Atomic Layer Deposition at RhySearch

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Contents

Summary

Atomic Layer Deposition (ALD) is a well-established coating technique in the semiconductor industry and is now becoming an increasingly attractive option in the field of optics for coating of components with complex geometries. In this paper we outline some fundamentals of ALD and the benefits and challenges it offers for optical designs. In addition we describe the deposition system and ALD process development at RhySearch.

1 Introduction

Atomic Layer Deposition is a chemical vapour technique to deposit thin films via alternating cycles of a material precursor and a co-reactant, enabling the deposition of a wide range of materials for different applications. The technique was developed in Finland in the 1970s and first applied commercially for components used in large displays [1]. After its adoption for DRAM in the early 2000s and subsequent use in 2007 as a gate material in CMOS processes, it is now well established as a standard process in the semiconductor industry. The surge of interest in the technique also drove an increased effort in precursor development to expand the range of available materials [2]. Since the early 2000s there has also been a significant increase in the number of manufacturers worldwide which are offering commercial ALD systems. For the optics community the potential of this technique is of growing interest as component geometries increase in complexity and given the potential of utilizing ALD for conformal deposition of such structures.

A typical ALD cycle consists of four steps, illustrated in Figure 1. First a gaseous precursor is injected to the deposition chamber (1), typically from a heated metal-organic compound. After a self-limiting surface reaction is complete any excess precursor and reaction by-products are removed in a purge step (2). A co-reactant is then used in step (3) to form the intended material. H_2O or O_3 are used for thermal ALD formation of oxides. Various plasma processes (O_2, N_2, or SF_6) can be used to form oxides, fluorides or nitrides via plasma enhanced ALD (PEALD). A final purge step (4) is used to remove by-products and the entire cycle is repeated to build up layers of the desired material.

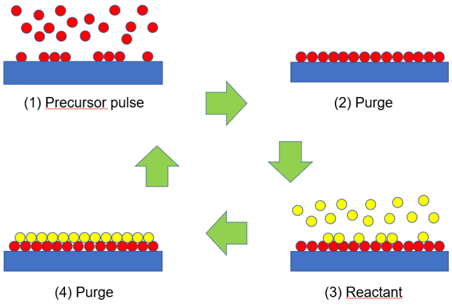


Figure 1: Schematic of a typical ALD cycle.

2 ALD for optics

The most appealing characteristic of ALD for the optics industry is that the technique enables conformal deposition of materials on complex structures and geometries. This is becoming increasingly relevant with respect to larger components such as spheres, prisms, and also for micro-optics [3]. Given that traditional Physical Vapour Deposition (PVD) methods are very directional with respect to the material source it is challenging to achieve uniform coverage on curved 3D components or on surfaces out of the line of sight of the source. Complex holders are then required to manipulate the components to achieve even coatings. ALD has the potential to simplify such setups and also to facilitate single and double-side coating of geometries and shapes which would not be possible using PVD.

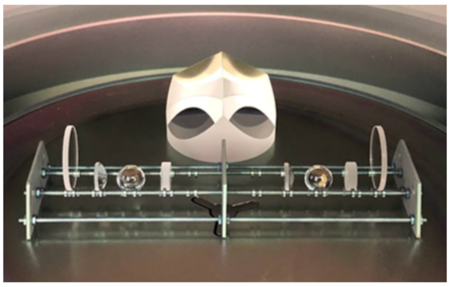


Figure 2: Optical components of various shapes coated in the ALD chamber at RhySearch.

ALD offers multiple options to tune material properties via alteration of process parameters. The refractive index and film density can be readily modified through varying deposition conditions such as the growth temperature. The technique enables fine layer thickness control with growth rates being typically on the order of 1Å per ALD cycle. Such attributes make ALD attractive for optical designs such as AR coatings and mirrors where multiple layers are stacked with varying thicknesses and refractive indices. For plasma enhanced ALD processes additional parameters such as plasma power are available for material tuning. PEALD also allows for deposition at lower process temperatures than for thermal ALD, which can be advantageous where temperature sensitive samples are involved. Another advantage of PEALD is that the increased reactivity of species present in the plasma also facilitates PEALD growth of materials using precursors where H_2O is not sufficiently reactive [4]. One example of this is the Bis(diethylamino)silane (BDEAS) precursor used for deposition of SiO_2.

ALD typically results in dense and pin-hole free films thus making it an attractive proposition for protective and barrier coatings, one example of this being the use of Al_2O_3 as an anti-corrosion layer. A further extension of the approach is the use of nanolaminates as protective coatings. Recently, quantized nanolaminates have been investigated for independently adjusting the refractive index and bandgap in optical coatings [5, 6]. Nanolaminate stacks consist of alternating layers of different materials with thicknesses in the nanometer or sub-nanometer range. ALD can achieve this with great ease and precision by simply varying the number of growth cycles for each material layer. Therefore one can very finely tune the properties and composition of the overall stack.

Some challenges remain for adoption of ALD in optical coating applications. The most obvious limitation of ALD is that the process is by nature much slower than PVD methods. As an example, one can compare a process on the ALD and Dual Ion Beam Sputter (DIBS) systems at RhySearch. The deposition time for 100nm of SiO_2 is $\sim$150 minutes by PEALD compared to $\sim$5 minutes using the DIBS. The longer deposition times are primarily due to the necessity to purge the reaction by-products after the precursor and co-reactant steps. This has inhibited the use of ALD for optical components where thicker coatings are frequently required. Efforts are underway to develop “fast” ALD tools to reduce process times, one example being the Spatial ALD system developed by LZH and Beneq [7]. Another issue, in particular for thermal processes using H_2O, is that elevated deposition temperatures are required, often in the region $\sim$300°C. This can restrict the use of certain ALD processes for applications where constraints exist with regard to processing temperature.

3 ALD system at RhySearch

The ALD system at RhySearch is a FlexAl tool from Oxford Instruments, as shown in Figure 3 below. This is capable of performing both thermal and remote plasma processes in a single chamber configuration. Further details are published by Faraz et al regarding the tool specifications [8]. Up to seven different precursors can be installed on the system at RhySearch. Thermal ALD of oxide materials is performed using H_2O with an additional process option provided by the integrated ozone generator. There is the facility for six different process gases allowing for deposition of oxides, fluorides and nitrides via PEALD processes. The loadlock and heated chuck permit deposition on various substrate diameters up to 200 mm. It is possible to apply a RF bias to the chuck for additional tuning of material properties during deposition. ALD of larger parts and one-off components is also possible on the system at RhySearch via the use of customized substrate carriers.

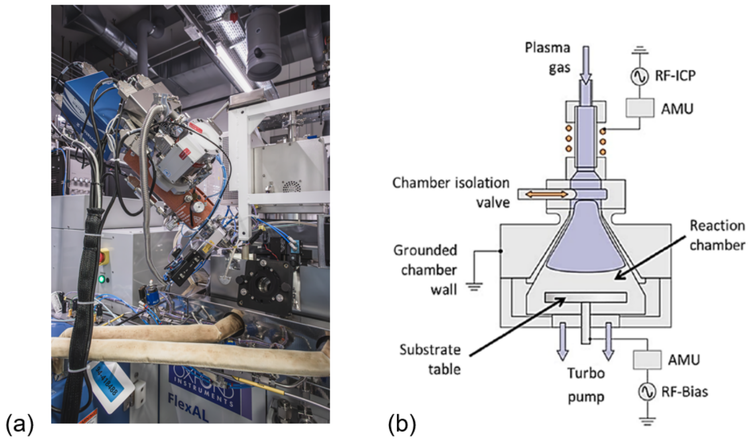
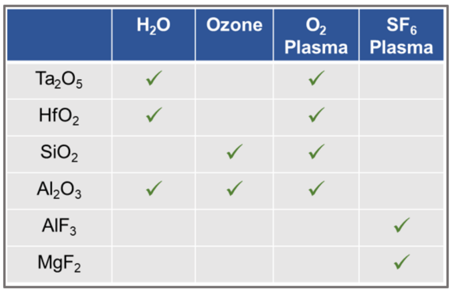


Figure 3: (a) the Oxford FlexAl in the cleanroom at OST (b) Schematic of the Oxford FlexAl deposition chamber[8].

4 ALD Processes at RhySearch

The material processes currently available at RhySearch are summarized in the table shown in Figure 4. The various process recipes are continually developed in order to optimize material properties which are characterized via several methods, a selection of which are described later. Several variables must be optimized including deposition temperature, pressure, gas flows, and in the case of PEALD processes the plasma power. For all processes particular attention is paid to the precursor and co-reactant dose times and purge times for each ALD half-cycle in order to minimize the total cycle time. This is particularly important for optical coating designs where multiple layers are employed resulting in potentially long processing times and increased material and tool costs. However, there are obvious limitations in the reduction of purge times as the inclusion of film impurities arising from the precursors or process gases must be minimized or eliminated. It is also a fundamental requirement that good film uniformity and density are maintained. The variety of test methods available in the Optical Coating and Characterization Lab (O2C) at RhySearch allow for in-house testing of multiple properties of the ALD materials [9].



	H_2O	Ozone	O_2 Plasma	SF_6 Plasma
Ta_2O_5	✓		✓	
HfO_2	✓		✓	
SiO_2		✓	✓	
Al_2O_3	✓	✓	✓	
AlF_3				✓
MgF_2				✓

Figure 4: ALD material processes available at RhySearch.

Ellipsometry is used for thickness calibration and uniformity mapping over the 200mm chuck area. Various optical characterization techniques are used to evaluate the optical quality of the films including Total Integrated Scattering (TIS), Laser Induced Deflection (LID) and Laser Induced Damage Threshold (LIDT). Atomic Force Microscopy (AFM) is used to extract information on film roughness and morphology.

Figure 5 below plots refractive index values measured using a Woollam variable angle spectroscopic ellipsometer for selected materials deposited using plasma processes in the FlexAl reactor at RhySearch. With refractive index values varying between 1.35 and 2.1 (at 633nm) one can utilize combinations of these layers in various designs such as AR coatings or mirrors. The extinction coefficients of the materials are also monitored to examine the effects of process parameter changes on losses in the layers. Further spectrophotometer measurements are employed to extract (n,k) values to provide relevant parameters for use in optical designs.

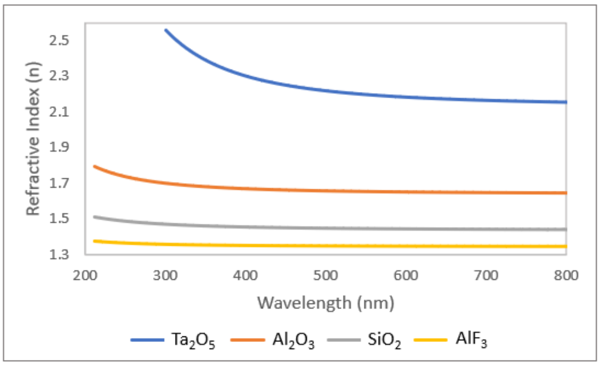


Figure 5: Refractive index plots for various plasma enhanced ALD materials at RhySearch.

Figure 6 shows LIDT and TIS data as measured in the O2C Characterization Center. LIDT provides information on the laser resistance of materials while TIS describes how much light is scattered by the material. The results shown are for SiO_2 deposited using a BDEAS precursor and O_2 plasma. An additional method is the use of LID which quantifies the absorption of materials and is an important parameter to assess the quality of the material. The availability of such characterization in-house at RhySearch provides vital feedback regarding the properties and quality of the deposited films and assists in ongoing monitoring and optimization of ALD processes.

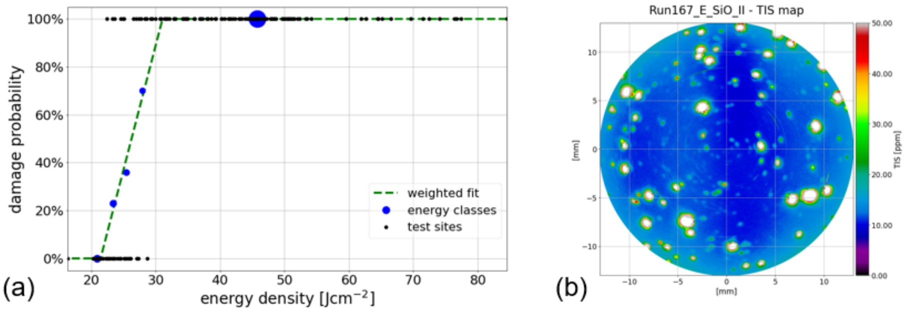


Figure 6: (a) LIDT and (b) TIS characterization of SiO_2 PEALD films.

As mentioned earlier the plasma enhanced ALD system offers a further option to fine tune the material properties via substrate biasing. This has been demonstrated previously for a similar Oxford FlexAl system by [10] and [8]. In those works the refractive index, growth rate and film density were all modified through variation of the substrate bias during the plasma step. This capability has been demonstrated on the FlexAl tool at RhySearch. In a SiO_2 deposition process using a BDEAS precursor and O_2 plasma, various substrate biases were applied during the plasma step in order to examine the effect on material properties. The results were in agreement with the work of [8] where the growth rate was reduced and the refractive index and film density increased. This illustrates a further capability on the tool at RhySearch to adjust critical properties of the deposited material.

Metal fluorides are of interest for applications in the visible and UV wavelength ranges given their properties of low refractive index, wide bandgap and high transparency. There are few reports on the growth of AlF_3 via ALD. [11] employed a thermal ALD process with trimethylaluminum (TMA) and Hydrogen Fluoride while [12] used a PEALD process with TMA and an SF_6 plasma. At RhySearch we have developed a process for deposition of high quality AlF_3 using an approach similar to that used by [12]. Through optimization of the PEALD process parameters, low loss, dense and smooth AlF_3 films were deposited. Figure 7 shows an image of an AFM measurement (0.5x0.5μm) performed in the O2C Characterization Center of an AlF_3 film on silicon. The layer exhibits a low roughness comparable to the underlying substrate, which is important to avoid effects such as scattering. Spectroscopic ellipsometry results indicate that the material has a low refractive index of 1.35 (@633nm).

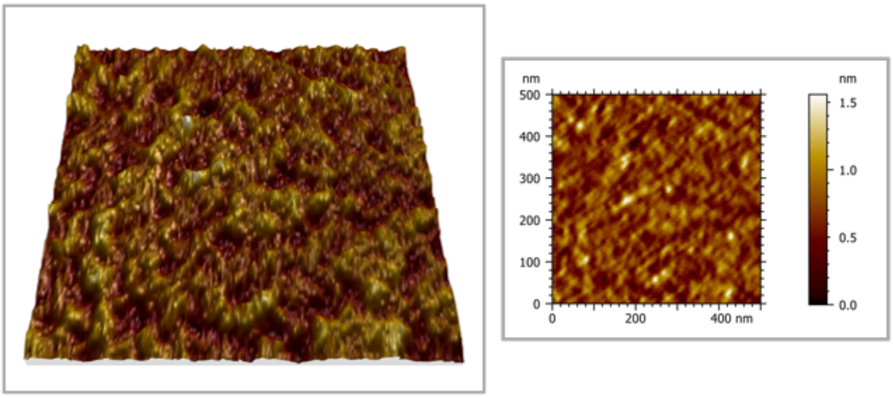


Figure 7: AFM of AlF_3 films deposited on Si via a PEALD process.

The deposition of materials on non-planar and high aspect ratio structures is one of the principal attractions of ALD. In order to provide an illustration of this, an Al_2O_3 film of ∼150nm thickness was deposited at RhySearch by thermal ALD (using TMA and H_2O) on a variety of test structures etched on a silicon wafer. In collaboration with Martin Stahel of the Ostschweizer Fachhochschule (OST) the coated structures were studied using Scanning Electron Microscopy (SEM). Figure 8 (a) shows an SEM image of holes etched into the silicon with dimensions of approximately 3μm width and 30μm depth, while 8 (b) focuses on a region near the base of adjacent holes. These images illustrate the conformality and thickness uniformity of the 150nm Al_2O_3 layer on the sidewalls and down to the bottom of these etched holes. The SEM image in Figure 8 (c) shows the sidewall and cavity coverage for a different feature with multiple etched rings of ∼30μm depth and ∼10μm spacing. Finally, for the etched free-standing columnar structures (∼30μm in height, and ∼8μm or 3μm in diameter) shown in Figure 8 (d), it was also possible to achieve excellent conformal coating on the individual columns with Al_2O_3.

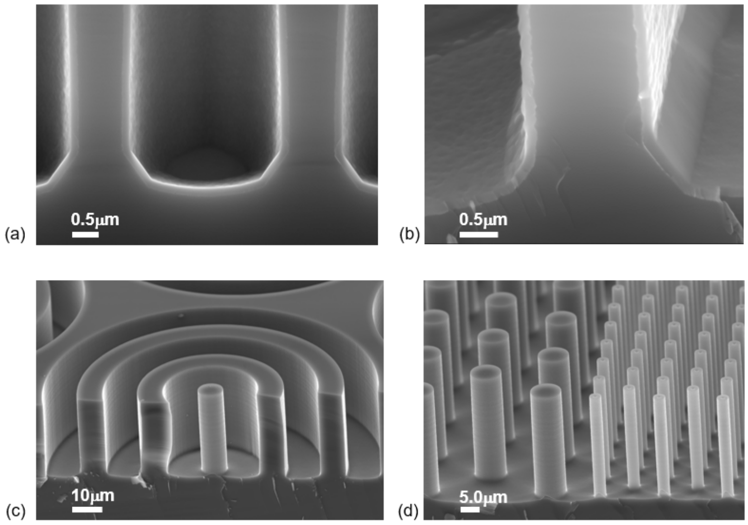


Figure 8: SEM of Al_2O_3 deposited via a thermal ALD process on features etched in silicon: (a) and (b) holes etched into the Si of approximately 4μm width and 30μm depth. (c) etched ring structure of ∼30μm depth and ∼10μm spacing. (d) columnar structures which are ∼30μm in height and ∼8μm or 3μm in diameter.

The results in Figure 8 show that this thermal ALD Al_2O_3 process can be implemented for a range of geometries and surface topologies. One example application of this at RhySearch is where Al_2O_3 layers have been deposited as protective coatings on components of various dimensions for customers and research partners. Additionally, while it is not the case for all materials, Al_2O_3 can be deposited via both thermal and plasma ALD over a wide temperature range, with PEALD processes at RhySearch ranging from below 100°C to 300°C, which is appealing for applications where the substrates or devices are temperature sensitive.

5 Summary

ALD represents a versatile and exciting technique to deposit a range of materials for use in diverse applications. With respect to the optics industry, while challenges remain regarding the deposition rate, ALD opens up new opportunities for applications and components where traditional PVD techniques are not suitable. The ALD facility at RhySearch offers a range of material and process options in addition to advanced in-house testing of ALD material properties in the O2C Characterization Center. High quality oxide and flouride materials are available for use in a range of applications such as optical designs and protection coatings. It is envisaged to expand the portfolio of materials and processes at RhySearch in order to realise the full potential of ALD for the future deposition needs of industry and research.

6 About RhySearch

The “Research and Innovation Centre Rheintal" (RhySearch) has been operating as a public institution on the campus Buchs of the Ostschweizer Fachhochschule (OST) since 2013. It is supported by the canton of St.Gallen and the Principality of Liechtenstein and comprises three main Labs: Optical Coating and Characterization, Ultra Precision Manufacturing, and Digital Innovation. RhySearch networks with existing research and educational institutions, forming a technology cluster that can manage large-scale research assignments and technology transfer. It also provides companies with a single contact point for comprehensive research and innovation support. Further information is available on the RhySearch website `https://www.rhysearch.ch/`.

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