Synthesis of self-assembled 3D nanostructures for UV-NIR broadband absorber

Mario Ziegler[1,2], André Dathe[3], Sophie Thamm[1], Lisa Stolle[1], Uwe Hübner[1], Dong Wang[2] and Peter Schaaf[2]

1 Leibniz Institute of Photonic Technology Jena (IPHT), Albert-Einstein-Straße 9, 07745 Jena, Germany
2 Chair Materials for Electrical Engineering, Institute of Materials Science and Engineering and Institute of Micro and Nanotechnologies MacroNano®, TU Ilmenau, Gustav-Kirchhoff-Str. 5, 98693 Ilmenau, Germany
3 Single-molecule Microscopy Group, Jena University Hospital, Friedrich-Schiller-University, 07745 Jena, Germany

In regard of green energy solutions, broadband absorbers in the visible spectra are necessary. Here, the assembly of materials with different geometries is a promising candidate to meet these demands. The so-called metamaterials can be tailored to fabricate structures with well-defined properties, which cannot be found in nature. Nevertheless, such structures require subwavelength features sizes in large areas. High resolution lithography, for instance electron beam lithography, can fulfill these demands, but those techniques are time-consuming and therefore expensive.

Here, we report on a cost-effective approach for the generation of high absorption three-dimensional silver-silica hybrid structures (figure 1), so-called metastable atomic layer deposition (MS-ALD) [1]. Unlike the conventional ALD, the coating of MS-ALD is not conformal to the substrate surface. So, the substrate surface does not have to be pre-patterned, which decreases the cost and the need for expensive fabrication tools. Rather, the structures in the MS-ALD process are generated using a self-assembly approach. The process consists of 2 individual steps. In the first step, a planar silver film is deposited using electron beam evaporation onto a flat glass substrate. In the second step, silica is deposited using plasma-enhanced atomic layer deposition (PE-ALD). As precursor we use tri-dimethyl-amino-silane (TDMAS) and oxygen plasma. In contrast to classical ALD, the process parameters of the PE-ALD are altered to generate a metastable silver oxide. The silver oxide subsequently decomposes to elemental silver and reactive oxygen along the ALD cycles. The reactive oxygen leads to further reactions with the TDMAS and causes the generation of the 3D structures.

The geometry of the formed nanostructures can be easily adjusted by tuning the deposition parameters, such as dose time of both precursors and cycle numbers (figure 2.) [2]. By doing so, we observed nanoporous and microporous sponge-like structures as well as nanowires with feature sizes of up to 10 µm. The structures consist of a 3D silica matrix and silver nanoparticles, which are randomly attached onto the silica surface. The resulting structures are matte black over the complete substrate surface and reveal a very high and broadband absorbance (>95 %) from the initial 220 nm up to 1550 nm (fig 1d).

[1] Ziegler et al., Adv. Mater. Technol. 2 (2017), 1700015
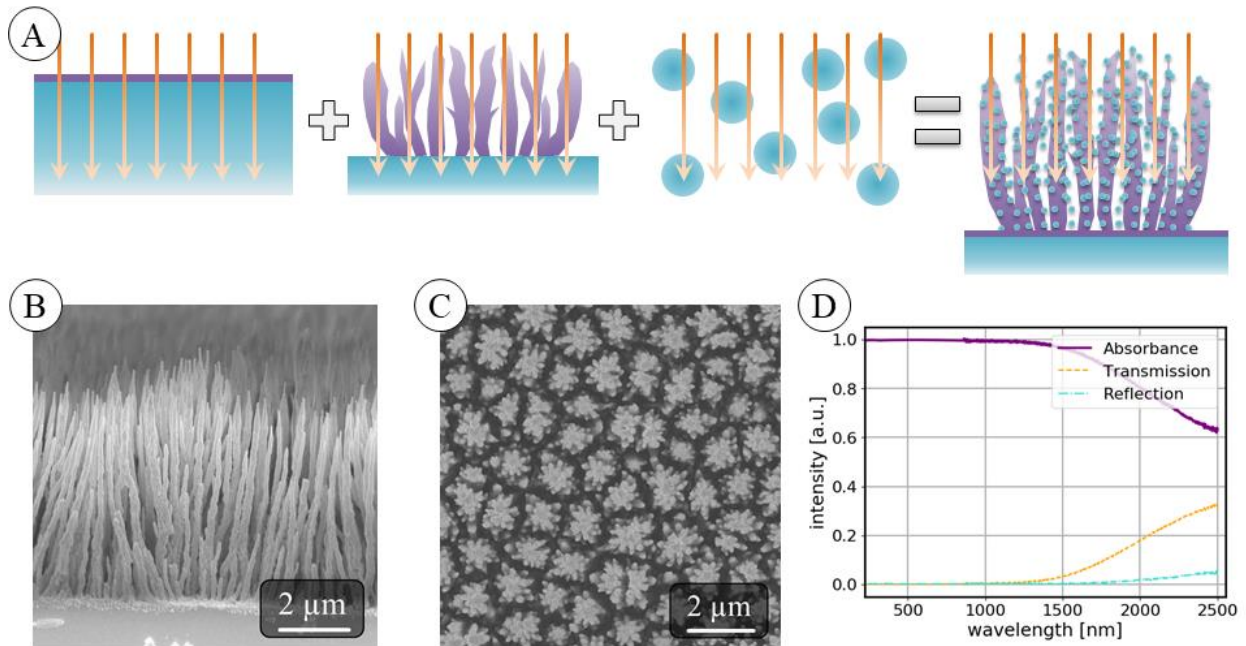[2] Ziegler et al., Materials Today Chemistry 10 (2018), 112-119

Figure 1. (a) Assembly of different geometries to generate broadband high absorption nanostructures (planar film, nanostructured film and nanoparticles, orange arrows indicate the absorbance), (b) cross section image and (c) top view image of the resulting structure generated using MS-ALD (50 ms dose time 1, 6 s dose time 2, 225 cycles, silver film thickness: 300 nm) and (d) corresponding absorption spectra of (c) revealing the high absorption from UV to NIR region.
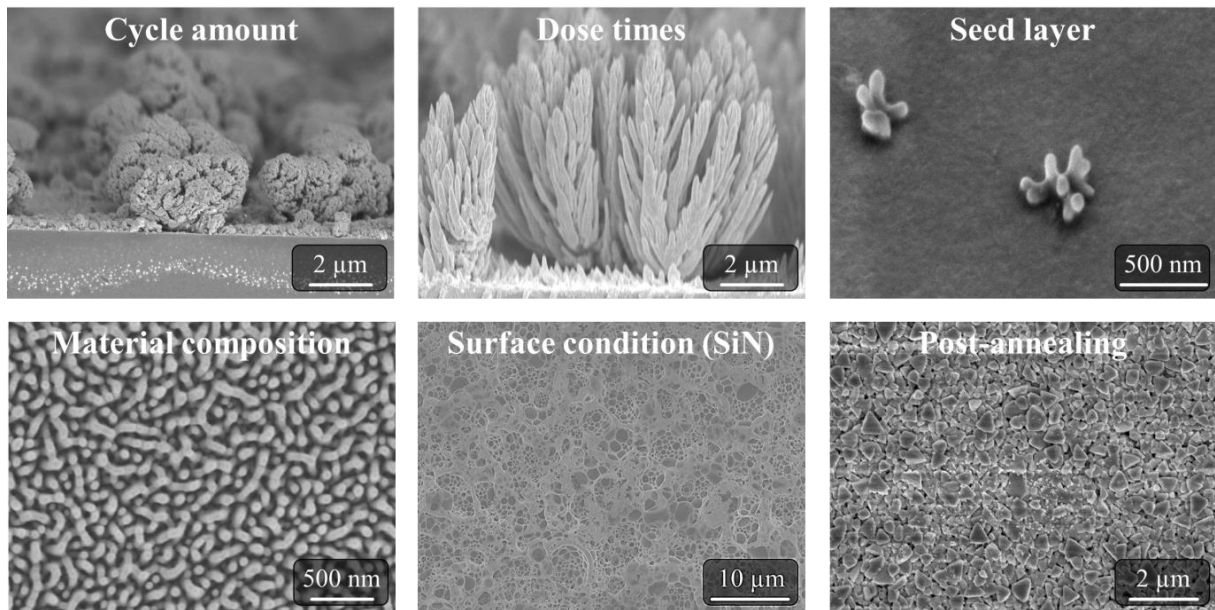

Figure 2. SEM images of hybrid-structures fabricated using metastable atomic layer deposition

Atomic Layer Deposition at the heart of an innovating strategy to fabricate stable and efficient photoanode for water photooxidation

Maxime E. Dufond[1], Gabriel Loget[2], S. Haschke[3], J. Bachmann[3] and Lionel Santinacci[1]

1 Aix-Marseille Univ., CNRS, CINaM, Marseille, France (dufond@cinam.univ-mrs.fr)
2 University of Rennes 1, CNRS, Rennes France
3 Friedrich-Alexander University Erlangen-Nürnberg, Germany

Water photosplitting is a promising way to transform the solar irradiation into a storable and transportable fuel (H_2). Si can be used as photoanode because it absorbs in the visible range and its electronic structure is suitable to drive water photooxidation. Though, Si suffers from a strong corrosion in KOH and a high reflectivity. The strategy is to combine Si microstructuring with ALD of a protective layer. TiO_2 is combined to Si due to its absorption in the UV range and its stability at high pH. TiO_2 is grown using TTIP and TDMAT at various temperatures (70-250°C) and annealed at 450°C. Numerous surfaces analyses have been employed to compare the physico-chemical properties. The influence of precursor nature and the temperature has been correlated to the Si/TiO_2 photoelectrochemical performances. The best layers (stability and efficiency) are achieved when TiO_2 is grown from TDMAT at 150°C. To further increase the efficiency a co-catalyst must be added. Ni is often associated to Si/TiO_2 due to its low cost and high activity. Usually, metallic Ni is deposited by PVD or electrodeposition but the quality of the films is not fully satisfying on tortuous substrates. Here a two-steps process has been developed: (i) conformal ALD of NiO on the nanostructured Si/TiO_2 photoanode and (ii) reduction to Ni by an annealing under H_2. In this case the efficiency of the multilayered photoelectrode is drastically improved (×300). This approach has been extended to another microstructured heterojunction Si/Fe_2O_3. Higher photoelectrochemical performances have been evidenced on hematite.

Atomic Layer Deposition at the heart of an innovating strategy to fabricate stable and efficient photoanode for water photooxidation

Maxime E. Dufond[1], Gabriel Loget[2], S. Haschke[3], J. Bachmann[3] and Lionel Santinacci[1]

1 Aix-Marseille Univ., CNRS, CINaM, Marseille, France (dufond@cinam.univ-mrs.fr)
2 University of Rennes 1, CNRS, Rennes France
3 Friedrich-Alexander University Erlangen-Nürnberg, Germany

The development of renewable energies is one of the most promising ways to decrease our detrimental impact on the planet. Water photosplitting appears to be a leading approach because it converts the intermittent solar irradiation into a storable and transportable fuel (i.e. H_2). By this technology, the fuel is sufficiently pure for a direct use in fuel cells and its combustion occurs without CO_2 generation. This concept has been demonstrated in the early 70's [1] and since then, this field has attracted an intense research effort because this technology is not scalable yet. In this work, we focus on the water photooxidation which is the reaction exhibiting the highest kinetic barrier and, to date, high efficiencies are reached solely with scarce materials (e.g. InP). One of the keys to improve the efficiency is the combination of alternative semiconductors and the surface micro- or nanostructuring. This approach leads to better properties such as an increase of the active area, an enhanced light trapping, a higher stability, and a better charge collection.

Here, silicon has been selected as photoanode because it has a suitable electronic structure ($E_g = 1.1$ eV) to absorb visible light and drive the reaction [2]. Unfortunately, this material suffers from two major drawbacks which are its instability in alkaline media and its high reflectivity. In order to reach beyond these drawbacks, the Si surface is anodically microstructured (pores and spikes) [3-4] and a thin protective TiO_2 layer is grown by Atomic Layer Deposition (ALD) to uniformly cover such high aspect ratio materials. This film is well-adapted due to its high stability in alkaline media and its wide bandgap ($E_g = 3.2$ eV). It absorbs light in the UV range and a synergic effect between n-Si and TiO_2 is expected to generate an appropriate band bending leading to a better photocurrent [5].

The TiO_2 growth has been performed using two Ti precursors (TTIP and TDMAT) at various temperatures (70-250°C) and an annealing in air at 450°C has been carried out. Numerous surfaces analyses have been employed to compare the morphology, the crystalline structure, the refractive index and the chemical stability. The influence of both precursor composition and the process temperature has been correlated to the Si/TiO_2 photoelectrochemical performances. The best layers (stability and efficiency) are achieved when TiO_2 is grown from TDMAT at 150°C.

To further increase the efficiency a co-catalyst must be added. Ni is often associated to Si/TiO_2 due to its low cost and high electroactivity [6-7]. Usually, metallic Ni is directly deposited by PVD or electrodeposition but the quality of the films is not fully satisfying on tortuous substrates. Here a two-steps process has been developed: (i) conformal ALD of NiO on the nanostructured Si/TiO_2 photoanode and (ii) reduction to Ni by an annealing under H_2. In this case the efficiency of the multilayered photoelectrode is drastically improved (×300).

This approach has thus been extended to another microstructured heterojunction Si/Fe_2O_3. Hematite is indeed interesting because of its lower band-gap ($E_g = 2.2$ eV). Higher photoelectrochemical performances have been evidenced and will be presented as conclusion.

[1] A. Fujishima and K. Honda, Nature 238 (1972) 37-38
[2] K. Sun et al., Chem. Rev. 114 (2014) 8662-8719
[3] L. Santinacci et al., ACS Appl. Mater. Interfaces 8 (2016) 24810-24818
[4] G. Loget et al., Mater. Chem. Front. 1 (2017) 1881-1887
[5] Y. J. Hwang et al., Nano Lett. 9 (2009) 410-415
[6] S. Hu et al., Science 344 (2014) 1005-1009
[7] M. T. McDowell et al., ACS Appl. Mater. Interfaces 7 (2015) 15189-15199
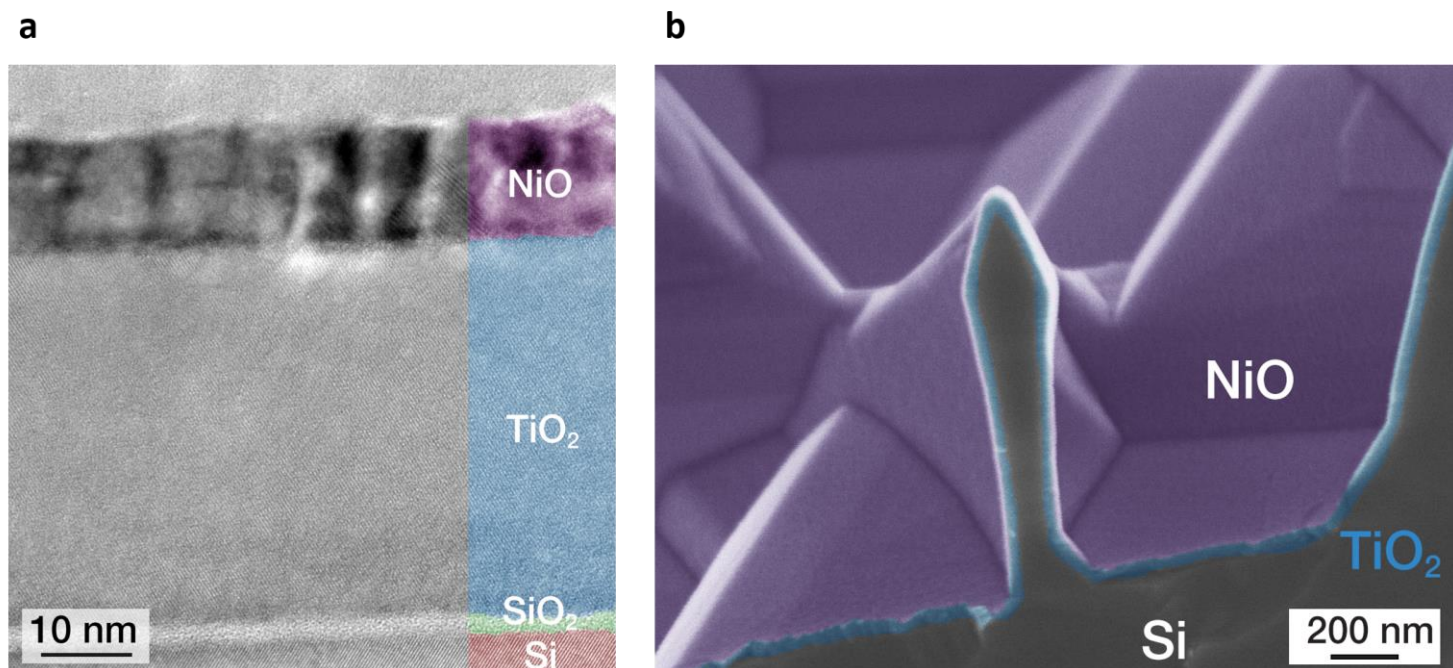
Figure 1. a) TEM image of the Si/TiO$_2$/NiO photoanode b) SEM image of the microstructured n-Si/TiO$_2$/NiO photoanode. Colors have been added for the sake of clarity.
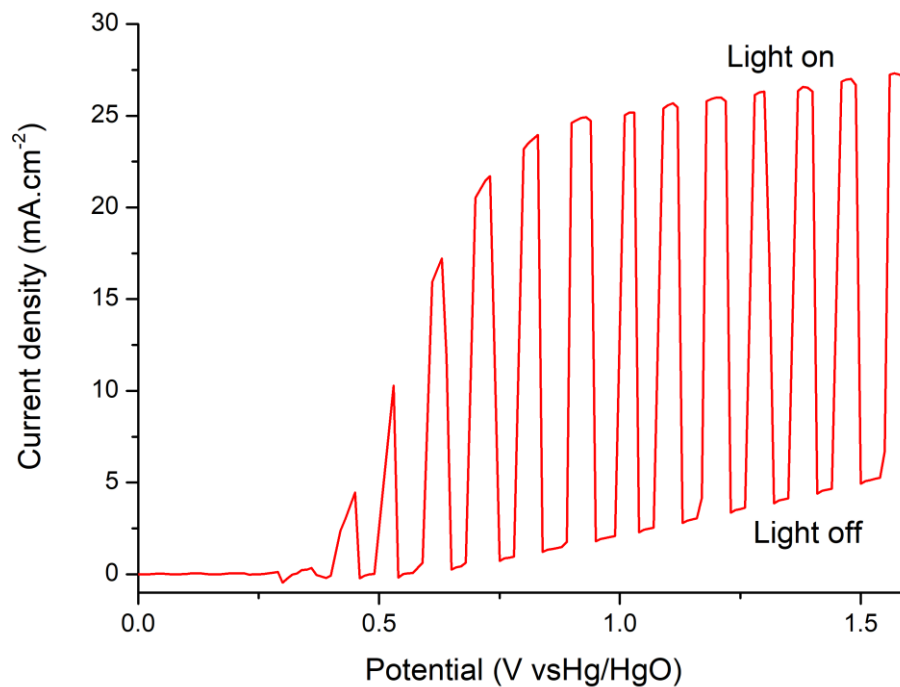

Figure 2. Linear sweep voltammogram of the final Si/TiO$_2$/Ni flat photoanode. Light has been chopped. Electrolyte KOH 1M, scan rate 20 mV/s.

Stability Enhancement of Silver Nanowire Networks with Conformal ZnO Coatings Deposited by Atmospheric Pressure Spatial Atomic Layer Deposition

Afzal Khan[1,2], Viet Huong Nguyen[1,3], David Muñoz-Rojas[1], Sara Aghazadehchors[1,4], Carmen Jiménez[1], Ngoc Duy Nguyen[4], Daniel Bellet[1]

1 Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, F-38000 Grenoble, France.

(*david.munoz-rojas@grenoble-inp.fr*)

2 Department of Physics, University of Peshawar, 25120 Peshawar, Pakistan

3 Univ. Grenoble Alpes, CEA, LITEN, INES, F-73375, Le Bourget-du-Lac, France

4 Département de Physique, CESAM/Q-MAT, SPIN, Université de Liège, B-4000 Liège, Belgium

Silver nanowire (AgNW) networks offer excellent electrical and optical properties and have emerged as one of the most attractive alternatives to transparent conductive oxides to be used in flexible optoelectronic applications. However, AgNW networks still suffer from chemical, thermal, and electrical instabilities, which in some cases can hinder their efficient integration as transparent electrodes in devices such as solar cells, transparent heaters, touch screens, and organic light emitting diodes. We have used atmospheric pressure spatial atomic layer deposition (AP-SALD)[1] to fabricate hybrid transparent electrode materials in which the AgNW network is protected by a conformal thin layer of zinc oxide. The choice of AP-SALD allows us to maintain the low-cost and scalable processing of AgNW-based transparent electrodes. The effects of the ZnO coating thickness on the physical properties of AgNW networks are presented. The composite electrodes show a drastic enhancement of both thermal and electrical stabilities. We found that bare AgNWs were stable only up to 300 °C when subjected to thermal ramps, whereas the ZnO coating improved the stability up to 500 °C. Similarly, ZnO-coated AgNWs exhibited an increase of 100% in electrical stability with respect to bare networks, withstanding up to 18 V. A simple physical model shows that the origin of the stability improvement is the result of hindered silver atomic diffusion thanks to the presence of the thin oxide layer and the quality of the interfaces of hybrid electrodes. The effects of ZnO coating on both the network adhesion and optical transparency are also discussed. Finally, we show that the AP-SALD ZnO-coated AgNW networks can be effectively used as very stable transparent heaters.[2]

[1] Muñoz-Rojas, D., Viet Huong Nguyen, Masse de la Huerta, C., Jiménez, C. & Bellet, D. Spatial Atomic Layer Deposition. in Intech open 1 (2019). doi:10.5772/32009

[2] Khan, A., Nguyen, V. H., Muñoz-Rojas, D., Aghazadehchors, S., Jiménez, C., Nguyen, N. D. & Bellet, D. Stability Enhancement of Silver Nanowire Networks with Conformal ZnO Coatings Deposited by Atmospheric Pressure Spatial Atomic Layer Deposition. ACS Appl. Mater. Interfaces 10, 19208–19217 (2018).

High temperature XRD and XRR studies on atomic layer deposited niobium oxide - silicon oxide nanolaminates

Mikko J. Heikkilä[1], Kaupo Kukli[1,2], Elisa Atosuo[1], Mikko Ritala[1], Markku Leskelä[1]

[1]*University of Helsinki, Department of Chemistry, Helsinki, Finland*
[2]*University of Tartu, Institute of Physics, Tartu, Estonia*

Multilayers and mixtures of Nb_2O_5-SiO_2 have been investigated *e.g.* in optical coatings wherein changes in composition enables tailoring of mechanical stress and refractive index of the multilayer. [1] Possible applications include also memristors [2], where either laminates or complete mixtures can be used, and other memory devices, where band gap of Nb_2O_5 can be adjusted by adding more insulating SiO_2 to the structure [3].

This work focuses on using high temperature x-ray diffraction (HTXRD) and x-ray reflectivity (HTXRR) to analyze nanolaminate structure upon annealing. Similar studies conducted earlier in our laboratory include *e.g.* analysis of multilayer structures of holmium-titanium-oxide with HTXRR [4] and using combined HTXRD+HTXRR for analyzing Al_2O_3/TiO_2-nanolaminates [5]. Based on these results, x-ray reflectivity adds valuable information to the diffraction data and helps in designing possible post deposition thermal annealings. More importantly, XRR allows one to detect amorphous layers present or formed during annealing. Related to the applications mentioned above, change in thickness or density has immediate effects on optical properties of multilayers, and change of structure from amorphous to crystalline or from a crystalline phase to another can have drastic effects to electrical properties via grain boundaries and changes in dielectric constant. Interdiffusion between adjacent layers might lead to stress relaxation or possibly new phases that are invisible to XRD due to small thickness but readily observed with XRR.

Multilayer structures were deposited at 300 °C from $Nb(OC_2H_5)_5$, $Si_2(NHC_2H_5)_6$, and O_3. The number of subsequent SiO_2 and Nb_2O_5 deposition cycles was varied in order to change the thicknesses of the constituent metal oxide layers. Results for a [10 x (5.5 nm Nb_2O_5 + 2.0 nm x SiO_2) + 5.6 nm Nb_2O_5] structure are shown in Figures 1 and 2 as an example. A crystalline phase is formed at around 575 °C, corresponding to an orthorhombic Nb_2O_5 phase, but the broad peaks indicate very small crystallites. The reason for this is obvious from Fig. 2 as the superlattice structure remains intact up to ~900 °C restricting the crystallite growth to the individual Nb_2O_5 layers with a thickness of ~5 nm. From Fig. 2 it is equally easy to see that at the temperature corresponding to the crystallization there is a decrease in bilayer thickness accompanied with an increase in Nb_2O_5 density. The destruction of the superlattice structure leading to complete mixing of the adjacent layers results in coalescence of layer thickness sized Nb_2O_5 crystallites into larger crystallites seen as narrowing of the Nb_2O_5 peak in Fig.1. Similar phenomenon was observed earlier in our study on Al_2O_3/TiO_2-laminates [5].

It is noteworthy that in a structure having a bilayer made of thinner Nb_2O_5 and thicker SiO_2 layer, crystallization is not observed in HTXRD until the complete mixing of the layers at ~900 °C takes place. However, XRR shows thickness changes starting above 400 °C and most likely nanocrystalline Nb_2O_5 is formed at similar temperature as seen in Fig.1. To conclude, without accurate knowledge of how bilayer component materials behave upon annealing, one might misinterpret their post thermal annealing results, in this case thinking that thin Nb_2O_5 layer remains amorphous up to 900 °C. Combining HTXRD and HTXRR gives more insight into what is actually happening.

[1] F. Richter, H. Kupfer, P. Schlott, T. Gessner, C. Kaufmann, *Thin Solid Films*, 389 (2001) 278–283
[2] M. D. Pickett, G. Medeiros-Ribeiro, R. S. Williams, *Nat. Mater.* 12 (2013) 114–117
[3] M. Santamaria, F. Di Franco, F. Di Quarto, *J.Phys.Chem.C*, 117 (2013) 4291–4210
[4] K. Kukli, J. Lu, J. Link, M. Kemell, E. Puukilainen, M. Heikkilä, R. Hoxha, A. Tamm, L. Hultman, R. Stern, M. Ritala, and M. Leskelä, *Thin Solid Films*, 565 (2014) 165–171
[6] M.J. Heikkilä, O.M.E. Ylivaara, E. Atosuo, R.L. Puurunen, M. Ritala, M. Leskelä, "*Properties of ALD grown Al₂O₃-TiO₂ laminates investigated by high temperature XRD/XRR and in situ wafer curvature measurements*", part of the results presented at EMRS Fall 2018, manuscript in preparation
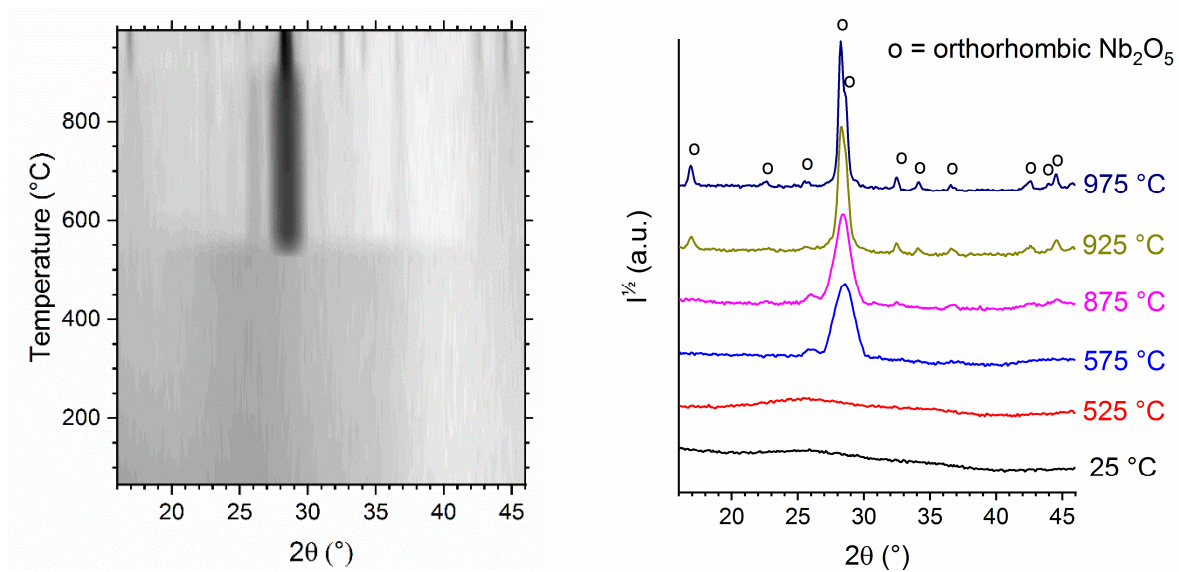
Figure 1. HTXRD data (left) and selected diffractograms (right) of the 10 x (5.5 nm Nb$_2$O$_5$ + 2 nm SiO$_2$) + 5.5 nm Nb$_2$O$_5$ structure
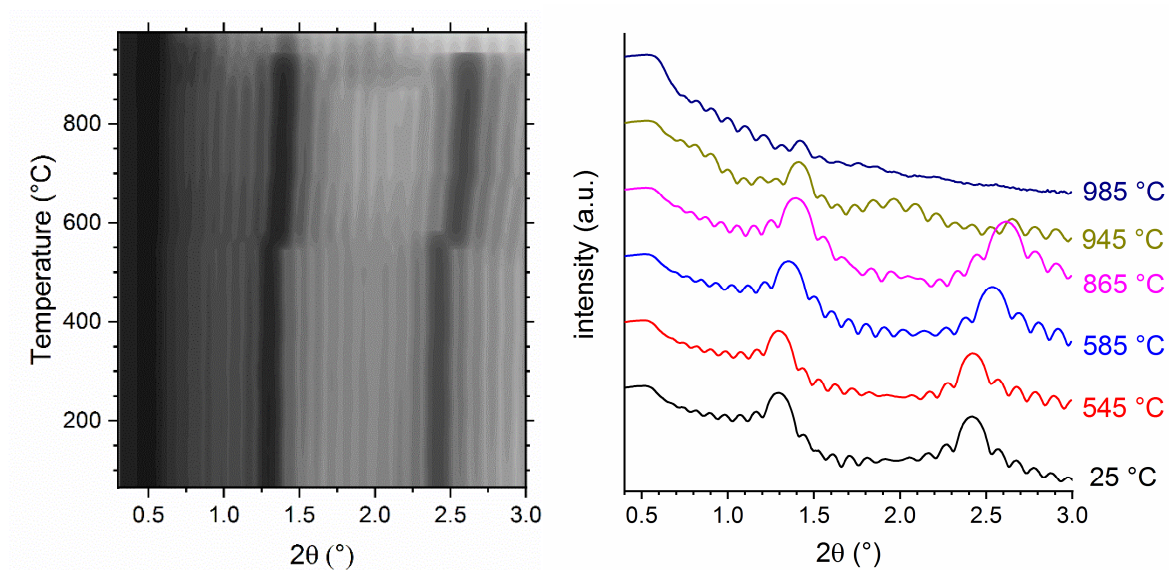
Figure 2. HTXRR data (left) and selected reflectograms (right) of the 10 x (5.5 nm Nb$_2$O$_5$ + 2 nm SiO$_2$) + 5.5 nm Nb$_2$O$_5$ structure

Atomic layer deposition of metal oxide nanolaminates exhibiting nonlinear electrical and magnetic polarization with tunable resistivity

Kaupo Kukli,[1,2] Marianna Kemell,[1] Mikko J. Heikkilä,[1] Helina Seemen,[2] Kristjan Kalam,[2] Aile Tamm,[2] Helena Castán,[3] Salvador Dueñas,[3] Joosep Link,[4] Raivo Stern,[4] Mikko Ritala,[1] Markku Leskelä[1]

[1] *University of Helsinki, Department of Chemistry, Helsinki, Finland, email: kaupo.kukli@helsinki.fi*
[2] *University of Tartu, Institute of Physics, Tartu, Estonia, e-mail: kaupo.kukli@ut.ee*
[3] *University of Valladolid, Department of Electronics, Valladolid, Spain*
[4] *National Institute of Chemical Physics and Biophysics, Tallinn, Estonia*

Multilayers and nanocomposites consisting of single and binary metal oxide thin films are of great interest as constituents of resistive switching and/or multiferroic memory cell structures for spintronics. Ferroelectric behavior in metastable HfO_2 has been described [1]. Electrical polarization in a metal oxide film, i.e., HfO_2, has also been coupled with resistive switching behavior [2]. However, the list of materials demonstrating magnetoelectric performance is rather short [3]. It is still desired that binary and doped binary multiferroics allowing ALD of uniform layers over arbitrarily shaped and large substrates were found.

It was at first necessary to seek saturative and remanent electrical and magnetic polarization, as well as switching resistance in materials with conveniently controllable composition. In our studies, combinations of oxides such as ZrO_2–HfO_2 [4], ZrO_2-Al_2O_3 [5], HfO_2-Al_2O_3 [6], ZrO_2-Co_3O_4, ZrO_2-Fe_2O_3, SiO_2-Fe_2O_3, SiO_2-Nb_2O_5, were grown. To achieve a material possessing well insulating properties in static regime to allow ferroelectric behavior and, at the same time, defective phase promoting ferromagnetism, appropriate relationship between polymorphic phase compositions and cation ratios in the films has to be found.

We have observed certain interrelationship between structural, compositional and dielectric properties of metal oxide films enabling saturative nonlinear polarization and coercivity in the same material under both electric and magnetic fields and, complementarily, memristive behavior with definitive memory windows between high and low resistance states. For instance, HfO_2-Al_2O_3 nanolaminates have demonstrated polarization loops analogous to those in ferromagnetics (Fig. **1**), ferroelectric materials (Fig. **2**), and memristors (Fig. **3**). A variety of thin films were grown, in this context, using ALD processes based on $ZrCl_4$, $HfCl_4$, $Nb(OC_2H_5)_5$, $Al(CH_3)_3$, $Si_2[NH(C_2H_5)]_6$, $Fe(C_5H_5)_2$, $Co(acac)_3$ as cation precursors. Magnetic and electrical performance of different materials grown by ALD will be discussed, comparatively.

[1] J. Müller, P. Polakowski, S. Mueller, T. Mikolajick, Ferroelectric hafnium oxide based materials and devices: Assessment of current status and future prospects, ECS J. Solid-State Sci. Tech. 4 (2015) N30-N35.
[2] B. Max, M. Pešić, S. Slesazeck, T. Mikolajick, Interplay between ferroelectric and resistive switching in doped crystalline HfO_2, J. Appl. Phys. 123 (2018) 134102.
[3] N. A. Hill, Why are there so few magnetic ferroelectrics? J. Phys. Chem. B 104 (2000) 6694-6709.
[4] K. Kalam, H. Seemen, M. Mikkor, P. Ritslaid, R. Stern, S. Dueñas, H. Castán, A. Tamm, K. Kukli, Electric and magnetic properties of atomic layer deposited ZrO_2-HfO_2 thin films, ECS J. Solid-State Sci. Tech. 7 (2018) N117-N122.
[5] K. Kukli, M. Kemell, H. Castán, S. Dueñas, H. Seemen, M. Rähn, J. Link, R. Stern, M. J. Heikkilä, M. Ritala, M. Leskelä, Atomic layer deposition and performance of ZrO_2-Al_2O_3 thin films, ECS J. Solid-State Sci. Tech. 7 (2018) P287-P294.
[6] K. Kukli, M. Kemell, H. Castán, S. Dueñas, H. Seemen, M. Rähn, J. Link, R. Stern, M. Ritala, M. Leskelä, Atomic layer deposition and properties of HfO_2-Al_2O_3 nanolaminates, ECS J. Solid-State Sci. Tech. 7 (2018) P501-P508.
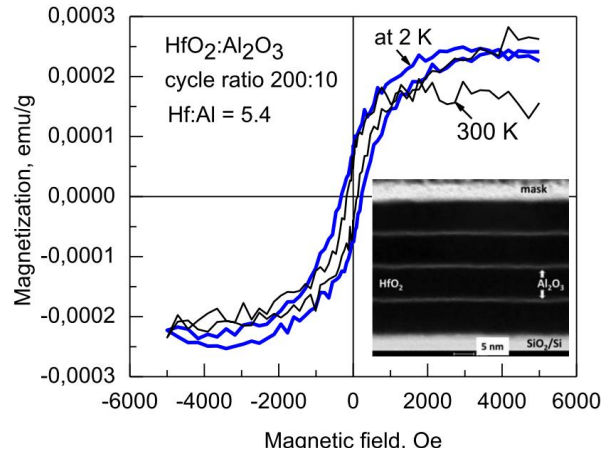
Figure 1. Room temperature (RT) and low-temperature magnetization-field loops measured from HfO$_2$-Al$_2$O$_3$ nanolaminate deposited using HfO$_2$:Al$_2$O$_3$ cycle ratio of 200:10. Inset represents the cross-section HRTEM image of the laminate structure.
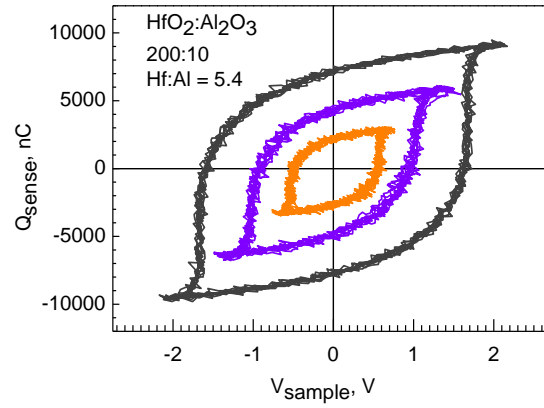

Figure 2. Charge polarization-voltage loops measured using Sawyer-Tower circuit from HfO$_2$-Al$_2$O$_3$ nanolaminate deposited using HfO$_2$:Al$_2$O$_3$ cycle ratio of 200:10. The electrode area was 0.204 mm^2.
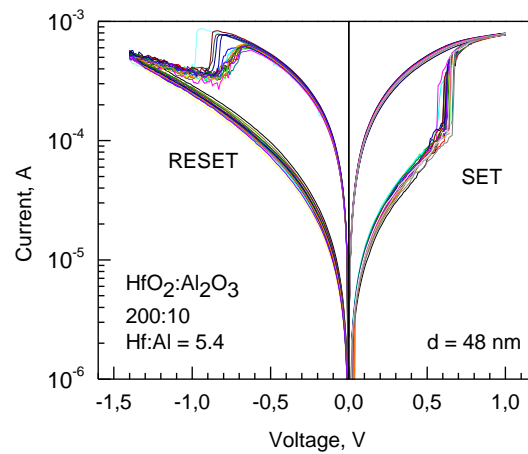

Figure 3. Electrical current versus applied voltage loops measured in switching resistance regime from HfO$_2$-Al$_2$O$_3$ nanolaminate deposited using HfO$_2$:Al$_2$O$_3$ cycle ratio of 200:10.

A new MOCVD process for SnO$_2$ using an amino functionalised tin alkyl precursor: Tuning of surface morphology for sensor related applications

David Zanders[1*], Engin Ciftyurek[2], Klaus Dieter Schierbaum[2], Anjana Devi[1]

1 Inorganic Materials Chemistry, Faculty of Chemistry and Biochemistry, Ruhr University Bochum, 44801 Bochum, Germany (david.zanders@rub.de)
2 Institute of Experimental Condensed Matter Physics, Department of Materials Science, Heinrich-Heine University Duesseldorf, 40225 Duesseldorf, Germany

Tin (IV) oxide (SnO$_2$) is a promising n-type semiconducting material with excellent electrical and optical properties.[1,2] Accordingly, thin films of SnO$_2$ are employed in a broad range of devices comprising such as photovoltaic cells[3] and gas sensors.[4] Regarding chemical sensing applications, SnO$_2$ thin films have become exceptionally attractive due to their outstanding performance that is based on their oxygen deficient surface nature which facilitates ideal conditions for reduction-oxidation reactions to take place.[5] As the properties of metal oxide semiconductor thin film surfaces are highly dependent on the employed deposition process, a wise choice must be made to this effect. Owing to the variability of applicable process temperatures accompanied by good layer thickness control as well as conformal and dense coverage, metal organic chemical vapor deposition (MOCVD) depicts a reliable and favorable route for the above mentioned applications.

A new and highly promising MOCVD process using an amino functionalized tin alkyl precursor, namely [Sn(DMP)$_4$] for the deposition of SnO$_2$ thin films was developed.[6] In-depth thermal characterization of the liquid precursor by thermal stress tests and stepped isothermal analysis evidenced volatility, robustness and allowed to correlate vapor pressure with the applied temperature (Figure 1a). The application of this precursor in MOCVD yielded high quality SnO$_2$ layers and the growth characteristics between 400 °C and 800 °C were investigated (Figure 1b). Morphological and structural features as well as composition were evaluated by XRD, AFM, SEM, RBS, NRA and XPS (Figure 1c) measurements. Optical band gaps of films with varying thicknesses were determined to be between 3.7 eV - 3.9 eV by UV-VIS measurements. In a combinatorial approach comprising temperature-dependent vdP, SEM, AFM and XRD, the profound impact of surface morphology and roughness on the electrical properties of thin ($\leq$ 50 nm) SnO$_2$ films was studied. All investigated films revealed hysteresis-free resistivity performance when heated to temperatures of up to 300 °C in atmospheric environment exhibiting minimum resistivities of 3.12 x 10^{-5} Ω m, which renders them as highly promising for chemical sensor applications in combination with their oxygen deficient surface nature as assessed by XPS.

[1] S. Das, V. Jayaraman, Progress in Materials Science, **2014**, 66, 112.
[2] M. Y. Maximov et al., Journal of Elec Materi, **2017**, 46, 6571.
[3] C. Beneking et al., Thin Solid Films, **1999**, 351, 241.
[4] J. Zhao, et al., Sens. Actuators B, **2010**, 145, 788.
[5] W. Gopel, Prog. Surf. Sci. **1985**, 20, 9.
[6] D. Zanders, et al., Adv. Mater. Interfaces. **2019**, 6, 1801540
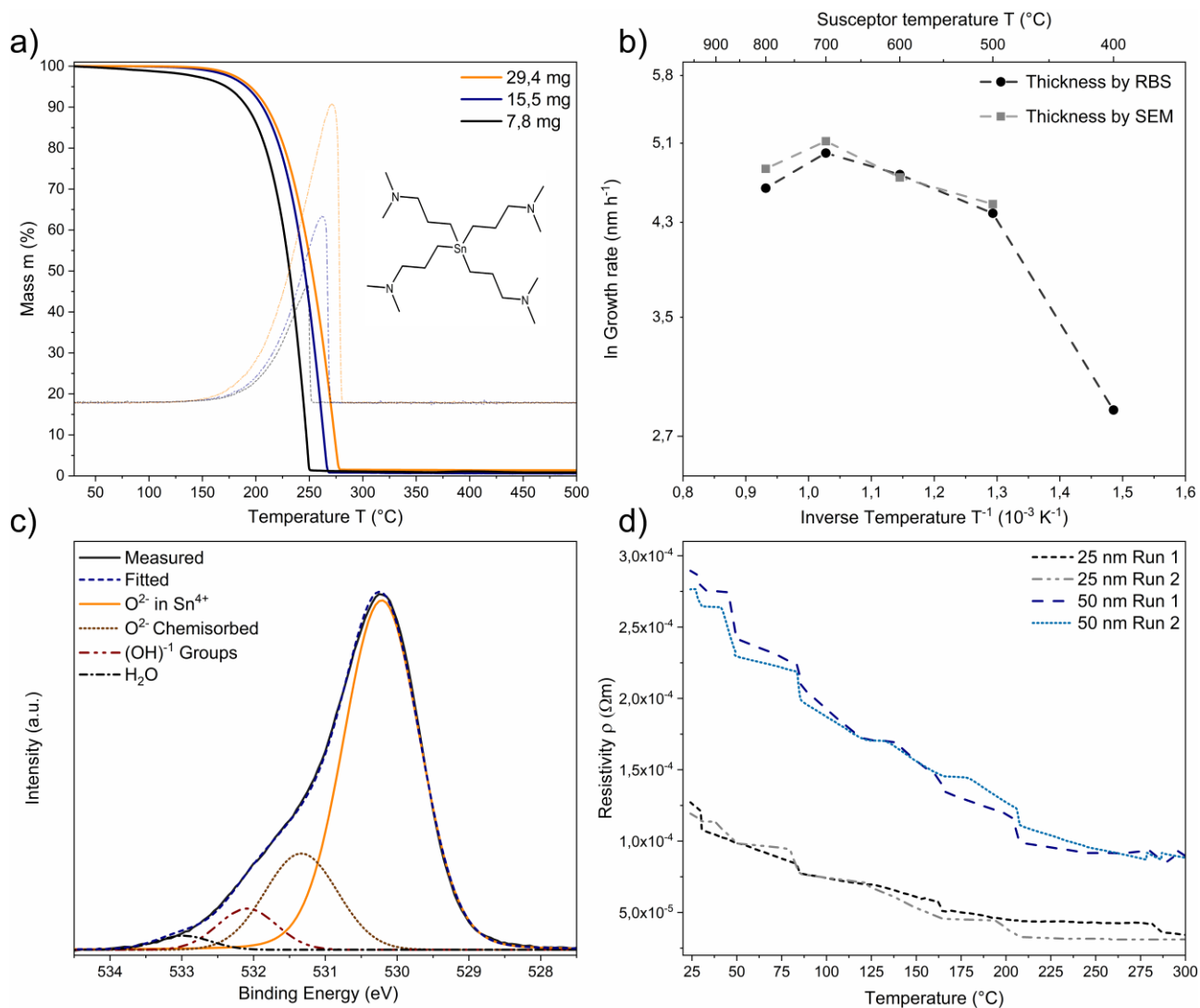
Figure 1: a) TGA of [Sn(DMP)₄] showing mass loss curves of the precursor. b) Arrhenius plot for SnO₂ films deposited on Si(100). c) High-resolution XPS spectra of a 50 nm SnO₂ thin film deposited at 600 °C on Si(100) using the O 1s core level spectrum of the as introduced film. d) Dynamic resistivity of 25 and 50 nm thick SnO₂ thin films as a function of temperature.

Pulsed CVD/ALD of amorphous GeSe for application as OTS selector

Ali Haider[1], Shaoren Deng[2], Elie Schapmans[1], Jan Willem Maes[2], Jean-Marc Girard[3], Gabriel Khalil El Hajjam[1], Gouri Sankar Kar[1], Ludovic Goux[1], Romain Delhougne[1], Matty Caymax[1]

1 IMEC, Belgium (ali.haider@imec.be)
2 ASM-Belgium, Belgium
3 Air Liquide Advanced Materials, France

One of today's most promising alternative concepts for scaled memory is RRAM (Resistive RAM) which is based on the electronic switching of a resistor element. [1] Despite the advances in RRAM structural designs to scale down the memory, sneak currents, which frustrates the accurate reading/writing of data in each cell, has remained a critical issue. An attractive approach is to add a selection device operating for example by means of the Ovonic threshold switching (OTS) mechanism to each memory element that suppresses sneak currents through highly nonlinear current-voltage (IV) characteristics. Amorphous germanium selenide (GeSe) is a well-known candidate for OTS selector which so far has only been grown by physical vapor deposition (PVD) for planar RRAM devices. [2] The 3D RRAM approach, which has the advantage of ultra-high storage density with low cost, calls for a uniform and highly conformal deposition technique to deposit this amorphous GeSe selector material on 3D structures.

Here, we report pulsed chemical vapor deposition (CVD) ('ALD') of amorphous GeSe by means of two Ge and Se sources: 1. Ge: dioxane-stabilized germanium dichloride. ($GeCl_2 \cdot C_4H_8O_2$) and Ge methoxide $Ge(OCH_3)_4$, and 2. Se: (bis(trimethylsilyl)selenide ($C_6H_{18}SeSi_2$) $(TMS)_2Se$ and bis(triethylsilyl)selenide ($C_{12}H_{30}SeSi_2$) $(TES)_2Se$. Initially, we performed chemisorption studies using total reflection X-ray fluorescence (TXRF) to study the kinetics of precursor chemisorption on Si substrate. Ge dichloride precursor chemisorption on Si substrate was found to show some under-dosing due to limited precursor supply. On the other hand, Se chemisorption is limited by low reaction efficiency as we learned from a much better within-wafer uniformity. The same measurements also show that Se precursors need Cl sites (from Ge precursor) for precursor ligand exchange reactions. Chemisorption of $(TMS)_2Se$ is much faster than $(TES)_2Se$ on a precoated $GeCl_x$ layer owing to its higher vapor pressure and better reaction efficiency of $(TMS)_2Se$ with Ge dichloride precursor. ALD tests with $GeCl_2 \cdot C_4H_8O_2$ and $(TMS)_2Se$ revealed that the growth per cycle (GPC) decreases with introduction of purge steps in the ALD cycle whereas a higher GPC is obtained in pulse CVD mode without purges. Based on this basic understanding of the process, we developed a pulsed CVD growth recipe (GPC=0.3 Å/cycle) of GeSe using $GeCl_2 \cdot C_4H_8O_2$ and $(TMS)_2Se$ as Ge and Se source, respectively. $Ge(OCH_3)_4$, on the other hand, didn't result in GeSe growth. TEM images reveal that ~20 nm grown GeSe layer is amorphous while EDX and RBS measurements revealed stoichiometric GeSe films with traces of Cl impurities. EDX mapping revealed uniform Ge and Se distribution throughout the film. Elastic recoil detection (ERD) measurements show ~5 % carbon inside the grown GeSe film. AFM images show an RMS surface roughness of 1.7-1.9 nm. GeSe grown on 3D test structures showed excellent film conformality.

[1] J. Zhou et al., IEEE Transactions on Electron Devices, **61**, 1369 (2014).
[2] A. Verdy et al., 2017 IEEE International Memory Workshop (IMW), Monterey, CA, 1-4 (2017).
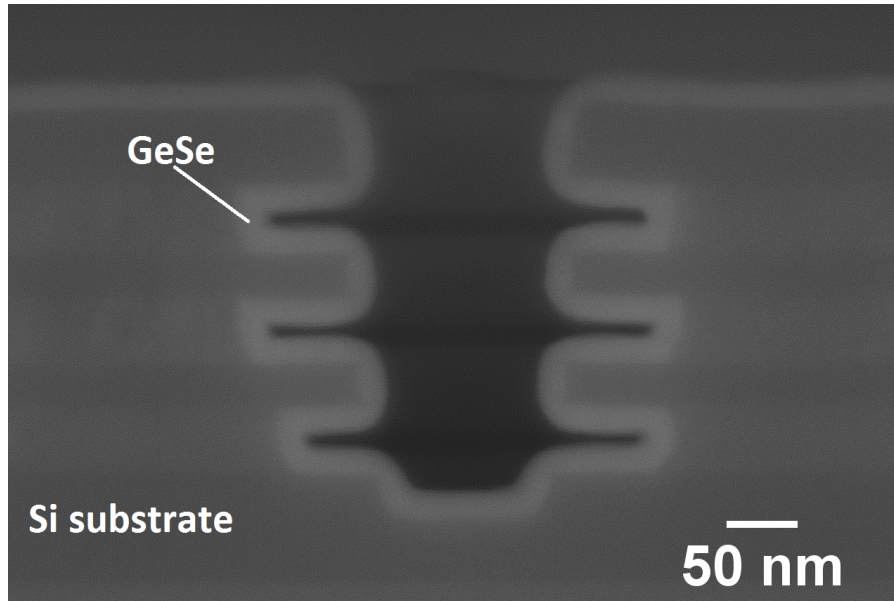[3] V. Pore et al., Journal of American Chemical Society, **131**, 3478 (2009).

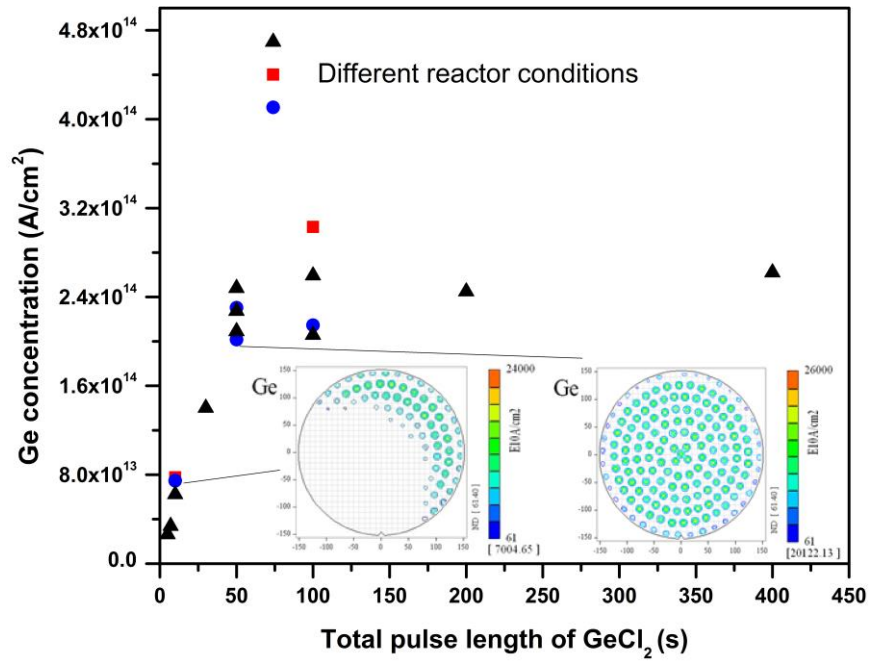**Figure 1**. Conformally grown pulsed CVD GeSe on 3D test structure

Figure 2. Ge chemisorption on SiO_X is slow (TXRF measurements), limited by precursor supply/slower injection

Drug elution system based on a sandwich layer structure grown onto commercially-available stents using atomic layer deposition

Mohammed T Ali[1], Kenneth Martin[1], Wisam Khider[1] Arun HS Kumar[1], Noel M Caplice[1]

Ian M Povey[2], Martyn E Pemble[2,3]

1. Centre for Research in Vascular Biology, University College Cork, Cork Ireland

2. Tyndall National Institute, University College Cork, Dyke Parade, Cork, Ireland

3. School of Chemistry, University College Cork, Cork, Ireland

Drug eluting stents (DES) represent one of the most active and rapidly changing technologies in the medical device industry with recent research focused on improving the scaffold and stent delivery platforms [1]. Initial DES used durable polymers that eluted over many months and were associated with immune activation but more recent designs have aimed at lower polymer loading, with thinner, lower profile polymer applications on stent struts and with shorter degradation periods. Alternatively, the polymer has been changed to a bio absorbable coating that achieves the same outcome of reducing exposure to the adverse effects of synthetic polymer. [2-5]. Despite these advances there remains a residuum of patients where polymer coating is associated with delayed healing and the potential for increased risk of late stent thrombosis. Thus the challenge remains to reduce or remove the polymer coating and to use less cytotoxic drugs that more selectively target smooth muscle cells and inflammatory cells without killing endothelial cells in the hope of getting a low restenosis rate but more rapid endothelialisation.

In this study we developed a drug-eluting inorganic stent coating in which an anti-restenotic drug was sandwiched between two ultra-thin (~5nm) layers ALD deposited titanium oxide (TiO_2) and aluminium oxide (Al_2O_3). This unique ultra-thin coating conformation also allows for flexibility in terms of stent coating thickness and design. In this proof of concept study we evaluated the hemato- and vascular compatibility of a TiO_2-drug-Al_2O_3 (TDA) sandwich DES compared to an ALD TiO_2-Al_2O_3 (TA)-only coated stent without drug as a control. It is demonstrated that the TA coated stent is significantly smoother that the Al_2O_3 only coated stent (Figure 1) and behaves well in a blood flow environment (Figure 2). Furthermore, the TDA stent has excellent bio- and hematocomptability, with minimal in-stent stenosis being observed 4 weeks after implantation, as compared to a control stent without drug.

1. S. Garg, C. Bourantas, P.W. Serruys, Nat. Rev. Cardiol. 10 (2013) 248-260.
2. J.R. Costa, A. Abizaid, R. Costa, F. Feres, L.F. Tanajura, A. Abizaid, L.A. Mattos, R.Staico, A.G. Siqueira D, Sousa, R. Bonan, J.E. Sousa, J. Am. Coll. Cardiol. Cardiovasc. Interv. 1 (2008) 545-551.
3. J.P. Loh, L.K. Pendyala, H. Kitabata, S. Badr, R. Torguson, F. Chen, L.F. Satler, W.O. Suddath, A.D. Pichard, R. Waksman, Int. J. Cardiol. 170 (2013) 43-48
4. G.V. Silva, M.R. Fernandes, R. Madonna, F. Clubb, E. Oliveira, P. Jimenez-Quevedo, R. Branco, J. Lopez, F.S. Angeli, R. Sanz-Ruiz, W.K. Vaughn, Y. Zheng, F. Baimbridge, J. Canales, C.O. Cardoso, J.A. Assad, R. Falotico, E.C. Perin. Catheter Cardiovasc. Interv. 73 (2009) 801-808
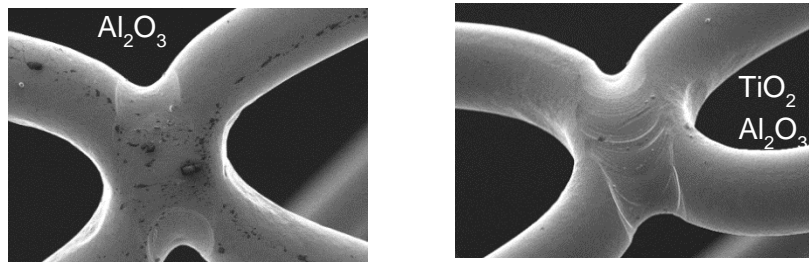5. N.G. Kounis, G. Hahalis, T.C. Theoharides, J. Interv. Cardiol. 20 (2007) 314-323.

Figure 1. C. SEM images of single Al$_2$O$_3$ coated and double (TiO$_2$ Al$_2$O$_3$) coated BMS showing relative smoothness of each.
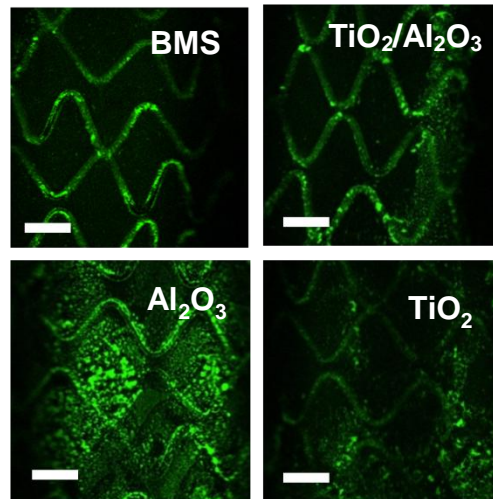

Figure 2. Fluorescently labelled platelets (mepacrine) attached to stent struts under varying bare metal stent (BMS) coating conditions and flowing exposure to arterial shear flow rates in an external flow chamber. The thrombus coverage for the TiO2-Al2O3 closely mimics that of the bare metal stent (BMC).

Developing upscalable routes to water splitting devices using chemical vapour deposition

Andreas Kafizas[1], Shababa Selim[1], Brian Tam[1], James Durrant[1], Christopher Blackman[2]

1 Department of Chemistry, Imperial College London, United Kingdom (a.kafizas@imperial.ac.uk)
2 Department of Chemistry, University College London, United kingdom

It is widely acknowledged that the release of CO_2 from the combustion of fossil fuels is the primary cause of Global Warming – an effect that has resulted in increased average temperatures, melted polar ice and a rise in sea levels [1]. To mitigate the potentially catastrophic results of climate change, the Intergovernmental Panel on Climate Change (IPCC) has set a set a target to restrict warming to 2 °C above pre-industrial era temperatures [2].

Sunlight is mankind's largest energy source, the amount reaching the surface of the Earth every hour being nearly twice the total energy consumed annually from fossil fuels, nuclear and all other renewable energy sources combined [3]. Photovoltaics are the fastest growing source of renewable energy; however, the mismatch between electricity supply and energy use has made energy storage increasingly important. One of the most promising approaches to both store solar energy, and renewably produce fuel, is solar water splitting - where water is converted into hydrogen fuel and oxygen gas [4]. Although solar-to-hydrogen efficiencies of 16% have been demonstrated [5], a durable, efficient and low-cost device is yet to be developed.

Recent work has shown that highly durable and low-cost metal oxide-based devices can be engineered, through the use of heterojunctions, to achieve high water splitting efficiency [6]. A heterojunction is the interface formed between two dissimilar semiconductors, and can promote the spatial separation of charge [7].

Chemical vapor deposition (CVD) is the go-to industrial method for growing large area coatings for a wide range of applications. Using CVD, one can increase the complexity of a device at little added cost, and grow a wide range of materials, with tailored nanostructure and heterojunction architecture that can remarkably improve device efficiency. In this talk we will present our recent work on two heterojunction systems: anatase-TiO_2/ rutile-TiO_2 and WO_3/ $BiVO_4$ (**Figure 1**). We will discuss how the CVD growth conditions were optimized to achieve water splitting activities that are amongst the highest ever reported for these systems.

[1] W. S. Broecker, *Science,* 80. (1975), 460–463
[2] M. New, D. Liverman, H. Schroeder, K. Anderson, *Philos. Trans. A. Math. Phys. Eng. Sci.* 369, (2011) 6–19
[3] O. Morton, *Nature* 443, (2006), 19–22
[4] A. Fujishima, K. Honda, *Nature* 238, (1972), 37
[5] J. L. Young, M. A. Steiner, H. Döscher, R. M. France, J. A. Turner, T. G. Deutsch, *Nature Energy*, 2, (2017) 17028
[6] K. Domen *et al.*, *Nature Materials*, 15, (2016), 611–615
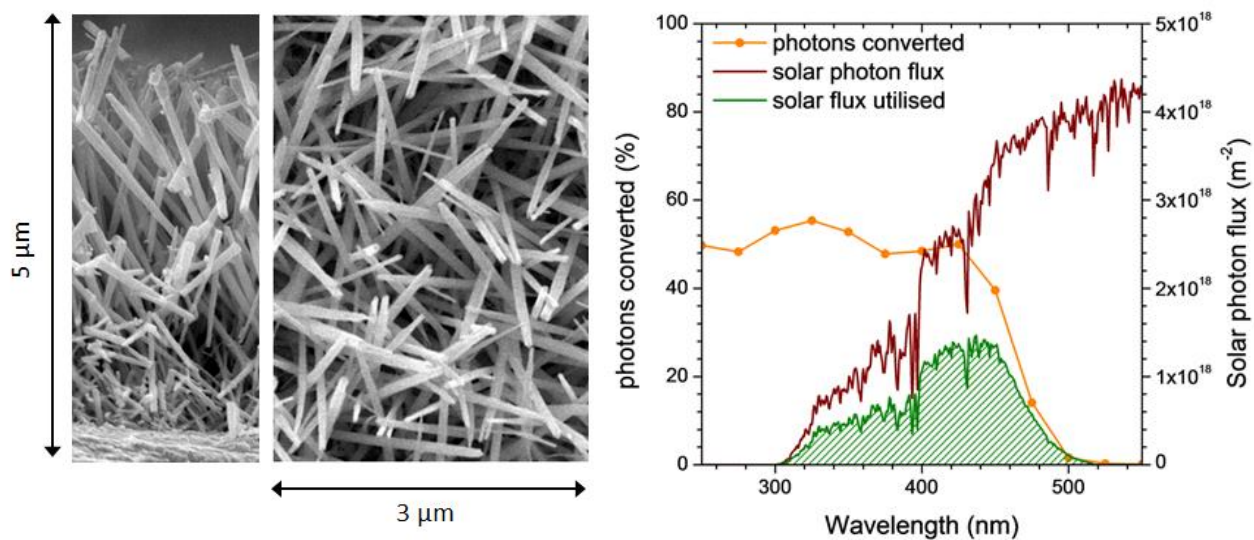[7] A. Kafizas *et al. Applied Catalysis B: Environmental*, 224, (2018), 904-911

Figure 1: (left) SEM images of WO₃/ BiVO₄ nanoneedlestructures deposited by an aerosol-assited CVD method. (right) Light conversion efficiency for driving the water splitting reaction alongside a calculation that shows the fraction of solar photons that would be converted.