Atomic Layer Deposition (ALD) for Optical Coatings

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ABSTRACT

This paper describes the use of ALD for optical coatings from the manufacturing and practical point of view. Especially features not existing with the PVD are covered, like capabilities to coat 3D surfaces, repeatable deposition of sub-nanometer thin films, creation of new film materials, use of many materials easily in the same process and to modify materials during the deposition. Items having importance for the industrial applications are shortly covered like cost, reliability and process integration. Novel methods to get high uniformity in large area and batch applications are introduced, opening scale up pathways. Factors mentioned above and natural 3D coating capabilities, set ALD into an enabling technology position and new coating possibilities are highlighted.

INTRODUCTION

People get their first exposure of the ALD often from the nanotechnology and semiconductor fields. Films there are often thin and typical production tools are single wafer or cluster tools. However, ALD was initially invented by industry to solve an industrial problem to make good ZnS film for Thin Film Electroluminescent (TFEL) Displays [1]. Production of these TFEL displays started in the middle of 1980's and is currently operated in Finland by Planar Systems, Inc. [2]. In fact origins of the ALD are in batch processing for film thickness over 1 µm, which fits well with industrial optical applications.

ALD technology is not competing with other coating technologies directly. ALD is an enabling technology for new products by providing coating and material features, which are not possible by other existing technologies. Coating of batches, large areas, complex 3D parts, double side coating and new coating materials and material structures are the main features of the ALD for the optical field.

Driving forces for the new industrial ALD optical applications can be roughly categorized as:

1. Coating of objects that are difficult or impossible for other methods.
2. Engineering of novel optical materials.

Additionally new processing technology enables good patenting possibilities. ALD is not yet in very wide industrial use beyond semicon, making unauthorized process duplication even more difficult.

MAIN TECHNICAL FEATURES OF ALD FILM COATING TOOL FOR OPTICAL APPLICATIONS

Pressure of the ALD process is in the range of 0.1 … 10 (hPa, Torr, mbar). Vacuum pumps are typically dry pumps, but conventional vane and roots stacks are also used. High vacuum pumps are not used due to various reasons (film growth inside the pump, low gas throughput, high cost). To be economically competitive systems need several m^2 of effective coating area. The amount of precursors is quite high in production and pumping system needs very good filtering systems to prevent pump contamination or film growth inside the dry pump. Gas flow is typically few SLM.

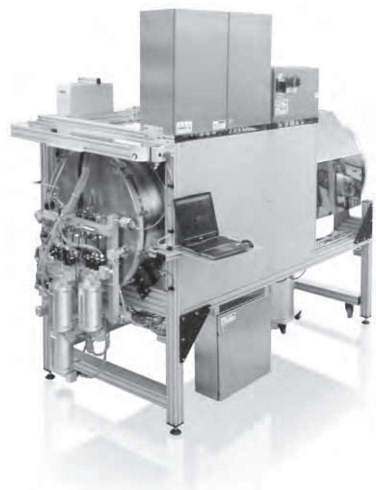

Figure 1: Example of industrial ALD batch coater for optical films. [3].

Typical ALD reactor uses traveling-wave principle. Nitrogen carrier gas flows through the system and precursors are dosed as vapor or gas pulses to this carrier flow. Carrier flow takes the precursor pulses as sequential vapor waves through the reaction chamber down to vacuum pump.

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ALD throughput (coated area/time) is high. CMOS industry and typical R&D use low throughput single wafer platforms. Industry beyond semicon use typically batch coaters. Coating can be done on both sides of the substrate or flat substrates can be loaded as back-to-back to double the capacity.

Both plasma enhanced and thermal ALD tools exist. Plasma is not easy to apply for the batch mode and thermal ALD is the preferred method for optical film production. Coating temperature is often in the range of 250-350 °C. This needs to be taken into account when coating substrates having low thermal expansion. Low temperature processes (T<120 °C) exist for Al_2O_3, ZnO, ZnO:Al and TiO_2. ALD uses chemical vapors or gas precursors reacting sequentially on the surface, producing solid film. Variety of precursors (often similar as with CVD or MOCVD) is available and the same film material can be processed using different precursors.

THIN SUB-NANOMETER FILMS WITH HIGH REPEATABILITY

Growth per cycle in ALD is limited to a single atomic layer. Coating can be less than, but never more than the fully saturated surface allows. Using process conditions in the full saturation regime gives high repeatability. This digital nature of the ALD allows deposition in open loop mode, without feedback. This reduces tool complexity and overhead costs. A single ALD cycle does not deposit a full monolayer of continuous film. Complete surface coverage often needs 3-5 cycles. Size of precursor molecule and molecules which are eventually left on the surface to form the deposited material are different than the size of the final molecule of the deposited film. Molecules actually block sites on the surface (steric hindrance), preventing full monolayer deposition. Continuous films need 4...6 Å thicknesses.

ENGINEERED NEW ARTIFICIAL MATERIALS

The capability to produce new materials is one of the most powerful features of the ALD. High level of deposition control opens good pathways to engineer new materials. ALD is very capable of creating materials requiring mixing of thin layers or uniform (co-) doping profiles.

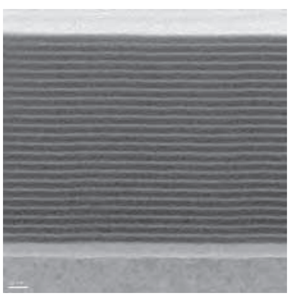

Figure 2: Film in this HR-TEM picture is not multilayer film stack, but engineered high index bulk material. White lines are <1 nm thick.

Modified TiO_2 for optical purposes [4] is a good example of artificial materials, demonstrating the use of sub-nanometer layers in ALD. Film is a low loss, high index, nanocrystalline yet optically amorphous like material. TiO_2 has a high refractive index, but in coating temperatures above 150 °C the films become crystalline, causing scattering and optical losses. Scattering from crystals can be prevented by keeping the crystal size small. The crystal size can be limited by depositing intermediate <1 nm layers of suitable material in the films.

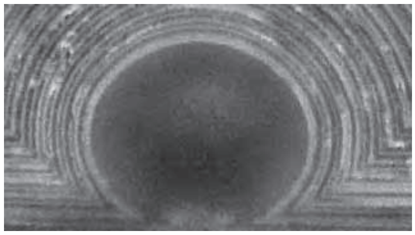

Figure 3: Conformal film stack. Individual layer thicknesses are on the order of 4 nm.

CONFORMALITY, ADHESION AND STRESS

Film grows up from the surface providing extreme conformality. Actually, film grows on surfaces as long as precursor molecules can reach the site. One needs to be aware of this powerful feature. If object includes zones where coating is not wanted some design feature needs to protect these zones. Adhesion of the ALD film is almost without exceptions strong (compared to PVD) due to chemical bond between the surface and the first layer(-s) of the growing film. Natural conformal property of the deposition further improves the adhesion. ALD films are dense, often demonstrated by resulting high refractive indexes. Stress of film is low because films grow through natural chemical reaction, without other than thermal energy.

UNIFORMITY OF DENSE PRODUCTION BATCH SETUPS AND LARGE AREAS

Concerning film uniformity, precursor temperature and flow path designs are main factors of the tool design. Additionally precursor can decompose or etch the deposited film; reaction by-products can reserve downstream sites or etch the film. ALD processes have typically optimum temperature range. High repeatability does not always mean that films are uniform. TiO_2 ($TiCl_4$+H_2O) is an example of a process providing quite uniform film in low capacity setups, but the uniformity suffers once loading capacity is increased. However there are methods to get very good uniformity also with TiO_2 [5].

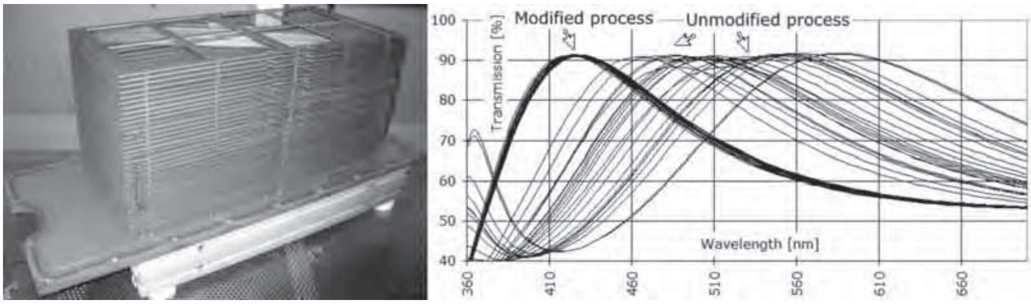

Figure 4: Example of the TiO_2 batch for uniform (±2%) coating. 36 shelves 240x500 mm^2 double side coating (8 m^2 of film). Transmission curves on the far right demonstrate transmission spread inside the batch without process modifications. On the left (thick bunch of curves) are results from the same locations with the next process using modifications.

Al_2O_3 deposited from trimethylaluminum (TMA) $Al_2(CH_3)_6$ and H_2O is in turn a good example of a process not having much uniformity issues. If the reactor is properly designed, it is difficult to not get reasonably high uniformity using the process. Generally speaking, to demonstrate or compare ALD coating systems by referring to results with Al_2O_3 may be misleading. Each coating material may have distinct requirements for the process. It is also important to note that the deposition temperature range depends on the coating system design. For example with TMA based Al_2O_3 some designs are limited to precursor decomposition range (<350 °C), while others can make good films with same precursors above 500 °C.

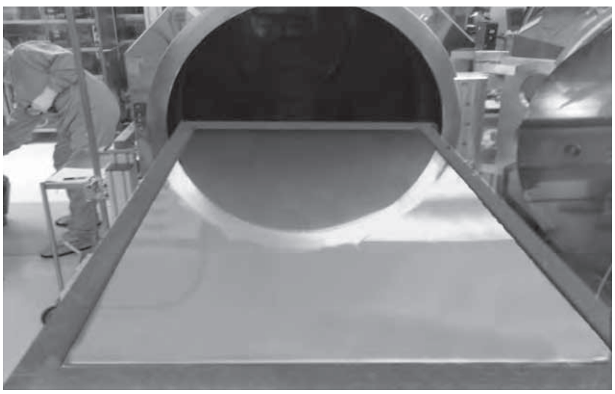

Figure 5: Larger area test setup for 1200x600 mm^2 glass using Al_2O_3 (±1% uniformity).

PROCESS INTEGRATION

Industrial production often needs films before (interface, barrier, seed, planarization, adhesion, stress, etc.) and after (passivation, protection, etc.) the active layers. ALD film is naturally pin-hole free and provides extremely good barrier properties. ALD coating tools are capable to process many materials and typically it is possible to integrate these pre- and post-coating steps to a single main ALD process. Compared to PVD this is a benefit, reducing the total processing costs and production flow complexity. Industrial ALD tools typically contain connections for more than eight precursors.

SCALE UP

ALD coats surfaces and throughput in area/time is high. However, ALD is a slow deposition method in time space, and thus it is often considered only suitable for <100 nm films with single wafer setups. Optical films are typically thick, often beyond 1 µm and the batch mode is a logical way to implement production. Thickest film stacks made by ALD have been about 45 microns thick (filter for optical telecom purposes). An important feature of the ALD is that the deposition rate in the batch or large area mode is typically on the same range as with the small single wafer mode. For example, the ALD cycle time was in the range of 1.5-2.5 s in both cases shown in Figures 4 and 5. ALD throughput is typically in the range of 1-3 µm / 24 h (40-130 nm/h) and some processes like SiO_2:Al [6] can reach the range of over 30 µm / 24 h in a traveling wave reactor.

RELIABILITY OF TYPICAL BATCH COATING TOOLS

Industrial ALD tools are near the 6 sigma reliability level. There is no need for complex process control instruments. Tools are typically controlled by the PLC and the only moving parts are valves and pump. ALD may sound scientific and complex, but in practice it is just dosing of vapors with purges between doses. However, ALD needs tool construction taking into account facts like valves dosing millions of cycles, good thermal design, and films growing on all exposed items. Furthermore, gas flow paths needs to designed well and good filtering is required before the pump. In contrast to PVD, ALD processes are generally speaking insensitive to small air leaks. Typical carrier gas inside the ALD system is nitrogen. Another air gas, oxygen is often non-reactive with precursors. The most harmful air leak item is water vapor. Largest Preventive Maintenance (PM) item is the cleaning of coated construction parts, as in any thin film coater.

NOTES OF THE ALD PROCESSING COST

ALD for optical applications uses typically low cost industrial grade chemicals and required direct labor and engineering overheads are low. Batch process is automated. Especially with thick optical films the process utilizes also night times, weekends and holidays, resulting high annual tool utilization rate. Downtime of the mature ALD system is small and it is mainly related to precursor refill and removal of few parts for cleaning using similar methods as PVD, like sandblasting. In most cases, the major part of the coating cost is related to the investment payback, and therefore tool suppliers need to work closely with customers to select or design an optimum ALD system setup to meet the throughput and cost targets for each case. In addition to batch tools also other industrial setups exist like in-line modules and special versions for powder coatings. Roll to Roll machines are under development for several applications.

ALD coating setup causes some new utility requirements, not existing with PVD. Pump exhaust lines typically need scrubber systems. Dry pump purge gas consumption can be high (tens of SLM), although the ALD system itself typically uses only a few SLM. However, dry pump use low purity gas and often dry air is adequate. Chemicals, including the waste, need attention and may need permits. Glove boxes may be required to fill precursor sources.

ALD has been using batch mode from the day zero, but semicon industry use single wafer or cluster platforms which do not fit well with the ALD. Often articles related to semiconductor production or R&D is the source for the "ALD is slow" comments. Speed should be distinguished from the throughput. In its natural batch mode, large ALD batch throughput (coating area / time) up and cost down. ALD fits very well in high capacity batch or large area production.

OPTICAL MATERIALS

Common optical materials are Al_2O_3, ZnO, ZnO:Al, TiO_2, SiO_2:Al [6], ZrO_2, Ta_2O_5, ZnS. Carbides and nitrides have good absorption for gray shade filter and decorative coating underlayer. Metals like Al, Ag, Au are not possible or not yet practical with ALD although especially Al is under wide research in semicon industry. Noble metals can be deposited using ALD. Generally speaking, metals are difficult for chemical deposition methods and PVD is the better choice.

Some fluorides are possible to make, but the cost and related safety items are limiting applications. Typically ALD gives fully stoichiometric films, which is a very good feature in most optical cases. Concerning impurities, in contrast to PVD, ALD as all chemical deposition methods leave some residues from precursors to deposited film. Typically impurity content is low and not important for optical properties. If process is close to borderlines, amount of impurities may increase to noticeable levels. Actually several common ALD precursors cause optical losses, often related to carbon residue. General R&D work with ALD is typically done for thin films only and results of hundreds of film interfaces and thick films are not studied. Chlorides are often the safer choice for optical applications than precursors containing carbon, small Cl and H residues do not typically cause noticeable effects.

APPLICATION CAPABILITIES FOR OPTICAL DESIGN

High repeatability and the capability to easily make thin continuous films down to 0.5-1 nm range provide tools for the optical designer to optimize multilayer stack designs and nanoscale materials. Photonics applications and quantum optics research benefit from the capability to make sub-nanometer films. ALD process development for new products takes more time than with PVD, but the payback comes from the fact that industrial high capacity ALD batch or large area coaters are capable to coat many micrometer thick optical stacks having sub-nanometer structures with competitive cost.

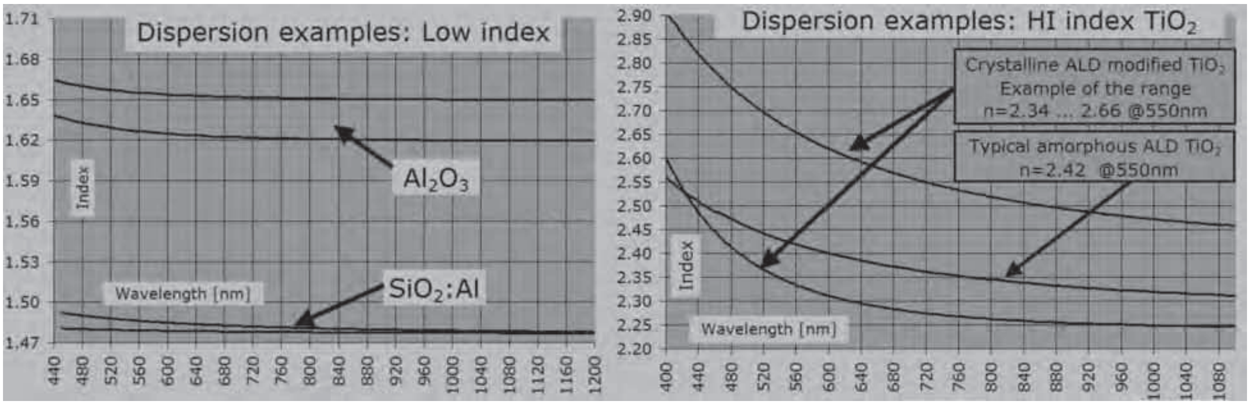

Figure 6: Dispersion ranges of typical optical ALD materials. Deposition temperature, precursors and possible nanoscale modifications are main sources for variations.

COMMENTS FOR PROCESS DEVELOPMENT

ALD is self purifying in the sense that precursor contaminants need to evaporate and chemically attach on the deposited surface to cause troubles. Typically 98...99% purity of the precursor is enough. If the product is developed using expensive ultrapure precursors, it is difficult to reduce purity when the production is started. Usually, it is better to start project with low purity precursors.

Small single wafer tool results can be dangerously misleading. ALD processes can include uniformity variations due to several reasons. Before making business decisions based on results from small wafers, the results should be verified at least in the flow direction. 300 mm is quite safe distance. ALD is very repeatable, but growth requires that precursors reach the surface. High aspect ratio trenches may need long exposure and purge times. Flow design of the reactor is important to get optimum exposure and to avoid long dosing times and lost precursor. For a flat surface cycle times should be below 3-5 sec. Fastest cycle times have been on the range of 0.2 … 0.3 sec.

Optical films need small tolerances. Although ALD growth is repeatable, it does not mean that the rate is same on all surfaces consisting of different materials. Especially crystalline materials tend to cause variations. Usually the filter process setup is somewhat iterative procedure with a few initial thinner filter depositions to get the precise deposition rates. Effects are not large, but need to be taken into account when targeting $<\pm 2$ %.

CONFORMALITY RELATED APPLICATIONS

Double side coating of flat wafers is a standard method with the ALD. Thin wafers can be coated easily, because bending of the wafer (e.g. due to stress with PVD) is not a problem. Precise coatings on both surfaces of a tubular object is a feature not available with other technologies. It is possible to coat optical filters inside tubes or holes using ALD. Nanoscale objects like particles, nanowires, nanotubes can be coated conformally with optical films using ALD. Conformal coatings in trenches, for example to planarize the surface, are used in optical components [7]. Photonic Crystals (PC) offer interesting features and ALD is one of the few technologies capable of making coatings inside 3D structures [8]. It is even possible to create objects consisting of optical material, by first coating the sacrificial mold structure and then etching, burning or otherwise destroying the mold.

LIGHT GENERATION, PHOTOVOLTAICS AND OTHER ELCTRO-OPTICAL APPLICATIONS

The classical ALD application is Thin Film Electroluminescent (TFEL) display from the Planar Systems Inc. [2]. Light is generated in the Mn doped ZnS phosphor layer. It is the most reliable display available, thanks to the solid state structure enabled by artificial insulator material made using Al_2O_3 and TiO_2 [9]. Photovoltaics applications have several active ALD areas related to optics and light in addition to barrier and passivation. Transparent and/or flexible electronics are one possible future ALD application area, having active R&D work ongoing.

DECORATIVE, BARRIER AND DOPING APPLICATIONS

The 3D coating feature makes ALD attractive for decorative coatings, although reaching the cost target can be demanding. nSILVER® [3] antitarnish film for silver combines optical and barrier requirements. It reduces the logistic costs (the need to polish silver in shops) of jewelry producers and mints. A large amount of possible ALD dopants are known, rare-earth elements included. Compared to PVD, ALD offers even wider doping possibilities with full freedom to vary doping profiles and materials during the film deposition. For example, erbium doping has been interestingly used in a wide range of emitting devices, thin film wave guide amplifiers and fiber preforms [10].

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