Atomic layer deposition for vapor sensor

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3 Abstract

Plasma-assisted atomic layer deposition is a thin film growth technique, with self-limiting periodic reactions. By this technique, thin film growth of metal oxide and other compounds will be investigated, with *in situ* and *ex situ* diagnostic analysis. The sensing mechanism between surface and gas molecules will be studied at the mean time. The aim of this project is the fabrication of gas sensors with ALD thin film. The goals of the final devices will focus on sensitivity, selectivity, miniaturization and so on.

4. Duration

The project will start on September 1st 2011 and will continue until August 2015 since this will be the applicant's time as a PhD student. The PhD student will spend proximately 2 years at PMP group of TU/e and another 2 years at Holst Centre.

5. Personnel

The personnel involved in this projects are both Plasma & Material Processing Group (PMP) at TU/e and Holst Centre

Prof. Dr. Fred Roozeboom (Project leader)
Dr. ir. Erwin Kessels (Group leader of PMP)
I.J.M.Erkens (PhD student)
Yizhi Wu (Applicant / PhD student)

Ms. Mercedes Crego Calama (Program Manager)
Mr. Sywert Brongersma (Principal Scientist)

6 Cost Estimates

The Funding is requested for one PhD positions. Furthermore, all specifically related need, such as substrates, gas precursors, and chemicals are also required from the budget. The equipment needed in this projects is already presented in laboratories of both PMP group at TU/e and Holst Centre at High Tech Campus. No other support will be required for this project.

Budget summary

	2011	2012	2013	2014	2015	Total
PhD students	1	1	1	1	1	
Postdocs	-	-	-	-	-	
Technicians	-	-	-	-	-	
Guests	-	-	-	-	-	
Personnel Costs	€36.000	€39.000	€43.000	€43.000	€47.000	€208.000
Running Budgets	€15.000	€15.000	€15.000	€15.000	€15.000	€75.000
Equipment	-	-	-	-	-	-
Total	€51.000	€54.000	€58.000	€58.000	€62.000	€283.000

7. Research Programme

7.1 Introduction

7.1.1 Motivation of gas sensor

Air pollution affects human health and the environment on the earth. For example, NO_2, produced by combustion of fossil fuels, is the main factor of ozone and acid rain. [1] A low concentration of NO_2 (4ppm) can anesthetize noses as well, which brings out the necessity of detecting NO_2 gas at low concentration scale. The gas sensing technique not only applies on world-wide air pollution issues, but also serves for human healthcare. For instance, in addition to the role in traffic and industrial pollution, NO is a signal of asthma in healthcare as well. The level of exhaled air from asthma patients increases significantly from 15 to 50 ppm NO before asthma occurs. If such change can be detected and sent to hospitals, a series of pre-treatment can be carried out before asthma happens. All above emphasize the importance and promising prospect of gas sensors.

Nowadays, various commercial sensors are already available, ranging from electromechanical to optical sensors. For example, NO_2 sensors, based on semiconducting metal oxide such as tin oxide, tungsten oxide, and zinc oxide, have been put into practice[2-4]. However, low sensitivity and the lack of selectivity are the bottlenecks of the development of gas sensors, which can be resolved by well-defined atomic layer at surface. Moreover, as predicted by Moore' law, which states that the number of transistors on integrated circuits double every 18 months, the miniaturization of electronic devices is the main trend in modern industry. All the aspects call for advanced technique to fabricate devices at atomic level.

7.1.2 Atomic Layer Deposition

Similar to Chemical Vapor Deposition (CVD), Atomic Layer deposition (ALD) is a thin film deposition technique, based on a sequence of periodic chemical reaction of precursors. The virtue of two self-limiting reactions gives rise to the ability of thin film growth at the atomic level. The mechanism of ALD is illustrated by Fig 1. The possibility of chemisorbed reaction depends on the available sites of surface groups. Ideally, a complete and homogenous monolayer is deposited after one consequent cycle. The advantages of ALD are listed as follows:

1. Precise control of thin film growth. The thickness can be derived from the amount of repetition cycles.
2. Purity. The selectivity of reactions on surface groups leads to high purity.
3. Highly uniform surface. The layer-by-layer growth ensures the flatness, with an RMS roughness of ≤ 1 nm [5].
4. Conformality. The morphology of surface can be maintained for application, e.g. large surface per area for solar cells.
5. Flexibility. By modifying precursors and reactants, the materials and composition can be tailored on purpose, e.g. doped thin film and different surface layers.
6. *In situ* diagnostic. Due to the virtue of self-limiting reactions, *in situ* measurement can be carried out at the intervals of half-cycles.

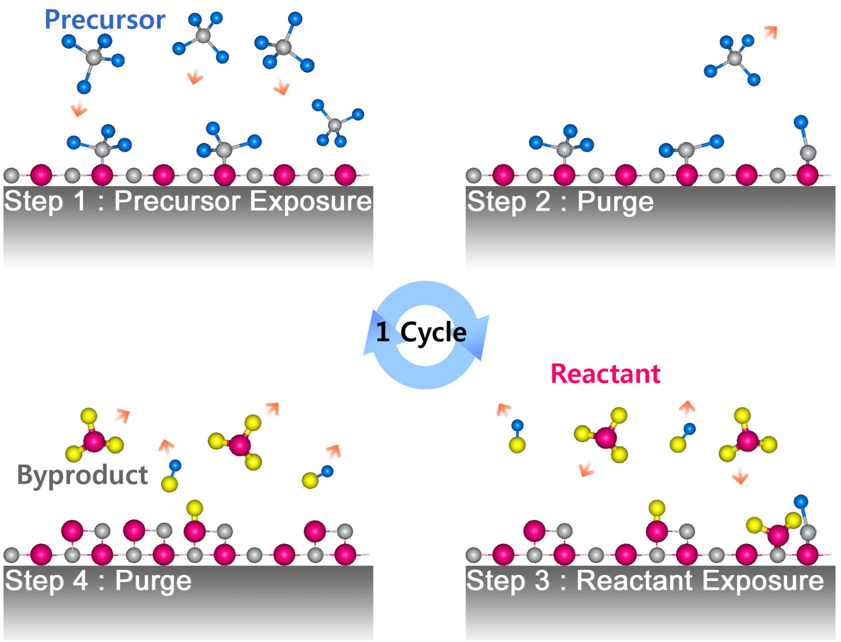

Figure 1. The Period of self-limiting reactions on ALD process. The periodic chemical reactions can be separated into two half-cycles. The first half-cycle starts with Step 1: self-limiting reaction between precursor and surface atoms, introducing new functional group for the following reaction. Step 2 is a purge process of removing volatile by-product by step 1 and the rest precursor. After the first half-cycle, a sub-monolayer forms by the chemisorbed new groups. The second half cycle consists of Step 3: Another self-limiting reaction between reactant and new groups, creating a new monolayer, and Step 4: purge process for by-product and the rest reactant. A complete monolayer forms after one periodic cycle, which gives rise thickness control at atomic level [6].

7.1.3 Plasma-Assisted Atomic Layer Deposition (PA-ALD)

In order to enhance the activity of ALD process, one approach is introducing plasma to support chemical reactions. On one hand, PA-ALD increases the versatility of precursors and reactants, some of which are limited by thermal energy due to the lack of sufficient activate energy. On the other hand, the energy supply from plasma allows to fabricate thin film at low temperature, which is necessary for application of temperature-sensitive devices. For example, O_3 as strong-oxidant is already under research to realize improved thin film properties at lower temperature than conventional thermal ALD, while O2 plasma source is also studied nowadays for similar purpose [7,8].
At the moment, several ALD operators are in operation at P&MP group, TU/e (Fig. 2), and similar setups are also available at Holst Centre. Based on thermal ALD, the virtues of PA-ALD are listed below: [5]

1. Improvement of the thin film density, impurity.
2. Deposition at lower temperature than thermal ALD
3. Efficiency of growth rate
4. Versatility of precursor choice
5. Good control of stoichiometry

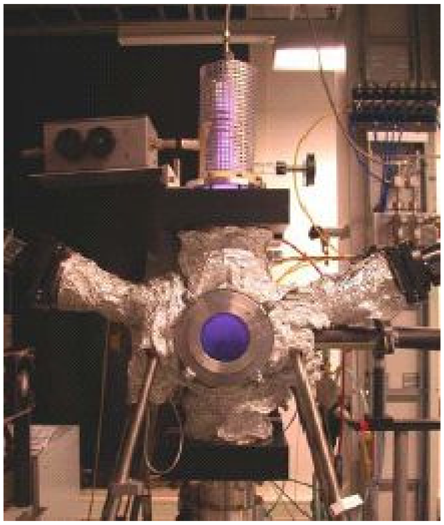

Fig. 2 Home-built ALD-I system (remote plasma, 4″ wafers, open-load). Experimental setup for fabrication of ALD thin film. Plasma is visible during ALD cycles. The optical access gives rise to *in situ* spectroscopy ellipsometry diagnose to investigate thin film growth.

7.2 Project Outlook

From the start of fabrication thin films to the end of device integration, this project consists a series of sub-topics during the whole process, which will bridge the gap from fundamental investigation to final industrial application. Challenges and innovations exist through out the entire process. This project can be divided into three parts: Fabrication of ALD thin film, investigation of sensing mechanism, integration of devices, as explained in details below.

7.2.1 Fabrication of ALD thin film

The versatility of precursors and reactants gives rise to a large freedom on the selection of thin film materials. The conventional ALD thin films are metal oxide. For example, aluminum oxide (Al_2O_3) has been investigated in PMP group, with the reactions as follows:

$$\mathrm{Al(CH_3)_3 + Al\text{-}(OH)^* \text{ — } Al\text{-}O\text{-}Al\text{-}(CH_3)_2^* + CH_4}$$
$$\mathrm{Al\text{-}(CH_3)^* + H\text{-}O\text{-}H \text{ — } Al\text{-}(OH)^* + H_2O}$$

However, ALD thin film materials are not limited within metal oxide. One of the challenges in this project will be modify thin film materials by investigating ALD processes and introducing novel precursors and reactants. For example, based on deposition process of TiO_2 growth, TiN can be deposited with other candidates of precursors. Besides metal oxide and nitride, ternary oxides like STO, BTO, BST and metal will be studied as well, because of their crucial roles in semiconductor industry.

PA-ALD provides more species of precursors compared to thermal ALD, due to the higher reactivity, Heteroleptic precursors are expected to replace traditional halide- and alkyl- based metallic precursors. In case of cyclopentadienyl (Cp) based Ti precursors [5], the Cp rings need stronger oxidants, such as Ozone and oxygen plasma, to dislocate from the surface.

The morphology and thickness of thin films play important roles on electron transport in devices, and will be investigated in the fabrication process. By controlling the ALD process and parameters, e.g. temperature, both amorphous and crystal film can be deposited. Responsivity is enhanced when film thickness approaches nanometer dimension. [9]. *In situ* and *ex situ* diagnostic techniques are utilized to comprehend the effects.

7.2.2 Sensing Mechanism

Sensing mechanism of semiconductors, as a fundamental study, determines the improvement of the responsivity, selectivity and response time of gas sensors, while such basic mechanism is still under active discussion [2]. One of the most common principles is the Debye length [10]. The Debye length describes the region of space charges near the surface where the surface species can affect the concentration of free charges. For example, the Debye length of SnO_2 is 30.6 Å at 250 °C [11]. The Debye length emphases the relationship between thickness effect and sensitivity of gas devices, which will be studied in this project as well. Recently, gas sensors in form of Field-effect transistors (FET) proves such mechanism [12], as illustrated schematically at Fig 3. A series of scientific questions about sensing mechanism still need further discussions, as listed below:

1. How does the reaction between target gas and surface charges take place? What is involved, atoms, radicals, or molecules?
2. What is the influence of pre-adsorbed species?
3. What is the redox mechanism?
4. Is the reaction in the whole thin film the same as on the surface?
5. Which species (mobile charges, fixed charges and ect.) play a role in the bulk, interface and surface?
6. Is the sensitivity optimized when the film thickness equals the Debye length?
7. How can the sensor reach ppb levels at room temperature?
8. What is the influence of morphology (amorphous, single crystal)?
9. What is the role of semiconductor-electrode contact?

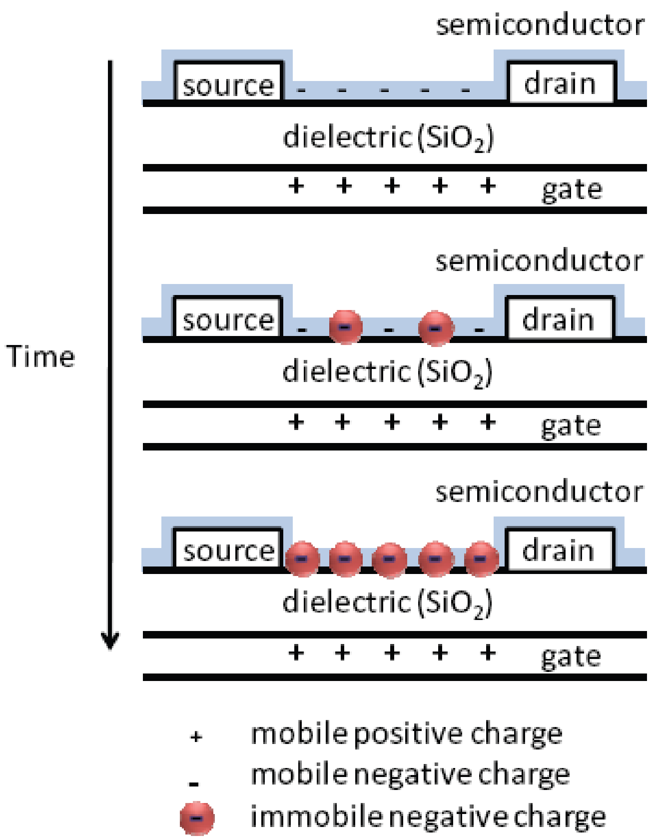

Fig. 3 Schematic representation of charge trapping process in FET. When a positive gate bias is applied, mobile negative charges accumulate on the surface, as a channel of drain current. In an NO_2 ambient at room temperature, the surface absorbs NO_2 due to large negativity of oxygen atoms. With time, electrons are trapped when the steady-state is reached, with a result of a smaller drain current compared to the original state. The time from the start to the steady-state is a function of NO_2 concentration.

7.2.3 Devices integration

The integration of gas sensors is still a open topic in this project, and will be carried out the Holst Centre at High Tech Campus. Nowadays, the forms of sensors are two-terminal chemiresistors, three-terminal metal-oxide-semiconductor field-effect transistors [12] (MOSFET) and so on, while the sensitivity can be magnified to 10 ppb in MOSFET. All these integrations will be investigated at the latter part of this project. The main goals of the application focus on:

1. Miniaturization
2. Low temperature application
3. Low energy consumption
4. High sensitivity
5. High selectivity
6. Fast responsivity

7.3 Innovations

The project contains a number of innovative elements .

7.3.1 Deposition of a hetero layer on the surface

Chemicals absorptions occur on the surface when target gas (e.g. NO) reacts with thin films. Due to the large electronegativity of oxygen atoms, charges transfer from metal oxide within Debye length and are trapped to the surface, which leads to deviation of conductance. Thus, the sensitivity of gas sensor depends on the selectivity and sensitivity of surface atoms and the electron density within the Debye length.

A more sensitive surface layer, different from previous atomic layers can be deposited by changing the precursors of the last couple of semi-reactions. For example, based on SnO_2 thin films, MgO can form by semi-reaction of precursors
$Mg(CH_3)_2 + SnO^* — Sn\text{-}O\text{-}Mg\text{-}CH3$

The electronegativity of alkaline earth metals, more positive than Sn, implies a higher sensitivity to oxide gas.

7.3.2 Doped ALD thin films

Thin film can be doped while growing, which can modify electron density of entire 2D material. For example, by inducing P_2O_5 among SnO_2 layers, a n-doped SnO_2 thin film can be deposited. After an annealing process, a homogeneous n-doped metal oxide can form, due to the atomic migration. As higher resistance leads to lower sensitivity [5], we can modify the conductance of thin film to increase the sensitivity in a wider gas concentration.

7.3.3 Buffer layer between substrate and thin film

TiO_2 thin film is amorphous below 300 °C and anatase crystalline above 300 °C [5], which states that temperature is one parameter to control the morphology. Meanwhile, by applying DC bias on the substrate can also modify crystal structure. Another innovation here is to insert buffer layer between substrate and thin film, since the misfit of lattice parameters may the reason of the structure differences. By introducing a buffer layer, we can

1. Modify the lattice parameter of substrate and thermal expansion, in order to control the morphology of thin film, and even crystal structure.
2. Prevent atomic diffusion between substrate and thin film, which may cause degradation of properties.
3. Modify the nucleation behavior. Shift the growth rate from delayed growth to immediate growth or even accelerated growth.

7.4 Plan of Work

The aim of the project is to investigate the application of gas sensors, starting from fundamental research of ALD process, with theoretical study of sensing mechanism, to the end of device integration of sensors.

Based on this scheme, the first phase will start from acquiring ALD setups, along with necessary *in situ* and *ex situ* diagnostic analysis. In this process, the PhD student will focus on: how to modify thin film materials (metal oxide, metal nitride, ternary oxide, with n- and p- doped); how to optimize thin film qualities (morphology, thickness, functional groups). The second phase is the integration and application of final devices. In this process, the student will focus on improvement of sensitivity, selectivity, and other aspects of sensors. Theoretical study of sensing mechanism will go through the whole process, which is crucial for understanding and improving gas sensors.

The time schedule of the 4 years PhD work is listed below.

Time	Research Tasks	Place
1st year	ALD process study, investigation of thin film materials	PMP group at TU/e
2nd year	Optimization of thin films with diagnostic analysis	
3rd year	Sensor devices integration, sensing characterization	Holst Centre
4th year	Optimization of devices, PhD thesis	

8. Infrastructure

This project will be carried out in both PMP group of Department of Applied Physics at TU/e and Holst Centre at High Tech Campus. Experiment setups are available at both places. PMP group, headed by Prof. W.M.M. Kessels, is well-equipped with technical personnel (5 technicians), vacuum systems, deposition and diagnostic equipment, including TU/e clean room. Holst Centre, equipped with similar setups, has diagnostic and measurement settings for gas sensors, including clean rooms shared with other groups of High Tech Campus.

Experiment carried out at PMP group will mainly focus on fabrication of ALD thin film and diagnostic analysis. Fabrication technique PE-ALD, will be applied with *in situ* analytical techniques simultaneously, as illustrated by Fig 4: spectroscopic ellipsometry (SE), (attenuated total reflection) Fourier transform infrared spectroscopy (FTIR), quartz crystal microbalance (QCM), quadrupole mass spectroscopy (QMS), optical emission spectroscopy (OES) and second harmonic generation (SHG). Some *ex situ* diagnostic measurements are available as well: state-of-the-art femtosecond laser system, atomic force microscopy (AFM), transmission spectroscopy, X-ray diffraction and reflectometry (XRD), Rutherford backscattering spectroscopy (RBS), elastic recoil detection (ERD), Raman spectroscopy, contact-angle measurement, and four point probe resistivity measurement.

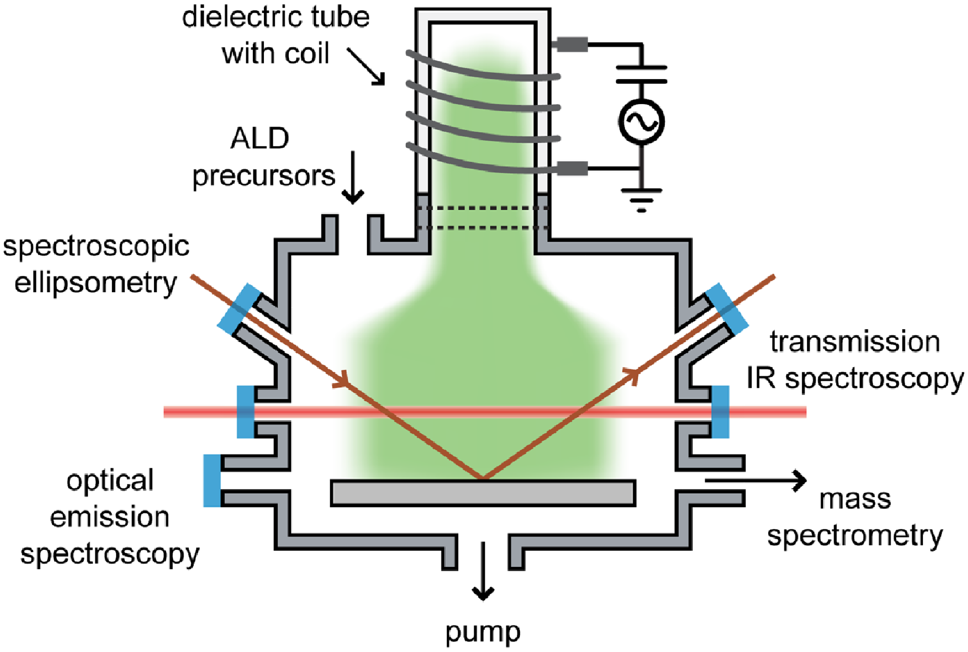

Fig. 4 Schematic representation of *in situ* setups in PE-ALD. Some *In situ* analytical techniques are denoted, while some others are not shown.

9. Application Perspective

From the road map of modern electronic devices, miniaturization is the main trend, where the Atomic Layer Deposition technique plays an important role. The high conformality implies the applications in nano-industry. The study of thin film compound, as done in the first phase of this project, will provide various of materials applicable for further application, such as metal nitrides, mixed metal oxides, doped semiconductors. The *in situ* and *ex situ* diagnostic analysis ensures the properties and qualities of the products. The research of sensing mechanism is a crucial topic in the field of gas sensor and general electronic interaction of thin film surface and gas molecules. This fundamental part will unravel the principles of solid state electronic interactions between surface and gas atoms.

The integration of sensor devices contributes to not only the industrial gas sensors but also the miniaturization of integrate devices. The perspectives of gas sensors lie in the pollution gas detections, sensing elements in integrated equipments, healthcare setups and so on. The fabrication process will help to understand fundamental technique questions, such as low-temperature integrations, electrodes contacts. In a word, the contributions of this projects go through the fundamental research of thin film fabrication technique and application of sensing devices in industry.

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