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Atomic layer deposition: an efficient tool for corrosion protection

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Abstract

Atomic layer deposition (ALD) is now a widely implemented thin film growing method. It is currently used in industrial fabrication processes of microelectronics and luminescent display technologies. Since compact and conformal films can be grown with a perfect control of the thickness, ALD is envisioned in numerous other applications fields such as energy, sensing, biomaterials and photonics. Although few reports can be found on its application to corrosion protection, it has been shown that qualities of ALD can be highly beneficial to this field. After a brief review of the principle of ALD and the effect of the main parameters on the properties of the films, this report attempts to show the interest of this technique to mitigate corrosion. Various examples of successful uses of ALD to protect metallic and non-metallic surfaces in different fields are reviewed.

Keywords: Atomic layer deposition, Corrosion, Thin film

Abbreviations

AAO, anodic aluminum oxide; ALCVD, atomic layer chemical vapor deposition; ALD, atomic layer deposition; ALE, atomic layer etching or atomic layer epitaxy; APCVD, Atmospheric pressure chemical vapor deposition; CVD, chemical vapor deposition; DLC, diamond-like carbon; DRAM, dynamic random-access memory; ED, electrochemical deposition; EDS, energy-dispersive X-ray spectroscopy; GPC, growth per cycle; HAADF-STEM, high-angle annular dark field -scanning transmission electron microscope; IPCE, incident photon-to-photocurrent efficiency, MIM, metal insulator metal; OLED, organic light-emitting diode; PE-ALD, plasma-enhanced atomic layer deposition; PECVD: plasma-enhanced chemical vapor deposition; PLD, pulsed laser deposition; PLGA, poly(lactico-glycolic acid); PVD, physical vapor deposition; T_{ALD} , operating temperature; TDMAT, Tetrakis(dimethylamino)titanium; TMA, trimethylaluminium.

Introduction

Although it has been firstly reported between the 1960s and 1970s [1, 2], atomic layer deposition (ALD) has really emerged after 2000. Initially called atomic layer epitaxy (ALE) because it consisted in growing a crystalline layer on a monocrystalline substrate or atomic layer chemical vapor deposition (ALCVD) because it belongs to this family of depositions, ALD is now the most common name. It is now seen as a powerful deposition technique because it exhibits numerous advantages such as compact and pinhole free layers, accurate control of the thickness, fine tuning of the chemical composition and excellent step coverage. In addition, ALD is usually carried out at low temperature (25 to 400°C) and easily scaled-up (up to m²). It can thus be applied to various types of materials at diverse scales. ALD is, however, slow as compared to other vapor phase techniques

(e. g. CVD, PVD, and PLD) or solution methods (e. g. sol-gel, spin coating, and ED). It is therefore, not yet appropriated to achieve thick layers (> 100 nm). The cost of precursors and the difficulties to grow all types of pure metallic layers limit also its integration in industrial processes. These drawbacks are gradually being eliminated thanks to intense efforts currently provided by the community. For instance, spatial-ALD and other sister techniques have considerably shortened the process duration [3, 4].

Due to the evident benefits, ALD is now studied in view of numerous and various applications. At present, it is applied in microelectronics for the fabrication of DRAM, MIM capacitors and high-*K* metal gates transistors or used during the device production processes to grow spacers, masking layers or interconnects [5, 6]. It is implemented as well in OLEDs encapsulation [7, 8] and it is envisioned in many other fields: energy storage and production (photovoltaics, batteries, fuel cells, thermoelectric, catalysis) [9–12], sensors [13, 14], filtration membranes [15, 16], biomaterials [17] and corrosion protection [18]. Surprisingly, the matter does not appear among the topmost investigated fields. However, when looking in details to other domains, it comes into sight that surface protection is often the targeted property of the film. Though few review on the subject can be found in literature (see e. g. Ref. [19, 20]).

The present article contributes therefore to account for the use of ALD in the field of corrosion mitigation. The principle of this deposition technique is briefly reported in the first section. Then, the expected advantages and limitations of those films for such objective are described. In the following, a large part of this paper is devoted to illustrations of the beneficial uses of ALD against corrosion of metallic and non-metallic surfaces. Note that it is not focused exclusively on the avoidance of pure corrosion processes but it describes more generally the surface protection against external alterations. Finally, some large-scale current applications will be presented before some

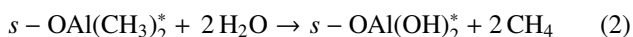
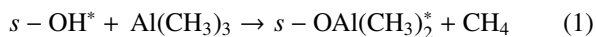
concluding remarks.

Atomic layer deposition

Principle of ALD

The section is not intended to describe in details the principle of ALD but it relates the basics of the method. For comprehensive descriptions, in-depth reviews can be found in literature (see e. g. Refs [21–23]). ALD is a deposition process that usually takes place in vapor phase but it has also been efficiently carried out in liquid [24]. It is a chemical, sequential, self-limited, surface process that requests an activation energy. The principle is schematically described in Figure 1 for the growth of Al_2O_3 . It starts by injecting the first precursor, a molecule containing the metal (here TMA), that chemically reacts with the surface (Figure 1a). Byproducts and excess of reactants are then pumped away and an inert gas (N_2 or Ar) is flowed to purge the chamber (Figure 1b). In the ideal case, the surface is next covered by a monolayer. The following surface reaction occurs when the second precursor (here H_2O) is injected and reacts with the chemisorbed molecules. The final product is then obtained (Figure 1c). Similarly to (b), the excess of water and the byproducts are evacuated by pumping and purging the reactor (Figure 1d). The targeted monolayer should be grown at this final step of so-called ALD cycle. By repeating this cycle (i. e. steps a, b, c, and d), one can grow the desired thickness with a high accuracy. Since the growth is cyclic, the deposition rate is not given according to the thickness per unit time as usually for other techniques (e. g. PVD, CVD or PLD) but rather according to the thickness achieved per each cycle: growth per cycle or GPC.

As mentioned above, ALD consists in chemical reactions occurring at the surface. It is therefore different from PVD, based on weak interactions (physisorption), that can lead to localized deposit accumulations. During ALD, amassing is not possible because when a precursor reacts at the surface no further chemisorption can proceed (Figure 1a). In opposition to CVD, no direct reaction between the two precursors takes place neither in the vapor phase nor at the surface since they are injected successively and a pumping/purging step separates those stages to avoid any contact. To grow the final film, two sequential surface reactions must proceed. In the case of Al_2O_3 , the successive reactions are described by Eqs. 1 and 2:



The star subscripts indicate a surface species and s stands for the surface. This sequential aspect of ALD also lead to a self-limited process. It gives a perfect control of the thickness anywhere on the substrates. If the recipe let sufficient time to the precursors to diffuse around the surface to find a free site, a perfect conformality is achieved. Trivially, this process can be compared to a car driver who wants to stop in a parking lot. When a car occupies a spot no additional vehicle can park there. By considering that cars move at the same speed (i. e. diffusion

rate for molecules), if the drivers have enough time to search for a free place, each parking lot aisle will be filled evenly. The second precursor can be compared to a caravan that can only be coupled to a parked car and not left directly on a free space.

The surface reactions involved in ALD request an activation energy. It can be provided by heating the sample (thermal ALD that is commonly named ALD) or using a plasma-assistance. In this latter case, the process, called plasma-enhanced atomic layer deposition (PE-ALD), generates highly reactive species (radicals, ions, electrons). In some cases, it allows for lower operating temperatures (T_{ALD}) and PE-ALD can lead to layers exhibiting better or different properties as compared to thermal ALD. Since the actives species exhibit a short lifetime, high-aspect ratio step-covering is more challenging.

Key parameters

The processes involved in ALD are activated reactions. Energy is therefore required and, thus, operating temperature critically matters. Figure 2 shows evolutions of GPC according to T_{ALD} . Under optimized conditions, a single layer is grown per ALD cycle, i. e. GPC is equal to one monolayer represented by the green horizontal dotted line on the plot. This is the ideal case that happens only in very seldom cases. The most important is that a single cycle does not lead to more than a monolayer. This self-limiting nature of the process prevents from local material accumulation and drives to conformal deposition. On Figure 2, when $T_{\text{ALD}} < T_{\text{min}}$, if GPC increases, it reveals a lack of energy and/or that the reaction kinetics is longer than the ALD cycle. The system requires more energy or longer steps to reach the optimized GPC. Conversely, if GPC decreases, condensation of the precursors on the surface and ligands are trapped in the layer. Again, T_{ALD} should be elevated to avoid such uncontrolled deposition. When $T_{\text{ALD}} > T_{\text{max}}$, GPC increases if precursors are decomposed at the surface and GPC decreases if they desorb before reacting due to lower sticking coefficient at such temperature. Note that T_{ALD} can also have an effect on the crystalline structure of the film. In this case, it is not correlated to the ALD process but to the thermodynamics of the grown material itself.

The reactivity and physical properties of the precursors are also determining. Except some specific recipes [25], ALD processes rely on two precursors that can be separated in two families according to whether they contain metal or not. Metal-containing molecules are liquid or solid at room temperature while the metal-free reactants are mainly gaseous (e. g. O_2 , O_3 , NH_3 , H_2S ...) except water. The precursors must be compatible with the three steps they undergo during the process: storing, travelling and reacting. First, they must be stable in their containers (called canisters) which can be heated to increase their saturation vapor pressure. Their volatility is decisive because when the high-speed valves are opened, part of the vapor in equilibrium with the solid or liquid phase stored in the canister travels through the equipment pipes to reach the reactor. They should react only at the surface of the sample in the chamber. An appropriate selection of chemicals is therefore requested because it is difficult for a metal-containing molecule

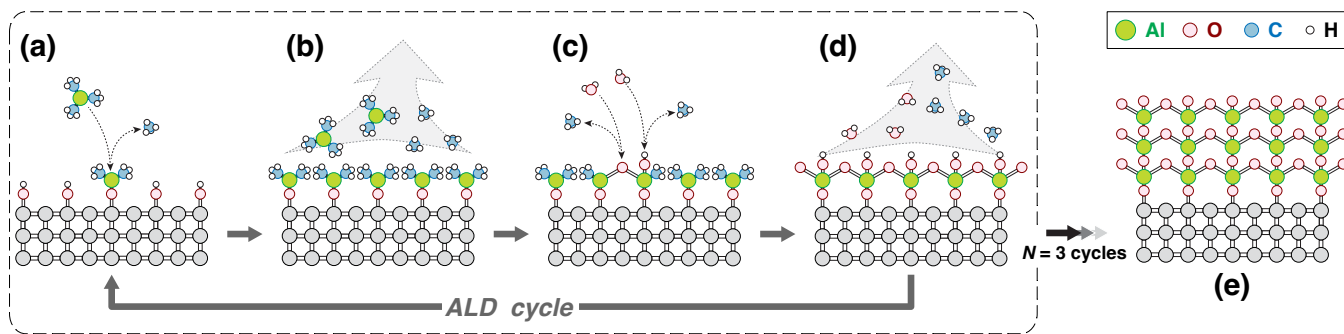


Figure 1: Principle of ALD illustrated by the growth of Al_2O_3 from trimethylaluminium (TMA) and water. (a) Pulse of TMA and chemisorption at the surface. (b) Purge and pumping of the by-products and TMA excess. (c) Pulse of H_2O and reaction with the remaining ligands of the TMA. (d) Purge and pumping of the by-products and H_2O excess. (e) Surface after 3 ideal cycles. The so-called ALD cycle corresponds to the steps (a,b,c,d,e) surrounded by the dashed line. The atom nature is indicated on the drawing.

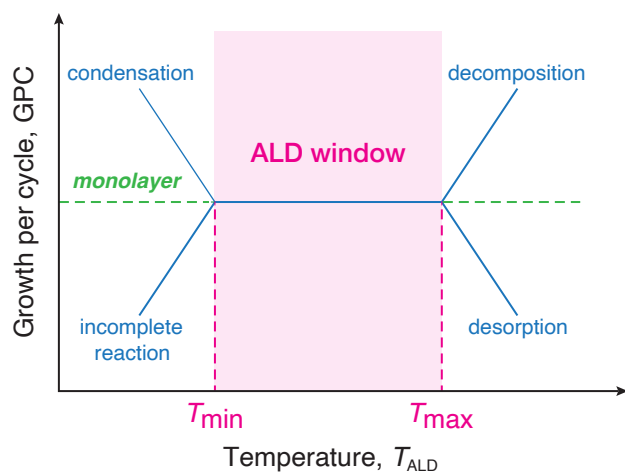


Figure 2: Schematic evolution of GPC with sample temperature. The pink area between T_{\min} and T_{\max} corresponds to the so-called “ALD window”.

to fulfill all the requirements. A large part of the field is therefore dedicated to the study of possible reactants. Among them, halides were firstly used but now the research is more focused on organometallics such as alkoxides, β -diketonates, alkylamides or amidinates (see e. g. Refs. [26, 27] for reviews). Halides are, in fact, deleterious for the pumping system since corrosive products such as HCl can be generated. They can also back-react with and be trapped in the growing layers, resulting in premature part failure.

Pressure is also a key parameter since it determines the number of active molecules in the chamber and can therefore drives the deposition rate. It is, however, often not controlled in numerous ALD tools because they are not frequently equipped with throttle valves.

As mentioned in the previous section, ALD can be thermally- or plasma-activated. In many systems, both approaches are possible. The selection depends on the available equipment, the expected properties and the substrate (topography or temperature sensitivity) on which the deposition is to be made. In the case

of non-planar surfaces, the thermal method is often preferred, but recent examples show that it is also possible to achieve conformal films on surfaces with relative high-aspect ratio [28–30]. In the car metaphor, it means the driver has more time to find a parking spot.

Finally, the ALD cycle timing is, obviously, a parameter to optimize to control the process. Pulse and purge phases should lead to the saturation of the available reactive sites. On high-aspect ratio surfaces, one can insert an additional stage between those steps. This so-called “exposure” stage consists of isolating the pumping from the reactor in order to let enough time to the precursors to diffuse within the substrate tortuosities as shown in Figure 3 [31–33].

Advantages and limitations of ALD for corrosion protection

Depending on the composition and geometry of a part, different corrosion protection methods apply. Prevention includes the following methods [34]:

- prevention through the proper form of the parts
- prevention by appropriate selection of materials
- protection by coatings
- protection by inhibitors
- electrochemical protection.

ALD is, obviously a coating method. The protection by coating can be achieved by forming a metallic film by electrodeposition, electroless plating, immersion, PVD, CVD or spray coating. Non-metallic inorganic layers can be the result of a conversion carried out by anodizing, phosphating or chromating the initial surface but it can also be the deposition of an external material such as enamel, ceramic or cement. Finally, an organic film such as painting, varnish or polymer can be applied to avoid contact with the aggressive medium. Except when galvanic coupling is involved in the protection process, coatings must be adhesive and fully cover the piece. ALD meets these requirements since the deposited molecules are chemically bonded to the substrate and also because the pinhole-free layers penetrate any tiny porosities with a perfect control of the thickness. Electrochemical-based techniques can also be

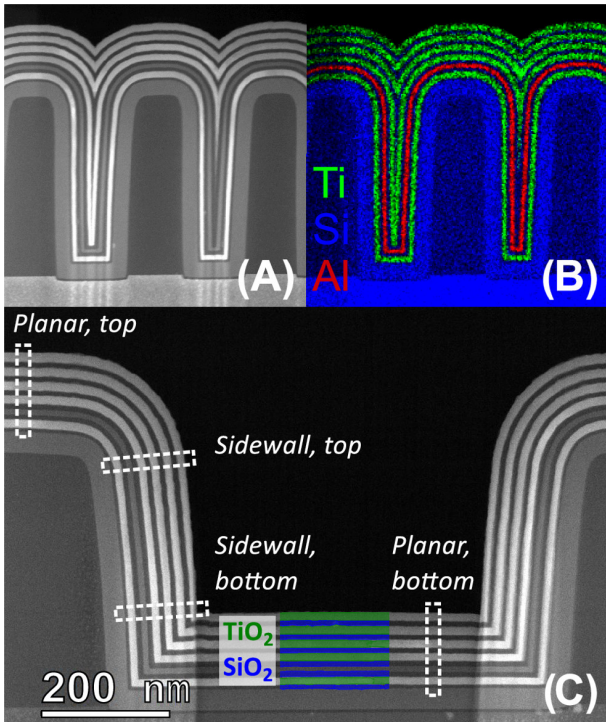


Figure 3: Cross-sectional HAADF-STEM images (A, C) and an EDS map (B) of a stack of alternated TiO_2 and SiO_2 layers and a single layer of Al_2O_3 , deposited on vertical trenches with different initial aspect ratios of approximately 4.3 (A, left), 5.6 (A, right), and 0.6 (C). All layers are grown at 200°C using plasma steps of 12 s. From reference [29]

highly conformal but they requires conductive or electrochemically active substrates while ALD is basically compatible with any materials. It is, however, not the perfect method. It also suffers from a low deposition rate that limits its application to thin layers (around 100 nm), some processes are not compatible with thermally sensitive substrates and the materials that can be grown is still limited. Up to now many recipes are available for oxides, nitrides and sulfides whereas deposition of metallic films is yet trickier. Despite these limitations, the numerous oxides and nitrides yet available constitute a wide range of protective films that are particularly interesting since they can be used as passivating layers.

With the development of molecular layer deposition (MLD) [35], it is now also possible to envision the growth of polymers or hybrid materials such as alucone (combination of alumina and organic compounds) [36]. In this ALD-derived technique, that follows the same principle, polymers or organic containing layers are grown sequentially. For instance, alucone is grown by replacing H_2O , as second precursor, with glycerol in the recipe describes in Eq. 2 [37]. MLD opens very interesting possibilities.

Although ALD exhibits significant benefits, it is often considered only for high added-values fabrication processes. Thus, anti-corrosion films have yet been reported in fundamental investigations that show the potential of the technique. More recently studies related to concrete application fields such as medical devices, plasmonic, sensing, astronomy and photoelectrol-

ysis are published. It is also used to avoid degradation or aging of air-sensitive devices such as OLEDs [38, 39] or perovskite-based photovoltaic cells [40]. This is not described, here, because it is not properly corrosion phenomena and it falls out of the scope of the present review.

Corrosion of metallic surfaces

General use of ALD

In 1999, Finnish groups have explored the use of protective films of Al_2O_3 , TiO_2 , Ta_2O_5 and $\text{TiO}_2/\text{Al}_2\text{O}_3$ multilayers on stainless steel. Though this alloy exhibits intrinsically a very good resistance against corrosion, this first article sets the basis for the use of the technique to prevent corrosion [18]. Since then, ALD has been applied to protect other metals and alloys such as steel, Al, Ag, Cu and Mg using mainly thin oxide layers but nitrides or multilayers, also know as nanolaminates, have been explored.

Resistance of stainless steel is significantly improved by depositing Ta_2O_5 or Al_2O_3 [41] as well as $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayers [42]. Such nanolaminates are interesting because they combine the properties of the different constituting materials while keeping a very limited total thickness. It has also been demonstrated that PE-ALD could lead to ultra-thin protective Al_2O_3 films (around 10 nm) on Al and Cr-steel exhibiting efficient corrosion suppressing properties as well as a good adhesion [43]. This was possibly attributed to a specific interlayer formed in PE-ALD (the effect of the interlayer is considered below in the section). Note that ALD is intuitively seen as a technique leading to adhesive coatings since a chemical bond is established between the substrate and the deposit. Nevertheless, one has to consider the usual parameters (e.g. thickness, stress, strain, surface energy...) because adhesion will not be optimal by this deposition method. Similarly, Al_2O_3 [44–46] and TiO_2 [47] films have proven to be effective in preserving regular steel. Although aluminum is protected by its native oxide layer, it may be necessary to further increase its stability. ALD of SiO_2 constitutes an efficient chemical corrosion protection of Al mirrors [48].

Optical components are often made of silver that is prone to tarnish. ALD of $\text{Al}_2\text{O}_3/\text{TiO}_2$ on Ag surfaces exhibits almost no porosity ($\approx 0.003\%$) as compared to the corresponding PVD process ($\approx 1\%$). A much better protection is thus obtained [49]. This is interesting for fabrication of sustainable optical components and it is highly valuable for observatories because they need to develop high performance and durable Ag-based mirror coatings for telescopes and instruments. ALD processes are thus implemented at large-scale to protect 0.9 m wide Ag mirrors using Al_2O_3 thin films [50]. It is shown that preservative coatings depend not only on the materials used but also on the deposition parameters such as T_{ALD} or activation type because this latter can modify the intermediate layers [51–53].

In many applications, copper migration or oxidation are frequent problems. Many routes have been used to overcome such degradation with varying degrees of success. ALD has recently emerged to conformally cover and/or passivate Cu surfaces.

Thin and ultra-thin Al_2O_3 layers have, of course, been grown for this purpose [54, 55]. In addition to the standard DC- and AC-electrochemical testing methods [56] that can be coupled to in depth surface analysis [57], such protective layers have been assessed by comparing of Cu electroplating, Cu wet etching and linear sweep voltammetry as techniques to probe the porosity of alumina [58]. Similarly to metals cited above, the role of surface preparation and interlayer effects on the final anti-corrosive behavior have been investigated [54, 59]. Other oxides such as TiO_2 , ZnO , HfO_2 , SiO_2 and ZrO_2 have also been investigated [60, 61] but it appears that Al_2O_3 and TiO_2 exhibit the best ability to protect Cu. Therefore, Al_2O_3 is often combined as bilayers to TiO_2 or sometimes SiO_2 as highly efficient barrier against corrosion [62, 61, 63]. Note that despite its intrinsic chemical stability, TiO_2 is not always as good as Al_2O_3 because of nucleation difficulties on Cu [63].

Magnesium alloys have been widely studied as materials for temporary implants, but their use has been limited by their corrosion rate. Recently, coatings have been proven to provide an effective barrier. TiO_2 , ZrO_2 and HfO_2 layers deposited on AZ31 Mg alloy have been assessed by in vitro electrochemical investigations. They have shown interesting stability and resistance against stress corrosion cracking combined with a good cytocompatibility [64, 65]. HfO_2 exhibits the best protective properties as well as the best compatibility [65]. ZrO_2 layers show also a very good behavior. They have been grown on AZ31 alloy by ALD in combination with subsequent PLGA grafting. PLGA is indeed biocompatible, biodegradable, and non-toxic and it should improve the action of the ceramic film. The synergetic effect is observed but strategy needs some improvement to avoid galvanic coupling [66].

As mentioned above, the interfacial layer can be decisive for the anti-corrosive properties. This has been initially demonstrated for ALD and PE-ALD of Al_2O_3 on steel [67]. The highest stability were reached with layers deposited on a clean uniform interfacial oxide, re-grown in between the plasma pre-treatment and the coating deposition. Similar findings were reported on Cu by removing the aged native oxide layer by H_3PO_4 treatment prior to ALD [54]. Again, the fresh re-grown oxide gives the best stability.

Combination of ALD with other techniques

It has been shown above that ALD is a powerful tool to grow compact protective layers. Corrosion mitigation by coating is, however, possible for a longtime, using other deposition methods. Combining ALD, which is a rather efficient technique to form ultra-thin films, with methods to reach higher thicknesses in a much shorter time may be a valuable strategy.

PVD coatings are known for their anti-corrosion and wear resistance properties. The films are often in the 1-10 μm range and they exhibit generally a non-negligible roughness. In 2009, it has been reported that TiAlN/TiN and TiCN coatings grown on steel by reactive arc evaporation in N_2 or C_2H_2 residual atmospheres had no resistance against corrosion. But when an additional thin Al_2O_3 film is deposited by ALD, it seals the PVD coating and the as-formed composite layer exhibits a longtime resistance against corrosion [69]. Similarly PVD hard coatings

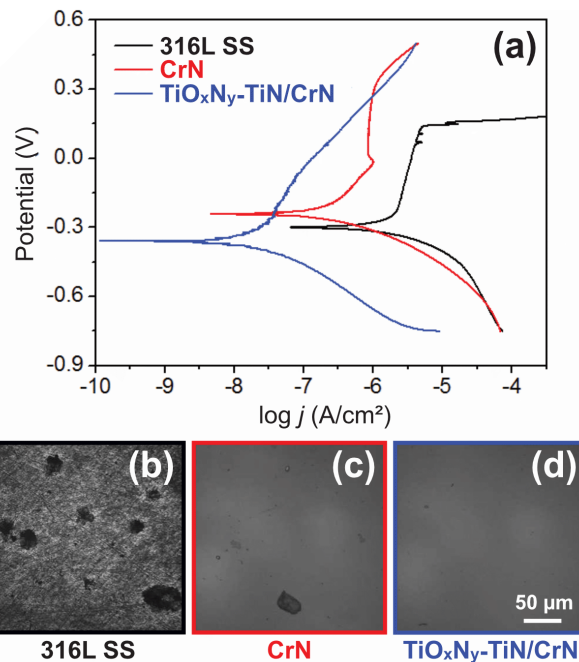


Figure 4: (a) Tafel curves of coated and uncoated steel substrates in 3.5 wt.% NaCl solution. Optical images of samples after the polarization tests: (b) bare 316L substrate, (c) CrN, and (d) CrN sealed with $\text{TiO}_x\text{N}_y\text{-TiN}$. Adapted from reference [68].

have been associated to a subsequent oxide or nitride deposition by ALD. DLC and CrN were sealed by $\text{Al}_2\text{O}_3/\text{Ta}_2\text{O}_5$ nanolaminate [70]. Conversely, Wan et al. have applied the reverse strategy by growing an Al_2O_3 blocking interlayer inserted between two CrN PVD layers grown on stainless steel [71]. One can also deposit the same protective oxide using the two complementary methods. Hybrid PVD/ALD TiO_2 coating has been grown successfully to protect Al-Si-Cu alloy [72]. As shown on Figure 4, ALD $\text{TiO}_x\text{N}_y\text{-TiN}$ layers give a very good corrosion resistance to CrN film grown on 316L alloy [68]. ALD-coated surfaces exhibits a significantly lower current as compared to bare and PVD-covered (Figure 4a) and no pitting corrosion is observed on Figures 4b,c,d.

Al alloy passivation by anodic aluminum oxidation (AAO) is well-spread protection approach. Such layers are porous and must be sealed to prevent corrosive substances such as chloride ions reaching the metal surface [73]. Two common solutions to this problem are painting/lacquering or polymer coating. Recently, ALD of chemically resistant $\text{Al}_2\text{O}_3/\text{TiO}_2$ nanolaminate has been proposed since it is an appropriate way to seal the AAO tortuosity using a little amount of material [74]. In this work, ALD was performed after an electrochemical treatment of the AA2024-T3 alloy to remove the inter-metallic phases. Such combination leads to excellent corrosion resistance: short-term anodic polarization up to 10 V and immersion in a salt solution for 7152 h (298 days).

Protection of 3D objects

Over the past decades, ALD has been proven to be the method of choice for coating 3D objects with various geome-

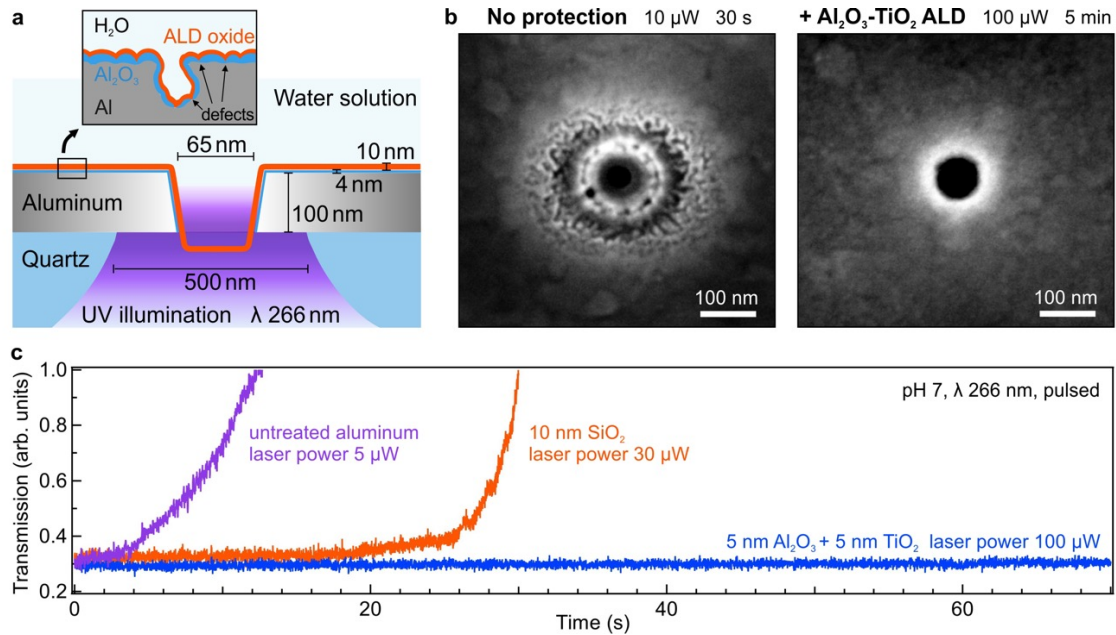


Figure 5: (a) Single aperture of 65 nm diameter milled in a 100 nm-thick aluminum film. The aperture is illuminated by a focused ultraviolet laser beam, and a water solution fills the aperture and the upper medium. The natural aluminum oxide (alumina) layer covers the aluminum bulk, but this layer is not fully dense or homogeneous on the surface, leaving defect sites for aluminum corrosion. The nanometer-thick extra oxide layer efficiently protects the aluminum surface. (b) Example of scanning electron microscopy images of a single aperture without and with a protective ALD layer (here, 5 nm of Al_2O_3 , followed by 5 nm of TiO_2 as capping). In the absence of protection, corrosion is clearly visible around the central aperture. (c) Transmitted intensity time trace for different nanoaperture samples and UV laser power. The stability of the time trace indicates corrosion resistance. From reference [75].

tries, such as wires/rods, powders/particles and holes/pores [76]. It has therefore naturally been employed to mitigate the corrosion of non-planar objects. It can be critical to protect nanoscaled materials since they can present different properties than their massive counter parts. Nanomaterials can, for instance, show an enhanced reactivity that could be deleterious for their stability. It is the case of Cu nanowires used as a promising thermal management solution of high power electronic devices that are prone to corrode at such scale [77]. A thin TiO_2 ALD coating prevents the dissolution while keeping the thermal properties of the nanowires.

It is peculiarly difficult for vacuum techniques to uniformly cover deposited particles and even trickier to surround unsupported particles while ALD is well-adapted. This approach has been applied in catalysis to avoid coking and sintering and thus maintaining a longer catalytic activity [78] and it appears suitable for corrosion prevention. Ag nanoparticles were, for instance, conformally coated with oxides in a fluidized bed ALD reactor to prevent their corrosion [79]. Although a thin layer of Ag_2O is present, the particles are protected when covered with 10 nm-thick ZrO_2 or HfO_2 layers and they keep their surface plasmonic activity [80]. ALD of Al_2O_3 on supported Ag nanoparticles was also efficient to improve the stability of the metallic clusters without degrading their plasmonic sensitivity. Cu powder can also be protected against corrosion by ALD of conformal thin Al_2O_3 and TiO_2 [81]. The stability of the powder was demonstrated from $\text{pH} = 0$ to 14 using the appropriate coating material: Al_2O_3 or TiO_2 .

Rough surfaces can be considered as nanostructured sub-

strates. ALD is also applied to protect those surfaces. Silver is present in many everyday life objects that can be in contact with the human body. Appropriate ALD coatings can mitigate Ag tarnishing of surfaces exhibiting a high roughness when they are immersed in artificial sweat [82].

ALD and PECVD of different oxides were compared as coating method to protect aluminum nanoapertures against UV photocorrosion [75]. Such Al nanoholes exhibits valuable UV plasmonic activity that is used for label-free detection of single molecule (here, streptavidin) with an improved signal-to-noise ratio. As shown in Figure 5, a 10 nm-thick $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer suppress the photocorrosion under the highly energetic UV laser irradiation while the other oxide fail. A thin SiO_2 film grown by PECVD shows a far less efficient protection at an even lower power. This work illustrates one of the interests of nanolaminates as protective films. Here, Al_2O_3 is transparent to UV while TiO_2 absorbs in this range. They are combined because the first suppresses any exchange with the underlying metal while the second brings chemical stability. As TiO_2 attenuates the light transmission, the thinnest possible layer is deposited, whereas this limitation does not apply to alumina. Other reasons may lead to the deposition of multilayers rather than single material films. The main idea is to combine the qualities of the materials while minimizing the impact of their limitations.

Corrosion of non-metallic surfaces

In the previous section, it has been shown that ALD is successfully used to suppress the degradation of various metallic

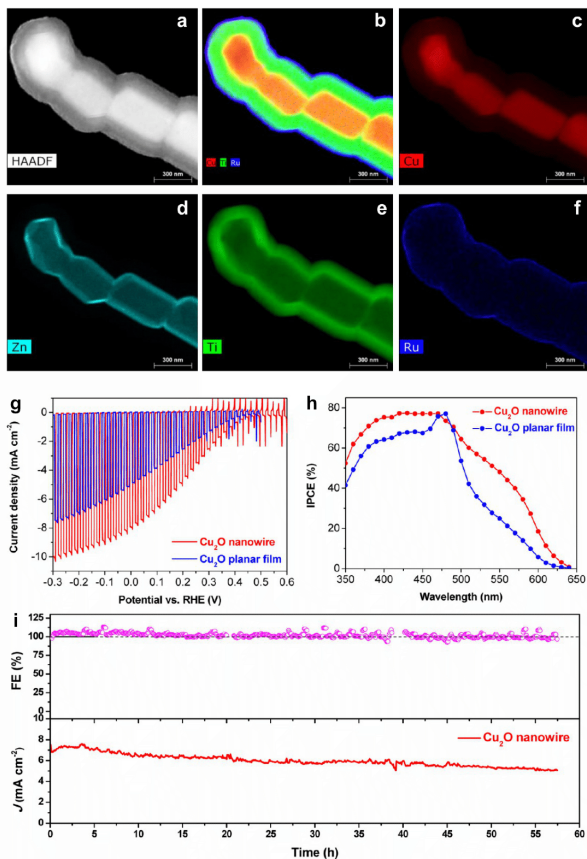


Figure 6: TEM and EDX characterization of the Cu_2O NW with overlayers. (a) HAADF image. (b) Combined elemental mapping image. (c, d, e, and f) element mapping of Cu, Zn, Ti, and Ru, respectively. Photoelectrochemical performance, stability, and Faradaic efficiency measurements. (g) j - V curves under simulated AM 1.5G chopped illumination and (h), IPCE spectra under monochromatic illumination of Cu_2O nanowires and planar devices. (i) Measured photocurrent and Faradaic efficiency for hydrogen evolution of Cu_2O nanowire device under constant bias at 0 V vs RHE and simulated AM 1.5G illumination. Adapted from reference [83].

surfaces. Non-metallic surfaces, i.e. semiconductors and insulators are also subject to corrosion and can be protected by ALD.

Many semiconductors are not stable when they are biased under illumination in the solutions used for water photosplitting. Silicon is a good example of this limitation. Although it has an indirect band gap, it absorbs light in the appropriate range to electrolyze water but it corrodes in KOH and it has been disconsidered [84]. Similar drawbacks are observed for III-V semiconductors that present the best suited optoelectronic features (e.g. InP, GaAs or ternary alloys) [85]. Conversely, semiconductive metal oxides are often stable on the whole pH range but they absorb light mainly in the UV range. Deposition of thin oxide layers onto such III-V or Si has thus been performed by PVD [86–88] or APCVD [89]. Metals, such as Ni or Fe, have also been deposited by PVD [90] or electroplating [91, 92] to cover Si with continuous films or dispersed particles and corrosion was mitigated or diminished. ALD has recently shown a great ability to protect photoelectrodes from corrosion [93].

Si photoanodes have exhibited long-lasting behavior when covered by thin TiO_2 [94–96] or Fe_2O_3 [95]. It also works on III-V materials as well as photocathodes such as InP [97] or Cu_2O that undergo the so-called cathodic decomposition [98]. As seen on Figure 6, it is also applied to nanostructured surfaces [95, 99, 100, 83]. The oxides are not only grown to mitigate the semiconductor corrosion but it is also expected to achieve a synergetic light-matter interaction. The covering oxide can absorb photons in the UV while the substrate collects light in the visible range [95]. The protective materials is mainly TiO_2 that can be grown after the co-catalyst deposition to protect the electrode components [101]. Note that it is however not the perfect material because depending on the deposition parameters the film can show a tiny porosity [102]. Elemental H diffusion can also occur through the layer during electrochemical polarization cycling that drives to the mechanical embrittlement [103] Note that other oxide films (Al_2O_3 , Nb_2O_5 , Ta_2O_5) have also brought interesting corrosion resistance in harsh environment to semiconductors with no specific targeted applications [104, 105].

The electrodes of Li-ion batteries are non-metallic compounds. During cycling processes, deterioration of the electrodes is often observed, which leads to a capacity degradation. The damages of the electrodes can be related to electrochemical phenomena but it is difficult to assimilate them to a corrosion of the electrode in the usual sense. Nevertheless, the ALD of thin oxide layers (mainly Al_2O_3) allows to keep the performance level and extend significantly their lifetime. This approach has been applied to Li-ion batteries to improve cathodes [106] and anodes [107] as well as other technologies such as Na-ion or Li-S batteries [108, 109]. ALD is well-adapted to the rough geometries of electrodes. It is further demonstrated by the deposition of AlF_3 on $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ powder serving as Li-ion cathode [110].

ALD processing is also used in gas sensor field but it mainly serves to enhance the detection sensitivity rather than prevent corrosion. Al_2O_3 films are, however, used in NO_2 gas sensors were encapsulated to prevent contact between H_2O and O_2 with the sensitive regions of the carbon-nanotube-based field effect transistors (i.e. metal contacts, single-walled nanotube, SiO_2 substrate) [111, 112]. SiN-based microelectrode array sensors have had a broad impact on studying the extracellular electrophysiological activity of neural and cardiac cells. Yet, they encounter corrosion in cell cultures. ALD of TiO_2 on the array was sufficient to suppress the corrosion but it also showed excellent cytocompatibility during a four-week culture with human embryonic stem cell-derived neuron [113].

Large-scale applications

Anti-corrosion coatings have already been deposited by ALD on everyday life objects used in various field of applications. They contribute to demonstrate the practical value of this technique. TiO_2 and Al_2O_3 thin films have shown enhanced corrosion barrier properties of Al food packaging when tested in beer electrolyte [114]. This was mainly ascribed to the absence of porosity on the two ALD coatings. ALD of different oxides

on various dental materials (metals/metal alloys, organic and ceramics) has been reported in a comprehensive review [17]. It describes the influence of different ALD thin films and their microstructure on the surface properties: corrosion-resistance, antibacterial activity, biofilm formation, and osteoblast compatibility. Mechanically robust microstructured TiO₂-coated stainless steel mesh has shown high corrosion resistance when used as high flux (1.43×10⁵ L·m⁻²·h⁻¹) oil-water separation in acidic, alkaline and Cl-containing solutions [115]. Due to the TiO₂ layer, the composite mesh exhibits also excellent photocatalytic capacity as well as self-cleaning and antifouling abilities. Other applications could probably be found on the market in a close future. Various ALD films can suppress Sn whisker growth and corrosion on printed circuit board assemblies [116]. Surgical scalpel blade were covered by a thin ZnO films exhibiting good adhesion and corrosion resistance. This is interesting because such coating is non-allergenic and it reduces bacteria multiplication [117]. Nanolaminate Al₂O₃/TiO₂ coating for Al alloys used in aerospace applications has shown exceptional corrosion resistance [118]. It exhibits no alteration after a 1000 h ISO 9227 salt spray test and demonstrates a maximum surface hardness of 5.5 GPa. The same coating also suffers negligible damage in an atomic oxygen test, which is comparable to 1 year of exposure to space in low Earth orbit.

Finally, it is difficult to process large parts by ALD because current reactors are designed for flat geometry. An interesting approach has been proposed to address such challenge. Sousa et al. [119] have proposed the concept of open-environment *in loco* ALD on an automobile. Similarly to spatial-ALD, a surface-mounted “ALD delivery head” is engineered to grow an Al₂O₃ film on the window of a parked automobile. This proof-of-concept demonstrates that ALD could be envisioned on large and complex parts.

Conclusion

According to its mechanism, ALD is intrinsically suitable for material protection. This review illustrates that qualities of this thin film deposition technique address the requirements of anti-corrosion coatings. It is, indeed, possible to form pinhole-free layers or to seal the porosity of protective coatings to avoid any tiny contact between the part and the external medium. The conformality of the coatings is also a key advantage to fight against corrosion because it means that any micro- or nanostructures can be covered with a compact layer. It is critical to perfectly protect the entire surface because local or pitting corrosion could be much deleterious than an homogeneous degradation process. The various examples illustrate how ALD can be used to successfully mitigate corrosion. It is important to note that in some cases the performances are not optimal when covering a surface with ALD. Among the few examples, one can cite the work of Diaz et al. [120] that have reported a better protection of stainless steel after depositing Ta₂O₅ by filtered cathodic arc deposition rather than ALD. Note also that intrinsic protective properties (i. e. electrochemical behavior) of the coatings are not changed by this deposition techniques. ALD is

a mean to deposit a pine-hole covered plane and tortuous surfaces and this is already a key advantage.

Although it has been shown that ALD can be very efficient against corrosion, it is not yet widely used in industry. It is indeed still difficult to compete with cheap and easily implemented methods such as electrochemical treatments, paintings or polymer coatings. Those techniques can commonly be applied to any part geometries while, except the nice example of *in loco* deposition, ALD is dedicated to planar pieces. Nevertheless, ALD can challenge other vacuum approaches (PVD, CVD). The recent developments (spatial ALD [2] or parallel precursor wave technology [121]) have pushed back the limits related to the low deposition rate. Al₂O₃ and TiO₂ are currently the most used protective materials but it has been shown, here, that there is room for other materials that can be interesting for specific applications. Although they can get oxidized, nitrides thin films present, indeed, very promising and complementary properties (e.g. mechanical properties and wear resistance).

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- Papers of particular interest, published within the period of review, have been highlighted as:
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