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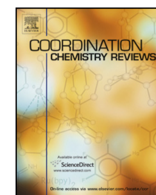

Review

Energy-enhanced atomic layer deposition for more process and precursor versatility

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ABSTRACT

Atomic layer deposition (ALD) is a popular deposition technique comprising two or more sequential, self-limiting surface reactions, which make up an ALD cycle. Energy-enhanced ALD is an evolution of traditional thermal ALD methods, whereby energy is supplied to a gas *in situ* in order to convert a traditional thermal ALD co-reactant to a highly reactive species with short-term stability. Therefore, energy-enhanced ALD encompasses plasma-enhanced ALD and ozone-based ALD techniques. In this article, we aim to provide insight into precursor considerations, such that the advantages of energy-enhanced ALD can be exploited. The examples of such advantages are that a wider variety of precursors can be used, and that deposition temperatures down to room temperature with a high growth-per-cycle can be employed. The precursor freedom is demonstrated here by Ti compounds of the general formula $[Ti(Cp^x)L_3]$ (Cp^x = alkyl-substituted η^5-cyclopentadienyl, L = OMe, O^iPr or NMe_2). Such heteroleptic cyclopentadienyl complexes allow for improved volatility by preventing oligomerisation and offering improved thermal stability, thereby leading to a longer storage life in bubblers and allowing for ALD at higher deposition temperatures than with analogous homoleptic precursors. However, experimental data show that $[Ti(Cp^x)L_3]$ compounds are not reactive with water during ALD but do react with plasmas

Abbreviations: 3c2e, 3-centre-2-electron bond; ALD, atomic layer deposition; BDEAS, bis(diethylamino)silane; CCP, capacitively-coupled plasma; Cp^{Me}, η^5-monomethylcyclopentadienyl; Cp*, η^5-pentamethylcyclopentadienyl; Cp^x, a general substituted η^5-cyclopentadienyl ligand; DFT, Density Functional Theory; DMAI, dimethylaluminium isopropoxide; E_{ads}, enthalpy of adsorption; Et, ethyl (CH_2CH_3); FT-IR, Fourier transform infrared (spectroscopy); GPC, growth per cycle; ICP, inductively-coupled plasma; ^{i}Pr, isopropyl ($CH(CH_3)_2$); MBE, molecular beam epitaxy; Me, methyl (CH_3); RF, radio-frequency; RT, room temperature; RT-ALD, room-temperature ALD; RTP, room temperature and pressure; s-OH, surface hydroxyl species; ^{t}Bu, *tert*-butyl ($C(CH_3)_3$); thd, 2,2,6,6-tetramethyl-3,5-heptanedionate; Ti-N-Prime, η^5-monomethylcyclopentadienyltris(dimethylamino)titanium(IV); Ti-Prime, η^5-monomethylcyclopentadienyltri(isopropoxy)titanium(IV); Ti-Star, η^5-pentamethylcyclopentadienyltri(methoxy)titanium(IV); TMA, trimethylaluminium; TTIP, titanium(IV) isopropoxide.

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and ozone. Density Functional Theory calculations suggest that this is because chemisorption is prevented by the steric hindrance of the cyclopentadienyl ligand. Further processing versatility afforded by energy-enhanced ALD is also observed with depositions at low temperatures (<200 °C) and even room temperature. Such low temperatures are often not considered viable for thermal ALD as there is insufficient thermal energy to drive reactions, resulting in low growth per cycle values and relatively high film contamination. The high reactivity of plasmas and ozone allows the deposition of good to fair quality films at low temperatures with a high growth-per-cycle, exemplified by $[Al(CH_3)_3]_2$ (TMA) and $[Al(CH_3)_2(O^iPr)]_2$ (DMAI) aluminium precursors. The considerations required for energy-enhanced room-temperature ALD (RT-ALD) are also presented here, using Al_2O_3, SiO_2 and TiO_2, from TMA, $[SiH_2(NEt_2)_2]$ (BDEAS) and $[Ti(O^iPr)_4]$ (TTIP), as examples. The essential criterion is that incoming metalorganic precursors and co-reactant gases must be reactive with the surface groups at room temperature. As long as this is met, then further desirable conditions for RT-ALD are a high precursor vapour pressure and short purge times. Using these examples, the advantages of energy-enhanced ALD with respect to precursor choices are highlighted.

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1. Introduction

1.1. Atomic layer deposition

Atomic layer deposition (ALD) is a derivative of chemical vapour deposition (CVD) that is driven by the reaction between functional groups on the substrate surface with incoming precursor molecules, rather than precursor decomposition [1,2]. This reaction mechanism means that once no more of the initial surface groups remain (or are made unreactive by steric shielding or geometric constraints), no further reactions occur. In essence, the reaction saturates, which is a key feature of ALD. Rather than a continuous flux of precursor gases, two or more precursors are introduced to the reaction chamber in pulses separated by purges, referred to as an ALD cycle. Typically, one ALD cycle comprises a precursor dose, which is usually a metal-containing precursor (e.g., a metalorganic compound or a metal halide), and a co-reactant dose, providing the second component of the material, such as oxygen for metal oxides [3–5] or nitrogen for metal (carbo)nitrides [6–8].

A schematic ALD cycle of the Al_2O_3 process from $[Al(CH_3)_3]_2$ (TMA) and an O_2 plasma is depicted in Fig. 1 as an example. During the metal precursor exposure (TMA dose), a TMA monomer undergoes a Brønsted acid-base condensation reaction (often referred to as a ligand-exchange reaction in ALD literature) with a surface hydroxyl (s-OH) species, resulting in a bond between the aluminium and oxygen on the surface and CH_4 as a reaction product. Furthermore, the remaining surface comprises only methyl (s-CH_3) groups, with which (excess) TMA will not react. In principle, this reaction will continue until only s-CH_3 remains (and no s-OH), which gives ALD its self-limiting nature. After this reaction is complete, excess precursor and reaction products are removed from the reaction chamber, either by evacuating, admitting a purge gas, or both. The second step involves a co-reactant exposure. Where water is the co-reactant, for example, similar ligand-exchange reactions to the TMA example above occur, which are hydrolysis reactions. Different reactions dominate when an O_2 plasma is the co-reactant. In this case of plasma-enhanced ALD of Al_2O_3 (Fig. 1, O_2 plasma exposure), the plasma undergoes combustion-like reactions with the s-CH_3, producing carbon dioxide and water as well as regenerating the s-OH groups such that the cycle can start again after a second purge [9]. Moreover, as water is a combustion-like reaction product, it can also undergo hydrolysis with remaining s-CH_3 groups, thereby adding a thermal ALD component to the surface reactions.

This cyclic nature of ALD affords stepwise growth of the desired material sub-monolayer by sub-monolayer. For this reason, ALD growth is reported in terms of growth per cycle (GPC) rather than growth rate [10]. (Technically, the growth rate would have to take the total cycle time into account.) This 'digital' growth offers several benefits, including thickness control to sub-nanometre precision, excellent film conformality and good uniformity over large-area substrates.

1.2. Thermal and energy-enhanced ALD

The classification of an ALD process can be described by the nature and reactivity of the precursors employed, which we present here using selected ALD processes as examples. For a complete list of reported ALD processes, the reader is directed to the review by Miikkulainen et al. [11].

The first examples of ALD (then known as atomic layer epitaxy, or ALE) involved the deposition of ZnS [12–14] and ZnSe [13,15,16], where the evaporated elements were used as precursors in a molecular beam epitaxy (MBE) reactor. However, the use of metal halide or metalorganic compounds in conjunction with a co-reactant is now standard. In general, the metal halide or metalorganic precursors and co-reactants are used in thermal ALD without the need for further preparation steps, i.e., they are generally purchased from chemical companies or synthesised in-house and used as supplied or prepared. (There is also an example of where a copper precursor was effectively generated *in situ* [17].) Thermal energy is typically supplied to the precursor in order to obtain a suitable vapour pressure for transport to the reactor. Furthermore, these compounds are most often used in combination with traditional co-reactants, which are typically small molecules, such as water or ammonia, or elemental gases, like oxygen or hydrogen [3,11]. The nature of the precursors allows for alternating condensation, during the precursor dose, and hydrolysis/solvolysis, during the co-reactant dose. Therefore, in addition to the heat supplied to the precursor, heat is also supplied to the substrate to drive these surface reactions. However, thermal energy is not always sufficient to afford complete surface reactions, which can lead to lower GPC values and higher impurity contents at the lower deposition temperatures [5,18,19] required for temperature-sensitive substrates or applications.

Many non-standard ALD chemistries are known, many of which were part of investigations to overcome problems with low reactivity. These chemistries are typically based on well-known techniques used in synthetic metalorganic chemistry. For example, "non-aqueous" reactions where organic molecules such as alcohols, esters and carboxylic acids have been employed as the oxygen-source in combination with metal alkoxide [20–25] and metal chloride [24,25] compounds in order to reduce impurities in metal oxide films. Furthermore, the reactivity between metal halides and alkoxy moieties was also exploited to obtain metal oxide films using metal alkoxides as the oxygen-source [26,27]. The overall ligand-exchange equation for the ALD process of aluminium chloride and

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