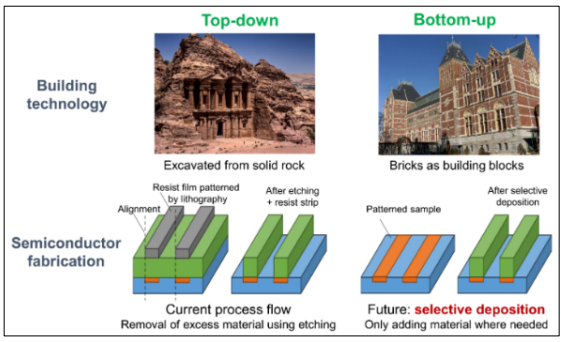
Bachelor End Projects
2021

Plasma and Materials Processing

10 February 2021

Area-selective atomic layer deposition for bottom-up fabrication of nanoelectronics

Short description: The ability of precursor ligands to block the adsorption of other precursors will be studied using spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy (XPS)



Background: To enable further downscaling of electronics following Moore's law, *bottom-up* fabrication schemes need to be introduced in the semiconductor industry. Semiconductor fabrication can be advanced drastically when it becomes possible to selectively add material *only* there where it is needed, instead of using the conventional top-down approach of removing excessive material. This strives for a new paradigm in the manufacturing of electronics, facilitating the continuation of Moore's law scaling for many more technology generations.

The focus of this project is on atomic layer deposition (ALD), a technique that enables layer-by-layer deposition of thin films with atomic-level control of the film thickness. ALD has recently become an important element of the semiconductor fabrication toolbox and being a true, enabling nanotechnology it is gaining ever more attention. The goal of this project is to make ALD growth *selective* to certain surfaces, such that the deposition only occurs at surfaces where it is needed.

Project: In the project you will investigate a three-step ALD cycle as shown in figure 1. The goal of the project is to find out how efficient the self-limiting adsorption mechanisms of an ALD precursor are for the blocking of other ALD precursors. Moreover, the influence of the size and reactivity of several precursor molecules on how much precursor adsorption can be blocked will be investigated. In this project you will work with ALD, SE and XPS and gain experience on working in a cleanroom facility.

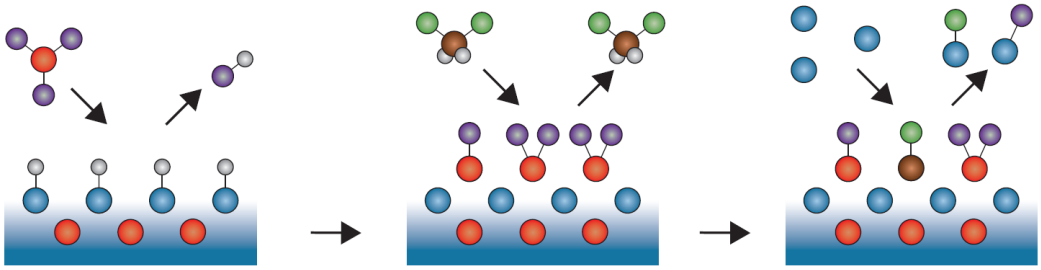


Fig. 1: *Schematic illustration of a three-step ALD process which suppresses the adsorption of molecules during the second step*

Location and supervision: You will perform experiments in the cleanroom that is located in spectrum. You will be supervised by Marc Merkx and Adrie Mackus.

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Marc Merkx:	**Flux 3.103**	m.j.m.merkx@tue.nl
Adrie Mackus	**Flux 3.112**	a.j.m.mackus@tue.nl

Studying Plasma Atomic Layer Etching reaction species using Quadrupole Mass Spectroscopy and Optical Emission Spectroscopy

Short Description: Understanding the mechanism of novel Atomic Layer Etch (ALE) processes for integrated circuit fabrication by utilizing Quadrupole Mass Spectroscopy (QMS) and Optical Emission spectroscopy (OES).

Background: Atomic layer Etching is set to become one of the key processes for further downscaling of integrated circuits (IC) allowing for the continuation of Moore's Law. First reported in 1988 ALE has witnessed a large increase in number of publications per year due to shrinking critical dimensions within ICs. To create these smaller critical features on a chip more accurate etch techniques are required. ALE is ideal for these etch processes due to its high level of etch control, smoothing effect and selectivity to the desired etched material. Production of Gate all around transistors and future technologies such as 3D NAND will be facilitated by ALE processes.

The focus of this project is on characterizing novel isotropic ALE processes for materials that are of interest to the semi-conductor industry. ALE is poised to become a key process for the realization of future technologies and as such understanding of the underlying process is required. The goal of this project is to better understand the reaction pathways and by-products produced during ALE.

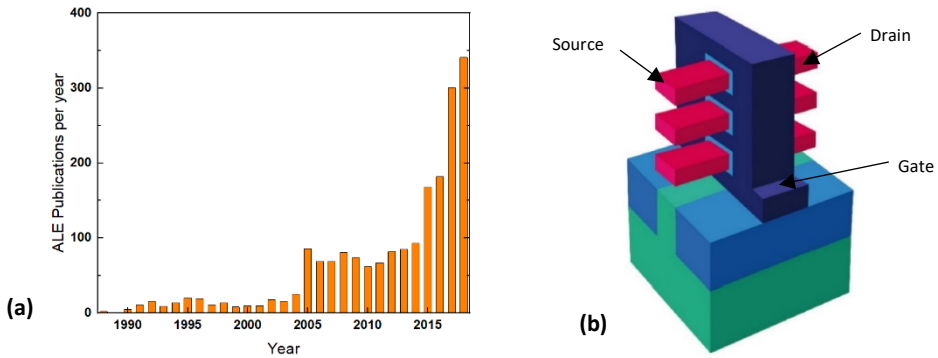

Fig 1: (a) Graph showing uptake in ALE publications, (b) Gate-all-around FET device that will require isotropic ALE to define the source/drain nanowires

Project: In this project an isotropic Plasma ALE process will be investigated using QMS and OES to identify reaction species. The aim is to understand what reaction by-products are produced during the plasma and precursor dosing steps to help determine a reaction pathway. Furthermore concentrations of reaction species will be monitored for different temperatures, plasma powers and pressures.

Location and supervision: You will perform experiments in the cleanroom that is located in spectrum. You will be supervised by Nick Chittock and Adrie Mackus.

If interested please contact:

Nick Chittock	**Flux 3.116**	n.j.chittock@tue.nl
Dr. ir. Adrie Mackus	**Flux 3.112**	a.j.m.mackus@tue.nl

Accurate ion energy control for plasma-enhanced atomic layer etching (ALE)

Introduction: Anisotropic plasma ALE is a processing technique for removing materials in a layer by layer manner using directional ions generated by a plasma. The aim of this research will be to investigate new approaches for anisotropic plasma ALE. A new approach can be performed by controlling ion energy distributions (IEDs) during plasma exposure through the application of arbitrary bias voltage waveforms to the substrate. The method relies on the concept demonstrated in our previous work whereby the use of low-frequency, arbitrary bias voltage waveforms can serve as a means for lowering the spread (or width) of IEDs, typically obtained by radio-frequency (RF) sinusoidal bias voltage waveforms (Figure 1). The narrowing of IEDs could (1) improve the precision of anisotropic plasma ALE by enabling removal of only a thin surface layer without removing any sub-surface material, (2) improve the selectivity of anisotropic plasma ALE by enabling removal of only one material without removing any other (different) material lying nearby. Such improvements in anisotropic plasma ALE are highly relevant for fabricating next-generation semiconductor devices.

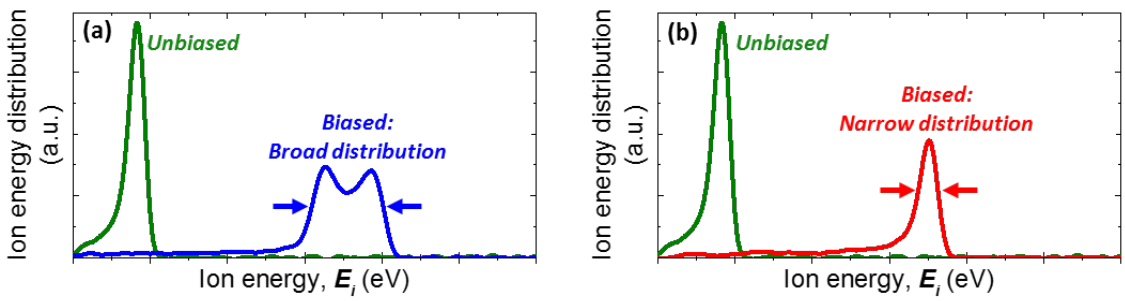

Figure 1. Schematics illustrations depicting ion energy distributions (IEDs) for a plasma exposed to a substrate biased using (a) a radio-frequency (RF: 13.56 MHz) sinusoidal voltage waveform and (b) a low frequency (kHz) arbitrary voltage waveform. They illustrate how narrow IEDs can be obtained for substrates that were either unbiased or biased with an arbitrary voltage waveform while also showing how broad IEDs can be obtained for substrates biased with a RF sinusoidal voltage waveform.

Project: The goals of this project are 1) to measure IEDs in plasmas with RF sinusoidal bias voltage waveforms and low frequency arbitrary bias voltage waveforms, 2) to measure and compare sputter yields of various materials (e.g. Co, Ru, Al_2O_3, etc.) obtained by sputtering substrates biased with RF sinusoidal voltage waveforms and low frequency arbitrary voltage waveforms. The plan for which measurements will be exactly performed depends on when the student is available for the project.

Location and supervision: The project will mostly consist of experimental work, which will be in the cleanroom located in the Spectrum building. You will by supervised by Shashank Balasubramanyam (Postdoc) and Adrie Mackus (Assistant Professor)..

For further information please contact

Dr. Shashank Balasubramanyam **Flux 3.116** s.balasubramanyam@tue.nl

Dr. ir. Adrie Mackus **Flux 3.112** a.j.m.mackus@tue.nl

Computational analysis of molecular interactions for area selective atomic layer deposition

Short description: Interactions between molecules for area-selective ALD will be computationally investigated via density functional theory calculations.

Background: Area-selective atomic layer deposition (ALD) enables bottom-up fabrication and can be used to minimize the number of the required processing steps during semiconductor production. One of the most promising area-selective ALD methods involves the sequentially dosing of the inhibitor, precursor and co-reactant molecules in ABC-type (i.e. three-step) cycles.[1] In this process, the introduction of inhibitor molecules plays an important role in determining area-selectivity of the growth process. Even the inhibitor and the precursor doses are not introduced to the system simultaneously, some undesired interactions can still happen between these species. Therefore, the synergy between the selected inhibitor, precursor and co-reactant is crucial for the successful application of the process.

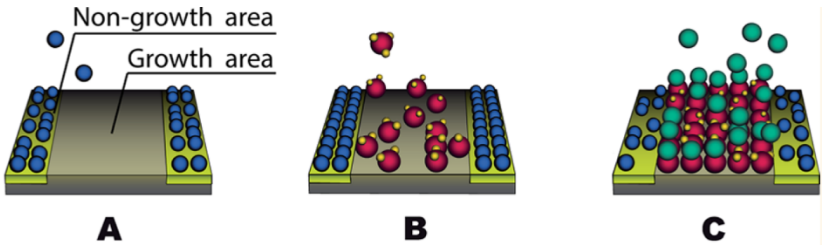

Figure 1. Schematic illustration of the ALD process in the ABC fashion, the introduction of inhibitor molecules in step A dominates the selectivity of the growth area.[1]

Project: This project aims to investigate the inhibitor-precursor and inhibitor-inhibitor interactions to shortlist possible precursor/inhibitor pairs for the area-selective ALD. For this aim, the energies of the candidate systems will be computed as a function of the distance between the molecules. Using this data the potential energy profiles along the interaction path will be prepared. For simplicity, simulations will be performed without the presence of a substrate.

You will get familiar with density functional theory calculations, and you will gain experience working with molecular simulations. Basic programming and command line knowledge are required for the project.

Reference:

1. Mameli, A., Merkx, M. J. M., Karasulu, B., Roozeboom, F., Kessels, W. E. M. M., & MacKus, A. J. M. (2017). Area-Selective Atomic Layer Deposition of SiO2 Using Acetylacetone as a Chemoselective Inhibitor in an ABC-Type Cycle. ACS Nano, 11(9), 9303–9311.

Location and supervision: The project will consist of computational work. You will work in the Plasma and Materials Processing (PMP) group and you will be supervised by İlker Tezsevin (Postdoc) and Adrie Mackus (Assistant Professor).

Interested? For further information please contact:

Dr. İlker Tezsevin	**Flux 3.116**	i.tezsevin@tue.nl
Dr. ir. Adrie Mackus	**Flux 3.112**	a.j.m.mackus@tue.nl

MoS_2 as a Cu diffusion barrier, tested by time-dielectric breakdown tests

Short description: The possibility to use MoS_2 as a barrier layer in Cu interconnect structures could enhance the industry to further scale down chips.

Background: Further downscaling of electronics is limited by the scaling of (among others) copper interconnects. When copper thicknesses are getting below 100 nm, the resistivity increases exponentially. This becomes a problem when the thickness of the copper is also limited by other factors. In interconnect structures there is a so-called barrier layer present which prevents Cu diffusion from the Cu line to the underlying material (often a dielectric). This barrier layer also needs to decrease in thickness. The problem is, however, that the conventional barrier fail when the thickness comes below 3 nm. Finding a new barrier which will work at lower thicknesses is thus the challenge.

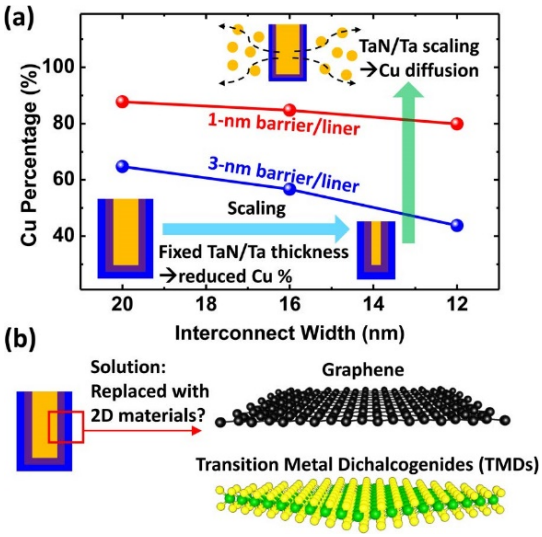

Figure 1. (a) Challenges of interconnect scaling—less cross-sectional area is occupied by Cu with interconnect width scaling. Thus, the total line resistance will increase significantly. Proportionally reducing TaN/Ta thickness is not a viable solution since Cu diffusion will occur. (b) Replacing TaN/Ta with 2D materials can be a promising solution to continue the required interconnect scaling. [1]

The focus of this project is on exploring the possibility of using MoS_2 as a barrier layer. The technique to create these thin layers is atomic layer deposition (ALD), a technique that enables layer-by-layer deposition of thin films with atomic-level control of the film thickness. ALD has recently become an important element of the semiconductor fabrication toolbox and being a true, enabling nanotechnology it is gaining ever more attention. The goal of this project is to use indirectly synthesized MoS_2, made by sulfurizing ALD grown MoO_3, as a barrier layer against Cu diffusion.

Project: The goal of the project is to find out if MoS_2 can serve as a barrier layer in Cu interconnects. You will work on time-dependent dielectric breakdown (TDDB) measurements to characterize the barrier properties. In the project you will also investigate an indirect ALD process, where you can make alterations in temperature of the different steps to investigate the influence on the barrier properties.

[1] Lo *et al.* Opportunities and challenges of 2D materials in back-end-of-line interconnect scaling. **J. Appl. Phys.** 128, 080903 (2020); https://doi.org/10.1063/5.0013737

Location and supervision: You will perform experiments in the labtuin and TDDB measurement lab which are both located in Spectrum. You will be supervised by Sanne Deijkers and Adrie Mackus.

If interested please contact:

ir. Sanne Deijkers	**Flux 3.096**	**j.h.deijkers@tue.nl**
dr. ir. Adrie Mackus	**Flux 3.112**	**a.j.m.mackus@tue.nl**

Metal oxide layers for perovskite solar cells

Introduction: A new type of solar cells based on perovskite compounds have rapidly developed, starting from 3.8% efficiency in 2009 and reaching over 25% in 2019 thus competing with market dominating crystalline silicon solar cells. Perovskite materials are compatible with low temperature processing and flexible substrates, allowing for a wide range of inexpensive processing techniques potentially allowing to lower the cost of solar cells. However, the stability of the perovskite solar cells is the main roadblock for upscaling, partially due to the utilization of organic transport layers. This project focuses on the replacement of organic charge transport layers with inorganic ones: metal oxides.

Metal oxides such as SnO_x and TiO_x can be used as electron transport layers (ETL); while NiO_x as hole transport layer (HTL). The configuration of a perovskite cell employing charge transport layers is shown in **Fig.1**. Atomic layer deposition (ALD) is a technique that has been successfully employed for the growth of metal oxide layers in perovskite solar cells.[2] ALD metal oxide films have demonstrated excellent electrical and optical properties. In addition, when deposited on the top of the solar cell or as one of the layers, they also show excellent encapsulating properties enhancing the stability of the cells.

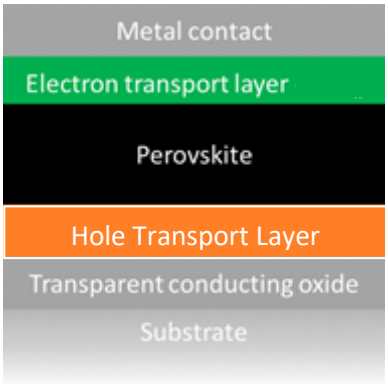

Figure 1: *Perovskite solar cell structure*

Project description: ALD of various metal oxides to be used in perovskite solar cells is currently being developed within our research group. Following our recent publication,[3] we have gained knowledge about interface modifications induced by ALD processing of metal oxides directly on the perovskite absorber. The student will work with us to research novel ALD metal oxides to be employed as charge transport layers and to optimize their properties to improve the perovskite solar cell performance and stability. Moreover, our research is not only limited to processing on top of the perovskite absorber but we are also in the process of investigating the interface created between the HTL and the perovskite with previously reported processes established by our group.[4] The student will work on either interfaces, top or bottom, and the resulting perovskite/metal oxide interfaces will be analyzed using X-ray diffraction, X-ray photoelectron spectroscopy, IR spectroscopy and spectroscopic ellipsometry together with electrical solar cell measurements to study the properties and performance of the transport layers in perovskite solar cells.

References: Brinkmann, K. O., et al., Nat. Commun. **2017**, 8, 13938; Zardetto, V., et al., Sustain. Energy Fuels **2017**, 1, 30–55; Bracesco et al., J. Vac. Sci. Tech.-A, **2020**, 38, 063206; Koushik, et al., J. Mater. Chem. C, **2019**, 7, 12532-12543

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Dr. Nga Phung	**Flux 3.116**	t.t.n.phung@tue.nl
Prof. Dr. Adriana Creatore	**Flux 3.107**	m.creatore@tue.nl

Electrochemical activation of cobalt phosphate-based electrocatalysts for H_2O splitting

Introduction: Shifting from fossil energy sources to renewable energy sources requires efficient ways to store renewable energy in chemical form. One way to do this is via electrolysis of water to form hydrogen, which can be converted back to electricity later or used as a feed stock for chemical processes. The efficiency of water electrolysis depends on the catalysts used for this process, and cobalt phosphate-based catalysts are particularly efficient in neutral conditions.

Recently, we discovered that cobalt phosphate thin films undergo a significant restructuring process during the electrolysis process. This enhances the surface area accessible to water and leads to a much more efficient catalyst. This restructuring process is strongly dependent on the initial composition of the cobalt phosphate film, which can be tuned accurately by means of Atomic Layer Deposition. However, much remains uncertain about the mechanism behind this restructuring process and if it is influenced by the film thickness or the substrate on which the film has been deposited

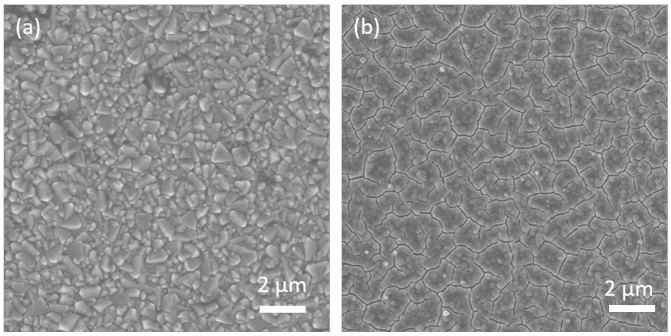

Figure 1: Scanning electron microscope images of a cobalt phosphate thin film a.) as deposited, b.) after long-term use as a water electrolysis catalyst

Project description: In this project you will investigate the structural changes occurring in cobalt phosphate thin films during water electrolysis. In particular, you will assist in the deposition of cobalt phosphate thin films and analyze their nanostructure by means of Raman spectroscopy and/or ellipsometric porosimetry, both as-deposited and after being used as a water electrolysis catalyst.

In this project you will closely collaborate with Gerben van Straaten (postdoc) and Tigran Khatarchjan (MsC.) who are working on further development of the deposition process and spectroscopic analysis techniques, and Marek Lavorenti (PhD) and Mihalis Tsampas from the Dutch Institute of Fundamental Energy Research (DIFFER) who will investigate the electrochemical performance of the deposited films.

References:

1) V. Di Palma et al., Electrochemistry Communications (2019), 98, 73-77
2) V. Di Palma et al., Journal of Vacuum Science & Technology A (2020), 38, 022416
3) R. Zhang et al., ACS Catalysis (just accepted)

For further information please contact

Dr. Gerben van Straaten g.v.straaten@tue.nl

Prof. dr. Adriana Creatore m.creatore@tue.nl

Molecular layer deposition of CO_2 adsorbing materials

Introduction: Mitigating the worst effects of climate change requires us to put a halt to the rising CO_2 levels. One promising approach is the direct sequestration of CO_2 from the atmosphere. This approach requires the development of systems that can efficiently store CO_2 at ambient conditions and release it with a minimal investment of energy. In collaboration with Carbyon B.V., we are developing methods to deposit ultrathin films of CO_2 adsorbing materials on porous scaffolds with low heat capacity.

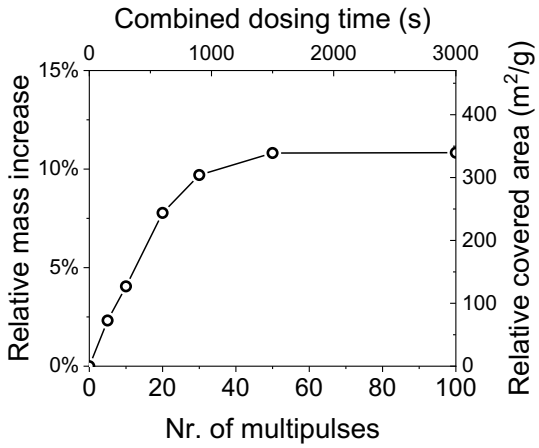

Figure 2: Mass gain of porous substrates as function of the amount of dosed precursor, showing saturation of the amount of absored material and thus self-limitng growth

A primary issue with porous materials is that uncontrolled growth of thin films can lead to pore clogging. One way to prevent pore clogging while still achieving high loading of CO_2 adsorbing materials is to use molecular layer deposition (MLD). In MLD, a molecule is dosed and then reacts with the reactive sites on the substrate surface. The result is a self-limiting reaction which continues until all sites have been covered, resulting in a mono-layer of the desired molecules. The molecule contains groups which can react reversibly with CO_2. Further growth can be achieved by dosing a second molecule which reacts with this molecular layer and provides new reactive sites.

Project description: This project focusses on the optimization of the deposition process of these ultrathin layers and the development of new methods to characterize them. You will oversee MLD depositions and analyze the effect of varying deposition conditions on the physical properties of these layers, both on flat model substrates and porous layers.

For further information please contact

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Ex situ study of CO_2 plasma conversion with optical diagnostics

Introduction: With the more and more apparent consequences of climate change, we have to look for new and innovative ways to reduce the CO_2 concentration in the atmosphere. A very appealing possibility is the plasma induced conversion of CO_2 into hydrocarbon fuels. If the plasma is generated with electricity from renewable energy sources these fuels are called solar fuels. Plasma is an ideal tool to conduct the most energy intensive step in the conversion process, namely the splitting of CO_2 into carbon monoxide and oxygen. Due to its non-equilibrium nature the plasma can split the CO_2 molecule in a very energy efficient way.

To tailor the plasma process a detailed understanding of the present molecular species and their interactions is therefore crucial. Furthermore, we want to assess the effectivity of the plasma. At PMP we use optical diagnostics to get the required information.

A rather obvious way to determine amount of converted CO_2 is by comparing the gas that enters the plasma with the one after the plasma.

Project description: You will perform an ex situ spectroscopic study on our plasma systems. That means you will determine the gas composition after the plasma processing by means of Fourier-Transform Infrared (FTIR) spectroscopy. You can do your measurement on two different plasma setups. On the one hand, we are currently building a completely new setup for a nanosecond repetitively pulsed (NRP) discharge. This new plasma source must be characterized thoroughly. On the other hand, we use a well-studied glow discharge but add oxygen to the carbon dioxide. This makes the whole system much more challenging in terms of e.g gas composition but also brings it closer to the application where one will rarely encounter a pure CO_2 gas stream.

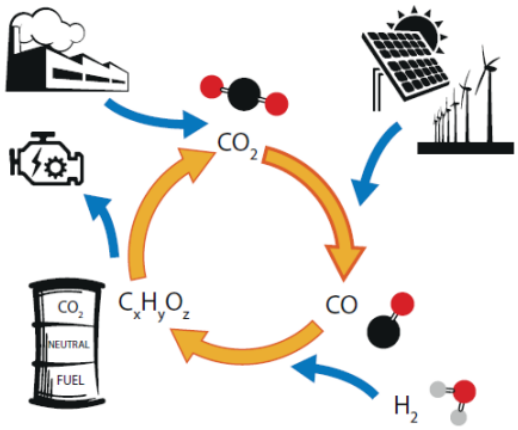

Figure 3: Mark Damen PhD Thesis 2020

References:

1. Montesano, C., et al., J. of CO_2 Utilization **2020**, 39, 101157
2. Grofulović, M., et al., PSST **2019**, 28, 045014

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In situ optical emission spectroscopic study of plasma for CO_2 conversion

Introduction: With the more and more apparent consequences of climate change, we have to look for new and innovative ways to reduce the CO_2 concentration in the atmosphere. A very appealing possibility is the plasma induced conversion of CO_2 into hydrocarbon fuels. If the plasma is generated with electricity from renewable energy sources these fuels are called solar fuels. Plasma is an ideal tool to conduct the most energy intensive step in the conversion process, namely the splitting of CO_2 into carbon monoxide and oxygen. Due to its non-equilibrium nature the plasma can split the CO_2 molecule in a very energy efficient way.

To tailor the plasma process a detailed understanding of the present molecular species and their interactions is therefore crucial. Furthermore, we want to assess the effectivity of the plasma. At PMP we use optical diagnostics to get the required information.

One characteristic of plasma is its light emission. By spectrally resolving and detecting the light, so-called optical emission spectroscopy (OES), information about the electron density, one of the most important parameters characterizing the plasma activity, can be obtained as well as atomic and molecular radical densities in the plasma.

Project description: You will perform an in situ OES study on two different plasma systems. On the one hand, we are currently building a completely new setup for a nanosecond repetitively pulsed (NRP) discharge. This new plasma source must be characterized thoroughly. On the other hand, we use a well-studied glow discharge but add oxygen to the carbon dioxide. This makes the whole system much more challenging in terms of e.g. electron density and gas composition but also brings it closer to the application where one will rarely encounter a pure CO_2 gas stream.

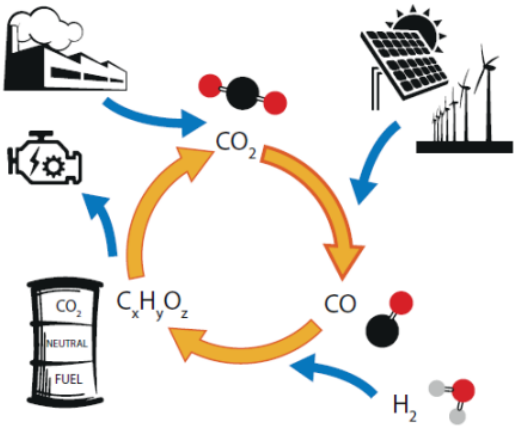

Figure 4: Mark Damen PhD Thesis 2020

References:

1. Montesano, C., et al., J. of CO_2 Utilization **2020**, 39, 101157
2. Grofulović, M., et al., PSST **2019**, 28, 045014

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Applied optical spectroscopy for characterization and outreach

Introduction: One of the most universal tools in the shed of a physicist is optical spectroscopy. Oversimplified it is about getting information from looking at light. Take for example the Fraunhofer lines in the spectrum of the sun. From these small dark absorption lines conclusions can be drawn about the sun's photosphere. But also, directly here at PMP optical spectroscopy is used. In plasma atomic layer deposition (ALD) processes it can be used to identify reactants and surface reaction products. Therewith, the process can be optimized or monitored. This and similar applications of optical spectroscopy often rely on the fact that atoms and molecules absorb and emit light at specific wavelengths according to the energy difference of involved levels. Since the energy levels are characteristic for the respective atom/molecule, it can therefore be identified.

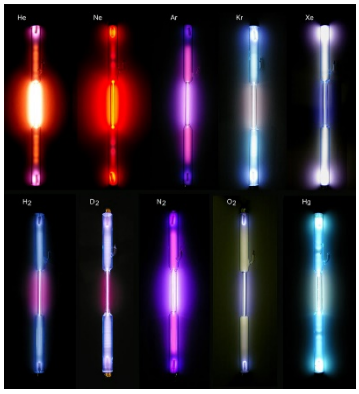

Figure 5: gas discharge lamps taken from www.ledwatcher.com

Project description: This project is an ideal opportunity to learn about the possibilities and challenges of optical spectroscopy in a hands-on way. The goal of the project is to build a compact and mobile setup for the characterization of optical elements like lenses, mirrors and light sources like gas discharge lamps by means of absorption as well as emission spectroscopy. While the light sources supply you with light on their own, passive elements like lenses must be illuminated with light. By comparing the light passing through/reflected by the optical element with the light that reaches your detector when no optical element is involved allows you to determine material properties. If build well, your setup will have lasting impact, since it will be used in daily lab work as well as in lectures like *Optical diagnostics*.

References:

1. Mackus, A. et al., J. Vac. Sci. Technol. A 28, 77 (2010); https://doi.org/10.1116/1.3256227
2. Engeln et al. 2020 Plasma Sources Sci. Technol. 29 063001; https://doi.org/10.1088/1361-6595/ab6880

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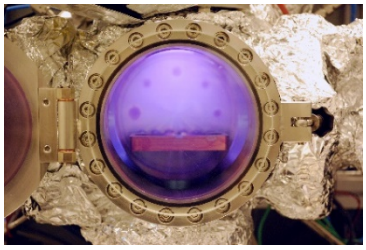
Role of Ions and Radicals during Plasma-assisted Atomic Layer Deposition in 3D Structures

Short description: Study film growth in 3D structures by plasma-assisted atomic layer deposition and explore how the film properties depend on the exposure to ions and radicals.



Background: Plasma-assisted atomic layer deposition (plasma ALD) is a technique used to grow ultrathin layers of materials that are used for instance in smartphones. As the name suggests, a plasma is used in this method, for example an oxygen plasma to grow an oxide (SiO_2, TiO_2, etc.). Among others, these plasmas contain ions (e.g., O_2^+) and reactive radicals such as atomic oxygen (O). The role of these different species during film growth can be investigated using 3D structures:

- Due to electric charging the ions are accelerated toward the substrate. The amount of 'exposure' of the surface to these energetic ions can affect the properties of the grown material (Fig. 1, left).
- The reactive radicals are usually needed for film growth, but can be lost through recombination when diffusing into a 3D structure. By looking at the penetration depth of the grown film, you can tell how far the radicals could diffuse before they recombined at the surface (Fig. 1, right).

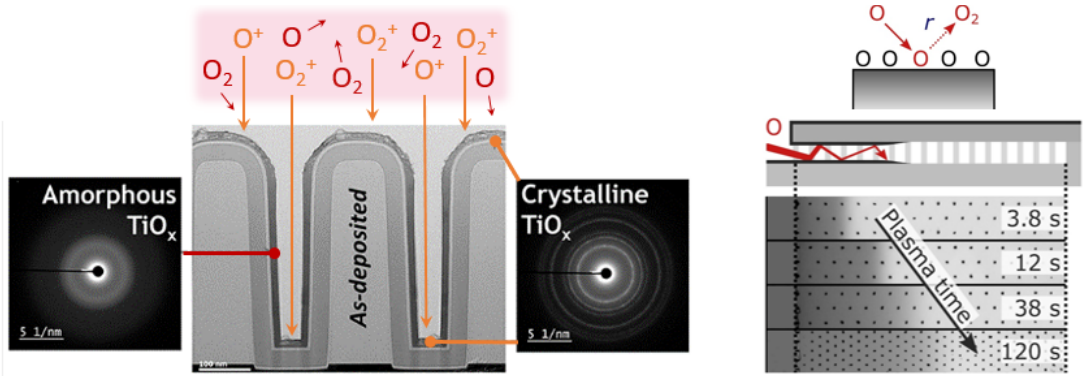


Figure 1: Left: Plasma ALD of TiO_x on a vertical trench showing ion-exposure-dependent material properties (adapted from Faraz et al., ACS Appl. Mater. Interfaces 10, 13158 (2018)). Right: Plasma ALD in a horizontal trench, where the film penetration is limited by the recombination of radicals at the surface (Arts et al., J. Phys. Chem. C 123, 27030 (2019)).

Project: Using plasma ALD, you will grow nm-thin films (of SiO_2, TiO_2 and/or Al_2O_3) in 3D test structures and investigate the film thickness and material properties using optical diagnostics. Furthermore, a specially-designed ion sensor can be used to relate the ion energy and flux to these film properties.

Location and supervision: The project will mostly consist of experimental work, part of which will be in the cleanroom in the Spectrum building. You will work in the Plasma and Materials Processing (PMP) group lead by prof. dr. ir. Erwin Kessels and you will be daily supervised by Karsten Arts.

Interested? For further information please contact:

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Ultra-thin Atomic Layer Deposited Interlayers in Hole-Selective Polysilicon Contact Structures

Short description: High-efficiency solar cell concepts rely on the quality of highly carrier-selective or passivating contacts. A well-known example is the contact comprising doped polycrystalline silicon (poly-Si) separated by an ultra-thin oxide layer from the absorber, known by the acronyms TOPCon or POLO. Conventionally, silicon oxide (SiO_x) is employed as the ultra-thin oxide layer in poly-Si contact structures.

Background: Due to its significant merits of processing uniform and conformal ultra-thin films with precise thickness control, over the last 10 years, atomic layer deposition (ALD) has received tremendous attention for application in Si solar cells. Specifically, ALD aluminium oxide (AlO_x) films (with thickness within the tunnelling range), have been shown to provide superior field effect passivation when compared to the conventional SiO_x tunnel layer, due to its negative interface charge density (Q_f). Aforementioned attributes make ALD AlO_x stand out as a promising candidate for application as an ultra-thin electron blocking layer in hole-selective poly-Si contact structures. However, it is crucial that poly-Si passivating contacts with ultra-thin ALD AlO_x showcase a good balance of the recombination parameter and the contact resistivity (R_{co}) of the contact for obtaining high carrier selectivity.

Project: In this work, we aim to reliably extract the R_{co} of hole-selective poly-Si contact structures based on two different ultra-thin oxide layers, namely SiO_x deposited by thermal oxidation and AlO_x by ALD (as a function of its film thickness). The second task of this project is to analyze passivating contact quality of both the stacks in terms of the implied open-circuit voltage (iV_{oc}). Toward the end of this project, the student will gain not only hands-on experience in a cleanroom for thin film material deposition and analysis, but also understanding of the working principles of solar cells.

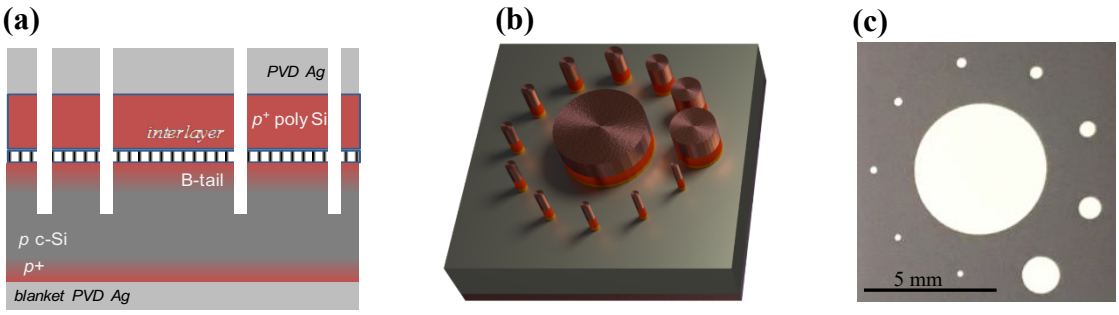

FIG. 1. (a,b) *Hole-selective poly-Si contact structure, where the layers (poly-Si, the ultra-thin oxide, and the diffusion tail) that are present between the front and back electrode are "laser etched" in order to fabricate the "stacks" for R_{co} measurements.* ***(c)*** *Top-view optical microscopy image of the fabricated contacts with different diameters.*

If you are interested, please contact us for further details.

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Surface passivation of germanium

Background: Semiconductors like silicon and germanium form a very useful group of materials with application ranging from the integrated circuits to solar cells. One of the challenges involving semiconductors are the electronic loses associated with its surface. The surface of a semiconductor facilitates the recombination electrons and holes present in the semiconductor. This recombination is in many cases responsible for decreased device performance. In the case of solar cells for example, recombination of electrons and holes result in a lower solar cell efficiency. Reducing the surface losses (passivation) is thus of importance. Covering a semiconductor surface with a thin film using for example atomic layer deposition (ALD) can greatly reduce these surface losses.

An alloy of silicon and germanium forms a versatile semiconductor. It is for example applied in today's MOSFETs (transistors). Recently it has been shown that the hexagonal crystal structure of silicon-germanium exhibits a direct bandgap making it a very interesting candidate for silicon compatible photonic circuits. While much is known about the surface passivation of silicon, germanium is less extensively studied. The aim of this project is therefore to study the surface passivation of germanium.

The project: The aim of the project is to study the surface passivation of germanium by thin films of a material called amorphous silicon. The project will include the deposition of thin films amorphous silicon on germanium, characterizing of the material, but also theoretical work on the physics involved. One can emphasize either of these aspects in the project depending on personal interest. A typical example of a surface passivation study can be found in the reference below.

Additional information:

Dingemans, G. , Seguin, R. , Engelhart, P. , Sanden, M. C. and Kessels, W. M. (2010), Silicon surface passivation by ultrathin Al_2O_3 films synthesized by thermal and plasma atomic layer deposition. phys. stat. sol. (RRL), 4: 10-12. doi:10.1002/pssr.200903334

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Atmospheric Plasma-Enhanced Spatial Atomic Layer Deposition

Background: Atomic Layer Deposition (ALD) is a gas-phase deposition technique which allows to achieve ultrathin, high quality layers (oxides, nitrides, metals) which are largely employed by the semiconductor industry as functional layers in, for example, transistors, computer chips, photovoltaic technology. In its conventional *temporal* mode, ALD is a deposition technique in which the substrate surface is exposed alternatively to the precursor and the co-reactant vapors in a cyclic manner. In particular, plasma-enhanced ALD makes use of plasma gasses as the co-reactant vapors which allows for lower deposition temperatures.[1] However, slow deposition rates and the need of expensive vacuum technology are the two distinctive drawbacks of temporal (PE)ALD. To overcome these limitations, atmospheric pressure plasma-enhanced *spatial* ALD has been developed as a novel, high-throughput and cost-effective technique (see Figure 1 for the basic principle). In fact, the spatial separation of the ALD half-reactions and the use of a dedicated atmospheric pressure dielectric barrier discharge (DBD) plasma source to generate the co-reactant allow for fast deposition rates at relatively low temperatures.[2]

Nowadays, the surface chemistry and the underlying reaction mechanism driving the spatial PEALD deposition of several oxides at atmospheric pressure are under investigations. To unveil these, optical emission spectroscopy (OES) and gas-phase Fourier Transform Infrared spectroscopy (FTIR) are being employed.

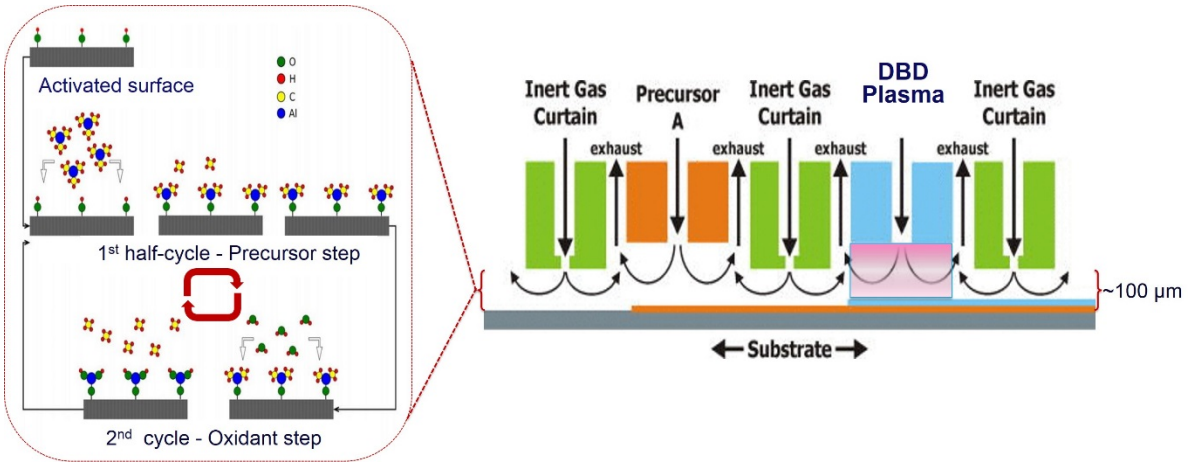

Figure 1 *Schematic of the basic principle of ALD (left) and of the atmospheric pressure Plasma-enhanced spatial ALD reactor present in TNO-Holst Centre, High Tech Campus 21, Eindhoven.*

Project: The goal of this project is to gain insights into the reaction mechanisms at the base of the atmospheric pressure plasma-enhanced spatial ALD deposition of oxides, such as Al_2O_3, SiO_2, ZrO_2, HfO_2. For these depositions, a metalorganic precursor and an O_2 DBD plasma are used. During the deposition, the formation of ALD reaction by-products will be investigated by means of OES and gas-phase FTIR as a function of different process parameters (temperature, plasma voltage, reactants gas flows). This study will give valuable information about the reaction mechanism at the base of the ALD process (see Figure 2). Furthermore, the influence of the different process parameters on the optical and structural material properties will also be investigated.

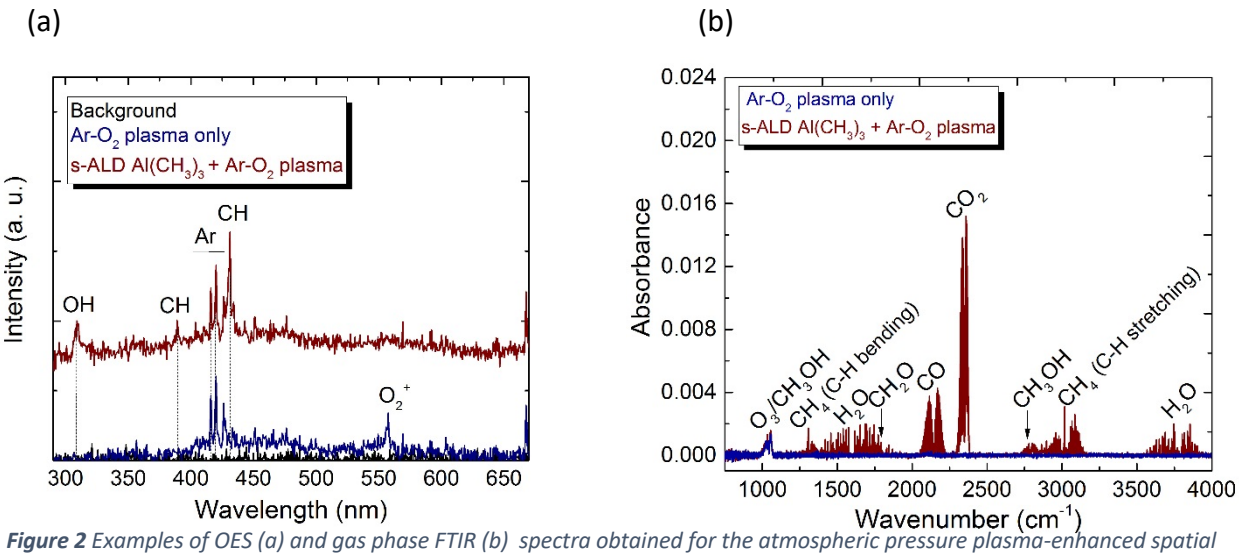

Figure 2 *Examples of OES (a) and gas phase FTIR (b) spectra obtained for the atmospheric pressure plasma-enhanced spatial ALD process of Al_2O_3 using $Al(CH_3)_3$ as the precursor and Ar-O2 plasma as the reactant.*

References

1. Profijt, H. B., et al., *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, **2011**, 29, 050801
2. Poodt, P., et al,, Adv. Mater., **2010,** 22, 3564

Location and supervision: The experiments will be carried out at the atmospheric pressure plasma-enhanced spatial ALD reactor (TNO-Holst Centre, Solliance building, High Tech Campus 21, Eindhoven) under the supervision of Maria Antonietta Mione (PhD student). The student will be part of the Plasma and Material Processing research group, Department of Applied Physics, TU/e.

For further information please contact

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Prof. Dr. Fred Roozeboom f.roozeboom@tno.nl ; fred.roozeboom@tue.nl

Developing the atomistic kinetic Monte-Carlo for Area Selective Deposition

Background: Micro-kinetics models are robust model to investigate the evolution of a chemical process, especially if the initial information are acquired by ab initio method. Area selective deposition (ASD) is a promising chemical process to deposit conformal thin film materials in below 5-nm thickness. Previously, we developed an atomistic kinetic Monte-Carlo based on ab initio DFT calculations [1], which could successfully provide new fundamental insight into the growth of material by ALD (e.g. Fig. 1). Currently, we are developing an ASD application to provide fundamental insight into the chemical process of ASD.

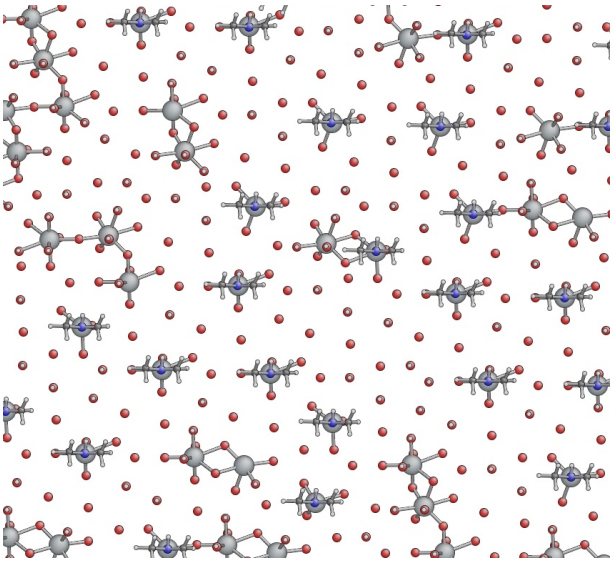

Fig. 1, top view of HfO_2 growth during the first cycle of ALD.

Project: The aim of the project is to implement more chemical reactions into the ASD application and to investigate the results of changing the reaction conditions. This will provide a robust method to describe the evolution of the starting surfaces during ASD. The ASD application is part of SPPARKS [2].

Location and supervision: The project will mostly consist of computational work, performed in the PMP group located in the Flux building. You will work in the Plasma and Materials Processing (PMP) group and you will be supervised by Mahdi Shirazi (postdoc) and Erwin Kessels (Professor). Some knowledge of C++ programming is required.

[1] M. Shirazi, S. D. Elliott, *J. Comput. Chem.*, **2014**, DOI:10.1002/jcc.23491.

[2] A. Slepoy, A. P. Thompson, S. J. Plimpton, *J. Chem. Phys.*, **2008**, DOI:10.1063/1.2919546.

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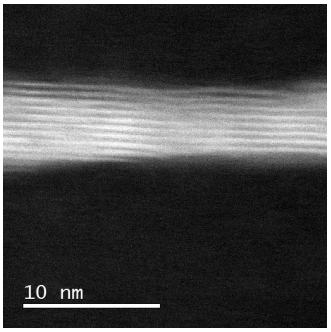
Improving electrical properties of atomic-layer deposition 2D MoS_2 by doping

Short description: In this project we will study e.g. Nb doping of the 2D transition-metal dichalcogenides (TMDs) such as MoS_2. You will be synthesizing these films using atomic-layer deposition (ALD) in the cleanroom and analyzing how the film properties vary with deposition condition. Apart from working with *state-of-the-art* deposition tools, you will get to know *go-to* thin-film analysis techniques such as SE, Raman, Hall, and 4PP. Apart from the experimental work, there is plenty of opportunity to perform theoretical work.

Background: For the fabrication of nano-electronics, good electronic properties (conductivity, carrier density, carrier mobility) combined with control over band-gap of materials are essential. For the next generation nano-electronics, 2D layered TMDs such as MoS_2 are promising because they retain good and predictable electronic properties down to a monolayer. You can see the individual layers of MoS_2 in the image to the right in a transmission electron microscopy (TEM) image.



ALD is a synthesis technique that in principle can meet all these requirements. However, the growth of these TMDs by ALD is in its exploratory stage and new deposition strategies need to be pioneered and understood. In the PMP group, the emphasis is placed on gaining a fundamental understanding of the material (growth) next to obtaining "good" material properties.

Project: You will do the deposition of the doped TMDs in the cleanroom varying initially only the doping density. After deposition, you will measure the film thickness by SE, crystallinity by Raman, and electrical properties using Hall and 4PP measurements. The aim is to get insight into the doping mechanism, how efficient the doping is, and which concentration gives the best material properties. The deposition will be performed together with a Postdoc (Miika). On the other hand, the analysis techniques mentioned above are very user friendly and you will be able to work independently with them rather quickly.

Supervision: You will work in the Plasma and Materials Processing (PMP) group under the daily supervision of Miika Mattinen (m.j.mattinen@tue.nl, Post-doc) in the group of Ageeth Bol (a.a.bol@tue.nl, Full Prof.).

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Ageeth Bol	**Flux 3.110**	**a.a.bol@tue.nl**

Efficient light emission from atomically thin semiconductors

Short Description: Single atomic layers of MoS_2 and WS_2 are promising materials for future electronic and photonic devices. While it has been demonstrated that these materials can emit light (luminescence) very efficiently, achieving this on large-area samples is an ongoing challenge. The goal of this project is to investigate how such large-area, highly luminescent layers of MoS_2 and WS_2 can be realized.

Background: Conventional semiconductor materials like silicon are isotropic: their material properties do not depend on direction. Two-dimensional materials, with graphene as the classic example, are fundamentally different. At the atomic scale, these materials consist of layers which have strong internal bonds while the interaction between the layers is only very weak. The most important consequence of this is that 2-D materials can be reduced in thickness to a single atomic layer while conserving their crystal structure and electronic and optical properties. The transition metal (Mo, W, …) sulfides are a family of 2-D materials that have semiconducting and luminescent properties at single atomic layers, which makes them highly interesting for next-generation electronics and photonics. Due to their inherently small thickness, these single atomic layers are highly sensitive to crystal defects and their environment. Current research focuses on how to control these parameters such that the full potential of 2-D materials can be unlocked.

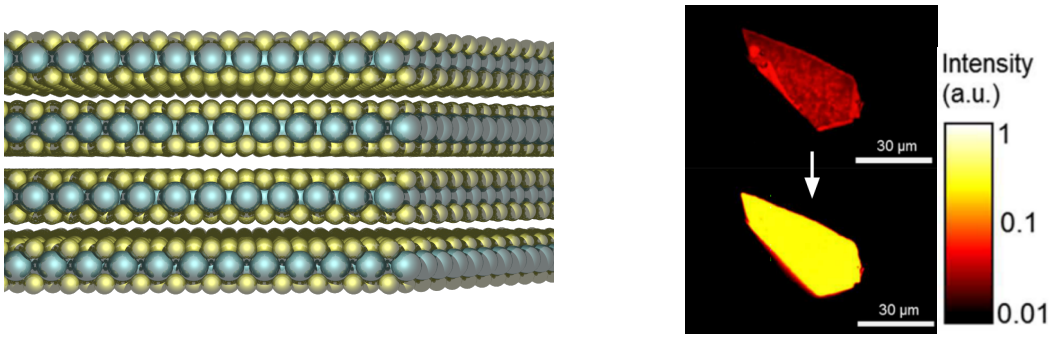

Figure 1: Left: Atomic-level structure of the 2-D semiconductor MoS_2. Right: highly enhanced light emission (luminescence) from small-size MoS_2 after chemical treatment.

Project: Learn to grow the 2-D semiconductors MoS_2 and WS_2 by the atomic layer deposition technique. Use various measurement techniques to study the light emission, crystal quality and composition of the grown material. Compare the grown materials to benchmarks to quantify their performance. Gain an understanding of the parameters that have the largest impact on the light emission and optimize the growth process such that luminescence is maximized.

Location & Supervision: The project is conducted in the group for plasma and materials processing (PMP). The responsible supervisor is prof. dr. Ageeth Bol, and the daily supervisor is ir. Jeff Schulpen. Atomic layer deposition performed in the Nanolab@TU/e cleanroom in the Spectrum building. Measurements are done both in the cleanroom and in other labs in Spectrum.

For further information please contact

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