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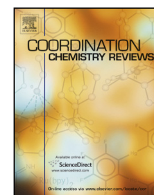

Review

Precursors as enablers of ALD technology: Contributions from University of Helsinki

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Abbreviations: acac, acetylacetonate; ALD, atomic layer deposition; CET, capacitance equivalent thickness; CHT, cycloheptatrienyl; CHD, cyclohexadiene; CMOS, complementary metal oxide semiconductor; CN, coordination number; Cp, cyclopentadienide; COD, cyclooctadiene; CVD, chemical vapour deposition; dien, diethylenetriamine; diglyme, bis(2-methoxyethyl) ether; DMAE, dimethylaminoethoxide; DRAM, Dynamic random access memory; EDS, energy dispersive spectrometry; EOT, Equivalent oxide thickness; FESEM, field emission scanning electron microscope; fod, 1,1,1,2,2,3,3-heptafluro-7,7-dimethyl-4,6-octanedione; FRAM, ferroelectric random access memory; GST, Germanium antimony telluride; hfac, hexafluoroacetylacetonate; HRTEM, high resolution transmission electron microscopy; me, methoxyethoxy; mmp, 1-methoxy-2-methyl-2-propanolate; MOCVD, metal organic chemical vapour deposition; MS, mass spectroscopy; MTHD, methoxy-2,2,6,6-tetramethylheptane-3,5-heptanedione, me; METHD, methoxyethoxy-2,2,6,6-tetramethylheptane-3,5-heptanedione; MOSFET, metal oxide semiconductor field effect transistor; NVRAM, non-volatile random access memory; PCRAM, Phase change random access memory; PEALD, plasma enhanced atomic layer deposition; Piv, pivalate; REALD, radical enhanced atomic layer deposition; SBT, strontium bismuth tantalate; SDTA, single differential thermal analysis; SEM, scanning electron microscope; SIMS, Secondary ion mass spectrometry; SOFC, solid oxide fuel cell; TG, thermo gravimetry; TGA, thermo gravimetric analysis; THF, tetrahydrofurane; tmhd, tetramethylheptanedione; Tp, tris(pyrazolyl)borate; Tp^{Et2}, tris(3,5-diethylpyrazolyl)borate; trien, triethylenetetraamine; triglyme, triethylene glycol dimethyl ether.

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ABSTRACT

The review focuses on ALD precursors of selected elements such as alkaline earth (Mg, Ca, Sr, Ba), group 4 metals, bismuth, silver, iridium, selenium, tellurium and antimony. These elements are needed in different high tech applications but are challenging for ALD. Their precursor design needs careful balancing between volatility, thermal stability and reactivity—the key properties of ALD precursors. The extensive studies showed that cyclopentadienyl based precursors of alkaline earth metals are versatile ALD precursors which react with both water and ozone forming oxide. Group 4 ALD chemistry has been studied very widely and many good precursors have been found for the oxide ALD. From a bunch of different compound types studied the most promising ALD precursor for bismuth is $Bi(OCMe_2{}^iPr)_3$ which shows stable ALD process with water at 150–250 °C. The success in depositing noble metal films by ALD can be attributed more to the reactant rather than the metal precursor. Ru, Pt, Ir, Rh and Os films can be deposited from various organometallic and metal organic precursors using O_2 as the other precursor. Typically temperatures above 225 °C are needed. Using O_3 as a reactant films can be deposited at lower temperatures. Noble metal oxides are obtained below approx. 200 °C and metallic films above that. By supplying both O_3 and H_2 as consecutive pulses, noble metal films can be deposited well below 200 °C. For silver phosphine stabilized carboxylato and β-diketonato complexes are thermally stable enough enabling hydrogen plasma enhanced ALD of silver metal films. Alkylsilyl compounds of selenium and tellurium are versatile ALD precursors for metal selenide and telluride films when combined with metal chloride precursors. The use of alkylsilyl compounds is not limited to group 16 elements but can also been used for group 15.

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1. Introduction

The success of ALD is built on chemistry. The great benefits of ALD (conformality, uniformity, atomic level thickness control, etc.) can be enjoyed only when proper precursors have been identified for the material of an interest. The precursors need to meet a number of requirements (Table 1) among which the combination of high reactivity and good thermal stability often sets major challenges. Volatility is important too, and though moderately volatile solids are used even industrially, liquids and gases are preferred for convenience.

The ALD chemistry has been approached from two directions: scientific curiosity and from needs of industry. Over the years the emphasis has been shifted toward the latter as the ALD has become better known and more widely used thin film deposition technique. For example, when we in 1993 studied $HfCl_4$ as a precursor for ALD of HfO_2 [1] this was done for comparison to the earlier studied $TiCl_4$ [2], and neither we nor anyone else had a clue that ALD HfO_2 would become a high-k gate oxide in the leading MOSFETs 15 years later. By contrast, our recent breakthrough in ALD of tellurides and selenides with their alkylsilyl compounds as precursors [3], was motivated by a request addressed to us from semiconductor companies via an ALD tool manufacturer that we collaborate with. On the other hand, also in 1990s we did application motivated precursor research but that focused on electroluminescent display materials rather than the current mainstream semiconductors. Soon after the results and knowledge gained in that research were successfully benefited in developing an ALD process for $SrTiO_3$ [4] that had gained increasing interest in IC applications because of its very high-k value.

ALD metal precursors have traditionally been grouped based on their ligands (Fig. 1): halides, β-diketonates, alkoxides, alkyl amides, alkyls, cyclopentadienyls, amidinates, guanidinates, etc. and even elements [5]. Inside these groups the precursor properties have been tuned to meet the ALD requirements by tailoring the ligands, particularly by changing the size of the ligands and by adding donor functionalities to the hydrocarbon groups of the ligands. Another option has been to add adduct ligand to the coordination sphere of the metals. A newer trend has involved heteroleptic metal complexes where two or more different ligands are used together for further tuning of the precursor properties.

In this paper we review some of our own contributions to the ALD precursor chemistry over the past 20 years. The aim of the review is not to present a balanced view of the field but to focus on studies and discoveries done at the University of Helsinki. Thus references to other studies are kept in minimum. A number of different kinds of precursor groups will be covered. Each chapter begins with a brief summary of applications of ALD films containing the given elements, thereby demonstrating how in ALD precursor chemistry basic and applied research are connected seamlessly. Properties (structure, volatility, thermal stability, reactivity) of precursors studied and main results from the film growth experiments are reviewed. About the ALD reaction mechanisms only some illustrative examples will be given since in situ reaction mechanism studies on ALD processes were reviewed in detail very recently by Knapas and Ritala [6].

2. Alkaline earth metals

Alkaline-earth metals are constituents of many technologically important materials. $SrTiO_3$ and $Ba_{1-x}Sr_xTiO_3$ are high permittivity dielectric materials for future DRAMs [7]. $BaTiO_3$ is not only a dielectric but also piezoelectric and ferroelectric material which may be used in e.g. ceramic multilayer capacitors and thermistor elements [8,9]. CaS, SrS and BaS are host materials for luminescent materials [10,11]. $SrBi_2Ta_2O_9$ is a ferroelectric material which may be used in FRAMs [12]. Strontium and barium are also constituents of the well-known superconducting cuprates $La_{2-x}Sr_xCuO_2$, $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_{8+x}$ [13]. Fluorides of magnesium and calcium are materials suited for optical coatings [14].

Especially the larger alkaline earth metals are challenging from the CVD/ALD precursor chemistry point of view: their compounds have a tendency to form oligomeric species which have low volatility. Thus sufficiently volatile, thermally stable and reactive compounds of alkaline earth metals are not that common.

Before the interest in ALD, a large variety of β-diketonates and also many other compounds had been used in CVD as precursors for alkaline earth metals. In addition a variety of compounds had been suggested as possible precursors due to their volatility [15]. These compounds include silylamides and phosphides, poly(pyrazaolyl)borates, alkoxides, β-ketoiminates, pyrazolates, pyrrolates and cyclopentadienyl compounds with and without neutral ancillary Lewis base ligands. Precursors used for ALD of alkaline-earth metal containing films are quite few and they are collected into Table 2. Basically the precursors have been restricted to

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