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Chapter 3

Inorganic-Organic Superlattice Thin Films by Atomic/Molecular Layer Deposition

Tommi Tynell and Maarit Karppinen

Abstract The combination of atomic and molecular layer deposition enables the fabrication of layered hybrid inorganic-organic structures with a high degree of controllability over the thickness and composition of individual layers. In addition to the increased potential for obtaining novel combinations of properties from the interplay of the inorganic and organic phases, layered hybrid structures offer opportunities for nanostructuring through the creation of superlattice structures where the organic layer thicknesses have been reduced to a single molecule. Even with very low organic content, this superlattice approach can lead to significant improvements in the inorganic host material's performance by influencing properties such as thermal conductivity or the electronic band structure.

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3.1 Introduction

Hybrid materials containing inorganic and organic constituents in a single structure form a field of research that has attracted growing attention in recent years due to the potential advantages that can be gained by creating materials that combine some of the properties typically associated with organic or inorganic materials separately. Flexible and/or transparent conductors are a typical example of material property combinations that could be achieved with simple hybrid materials consisting of inorganic phases suspended in an organic matrix, but the field contains a wide variety of structure types that can offer solutions to various materials science challenges. Other examples of inorganic-organic hybrid structures include metal-organic frameworks that could be utilized in applications ranging from gas storage to catalysis and gas separation, or layered hybrid solar cells consisting of conducting polymer layers and inorganic semiconductor layers. As the research and understanding of hybrid materials progresses further, their impact on the design of functional materials should spread to many new fields of materials research.

Even very small amounts of organic components can bring about dramatic changes in the properties of a hybrid material, and fabricating layered materials with thin organic layers within the inorganic structure can be an effective way to introduce new characteristics to a material without impairing its original properties. Thin films form a particularly interesting medium for investigating the magnitude of the achievable benefits because of the possibility of optimizing the structure for the utilization of various nanoscale effects on the material’s physical characteristics. Although this approach has a lot of potential, it is often difficult to incorporate both inorganic and organic components into a practical thin film deposition process in a controllable fashion. Perhaps the most suitable thin film deposition technique for this purpose is atomic layer deposition (ALD) combined with molecular layer deposition (MLD) due to the relative simplicity of fabricating layered hybrid films and the wide availability of a variety of inorganic and organic precursors.

While MLD, a version of ALD for deposition of organic thin films, has not quite enjoyed the sort of increased attention from the research community that ALD has in the course of the last decade, the combination of ALD and MLD for fabrication of hybrid inorganic-organic thin films is now being increasingly explored as a novel technique for making a range of exotic layered structures in a relatively simple manner [1]. The viability of the approach has been demonstrated with a plethora of different material combinations that highlight the potential of a practically endless variety of structures that can be made and tuned for a specific application. This chapter provides an overview of hybrid superlattices and the use of ALD and MLD in their fabrication.

3.2 Atomic and Molecular Layer Deposition

Atomic layer deposition is a chemical thin film deposition technique that is based on self-limiting surface reactions by sequentially pulsed precursor chemicals. Inert gas purges between the precursor pulses are used to purge the reactor of excess precursor molecules and reaction by-products to ensure that reactions only take place on the surface of the substrate. Due to this separation of the precursor pulses, the technique enables the deposition of single atomic layers at a time, affording a great deal of controllability over the composition of the layers and the thickness of the thin film. This controllability has brought about a significant increase in the use of ALD in various high-tech applications since the turn of the century as the requirements for the components of microelectronics have grown ever more stringent, which in turn has encouraged research in the field and enabled ALD to mature as a technique for the creation of various nanostructures [2-4].

The ALD technique can be used to deposit a variety of different compound types, restricted mainly by the availability of appropriate precursor chemicals of sufficient reactivity, but oxides are a particularly common class of compounds in ALD due to the good applicability of water, ozone or oxygen plasma as oxidizers for a number of metal-organic precursors. ALD processes have been developed and optimized for most of the common simple binary oxides and a number of more complex ternary oxides as well. A typical ALD process for the deposition of ZnO is shown in Figure 1, illustrating the way the growth proceeds in a step-like manner through the repetition of so-called ALD cycles.

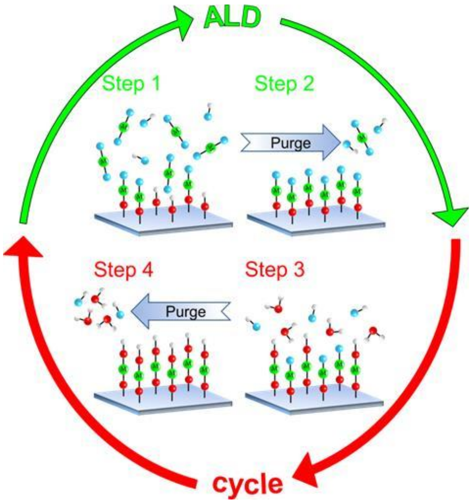


Fig. 1. Basic ALD cycle for depositing thin films of binary inorganic compounds. One ALD cycle consists of four separate gas pulsing steps:
Step 1: first precursor (e.g. DEZ) pulse
Step 2: inert gas (typically N_2) purge
Step 3: second precursor (e.g. water) pulse
Step 4: inert gas purge
The basic ALD cycle is then repeated as many times as needed to produce the desired film thickness.

The ALD process shown in Figure 1 is an idealized description, and in actual depositions the growth of the film layers is determined by a multitude of factors that affect the reactivity of the precursor chemicals and the degree of surface coverage that can be achieved. The most important parameter for an ALD process is the deposition temperature, which should be high enough to ensure good reactivity of the precursor chemicals with the surface species on the film surface, but not too high to avoid decomposition or desorption of the precursors. These temperatures determine the limits of the so-called ALD window, i.e. the temperature range where the film deposition rate is roughly constant, indicating that stable film growth has been achieved. In order to ensure complete coverage of the deposited surface, the pulse and purge lengths of precursors should also be long enough to allow sufficient time for access to the reactive sites on the film surface. The separation of the precursor pulses from each other also means that the length of the pulses can be made as long as needed, enabling the conformal deposition of very complex and high-aspect ratio surfaces. These properties make the ALD method an ideal fit for applications where conformality, precise thickness control and good step coverage are needed. Due to the self-limiting reactions and saturation of the reactive surface the technique is also very well suited for the fabrication of various multilayered structures.

Post-deposition annealing of ALD-grown thin films is a common step to improve the crystallinity of the films, but it is also used as an integral step in the synthesis process of ternary oxides to facilitate the formation of the intended structure. Thus, while ALD deposits thin films a single atomic layer at a time, the technique is not limited to layered or otherwise simple structure types. Similarly post-annealing can help offset problems with the typical way of doping ALD-grown oxide thin films, i.e. the addition of single layers of another oxide into the film in appropriate ratios, a method which can lead to localization of the doping electrons.

The ALD technique can also be used to deposit entire molecules instead of atomic layers, in which case the term MLD or molecular layer deposition is typically used. The principle behind the deposition is exactly the same as with ALD, but the precursors and deposition parameters are chosen so that one cycle of MLD deposits a single layer of a molecular species that can range from simple short-chain hydrocarbons and compact aromatic compounds to quite large and complex molecules. The MLD variant can be used alone to deposit purely organic thin films by using two or more molecular precursors, but an increasingly common approach has been to combine it with ALD, i.e. use a process containing both ALD and MLD cycles to fabricate inorganic-organic hybrid thin films [1, 5-7]. Due to the nature of the ALD/MLD technique, the resulting hybrid thin films will be layered in nature, consisting of alternating inorganic and organic layers of various thicknesses. Figure 2 illustrates the way ALD and MLD methods can be combined for the deposition of hybrid inorganic-organic films.

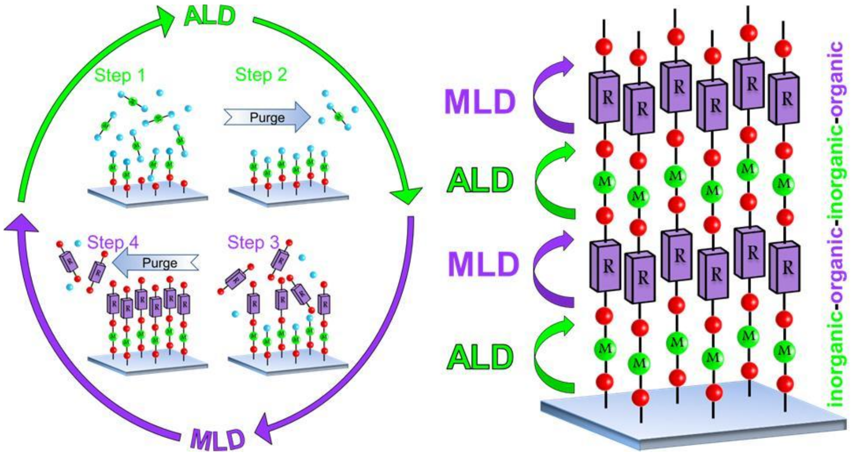
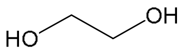
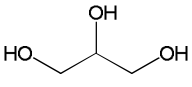
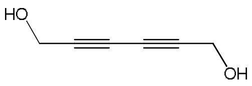
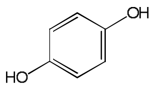
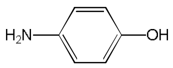
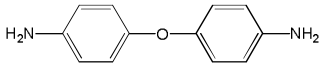


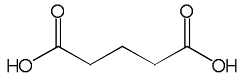
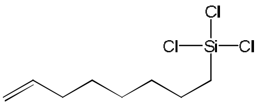
Fig. 2. The deposition of hybrid inorganic-organic thin films with a combination of ALD and MLD [8]. The deposition cycle in ALD/MLD consists of the following gas pulsing steps:
Step 1: inorganic precursor (e.g. DEZ) pulse
Step 2: inert gas (typically N_2) purge
Step 3: organic precursor (e.g. HQ) pulse
Step 4: inert gas purge
Like in conventional ALD, the ALD/MLD cycle is repeated as many times as needed to produce the desired hybrid film thickness.

In essence, the principle of depositing inorganic or organic layers with ALD or MLD is exactly the same, so combining the techniques for hybrid film deposition is simple and straightforward. A common style of hybrid thin film fabrication has been to alternate single ALD and MLD layers so that every other layer is inorganic/organic. However, the nature of the deposition technique makes it easy to use any desired layer ratio, and for optimizing the film's properties it is typically necessary to utilize different ratios of inorganic to organic layers as large amounts of organic layers tend to result in films with very high electrical resistance, which makes them unsuitable for many electrical applications. Therefore, the focus of many studies is now shifting to either structures with very high inorganic to organic layer ratios [9-11] or to ones combining inorganic portions with portions of 1:1 hybrid materials (so-called nanolaminates) [12-14].

A variety of inorganic as well as organic precursors have been utilized in ALD/MLD processes together with highly varied ratios of inorganic to organic layers. The choice of the organic precursor to use in hybrid deposition processes is an important one, as it will have a large impact on the properties of the hybrid material. Highly conjugated molecules are a common choice for the MLD precursor because of the generally better electrical properties and their importance in many applications. Benzene rings, which combine conjugated Π bonds with a rigid structure, are often a part of good MLD precursors for hybrid depositions due to the potential for good electrical properties and the added tendency of avoiding unwanted double reactions of the precursor molecules on the surface during deposition. Some common MLD precursor molecules that have been used in ALD/MLD hybrid studies are presented in Table 1.

Table 1. Some of the common precursor molecules used to fabricate hybrid inorganic-organic thin films with ALD/MLD [1]

Organic Precursor	Name	Inorganic Species	Ref.
	Ethane-1,2-diol	Al, Ti, Zn, Zr	7, 15-20
	Propane-1,2,3-triol	Al, Ti, Zn	19, 21
	Hexa-2,4-diyne-1,6-diol	Ti, Zn	22, 23
	Hydroquinone	Al, TiO_2, Zn, ZnO	6, 9, 10, 21, 24-28
	1,4-aminophenol	Ti, Zn, ZnO	8, 28-30
	4,4'-oxydianiline	Ti, ZnO	13, 28, 31

	Pentanedioic acid	Al	6, 32, 33
	7-octenyltrichlorosilane	Al, Ti, Zn, Zr	12, 34-37

As can be seen from the established organic precursors for MLD, the key to a molecule's applicability (assuming a suitable temperature range for sublimation in vacuum) is dual reactivity, i.e. the molecule should have two functional groups that can react with the surface species left on the film surface after the preceding precursor pulse. A rigid structure would also be beneficial in avoiding double reactions with the surface, but otherwise there are no specific requirements for the precursor structure. Needless to say, this enables the utilization of a practically limitless range of organic molecules that can be used in fabricating hybrid thin films with ALD/MLD. In practice, molecules containing a hydroxyl group as the reactive functional group are most commonly used as the MLD precursor in hybrid processes. This is due to the suitability of ALD for fabrication of oxide thin films and the corresponding wide availability of precursor molecules that are highly reactive with water (and thus also with the hydroxyl groups of the MLD precursors). There are no particular restrictions apart from reactivity on the precursors for the inorganic parts that can be used together with the MLD precursors, though hybrid films based on Al, Ti and Zn or their oxides are very common because of the availability of extremely reactive precursors that facilitate film formation through reaction with the hydroxyl groups of the MLD precursors.

3.3 Exceptional Features of Superlattice Structures

Superlattices, i.e. layered structures consisting of periodically repeating layers of two or more different compounds, are a relatively simple form of nanostructuring that has been utilized in many applications to create materials with properties uniquely suited to the required task. These applications take advantage of the possibility to control some of the physical properties of the material, such as optical, mechanical or electrical properties, by the choice of materials used in the layers and careful control of the thicknesses of individual layers. By making the layers of one material thin enough (nm scale) it is possible to bring about quantum confinement effects within the material, forming a structure which is usually called a quantum-well superlattice. However, for many applications it is not necessary to achieve the extremely thin dimensions required for the observation of quantum effects to see marked improvements in a number of physical properties of the material.

One common use for superlattice structures is in the field of thermoelectric materials, where the dimensions of the layered structure can be tailored to induce improvements in thermoelectric performance by reducing the lattice thermal conductivity of the superlattice structure by making the dimensions of the individual layers smaller than the mean free path of the phonons that are responsible for much of the thermal conductivity through the material. Since electron mean free paths are typically much shorter than those of phonons, it is possible to fabricate a superlattice structure that hinders the movement of phonons much more than electrons, thereby causing a lesser impact on the electrical properties of the material [38-40]. This principle is illustrated in Figure 3.

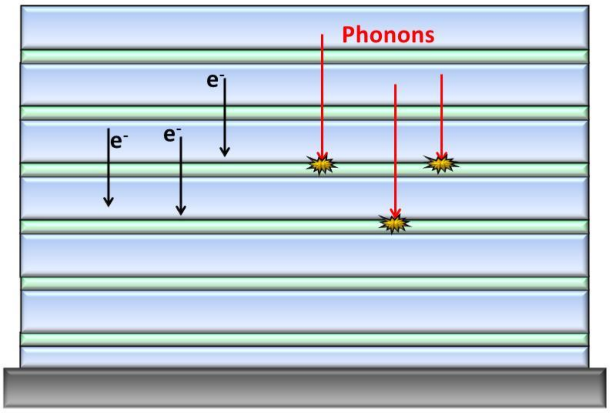


Fig. 3. A superlattice can be used to reduce the thermal conductivity of a material without adverse effects on the electrical properties by utilizing the different mean free path lengths of electrons and phonons

Even more dramatic benefits for thermoelectric applications can be achieved by fabricating superlattices utilizing quantum confinement effects, which could be quantum well superlattices or even layers of quantum dots within a parent material. These approaches have been theoretically predicted to enable a thermoelectric performance several times higher than current state-of-the-art materials, and experimentally produced conventional and quantum well or quantum dot superlattices have already been demonstrated to be capable of reaching significantly enhanced values of the thermoelectric figure of merit [41-45].

Other common uses for superlattice structures include optical and optoelectronic applications, where combining several different material layers into one device is an efficient way to tune its optical properties according to the specific demands of the application. In the field of photovoltaics such structures are used to construct multi-band-gap solar cells that are able to utilize a larger range of light wavelengths more efficiently through the inclusion of several material layers with appropriate band-gaps into the same cell [46,47]. Similarly, light-emitting diodes often utilize superlattice structures, taking advantage of the relative ease of tuning their optical properties through appropriate selection of materials and layer dimensions [48-50].

Hybrid superlattices of inorganic and organic layers are still a relatively unexplored field, and while there are a number of studies published on the subject, the available research on hybrid superlattices is still limited in scope compared to the wealth of literature available on conventional superlattices. Many of the early studies have concentrated on laying the groundwork for further study by focusing on the basic chemistry and physics involved with such hybrid structures, though studies with more strongly application-oriented objectives are growing more common [51-54]. For example, the suitability of organic molecules for tuning the band gap properties of semiconductors has been demonstrated with a hybrid material consisting of ethylenediamine together with ZnTe and ZnSe, fabricated by using a solvothermal synthesis method [55]. In a similar fashion to superlattices composed of different semiconductor materials, the interaction between the valence and conduction bands of the semiconductor and the molecular orbitals of the organic part in a hybrid superlattice can be used to influence the electrical properties of the parent semiconductor material, as is demonstrated in Figure 4.

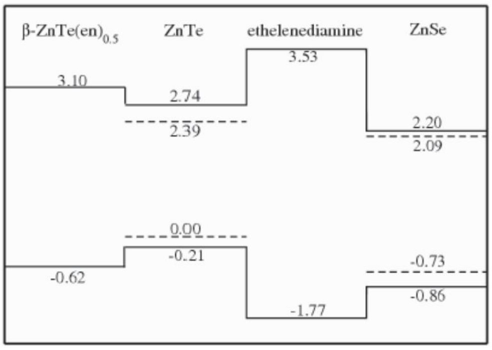


Fig. 4. The interaction between the molecular orbitals of organic layers and the valence and conduction bands of a semiconductor in a hybrid superlattice structure. Reprinted figure with permission from Y. Zhang *et al.*, Phys. Rev. Lett. **96**, 026405 (2006). Copyright 2006 by the American Physical Society [55]

A similar effect has also been observed in ALD/MLD-fabricated hybrid superlattices, where the addition of single hydroquinone layers into TiO_2 was found to influence the optical band gap of the material, most likely through orbital interactions between the organic and inorganic species [11]. This type of band gap tuning could also confer obvious benefits to solar cell applications and other optoelectronic fields, and the availability of an essentially limitless variety of organic molecules with different orbital characteristics offers tremendous potential for the tuning of the electrical and optical properties of hybrid materials. In addition, the different mechanical characteristics of organic materials can be exploited to confer other benefits to the performance of hybrid materials in specialized applications such as when flexibility is required of the material. Thin film transistors (TFT) are an example of an application where optimization of the electrical properties is essential, while properties such as flexibility of the device or the possibility to print the material can offer added value, so hybrid materials have already drawn some interest as the material basis for the required components. There are a fairly large number of studies published on the use of hybrid material combinations in TFT applications, though they most commonly relate to the use of polymers as active components of otherwise inorganic transistors [56-58] or conventional hybrid components that can for instance enable a part of the transistor to be printed [59]. Some studies have, however, reported on the application of hybrid superlattices as the dielectric layer in TFTs, fabricated as alternating layers of an oxide material and an organic phase consisting of relatively large molecules [60,61].

3.4 Hybrid Inorganic-Organic Superlattices via ALD/MLD

The combination of ALD and MLD has been used to deposit a variety of different combinations of hybrid materials, but many of these are not reported as superlattices even though the nature of the deposition technique means that the resulting hybrid structure is, in fact, often layered in nature and thus can be thought of as a hybrid superlattice. Instead, the terms *alloy* or *nanolaminate* are often used to describe the hybrid films, partly because it is not always certain that the inorganic and organic parts grow in neatly stacked layers, particularly in the case of very complex organic precursors, and partly because a common approach has been to grow stacks of a 1:1 hybrid material (i.e. alternating single layers of a metal and an organic molecule) and stacks of a corresponding metal oxide. Moreover, in the case of 1:1 hybrids it is often more appropriate to consider the structure as a hybrid material instead of a superlattice consisting of layers of two distinct phases. The differences between the different structure types are illustrated in Figure 5. From the perspective of developing materials for novel applications, nanolaminates and superlattices can be utilized in a variety of ways to tune the overall material properties and thus offer a greater deal of versatility than simple 1:1 hybrids. Accordingly, this section will concentrate on hybrid structures that can be defined as superlattices or nanolaminates, although some discussion will also be devoted to simpler hybrid structures fabricated with ALD/MLD as they are very closely related to hybrid superlattice structures.

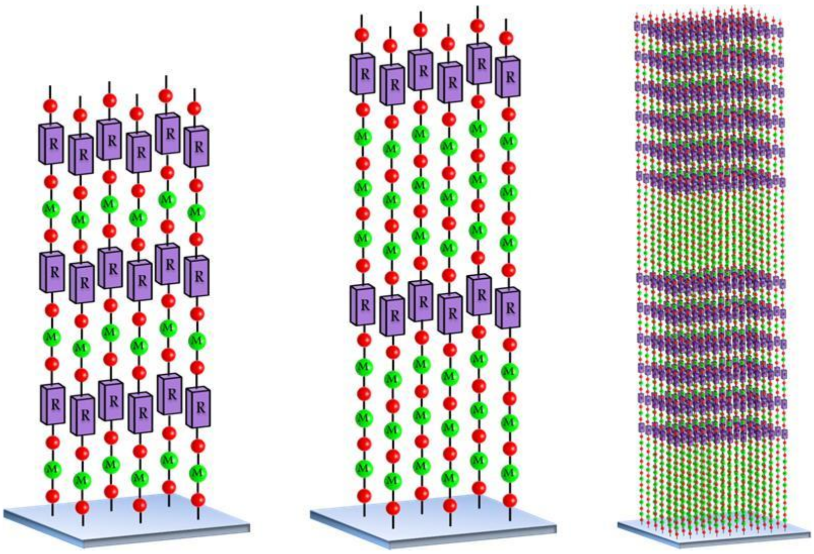


Fig. 5. ALD/MLD-grown hybrid (left), superlattice (middle) and nanolaminate (right) thin films

At its simplest, a hybrid superlattice structure can be fabricated by depositing stacks of an inorganic material (typically an oxide semiconductor) separated by single layers of a rigid, bifunctional organic molecule. The advantage of this approach is that with a suitably reactive organic precursor it is possible to easily fabricate simple hybrid superlattices from a vast number of inorganic compounds that have well-defined ALD processes. An illustration of a typical simple inorganic-organic superlattice structure is presented in Figure 6 for the ZnO:HQ hybrid (HQ stands for hydroquinone).

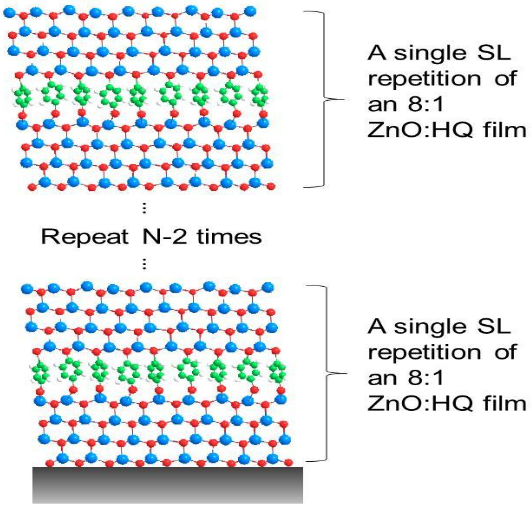


Fig. 6. A simple superlattice structure consisting of single hydroquinone layers between stacks of ZnO with a ZnO:HQ ratio of 8:1. [T. Tynell *et al.*, J. Mater. Chem. A **2**, 12150 (2014)] Reproduced by permission of The Royal Society of Chemistry [62]

Although it is difficult to observe quantum confinement effects in a hybrid structure of the type shown in Figure 6, it is possible to see other benefits from the inclusion of the organic layers, namely a marked reduction in the thermal conductivity of the thin film, as already demonstrated for ZnO:HQ hybrid superlattices [62]. Despite the relatively small amount of organic layers in the ZnO:HQ hybrid, there were also clear effects on the electrical properties, with the organic layers causing a reduction in electrical conductivity. However, considering that the magnitude of the reduction in thermal conductivity was much larger and that the electrical conductivity reduction can be offset with doping, the hybrid superlattice structure provides a means to improve the performance of ZnO for instance in thermoelectric applications. Although not extensively researched yet, the above influences are not limited to ZnO or hydroquinone only, but should be applicable to a vast number of different inorganic/organic material combinations.

The strength of the ALD/MLD approach in creating superlattice structures stems from the nature of the deposition technique, i.e. the high degree of controllability that is afforded by the self-limiting reaction steps and separation of the precursor reaction steps. Therefore, the advantages of the technique such as conformality and good step-coverage apply not only in regards to the whole film but also to single layers provided that the deposition conditions and other parameters are chosen properly. Thus, a single layer of an organic (or inorganic) constituent can be created simply by inserting a single pulse of the organic precursor into the deposition program while the periodicity will be determined by the thickness of the inorganic layers. The approach also enables the addition of doping layers into the film structure as is demonstrated in the process scheme in Figure 7.

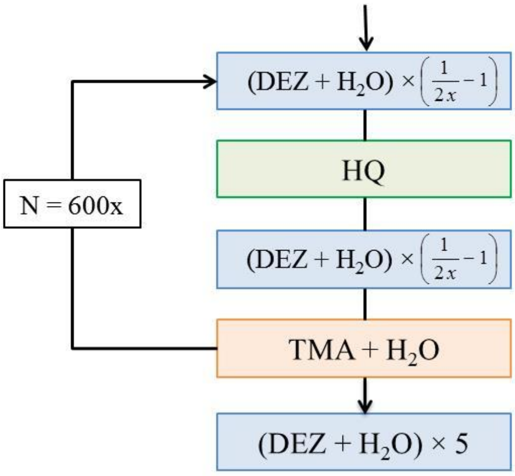


Fig. 7. A description of an ALD/MLD process for the deposition of ZnO-based hybrid superlattice thin films, with added Al_2O_3 layers from pulses of trimethyl aluminum (TMA) and H_2O for doping purposes [9]

The process described in Figure 7 was used to deposit thin films roughly corresponding to the formula $Zn_{1-2x}Al_xHQ_xO$, where N repetitions of a basic building block were used to obtain hybrid superlattice films of Al-doped ZnO and hydroquinone [9]. Note that the addition of five DEZ/H_2O pulses at the end of the process slightly skews the doping amount of the films from the nominal value, but it was deemed necessary to avoid the capping layer consisting of Al_2O_3. Doping of the inorganic phase is often necessary for electronic applications to offset the effects of the organic layers as was discussed above. The manner in which this is achieved in ALD is similar to the introduction of the organic constituents, i.e. single layers added in a suitable ratio to the deposition program. This generally does not affect the superlattice structure because the doping layers will integrate into the inorganic parent structure more smoothly than the organic layers, simply because of the very different nature and size of the organic molecules as compared to typical doping species. Moreover, the objective of doping the inorganic structure does not necessitate that the doping species form a complete layer within the parent structure, so the used pulse lengths and other process parameters for dopants are therefore often such that doping is achieved without the creation of distinct dopant layers in the film.

The usage of organic layers in the superlattice structures also enables a number of different approaches in designing the layer structure. Whereas in the above examples in Figures 5 & 6 the organic layers consist of disparate single molecules that together form a layer, it is possible with the proper choice of precursors and deposition parameters to fabricate polymerized organic layers, where the molecules forming the organic layer form bonds with each other. An example of such a structure is presented in Figure 8.

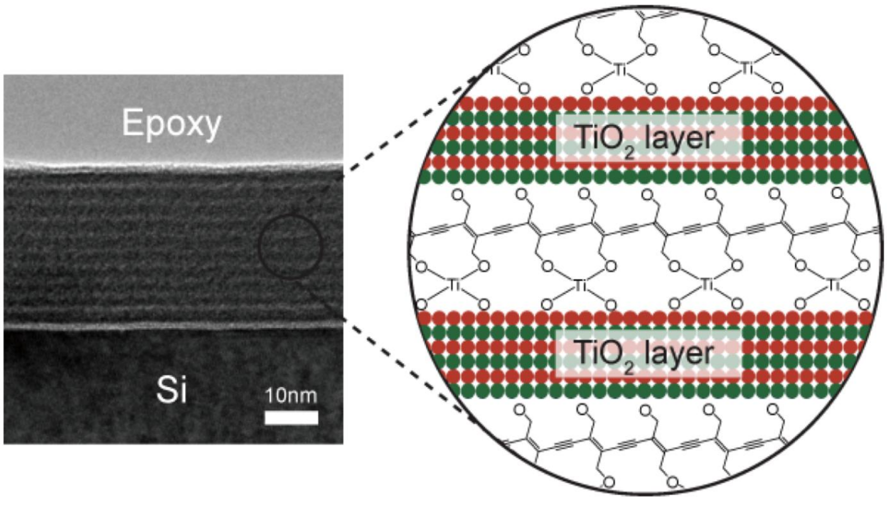


Fig. 8. A hybrid superlattice consisting of stacks of TiO_2 separated by single polymer layers. Reprinted with permission from Ref. [63]

The polymer layers in the above hybrid structure were fabricated by depositing monomers of the desired polymer on top of the top TiO_2 layer and then exposing the film to ultraviolet radiation, causing the monomer layer to form the polymer shown in Figure 8. After the polymerization step, the deposition proceeded with the addition of more TiO_2 layers. This result demonstrates another possibility in exploiting the unique properties of organic materials in ALD/MLD processes and the polymerization approach could prove to be useful in improving the electrical properties of a hybrid superlattice structure. The polymerized layers in Figure 8 would also be expected to be relatively rigid compared to the unpolymerized molecular layers, affecting the mechanical properties of the hybrid thin film.

Although the growth of hybrid superlattices by the ALD/MLD process sets various requirements for the precursors that can be used in the deposition process, the use of added steps in the ALD/MLD cycle can add more flexibility to the choice of precursor chemicals, particularly for the MLD part of the cycle. These added steps are aimed at improving the reactivity of the molecules, typically by changing the functional groups to better suit the desired deposition process. This approach also enables the fabrication of organic structures that might be difficult or even impossible to create using conventional single-precursor methods because of the unavailability of suitable precursor chemicals. The nature of the ALD/MLD technique allows any number of additional steps to be easily added into the reaction sequence, though exceedingly complex deposition processes also increase the risk of unintended side-effects. An example of a process utilizing added reaction steps for precursor modification is presented in Figure 9.

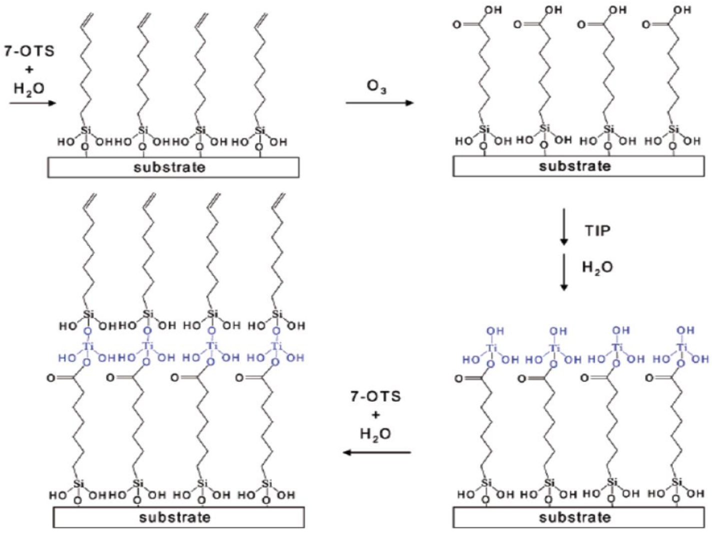


Fig. 9. Reaction diagrams describing the deposition of a hybrid thin film using 7-octenyltrichlorosilane with oxidizing reagents. Reprinted with permission from B. H. Lee *et al.*, J. Am. Chem. Soc. **129**, 16034 (2007). Copyright 2007 American Chemical Society [12]

In the above deposition process H_2O and ozone (O_3) are used to modify the reactivity of the MLD precursor, 7-octenyltrichlorosilane, both in the pulsing stage of the precursor, where simultaneous H_2O pulsing is used to convert the $SiCl_3$ group at one end of the molecule into a $Si(OH)_3$ group, and after the MLD pulse, where ozone is used to get a carboxylic acid group from the C=C group of the reacted precursor on the film surface. Additions such as these can enable the use of otherwise unreactive molecules in the ALD/MLD process but could also be exploited as a way to influence the properties of a hybrid material with an established deposition process.

In addition to the fabrication of single organic layers to fabricate hybrid superlattice structures, another approach enabled by ALD/MLD is to deposit a number of organic/inorganic layers to create a thicker layer of a hybrid material which forms one phase of the superlattice. In this case the superlattice is formed from layers of this hybrid phase within layers of an inorganic parent phase, although due to the unconventional nature of the hybrid layers the term *nanolaminate* is typically used instead of superlattice (cf. Figure 5). The fabrication of such nanolaminates affords even greater freedom in adjusting the layer structure and thus in tuning the material properties of the resulting thin film. With thicker hybrid layers the proportion of the organic phase can also be made much larger in the nanolaminates, which could be beneficial especially when the intent is to confer some properties of the organic phase into the material such as in the case of flexible electronic materials. TEM images of a number of hybrid nanolaminates in Figure 10 demonstrate the versatility of layer-structures that can be achieved with this technique.

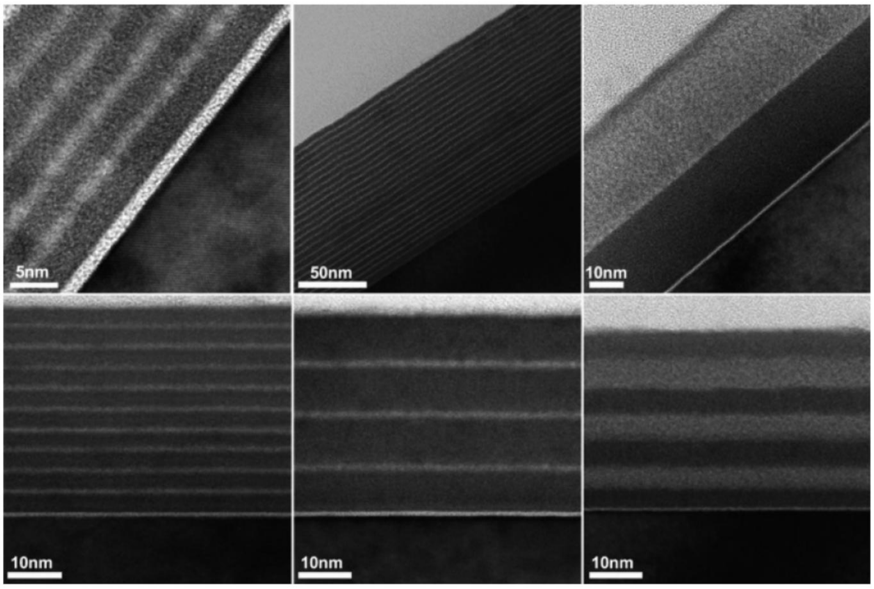


Fig. 10. TEM cross-sectional images of hybrid nanolaminates deposited on silicon substrates (see Figure 9 for the reaction). The light color in the TEM images corresponds to organic/hybrid layers. Reprinted with permission from B. H. Lee *et al.*, J. Am. Chem. Soc. **129**, 16034 (2007). Copyright 2007 American Chemical Society [12]

TEM images such as those in Figure 10 can be difficult to obtain due to the sensitivity of many organic molecules to atmospheric moisture, but when available the TEM images have shown that ALD/MLD superlattices result in very well defined layer structures. The images also demonstrate that using TEM it is possible to directly observe even single organic layers in the hybrid superlattice structure, although in this case the organic molecules employed are rather long and thus form a particularly thick monolayer (see Figure 9).

A potential application for hybrid nanolaminates has been identified in the field of bio-based packaging materials, where the mechanical properties of hybrid inorganic-organic materials can be utilized in moisture barrier coatings to increase the flexibility of the barrier coatings without sacrificing the barrier properties. Nanolaminates are perhaps better suited for this application than hybrid superlattices due to the possibility of creating thicker hybrid layers to maximize the flexibility gains while avoiding some of the problems of sensitivity to air that might arise with hybrid superlattices of very high organic content. The viability of this approach was recently demonstrated for Al_2O_3 coatings, a common barrier material against water and oxygen, when barrier coatings consisting of alucone (Al hybrid) layers sandwiched between Al_2O_3 layers were found to be more resistant to crack formation upon bending while still maintaining barrier properties comparable to those of Al_2O_3 alone. The applicability of this approach is further enhanced by the advantages of ALD when coating packaging materials, i.e. the reaction temperatures can be kept relatively low, the conformality of the films is very good even on very complex surfaces and the film be made pinhole-free, enhancing the performance of the barrier coating.

Taking the complexity of hybrid thin films a step further, it is possible to use several organic precursors in succession to widen the range of available organic layer structures even further. This approach makes available the entire breadth of organic structures with potentially beneficial influences on the properties of the hybrid material, although some structures will undoubtedly require substantial effort to achieve and optimizing the process for a particular process with several organic precursors is challenging. Nonetheless, the potential benefits from obtaining functional materials with improved properties are large enough to make the development of such processes worthwhile in some cases. An example of such an MLD process with several different organic precursors is presented in Figure 11.

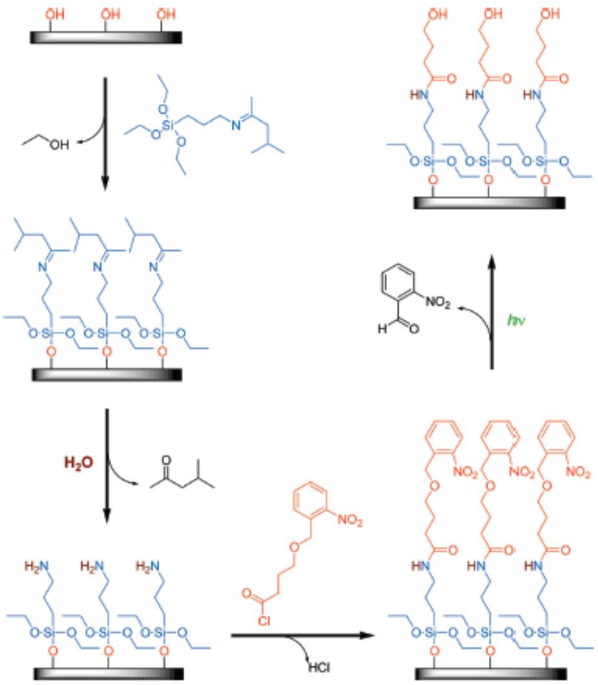


Fig. 11. An MLD reaction diagram demonstrating the use of two organic precursors and other intermediate steps to obtain complex organic layers. Reprinted with permission from S. M. George, B. Yoon and A. A. Dameron, Acc. Chem. Res. **42**, 498 (2009). Copyright 2009 American Chemical Society [64]

The process in Figure 11 features two organic precursors as well as intermediate steps where either H_2O or ultraviolet radiation is used to modify the deposited organic structure. The only limitations in designing processes for a particular organic structure are the availability of suitable precursor chemicals and the capabilities of the ALD/MLD equipment used. The latter is usually a minor concern, since most modern ALD reactors can easily accommodate at least four (and often more) different precursors in a single process, but the custom setup required for the ultraviolet light exposure limits the usability of this particular reaction process. It does, however, serve to highlight the versatility of the ALD/MLD technique in the design and fabrication of a huge range of different inorganic-organic layered structures that can be tuned to a large extent to match the needs of a particular application.

3.5 Verification/Characterization of Hybrid Superlattice Structures

The most robust method of determining the structural characteristics of superlattices, such as periodicity and thickness of individual layers, is cross-sectional transmission electron microscopy (TEM), and the technique is often utilized in studies of superlattice structures. However, in the case of inorganic-organic hybrid structures the organic constituent sometimes makes the use of TEM very difficult or even impossible due to the sensitivity of many organic molecules to atmospheric moisture. Moreover, in superlattices where the organic layers consist of single molecular layers it can be hard to differentiate the different layers in cross-sectional TEM (although with relatively thick organic layers it is not a concern, as was demonstrated in the TEM images in Figure 10). Therefore, X-ray reflectivity (XRR) is typically the best choice for characterization of hybrid superlattice structures. The technique utilizes the different electron density between a thin film and substrate to obtain a reflection pattern from which the thickness of the film can be worked out. In the case of a superlattice structure, the different layers give rise to interfering reflections that result in a distinctive pattern according to the number of superlattice repetitions (N). Thus, the XRR pattern directly displays the number of electronically distinct layers in the film, as displayed in the XRR patterns collected in Figure 12.

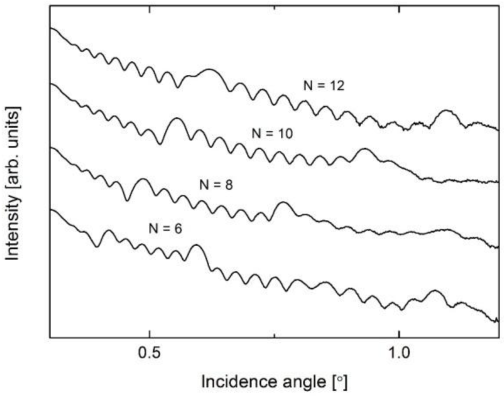


Fig. 12. Partial XRR patterns of a number of ZnO:HQ superlattice thin films with different amounts of HQ layers

The number of peaks within the characteristic superlattice peak pattern, as can be seen in Figure 12, corresponds very well to the number of organic layers in the hybrid films, and so provides a simple alternative method for structural characterization of hybrid superlattices. The technique is particularly suited for hybrid superlattices due to the typically very different electron density between the organic and inorganic phases in the structure, making it possible to make out even single organic layers in the material, as demonstrated in Figure 12.

Another important tool in characterizing inorganic-organic hybrid superlattices is Fourier transform infrared spectroscopy (FTIR), used for the determination of chemical bonds, particularly in organic compounds. The technique is fairly commonly used in ALD in an *in-situ* setup to analyze the evolution of the chemical bonds on the surface of the film as precursors are pulsed into and purged out of the reactor. In the case of hybrid films, FTIR can also provide valuable information on the make-up of the thin films after the deposition, as the obtained signals from various organic bonds are often rather strong and can be observed even with very small amounts of the organic species in the film. Thus, by using a combination of FTIR and XRR analysis it is possible to verify, in a non-invasive manner, the existence of the superlattice structure and the deposited organic molecules in the same film, thereby demonstrating with considerable confidence that the hybrid superlattice fabrication was succesful. An example of FTIR used for this purpose is given in Figure 13.

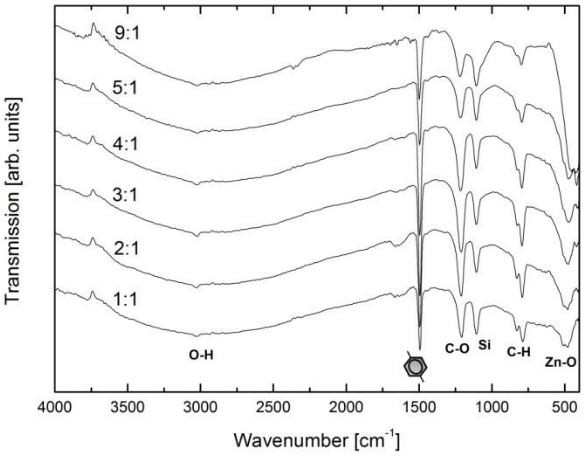


Fig. 13. FTIR patterns of ZnO:HQ thin films with varying ZnO to hydroquinone layer ratios. The peaks of the bottom pattern have been labelled according to the chemical bonds which they represent. Reprinted from Thin Solid Films **551**, T. Tynell and M. Karppinen, *ZnO:Hydroquinone superlattice structures fabricated by atomic/molecular layer deposition*, 23-26, Copyright 2013, with permission from Elsevier [10]

The FTIR patterns in Figure 13 clearly show all the relevant bonds associated with the hydroquinone molecule (i.e. the C-C stretches of the benzene ring, the C-H stretches and the C-O stretches), serving as proof that the molecule has been deposited whole instead of decomposing and leaving a different chemical species in the film. In addition to confirming the deposition of the intended organic molecules, FTIR spectra can also provide other information on the structure of the hybrid film. In the case of the ZnO:HQ films in Figure 13, the wide O-H peaks could be interpreted as a sign of incomplete surface coverage in the ZnO-HQ interface, as the peaks could originate from unreacted O-H bonds on the ZnO side of the interfaces. The main limitation of the FTIR technique in analyzing hybrid superlattices comes from the difficulty in obtaining observable peaks when the ratio of inorganic to organic layers is very high. Although the sensitivity of FTIR is generally very good, it is not unusual to have inorganic to organic ratios of 99:1 or higher, which is usually too high to confirm the character of organic layers using FTIR alone.

3.6 Summary & Outlook

The combination of ALD and MLD to deposit hybrid inorganic-organic superlattice thin films is a novel way to create materials with unusual combinations of properties and provides a relatively simple way of tailoring those properties to the needs of the application by manipulating the thickness and number of layers in the superlattice. Although the research into the possibilities of this method is still at a relatively early stage, the potential combinations of inorganic and organic layers are essentially limitless. Accordingly, ALD/MLD hybrid materials are drawing increasing interest from the research community and the technique has been used to develop materials for a variety of applications from flexible moisture barriers to electronic and thermoelectric applications. At the same time the ALD method itself has been experiencing increasing interest as a thin film deposition method capable of fabricating some of the more demanding parts of high-end electronics. Therefore, the use of ALD and MLD for hybrid film fabrication is sure to become more common as materials with ever more stringent property requirements become necessary for new applications.

Now that the groundwork of hybrid thin film fabrication has been mostly done by demonstrations of the feasibility of the ALD/MLD approach and the usage of numerous organic precursors, future work will no doubt be more application-oriented. The versatility of the ALD/MLD technique ensures its feasibility for a number of applications, but the most promising ones at the moment are electronic and optoelectronic applications as well as various barrier layers. The added flexibility from introduction of the organic species is likely to be the main advantage of hybrid films for the near future, but as the technique matures, the electronic applications should become more prominent along with other emerging applications.

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