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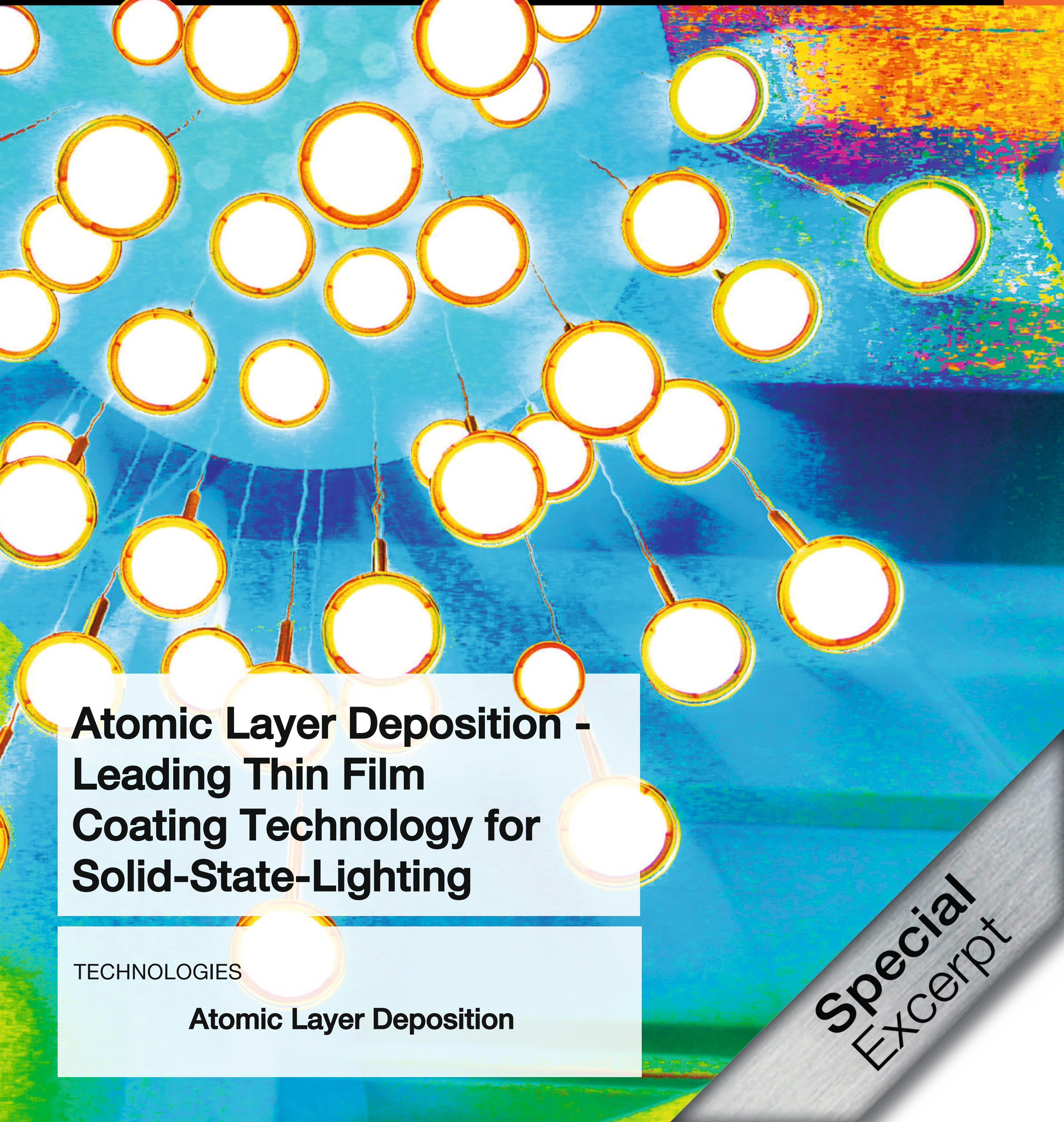

Atomic Layer Deposition - Leading Thin Film Coating Technology for Solid-State-Lighting

TECHNOLOGIES

Atomic Layer Deposition

Special Excerpt

Atomic Layer Deposition – Leading Thin Film Coating Technology for Solid State Lighting

Atomic Layer Deposition was invented in the 70's as a way of depositing conformal phosphor layers for electroluminescent displays. In the new millennium, it became a key enabler of microelectronic devices and is now an industry mainstay for DRAM, MEMS and NAND devices. Additionally, ALD offers many advantages for the production of display devices – LEDs, micro-LEDs and organic-LEDs. Picosun Group is a leader in applying ALD in the field of Optoelectronics and Picosun's Marketing Manager, Minna Toivola D.Sc.(Tech), will introduce this interesting technology, explain how it works, show its opportunities and applications and demonstrate its advantages over other coating technologies for similar applications.

Since LEDs were introduced to large-scale commercial use in the 1990's and early 2000's, they have revolutionized lighting and become a ubiquitous technology everywhere we go. From household lightbulbs, flashlights and mobile device displays to car lamps, TVs and large outdoor video screens, it is hard to imagine a world without LEDs.

Despite the obvious benefits, there is still room for improvement in LED brightness, efficiency and manufacturing costs, especially in demanding large volume, high power applications such as street lighting. LED chips and LED phosphors are also moisture-sensitive and small LEDs can be sensitive to high temperatures. These same attributes apply also and especially for emerging solid-state lighting (SSL) devices such as micro- and mini-LEDs, as well as OLEDs. A thin film coating technology called Atomic Layer Deposition (ALD) offers various solutions to the challenges in conventional LED, mini/micro-LED and OLED manufacturing. This article gives an overview of ALD, how it differs from other thin film coating methods, and what it can offer to SSL industries. The impact of implementing ALD to process flows of LED devices can be as significant as converting lighting from traditional to LED based, meaning increased energy efficiency, extended lifetime, cost savings and chip size reductions.

The Basics of ALD and Its Benefits Over Other Thin Film Coating Technologies

ALD is an advanced, sophisticated thin film coating method that, nowadays, is a mature, key enabling technology in all modern semiconductor device manufacturing. ALD was invented in Finland by Doctor of Technology, Tuomo Suntola, in 1974. Back then the technology was way ahead of its time and it took until the mid- 2000's when it was incorporated for the first time by Intel into transistor manufacturing. Since then, the utilization of ALD and the number of its applications have skyrocketed throughout the industrial field.

ALD belongs to the group of chemical vapor vacuum coating methods, but its film growth process differs from the more well-known techniques of the same family such as Chemical Vapor Deposition (CVD) or Physical Vapor Deposition (PVD). In ALD, the precursor chemicals from which the desired thin film material is formed are introduced to the reaction chamber in gaseous form as sequential pulses, separated by a period of purge with inert gas. In compound AB formation, precursor containing the A atoms reacts first with the object-to-be-coated by surface adsorption reaction, covering all available reaction sites. The A atoms stick to the surface and inert gas flushes off reaction by-products and excess precursor. Next, precursor containing the B atoms is introduced to the reaction chamber where it, in turn, reacts with the A atoms on the surface, forming the first layer of compound AB. Again, inert gas flushes the reaction chamber and the first ALD cycle is completed. These cycles are repeated till the desired film thickness is achieved and, as the thicknesses of individual atomic/molecular layers of the compounds are well-known, the total film thickness can be controlled with digital repeatability and accuracy (**Figure** 2). The typical ALD film thicknesses vary from a single atom layer to a few tens or hundreds nanometers.

Due to this self-limiting, surface-controlled film growth mechanism, ALD has various benefits over other thin film coating technologies, such as superior uniformity down to sub-nanometer levels and unmatched conformality even over nanoscale surface details such as deep trenches, voids, cavities and high steps (**Figure** 3).

In other methods such as CVD or PVD, the precursors are pulsed to the reaction chamber at the same time. This means that they react with each other already before hitting the surface, forming relatively thick films which are not uniform, cannot reach for example the insides of high aspect ratio trenches, and often contain mi-

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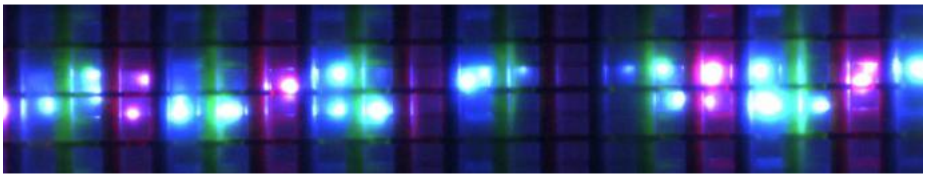

Figure 1: Micro-LEDs (image credit Picosun customer, Prof. Hao-Chung Kuo, NCTU Taiwan)

croscale cracks and pinholes. As ALD films grow "up" from the surface atomic layer by atomic layer, they are inherently dense, pinhole- and crack-free and their composition can be tailored down to atomic level. This makes it possible to create, in addition to single material layers, a plethora of mixed, doped and graded films, film stacks and nanolaminates. This allows endless opportunities for surface modification and functionalization with completely new electrical, optical or physical properties (**Figure** 4).

The list of materials that can be deposited with ALD is wide, the most typical being oxides, nitrides, sulfides, fluorides and metals (even noble metals and platinum-group metals can be deposited). Some of the most often used ALD materials, especially in semiconductor industries, are Al_2O_3, TiO_2, SiO_2, HfO_2, Ta_2O_5, ZrO_2, TiN and AlN.

ALD process temperatures are moderate, typically between 100–400 °C, which makes the method suitable also for temperature-sensitive substrates and devices. Using special techniques such as plasma-enhanced ALD (PEALD), some processes can be run even at close to room temperature. ALD does not need high vacuum, typically the processes take place at 1–10 hPa.

In ALD, film growth is slower compared to e.g. PVD or CVD, but the film quality compensates this. With ALD, the desired surface functionality can be obtained with much thinner films than in PVD or CVD, which also saves precursor materials and costs. For example, in barrier applications, ALD film can result in over ten times better barrier performance with one tenth of a barrier thickness compared with the same material deposited with plasma-enhanced CVD (PECVD) or PVD. Modern, industrial scale, fully automated batch ALD reactors can accommodate large numbers of substrates per run, which further diminishes manufacturing costs and allows fast, high volume production. As ALD is already a production-proven, routine method in other wafer-based semiconductor industries, it is easy to integrate to LED manufacturing as well (**Figure** 5).

ALD in Conventional LED Manufacturing

In conventional LEDs, the main applications of ALD relate to improving the LEDs' light extraction efficiency and the device lifetime and reliability. In these industries, ALD is already used in high volume manufacturing by several leading players.

Passivation Layers

ALD passivation layer on the LED surface "blocks" traps and defects which could cause leakage/parasitic currents. This improves light emission intensity. Superior performance and extremely low leakage current was achieved with Al_2O_3/SiO_2 ALD stack coating, compared to single layer SiO_2 deposited with PECVD method [1]. Both ALD Al_2O_3 and SiO_2 have near zero

Figure 2: The principle of ALD film formation (image credit Picosun)

absorbance on visible light wavelengths which makes them especially suitable for surface passivation of lighting devices.

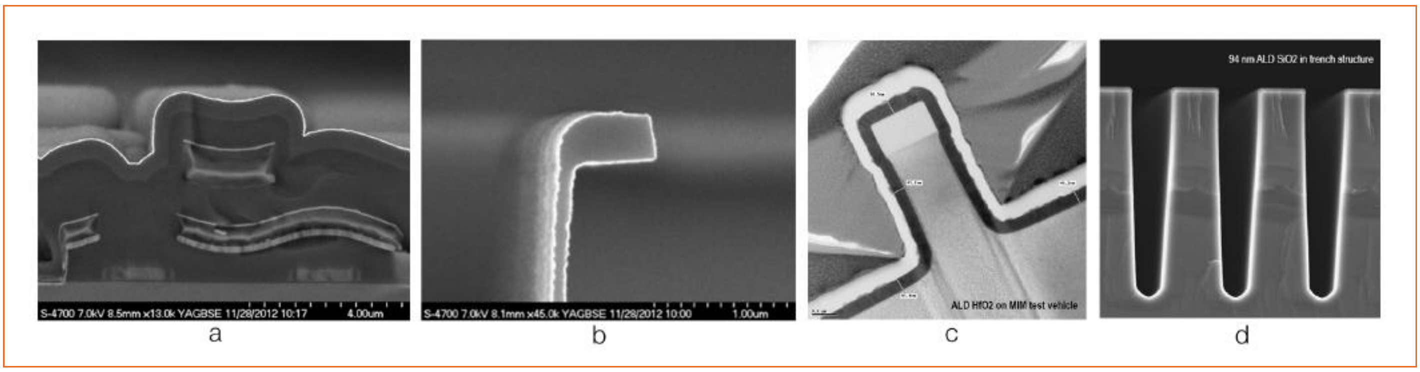

Figure 3: Examples of ALD films' excellent uniformity and conformality. SEM-micrographs a) and b): Conductive ALD layers on and inside MEMS (microelectromechanical system) structures (image credit Picosun customer Fraunhofer IMS, Germany); c) 45 nm ALD HfO_2 inside MIM (metal-insulator-metal) capacitor test structure (image credit Picosun); d) 94 nm ALD SiO_2 inside trench structure (images credit Picosun)

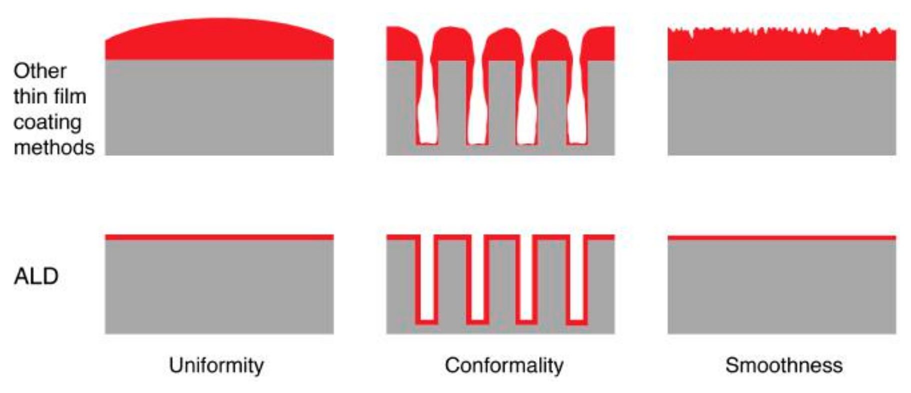

Figure 4: Benefits of ALD over other thin film coating methods (image credit Picosun)

Moisture Barrier Layers

ALD coating also works as a barrier layer against moisture and gases, thus improving LED lifetime and reliability. ALD ensures hermetic encapsulation against ambient conditions, with superior barrier performance compared to other methods. Typically, nanolaminates of various ALD oxides are used in this application. Employing a nanolaminate instead of a single-material layer gives extra protection by creating tortuous path for water molecule diffusion pathways caused e.g. by grain boundaries in the film.

Below two examples of Picosun's ALD films as moisture barriers:

Example 1:

- Reference: 330 nm PECVD SiO_2: water vapor transmission rate (WVTR) $\approx 10^{-3}$ g/m^2/d.
- Picosun's 40 nm ALD barrier layer: WVTR = 2×10^{-5} g/m^2/d (customer data, limited by measurement time).

⇒ ALD film exhibits 100× higher performance at 1/8 film thickness [2].

Example 2:

- Reference: PEN/PET: WVTR $\approx 10^{-1}$ g/m^2/d.
- Picosun's ALD nanolaminate: WVTR = $4 \ldots 5 \times 10^{-5}$ g/m^2/d (customer data, limited by time and device glue life, not ALD film barrier properties).

⇒ ALD film exhibits 2000× higher performance compared to reference material [2].

ALD is an ideal method also for protecting moisture-sensitive LED phosphors against ambient conditions. ALD forms uniform, conformal, continuous and crack-free coating on each phosphor particle individually, without agglomeration or sintering. Ultra-thin ALD films are practically massless and dimensionless so they keep the particle size, weight and surface area close to original. ALD films do not decrease the amount of light emitted by the phosphors, or their quantum efficiency. ALD films can be deposited on both hydrophilic and hydrophobic surfaces, ceramic, metallic, and organic particles with sizes down to sub-micron range. As a gentle, gas-phase coating method with moderate process temperatures, ALD eliminates the risks for microscopic surface damage to the coated particles and makes the method suitable also for sensitive materials. Below third example of ALD's superiority as moisture barrier encapsulant in LED applications:

Example 3:

- Coated surface: LED phosphor powder, immediately unstable in air.
- Coating each grain of phosphor with a perfectly conformal ALD film of less than 40 nm thickness hermetically seals the grains' surface.

⇒ ALD-coated phosphor has lifetime over 1400 hrs at 100% RH / 100 °C [2].

Transparent Conductive Oxide Layers

Transparent conductive oxide (TCO) layers are applied as electrodes/current collectors on LEDs to distribute and deliver the electrical carriers into the structure. Typical TCO material in LED applications is indium-doped tin oxide (ITO), but due to the scarcity of indium metal, alternatives have been widely investigated. Aluminum-doped zinc oxide (AZO), which has high transmittance over visible wavelengths and which resistivity can be optimized by tuning the aluminium content and process temperature, is one potential candidate. ALD-deposited TCO layers in general are especially ideal for novel LED architectures where nanoscale surface patterning such as nanorods, -spheres or -pyramids have been employed to enhance the light extraction efficiency.

Figure 5: PICOSUN® P-300BV, an example of an ALD reactor developed specifically for LED applications (images credit Picosun)

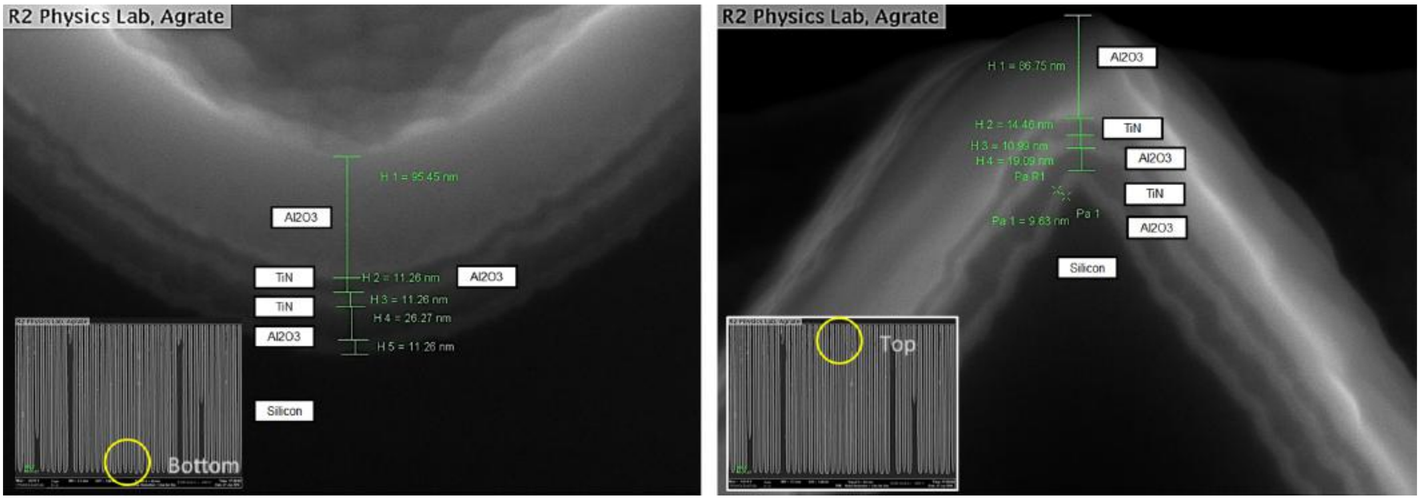

Figure 7: SEM-micrographs of highly conformal ALD Al_2O_3 – TiN – Al_2O_3 – TiN – Al_2O_3 nanolaminates in deep trench structures (images credit STMicroelectronics, Italy, in collaboration with Picosun in the EU-project "R2Power300")

Silver Mirror/Reflector Protection

Most LED designs employ thin silver film on the "bottom" of the LED stack to reflect back the light emitted towards the substrate. This improves the LED's brightness but the silver mirror is sensitive to tarnishing caused by moisture and chemical vapors. Also, especially under high electric fields, silver may start to diffuse to the neighbouring layers and thus degrade the LED performance. ALD thin film coating efficiently protects the silver from tarnishing and prevents silver diffusion.

ALD-coated LED reflectors have shown extreme durability even in high temperature acid vapor tests (HNO_3, 75 °C, 24 hours), due to the unmatched structural integrity and conformality of the ALD film [2]. Typical ALD materials used in this application are SiO_2, Al_2O_3, and their combinations. HfO_2 is also a potential candidate as it has excellent etch resistance even in extreme conditions.

Figure 6: Uncoated (left) vs ALD-coated silver mirror (right) aged four years at room temperature and moisture (image credit Picosun/Dr. Tero Pilvi, doctoral dissertation, University of Helsinki, 2008)

Optical Layers

Optical layers such as antireflection (AR) films and distributed Bragg reflectors (DBR) are often used in LEDs to improve light extraction efficiency [1]. ALD, with its superior uniformity, conformality, and the possibility to create atomic level tailored, multilayer film stacks with digitally repeatable layer thickness control down to sub-nanometer levels is an ideal method to manufacture optical coatings on non-planar samples and devices. ALD offers infinite possibilities to design optical stacks optimized for the desired wavelengths, just with varying the individual sub-layer materials and thicknesses. Some ALD films, for example AZO, can even combine two functions by acting both as the current collecting TCO layer and as the AR film (**Figure** 7).

Dielectric Insulation Layers

In semiconductor industries, especially transistor manufacturing, ALD has been used for years to deposit ultra-thin gate dielectric layers, thus promoting the constant miniaturization of the components. ALD's superior conformality and thinness can be utilized to deposit dielectric insulation for LEDs as well. For example, Al_2O_3/SiO_2 ALD dielectric reduces the thickness of the insulation layer and improves light extraction efficiency.

ALD's Specific Benefits for Mini- and Micro-LEDs

Mini- and micro-LEDs are new LED technologies that show significant potential as the enablers of future lighting and display solutions [3]. Micro-LEDs especially have excellent performance compared to other technologies such as liquid crystal or conventional LED displays, such as compact size, low power consumption, flexibility, fast response, ultra-high resolution, superior brightness and energy efficiency, and greater contrast and color saturation. Micro-LEDs are ideal for small displays in e.g. smartphones and smart watches, but high manufacturing costs and reliability issues have been the downsides of the technology this far.

Mini- and micro-LEDs are similar to the conventional LEDs when it comes to the operating principle and basic materials, but the manufacturing methods and structural details differ. Especially micro-LEDs are orders of magnitude smaller than conventional LEDs and they often employ microscopically patterned surfaces to maximize light output. Here, ALD shows again its beauty when ultra-thin functional or protective layers must be deposited evenly and conformally on these tiny surface details.

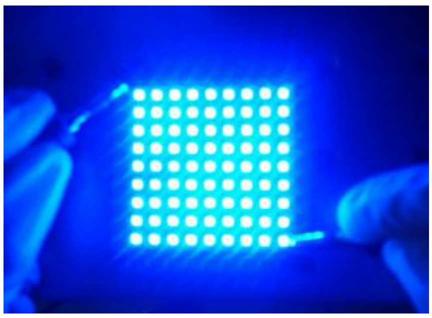

Figure 8: Flexible white mini-LED sheet (image credit Picosun customer, Prof. Hao-Chung Kuo, NCTU Taiwan) [4]

As the most of the ALD's applications in mini- and micro-LED manufacturing are analogous to those in conventional LEDs (passivation, moisture barriers, TCO films, optical layers, etc), this chapter highlights those uses where ALD has exceptional benefits just for these emerging LED technologies.

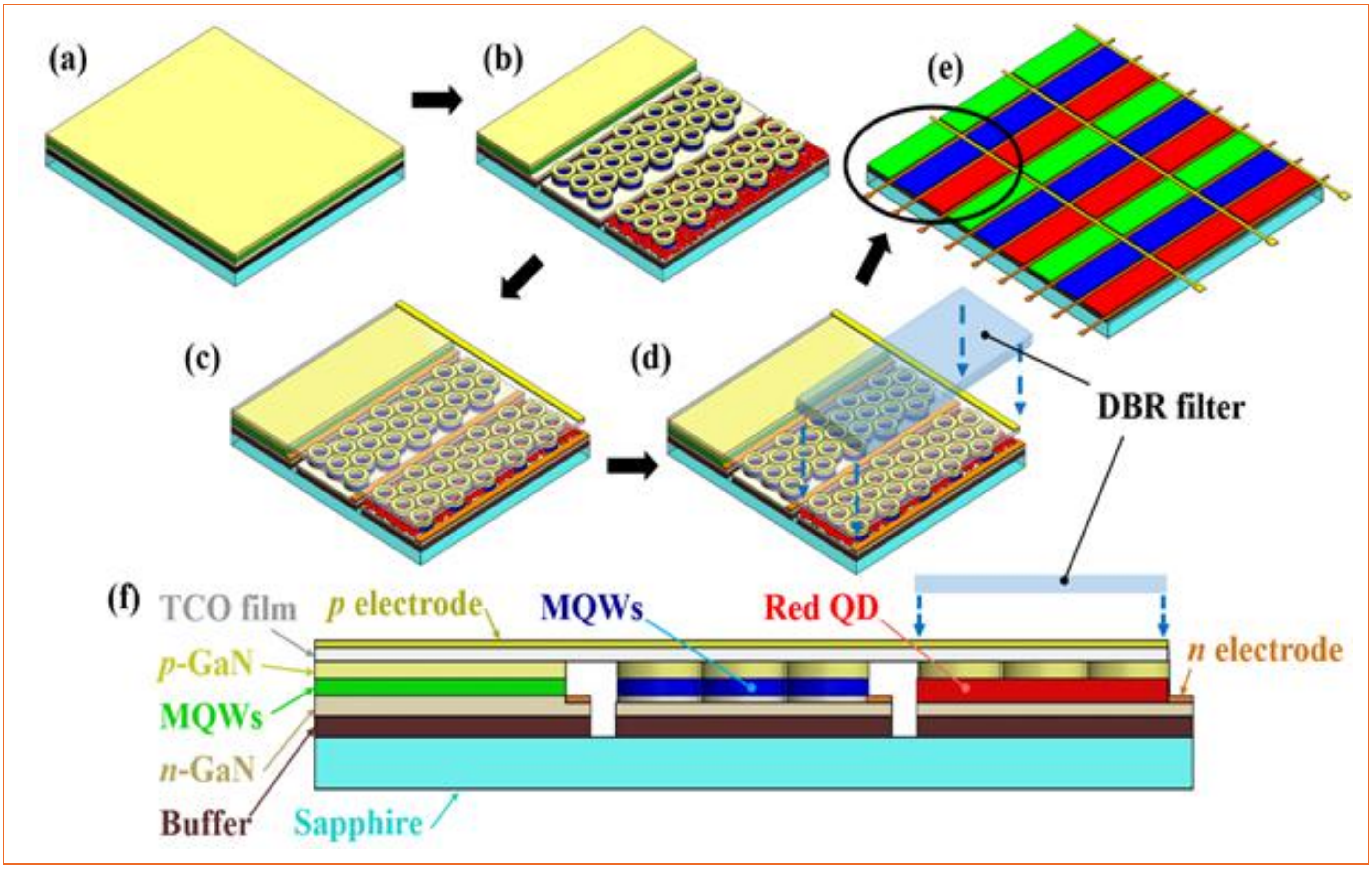

Figure 9: Manufacturing process of quantum dot nanoring micro-LEDs (image credit Picosun customer, Prof. Hao-Chung Kuo, NCTU Taiwan) [7]

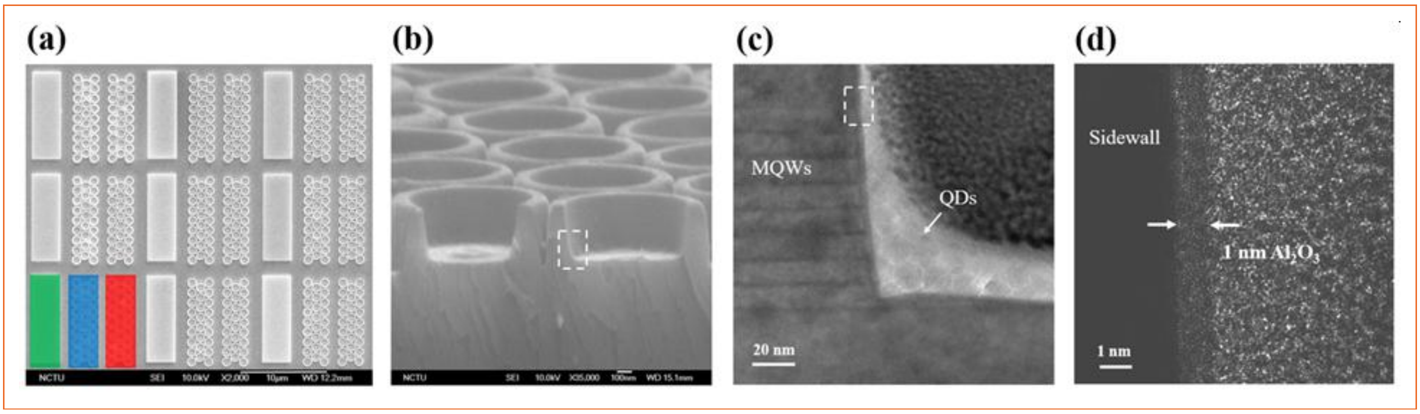

Figure 10: Quantum dot nanoring micro-LEDs: (a) SEM image of an RGB pixel array (top view); (b) SEM image of a nanoring micro-LED with 30° tilt angle; (c) TEM image of the contact area between multiple quantum wells and quantum dots; (d) TEM image of 1 nm Al_2O_3 deposited on the sidewall of a nanoring micro-LED with ALD (image credit Picosun customer, Prof. Hao-Chung Kuo, NCTU Taiwan) [7]

Sidewall Passivation and Light Confinement

Macroscopic, conventional LED chips are more or less "flat", but due to the shrinking dimensions, in micro-LEDs 3D geometrical aspects get highlighted. This means not only the phenomena occurring on the top of the LED matter, but those on the sides as well. Because of the minuscule dimensions and micropatterning, resulting in steep sidewalls, sharp angles and deep trenches with high aspect ratios, advanced surface treatment methods are called for.

Micro-LED manufacturing also utilizes flip-chip approach and chip-scale packaging, which makes sidewall protection even more important.

On all microscale devices, in general, surface passivation to eliminate traps and defects generated during the manufacturing process is needed when maximum performance and improved lifetime of the device are desired. In micro-LEDs especially, non-radiative recombination on sidewalls and subsequent loss of light intensity may be significant problem which must be solved.

A good passivation film must cover conformally all microscopic surface details and this is where traditional thin film deposition methods easily fail. ALD is able to form ultra-thin, conformal, uniform, reliable and pinhole-free passivation layer over the smallest nanoscale architectures of the micro-LED, while not interfering with the light output. Superior performance of ALD passivation, compared to PECVD, has been reported, where ALD resulted in lowest leakage currents and uniform light emission even for the smallest, only 20 µm × 20 µm micro-LEDs [5].

Another aspect related to the micro-LED sidewall, especially in chip-scale packaging, is light "leakage" through it. This can also be prevented with ALD by depositing thin reflecting layer, for example DBR stack made of alternating SiO_2/TiO_2 or Al_2O_3/TiO_2 films on the LED sides. This directs all light "out" from the top surface and improves notably the LED intensity.

ALD Passivation for Elimination of Manufacturing Damages

In micro-LEDs, especially novel architectures with sophisticated 3D details such as nanorings [6], surface damage caused by reactive ion etching may lead to notable decline of device performance. ALD surface passivation mends these damages, traps and defects, not only restoring the light intensity but boosting it to superior levels. At Picosun customer site, National Chiao Tung University (NCTU), Taiwan, light-emitting intensity of quantum dot nanoring micro-LEDs has been enhanced by 143.7% by using ALD passivation layers [7] (**Figure** 9, **Figure** 10).

ALD Applications for OLEDs

In OLEDs, the light-emitting layer is made of electrically active polymer materials. OLEDs generate soft and diffuse light over large area, they have excellent contrast ratio and bright colors, and they can be manufactured on lightweight, flexible substrates, but due to the organic core layer, their efficiency and lifetime are lower than those of other SSL devices. The organic, light-generating layer is extremely moisture-sensitive which is why hermetic encapsulation of the structure is essential for long operating life. ALD films' superior moisture barrier properties, as presented earlier in this article, make them a promising candidate to be utilized in OLED encapsulation. Ultra-thin, optically transparent ALD films are also well suitable for flexible substrates.

Naturally, other applications of ALD as presented in the previous chapters here are again valid for OLEDs as well: TCO layers, optical layers and passivation films. As ALD process temperatures are modest, and the method is gas-phased and gentle to the surface, it is very well suitable for plastic-based organic electronics such as OLEDs.

Summary and Conclusions

ALD is, by far, the most advanced and sophisticated thin film coating technology of today. Its key benefits over other methods – the films' superior conformality, uniformity, structural integrity and excellent barrier properties – combined with the modest process temperatures and surface-friendly film formation make it an ideal technique to manufacture functional and protective layers for LEDs. Especially for new technologies such as micro-LEDs, where manufacturers operate on micrometer or nanometer dimensions and totally new challenges emerge, ALD offers unrivaled possibilities to improve the device efficiency, light output, operational lifetime and reliability. ■

References

[1] Guo et. al., Optics Express, Vol. 21, No. 18, p. 21456 (2013)
[2] Picosun customer data
[3] Wu et. al., Applied Sciences, Vol. 8. p. 1557 (2018)
[4] Sher et. al., Optics Express, Vol. 23, No. 19, p. A1167 (2015)
[5] Wong et. al., Optics Express, Vol. 26, No. 16, p. 21324 (2018)
[6] Wang et. al., Scientific Reports 7:42962 (2017)
[7] Chen et. al., Photonics Research, Vol. 7 No. 4, p. 416 (2019)

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