Synthesis of Calcium(II) Amidinate Precursors for Atomic Layer Deposition through a Redox Reaction between Calcium and Amidines

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

Citation

Published Version
doi:10.1002/anie.201602406

Citable link
http://nrs.harvard.edu/urn-3:HUL.InstRepos:29626196

Terms of Use
This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA
Synthesis of Calcium(II) Amidinate Precursors for Atomic Layer Deposition through a Redox Reaction between Calcium and Amidines

Sang Bok Kim, Chuanxi Yang, Tamara Powers, Luke M. Davis, Xiabing Lou, and Roy G. Gordon*
Calcium plays an important role in a wide variety of multicomponent materials, including nonlinear optics, phosphors, dielectrics, high-temperature superconductors, colossal magnetoresistance materials, planar waveguides, laser windows, and fiber optics. Promising potential applications of calcium oxide, owing to its wide band gap of 6.8 eV, include alloys with HfO$_2$ for gate-capacitor dielectrics in metal-oxide-semiconductor field-effect transistors (MOSFETs), and alloys with MgO as an epitaxial gate insulator in GaN-based high-electron-mobility transistors (HEMTs). Calcium sulfide may have utility as an alloy with the strong visible-light absorber SnS; the addition of calcium to SnS to form Sn$_x$Ca$_y$S stabilizes the desirable but unstable cubic (rock-salt) phase of this material.

For many of these applications, especially in electronic devices, a method to deposit uniform thin films at modest temperatures is required. Atomic layer deposition (ALD), a modified form of chemical vapor deposition in which precursors are delivered in pulses, provides a route to conformal thin films of metals, metal oxides, and metal chalcogenides on nanostructured substrates. During each pulse cycle, one precursor reacts with the growth surface until the surface is saturated, and then by-products and unreacted precursor are removed by purging with inert gas.

This process is repeated alternately, and the self-limiting character (film growth through surface saturation) allows for accurate and reproducible control of film thickness with excellent large-area uniformity and conformality. Other requirements for an ALD precursor are self-limited reactivity with the growth surface, high volatility, high thermal stability, and the formation of only stable and noncorrosive by-products.

ALD affords a constant film-growth rate within a temperature window; at lower temperatures, the precursor may not react with the surface or may condense without any surface reaction, whereas at higher temperatures, the precursor may decompose. The available ALD window is critically important in the selection of precursors for multicomponent thin films whereby the temperature range is defined by the overlap of the individual component ALD windows. Therefore, a major goal of ALD precursor development is increasing the growth window, and this goal is especially urgent for calcium because Ca has mostly been alloyed with metal chalcogenides and metal oxides for functional-materials applications.

The most widely employed ALD Ca precursor, commercially available trimeric [Ca$_m$(tmhd)$_n$] (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate) has an ALD window of 325–400°C for the ALD of CaS with H$_2$S as a coprecursor. One alternative precursor, [Ca$(i$Pr$_2$)$_2$C$_2$] (Pr$_2$C$_2$ = 1,2,4-trisopropylcyclopentadienyl) has a somewhat lower window in the ALD of CaO films with H$_2$O as a coprecursor (200–300°C, 1–2 atom % carbon), but has not seen widespread adoption.

Several other types of volatile Ca$_k$ complexes (fluoroalkoxides, fluorinated $\beta$-diketonates, $\beta$-diketiminate and aminodiboranates) have been reported, but not employed in ALD reactions. To complement the currently known Ca ALD precursors, we chose to explore the amide ligand system. Amidinate ligands have high basicity, and amidinate complexes have been shown to react readily with proton sources, such as H$_2$O and H$_2$S, for the ALD of a variety of transition-metal and lanthanide oxides and sulfides. Although several Ca$_k$ amidinate complexes are known (Scheme 1), none are appropriate for ALD. All of the ligands contain bulky aryl groups, which typically afford compounds of very low volatility.

Herein, we report the synthesis of Ca$_k$ alkyl amidinates with excellent thermal stability and volatility, and demonstrate the utility of the Ca$_k$ amidinate precursors for the ALD of CaS. Dimeric bis(N,N-diisopropylformamidinato)calcium(II) (1; 57% yield; distills at 110–115°C, 0.2 torr) and dimeric bis(N,N-diisopropylacetamidinato)calcium(II) (2; 59% yield; sublimes at 120–125°C, 0.1 torr) were prepared in the presence of ammonia by an atom-economical redox reaction between Ca metal and the free amidines (Scheme 2). This direct synthesis avoids the involvement of other metals and reduces the possibility of incorporating trace metal contaminants into thin films. The mechanism probably follows that of the reaction of Ca with HN(SiMe$_3$)$_2$ to form Ca[N(SiMe$_3$)$_2$](THF)$_2$. 1 and 2 are the first nitrogen-only coordinated Ca$_k$ complexes that satisfy the ALD requirements of high volatility and thermal stability. For example,
although homoleptic \( \text{β}-\text{diketiminate} \) \( \text{Ca}^{II} \) complexes are appreciably volatile, they decompose at about 180°C and are therefore not suitable for ALD.[16] Single-crystal X-ray analysis[27] (Figure 1; see also Tables S1–S3 in the Supporting Information) showed that, in the solid state, \( \text{1} \) is a homoleptic dimer in which each Ca center is coordinated by one terminal bidentate amidinate and two bridging amidinates. One of the bridging ligands (N(5) and N(6)) coordinates to both Ca centers in an asymmetric fashion (\( m-h_2 \)). The other bridging ligand (N(7) and N(8)) coordinates in an asymmetric fashion (\( m-h_1 \)). Therefore, formally the coordination number at Ca(1) is six, whereas the coordination number at Ca(2) is only five, as found in one previously reported Ca(II) amidinate.[21a] Interestingly, the sixth (vacant) coordination site of Ca(2) appears to be filled by an agostic interaction with C(24): The Ca–H distances of 2.80 and 2.84 Å fall at the long end of the range typically described as agostic.[26] The Ca–N bond lengths (see Table S2) are consistent with those found in other Ca(II) amidinates. The terminal Ca–N distances of 2.323(3)–2.375(3) Å fall at the short end of the range reported for terminal amidinates, 2.306(5)–2.525(3) Å,[24] with most distances in the range 2.36–2.44 Å.[21a,24,25] The Ca(2)–N distances (2.324(3), 2.325(3) Å) are shorter than the Ca(1)–N distances (2.347(3), 2.374(3) Å), as should be expected from the lower coordination number of Ca(2). The bridging Ca–N distances (2.400(3)–2.633(3) Å) are slightly shorter than those found in the only previously reported bridging amidinate (2.445(3)–2.650(3) Å).[21a] The Ca(1)–N(8) distance of 2.407(4) Å reflects the \( h_1 \) nature of this nitrogen atom, and the Ca(2)–N(8) distance of 3.545(4) Å is nonbonding. Although extreme disorder and weak diffraction thwarted the refinement of several data sets for \( \text{2} \), the connectivity of \( \text{2} \) does appear to be the same as found in \( \text{1} \). \( ^{1} \text{H} \) and \( ^{13} \text{C} \) NMR spectroscopy clearly showed that \( \text{1} \) and \( \text{2} \) maintain dimeric structures in solution (see Figures S1 and S2 in the Supporting Information).

Thermogravimetric analysis (TGA) was used to investigate the volatility and thermal stability of \( \text{1} \) and \( \text{2} \). Under a linear temperature ramp, quantitative, single-step weight loss was observed in the temperature range 150–275°C for \( \text{1} \) and 175–290°C for \( \text{2} \) (Figure 2a). Therefore, both \( \text{1} \) and \( \text{2} \) can vaporize without decomposition (i.e., \( \text{1} \) and \( \text{2} \) are thermally stable) in those temperature ranges on the time scale of the TGA experiment. With a larger sample and faster heating rate, the weight-loss window was elevated as expected, and quantitative, single-step weight loss occurred in the range of 300–400°C (Figure 2a). The excellent thermal stability of both complexes to at least 350°C meets an important requirement for ALD, namely, thermal stability during mass transport to the substrate surface at film-growth temperatures. 

Evaporation rates for \( \text{1} \), \( \text{2} \), and [Ca(3)(tmhd)₆] obtained from isothermal TGA experiments (Figure 2b; see also Figure S5), show that the evaporation rates (i.e., volatilities) follow the order \( \text{1} > \text{2} > \text{[Ca₃(tmhd)₆]} \). Notably, the evaporation rate of \( \text{1} \) was approximately 37 times higher than that of [Ca₃(tmhd)₆] at 225°C, at which temperature both compounds
are liquid (m.p. of 1: 110–116°C; m.p. of [Ca₃(tmhd)₆]: 220–223°C). The slopes of the logarithms of evaporation rate versus inverse temperature in Figure 2b indicate that the enthalpy of vaporization is lower for 1 and 2 than for [Ca₃(tmhd)₆].

In initial tests of the reactivity of the new compounds, CaS films were deposited by ALD by using the vapor of 1 or 2 and H₂S. For both compounds, the precursor was maintained at 140°C. At this temperature, 1 (m.p.: 110–116°C) is a liquid, from which it evaporates at a high and consistent rate (Figure 2b). This rate of evaporation from the liquid surface is consistently reproducible, because its surface area is fixed by its container. In contrast, 2 is a solid (m.p.: 170–174°C) at the evaporator temperature; therefore, its vaporization rate is lower and is determined by its surface area, which changes with time as the material evaporates, and thus is less reproducible.

The ALD of CaS by using the vapor of 1 with H₂S as a cocoreactant produced pure CaS films within the temperature range of 150–280°C (Figure 3). The thickness of the CaS from 1 was constant over the whole length of the gas flow in the reactor (30 cm). Thus, the surface reactions of 1 were saturated over the whole substrate surface. In contrast, the films from 2 became thinner toward the end of the gas-flow path. Thus, the lower vapor pressure of 2 was not high enough to saturate its surface reactions near the end of its gas-flow path. The following discussion therefore focuses on ALD with 1.

At temperatures below 150°C (Figure 3a), the thickness increased owing to incomplete removal of the ligands or physical adsorption of the precursor. At temperatures over 280°C, the thickness increased owing to decomposition of the precursor. Carbon was also detected in these higher-temperature films, which is another indication that the ALD window lies below 280°C. Thus, the deposition operates as an ideal ALD process in the temperature range from 150 to 280°C.

The observed ALD window covers a significantly lower and wider temperature range as compared to that with [Ca₃(tmhd)₆] (325–400°C)[11a,b] and [Ca₃(tmhd)₆(tetraen)] (300–350°C).[11b] This dramatic

![Scheme 2. Synthesis of Ca₃ amidanates by a redox reaction between Ca metal and an amidine. a) Plausible redox reaction mechanisms for Ca and the amidine. b) Synthesis of 1 and 2.](image)

![Figure 1. Solid-state structure of 1 with the thermal ellipsoids set at the 30% probability level; hydrogen atoms and the minor positions (15%) of the disordered bridging ligands are omitted for clarity. Selected distances (Å): Ca(1)–N(1) 2.347(3), Ca(1)–N(5) 2.633(3), Ca(1)–N(7) 2.619(3), Ca(1)–N(8) 2.407(4), Ca(2)–C(24) 3.102(6).[27]](image)

![Figure 2. Thermogravimetric analysis. a) TGA curves (ramp from room temperature to 550°C) of 1 (solid line: 9.6 mg, 10°C/min; dashed line: 8.0 mg, 20°C/min), 2 (dashed line: 9.6 mg, 10°C/min; dotted line: 8.0 mg, 20°C/min). b) Plot of evaporation rate (mg/min) versus temperature (°C).](image)
improvement to the ALD window should enrich the ALD study of alloys of CaS with other metal chalcogenides or oxides because the ALD of metal sulfides and oxides has often been performed below 300°C.\(^{[11,12]}\) The growth rate in the ALD window (Figure 3a) was found to be 0.87 Å per cycle\(^{-1}\), which is significantly higher than that reported for Ca\(_2\)((tmhd)\(_6\)) (0.50 Å per cycle\(^{-1}\)).\(^{[11,12]}\) In X-ray photoelectron spectroscopy (XPS) experiments for the CaS films grown in the ALD window, carbon was not detected (see Figure S6). However, in the CaS films grown at temperatures outside the ALD window (130, 296, 312°C), carbon was detected (see Figure S6). Figure 3b shows the SEM image of a typical columnar and highly crystalline CaS film grown at 212°C. The XRD pattern of this film (Figure 3c) shows only the (111) and (222) reflections of cubic CaS, thus indicating preferential orientation during film growth.\(^{[11,12]}\) The electron diffraction pattern of a CaS film from TEM experiments also indicates that the deposited film has the cubic (rock-salt) structure (Figure 3d; see also Figure S8).

In summary, volatile and thermally stable homoleptic, dimeric Ca\(^{111}\) amides were synthesized in one step through a redox reaction between calcium metal and amidines without any involvement of potential trace metal contaminants. This synthetic procedure may be applicable to Sr or Ba precursors because reactions of Sr and Br with HN(SiMe\(_2\))\(_2\)(THF) or Ba[N(SiMe\(_2\))\(_2\)](THF), in the presence of ammonia,\(^{[10]}\) we are currently exploring this possibility. Precursor \(1\) is a thermally stable liquid at its evaporation temperature, thus ensuring the rapid, stable, and reproducible delivery of vapor. The observed ALD window for CaS with \(1\) and H\(_2\)S is approximately twice as wide and begins 150°C lower than the window reported for commercially available and widely employed [Ca\(_2\)((tmhd)\(_6\)]\(_{2}\). Through improved volatility and lower reaction temperatures, compounds \(1\) and \(2\) provide the opportunity for increased usage of Ca in ALD, especially for the synthesis of multicomponent materials.

**Acknowledgements**

This research was supported in part by the Office of Naval Research (ONR) under contract number ONR N00014-10-1-0937. This study was performed in part at the Center for Nanoscale Systems (CNS) at Harvard University, a member of the National Nanotechnology Infrastructure Network (NNIN), which is supported by the National Science Foundation under NSF award no. ECS-0335765. We are grateful to Prof. T. A. Betley for letting us use his FTIR instrument.

**Keywords:** amidines · atomic layer deposition · calcium · redox chemistry · thin films

**How to cite:** Angew. Chem. Int. Ed. 2016, 55, 10228–10233

Angew. Chem. 2016, 128, 10384–10389

[27] CCDC 1442724 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.