and properties of more complex nanostructures.

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In Situ Synchrotron-based XRF and GISAXS Study of ALD Encapsulation of Supported Nanocrystals

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Colloidal semiconductor nanocrystals or quantum dots (QDs) are actively investigated for applications in opto-electronic devices such as light emitting diodes, amplifiers or lasers and photovoltaic cells. For many applications, QDs need to be embedded in a solid matrix, either to reduce degradation or to allow efficient injection or extraction of electron-hole pairs.

Here, we study the encapsulation of CdSe/CdS/ZnS core/shell/shell QDs in a ZnO matrix. The ≈ 6 nm QDs are terminated by oleic acid ligands, enabling Langmuir-Blodgett deposition of a hexagonally ordered monolayer on a silicon support. By using *in situ* x-ray fluorescence (XRF) and grazing incidence small angle x-ray scattering (GISAXS) at the NSLS synchrotron of Brookhaven National Laboratory, we show the inhibition of ZnO growth on as-deposited QDs. Previous studies, however, have shown that it is possible to use thermal ALD of Al_2O_3 to encapsulate similar QDs [1]. Therefore, a pretreatment of the QDs with a single pulse of trimethylaluminium vapor is used to trigger the ZnO growth. This pretreatment however comes with an Al-for-Zn cation exchange at the QD surface, involving the conversion of approximately one third of the original ZnS shell and leading to a reduction by half of the photo-luminescence quantum yield. Additionally, analysis of the evolution of the GISAXS pattern during ALD shows that the QD ordering in the monolayer is not affected by ZnO coating. These results illustrate the important interplay between highly reactive ALD precursors and the QD surface.

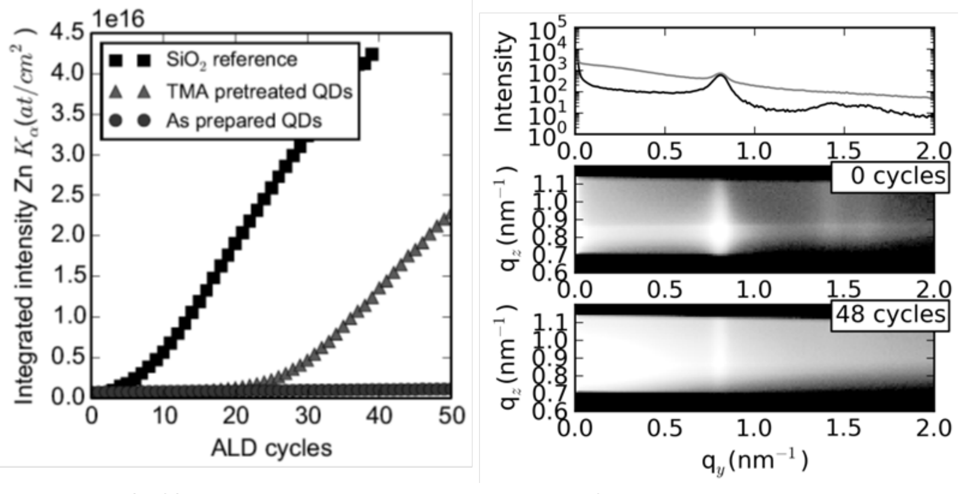

Figure 1: (left) The integrated XRF intensity of the Zn Kα line indicating the amount of deposited ZnO during the encapsulation process. The growth on SiO_2 is added as a reference. (right) Gisaxs pattern before and after 48 ALD cycles of ZnO growth and TMA treatment, showing the conservation of order during encapsulation.

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POSTERS

Thorsten Cottre, Andreas Hajduk, Technical University Darmstadt, Germany
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BOREAS: Polarization-dependent Soft X-ray Absorption and Resonant Scattering Beamline

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Monitoring of Atomic Layer Deposition by Infrared Spectroscopy

ALD of Titanium Dioxide Films Used as Protective Coatings for Photoelectrochemical Cells

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Solar-driven hydrogen production via water splitting offers the possibility to convert solar energy directly into a chemical fuel and is therefore a promising candidate for a sustainable energy solution in the future. The so far highest reported solar-to-hydrogen conversion efficiencies are achieved by photoelectrochemical cells using tandem solar cell as photoelectrodes. Nevertheless, the semiconductors used in these tandem structures, like silicon and III–V semiconductors, easily corrode under operating conditions. This presents a major obstacle for their use as efficient and stable photoelectrodes for water splitting.

In this study we used atomic layer deposition (ALD) to produce thin titanium dioxide films as protective coatings for tandem solar cells. The precursors used for the ALD process were titanium tetrachloride and water. The films were deposited in a self-built ALD reactor, which is part of an integrated system for surface preparation and analysis. For the optimization of the ALD process in-situ X-ray photoelectron spectroscopy (XPS) measurements were combined with ex-situ ellipsometry measurements. To characterize the film morphology scanning electron microscopy (SEM) was used. The effectiveness and stability of the titanium dioxide protective layers was investigated via electrochemical methods.

Our measurements show that the produced ALD titanium dioxide passivation layers possess a high stability in 0.1 M KOH solution. Furthermore, the ALD passivation layers do not decrease the efficiency of silicon thin-film tandem solar cells significantly and are thus suitable protective coatings for photoelectrochemical cells.

In addition to the measurement techniques outlined above synchrotron radiation photoemission spectroscopy (SXPS) measurements were carried out. In these experiments clean $GaInP_2$ surfaces were exposed to acidic and alkaline aqueous solutions to study their stability in electrolytes that are used for water splitting. The results from the SXPS measurements show that clean $GaInP_2$ surfaces are not stable in aqueous solutions even for a short period of time. Therefore, protective coatings to passivate the $GaInP_2$ surface without altering the semiconductor's electronic properties are needed. To this end, titanium dioxide coatings on $GaInP_2$ deposited by ALD should be investigated in further synchrotron radiation experiments. These future studies will focus on the $GaInP_2/TiO_2$ interface as well as on the TiO_2/electrolyte interface.

In Situ GISAXS Characterization of ALD in Mesoporous Thin Films

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Mesoporous materials are of interest to a broad range of applications such as the development of optical, electronic and sensor devices, and catalytic surfaces. For many of these applications, the interior surface of the porous material needs to be functionalized. ALD has become an attractive technique for tailoring porous materials because of its ability to produce conformal coatings [1]. We present a synchrotron-based *in situ* study of TiO_2 ALD in mesoporous thin films using grazing incidence small angle x-ray scattering (GISAXS).

GISAXS is a powerful technique for the morphological characterization of nanoscopic features (particles, pores, granules) at surfaces, at buried interfaces or in thin films. In the case of mesoporous thin films, the technique can reveal information on the ordering and spacing of the pores. A GISAXS experiment consists of measuring the diffuse scattering around the specularly reflected beam at a fixed incident angle. A typical dynamical feature of diffuse scattering is the Yoneda peak, i.e., an enhancement of the scattered intensity at the exit angle which equals the critical angle of the scattering medium.

Fig. 1 shows the GISAXS spectrum measured on the uncoated titania film containing ink-bottle shaped mesopores with ~3 nm wide pore necks. The interference pattern revealed an anisotropic pore structure in the film, in accordance with an electron tomography study of the porous film. During ALD of TiO_2 in the mesopore network, the critical angle of the material was probed *in situ* using GISAXS (Fig. 2). During the first ca. 24 ALD cycles, the critical angle, which is proportional to the square root of the average electron density of the mesoporous thin film, increased gradually, indicating film densification. Thereafter, the critical angle remained constant, meaning that the density of the film no longer changed. This result is in agreement with *in situ* XRF data showing the amount of Ti atoms deposited in the film [2]. This work demonstrates that both XRF and GISAXS are suitable for *in situ* monitoring the filling of mesoporous thin films by ALD [3].

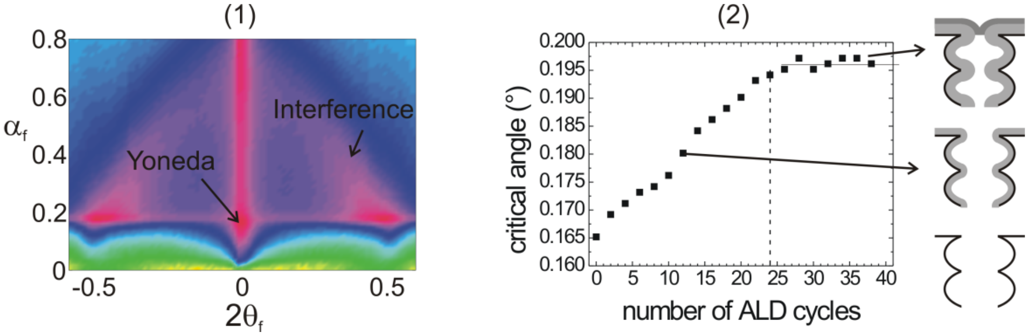

Figure (1) GISAXS spectrum measured on a mesoporous titania film. (2) Evolution of the critical angle of a mesoporous titania film during TiO_2 ALD, as measured by in situ GISAXS.

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Near Ambient Pressure Photoemission at the ALBA Synchrotron

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CIRCE is a soft X-ray beamline with two end stations in different branches, dedicated to Photoemission Electron Microscopy (PEEM) and Near Ambient Pressure Photoemission (NAPP).

The NAPP is based on X-ray Photoelectron Spectroscopy (XPS), a technique to probe the chemical composition and the electronic state of surfaces of materials. Because of the vacuum requirements of the detectors used and the strong interaction of photoemitted electrons with gases and liquids, XPS has been traditionally performed under high or ultra-high vacuum conditions. This restriction was overcome by Salmeron and Schlögl groups who develop a differentially pumped electron energy analyzer with electrostatic lenses, now available commercially, that allows to extend the standard UHV XPS technique to sample pressures up to the milibar range [1] and thus to study the occupied and unoccupied electronic structure of solid-gas and liquid-gas interfaces. The surface reactivity and structure in more realistic environments can reveal dramatic differences with respect to traditional solid-vacuum studies. The possibility to get information in situ during the reactions or processes of interest has a great impact in heterogeneous catalysis, fuel cells, photovoltaics, batteries, corrosion, biological systems and many other fields.

The NAPP capabilities [2] will be described and illustrated with some examples of recent research studies and the first published results related to catalytic studies on the Ethanol Steam Reforming (ESR) reaction [3].

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The Use of Metals Deposited by Atomic Layer Deposition for 3D Microelectronic Devices

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The ever-evolving information technology is based upon a single simple concept: device scaling. New technologies have been steadily developed in order to enable this continuous scaling process from 100 micron long devices about 60 years ago to about 10 nm long device today.

PVD and CVD have been commonly used for thin films deposition up until now. These techniques, although thoroughly studied, have several drawbacks which make them less applicable for 3D semiconductor device. Among the problems associated with these methods is the lack in the ability to deposit conformal, uniform and thickness-controlled thin films in addition to shadowing problems (associated only with PVD).

On the contrary, atomic layer deposition (ALD) and specifically plasma assisted ALD (PEALD), are known and being utilized for the deposition of highly uniform, conformal ultra-thin films due to their self-controlled nature. Hence, these techniques have become more favorable in the semiconductors industry over the years, offering a broad spectrum of possible materials to deposit including various metals.

The integration of ALD metallic films in a Field Effect Transistor structures a critical issue for the fabrication of the next generation of electronic devices – 3D structure Field Effect Transistors (3D FET), e.g. multi-gate and *gate-all-around* nanowire FETs. In compare to the planar devices, 3D FETs allow a better electrostatic gate over channel control relative to the planar devices, which improves the device gate controllability, reduces the short-channel effects, sub-threshold characteristics and drain leakage current. Therefore 3D FET devices are introduced in the most advanced Si devices and are certainly considered as the next step in the evolution of electronic device integration circuits technology. The introduction of 3D FET devices and high mobility semiconductors (InGaAs and Ge) is expected to provide the additional scaling of the Complementary Metal Oxide Semiconductor (CMOS) technology mainly for digital electronic applications. In high power electronics, the use of 3D FET technology allows to obtain the highly required normally-off AlGaN/GaN High Electron Mobility Transistors (HEMT) at nano-scaled gate dimensions. The particular choice of the metal is of great importance in Schottky gate devices as well as in insulated gate devices. Both Schottky gate devices and insulated gate devices are reported within the GaN technology, whereas only insulated gate devices are feasible using the InGaAs material for high-speed applications. In this light, ALD metallization should be developed for both gate and Ohmic contacts, for both types of devices/semiconductors.

Here we will present some of our preliminary results for the deposition of nickel and platinum metals by atomic layer deposition, which will be used in the future as a proof of concept for selective metallization as part of 3D semiconductor devices fabrication.

The Non-Crystalline Diffraction Beamline at ALBA

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Small Angle X-ray Scattering (SAXS) experiments provide structural and dynamic information of large molecular assemblies like polymers, colloids, proteins and fibres. A wide range of fields (medicine, biology, chemistry, physics, archaeological, environmental and conservation sciences and materials) can be covered by this technique. SAXS is a very powerful technique that is used to study the supramolecular organization in biological systems, the structure and function of muscle filaments, corneal transparency, biological membranes, polymer processing, self-assembly of mesoscopic metal particles, colloids, inorganic aggregates, liquid crystals and devices.

Recording simultaneously SAXS and WAXS (Wide Angle X-ray Scattering) results in a length scale which ranges from a few microns to a few angstroms.

Phase Transitions in Compositionally Graded Ferroelectric Superlattices

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Elastic strains in thin films and artificial superlattices composed of alternating layers of ferroelectric compounds provide a new route to enhance the properties of known ferroelectrics and create materials with superior properties for device applications.

The series of ferroelectric $BaTiO_3/Ba_{1-x}Sr_xTiO_3$ (BT/BST-x) superlattices deposited on (001)MgO substrate using a pulsed laser deposition technique. The lattice parameters of the alternating layers and orientation relationships between the layers and the substrate were determined by X-ray diffraction.

Near- and sub-Terahertz dynamics of soft and Debye-type central modes was studied by the polarized Raman spectroscopy in the BT/BST-x superlattices in the temperature range of 80-500 K where system undergoes the following sequences of phase transitions: paraelectric-tetragonal-monoclinic in BT layers and paraelectric-orthorombic-monoclinic in BST-x layers. Due to relatively large periodicity the stress gradients exist in these BT/BST-x superlattices in the direction normal to the substrate and the phase transitions in alternating BT and BST-x layers occur at different temperatures and depend on chemical composition of the BST-x layers. It was shown that temperature evolution of the low-frequency Raman spectra can be described within the model of coexisting damped harmonic oscillator and Debye relaxator.

The occurrence of the pronounced central mode can explain the recently observed relaxor-like dielectric anomalies in BT/BST-x superlattices. We demonstrate that variation of chemical composition of the BST-x layers allows to tune distortions in alternating layers and to modify the shape of the dielectric permittivity as a function of temperature.

This study was supported by the Russian Science Foundation (grant N 14-12-00258).

CLÆSS: the Core Level Absorption & Emission Spectroscopies Beamline at ALBA

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X-ray absorption spectroscopy (XAS) is an element selective local probe to access to the structure and electronic properties of the matter, in all its forms: crystals, glasses or amorphous, liquids, and gases.

This is a pure synchrotron technique, not accessible in research laboratories, due to its intrinsic necessity to tune constantly the incoming photon energy as well as the required high photon flux. Due to its intrinsic versatility, this technique attracts a large and growing community of users comprising environmentalists, electrochemists, biologists, material and catalysis scientists, etc.

CLÆSS is the general-purpose absorption spectroscopy beamline at the ALBA CELLS Spanish synchrotron. Its optical layout is presented here along with its powerful capabilities for collecting absorption spectra with high signal to noise ratio in a unusually wide energy range (2.4 - 63.2 keV). Continuous energy scanning for quick-scans are available below 30 keV, allowing collecting x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectra in 3-5 and 8-10 min respectively.

The fully automation of the beamline allows performing successive measurements in different conditions without attending to the beamline. The different experimental setups available to users are reported and examples of XAS measurements are presented, showing the performances of the beamline in different standard conditions.

Visualizing the Incipient Growth of ZnO Ultra-thin Films on InGaAs for Tailoring Contact Resistivity

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For tailoring non-alloyed contact resistivity on InGaAs, ZnO is one of the most performing materials. A low resistance Metal Insulator Semiconductor contact is obtained by inserting a ZnO ultra-thin film (Insulator) between the metal and the InGaAs semiconductor allowing an efficient depinning of the Fermi level.

Atomic Layer Deposition (ALD) is a suitable method for the depositing ultra-thin ZnO films on InGaAs and opens the possibility for studying ZnO film formation and growth at the initial stage. The MOON reactor (MOCVD/ALD growth of Oxides Nanostructures) is an instrument, which can be moved to the synchrotron centre for performing in situ, during growth X-ray experiments (Surface X-ray Diffraction, X-ray absorption, Grazing Incidence Small Angle Scattering, X-ray Fluorescence and Reflectivity).

We report on preliminary results obtained recently at beamline ID3 (ERSF, France). ZnO layers were deposited by ALD on $In_{0.53}Ga_{0.47}As$ substrates with di-ethyl-zinc and nitrous oxide precursors.

Two-dimensional in-plane reciprocal space maps were measured for six different samples at different growth temperatures and different numbers of ALD cycles. The $In_{0.53}Ga_{0.47}As$ HK-reciprocal space map reveals that the growing ZnO layer undergoes an amorphous to crystalline transition. We have detected a different ZnO growth behavior when the samples are glued with Ag paint and detected a noticeable X-ray beam effect when the beam is on the precursor injection.

Untangling Diffraction Contributions from Epitaxial Thin Films

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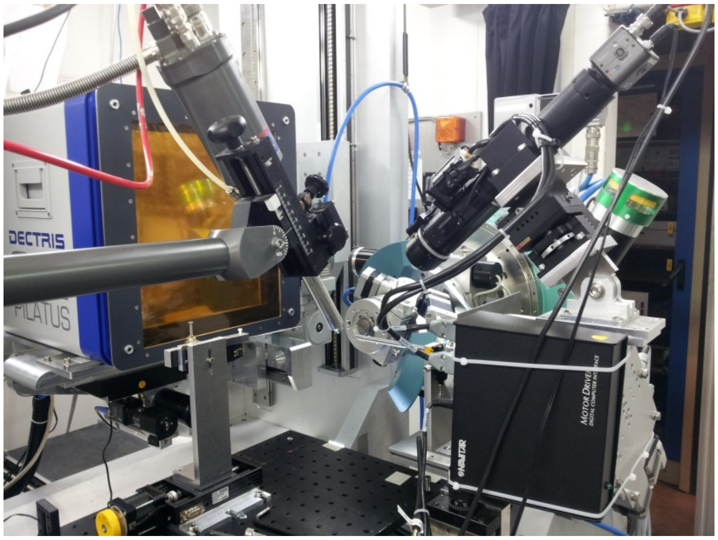
Determination of crystallographic structure of epitaxial thin films with respect to its substrate, is important for evolved understanding and continued research on films of nanoscale thickness. Tailoring functional properties is often not possible without a general understanding of growth direction, interface crystallinity and crystalline quality. Using home lab equipment, this is traditionally a time-consuming and difficult task. Depending on the crystallinity, type of material and dimensions of the films, synchrotron light is sometimes necessary to get a date set with the quality needed for understanding the crystal properties.

In cooperation with the Swiss-Norwegian Beamlines at ESRF, a setup for mapping out large parts of the reciprocal space has been constructed. The samples are aligned using a four-axis goniometer and the diffracted intensity is measured on a Dectris Pilatus detector. The high brilliance of the synchrotron light in addition to the fast acquisition times and low noise of the Pilatus detector allows for fast mapping of a large portion of the reciprocal space. The setup also includes a small furnace for *in situ* studies of crystallization, opening for new insight on the crystallization mechanisms of atomic layer deposited thin films.



Setup for thin film measurements at SNBL@ESRF.

Atomic Layer Deposited HfO_2-based Magnetic Tunnel Junctions

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Magnetic tunnel junctions (MTJs) consist of two ferromagnetic electrodes separated by a thin insulating tunnel barrier. In these devices, the tunnel magnetoresistance effect can be observed, i.e. different electrical resistance values of the tunnelling current for the parallel and antiparallel alignment of the magnetizations of the two electrodes [1]. Ever since this effect was observed at room temperature in 1995, it was used in many spintronic devices such as read heads in hard disk drives. In most cases, the required layer stacks are prepared by sputter deposition and subsequent optical/electron-beam lithography to define the tunnel junctions. However, a combination of atomic layer deposition (ALD) and sputtering would lead to new options for the preparation of MTJs. In particular, with respect to thin film quality and large-scale production, which is required for industrial applications. Here, we combined sputter deposition of the ferromagnetic Co-Fe-B electrodes and ALD preparation of the HfO_2 tunnel barrier [2]. The barrier was prepared using tetrakis (dimethylamido) hafnium and water as precursors. Prior to and after the deposition, the sample was stored for 6 h under a constant argon-hydrogen flow (200°C) to allow the removal of any oxidized surface layer at the CoFeB/HfO_2 interface that may have formed. We investigated the TMR ratio, the temperature- and bias voltage dependence and compared the junction properties with sputtered magnesia and alumina based MTJs. Figure 1 depicts the room temperature TMR ratio of a HfO_2 based tunnel junction. In addition, we studied the structural properties via high-resolution transmission electron images and observed a polycrystalline/amorphous electrode barrier system. Finally, the barrier parameters are discussed within the framework a trapezoidal tunnel barrier and the temperature and bias voltage dependence in the context of magnon and phonon excitations [3].

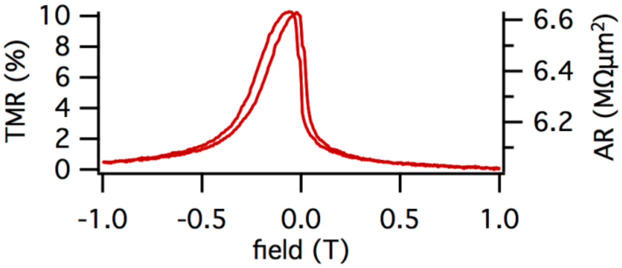

Figure 1: Tunnel magneto-resistance ratio of a HfO_2-based magnetic tunnel junction at 300K and an applied bias voltage of 10mV.

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BOREAS: Polarization-dependent Soft X-ray Absorption and Resonant Scattering Beamline

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BL29 is a soft X-ray beamline dedicated to polarization-dependent spectroscopic investigations of advanced materials of fundamental as well as applied interest.

The main techniques available at BOREAS beamline are soft-X-Ray Absorption Spectroscopy (XAS/NEXAFS), X-Ray Magnetic Circular/Linear Dichroism (XMCD/XMLD), and Soft X-ray Magnetic Resonant Scattering (SRXMS).

The beamline is equipped with two state-of-the-art end-stations: a High-field vector magnet (HECTOR) dedicated to soft-X-Ray Absorption Spectroscopy techniques NEXAFS, XMCD or XMLD with an applied magnetic field of up to 6T along the beam direction and 2T in arbitrary direction, and a UHV reflectometer (MARES) for scattering and reflection approaches including resonant soft X-ray reflectivity, resonant magnetic scattering and GISAXS with the possibility to apply magnetic field up to 2T.

The variable-polarization source and monochromator are capable to deliver circularly and linearly polarized X-rays in the wide energy range 80-4000 eV covering the magnetism-relevant $L_{2,3}$ and $M_{4,5}$ absorption edges of the 3d, 4d metals and 4f rare earths. Experiments performed at BL29 usually involve magnetic materials composed of 3d metals and rare earths, magnetic or superconducting oxides, semiconductors, Silicon and Carbon based materials such as Graphene or organic molecules, ferro-electric, piezo-electric or multiferroic materials in bulk single-crystals, thin films, multilayers or surface-supported nanostructures/adatoms.

BOREAS beamline instrumentation and an advanced X-ray optical design, which are in service at these two complementary endstations, make possible soft X-ray (magnetic) circular and linear dichroism (XMCD/XMLD) measurements, and other related characterization techniques at the frontier of materials science studies and X-Ray Science.

Monitoring of Atomic Layer Deposition by Infrared Spectroscopy

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Infrared spectroscopy is a powerful tool to study the reaction mechanisms responsible during atom layer deposition. The technique allows focusing on the initial surface reaction mechanisms of thin film growth under various deposition conditions. Examples are the deposition of metal oxide films with precise control of the composition at the atomic scale.

The MIRAS beamline, housed at the ALBA synchrotron light source, is a new state of the art infrared spectroscopy beamline with the option to measure thin film growth under various sample conditions. A spectral range between 2 and 20μm can be approached. Sample maps with spatial resolution of around 3 μm can be recorded with the combination of a Fourier transform infrared spectrometer and a microscope. As an outlook, it could be possible to monitor *in-situ* atomic layer deposition during the growth process.