Atomic Layer Deposition (ALD) is a chemical vapor coating technique that has recently been adapted for precision laser optics to perform highly conformal multilayer coatings on complex 3D substrates like hemispheres, axicons or multi-sided prisms. Here, we explain some ALD fundamentals and describe the way from idea and single-layer films to simple anti-reflection coatings and even more ambitious designs, like non-polarizing beam splitters, performed on complex optical substrates.

In laser systems, non-planar, i.e. 3D shaped optics (Fig. 1) are needed to image or transform laser light with respect to a certain application. For instance, an axicon converts the point-source laser beam into a ring of light used for laser eye surgery or optical trapping [1]. Starting from strongly curved lenses to custom made aspheres and multi-sided prisms, these optical elements all aim at light shaping. Thin-film coatings are needed to enhance the performance of almost all optical components, e.g. reduce transmission losses with anti-reflection coatings or reflect beams with mirror coatings.

Unlike standard planar substrates, the challenge for all curved or 3D optics is to deposit a coating with superior uniformity over the shape with reasonable effort. The common techniques of physical vapor deposition (PVD) show constraints in this regard. The coating material comes uni-directionally from the PVD point source like the evaporation crucible or the sputtering target. This leads to a gradient thickness distribution, shadowing effects and no deposition on the “dark side of the moon”. To reach a high level of conformity with PVD, the effort needs to be made to specifically twist, turn, rotate or otherwise move the substrates and to additionally shape the vapor intensity through shadowing masks. This comes with an extensive load of mechanical work and process optimization and requires tight control of the process parameters. In the end, this may still not lead to a sufficient result. Adjusting the coating design is of limited benefit and can impact negatively on the spectral performance of the coating.

ALD overcomes those constraints and has proven its suitability for high precision and uniformity in other fields, where the challenge was not only to achieve conformity over the outer shape, but within the semiconductor microstructures at nanometer scale. Additionally, the ALD technology has reached a high level of reliability, qualifying it for serial production of expensive laser optical coatings.

Being introduced to the field of laser optics, ALD has its foremost advantage in the ability to coat complex optical geometries, which...
most often require anti-reflection layers, i.e. rather simple designs (Fig. 2). Due to the superior thickness control in ALD, this technique has the potential to compete with high precision PVD methods like sputtering that can realize sophisticated coating designs of many non-quarter-wave layers. A standard process like electron-beam evaporation still is the mostly used and versatile coating technique, but is limited for complex coating designs or substrate shapes.

**ALD history**

The ALD principle, a solid film growth in a sequential, self-limiting, layer-by-layer deposition mode, was independently developed twice: in the early 1960s in St. Petersburg, Soviet Union, under the name “molecular layering” and in the 1970s in Finland under the name “atomic layer epitaxy” [2]. The first practical application for ALD was established by Tuomo Suntola and co-workers in the middle of the 1970s and aimed at the deposition of high quality polycrystalline zinc sulfide thin films for electroluminescent flat panel displays. The first such display presented in 1980 at the conference in San Diego, USA, was such a great success that, after its presentation, the developer’s team got more than three thousand requests for it. The first industrial scale display fabrication by using ALD manganese-doped zinc sulfide luminescent layers and aluminum-titanium oxide dielectrics started in 1983.

For a long time, ALD research was mainly focused on electroluminescent materials. In the late 1990s and 2000s, the interest in elemental semiconductors and oxide materials manufactured by ALD increased, mainly driven by silicon-based microelectronics. ALD was recognized for producing conformal and ultra-thin films with exact composition and thickness control at the sub-nanometer level [3, 4]. Little by little, the material choice has been enlarged and the application areas have been extended to semiconductor devices, photovoltaics, catalysis and others.

**ALD fundamentals**

As mentioned above, ALD is a special type of chemical vapor deposition (CVD) techniques, in which surface reactions play the crucial role. In these reactions, two gaseous chemicals, called precursors, meet each other only at the surface and recombine into the desired material. For example, a typical ALD process (Fig. 3) starts with arriving and chemisorption of the precursor A on the substrate surface. After all available surface sites are covered, a purge step removes the excess of the precursor A. Therefore, the deposition is surface-controlled and extremely conformal. Now the precursor B is introduced and reacts with the adsorbed precursor A, resulting in a solid film plus reaction byproducts. The final purge removes the byproducts and excess of the precursor B. The chemical nature of the growth process is responsible for the resulting fully stoichiometric materials. To achieve thicker films or to grow more layers, the described sequence has to be repeated n times with the same or other precursors. In most cases, the excessive dosage of precursor A or B does not increase the deposition rate. This self-limitation is an important feature of ALD and ensures a high repeatability of the deposition process.

Unlike continuous CVD, the sequential layer-by-layer thermal ALD (Fig. 3) provides a perfect film
thickening and growth for SiO$_2$, Al$_2$O$_3$ and Ta$_2$O$_5$ de-
positioned with ALD
and ion beam sputtering (IBS)

control allow ALD to create new
artificial materials, like thin and
ultra-thin multilayer systems (so
called nano-laminates), films
modified via sub-nanometer thin
dopant layers or tailored mixtures.
In combination with a broad spec-
trum of nowadays available stan-
dard optical materials like SiO$_2$,
Al$_2$O$_3$, TiO$_2$ or Ta$_2$O$_5$, ALD is a very
promising coating option for chal-
lenging laser optics. It opens a way
to coat nearly every 3D optic for
laser applications, even with a high
aspect ratio or strongly curved,
where all surfaces can be coated
at once and selected ones can be
protected.

**ALD for optical coatings**

The initial approach to use ALD
for optical coatings is to compare
commonly used PVD coating ma-
terials with their ALD pendants.
Therefore, the optical constants
and growth rate of single SiO$_2$,
Al$_2$O$_3$ and Ta$_2$O$_5$ films as common-
ly used materials were observed
first.

The single layer films with a total
thickness of about 200 nm were
deposited by thermal ALD at tem-
peratures between 200 and 300 °C.
The typical ALD growth rate,
roughly 0.05 – 0.10 nm per cycle,
ensures a high deposition precision
and thickness control. Empirically
determined refractive indices for
SiO$_2$, Al$_2$O$_3$ and Ta$_2$O$_5$ are shown in
Fig. 4.

A raw comparison of ALD made
films with ion beam sputtering
(IBS) deposited materials shows
that they are not absolutely identi-
cal, but can easily be implemented
into optical designs. In addition,
good film purity, very low level
of absorption and a particle free
growth make ALD a very promi-
sing method for challenging optical
applications [6]. Further upscaling
to multilayer stack coating designs
can be done on planar or 3D optics
with respect to suitable deposition
parameters and reactor designs.

For example, based on the re-
fractive index values and growth
rates, an antireflective coating cen-
tered at 266 nm can be produced by
using thermal ALD. A pragmatic
design consists of a stack of four
alternating SiO$_2$ and Al$_2$O$_3$ layers
and has a total thickness of about
180 nm. The sample, measured
against air at 8° angle of incidence,
shows a reflectance of less than
0.1 % (Fig. 5).
The good match with the theoretical design motivated to explore ALD capabilities on more complex optical designs. For that purpose, a non-polarizing beam splitter (NPBS) has been chosen, a design normally done by IBS. The optics have to provide a splitting ratio of 50% at 400 nm for both s- and p-polarized light, at 45° angle of incidence (dotted lines in Fig. 6). The entire film stack is made of alternating 23 layers of Al₂O₃ and Ta₂O₅ with a total thickness of about 1.2 µm. The processing time was around 24 hours and seems to be too long. But taking into account that the ALD deposition rate in the batch mode is typically almost in the same range as for the single substrate mode, the ALD method becomes a winner with a higher throughput (coated area per time) compared to standard PVD techniques. Nevertheless, the measured sample characteristics meet the optical requirements at 400 nm and also the side bands are in good accordance with the design. The final coating (solid lines) matches the theoretical design (dotted lines) well, as presented in Fig. 6.

This example shows the potential of ALD as mentioned in Fig. 2. Considering the strong advantage of ALD, even complex surface geometries will not have a big influence on the deposition precision. Therefore results presented here can directly be applied to non-planar, i.e. 3D-shaped optics.

Conclusions and outlook

Looking at the whole segment of optical coatings, those for laser components represent a small niche that is mostly served by using PVD methods. Within that niche, ALD is introduced as a next stage of specialization. It has the potential for high design precision and low defect density, also good spectral performance, but its main advantage is the shape independent uniformity. At Laseroptik, this method helps to fill a technological gap in the broad portfolio of capabilities to serve customers with so-called 3D optics.

ALD's future potential is to develop into areas with substrate geometry and coating design being both complex. In this context, ALD can also be interesting regarding the deposition of ultra-thin intermediate layers, e.g. for sophisticated mirror designs for dispersion control in femtosecond lasers. Or they can be made of metals like Au, Ag or Al, needed for broadband designs. While ALD is capable of accurately depositing these layers, the challenge will be to monitor the film growth and to control it. Apart from metals, there are also attempts to deposit fluorides [7], but still with various challenges and even more chemical safety requirements than with standard precursors.

The production efficiency seems to be relatively poor when one just takes into account the growth rate of ALD. But having all sides coated at once and running highly reliable processes unattended, helps to relativize the ironic remark of semiconductor ALD users, when they define it as "Awfully Lame Deposition".

References