

The surface chemistry of thin film atomic layer deposition (ALD) processes for electronic device manufacturing

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Atomic layer deposition (ALD) is poised to become one of the dominant technologies for the growth of nanometer-thick conformal films in microelectronics processing. ALD is particularly suited for the deposition of isotropic films on complex topographies under mild conditions and with monolayer control. However, many questions concerning the underlying surface chemistry need to be answered before this film deposition methodology can find widespread use. Here we highlight some recent examples of surface-science studies of ALD processes aimed to provide a basic understanding of that chemistry.

Introduction

Conformal films, that is, thin films that closely follow the shape of the underlying structures they cover, are crucial components in a variety of modern technologies, and are widely used as optical, optoelectronic and magnetic storage devices, tribological, heat and corrosion barriers, biocompatible prostheses, membranes, and catalysts. They are particularly

important in microelectronics, where they are used as conductor or insulator layers and as diffusion, adhesion, or protection barriers; the growth of such thin films is required to build capacitors, metal interconnects, diodes, transistors, and other elements within integrated circuits. In the past film growth for these applications has relied on the use of physical deposition methods, but those, being intrinsically directional, are ill suited for the requirements of modern electronic devices, which are now routinely prepared with sub-100 nm individual structures of very high aspect ratios and many narrow

and deep holes and trenches. Chemical-based processes, which are intrinsically isotropic, can better handle film deposition on rough surfaces.

One promising method for the chemical growth of thin films is atomic layer deposition (ALD).^{1,2} In ALD, two self-limiting and complementary reactions are used sequentially and in alternating fashion to slowly build up solid films one monolayer at the time.^{3–7} ALD was in fact developed in the late 1970s under the name of atomic layer epitaxy (ALE) for the manufacturing of flat-panel displays and the preparation of III–V compounds, but really took off in the mid-1990s in connection with the manufacturing of high aspect ratio integrated circuits. ALD offers many advantages over other film growth processes, including great control over film thickness and lax requirements in terms of reactor design and deposition conditions, but also presents some limitations, mostly associated with the incorporation of impurities and the limited control over film crystallinity.^{4,8} These problems may be addressed by choosing appropriate chemical precursors and deposition conditions,⁹ but that requires a good understanding of the surface chemistry involved. Little work has been carried out to provide that basic knowledge to date, even if that is starting to change. Here we introduce a few examples of key ALD processes of interest to the microelectronics industry to illustrate the need for more fundamental surface chemistry studies.

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Francisco Zaera was born in 1958, and received his Licenciata and PhD degrees in 1979 and 1984 from the Simón Bolívar University in Caracas, Venezuela and the University of California, Berkeley, respectively. After spending two and a half years as an Assistant Chemist at Brookhaven National Laboratory, he moved to his present position as professor of chemistry at the University of California, Riverside in 1986. Prof. Zaera has received several awards, including the 2001 American Chemical Society George A. Olah Award in Hydrocarbon or Petroleum Chemistry, the 2003 North American Catalysis Society Paul H. Emmett Award, and the 2008 American Chemical Society Arthur W. Adamson Award for Distinguished Service in the Advancement of Surface Chemistry. He has held several editorial responsibilities, including his present post as Senior Editor of Journal of Physical Chemistry, and several professional offices. Prof. Zaera has published over 230 publications, and presented over 150 invited talks. His research interests are in the areas of surface chemistry, with emphasis in heterogeneous catalysis and materials chemistry.

Deposition of metal films

The deposition of thin transition-metal films is required at several stages of microelectronics manufacturing, for use as contact plugs, in ferroelectric (FRAM) and dynamic (DRAM) random access memories, and for dual-gate metal-oxide-semiconductor field effect transistors (MOSFETs), diffusion barriers, and interconnects.^{3,4,8,10,11} Examples of metal ALD processes well discussed in the literature include those for the growth of tungsten films using WF_6 and Si_2H_6 ,¹² and of other transition metals using organometallic precursors and either an oxidizing⁸ or a reducing³ agent.

One metal ALD application that has gained interest recently is for electrical interconnects. In the past those have been made out of aluminium, but more recently copper has drawn much attention because of its lower bulk resistivity and superior electromigration resistance.¹³ The deposition of thin copper seed layers could perhaps be best accomplished by ALD,¹⁴ but, to date, there are no copper precursors available to produce films with acceptable adhesion properties.¹⁵ Even though several families of organo-copper organometallic compounds have been advanced for this application (Fig. 1),^{3,8,16–18} they all suffer from severe shortcomings. One main issue here, as with most organometallic precursors, is the need to avoid ligand decomposition on the surface, because that usually leads to the incorporation of impurities in the growing film and destroys the ALD-type growth and conformality. For instance, in the case of copper acetamidinates (Fig. 1), which can be used alternately with

hydrogen to deposit Cu films of reasonably good quality,^{19,20} our initial studies using temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) have suggested that alkyl substituents with β hydrogens may be prone to dehydrogenation reactions to produce olefins and surface acetamide moieties (Fig. 2).²¹ This is undesirable, but could potentially be avoided by blocking all β positions in the alkyl moieties of the ligand, a hypothesis that remains to be tested.

Another option for copper deposition is to use compounds based on the well-established CupraSelect® Air Products copper CVD precursor 1,1,1,5,5,5-hexafluoro-2,4-pentanedionatocopper(i)-trimethylvinylsilane, or $\text{Cu}(\text{hfac})(\text{tmvs})$ for short (Fig. 1).²² The problem in this case is that the original compound undergoes facile disproportionation, a reaction highly desirable for regular CVD processes but which limits its use for ALD applications. To address this limitation, the Air Products team has recently developed new compounds where the *tmvs* and *hfac* ligands are linked *via* a small hydrocarbon chain (Fig. 1) in the hope of preventing the easy thermal release of the former moiety.²³ Again, the surface chemistry of the new compounds has by and large been untested as yet.

A more general issue related to the surface chemistry of copper ALD (and CVD) refers to the relative advantages and disadvantages of using $\text{Cu}(\text{i})$ vs. $\text{Cu}(\text{ii})$ complexes.²⁴ $\text{Cu}(\text{i})$ compounds tend to disproportionate easily, which is why they have been chosen for low-temperature CVD processes.^{25,26} However, that disproportionation wastes

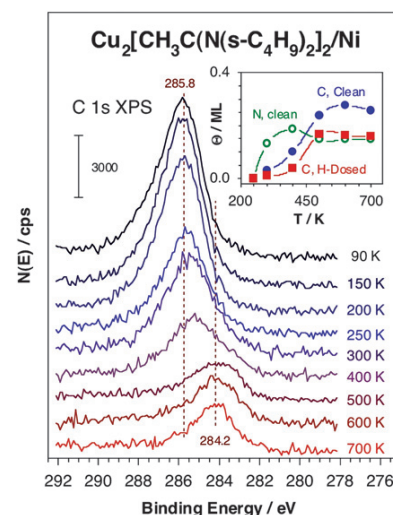


Fig. 2 X-Ray photoelectron spectra (XPS) data from bis[(*N,N'*-di-*sec*-butylacetamidinate)-Cu] adsorbed on a nickel surface.²¹ Main frame: C 1s XPS spectra as a function of annealing temperature showing both the loss of signal intensity above 200 K due to molecular desorption and a shift in the remaining peak because of further surface conversion. Inset: estimated coverages of the new surface species identified by XPS. Three things have become apparent from the surface-science data: (1) the amidine ligands already detach from the Cu complex by 200 K; (2) they decompose at ~300 K to form *sec*-butyl groups, which later dehydrogenate to produce butene; and (3) hydrogen pre-dosing leads to the inhibition of these reactions, delaying them to higher temperatures and lowering their yields.

half of the reactant, and can also lead to undesirable side reactions. More importantly, it provides a channel for continuous reactivity, thus forfeiting the self-limiting nature of ALD processes. In terms of $\text{Cu}(\text{ii})$ precursors, they are often more stable than their $\text{Cu}(\text{i})$ counterparts, but, accordingly, require higher temperatures for activation.^{27,28} High process temperatures are in general not desirable, but in this case may help inhibit the decomposition of the copper complex, thus requiring a separate hydrogen treatment for the removal of the ligands (a plus in ALD).²⁹ A full assessment of the pros and cons of using the different $\text{Cu}(\text{i})$ and $\text{Cu}(\text{ii})$ precursors will require more basic surface chemistry studies.

Finally, the use of fluorinated ligands has been a common way to make copper compounds, which tend to be quite heavy, volatile enough for practical applications

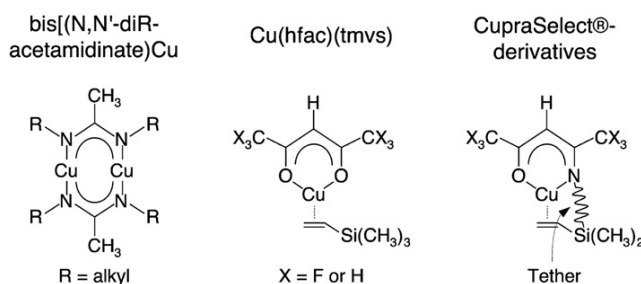


Fig. 1 Selected organocopper precursors for the atomic layer deposition (ALD) of copper films. From left to right: copper amidinates,^{19,78} Air Products' CupraSelect® copper CVD precursor (1,1,1,5,5,5-hexafluoro-2,4-pentanedionatocopper(i)-trimethylvinylsilane),^{22,30} and tethered derivatives of that CupraSelect® compound.²³ The surface chemistry of these compounds is by and large still unknown.

in ALD.³⁰ However, that sometimes opens new undesirable reaction channels, in particular surface etching. The specific nature of the fluorinated groups that leads to such etching has not yet been determined, though, and some fluorinated copper complexes appear to induce minimal surface damage.²⁴ Other volatile non-fluorinated compounds have been designed recently for these applications as well.¹⁸ It would be useful to know about the surface reactivity of all those compounds in order to make educated decisions on their potential for ALD and on how to modify them to improve their performance.

Deposition of metal oxides

There is also renewed interest in the growth of high-*k* dielectric thin films by ALD to replace the silicon oxide layers used nowadays in devices such as complementary metal–oxide–semiconductor (CMOS) integrated circuits, high-performance MOSFETs, and DRAMs.^{31–33} This is in fact the current major application of ALD nowadays. The semiconductor industry has narrowed down the choices for this to a few metal oxides, most notably those of hafnium.^{34,35} However, a number of practical issues regarding the optimal growth of films of those materials using ALD remain unresolved.⁵ As in the case of metal ALD, one of the main problems here is the incorporation of impurities during deposition due to the decomposition of the precursor ligands on the surface. Many types of precursors have been tested for this application, including metal halides,³⁶ alkylamides,³⁷ alkoxides,³⁸ and cyclopentadienyl complexes,³⁹ but no clean chemistry, with no side reactions involving the ligands, has been identified yet. The surface conversion of most of the precursors available is at present poorly understood.

Particular effort has been placed on the use of metal alkylamides. Metal alkylamides tend to have high vapor pressures, require low film growth temperatures, produce non-corrosive byproducts, and sometimes deposit fewer impurities than metal halides (carbon and hydrogen instead of halogen atoms).^{37,40} They also seem to produce smoother films, lead to better growth rates, and be reactive in desirable ALD temperature windows.⁴¹

However, those molecules tend to be unstable at the temperatures needed for deposition, and the final quality of the films they produce depends critically on such process parameters as the length and pressure of the pulses and the deposition temperature used.^{42,43} No comprehensive molecular understanding is available at present of the origin of these variations, but incomplete reaction between the adsorbed alkylamide species and the oxidant in the second half-cycle of the ALD processes has been proposed to be the likely reason for the increased impurity content and deterioration of the film properties observed at low temperatures.^{44,45} Results from studies using secondary ion mass spectrometry (SIMS) suggest that thermal decomposition of the precursor may be the main culprit at higher temperatures.⁴³

One limitation with the alkylamide precursors is the relatively low strength of their Hf–N bonds, which restricts the ALD growth temperature to 250–300 °C.³⁷ Quantum mechanics calculations have suggested that activation of these compounds occurs *via* the formation of rings involving one or two surface atoms, the hafnium center, and either oxygen or nitrogen atoms (Fig. 3),⁴⁶ but no evidence is available yet to support this claim. Also, it is not clear what the subsequent surface chemistry may be, and alternative mechanisms have been advanced in the organometallic literature for the decomposition of these alkylamide metal precursors,^{47,48} even if those have not yet

been properly considered in ALD studies. Answering these questions should help better address the design of proper precursors for this application.

New and novel non-amide precursors have also been introduced in recent years to address the limitations of the alkylamides. Some of those have displayed excellent self-limiting deposition behavior at high temperatures with negligible incorporation of impurities,^{39,49} but they still have the potential of depositing lower quality films if the deposition conditions are changed; the mechanism by which they decompose on the surface and leave the metal behind is still not known. The availability of new families of precursors certainly widens the options for high-*k* dielectrics film growth, but also adds to the complexity of the problem. Understanding the surface chemistry of all these hafnium precursors (and those of other metals) could help decide on their relative promise in ALD applications.

Another aspect of the ALD of metal oxides to which fundamental surface chemistry studies could contribute is that of the initial nucleation of the films on the surface of the substrate.^{33,50} One point that has been briefly discussed in the literature in connection with this issue is that of the role of hydroxyl surface groups in facilitating the initial activation of the metal precursor.^{46,51} In general an enhanced reactivity has been observed on OH-terminated surfaces with a variety of precursors,^{41,52} even if the opposite trend has also been reported on occasion.⁵³ In

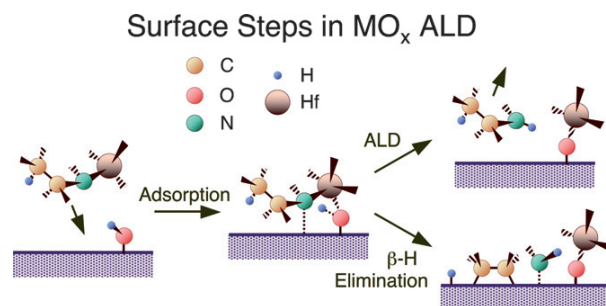


Fig. 3 Schematic representation of some of the proposed key surface elementary steps during the adsorption of hafnium alkylamide ALD precursors on hydroxyl-terminated surfaces. Based on calculations for similar systems, adsorption is proposed to take place *via* two dative bonds, one from the oxygen of the surface OH groups to the metal center and another from the nitrogen of one of the ligands of the precursor to the surface. Also shown is the potential competition between the desirable reductive elimination of one of the amine moieties with hydrogen *versus* an undesirable β -hydride elimination side step. These are at present only hypotheses in need of corroboration; understanding the underlying chemistry of ALD at this level may help design better precursors and choose better operating conditions.

fact, based on *in situ* infrared spectroscopy studies, it has been proposed that on hydrogen-terminated silicon surfaces the observed induction period in the initial stages of deposition may be due to a slow replacement of Si–H surface species by Si–OH groups.⁵⁴ The initial reaction of the precursor with the surface may take place by interactions of the sort illustrated in Fig. 3, but direct confirmation of ideas like this is still in the future. Resolution of this issue may lead to new proposals on preconditioning of the surface prior to ALD film growth. Finally, deposition of mixed oxides, as recently proposed, requires a further understanding of the interplay of the sets of precursors to be used. That increases the complexity of the chemistry involved, but also adds much flexibility to the design of ALD processes.^{55,56}

Deposition of metal nitrides

A third area of active research in ALD for microelectronics applications is in the deposition of metal nitride films.^{4,8} Specifically, titanium and tantalum nitride layers are used as barriers to prevent the diffusion of copper into the silicon substrate.^{15,57,58} The ALD of those films has been studied in great detail already by using a wide variety of techniques, including quartz crystal microbalances (QCM), Fourier transform infrared spectroscopy (FTIR), and mass spectrometry (MS), but some problems have not yet been resolved. In the case of TaN, perhaps the most promising barrier material so far, the remaining difficulties include the need to deposit a Ta layer prior to the TaN film growth to improve adhesion, the required use of a strong reducing agent, and the difficulty in controlling the stoichiometry and crystallinity of the growing material.^{10,59} A particularly important issue here has to do with the possible growth of two different TaN *vs.* Ta₃N₅ crystalline phases, something that can be easily assessed by X-ray diffraction techniques.^{60,61} Moreover, as with most other ALD processes, there is the issue of impurities incorporation, which in this case leads to films with unacceptably high resistivities.^{59,60,62}

The growth of titanium nitride from TiCl₄ and NH₃, arguably one of the most

studied ALD processes of all,^{63–66} can serve to illustrate how far we are still from understanding the surface chemistry of ALD systems. The most important practical limitations in this case are the modest reactivity of the ammonia used as the second reactant, which leads to slow deposition rates, and the 1–2% residual chlorine that is always incorporated in the growing films. Many processes are also inadvertently designed to run in a non-ALD mode, perhaps because of insufficient precursor exposure, insufficient purging or pumping between half cycles, and/or too low or too high deposition temperatures. All those problems could be better addressed if a more complete understanding of the underlying chemistry were available. For instance, it is surprising that the identities of both the reducing agent and the oxidation byproducts of the overall process have not yet been established.^{4,67} In connection with this, our recent work using XPS has pointed to the formation of a thin Ti₃N₄ layer on top of the growing TiN film all throughout the deposition process, implying that reduction may occur during the TiCl₄, not ammonia, half-cycle (Fig. 4).^{21,68,69}

It is important to be able to control the stoichiometry of the films and to avoid the formation of Ti₃N₄, because that is believed to play a crucial role in the

properties of diffusion barriers.^{1,59} Our results also point to the relative importance of finding new metal precursors before looking for alternatives for the ammonia half-step.^{70,71} A number of titanium precursors have in fact been tested for metal nitride ALD in recent times.^{72,73} However, so far, all the chemicals tested have led to the growth of low-density films with high levels of impurities and unacceptable adhesion to copper.⁷⁴ A number of potential nitrogen-containing organometallic complexes have also been identified for the deposition of nitrides of Ta, Hf, and Zr,^{75,76} but their chemistry is equally poorly understood, and their viability for ALD still in question. A separate question also unanswered to date is that of the origin of the induction process often observed in the initial stages of film growth, which can lead to undesirable three-dimensional island formation.⁷⁷ Resolving this issue could help extend the use of TiN and other metal nitrides as barrier films on silicon oxide and other dielectrics and on plug materials such as tungsten.⁴

Concluding remarks

In this brief Highlight we have provided only a few examples of the many potential applications of ALD in the semiconductor industry. Chemical deposition

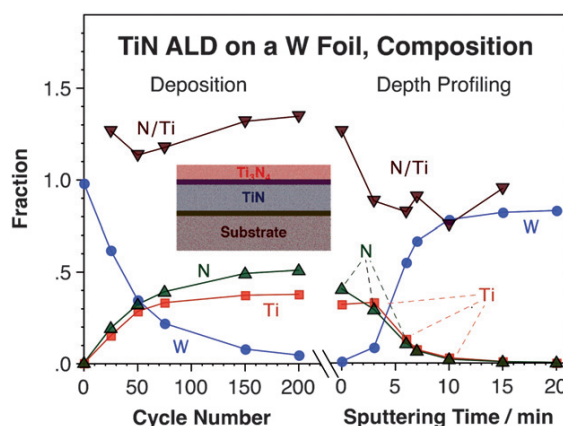


Fig. 4 Summary of the XPS data obtained in studies of the ALD of titanium nitride films using TiCl₄ and ammonia. The data correspond to the W (the substrate), N, and Ti average atomic surface concentrations and the N/Ti atomic ratio measured as a function of the number of ALD cycles during film growth (left) and the sputtering time once a thick film had been grown (right).⁶⁸ N/Ti ratios higher than unity were always observed during growth but not after light sputtering, indicating the formation of a thin Ti₃N₄ layer on top of the growing TiN film. The results suggest that the reduction of the titanium ions occurs *via* disproportionation of the TiCl₄ precursor, not by reaction with ammonia as commonly thought. Reprinted with permission from Elsevier.

methods such as ALD are certainly more complex than the physical counterparts used nowadays, and introduce new problems into the film growth process such as the potential lack of initial reactivity with the substrate and the incorporation of impurities in the deposited materials. On the other hand, they afford the growth of isotropic films as required for the manufacturing of future micro-electronic devices, with their increasing rough topographies and high aspect ratio features. The availability of many organometallic compounds as potential precursors for ALD offers great flexibility in the design of these processes, but also requires a better knowledge of the surface chemistry involved. Fundamental studies in this area are still in their infancy, and will need a heavier involvement from the surface science community if faster progress is to be achieved.

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