

## ALD Fundamentals

### Room Grand Ballroom E-G - Session AF3-MoA

#### Growth and Characterization I

**Moderators:** Somilkumar Rathi, Eugenius, Inc., Sumit Agarwal, Colorado School of Mines

4:00pm **AF3-MoA-11 Understanding Elemental Steps of ALD on Oxidation Catalysts**, *Kristian Knemeyer, M Piernawieja Hermida, R Naumann d'Alnoncourt*, Technische Universität Berlin, Germany; *A Trunschke, R Schlögl*, Fritz Haber Institute of the Max Planck Society, Germany; *M Driess*, Technische Universität Berlin, Germany; *F Rosowski*, BASF SE, Germany

Since the invention in the 1970s, Atomic layer deposition (ALD) has been extensively studied. Over the course of 40 years, its benefits for the microelectronic industry have been spread to numerous different fields such as medicine, batteries and catalysts[1]. Despite being applied and investigated for such a long time the deposition mechanism is barely understood. Typically, ALD is applied by performing hundreds of cycles to grow layers in the range from nanometers to micrometers and most of the times the first cycles show different growth behavior than the following ones. The first cycles might not be of interest for depositing films but they are crucial for us, as our aim in catalyst synthesis and modification is a film thickness in the nm range which is achieved with only few cycles.

We focused on understanding the first cycles of ALD on vanadium pentoxide as oxidation catalyst. Phosphorous oxide ALD on  $V_2O_5$  was conducted with two different precursors ( $P^{5+}$  and  $P^{3+}$ ) and then compared to the highly investigated mechanism of TMA/ $H_2O$ . ALD was performed in a magnetic suspension balance to track the mass gain in situ[2]. Surface species were analyzed not only by  $^{31}P$ -NMR but also by in-situ DRIFTS measurements of the second half cycle. XPS was conducted to determine oxidation states of bulk and surface species after each half cycle. STEM-EDX shows highly distributed P on the surface and no additional phases were found. With the combination of these analytics we will show that the ALD mechanism depends heavily on the substrate and that ALD on oxidation catalysts is clearly different than on typical catalyst supports, such as  $SiO_2$  or  $Al_2O_3$ .

[1] J. Lu, J. W. Elam, P. C. Stair, Surf. Sci. Rep. **2016**, 71, 410

[2] V. E. Strempele, D. Löffler, J. Kröhnert, K. Skorupska, B. Johnson, R. Naumann D'Alnoncourt, M. Driess, F. Rosowski, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **2016**, 34, 01A135.

4:15pm **AF3-MoA-12 Advanced Lateral High Aspect Ratio Test Structures for Conformality Characterization by Optical Microscopy**, *Olli Yliivaara, P Hyttinen*, VTT Technical Research Centre of Finland Ltd, Finland; *K Arts*, Eindhoven University of Technology, Netherlands; *F Gao*, VTT Technical Research Centre of Finland Ltd, Finland; *E Kessels*, Eindhoven University of Technology, Netherlands; *R Puurunen*, Aalto University, Finland; *M Utriainen*, VTT Technical Research Centre of Finland Ltd, Finland

Atomic Layer Deposition (ALD) is a key technology in 3D microelectronics enabling conformal coatings into deep microscopic trenches and high aspect ratio cavities. However, conformality characterization in 3D trench walls is challenging and requires sample preparation. The MEMS-based all-silicon Lateral High Aspect Ratio (LHAR) test structure, developed at VTT, named PillarHall<sup>®</sup> [1-3], provides a fast and accurate substrate and characterization concept for the thin film conformality analysis [4,5]. The most important outcome from the PillarHall<sup>®</sup> characterization is the film saturation profile, which provides valuable data for reaction kinetics modelling and quantifying conformality. Since the LHAR enables utilization of planar metrology instruments, multiple approaches are compatible.

In this study, we focus on characterization methods suitable to extract the saturation profile and show the advantage of simple optical microscopy image analysis. Studied material was prototypical ALD  $Al_2O_3$  (40-50 nm thick layers) made in two separate research facilities. The study consisted of SEM/EDX planar view, micro-spot reflectometry and ellipsometry and optical microscopy image analyses. These experiments were carried out by two research labs and supported by leading edge optical metrology tool vendors, Semilab Ltd, JA Woollam and Filmetrics.

We also introduce advanced LHAR 4<sup>th</sup> generation design, which enables characterization of the penetration depth profile with distinct advantages. Namely, new pillar design enables employment of optical line scanners up to 50  $\mu m$  spot sizes. Furthermore, internal distance indicators support

positioning the characterization tools more accurately. These features are illustrated in Supplementary Material Fig S1.

The results show that the gray-scale optical microscopy image analysis with the thickness determination in opening area gives similar results as the reflectometry or ellipsometry line scans, within the accuracy limits. Optical thickness/ $\lambda$  of the film is a limitation for the image analysis, but designing the experiments properly, the grayscale optical micrograph can be a powerful, widely compatible and easy method for conformality analysis.

Support from Semilab Ltd is gratefully acknowledged.

#### References

[1] F. Gao et al., *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **33**, 010601 (2015).

[2] R. Puurunen and F. Gao, 2016. doi: 10.1109/BALD.2016.7886526

[3] M. Mattinen et al., *Langmuir*, **32**, 10559 (2016).

[4] M. Ylilampi et al., *J. Appl. Phys.*, **123**, 205301 (2018).

[5] V. Cremers et al., *Applied Physics Reviews*, in press (2019).

4:30pm **AF3-MoA-13 Dopant Concentration Analysis of ALD Thin Films in 3D Structures by ToF-SIMS**, *A Kia, Wenke Weinreich*, Fraunhofer-Institut für Photonische Mikrosysteme (IPMS), Germany; *M Utriainen*, VTT Technical Research Centre of Finland Ltd, Finland; *R Puurunen*, Aalto University, Finland; *N Haufe*, Fraunhofer-Institut für Photonische Mikrosysteme (IPMS), Germany

Self-limiting nature of atomic layer deposition (ALD) proposes a unique deposition mechanism which can produce extremely good step coverage within high aspect ratio (HAR) structures. This layer-by-layer deposition method also provides fine control on different features of deposition techniques such as controlling the dopant distribution in the direction of growth.

The quantity of dopant per layer is controlled, by applying saturation coverage delivering adequate dose rate for each precursor/reactant mixture. There are different parameters that contribute to control the dopant concentration in both 2D and 3D structures. To understand the reasons and characterize the precursors' behavior in deep trench structures, we used dynamic SIMS. Time of flight secondary ion mass spectrometry (ToF-SIMS) is a well-known method due to high detection sensitivity for the measurement of concentration levels of the dopant materials. Nevertheless, due to the geometry of the vertical HAR structures, it is challenging to characterize samples by ToF-SIMS. The absence of a simple and immediately available 3D structure for analyzing thin films produced by ALD has led most studies being made on flat surfaces.

A potential approach to circumvent the challenges is a MEMS-based all-silicon lateral high aspect ratio (LHAR) test structure, PillarHall<sup>®</sup> developed at VTT<sup>[1-2]</sup>. After removal of the top membrane (Fig.a-c) the LHAR test chip enables utilization planar characterization tools to examine the properties of deposited thin film on the 3D trench wall. This study focuses on semiquantitative characterization of different doping concentrations of La-doped  $HfO_2$  with using LHAR. The LHAR Test Chips (LHAR3-series, AR2:1-10000:1, 500nm gap height) were used on carrier wafers in a 12 in wafer ALD process (Jusung Eureka 3000).

The findings show that the main difficulties with respect to the geometry for elemental analysis in non-planar structures can be resolved with LHAR. In particular, with the power of ToF-SIMS in data imaging (Fig.d) and integrating of data point from interested area (Fig.e), we are able to quantify doping profile along with understanding the properties of the trench wall in depth penetration.

#### REFERENCES

[1] Gao et al., *J. Vac.Sci.Technol. A*, **33**(2015) 010601.

[2] Puurunen et al., AF-SuA15,ALD 2017,Denver,USA.

4:45pm **AF3-MoA-14 Metallic Ruthenium Coating on  $SiO_2$  Powder by Atomic Layer Deposition using  $H_2O$  Reactant.**, *H Lee, Chi Thang Nguyen*, Incheon National University, Republic of Korea

Ruthenium has been many times studied by atomic layer deposition (ALD) for various applications, such as metal-insulator-metal capacitors (MIMCAP), diffusion barriers, and electrodes for dynamic random access memory (DRAM), due to its good thermal and chemical stability, high conductivity (resistivity of Ru  $\sim 7.4 \mu\Omega.cm$ ) and high work function (4.7 eV). Most of the ALD Ru films reported were deposited by the oxidants such as  $O_2$  and  $O_3$ , and the main mechanism of Ru deposition was combustion

reactions by the oxidant. So, Ru oxide phases were unintentionally formed under overexposure condition of oxidant. In this study, we used H<sub>2</sub>O as a reactant to deposit metallic Ru film by ALD. We proposed an abnormal reaction mechanism between H<sub>2</sub>O and the new beta-diketonate Ru precursors (5-methyl- 2,4- hexanediketonato) Ru(II), Carish, C<sub>16</sub>H<sub>22</sub>O<sub>6</sub>Ru led to the formation of Ru metallic film without the appearance of oxide phase under overexposure condition of the reactant. The formation of metallic Ru film by H<sub>2</sub>O was analyzed with experimental and theoretical approaches, including the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and Density functional theory (DFT). Also, the cyclic voltammetry (CV) testing was performed on ALD Ru on SiO<sub>2</sub> powders.

5:00pm **AF3-MoA-15 Low Energy Ion Scattering Study of Pt@Al<sub>2</sub>O<sub>3</sub> Nanoparticle Coarsening**, Philipp Brüner, IONTOF GmbH, Germany; E Solano, ALBA Synchrotron Light Source, Spain; C Detavernier, J Dendooven, Ghent University, Belgium

Coarsening of dispersed Pt nanoparticles has been shown to occur at elevated temperatures [1], leading to the formation of larger particles, and consequently a reduction of the total number of particles. This has important consequences in real-world applications of Pt nanostructures, such as heterogeneous catalysis, where a high number of small, highly dispersed particles are desirable to maintain high catalytic activity.

One attempt to prevent coarsening is to coat the Pt nanoparticles by a thin Al<sub>2</sub>O<sub>3</sub> shell deposited by atomic layer deposition (ALD). Advanced surface analytical techniques are required to study the resulting complex structures. In this study, low energy ion scattering (LEIS) is used to support existing data obtained by grazing incidence small angle X-ray scattering applied to Pt nanoparticle model systems prepared by ALD [1]. In LEIS, the energy spectrum of noble gas ions scattered from the sample surface is recorded. The evaluation of elemental peaks in the resulting spectra allows the quantification of the elemental composition of the first atomic layer [2]. This extreme surface sensitivity of just a single atomic layer, combined with composition analysis, is unique to LEIS and makes it especially useful in the study of nanoscale systems. In addition, sub-surface scattering signal from deeper layers gives information about sample composition and layer thickness up to depths of 10 nm.

We show how the monolayer surface sensitivity of LEIS enables the precise determination of the areal density of the deposited nanoparticles and the particle surface coverage of sub-monolayer Al<sub>2</sub>O<sub>3</sub> shells. Furthermore, cracking of the shells by annealing has been observed. By measuring layer thickness values, average particle sizes are determined, which give insight into coarsening processes. The thickness of Al<sub>2</sub>O<sub>3</sub> shells can be determined precisely over a wide range of values, including ultra-thin sub-monolayer shells after just five cycles of Al<sub>2</sub>O<sub>3</sub> deposition.

The results demonstrate that the effectiveness of the Al<sub>2</sub>O<sub>3</sub> shell depends on the process conditions during the deposition of the Pt nanoparticles. MeCpPtMe<sub>3</sub> was used as a precursor, with either O<sub>2</sub> gas or N<sub>2</sub> plasma as reactants [3]. In the former case, even a sub-monolayer Al<sub>2</sub>O<sub>3</sub> shell can completely prevent particle coarsening. In the latter case, the N<sub>2</sub> plasma based Pt process results in a denser collection of smaller Pt nanoparticles and stabilization with an Al<sub>2</sub>O<sub>3</sub> overcoat is proven to be more difficult.

[1] *Nanoscale*, 2017, 9, 13159-13170

[2] "Low-Energy Ion Scattering" in *Characterization of Materials - Second Edition* ISBN 978-1-118-11074-4 - John Wiley & Sons.

[3] *Nat. Commun.* 8 (2017) 1074

5:15pm **AF3-MoA-16 Physical and Electrical Characterization of ALD Chalcogenide Materials for 3D Memory Applications**, Vijay K. Narasimhan, V Adinolfi, L Cheng, M McBriarty, Intermolecular, Inc.; M Utraiainen, F Gao, VTT Technical Research Centre of Finland Ltd, Finland; R Puurunen, Aalto University, Finland; K Littau, Intermolecular, Inc.

In three-dimensional memory integration schemes, like those used for current NAND Flash memory technologies, the active layers of the memory devices are filled into vias with aspect ratios of 40:1 or greater. It is important for the deposited films to demonstrate consistent properties all the way through the depth of the via. Recently, novel ALD chalcogenide materials have emerged [1-3] that could be used as phase-change memory (PCM) and ovonic threshold switch (OTS) selectors. ALD chalcogenides are attractive because they could be compatible with 3D integration schemes; however, the properties of these films in high-aspect ratio structures have not been extensively investigated.

In this study, we use PillarHall® Lateral High Aspect Ratio (LHAR) test chips [4-6] to elucidate the properties of ALD chalcogenides on a trench wall

using standard in-plane metrology techniques without fabricating full device stacks. The PillarHall all-silicon LHAR test chip includes multiple trenches in the aspect ratio range 2:1 - 10000:1 with constant 500 nm gap height [6]. LHAR chips are used as substrates for ALD binary and ternary chalcogenide films using HGeCl<sub>3</sub>, [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>Te, [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>Se, and (C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub>Te as precursors. Using optical microscopy, scanning electron microscopy with energy-dispersive x-ray spectroscopy, and scanning-probe techniques, we describe the chemical, physical, mechanical, and electrical properties of these films. We show that the thickness and atomic composition of certain chalcogenide films changes dramatically inside of high-aspect ratio features (Fig. S1). Furthermore, we perform optical profilometry on silicon micro-membranes on the PillarHall test chips (Fig. S2) to rapidly estimate the ALD film stress on the microscopic level, which is not directly measurable in devices today despite its importance in 3D architectures. We use these results to comment on the ALD reaction kinetics and discuss implications for future research on ALD chalcogenide films.

Combining high-aspect ratio and stress measurements on a single test chip can accelerate R&D of ALD chalcogenides for applications in PCMs and OTSs as well as other microscopic 3D applications of ALD thin films.

References

[1] T. Gwon *et al.*, *Chem. Mater.* 29, 8065 (2017).

[2] W. Kim *et al.*, *Nanotechnology*, 29, 36 (2018).

[3] L. Cheng, V. Adinolfi, S. L. Weeks, Sergey V. Barabash, and K. A. Littau, *J. Vac. Sci. Technol. A*. ALD2019, 020907 (2019).

[4] F. Gao, S. Arpiainen, and R. L. Puurunen, *J. Vac. Sci. Technol. A*. 33, 010601 (2015).

[5] M. Ylilammi, O. M. E. Ylivaara, and R. L. Puurunen, *J. Appl. Phys.* 123, 205301 (2018).

[6] O.M.E Ylivaara *et al.*, *Proc. 18th Int. Conf. At. Layer Depos.* (2018).

5:30pm **AF3-MoA-17 The Tailoring of the Single Metal Atom-Oxide Interface**, Bin Zhang, Y Qin, Institute of Coal Chemistry, Chinese Academy of Sciences, China

The metal-oxide interface plays important roles in the metal-based heterogeneous catalyst. By sample tailoring the types of interface, size and crystal structure of metal and oxides, etc, the catalytic performance of the catalyst changes dramatically. Thus, the preciously tailoring the metal-oxide interface in atomic scale is a key and most important strategy to design an effective metal-based catalyst. Atomic layer deposition (ALD) is a promising and controllable approach to precisely design and tailor the metal-oxide interface because of its atom-level thickness control, excellent uniformity and conformality and good repeatability in film or particle deposition. Recently, we have developed new strategies for the tailoring of the interface structure by building a serial of nanostructures, such as the core-shell structures, inverse oxide/metal structure, porous sandwich structure, multiple confined metal nanoparticles in oxide nanotubes, and tube-in-tube structure with multiple metal-oxide interfaces. In many case, the metal-oxide interface forms at the cost of metal surface sites through ALD overcoating or modification. In order to increase the ratio of metal-oxide interface and utilization of metal, the building of single metal atom-oxide interface with high loading of metal is a good but challenge strategy since the unstability of single atoms. We have realized this in many ways, such as developing new ALD deposition approaches, depositing oxide site in advance, and changing the deposition dynamic conditions etc. Pt/FeO<sub>x</sub>, Cu-TiO<sub>2</sub>, and Pt-CeO<sub>2</sub> single metal atom-oxide interface showed high catalytic performance in selective hydrogenation with high efficiency.

References

1. H. Ge, B. Zhang, X. Gu, H. Liang, H. Yang, Z. Gao, J. Wang, Y. Qin, *Angew. Chem. Int. Ed.* 2016, 55: 7081-7085.

2. Z. Gao, M. Dong, G. Z. Wang, P. Sheng, Z. W. Wu, H. M. Yang, B. Zhang, G. F. Wang, J. G. Wang, and Y. Qin, *Angew. Chem. Int. Ed.* 2015, 54: 9006-9010.

3. J. K. Zhang, Z. B. Yu, Z. Gao, H. B. Ge, S. C. Zhao, C. Q. Chen, S. Chen, X. L. Tong, M. H. Wang, Z. F., and Y. Qin, *Angew. Chem. Int. Ed.* 2017, 56: 816-820.

4. B. Zhang, Y. Qin, *ACS Catal.* 2018, 8, 10064-10081.

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