Characterization of Atomic Layer Deposition and Etch processes for Ruthenium films

Short description: Understanding processes for the growth and removal of Ru films, which are relevant for the semiconductor industry.

Background: Atomic layer deposition (ALD) is a film deposition technique which allows for deposition of ultrathin films with a good control over the film thickness, uniformity and conformality. Due to these unique features, it has found application in the semiconductor and photovoltaic industries. Currently, the method is being developed to enable area-selective ALD, meaning that material can be deposited only on areas where required. This development is driven by the semiconductor industry, since area-selective ALD allows for bottom-up device fabrication, making some commonly used lithography steps unnecessary. Recently the PMP group showed that by combining ALD with etching, area-selective ALD of Ru can be achieved (See Figure 1), which could become important for fabrication of integrated circuits.

Project: The goal of this project is to better understand the underlying mechanisms of the ALD and etch processes as shown in Figure 1, and to further improve the method to optimize the selectivity. Therefore additional investigations will be done using a variety of diagnostic methods. In this project, you will get familiar with both ALD and thin film characterization techniques, and you will gain knowledge on materials science.

Location and supervision: The project will mostly consist of experimental work, performed in the main lab of the PMP group located in the Spectrum building. You will work in the Plasma and Materials Processing (PMP) group and you will be supervised by Martijn Vos (PhD student) and Adrie Mackus (Assistant Professor).

Interested? For further information please contact: Ir. Martijn Vos (Flux 3.096, m.f.j.vos@tue.nl), or Dr. ir. Adrie Mackus (Flux 3.112, a.j.m.mackus@tue.nl).

Figure 1. (left) ALD leads to Ru growth on two different areas (Pt and SiO$_2$), and is non-selective in this case. (right) When Ru ALD is combined with etching steps, area-selective growth of Ru can be achieved on top of Pt, while SiO$_2$ is left clean.
Quadrupole mass spectrometry studies during growth of aluminum fluoride films

**Short description:** Using quadrupole mass spectrometry (QMS) the reaction mechanisms during atomic layer deposition (ALD) of Aluminum Fluoride (AlF₃) will be studied.

**Background:** Atomic layer deposition (ALD) is a film deposition technique which allows deposition of ultrathin films with a good control over the film thickness, uniformity and conformality. Although the technique is relatively new, it has already found application in the semiconductor and photovoltaic industries, due to its unique features. Recently ALD of metal fluorides has received increased attention, since metal fluorides are typically very transparent materials and have possible applications in optics, batteries and solar cells.

A powerful diagnostic to study ALD processes is quadrupole mass spectrometry (QMS). QMS relies on the separation of ions based on their mass-to-charge ratio (m/z) and can be used to study the presence of certain species in an ALD reactor. By following specific m/z ratios over time, it is possible to determine the reaction products which are released during the ALD process (see Figure 1).

**Project:** The goal of this project is to get a better understanding of the reaction mechanism of AlF₃ ALD. This ALD process uses Al(CH₃)₃ and SF₆ plasma and was recently developed and published by the PMP-group (see Vos *et al.* Applied Physics Letters 111, 2017). In a follow-up publication the reaction mechanism of this new process will be studied in more detail and for this a well-defined set of QMS measurements is needed. The measurements will be performed on the FlexAL1 reactor, which is a commercial ALD reactor from Oxford Instruments, located in the cleanroom of the TU/e (see Figure 1).

![Figure 1. (Left) Example of time-resolved QMS data collected during AlF₃ ALD, showing the production of HF and CFₓHᵧ species. (Right) ALD tools inside the cleanroom, with the FlexAL1 reactor on the right.](image)

In this project, you will get familiar with both ALD and QMS, and you will gain experience working in a cleanroom facility. In addition, the project will require the processing of large amounts of data, for instance with the help of Matlab.

**Location and supervision:** The project will mostly consist of experimental work, which will be in the cleanroom located 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 Martijn Vos (PhD student).

**Interested? For further information please contact:**

Ir. Martijn Vos  m.f.j.vos@tue.nl
Dr. ir. Adrie Mackus  a.j.m.mackus@tue.nl
Comparison of plasmas of different ALD reactors

Short description: Using various diagnostics, such as optical emission spectroscopy (OES) and a retarding field energy analyzer (RFEA) plasmas of different deposition tools will be studied and compared.

Background: Inductively coupled plasmas (ICP) are widely used in the semiconductor industry for deposition of materials and cleaning or functionalization of substrates. The PMP-group is equipped with two sets of (nearly) identical deposition tools that are equipped with an ICP source: the ALD1 & ALD2 and the FlexAL1 & FlexAL2 (see Figure 1). Both the ALD – and the FlexAL reactors are theoretically identical and should give very similar results. In practice it is however found that their plasmas have slightly different properties and similar experiments on different reactors result in different results.

Project: The goal of this project is to get a better understanding of the differences between the plasma properties of the different reactors and try to answer why different results are obtained when doing the same experiments. This means that the plasmas of the ALD1 & ALD2 will be compared with each other, as well as the plasmas of the FlexAL1 and FlexAL2.

Using a combination of techniques (e.g. RFEA, a Langmuir probe and OES) important plasma parameters, such as ion energy, ion flux and electron temperature will be measured. Furthermore, the plasmas will be compared by performing several experiments. The quality of thin Al₂O₃ films, deposited on the different reactors, can for instance be compared by doing so-called passivation studies. Insight in the strength of the plasmas can be gained by plasma-etching poly(methyl methacrylate) (PMMA) and measuring the thickness of the PMMA as a function of plasma exposure time. A third example is to investigate plasma functionalization of graphene, which is dependent on the plasma 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 Martijn Vos.

Interested? For further information please contact:

Ir. Martijn Vos: m.f.j.vos@tue.nl
Dr. ir. Adrie Mackus: a.j.m.mackus@tue.nl
Plasma-surface Interactions and Their Role in Plasma-Enhanced ALD Using NH$_3$ Plasmas

**Background:** ALD is a cutting-edge method to deposit thin films that is currently being adopted in the semiconductor, solar cell and chemical industries. It relies on the exposure of a substrate to a gas to form a monolayer of adsorbed precursors on the surface. This monolayer is then exposed to a coreactant which converts it to a layer of the desired product, typically an oxide, nitride or metal. By repeating this process thin films can be built up atomic layer by atomic layer, allowing for excellent control over the film thickness even for large, complex substrates.

In plasma-enhanced ALD the coreactant is a plasma, a complex mixtures of free electrons, neutral gas molecules, radicals and ions, and the properties of the deposited films depend on the chemical make-up of the plasma. One of the factors affecting the make-up of the plasma is reactions happening between plasma species at surfaces inside the reactor, leading to a feedback loop where film deposition changes the properties of the plasma, which then affects the film deposition process. One example where this is believed to play a role is in ALD of metals using NH$_3$ plasmas. A number of metals, most notably Cobalt, can catalyze the decomposition of ammonia into hydrogen and nitrogen, which can lead to changes in the plasma chemistry as the deposition progresses. At this point, little is known about how these plasma-surface interactions change the composition of the plasma under realistic conditions and how this affects the ALD process.

**Project:** The goal of this project is to shed light on how surface-plasma interactions affect the chemical properties of NH$_3$ plasmas. To do so you will employ a variety of spectroscopic methods to study the chemical reactions happening in the plasma and at the plasma-surface interface and how they change as Cobalt is deposited. Based on these insights you will advise us on how to better control and optimize plasma-enhance ALD processes.

**Location and supervision:** You will work in the Plasma and Materials Processing (PMP) group lead by prof. dr. Erwin Kessels. Your project supervisor and daily supervisor will be dr. Adriana Creatore and Gerben van Straaten, respectively.

**For further information please contact:**

Gerben van Straaten  g.v.straaten@tue.nl  
Dr. Adriana Creatore  m.creatore@tue.nl
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. 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.

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](image.png)

*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 Al₂O₃, SiO₂, ZrO₂, HfO₂. For these depositions, a metalorganic precursor and an O₂ 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 Al₂O₃ using Al(CH₃)₃ as the precursor and Ar-O₂ plasma as the reactant.

References

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.

Interested? Please, contact us for more information:

MSc Maria Antonietta Mione  m.a.mione@tue.nl
Prof. Dr. Ir. W. M. M. Kessels  w.m.m.kessels@tue.nl
Prof. Dr. Fred Roozeboom  f.roozeboom@tno.nl; fred.roozeboom@tue.nl
Optical emission study on an atomic layer deposition system.

Short description: in this project, you will investigate the properties of a radio-frequency plasma for atomic layer deposition (ALD) using optical emission spectroscopy (OES). This spectroscopic technique is a powerful and non-invasive diagnostic tool that can be used to monitor plasma mediated processes.

Background: ALD is a method to deposit (ultra-)thin films and it has a growing number of applications in nanotechnology and semiconductor processing. Plasma steps are used in ALD processing. In the plasma, a zoo of reactive and energetic species is formed and a better understanding of the type and amount of radicals produced is desirable.

Project: OES will be used to investigate plasma parameters such as gas and electron temperature. In ALD process is of particular interest the quantification of reactive species. OES can be used as an analytical tool to monitor or measure radicals formed by the plasma. In particular, by using actinometry is possible to determine ground-state densities of reactive species. The technique relies upon normalization of the radical emission intensity to that from an inert gas (the actinometer) in order to compensate for changes in the electron density or energy distribution.

Location and supervision: You will work in the Plasma and Materials Processing (PMP) group lead by prof. dr. Erwin Kessels. Your project supervisor and daily supervisor will be Dr. Richard Engeln and Luca Matteo Martini (PostDoc), respectively.

For further information please contact:

Luca Matteo Martini  l.m.martini@tue.nl
Dr. Richard Engeln   r.engeln@tue.nl
ALD Nucleation Studies to Deposit Ultrathin Films

Introduction: As semiconductor devices become smaller, thinner and thinner films are needed in various parts of the device. Typically, ultrathin film growth produces discrete islands which grow until merging together to form a continuous film. This limits the minimum thickness of a closed film. Atomic Layer Deposition (ALD) is used heavily in the electronics industry to deposit thin films. The ALD nucleation process depends on the surface chemistry of the substrate. As required film thicknesses decrease, it is becoming increasingly difficult to deposit closed films of the desired thickness.

The nucleation process for ALD needs to be better understood to allow deposition of thinner closed films. Important questions remain about the exact mechanism which limits the density of islands. Because various physical processes affect ALD nucleation, experimental data is needed to determine which ones are relevant. This requires imaging small (~5 nanometer) islands produced by ALD.

Atomic Force Microscopy (AFM) allows imaging of very small features. It moves a tip with a radius of curvature between 1 and 50 nm across a surface, measuring the surface topography. AFM allows us to image islands deposited by ALD:

![AFM Image](image)

Project: In this project, you will learn to use the AFM to image surfaces with small islands of material deposited by ALD. You will compare this data to theoretical models. This will allow greater understanding of ALD nucleation, such as how many new islands appear per cycle, the rate at which the islands grow, and what fraction of the available sites on the surface contribute to the ALD process.

References:


If interested please contact:

David Kane    d.a.kane@tue.nl
Adrie Mackus   a.j.m.mackus@tue.nl
Characterization of functional materials for Lithium Ion batteries by Atomic Layer Deposition

Introduction: Rechargeable lithium-ion batteries dominate the current battery market. They are in widespread use because of their high energy and power densities. The classical lithium-ion battery systems employ a liquid electrolyte to facilitate Li-ion transport between the electrodes. However, the presence of this organic solvent poses a significant safety risk, restricts the temperature window, and prevents easy miniaturization.

Switching to a solid-state electrolyte could relieve these issues (Fig. 1a). As such, solid-state thin-film batteries might offer an alternative for the current “wet” lithium-ion batteries. In addition to their increased safety and operational range, they allow easy miniaturization and on-chip integration, which enables their use for medical implants and various sensor systems.

A major bottleneck in the further development of an all-solid-state Li-ion battery is its high internal resistance, which stems from the low Li-ion conductivity in the solid electrolyte. This leads to an inefficient charging and discharging of the battery due to power losses. However, stable solid electrolytes with high ionic conductivities are currently not available. Possible approaches to reduce the internal resistance of the battery are (i) to reduce the electrolyte and electrode thicknesses and (ii) to increase the internal surface area of the battery ($R = \rho l/A$). Such an approach is followed in the development of so-called 3D batteries, whereby the current collectors, electrodes and electrolyte are conformally deposited on high-aspect ratio structures (Fig. 1b).

Atomic layer deposition (ALD) is very suitable for the fabrication of potential next generation Solid-state Lithium-ion micro-batteries as it allows for the fabrication of very thin (typically < 100 nm), uniform, conformal and pin-hole free films. 1 A large variation of Lithium-ion battery materials is already being deposited by ALD 2.

![Fig. 1: (a) Solid state lithium ion battery schematic and (b) concept of 3D solid-state batteries](image)

Project: By varying the ALD deposition parameters, film properties can be tuned. In addition to the conformality and uniformity, the quality of the films is also determined by the stoichiometry, crystallinity and conductive properties of the films, 3 all of which are very important to address when considering the practical use of these films in a Lithium-ion battery.

Within the scope of the development of lithium ion battery materials, material analysis is essential. A wide range of diagnostic tools could be employed to characterize the deposited layers. Within the scope of this bachelor project, one or more characterization techniques will be exploited to determine the quality of such ALD films. The main focus will be on the analysis of the measurement data as well
as the in-depth understanding of the results. Possible characterization techniques could be X-Ray Photoelectron Spectroscopy which is typically used to accurately determine the chemical binding state present in a material, X-Ray Diffraction, used to identify the crystalline phase of a material or Spectroscopic Ellipsometry, with which optical constants and film thickness can be measured. Another task could be to assist with the development of a new ALD process.

References:


Location and Supervision: During the project you will obtain experience in the Nanolab (cleanroom) and with some of the techniques described above (depending on your personal interest and the progress). Your daily supervisor will be Norah Hornsveld (PhD candidate).

If interested please contact:

Msc. Norah Hornsveld  n.hornsveld@tue.nl
Dr. Adriana Creatore  m.creatore@tue.nl
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 work in the area-selective ALD subgroup, which is led by Adrie Mackus. Your daily supervisor will be Marc Merkx.

If interested please contact:

Marc Merkx   m.j.m.merkx@tue.nl
Adrie Mackus   a.j.m.mackus@tue.nl
Modelling of atomic layer deposition of 2D materials: a multi-scale modelling study

Introduction: Recently, the two-dimensional (2D) transition-metal dichalcogenides (TMDs) (MX$_2$, such as M=Mo, W, etc. and X=S, Se, and Te) have attracted scientific and technological interest. Unlike graphene, 2D-TMDs can exhibit metallic or semiconducting properties, depending on the transition metal or chalcogen in the crystal. The combination of an ultrathin body with semiconducting properties makes 2D-TMDs key candidates for future electronic and optoelectronic nano-device applications. To make the 2D-TMDs viable for future applications, a reliable and scalable synthesis of wafer-scale thin films with atomically controlled layers is the prerequisite.

Atomic layer deposition (ALD) employs alternating cycles of self-limiting chemical reactions between gaseous precursors and a solid film to deposit material in an atomic layer-by-layer fashion. In ALD of 2D materials, an ultra-thin film of Mo/WS$_2$ is deposited by means of (C$_{12}$H$_{30}$N$_4$W/Mo) precursor and a H$_2$S/H$_2$ gas mixture at relatively low temperature (< 500 K). The process initially involves the interaction of gaseous precursors with the passivated SiO$_2$ or Al$_2$O$_3$ substrate (hetero-deposition). This results in the formation of a sub-monolayer Mo/WS$_2$ at the surface. The process follows with the interaction of gaseous precursors with partially formed monolayer of Mo/WS$_2$ (homo-deposition).

Project: In this project, an integrated density functional theory (DFT) and kinetic Monte-Carlo calculation (KMC) modelling approach is employed to provide thermodynamic insight into the formation of flakes of the prototypical 2D materials. DFT calculations are performed to investigate the chemical reactions of ALD. This includes the adsorption of metal precursors, the elimination of ligands, the densification of metal precursor, the cooperative effect and the formation of flakes of 2D material at the surface. The Vienna *ab initio* software package (VASP) is employed to provide the reaction energies and activation energy of ALD reactions.

If interested please contact:

Mahdi Shirazi  
m.shirazi@tue.nl

Wilhelmus M. M. Kessels  
W.M.M.Kessels@tue.nl

Ageeth A. Bol  
a.a.bol@tue.nl
Electrical studies of ALD MoS2 films

**Introduction:** There has been a growing interest in recent years over Transition Metal Di-Chalcogenide (TMDC) semiconductors with chemical formula of MX₂ in which 'M' can be Mo, W, or Sn and 'X' can be S, Se or Te. This family of materials exhibits 2-Dimensional properties with excellent control over the bandgap depending on its number of layers. Amongst TMDCs, MoS₂ is the most extensively studied semiconductor in both electrical and optical contexts. There are different methods to obtain few layer MoS₂ films, namely; exfoliation (using the scotch tape) and Chemical Vapor Deposition (CVD) none of which can bring in uniform and reproducible film in large areas suitable for future electronic and optical device schemes.

PMP, and more specifically our sub-group, is growing different 2D materials including MoS₂ by means of Atomic Layer Deposition (ALD) technic in order to obtain reproducible, uniform and large-area-scale films. This is followed by a fundamental study over the material quality. However, the electrical properties of the grown films has yet to be optimized and the growth conditions has to be modified accordingly. To serve this purpose, different electrical measurements are carried out on test samples. The as-grown films are first characterized using Four Point Probe or Hall set-up. Then, simple transistor structures are fabricated and electrically measured to monitor the electrical performance in a real device. See the figure below.

![Figure. Left –Layered structure of MoS2, Right-Schematic of one of the earliest and successful MoS2 transistors from exfoliation technic by: B. Radisavljevic et. al, NNANO 2011, Vol.6, No. 279](image)

**Project description:** The student will be provided simple test structures fabricated out of ALD MoS₂ films with different deposition conditions on possible different substrates to measure the conductivity and mobility of the films by means of Four Point Probe/Hall setup and/or I-V probe station. During this 8 weeks period he/she will gain knowledge over MoS₂ electrical properties.

**If interested please contact:**

Reyhaneh Mahlouji  
R.mahlouji@tue.nl

Ageeth A. Bol  
a.a.bol@tue.nl
Sulfurization of ALD grown Transition Metal Oxides

Transition Metal Dichalcogenides (TMD’s) are a new group of 2D materials like Graphene, which are emerging as potential materials for a wide range of future applications. Our group focuses on growing 2D TMD’s using Atomic Layer Deposition (ALD) with properties suitable for high-end opto-electronic devices. We also employ the Chemical Vapour Transport (CVT) method to form TMD’s which is a two-step process in which first transition metal oxides are deposited using ALD, which is followed by sulfurization where oxygen atoms in the film are replaced by sulfur atoms. This is a challenging process to optimize as we need to obtain mono or few monolayer (<1nm) thick TMD’s.

Objective: To optimize sulfurization of transition metal oxides to form high quality TMD’s and achieve uniform large area mono or few layer thick TMD with significantly large grain size.

Project Description: In this project you will be acquainted with atomic layer deposition equipment utilized in our group to deposit Transition metal oxides (Nb₂O₅, TiO₂) and you will be introduced to various analysis techniques such as Raman Spectroscopy, Photoluminescence, Scanning Electron Microscopy and Atomic Force Microscopy to study TMD’s. Sulfurization of ALD grown transition metal oxide into TMD’s (NbS₂, TiS₂) will be executed using both a tube furnace and an ALD tool.

Key Publications:

Location & supervision: You will work in the 2D materials subgroup of PMP, led by Dr. Ageeth Bol. Your daily supervisor will be Saravana Balaji Basuvalingam.

If interested please contact:
Saravana Balaji Basuvalingam  s.b.basuvalingam@tue.nl
Ageeth A. Bol  a.a.bol@tue.nl