DS 23: Trends in atomic layer deposition II (Focused session – Organizer: Nielsch)

Time: Wednesday 17:30–19:45 Location: H 0111

Invited Talk DS 23.1 Wed 17:30 H 0111

Functional complex oxide materials by atomic layer deposition — •Maarit Karppinen — Laboratory of Inorganic Chemistry, Department of Chemistry, Aalto University, Finland

Complex oxides of 3d transition metals play central roles in many important future applications related to e.g. spintronics and sustainable energy technologies. The apparent examples include but are not limited to the emerging spintronic devices based on manganese oxides, high-Tc superconductors based on copper oxides, next-generation thermoelectric devices based on cobalt oxides, solid-oxide fuel cells based on a tailored combination of various oxide materials, Li-ion batteries based on oxides of cobalt, manganese, iron, titanium, etc. The present lecture is a short summary of the ALD (Atomic Layer Deposition) research carried out on various complex oxide materials in our laboratory, such as hexagonal and orthorhombic forms of RMnO$_3$ (R = rare earth element) [1,2], [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] [3], and MnCo$_2$O$_4$ [4]. All the fundamental elements of basic research on such thin-film materials are discussed: (i) ALD process development to obtain high-quality thin films of the desired metal composition, (ii) post-deposition treatments to obtain the desired phase in crystalline form and to control the oxygen stoichiometry, and (iii) basic chemical and physical property characterizations of the films.

[1] K. Uusi-Esko, J. Malm & M. Karppinen, Atomic layer deposition of hexagonal and orthorhombic YMnO$_3$ thin films, Chem. Mater. 21, 5691 (2009).

[2] K. Uusi-Esko & M. Karppinen, Extensive series of hexagonal and orthorhombic RMnO$_3$ (R = Y, La, Sm, Tb, Yb, Lu) thin films by atomic layer deposition, Chem. Mater. 23, 1835 (2011).

[3] J. Lybeck, M. Valkeapää, S. Shibasaki, I. Terasaki, H. Yamauchi & M. Karppinen, Thermoelectric properties of oxygen-tuned ALD-grown [Ca$_2$CoO$_3$]$_{0.62}$[CoO$_2$] thin films, Chem. Mater. 22, 5900 (2010).

[4] K. Uusi-Esko, E.-L. Rautama, M. Laitinen, T. Sajavaara & M. Karppinen, Control of oxygen nonstoichiometry and magnetic property of MnCo$_2$O$_4$ thin films grown by atomic layer deposition, Chem. Mater. 22, 6297 (2010).

Topical Talk DS 23.2 Wed 18:00 H 0111

Uniform ZnMnO and ZnCoO films grown by Atomic Layer Deposition — •Marek Godlewski[1,2], Małgorzata Łukasiewicz[1], Aleksandra Wójcik-Głodowska[1], Elzbieta Guziewicz[1], and Bartłomiej Witkowski[1] — [1]Institute of Physics PAS, Al. Lotników 32/46, 02-668 Warsaw, Poland — [2]Dept. Mathematics and Natural Sciences College of Science, UKSW, Dewajtis 5,

Despite many efforts, origin of a ferromagnetic (FM) response in ZnMnO and ZnCoO is still not clear. It is believed that FM response reported for these two alloys is due to inclusions of foreign phases (TM oxides), defects or metal accumulations, rather than volume properties of investigated samples. Thus, control of uniformity of investigated samples is crucial.

Atomic Layer Deposition (ALD) enables deposition of uniform ZnMnO and ZnCoO films. This is possible by reduction of a growth temperature, selection of Mn and Co precursors, and use of optimized ratios of the relevant ALD cycles, as will be discussed in details. Importantly, uniform films of ZnMnO and ZnCoO remain paramagnetic even at increased concentration of magnetic ions. Magnetic investigations show the FM response for films deposited on purpose with a non-uniform Mn (Co) distribution. This enables us to discuss the origin of FM in ZnMnO and ZnCoO.

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Topical Talk DS 23.3 Wed 18:30 H 0111

Atomic layer deposition of oxide thin films for non-volatile memory applications — •Susanne Hoffmann-Eifert — Peter-Grünberg Institut (PGI-7), Forschungszentrum Jülich and Jülich-Aachen Research Alliance (JARA-FIT), Germany

The fast growing market for portable electronic devices demands for non-volatile memory circuits with high speed data access and high reliability in combination with low power consumption. One promising concept is the resistive switching random access memory (RRAM). Films from transition metal oxides sandwiched between metal electrodes often show binary stable electric resistance states which can be switched by applying a certain voltage. Decisive for a stable device operation are a homogeneous microstructure and a controlled defect density in the oxide films of a few nm in thickness. Atomic layer deposition (ALD) can fulfill these requirements by its unique surface-reaction controlled self-limiting growth.

The talk will comprise recent results on ALD transition metal oxide thin films integrated into cross point MIM structures for future resistive switching applications. TiO2 thin films were grown from water based thermal ALD processes utilizing different alkoxide and amide based Ti sources. For ZrO2 thin films an amide type precursor was used in ozone and water based ALD processes. In addition, selected works on ALD HfO2, Nb2O5 and Ta2O5 thin films utilized in switching cells will be summarized. The examples highlight the importance of atomic layer deposition for the new non-volatile memory concept of resistive switching RAM.

DS 23.4 Wed 19:00 H 0111

Investigation of Morphology and Resistive Switching in ZrO2/TiO2 Films Grown by Atomic Layer Deposition — •Irina Kärkkänen[1], Mikko Heikkilä[2], Jaakko Niinistö[2], Mikko Ritala[2], Markku Leskelä[2], and Susanne Hoffmann-Eifert[1] — [1]Peter Grünberg Institute, Research Center Jülich , 52425 Jülich, Germany — [2]Laboratory of Inorganic Chemistry, University of Helsinki, Finland

Thin films from transition metal oxides have become of increasing interest for various applications, especially in high-k and resistive switching devices. In this work, we studied the influence of processing on the structural, morphological and electrical properties of ZrO2 and combination of ZrO2/TiO2 in the form of laminates and bilayers. The films were deposited from Zr(NEtMe)4 (TEMAZ) and Ti(OiPr)4 (TTIP) by atomic layer deposition using ozone or water as the oxygen sources. Deposition temperatures were 200°C, 240°C, and 280°C. The films were characterized with x-ray diffraction, x-ray reflectometry, atomic force microscopy, scanning electron microscopy, and electrical measurements. Differences in structure and electrical properties were found depending on type of oxygen source. Ozone grown ZrO2 films showed an(111) oriented cubic structure, whereas the ones deposited with water were polycrystalline with a cubic/tetragonal mixed phase in thicker films. Resistive switching of metal-insulator-metal structures was scrutinized. Structures like Pt/ZrO2/Ti/Pt, Pt/ZrO/TiO2/Ti/Pt, and Pt/TiO2/ZrO2/Ti/Pt showed different kinds of resistive switching behavior.

DS 23.5 Wed 19:15 H 0111

ALD of metal oxides and fluorides for optical applications — •Matti Putkonen[1,2], Adriana Szeghalmi[3], Mato Knez[3], and Timo Sajavaara[4] — [1]Beneq Oy, P.O. Box 262, FI-01511 Vantaa, Finland — [2]Laboratory of Inorganic Chemistry, Aalto University School of Science and Technology P.O. Box 16100, FI-00076 Aalto, Espoo, Finland — [3]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle (Saale), Germany — [4]Department of Physics, P.O. Box 35 (YFL), FI-40014 University of Jyväskylä, Finland

Atomic layer deposition (ALD) is a mature technology and there is increased number of ALD enabled applications, such as optical coatings.

For high index materials there are several possibilities but for low index materials deposited by ALD the selection is still more limited. The lack of industrially viable process for low refractive index materials, such as SiO$_2$ and metal fluorides is still the limiting factor.

In this presentation we show data concerning the SiO$_2$ deposition by thermal and plasma ALD using novel precursors as well as deposition of metal fluorides by using chemistry based on the traditional metal oxide ALD chemistry using either fluorinated metal β-diketonates or fluorinated hydrocarbons as a fluorine source. [1] The depositions were carried out by using Beneq TFS 200 and P400 ALD tools. The films were analyzed by TOF-ERDS, RBS, XRD and AFM. Optical properties of the deposited films were also measured at UV region. In this presentation we also discuss the ALD process requirements when these processes are transferred to large surface area coatings.

1. M. Putkonen et. al. J. Mater. Chem. 21 (2011) 14461.

DS 23.6 Wed 19:30 H 0111

Thermoelectric Characterization of Sb$_2$Te$_3$ Thin Films Deposited by ALD — •Sebastian Zastrow[1], Christian

Schumacher[1], Matthias Regus[2], Stephan Schulz[3], and Kornelius Nielsch[1] — [1]University of Hamburg — [2]University of Kiel — [3]University of Duisburg-Essen

Thermoelectric materials can be used as temperature sensors or peltier cooling devices as well as to recover a part of the massive losses of energy due to the waste heat generated in fossil-fuel driven power plants and vehicles. Antimony Telluride (Sb_2Te_3) is a p-doped semiconductor and in the focus of interest for room temperature applications because of its thermoelectric peak performance at around 350 K. However, thermoelectric properties of Sb_2Te_3 ALD thin films have not been reported yet. Based on the work of Pore *et al.*, Sb_2Te_3 is deposited with a home-made reactor on SiO_2 by using $(Et_3Si)_2Te$ and $SbCl_3$. The surface roughness as well as the growth rate depend strongly on the deposition temperature as reported by Cu *et al.* To check the preferential growth directions and the composition, XRD and EDX measurements are carried out. The thermoelectric properties are influenced by the deposition parameters. Therefore, spatial scans of the Seebeck coefficient are performed and the electrical resistivity is measured. In order to enhance the thermoelectric performance, a first optimization by short annealing processes is done under helium atmosphere up to 570 K.

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