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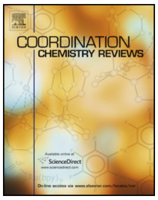

Review

Metal ALD and pulsed CVD: Fundamental reactions and links with solution chemistry

David J.H. Emslie*, Preeti Chadha, Jeffrey S. Price

Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, ON L8S 4M1, Canada

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ABSTRACT

Atomic layer deposition (ALD) is a thin film deposition technique which operates via repeated alternating and self-terminating surface-based reactions between a precursor and a co-reactant, separated in time by purge steps. This technique is particularly well-suited to the deposition of highly uniform and conformal thin films, even on surfaces with nano-scale high aspect ratio features. Furthermore, use of a metal precursor *and* a co-reactant in ALD and the related technique of pulsed-CVD (pulsed-chemical

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Abbreviations: acac, acetylacetonate; AES, atomic emission spectroscopy; ALD, atomic layer deposition; allyl, C_3H_5; allyl^R, CH_2CRCH_2; allyl^{R2}, RCHCHCHR; amd^R, RNCMeNR amidinate; amd$^{R,R'}$, RNCR'NR amidinate; ^{n}Bu, *n*-butyl; ^{s}Bu, *sec*-butyl; ^{t}Bu, *tert*-butyl; CHD, 1,3-cyclohexadiene; CMOS, complementary metal–oxide–semiconductor; COD, 1,5-cyclooctadiene; COT, cyclooctatetraene; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; Cp$'$, methylcyclopentadienyl; Cp^{Et}, ethylcyclopentadienyl; CVD, chemical vapour deposition; dmamb, 1-dimethylamino-2-methyl-2-butanolate ($OCMeEtCH_2NMe_2$); dppe, 1,2-bis(diphenylphosphino)ethane; DRAM, dynamic random-access memory; Et, ethyl; fod, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionate; hfac, 1,1,1,5,5,5-hexafluoroacetylacetonate; IPSA, *N*-isopropyl-2-salicylaldiminate; IR, infrared; ITO, indium tin oxide; LIALD, liquid injection ALD; LICVD, liquid injection CVD; Me, methyl; MIM, metal–insulator–metal; MOS, metal–oxide–semiconductor; nacnac^R, MeC(=NR)CHC(=NR)Me β-diketiminate; nacnac$^{cycle\text{-}R,R'}$, R$'$C(=NR)CH{C=N(CH_2)$_3$}; NHC, *N*-heterocyclic carbene; od, 2,4-octanedionate; OTf, triflate; PEALD, plasma-enhanced ALD; Ph, phenyl; Pin, pinacolate ($OCMe_2CMe_2O$); ^{i}Pr, *iso*-propyl; PVD, physical vapour deposition; PyrIm^R, (NC_4H_3)CH=NR 2-pyrrolylaldimine; QCM, quartz crystal microbalance; QMS, quadrupole mass spectrometry; SAM, self-assembled monolayer; TEM, transmission electron microscopy; TFEL, thin film electroluminescent; thd, 2,2,6,6,-tetramethyl-3,5-heptanedionate; UHAR, ultra-high aspect ratio; UHV, ultra-high vacuum; VTMS, vinyltrimethylsilane; XPS, X-ray photoelectron spectroscopy.

* Corresponding author. Tel.: +1 905 525 9140; fax: +1 905 522 2509.
E-mail address: emslied@mcmaster.ca (D.J.H. Emslie).

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vapour deposition), provides the potential for deposition of materials that may be inaccessible using CVD methods that rely upon the thermal decomposition of a single metal precursor. This review surveys the different classes of co-reactant used for thermal metal ALD/pulsed-CVD with a focus on the reaction chemistries known or proposed to be involved. Parallels are drawn between surface-based metal ALD/pulsed-CVD reactivity and solution-based reactivity including electroless deposition, solution-based nanoparticle synthesis, and the synthesis of zero-valent complexes bearing labile ligands. Also described are applications of solution screening and solution mechanistic studies to the identification of promising new ALD/pulsed-CVD reactivities, and the generation of initial mechanistic hypotheses as to the fundamental reaction steps involved in metal ALD/pulsed-CVD. A primary goal of this review is to provide a unique reactivity-based perspective of metal ALD/pulsed-CVD. In addition, we have endeavoured to illustrate commonalities between solution-based and surface-based reactions relevant to metal deposition, and to highlight beneficial applications of the former to the development of the latter.

1. Introduction

1.1. Thermal ALD and pulsed-CVD

For many years, PVD and CVD have been central techniques for the deposition of thin metal films with a broad range of applications. However, the directional nature of these methods can lead to difficulties in: (a) obtaining ultra-thin films of uniform thickness, and (b) deposition of conformal films within nano-scale high aspect ratio features (e.g. trenches or vias), and these difficulties are becoming increasingly significant in the microelectronics industry as a result of rapidly decreasing device dimensions. Furthermore, while CVD offers improved conformality relative to PVD, it suffers from: (a) the potential for particle formation due to reactions occurring in the vapour phase rather than on the substrate surface, (b) in the case of solid precursors, dependence of film growth rate on precursor particle size, and (c) unavailability of precursors for deposition of certain materials, including many of the transition metals [1,2].

ALD is a technique related to CVD which largely overcomes the limitations outlined above, although the overall deposition rate is generally much lower than that of CVD. In ALD, a volatile metal precursor is employed, as in CVD, but in this case, the substrate temperature and precursor thermal stability are such that the precursor does not undergo thermal decomposition upon contact with the substrate. Instead, deposition is achieved by repeated alternating self-terminating surface-based reactions between a metal precursor and a co-reactant [1–10]. In thermal ALD, the co-reactant is a ‘stable’ entity (e.g. H_2, H_2O, O_2 or O_3), while in plasma-enhanced ALD (PEALD), the co-reactant is plasma-generated (e.g. H, O or N atoms). Potential drawbacks of PEALD are that it introduces additional complexity to an ALD reactor, exposure to plasma-generated ions and UV-radiation can cause damage to the substrate and/or the growing film, and conformal deposition inside high aspect ratio features is difficult; this is especially the case for metal deposition using hydrogen plasma, since hydrogen radicals have particularly high recombination rates on most metal surfaces [11,12]. On the other hand, a major advantage of PEALD is that it can be used to deposit a range of materials at low temperature, due to the high reactivity of species such as atomic hydrogen, oxygen and nitrogen. For example, while thermal ALD of silver metal has not yet been reported, PEALD of silver metal has been achieved using hydrogen plasma in combination with $[(\text{fod})\text{Ag}(\text{PEt}_3)]$ at 120 °C. The silver precursor was delivered at 106 °C, and undergoes surface-based thermal decomposition above 140 °C [13], rendering it unsuitable as a candidate for thermal ALD of silver films using less reactive molecular hydrogen in place of atomic hydrogen. This example highlights a fairly general challenge in the development of new thermal metal ALD processes that rely on the existing suite of co-reactants; the availability of metal precursors with sufficiently high thermal stability and reactivity. PEALD is one way to utilize metal precursors of limited thermal stability, and the development of more reactive co-reactants for thermal ALD is another. In this review, only thermal ALD will be discussed, and from herein the term ALD is used to mean thermal ALD unless otherwise specified.

The reactions in ALD are designed to yield only volatile byproducts, and these, as well as excess metal precursor/co-reactant, are removed in inert gas purge steps between metal precursor and co-reactant pulses. The defining characteristic of ALD is that the metal precursor and the co-reactant are adsorbed and/or react with the surface in a *self-limiting* fashion. Therefore, so long as sufficient vapour doses of the metal precursor and co-reactant are delivered to ensure maximum surface coverage and complete reaction, the thickness of the deposited film will depend only on the number of precursor/purge/co-reactant/purge cycles, and the film will grow conformally on all exposed surfaces on which nucleation can occur, including the surfaces of high aspect-ratio features. If self-limiting behaviour cannot be achieved, even in cases where ALD reactivity is accompanied by a minor parasitic CVD process, the overall process is termed pulsed-CVD [1–10].

Although ALD offers advantages not conferred by pulsed-CVD, in both cases use of a metal precursor *and* a co-reactant provides access to a broader range of deposition chemistries than CVD involving thermal decomposition of a single metal precursor. Consequently, both ALD and pulsed-CVD provide the potential for deposition of materials that are inaccessible using single precursor CVD, as well as enhanced potential for the development of deposition reactions capable of operating at low temperature.

1.2. A brief introduction to metal ALD/pulsed-CVD

Relative to metal oxide and metal nitride ALD, examples of thermal metal ALD are far less common. In fact, as illustrated graphically in Fig. 1 (see Section 2 of this review for references), thermal metal ALD has thus far only been achieved for the least electropositive transition metals: the noble metals not including silver and gold, 1st row congeners of the noble metals, and the group 6 elements molybdenum and tungsten. Beyond this, pulsed-CVD has been reported for Ti/Al alloy (under UHV conditions), Mn, and Ag; vide infra.

From the above discussion, it follows that a major challenge in ALD is the development of suitable reaction chemistry for deposition of metals not yet accessed by ALD. However, even for metals that have previously been accessed by ALD, various features of the precursors, the deposition process and/or the resulting films may prevent commercial application. These include: (a) difficulties in precursor scale-up, (b) insufficient precursor or co-reactant thermal stability, (c) an ALD temperature that is too high to be compatible with the desired substrate (temperatures of 200–400 °C are common; vide infra), (d) an ALD temperature that causes agglomeration of thin metal films [15,16], (e) deposition of metal films