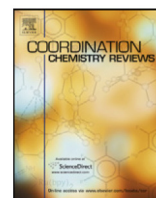




ELSEVIER

Contents lists available at ScienceDirect

## Coordination Chemistry Reviews

journal homepage: [www.elsevier.com/locate/ccr](http://www.elsevier.com/locate/ccr)

## Review

## Theoretical design and computational screening of precursors for atomic layer deposition

Guoyong Fang<sup>a,b,\*</sup>, Lina Xu<sup>a</sup>, Yanqiang Cao<sup>b</sup>, Aidong Li<sup>b</sup><sup>a</sup> Key Laboratory of Carbon Materials of Zhejiang Province, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China<sup>b</sup> National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China

## Contents

1. Introduction .....	94
2. Bond strength between the metal and the ligand of the precursor .....	95
3. Thermolysis energy and barrier and chelation energy of the precursor .....	95
4. Hydrolysis energy of the precursor and Lewis/Brønsted basicity of the ligand .....	98
5. Formation energy of the precursor and energy change for electron reduction .....	99
6. Computational screening process for precursors .....	99
7. ALD reaction mechanism and surface reactivity of the precursor .....	100
8. Conclusion and outlook .....	102
Acknowledgements .....	103
References .....	103

## ARTICLE INFO

## Article history:

Received 20 March 2016

Accepted 26 May 2016

Available online 3 June 2016

## Keywords:

Atomic layer deposition

Precursor design

Computational screening

Surface reactivity of the precursor

## ABSTRACT

An effective precursor is a prerequisite and key to the success of atomic layer deposition (ALD). Currently, the design of more effective precursors is an important aspect of the development of ALD technology. In this review, theoretical design and computational screening methods for ALD precursors are discussed. Theoretical calculations can predict many properties of precursors, such as the bond strength between the metal and the ligand, the thermolysis energy and barrier, the chelation energy, the hydrolysis energy, the formation energy, and so on. Most of these calculated data are related to the stability and reactivity of the precursor, which can be used in the design and computational screening of new ALD precursors. In addition, precursor design and screening require consideration of the ALD reaction mechanism in order to predict the true reactivity of the precursor with the surface, namely the surface reactivity of the precursor, which reflects the essence of ALD technology. Such theoretical efforts are expected to provide guidance for the design of more effective precursors and thereby lead to an improvement of ALD applications.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

As a nanofabrication technique, atomic layer deposition (ALD), formerly named atomic layer epitaxy (ALE) or molecular layering (ML), has been widely used for the growth of various materials, such as oxides, nitrides, sulfides, metals, semiconductors, and organic and organic–inorganic hybrid materials [1–19]. In industry, ALD was initially used for the manufacture of electroluminescent flat panel displays [6]. With the scaling down of device dimensions, ALD was successfully applied in the area of microelectronics, such as in complementary metal oxide semiconductors (CMOS) and dynamic

random access memory (DRAM) [1–5]. Thereafter, ALD applications were further extended to the fields of catalysis, coatings, and energy conversion, storage, and utilization [1–5].

The success of ALD relies heavily on the precursors. Only suitable precursors can grow ALD thin films [1–9]. To date, ALD precursors have mostly been derived from chemical vapor deposition (CVD) precursors [2,4,20]. The design of new precursors is still an important development direction in ALD technology. In general, the most important characteristics of ALD precursors are good volatility, thermal stability, and high reactivity [2,4,6]. When discussing the concept of stability of the precursor, it is necessary to distinguish between thermodynamic stability and kinetic stability. The former is essentially related to bond energies of the precursor, whereas the latter is related to reaction barriers and rates. In principle, the precursor must be sufficiently stable to volatilize

\* Corresponding author. Tel.: +86 577 8668 9300.

E-mail address: [fanggy@wzu.edu.cn](mailto:fanggy@wzu.edu.cn) (G. Fang).

and reach the surface intact without decomposition; that is, it must be thermodynamically or energetically stable. When the volatility and thermal stability of the precursor are considered, a strong bond between the metal (M) and the ligand (L) is often preferred. However, if the precursor is too stable or the M–L bond is too strong, the precursor may be unreactive, namely kinetically stable, since a high activation energy will be required to break the M–L bond for proton-transfer, hydrolysis, or ligand-exchange reactions between the precursor and the surface. When the reactivity of the precursor is considered, a weak M–L bond may be preferred. According to the focus of theoretical design and computational screening, members of a series of precursors are often compared to obtain their relative stabilities or relative reactivities by varying metals and ligands or substituents.

In the past few decades, because of the ingenuity and hard efforts of many chemists, many suitable precursors for ALD have been devised and synthesized [2,4]. For example, Gordon et al. designed and synthesized a series of amidinates for transition metal ALD [13,21]. Hatanpää et al. focused on ALD precursors of alkaline-earth and group 4 metals [22]. Barry et al. studied amidinate and guanidinate precursors of group 13 and coinage metals [23]. Carmalt et al. also synthesized group 13 alkoxide precursors [24]. Devi et al. designed and synthesized a series of group 4 and rare-earth metal precursors [25]. Most of these studies were based on experiments, such as Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), thermogravimetric analysis (TGA), and X-ray crystal studies. Recently, the special issue “CVD and ALD precursor design and application” in *Coordination Chemistry Reviews* provided a good summary of previous work on ALD precursors [26–38].

In this paper, we review theoretical advances on the design of ALD precursors from the viewpoint of computational chemistry. Some theoretical calculation and computational screening methods for ALD precursors are discussed. Furthermore, a more reliable computational screening method is proposed. Through theoretical calculations, many properties of precursors can be predicted, such as the M–L bond strength, the thermolysis energy and barrier, the chelation energy, the hydrolysis energy, the formation energy, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the energy gap between these orbitals, which are related to their stabilities and reactivities [39–48]. On the basis of these data, computational screening can offer a convenient and rapid approach for the theoretical design of new ALD precursors [48]. In addition to the stability and reactivity, a more reliable method for precursor design is to consider the ALD reaction mechanism in order to predict the true reactivity of the precursor with the surface [49–62]. This is the essence of ALD technology, and can be termed the surface reactivity of the precursor. Table 1 summarizes theoretical advances on the design and computational screening of ALD precursors, including different metals and ligands. Most such theoretical calculations have been based on density functional theory (DFT) with different functionals, such as B3LYP, PW91, BP86, PBE, PBE0, and M06-2X [39–62]. The electrons of all elements are represented by using atomic-orbital and plane-wave basis sets, effective core potential (ECP), and projector-augmented wave (PAW) methods. In the rest of the paper, we describe pertinent theoretical work and computational screening methods concerning the design of ALD precursors.

## 2. Bond strength between the metal and the ligand of the precursor

A method for computational screening of ALD precursors is based on the bond strength between the metal atom (M) and the ligand (L) [39]. For a facile ALD reaction, an ideal precursor should have a

relatively weak M–L bond, which leads to a relatively high reactivity. By comparing the energies required for bond breaking among different precursors, those having favorable driving forces for reaction can be predicted [39].

The bond strength can be characterized by the bond-dissociation energy ( $E_{\text{BDE}}$ ) of the coordination bond (M–L) of the precursor, calculated according to the following formula:

$$E_{\text{BDE}} = E_{\text{metal}} + E_{\text{ligand}} - E_{\text{precursor}} \quad (1)$$

where  $E_{\text{precursor}}$ ,  $E_{\text{ligand}}$ , and  $E_{\text{metal}}$  represent the energies of the precursor, the ligand, and metal atom, respectively. For a precursor with two ligands, the first and second bond-dissociation energies can be calculated. The bond-dissociation energy should not be confused with the bond energy, which is the average value of the bond-dissociation energies for all bonds of the same type in a molecule. Except in the case of diatomic molecules, the bond-dissociation energy is different from the bond energy.

On the basis of bond strengths, a series of strontium (Sr) and barium (Ba) precursors ( $\text{ML}_2$ ) has been evaluated for ALD growth of SrO and BaO by means of DFT calculations at the B3LYP/6-311G + LanL2DZ level [39]. These precursors included  $\beta$ -diketonate and cyclopentadienyl (Cp) compounds, such as acac, hfac, tmhd, fod, Cp,  $\text{Me}_5\text{Cp}$ ,  $\text{PrMe}_4\text{Cp}$ ,  ${}^i\text{Pr}_3\text{H}_2\text{Cp}$ , and  ${}^t\text{Bu}_3\text{H}_2\text{Cp}$  (Fig. 1).

According to the first and second bond-dissociation energies, Cp-based ligands have weaker bonds with metals than  $\beta$ -diketonate precursors. The bonds between Cp rings and a metal are further weakened when methyl (Me) or propyl (Pr) groups are appended on the Cp ring. The trends for both Sr and Ba precursors are similar.  $\text{PrMe}_4\text{Cp}$  and  $\text{Me}_5\text{Cp}$  complexes are expected to be the best precursors for the ALD growth of SrO and BaO films, whereas  $\beta$ -diketonate precursors would seem to be unfavorable.

In fact, this prediction is instantly obvious when comparing  $\text{pK}_a$  values and associated proton equilibria of water, Cp anions, and  $\beta$ -diketonate anions. In particular, the  $\text{pK}_a$  values of water and  $\beta$ -diketonates imply unfavorable proton transfers, whereas that with Cp is favorable. From the viewpoint of organometallic chemistry, the strongly electronegative fluorine will strengthen the M–L bond between the metal and  $\beta$ -diketonate, whereas an electron-donating methyl or propyl group will weaken the  $\sigma$ – $\pi$  coordination bond between the metal and the Cp ring.

The introduction of a tetrahydrofuran (THF) ligand does not have a significant impact on the bond energy between Ba and the ligand. In fact, THF is only weakly bound to Ba and readily detaches from the precursor with increasing temperature. Thus, precursors with THF as a ligand should show similar behavior to those without it. The results of subsequent ALD experiments further verified that SrO films could be deposited with precursors bearing  $\text{PrMe}_4\text{Cp}$  or  $\text{Me}_5\text{Cp}$  using  $\text{H}_2\text{O}$  or  $\text{O}_2$  as an oxygen source, whereas no films could be grown with  $\beta$ -diketonate precursors under similar conditions, thus supporting the prediction [22,39]. However, it should be pointed out that this screening method based on weak bonds between the metal and ligand only evaluated the initial and end points of the reaction to compare thermodynamic driving forces for breaking various bonds in the precursor and neglected the ALD reaction mechanism and kinetic factors.

## 3. Thermolysis energy and barrier and chelation energy of the precursor

Another method for screening ALD precursors is to examine their thermal stabilities and thermolysis mechanisms [40–43]. Theoretically, a precursor with a stronger M–L bond and higher stability will be less reactive, having to overcome a higher reaction barrier to undergo thermolysis. Quantum chemical calculations can yield the reaction energy and activation barrier for thermolysis, the

Download English Version:

<https://daneshyari.com/en/article/1300206>

Download Persian Version:

<https://daneshyari.com/article/1300206>

[Daneshyari.com](https://daneshyari.com)