

Review

Mechanisms of surface reactions in thin solid film chemical deposition processes[☆]Francisco Zaera^{*}

Department of Chemistry, University of California, Riverside, CA 92521, USA

Contents

1. Introduction	3177
2. Reaction stoichiometry	3179
3. Changes in metal oxidation state	3180
4. Role of co-reactant	3181
5. Thermal decomposition of ligands on the surface	3184
6. Role of the nature of the surface on the chemistry of ALD	3187
7. Nature of the film grown by ALD	3188
8. Concluding remarks	3188
Acknowledgement	3190
References	3190

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ABSTRACT

In this review, key aspects of the surface chemistry associated with atomic layer deposition (ALD) are discussed. It is argued that, in spite of its central role in defining the efficacy of these film deposition processes, little is known about the mechanisms of the chemical reactions involved in ALD. Even the most basic information, the stoichiometry of the overall process in particular, is in many instances unknown. Limited understanding is also available on the redox chemistry that affords the growth of metallic and other types of films from inorganic compounds containing elements in different initial oxidation states. The role of co-reactants in ALD is often misinterpreted: in many instances, these may not be the reducing agents they are set out to be, but rather are needed to remove the auxiliary moieties formed upon adsorption of the main precursor from the surface. These auxiliary surface species may be the original ligands in the ALD precursors, but quite often are new surface species formed upon thermal activation of the original compounds, a conversion that usually follows complex reaction networks. Reactivity in ALD is also controlled by the nature of the substrate, where specific nucleation sites are often responsible for the initial deposition and where a change in chemistry may take place as the first layer of the growing film is formed. Finally, solid-state chemical reactions may take place after deposition, leading to the formation of new layered structures. Examples from our own laboratory are used in this review to illustrate all these issues and to exemplify the type of surface-science experiments that can be performed to shine light on them. We contend that a basic molecular-level understanding of the surface chemistry that underpins ALD processes should afford a better approach for the selection of ALD precursors and co-reactants and for the optimization of the ALD operating conditions. One of the objectives of this review is to encourage the surface-science community to take on this challenge.

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1. Introduction

Thanks in great part to their isotropic nature, chemistry-based processes for solid film depositions have gained much interest in connection with several industrial applications in recent years. In the microelectronics industry in particular, they can be used to grow thin films conformally and to coat topologically complex surfaces in order to create conducting or insulating layers or

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^{*} Tel.: +1 951 827 5498.

E-mail address: zaera@ucr.edu

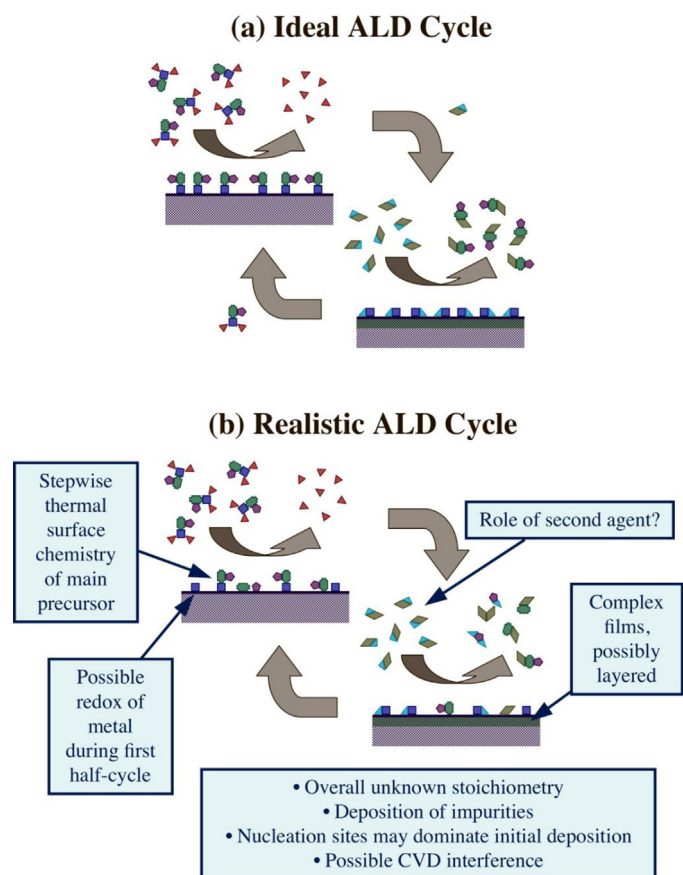


Fig. 1. Schematic representation of typical atomic layer deposition (ALD) cycles. (a) Idealized cycle, where two reactants are fed sequentially and allowed to react on the surface until monolayer saturation occurs and all thermal conversion stops. The adsorbate from each half-cycle reacts in a complementary way with the reactant provided in the other half-cycle to form the desired surface compound and cleanly eliminate the ancillary ligands. (b) Realistic cycle, indicating some of the possible deviations from the ideal model, including ill-defined stoichiometries, complex redox chemistry, possible side reactions, different reactivity on different surface sites, and the formation of multicomponent and complex films.

to introduce diffusion, adhesion, or protection barriers. Standard chemical vapor deposition (CVD) methods have been available for these uses for some time already [1,2], but recent interest has focused on a variation known as atomic layer deposition (ALD) where the overall chemical process is split into two or more self-limiting and complementary reactions in order to gain better control over the film growth at a submonolayer level (Fig. 1a) [3,4]. ALD has been identified as one of the most promising technologies for the deposition of thin films in future modern microelectronics manufacturing [5,6].

One advantage of CVD and ALD is that they offer many options in terms of the selection of the compounds and reactions to be used to deposit a particular material on surfaces. On the other hand, most of those options require complex chemistry, often including undesirable side reactions that may lead to the incorporation of impurities in the grown layer or to surface etching, and more generally to poor film quality (Fig. 1b). To avoid such complications, early chemical deposition processes were designed around simple precursors such as metal halides [7]. Unfortunately, many elements do not form such simple compounds; for the delivery of late transition metals, for instance, it is often necessary to use organometallic or metalorganic compounds. Another consideration when choosing CVD or ALD precursors is that they not only are required to follow clean surface conversion to the desired film material, but also need to be sufficiently volatile and stable so that they can be easily

delivered intact to the deposition reactor. Much of the modern work in ALD is focused on designing, synthesizing, and testing viable new precursors that fulfill those requirements [8].

In spite of the limitations mentioned above, the field of ALD has blossomed in recent years. As the microelectronics industry advances toward the 14 nm node and beyond, the need for the controllable deposition of thin films conformally is becoming increasingly pressing, and ALD is developing as one of the few options available to tackle this issue. Moreover, the applications of ALD are being extended well beyond its original uses into other fields such as the manufacturing of optical and magnetic devices, flat panel displays, catalysts, protective coatings, and textiles, and also to areas related to the conversion (solar cells), utilization (fuel cells), and storage (batteries and supercapacitors) of energy [9–11]. Much work is being dedicated to the identification, testing, and assessing of the use of ALD for such practical applications. An increasing number of synthetic research groups are also developing new promising precursors for the delivery of virtually every element in the periodic table in these chemical-based deposition processes. It would be highly desirable to have a good understanding of the surface chemistry underpinning the ALD processes in order to design precursors in a rational way, from first principles.

Unfortunately, studies in this direction have lagged those on the more practical aspects of film deposition, although that is starting to change [12]. There have certainly been important contributions in this area worth mentioning here. For one, there have been a number of insightful reports on the characterization of the overall stoichiometry of the reactions that take place in each ALD half cycle by using quartz crystal microbalances (QCM), a technique used to follow the changes in mass that occur on the surface upon exposure to each of the reactants [13,14]. It should be noted, however, that QCM measurements do not provide any chemically specific information. A complementary approach to QCM in these studies is the use of mass spectrometry for the detection of the gas products downstream from the ALD reactor [13]. Mass spectrometry is certainly a powerful technique, employed in alternative ways in temperature-programmed desorption, molecular beams, and GC/MS analysis in our laboratory, but it is sometimes difficult to differentiate among the several desorbing species that may be produced in ALD systems using complex metalorganic precursors. Also, some of the gas-phase species generated during ALD processes may not be stable and may undergo further conversion before detection. In terms of the characterization of surface intermediates, perhaps the most explored approach has been the use of infrared absorption spectroscopy (IR) [15,16]; it is unfortunate that, to date, this technique has not lived up to its potential in ALD studies, perhaps because the experiments are not easy to carry out and the data not always straightforward to interpret. Overall, more mechanistic studies are still needed to develop a more complete picture of the mechanistic details of ALD reactions, possibly combining several techniques and approaches.

We in our laboratory have taken a modern surface-science approach to the study of the mechanism of the surface reactions associated with ALD processes, by using a combination of surface-sensitive analytical techniques such as X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), low-energy ion scattering (LEIS), and IR to investigate the details of those reactions at a molecular level [12,17–20]. Our initial focus has been on applications of ALD for the back-end-of-line processing in integrated circuit fabrication, where the individual devices (transistors, capacitors, resistors, etc.) made on the silicon wafer are wired together [21]. The surface chemistry of a number of the copper precursors proposed in the literature for this use, including copper acetamidates [22–24] and copper acetylacetonates [25], has been investigated. In addition, the surface processes involved in the formation of early transition-metal nitrides, titanium and tantalum

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