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A flexible research reactor for atomic layer deposition with a sample-transport chamber for in Vacuo analytics

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Abstract: A modular reactor for thermal atomic layer deposition (ALD) was designed, which allows changes of all reactor components in order to obtain a flexible set-up for research purpose. A sample transport chamber is included for dual purpose. It allows for *in vacuo* transport of samples to analytical devices such as an XPS instrument. Surface activation of the samples is possible in the same chamber via an irradiation-induced approach.

Keywords: Atomic Layer Deposition, Reactor Design, *in Vacuo* Sample Transport, UV Irradiation

1. Introduction

Atomic layer deposition (ALD) is a method for gas phase deposition of conformal films with control over thickness and chemical composition at atomic level. It is known to produce nearly defect free thin films making it a valuable tool for production of e.g. high-quality dielectrics, luminescent films or gas permeation barriers [1]. The latter ones are in the focus of our research, which deals with technically feasible methods for producing gas barrier laminates. For protection of electronic devices like thin film solar cells single barrier SiO_2 films with water vapor transmission rates (WVTR) below 10^{-2} g m^{-2} d^{-1} were prepared with an irradiation-induced approach [2]. Al_2O_3 thin films produced by different ALD processes exhibit WVTRs below 10^{-3} g m^{-2} d^{-1} [3] and are thus extremely interesting for gas barrier research purpose [4]. In addition to that it comprises an interesting tool for preparing 2D or 3D nanostructures [1d], which are of interest for our institution with respect to areas like the surface modification of fuel cell electrodes, of membranes for waste water treatment or of medical implants.

We evaluated different reactor concepts and construction designs to design an ALD reactor, which is modular and thus adaptable for those various research interests on a cost efficient basis. Herein we describe the design of a reactor for thin film deposition from the gas phase which complies with the flexibility demand of a research institution. It is based on the hot wall viscous flow tubular reactor already described by S. M. George in 2002 [5]. It is extended to a modular setup for higher variability in process and precursor choice. In addition, it enables *in vacuo* transport to analytical devices that allow attachment of CF flanges to their own sample transport system. Radiation-induced substrate preparation is possible in addition to standard preparation procedures.

Designs of reactors for atomic layer deposition have been described in the literature for various special and highly defined foci: concepts for *in situ* analytical studies with XPS [6], spectroscopic ellipsometry [7], mass spectrometry [8], etc. and a transportable reactor for *in situ* synchrotron photoemission studies [9]. Especially within the last decade gas flow characteristics of different reactors have been numerically simulated [10]. Roll-to-roll variants of the process are being developed [3]. Various commercial designs are offered, which are highly adapted to industrial needs of deposition speed and reproducibility.

2. Design and Construction

2.1. Overview

The basic idea of the ALD process is to introduce reactant gases in a timely or spatially separated regime into the reaction chamber. This separation allows sequential self-limiting chemical surface reactions and prevents gas phase reactions

between the precursors as well as transport limitations of film growth.

Due to self-limiting surface reactions in each precursor/purge sequence, also called a half-cycle of the ALD-process, a maximum of one monolayer can be deposited on the surface. Sequentially pulsing of appropriate precursors of complementary chemical reactivity will lead to the homogeneous growth of the desired material on all surfaces of appropriate temperature and chemical functionality. Even on high aspect ratio substrates thin conformal layers, which are extremely poor in defects, are thus formed in an ALD process.

A scheme of the herein described viscous flow reactor is shown in Figure 1. It principally consists of the modules gas supply, flow tube, handling cross, heating devices, and vacuum system. All of them are discussed in detail in the following sections.

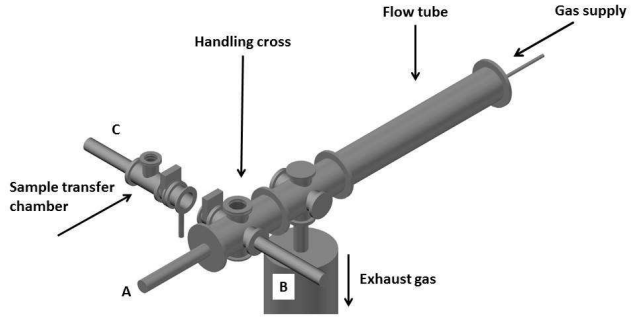


Figure 1. *Modular setup of the hot wall ALD flow tube reactor; A, B, C denominate the three transfer arms for explanation in chapter 2.5.*

Where not stated differently, the whole reactor has been constructed of standard vacuum stainless steel (AISI 304L) components connected with CF flanges and silver coated copper gaskets. Connections that are opened on a regular basis are set using ISO-K clamping flanges. For sample sizes up to 20·20·5 mm^3 a system with inner diameter of 40 mm is sufficient in order to minimize cost (flanges of diverging size are stated within the text). If bigger samples or sophisticated three-dimensional samples are to be considered, flange size has to be adjusted accordingly.

2.2. Gas Supply

The most common setup to introduce precursor pulses into a reactor chamber is to use a gas piping system combined with special ALD diaphragm valves with high speed actuation (opening or closing time of max. 5 ms). Since for research purpose we did not aim at optimized cycle times, we chose standard pneumatically actuated diaphragm valves for ultra-high purity applications. We determined the minimum possible pulse duration to be 25 ms, if time delay caused by pneumatic actuation is considered. Two precursor lines were equipped with special high-temperature formatted valves, which allow heating up to 300 °C (elgiloy® diaphragms).

Gas pipes for carrier and reactant gases have been constructed from ¼ in. x 0,035in. AISI 316/316L stainless steel piping using VCR® metal gasket face seal fittings for connections, which allow easy maintenance and flexible experimental setups.

For the carrier and purge gas we use nitrogen of purity 5.7 which at first flows through an activated charcoal trap to remove hydrocarbon residues and then through an oxygen/moisture trap consisting of catalyst coated molecular sieve. The gas flow is then split into six lines, four for liquid/solid precursor sources, one for reactant gas line and one for purge gas line. Each of them runs through a mass flow controller surrounded by two diaphragm valves actuated manually for easy cut-off during maintenance.

The setup for introducing precursor gas pulses into the carrier gas stream follows downstream of mass flow control for each of the liquid/solid precursor lines. We extended the principle valve setup by S. M. George et al. [5] by one additional valve, valve 3 in figure 2, in front of the precursor container in order to be able to use bubbler systems for lower vapor pressure precursors. We propose a gas switching setup shown in Figure 2.

Valves are normally off and opened by the corresponding signals from the valve controlling unit. In the off mode for the respective precursor only valve 1 (three-way valve) is open. The carrier gas is lead through the valve to a mechanical pump keeping the pressure of the line constant and avoiding back-pressure.

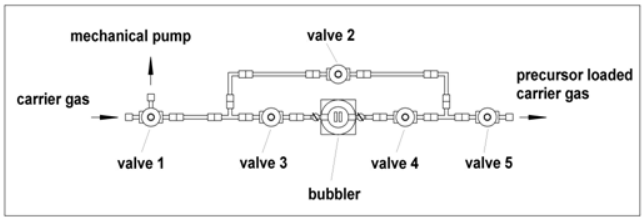


Figure 2. *Gas switching setup viable for bubbler use*

In the purge mode of the pulse sequence, only valves 2 and 5 are open purging the line/reactor with carrier gas, the pump outlet for valve 1 is closed, the gas flow is directed towards the gas switching system. This step is important to avoid pipe plugging, which would occur in the piping downstream of valve 5, where all precursor lines are reconnected to form one inlet into the reactor tube. If residual precursor is not purged from this reconnecting tube, it might react with the next precursor pulse in the gas phase. For injection of a precursor pulse, valve 2 closes instantaneously with the opening of valves 3 and 4 for the duration of the pulse and falls back into the purge mode after desired pulse duration.

2.3. ALD Reactor – Flow Tube

All parts within the flow tube are made of AISI 304 stainless steel. The flow tube itself consists of an 800 mm long tubular reactor of an inner diameter of 76 mm. The surface of the flow tube was electro-polished. At both ends, the reactor tube is terminated by 100 mm standard CF flanges.

At 400 mm, it contains a stainless steel sample stage, on which the sample holder can be placed. The principle of sample placement into the reactor is shown in Figure 3.

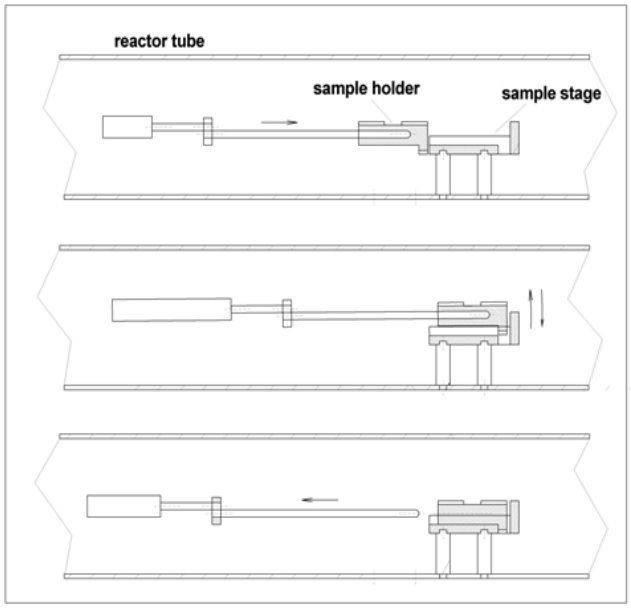


Figure 3. *Scheme for sample placement and removal into/from the reactor tube*

2.4. Heating Devices

If reaction temperatures up to a maximum of 300 °C are sufficient for the ALD process and highest possible flexibility is desired, a simple heating system built from glass yarn fabric heating mats and tapes has been shown to be sufficient. Both are commercially available in various dimensions with integrated NiCrNi temperature sensors and can simply be wrapped around reactor walls, gas piping and valves.

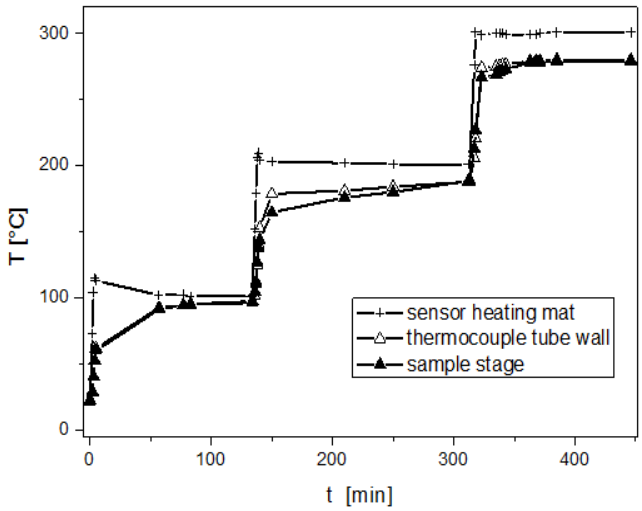


Figure 4. *Temperatures measured in the heating mat, the tube wall and on the sample stage after sequentially increasing the desired temperature to 100, 200 and 300 °C, p = 2 mbar, N_2 atmosphere*

As close as possible to the sample stage, a holding fixture is introduced into the reactor wall to accommodate a Pt100 resistance temperature detector for monitoring the temperature of the sample. The sample temperature is measured in the holding fixture described in chapter 2.3. During experiments for determination of the temperature regime of the flow tube, an additional thermocouple was placed on the sample holder. Results of these experiments are shown in Figure 4. The flow tube needs on average 70 minutes to reach a stable temperature within ±1 °C precision. After that, the average temperature difference between the temperature on the sample stage and the Pt100 detector is 1 ± 1 °C which allows sufficient temperature control of the ALD process.

In optimal reactor conditions, the temperature in the reactor is advised to be 10 °C higher than in the precursor piping and 20 °C higher than in the bubbler from experience.

If higher temperatures than 300 °C are needed for special processes and/or precursors, we highly recommend commercial heating mantle systems, which are individually tailor-made by manufacturers for the very precise dimensions of reactor and gas pipes. For high temperature processes, a cooling system for flanges has to be considered in order to keep connections gas-tight over many temperature cycles.

2.5. Handling Cross / Sample Transport Chamber

In order to avoid reactions of the sample with ambient air during transport to XPS analysis, we designed a sample transport chamber. It allows simple manual transport of the sample at ALD process conditions (≈ 1 mbar). Once detached from the vacuum pump, the chamber stays at that pressure over a period of up to three hours. It can then be attached to analytical devices, which allow attachment of CF flanges to their very own sample loading setup.

A handling cross was attached behind the exit of the reactor to direct the prepared sample. Using the process sample holder and transfer arm A, the sample can be de-loaded directly to the atmosphere. If in vacuo transport to analytical devices is wanted, transfer to the transport chamber is achieved via transfer arm B directly onto the XPS-sample holder attached to transfer arm C (see Figure 1), the chamber would be attached to the sample cross, like in setup I in fig. 5.

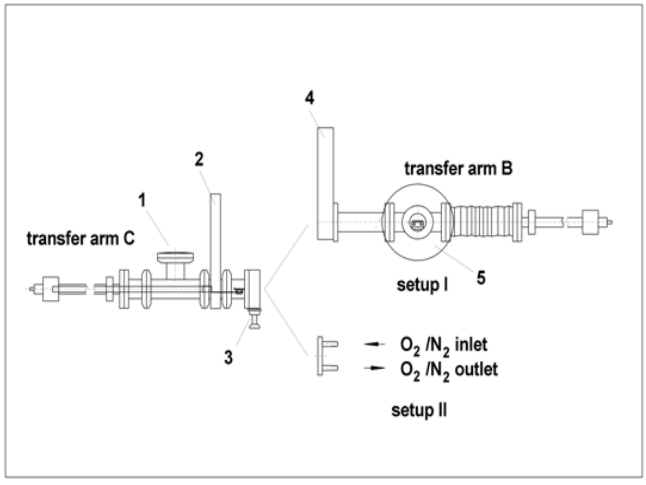


Figure 5. *Side view of possible setups of the sample transport chamber: setup I: sample transport for XPS analysis, setup II: sample surface activation; 1: quartz window, 2 and 4: gate valves, 3: connection to vacuum pump, 5: flow tube.*

An additional feature of the transfer chamber is a quartz window, situated directly above the sample holder. After sample loading and directly before the ALD process, the surface of the sample can thus be activated for chemical reactions e.g. by treatment with UV light in O_2/N_2 gas mixtures. For that purpose, a blank flange was equipped with two connections for in- and outlet of the gas mixture and can be attached to the transfer chamber during sample preparation. Then the sample can be loaded into the reactor without contact to air (Figure 5, setup II).

2.6. Vacuum System and Exhaust Gas Management

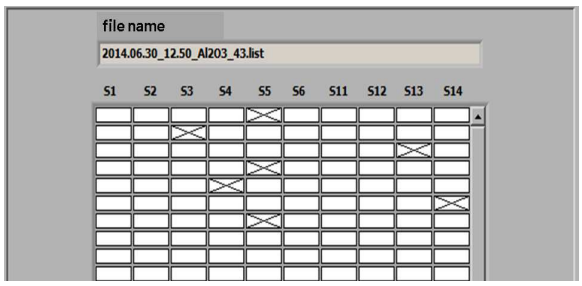
Inherent to the ALD process, it is necessary to keep up a constant flow distribution of precursor and purge gas through the reactor in order to obtain best possible separation of the precursors. Commonly used pressure regimes range between one to several mbar achieved with vacuum pumps. In our case a ceramic pump is used to avoid back-diffusion of pump oil into the reactor chamber and incorporation into deposit. To protect the pump from accidentally formed or abraded particles, we use particle filters with a pore size of 2 µm directly in front of it.

To prevent precursor mixing within the exhaust line which in our case is of ten meters length in total, we usually run the process with a purging gas flow of 600 ml · min^{-1} (T = 23 °C, p = 2 mbar). Using this construction during the ALD of Al_2O_3 from Me_3Al and water, we did not observe precursor condensation at the exit of the reactor flow tube. For precursors with a lower vapor pressure, this problem might arise and might make heating of the exhaust tubing necessary.

In ALD processes only a small percentage of the dosed precursor is actually used for layer deposition, the majority is going through the pump and has to be removed from the exhaust gas before release to the atmosphere. Therefore, behind the pump the exhaust gas runs through a system of gas washing bottles that can be filled with water, bases, or acids according to the removal process necessary for the desired precursor substance. We use a safety bottle to prevent backflow of water into the exhaust tubing, followed by a gas wash bottle and a second one equipped with a glass frit at the outlet in order to enable optimal distribution of the gas throughout the solution.

2.7. Software

The designed software operates all mass flow controllers as well as the valves individually, the latter ones via pneumatic impulses supplied by a valve controlling unit. It allows individual setting of the gas flow of each gas line, of the pulse lengths for each valve, of the pulse sequence of the ALD cycle, of a purge gas pulse for reproducible starting conditions, as well as of the cycle number. Thus, all needed parameters are adjustable individually to fully control the ALD processes. An exemplary experimental setup for the standard Al_2O_3 ALD process and a XPS depth profile of the resulting Al_2O_3 film are shown in Figure 6.



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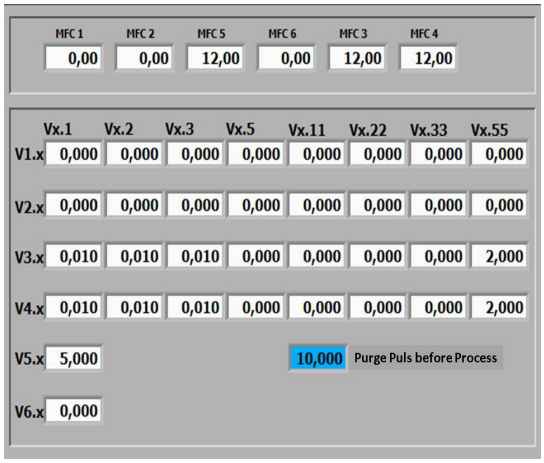

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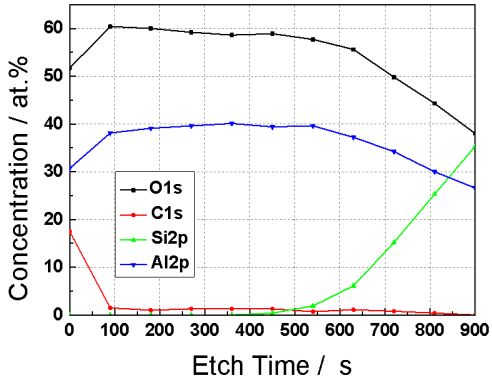

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Figure 6. *a) Screenshots of the input mask for set up of ALD experiments, the upper part defines the order, in which the valves defined in the lower window are opened. The length of the pulses is defined in the lower window (unity: s); b) XPS depth profile of a 40 nm thick Al_2O_3 thin film, for experimental details see [11]*

3. Conclusion

A description of a modular reactor for thermal atomic layer deposition has been given. The design allows for deposition temperatures of up to 300 °C with up to five precursors, one of them to be gaseous. A handling cross allows for *in vacuo* transfer of the sample to sample holders for external analytics which allow attachment of standard flanges to the sample transport system. The very same transport chamber allows for irradiation induced sample preparation *in vacuo*.

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[11] To verify the reactor Al_2O_3 films were deposited with the instrument described above. $AlMe_3$ (pur. ≥ 98 %) was used as obtained from Strem Chemicals Inc., Millipore ® grade water was degassed before filling of the precursor containers. Containers were kept at room temperature during deposition. Nitrogen was used as a carrier gas at a flow rate of 600 ml/min. Pulsing times were 1 s for the precursors and 4 s for purge gas. The deposition temperature was 200 °C. X-ray photoelectron spectra (XPS) were measured using an AXIS ULTRA Probe instrument from KRATOS Analytical Ltd., Manchester, UK, equipped with a monochromatic Al Kα X-ray source (15 kV, 10 mA) and a magnetic immersion lens. Depth profiles were determined by alternating XPS measurements and stepwise depth sputtering with an Ar^+ beam (1 kV, area 2 2 mm^2).