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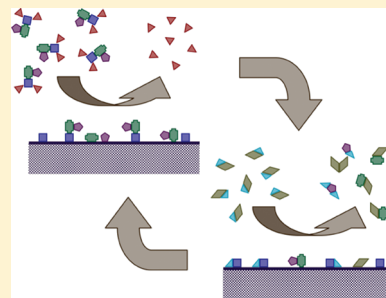
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The Surface Chemistry of Atomic Layer Depositions of Solid Thin Films

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ABSTRACT: Atomic layer deposition (ALD) is one of the most promising methodologies available for the growth of solid thin films conformally on complex topographies and with atomic-level control on thickness. However, as a chemical process, ALD can lead to the incorporation of impurities and to the growth of poor-quality films. Here we discuss some possible complications associated with the chemistry of ALD, including its ill-defined stoichiometry, the stepwise and extensive surface conversion possible with the ligands of most ALD metalorganic precursors, the need for the reduction or oxidation of the deposited elements, the poor understanding of the role of the coreactants, the dominant activity of specific minority surface sites in starting ALD processes, and the development of complex layered or three-dimensional structures within the deposited films. The resolution of these issues should help with the development of a more systematic approach for the selection of ALD precursors and for the design of ALD processes.



A wide variety of industrial processes require the deposition of thin films of many compositions on solid surfaces, of metals, oxides, oxinitrides, nitrides, sulfides, and chalcogenides, among others. In many instances, this is accomplished by physical means such as vapor or sputtering deposition, but if conformality to surfaces with complex topographies is required, chemical alternatives, which are isotropic in nature, may be preferred. Additional high atomic-level control on the thickness of the grown films in such chemical vapor deposition (CVD) methods can be achieved by atomic layer deposition (ALD), where the overall reaction is split into two self-limiting and complementary half steps.^{1,2} Ideally, ALD cycles consist of an initial exposure of the surface to the precursor used to deliver the main desired element (typically a metal atom) followed by reaction with a second agent to remove the excess ligands from the adsorbed precursor and to add any missing elements (oxygen, nitrogen, carbon, chalcogen atoms) to the solid film (Figure 1). The use of ALD is becoming ubiquitous in microelectronic manufacturing, and it is being extended to other fields such as the manufacturing of optical and magnetic devices, flat panel displays, and catalysts, and also to uses in energy conversion (solar cells), utilization (fuel cells), and storage (batteries and supercapacitors).

ALD does provide the control on film thickness and conformality required in many modern applications, but also suffers from a number of limitations. Because ALD is a chemical process, it can be complex, and it may include side, undesirable, reactions leading to the growth of films with poor structural, mechanical, or electrical properties, and also to the incorporation of detrimental impurities. Moreover, there is an intrinsic contradiction associated with the choice of chemical precursors for ALD: they need to be volatile but sturdy in order to facilitate their handling, yet they also need to be able to react once adsorbed on the surface where the film is to be grown. To fulfill these requirements, many of the early ALD processes

Idealized Atomic Layer Deposition (ALD) Cycle

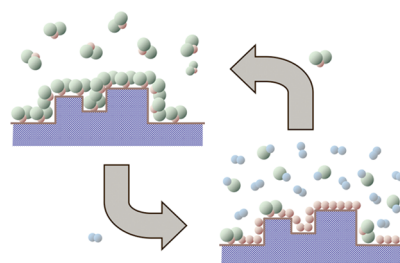


Figure 1. Schematic representation of idealized ALD processes, highlighting the self-limiting and complementary nature of the reactions involved in each of the two half-cycles. Typically, in modern ALD processes, the first half cycle uses a metalorganic precursor to deliver the main element to be deposited, whereas the reactant in the second half-cycle provides the missing elements for film growth and helps remove undesirable surface species.

relied on simple precursors such as metal halides.³ There were some great successes in depositing thin films with such precursors, but the range of elements that could be delivered was limited; it soon became clear that more complex compounds, including metalorganic complexes, needed to be considered as potential precursors if the range of elements to be delivered in ALD processes was to be widened. Much of the modern work in ALD is focused on designing, synthesizing, and testing new precursors for ALD. The idealized goal is to prepare complexes with ligands able to detach upon adsorption while retaining their molecular integrity in order to avoid the

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side reactions that may lead to the deposition of impurities on the growing films.

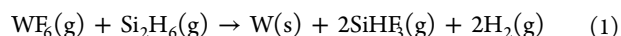
One problem with using metalorganic precursors in ALD is that, in many instances, their ligands are not very stable and may decompose easily upon thermal activation, possibly leading to a messy set of competing reactions on surfaces. The idealized picture of ALD described above is seldom fulfilled. As we discuss in this Perspective, the overall reactions responsible for film deposition often display ill-defined stoichiometries. In addition, the surface conversion of the main metalorganic ALD precursor may lead to the formation of a number of intermediates over a range of temperatures, with possible detrimental effects on the film growth. In some instances, the elements being deposited need to be reduced or oxidized, a process that may or may not happen directly during the adsorption of the precursor. The role of the second ALD agent is presumed to include cleaning of the surface from undesirable contaminants, but it is often not fully understood. ALD is likely to be initiated on specific minority surface sites, the identity of which is not always known, and those may exert great control on the evolution of the subsequent film growth. Finally, the deposited films may develop complex heterogeneous structures, possibly involving layered distributions of their constituent chemical elements, or even three-dimensional (3-D) structures. These issues need to be better characterized at a molecular level if a more systematic approach to the selection of ALD precursors and to the design of ALD processes is to become viable.⁴ Below, we briefly survey the state of our knowledge in terms of the surface chemistry associated with ALD processes, and provide a personal view of the outstanding issues in this area and of the future of this field.

To fulfill the promise of ALD as the thin film growth approach of the future, the surface chemistry involved needs to be better understood at a molecular level. That surface chemistry is likely to be much more complex than implied in the nominal description of ALD processes.

Reaction Stoichiometry. In most CVD and ALD processes, even the stoichiometry of the overall reaction is unknown. Only in a handful of cases has there been a concerted effort to identify the gas-phase byproducts of the reaction and, in those, multiple products have been often detected, in nonstoichiometric yields that may vary, in relative terms, depending on the reaction conditions. In the case of ALD, additional complications arise from the fact that the same products are sometimes detected in both halves of the cycle. In general, it appears that most CVD and ALD processes may not involve one single stoichiometric reaction but rather a mixture of competing pathways.

One case that nicely illustrates this issue is that of the deposition of tungsten films using tungsten hexafluoride and a silane, either SiH_4 or Si_2H_6 . Tungsten films are desirable in many applications, for making filaments and for filling contact holes and vias in microelectronic circuits, among others. The reaction between WF_6 and silane was initially introduced in CVD mode,⁵ but was later adapted to operate in ALD fashion

as well.⁶ With disilane, the stoichiometry of the overall reaction was initially suggested to be



However, early mass spectrometry experiments showed that such description is incomplete, since, in addition to SiHF_3 , SiH_4 and SiF_4 (as well as H_2 and HF) are also detected as gas-phase products in these processes depending on the experimental conditions used.⁷ Moreover, similar WF_6 /silane mixtures have been reported to lead to the growth of tungsten silicide films as well.⁸ On the basis of a series of elegant experiments involving quartz crystal microbalance (QCM) uptake measurements (Figure 2),^{9,10} surface characterization using infrared absorption⁶

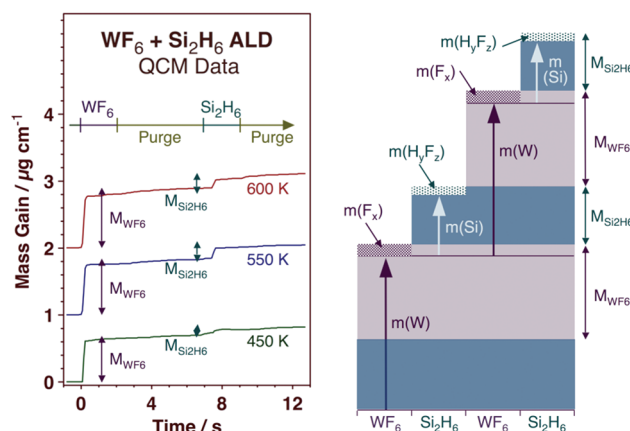
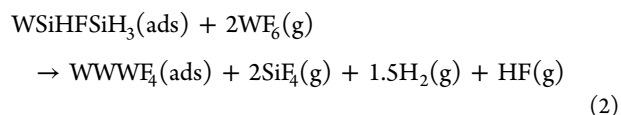


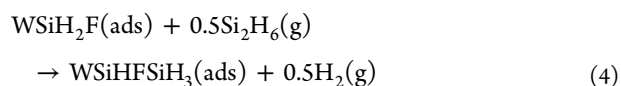
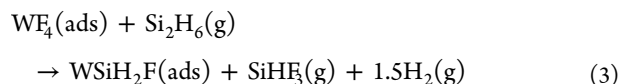
Figure 2. Results from a QCM study of the mechanism of the ALD of tungsten films using WF_6 and Si_2H_6 .⁹ Left: Experimental data for the mass gains monitored at 450, 550, and 600 K during a single ALD cycle. Right: Interpretation of the data, illustrating the sacrificial role of the silicon species: Si_2H_6 strips the $\text{WF}_x(\text{ads})$ of its fluorine atoms and creates new $\text{SiH}_x\text{F}_x(\text{ads})$ surface species, which then react with WF_6 in the next cycle to replenish the $\text{WF}_x(\text{ads})$ layer. Figure courtesy of Francois Fabreguette and Steven George, adapted from ref 9 with permission. Copyright 2005 Elsevier.

and Auger electron spectroscopies,^{11,12} and gas-phase product identification using mass spectrometry,^{10,12} George and co-workers have more recently proposed the following stoichiometries for this ALD process:

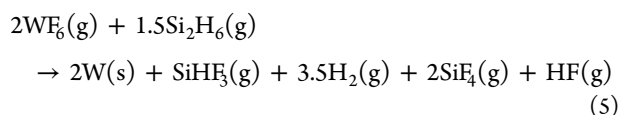
First half cycle:



Second half cycle:



Overall:



In this scheme, the two steps in the second half of the ALD cycle (3 and 4) compete with each other with relative rates controlled by the temperature of reaction, and the overall stoichiometry varies accordingly; eq 5 is only one representative case from all possible combinations. However, although this mechanism explains the formation of many of the surface and gas-phase species observed experimentally, by the own account of the authors of that work, it is still incomplete. For instance, SiF_2 species may also be produced at high temperatures, and, in the fluorosilane elimination chemistry, disilane insertion into Si–H bonds may introduce a CVD contribution on top of the W ALD. Furthermore, a similar ALD process with MoF_6 appears to follow a very different mechanism.¹³ Additional work is needed to pin down some important unanswered questions regarding the stoichiometry of this particular process. Much less is known about the stoichiometry of most other ALD processes.

The stoichiometry of ALD is usually not known, and likely to not be simple. Moreover, ALD precursors often decompose on the surface in several steps and over a wide range of temperatures, in processes that typically generate new surface intermediates. An assessment is needed of the effect of those intermediates on the rate of deposition and on the quality of the deposited films.

Stepwise Surface Decomposition of Precursors. Additional complications in CVD and ALD processes arise from the fact that the ligands in the precursors used for the deposition of the main element may display complex and stepwise surface chemistry, possibly encompassing a wide range of temperatures. This may be particularly true with the bidentate and π -bonded organic ligands predominantly used to deliver transition metal atoms.^{3,14} Such complex surface chemistry is illustrated by the behavior of copper acetamidinate on metal surfaces. Copper films are ideal for interconnects in microelectronic circuits, but their clean deposition has proven challenging. Amidinates are stable ligands that have shown great promise in ALD for the deposition of copper and a wide range of other metals.¹⁵ However, a recent surface-science study in our group has indicated that, upon activated adsorption on solid metal surfaces, copper(I)-*N,N'*-di-*sec*-butylacetamidinate undergoes a series of decomposition steps, including an initial dimer-to-monomer conversion, dissociation to a smaller acetamidinate around 200 K (which is then hydrogenated to *N-sec*-butylacetamidine at 300 K), and further conversion to acetonitrile and butene above 400 K (Figure 3).^{16–19}

The stepwise thermal decomposition of metalorganic precursors on surfaces contravenes the idealized vision of ALD processes, where the ligands are used to volatilize the metal atoms but are expected to remain intact during the first half of the cycle and to be removed cleanly by the second reactant in the second half. Their possible thermal decomposition on solid surfaces brings about a series of new questions, mostly related to the potential deposition of

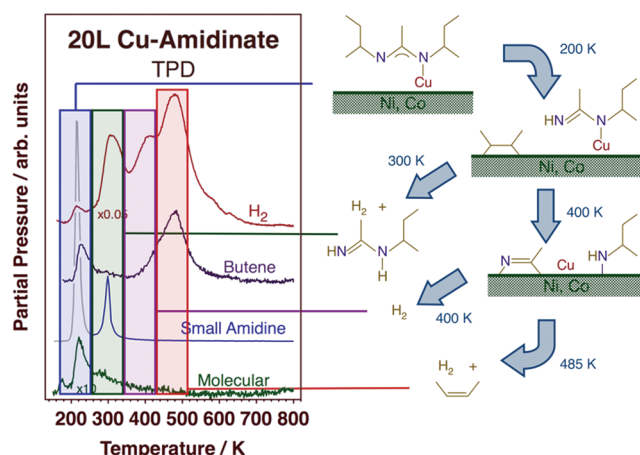


Figure 3. Left: TPD data from copper(I)-*N,N'*-di-*sec*-butylacetamidinate adsorbed on a Ni(110) surface.¹⁸ The data indicate stepwise decomposition, with sequential desorption of the molecular precursor, *N-sec*-butylacetamidine (labeled small amidine), and butene; H_2 desorption is also observed in all temperature ranges. Right: Proposed reaction mechanism indicating the key steps that account for the observed chemistry, including dissociation to a smaller acetamidinate around 200 K (and its hydrogenation to *N-sec*-butylacetamidine at 300 K), and further conversion to acetonitrile and butene above 400 K. Reproduced from ref 18 with permission. Copyright 2011 American Chemical Society.

impurities during film growth. On the other hand, some of the steps in reaction schemes such as that in Figure 3 may in fact be desirable. For instance, the two species that form in that case at approximately 200 K upon scission of the first C–N bond, a smaller amidinate and an olefin, may still be easily removable from the surface (a fraction of the new amidinate is hydrogenated to an amidine and released to the gas phase by 300 K), and, at the same time, their formation may reduce the footprint of the precursor on the surface, affording a higher packing density of metal atoms on the surface per cycle.

This balance between clean elimination of organic fragments and irreversible decomposition to hard-to-remove surface species is likely to shift to the latter with increasing temperature. Consequently, the key question in the design of ALD processes is the identification of where the threshold temperature is for fast and clean film deposition. In our example in Figure 3, it is possible that even the next step, the scission of a second C–N bond to produce acetonitrile and an amido surface intermediate, which occurs around 400 K, is still beneficial for film growth, but that after the elimination of butene seen at 485 K, the remaining surface species may lead to atomic carbon and nitrogen deposition on the surface. Also, continuous exposure of the surface to the precursor at such high temperatures may result in non-self-limiting behavior, and to the deposition of multiple layers of the metal in a single ALD cycle.¹⁷ It is quite possible that, in this copper deposition using the copper(I)-*N,N'*-di-*sec*-butylacetamidinate precursor, 485 K represents an upper temperature limit for the effective ALD of copper on nickel or cobalt surfaces. Of course, the exact ALD temperature range depends on the specific details of the process being considered, and can change with changing precursors (even with small changes in similar ligands) or with the nature of the surface: on copper substrates, for instance, where the growth must take place after deposition of the first layer, butene elimination occurs at 550 K, indicating that the ALD threshold temperature may be higher than on nickel.¹⁹

Systematic mechanistic studies such as this need to be performed to identify appropriate trends in terms of the surface chemistry and temperatures involved in ALD as a function of the ligands used in the precursors, and to provide some guiding principles on how to optimize their behavior.

Changes in Metal Oxidation State. In many ALD processes, the metal center in the precursor used for deposition is required to undergo an oxidation or reduction step. This is certainly the case when metallic films are to be deposited using non-zerovalent metalorganic complexes. In those cases, it is commonly believed that the second ALD agent is the one responsible for the promotion of the redox chemistry. However, recent surface-science studies on several different ALD processes have indicated that changes in oxidation state in the metal can occur during its own deposition, prior to the addition of the second reactant. For instance, it has been established that the Cu^+ atoms deposit by adsorption of copper acetamidate precursors on nickel, cobalt, or copper surfaces are reduced to their metallic state upon heating above 400 K, as the organic surface species resulting from activation of the amidinate ligands decompose into smaller surface species.^{17–19}

Another good example of this redox chemistry is seen in the ALD of early transition-metal nitrides. The deposition of titanium, zirconium, and hafnium nitrides, for instance, is typically performed by using M^{4+} complexes, even if the final films require an MN stoichiometry (with the metal in a +3 oxidation state). Such films have been used as protective hard coatings, and may also be employed as diffusion barriers in microelectronics. In the ALD of these materials, it has generally been assumed that it is the agent used in the second half-cycle, often ammonia, that reduces the metal center, but the chemistry by which this is supposed to occur has never been postulated. In fact, metal reduction may happen upon adsorption of the precursor itself. In the case of $\text{TiCl}_4 + \text{NH}_3$, for instance, we have shown that even though there is always a superficial Ti_3N_4 layer on top of the growing TiN film, some of the titanium atoms are reduced to the +3 state immediately upon the activated adsorption of the TiCl_4 agent, before any ammonia is added.^{4,20} Similar behavior has been seen with zirconium and tantalum precursors as well.²¹ As per the surface reactions that may lead to such metal reduction upon adsorption, newer gas-chromatography/mass-spectrometry (GC/MS) experiments with metal amido precursors suggest reductive-elimination and/or insertion steps. For instance, the evolution of tetramethylhydrazine, a product of the coupling of two dimethylamido ligands, has been identified during thermal activation of tetrakis(dimethylamido)titanium (TDMAT) by the data in Figure 4.^{22,23} It is quite possible that similar reductive elimination steps are also responsible for the reduction of late transition metals such as copper during their deposition using metalorganic complexes, as in the acetamidate example discussed above.

Oxidation state changes may be required for the deposition of metal oxides as well. One example of this is the case of the growth of In_2O_3 films using $\text{In}(\text{+1})$ cyclopentadienyl complexes.²⁴ In fact, even if there is no requirement for net oxidation state changes in the overall stoichiometry of ALD processes, redox reactions may still occur in each half cycle. This may be the case during the ALD of oxides of early transition metals such as zirconium or hafnium, which have gained recent interest as high k materials. Those oxides can be deposited by using the same precursors employed in metal nitride film growth, amido complexes in particular, and water

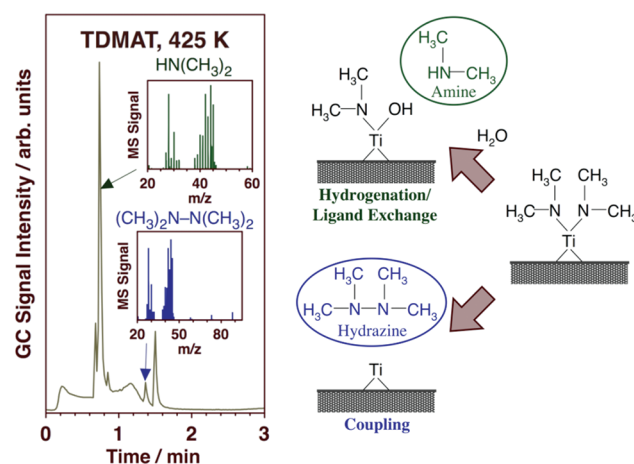


Figure 4. Left: GC/MS characterization of the gas-phase products that form during the thermal activation of TDMAT on the silicon oxide surfaces of a glass vial at 425 K.²³ The mainframe reports the main GC trace, whereas the insets show the mass spectra of the most important products. Right: Reaction scheme to account for those products: dimethylamine from hydrogenation of a single dimethylamido ligand, and tetramethylhydrazine from coupling of two of the ligands. The latter reductive elimination step can explain the reduction of the Ti center required to ultimately make TiN films. Adapted from ref 23 with permission. Copyright 2011 The Electrochemical Society.

(or ozone) instead of ammonia as the second reactant.^{25,26} In principle, since in both the initial precursors (tetrakis(ethylmethyamido)hafnium, for instance) and the final oxide films the metal is in a +4 oxidation state, the overall chemistry could be explained simply in terms of ligand exchange steps where water molecules replace the amido ligands.²⁷ That may in fact be the dominant mechanism in CVD processes.²² However, in ALD, the amido precursors can undergo significant surface chemistry during their adsorption in the first half cycle, including the reducing reactions discussed above.^{22,23} It is therefore possible that even in this case redox reactions may take place during both halves of the deposition cycles.

Role of the Second ALD Agent. If the redox chemistry in many ALD processes already occurs in the first half-cycle, during the activated adsorption of the metal precursor, it is worth asking what the role of the second ALD agent may be. One obvious function is to provide the missing element(s) required to deposit metal nitrides, oxides, carbides, sulfides, phosphides, and so forth. This has clearly been shown with ammonia and with water, for metal nitride and metal oxide deposition, respectively, even in cases where the metal precursor already contains all needed elements. With amido precursors, for instance, ammonia has been shown to displace some of the ligands via transamination steps and to provide the nitrogen that is ultimately incorporated into the metal nitride films.^{28,29} Similar steps with water may also lead to the generation of hydroxyl groups on the surface, which may then play a central role in the ligand displacement mechanism.³⁰

The second ALD reactant can also inhibit the decomposition of the surface species that form upon activation of the metal precursor, and/or modify the selectivity of the surface reactions available to those toward more benign pathways. For instance, the addition of ammonia during pentakis(dimethylamido)tantalum (PDMAT) adsorption on tantalum substrates was shown to increase the formation of dimethylamine at the expense of methane formation.³¹ The first, a hydrogenation product, is more desirable than the second, since methane

production involves the scission of C–N bonds and possibly leads to the formation of highly dehydrogenated and hard-to-remove nitrile surface species. It should be mentioned, however, that this effect may be more relevant in CVD processes, where both reactants are fed simultaneously during film deposition. In ALD, such effects may at best be indirect, induced by the surface species that may form from activation of the second reactant, which may modify the adsorption process of the metal precursor in the following ALD half-cycle. Some inferences have been made along these lines concerning a few ALD processes, and the suggestion has been made that the second reactant may precondition the surface for better film growth.³² However, to the best of our knowledge, no direct evidence for such behavior has been demonstrated to date.

It is often believed that the redox chemistry required in many ALD processes is promoted by the second reactant, but recent evidence suggests that, at least in some instances, it may occur upon adsorption of the main precursor instead. The second reagent is still required for surface cleaning and to provide any missing elements, but its surface chemistry has only been cursory outlined.

Another key role of the second reactant in ALD is to clean up the surface of any undesirable organic species in order to prepare it for the next ALD cycle and to prevent the incorporation of impurities in the growing film. Hydrogen-containing reactants, including H_2 , may hydrogenate unsaturated or surface-coordinated organic ligands such as σ -bonded alkyls, alkoxides or amido groups, bidentate diketones, amidinates or guanidates, or π -bonded cyclopentadienyls or aryls.³² However, this type of hydrogenation reaction has often proven inefficient, perhaps because the hydrogenating agents used (H_2 , NH_3) are sometimes difficult to activate on the surface,³¹ or because, once activated, they easily and reversibly desorb.^{17,19} With more elaborate reducing agents such as silanes, boranes, or phosphides, undesirable elements may also be deposited on the surface. Plasmas are employed in many instances to generate highly reactive reducing agents,³³ but plasma chemistry is in general more difficult to control than thermal processes. Almost no fundamental studies have been performed on any of these hydrogenation reactions in connection with ALD processes, even though extensive surface-science work is available in this area already.^{34,35}

Alternatively, organic ligands may be burned off the surface by using an oxidizing agent such as O_2 , ozone, or water. If the final films to be grown are metal oxides such as Al_2O_3 or HfO_2 , the oxidant may serve as the source of the oxygen as well,^{30,36–38} although in some instances the two functions—ligand removal from the surface and metal oxidation—require different chemicals.²⁴ On the other hand, if reduced metal films are what is desired, the use of strong oxidants may be contraindicated, except perhaps in cases of hard-to-oxidize late

transition metals such as platinum and other noble metals.^{39,40} An interesting mechanistic twist to these oxidation processes is that, often, the gas-phase oxidation products (CO_2 and H_2O) are seen during both halves of the ALD cycle (Figure 5). This

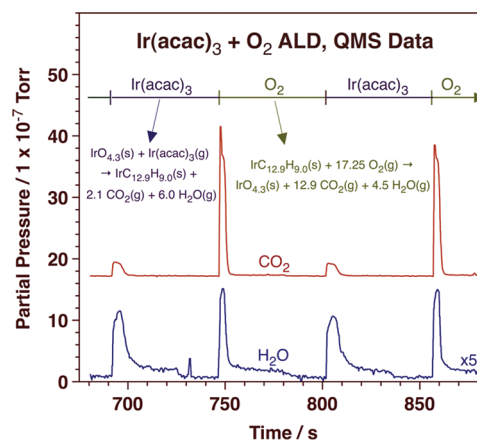


Figure 5. In-situ mass spectra of the gas-phase products from ALD of iridium oxide films on a glass substrate at 575 K using $Ir(acac)_3$ and O_2 .⁴⁰ Shown are the traces for the evolution of CO_2 (44 amu) and H_2O (18 amu) during the dosing of the two reactants in alternating cycles, as indicated by the timeline on the top (in pulses 20 s long, followed by pumping). To note here is the evolution of both oxidation products—water and carbon dioxide—in both halves of the ALD cycle, implying the complex stoichiometries for each half cycle provided in the figure. Figure courtesy of Kjell Knapas and Mikko Ritala, adapted from ref 40 with permission. Copyright 2011 American Chemical Society.

implies that some reducible species must remain on the surface after the end of the oxidant pulse, ready to react with the metal precursor in the next half cycle. Several surface species have been proposed in mechanistic studies of these processes, including coordinatively unsaturated metal oxide sites, chemisorbed oxygen, and hydroxyl or carbonate groups,^{39,40} but direct evidence for those is still lacking. Also, in the case of platinum deposition using (trimethyl)methylcyclopentadienyl platinum(IV) + O_2 , methane formation has been observed (in addition to the expected CO_2 and H_2O combustion products).^{41,42} It has been suggested that such CH_4 is formed via displacement of methyl groups in the precursor by surface hydroxyl groups, potentially made during the previous oxidation half-cycle (either as intermediates toward water production or by water decomposition). One possible consequence of all this chemistry is that each half reaction may not be entirely self-limiting, and that a continuous CVD process may be operational on top of the ALD cycle. It should also be noted that most of the chemistry discussed above has been inferred from mass spectrometry detection of gas products, and awaits surface-science corroboration.

Surface Reactivity and Nature of the Grown Films. Another key aspect of the chemistry of ALD processes is the role that the underlying surface plays in initiating the film deposition, controlling the deposition rate, and defining the nature of the grown films. In this ALD chemistry, the surface could be viewed as another reactant. During the deposition of metal films (or if the initial substrate is metallic), the dissociative uptake of the precursor may be controlled by the ability of that metal to adsorb and/or transform the associated organic ligands. The delocalized nature of the valence electrons

(conduction band) of metals means that these reactions may differ from those seen in discrete molecules.^{34,35} On the other hand, on oxides and other insulating and semiconductor surfaces, the bonds within the atoms of the solid may be more covalent in nature, and the interaction between surface sites and adsorbates more localized. In those instances, bonding to the surface may resemble bonding in isolated compounds, may involve specific surface sites, and may be described by known steps in discrete molecular systems. Minority sites may dominate the initial deposition chemistry, a fact that sometimes manifests itself by induction periods before film growth is observed.

In this regard, much has been made of the idea that hydroxyl surface groups may be the initiating sites for ALD on most oxide substrates. Direct evidence of this fact has been difficult to obtain, but the collective literature on this point is fairly compulsive.^{36,43–46} Typically, the reactivity of OH surface groups with metal complexes is viewed as a displacement reaction, where the coordination of the metal to the surface occurs via bonding with the electron lone pair of the oxygen atom and is accompanied by the release of another ligand from the original precursor (perhaps after hydrogen transfer from the OH moiety). Special surface groups such as these hydroxyl species act as nucleation sites, and can direct the subsequent progress of the film growth, possibly causing preferential 3-D deposition around them. In more general terms, from a kinetic standpoint, the morphology of the growing films may be defined by the rate of reactivity of the precursor on the initial substrate relative to that on the surface of the deposited material: a faster deposition on the former may lead to smooth layer-by-layer deposition, at least in the initial stages, whereas a faster rate on the latter may lead to 3-D growth and a more granular texture of the films instead. These effects are often glossed over in ALD studies, although a few clever experiments have been performed to address the issue of film nucleation.^{3,47,48}

Minority surface sites may dominate the initial chemistry of deposition and define the nature of the films. Those may grow in 3-D fashion, and also develop complex spatial profiles in terms of chemical composition.

Finally, compositional and structural changes may occur within the top few layers of the growing films as they are deposited, sometimes leading to the development of chemically nonuniform and complex structures. The case of the continuous presence of a Ti_3N_4 layer on top of TiN films grown by using $\text{TiCl}_4 + \text{NH}_3$ cited earlier in this Perspective provides one example of this behavior.^{4,20} We have recently reported on another case where manganese deposition on silicon wafers leads to a layered mixed structure consisting of sequential thin slabs of manganese silicide, mixtures of manganese and silicon oxides, and manganese silicate on top of the underlying silicon substrate (Figure 6).^{49,50} The formation of such complex structures implies atomic diffusion from the surface into the bulk to depths of up to a few nanometers, a phenomenon that may be aided by the chemical gradients set by the adsorbates and deposition process. The nature of the final manganese-containing films is of great

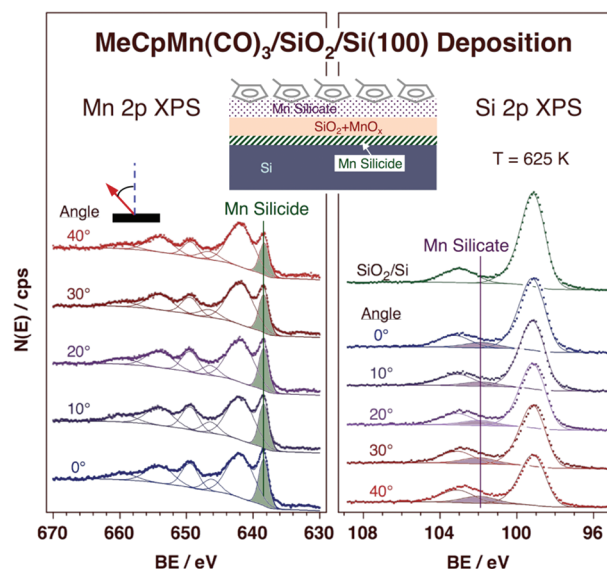


Figure 6. Mn 2p (left) and Si 2p (right) XPS as a function of detection (takeoff) angle for films obtained by dosing MeCpMn(CO)_3 on a $\text{SiO}_2/\text{Si}(100)$ wafer at 625 K.⁴⁹ In addition to silicon and manganese oxides, new signals were identified in these data for manganese silicide and for manganese silicate. The angular dependence of the relative intensities of the different XPS peaks points to the formation of the layered structure depicted in the figure. Adapted from ref 49 with permission. Copyright 2011 American Chemical Society.

relevance to their performance, as self-forming diffusion barriers, as materials for supercapacitors and batteries, for catalysis, and to take advantage of its magnetoresistance effect. Similar arguments may apply to films of other materials.

Experimental Tools. The discussion provided above is intended to point to the relevance of the mechanistic details of the surface chemistry of ALD to the overall performance of these film-deposition processes. Knowledge on the mechanism of ALD reactions on surfaces should help in the selection of better precursors and in the optimization of their performance. In spite of the fast-growing importance of ALD in many industrial applications, though, comparatively little work is being directed at elucidating such mechanistic details. These are not simple systems, but there are already a number of experimental and theoretical tools available to tackle the type of questions posed in this Perspective.

Much of the ALD mechanistic information obtained to date has relied on the use of QCM to follow the changes in mass that occur on the surface upon exposure to each of the reactants in the ALD cycle.^{51,52} An example of the type of data obtained from such studies is provided in Figure 2.⁹ QCM measurements are quite valuable, but are limited by the fact that they do not provide any chemically specific information. Changes in mass on the surface can in principle be interpreted as due to the deposition or desorption of individual surface species, but this association is often difficult to make in ALD processes because the reactions may not be stoichiometric.

Another useful, and complementary, technique is mass spectrometry, used for the detection of the products that desorb into the gas phase.⁵¹ Figure 5 shows an example of how such approach may be used in situ during each step of the ALD process.⁴⁰ One limitation here is that it may be difficult to differentiate among the mass spectrometry signals of the several desorbing species that may be produced from the complex chemistry expected with many organic ligands, although that

limitation may be addressed by performing ex-situ analysis of the gas products of ALD using GC/MS, as illustrated in Figure 4.^{22,23} It is also important to keep in mind that some of the gas-phase species generated during ALD processes such as radicals may not be stable and may undergo further conversion in the gas phase, upon collision with the walls of the reactor, or in the ionizer of the mass spectrometer before detection. Another typical in situ surface-science application of mass spectrometry that has yet to find widespread use in the study of ALD chemistry is temperature-programmed desorption (TPD), where the gas-phase products from surface reactions are recorded as the temperature of the surface is ramped;^{53,54} an example of data obtained this way is provided in Figure 3.¹⁸ A third option is to use mass spectrometry in molecular beam studies as a way to gather more accurate isothermal kinetic information on individual ALD reactions.³¹

Many surface-science techniques are already available for the study of the chemistry of ALD. The field could greatly benefit from engaging the surface-science community and enticing it to work toward a better understanding of the mechanisms of ALD reactions.

It is more difficult to characterize the chemical nature of the species that form on the surface during each step of ALD processes. The most common spectroscopy used for this purpose has been infrared absorption spectroscopy, a versatile technique that may be implemented in situ in ALD reactors, and that can be made to operate in transmission, reflection-absorption (RAIRS), or attenuated total reflection (ATR) modes.^{41,55,56} The vibrational information provided by infrared absorption spectroscopy is quite sensitive to the molecular details of the species being probed, and is ideally suited to follow subtle chemical or structural changes in organic fragments.⁵⁷ An example of the detailed chemistry that can be established using this technique is illustrated by the data in Figure 7, which show that β -hydride elimination steps on amido ligands occurs selectively at ethyl (versus methyl) moieties.⁵⁵ It is unfortunate that, to date, infrared absorption spectroscopy has not lived up to its potential in ALD studies: only a few systems have been characterized this way, and the results in most instances have been inconclusive. Much more effort is needed to improve on the performance of infrared absorption spectroscopy in ALD studies.

Even though ALD-grown films are sometimes analyzed post mortem by other surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Rutherford backscattering (RBS), low-energy ion scattering (LEIS), and secondary ion mass spectrometry (SIMS), those techniques have seldom been used for mechanistic studies of ALD processes. This is at present an undeveloped area of research. The potential is there: many surface-sensitive techniques are readily available for this type of study, and methodology for the characterization of analogous problems in heterogeneous catalysis has been widely developed and tested.^{58,59} High-probability reactions can be easily studied directly in the ultrahigh vacuum (UHV) environments required for the operation of the majority of modern surface-sensitive

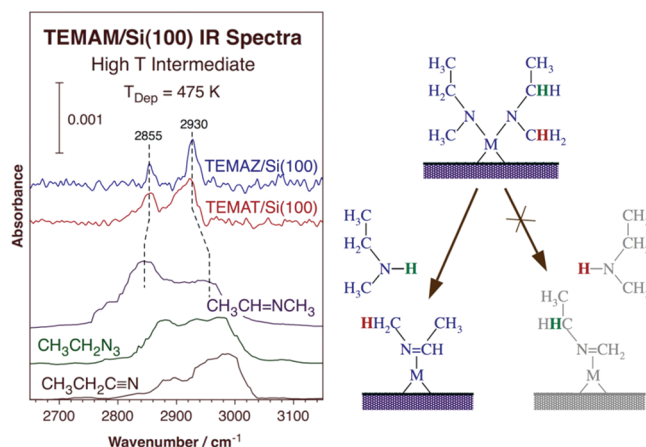


Figure 7. ATR infrared absorption spectra in the C–H stretching vibrational region for tetrakis(ethylmethylamido) zirconium (TEMAZ) and titanium (TEMAT) precursors adsorbed on Si(100) at 475 K.⁵⁵ Comparison with reference spectra (the three bottom traces) led to the assignment of the surface species to adsorbed N-methylethylidenimine. This indicates the occurrence of a β -hydride elimination step selectively at the ethyl moiety of the ethylmethylamido ligand, as illustrated in the reaction scheme shown on the right. Reproduced from ref 55 with permission. Copyright 2009 American Chemical Society.

spectroscopies, but even low-probability reactions requiring high gas exposures, as is often the case in ALD, can be probed in instruments equipped with appropriate reactors coupled via sample transferring mechanisms.⁶⁰ In this Perspective, we have identified a number of critical chemical questions in terms of reaction stoichiometry, stepwise thermal decomposition of precursors, redox requirements, the role of the auxiliary ALD reagents, surface active sites, and the chemical nature of the resulting films in need of answers. Those would certainly help enormously in the development of a systematic approach to the selection of ALD precursors and to the design of ALD processes. We encourage the surface-science community to rise to this challenge and offer its expertise to resolve these issues.

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Notes

The authors declare no competing financial interest.

Biography

Francisco Zaera received his Ph.D. from the University of California, Berkeley, in 1984, and worked at Brookhaven National Laboratory before joining the University of California, Riverside, where he is presently a Distinguished Professor of Chemistry. He is also a Senior Editor for *The Journal of Physical Chemistry*. More information about Prof. Zaera can be found at <http://research.chem.ucr.edu/groups/zaera/>.

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