ALKALINE EARTH CYCLOPENTADIENYL COMPOUNDS AS PRECURSORS FOR ATOMIC LAYER EPITAXY

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Larger alkaline earth metals do not have many volatile compounds, the most well-known being β-diketonates (1). The β-diketonates have a few disadvantages: they form easily oligomers which limit the volatility, they are too less reactive at temperatures where they are thermally stable and at temperatures where the reactivity is sufficient they are unstable. β-Ketoiminato complexes form another group of volatile alkaline earth compounds (2). Alkaline earth alkoxides are usually thermally unstable and better results have been obtained with aryl oxides and donor functionalized alkoxides (3). Forth group of alkaline earth complexes showing some volatility is formed by alkyl silyl amides (4). It has been reported recently that η^2 coordinated pyrazolato ligands form volatile complexes with calcium (5). Recently, the cyclopentadienyl compounds of alkaline earth metals have gained attention.

Our group has studied alkaline earth Cp compounds as ALD precursors for few years (6-8). In this paper a summary of Sr and Ba cyclopentadienyl compounds synthesized and studied in deposition of SrS, BaS, $SrTiO_3$ and $BaTiO_3$ films by Atomic Layer Deposition (ALD) is presented. Different alkyl substituted (methyl, isopropyl, *tert*-butyl) cyclopentadienyl and indenyl ligands were synthesized and coordinated to Sr and Ba. The compounds were tried to stabilize by adding neutral ligands like THF, dien, trien, diglyme, and triglyme. In addition, N and O donor functionalities were added to the Cp ring by using $Me_2NHCH_2CH_2C_5Me_4$ and $EtOCH_2CH_2C_5Me_4$ as ligands. The compounds were characterized by NMR and mass spectroscopy, and crystal structures of several compounds were determined. ALD deposition and characteristics of SrS, BaS, $SrTiO_3$ and $BaTiO_3$ films made from different precursors will be presented.

The results show that alkaline earth cyclopentadienyl complexes form monomeric structures and show high enough volatility and thermal stability that they can be used as precursors in ALD. Their advantages are: low deposition temperature to sulfide films, reaction with water to form ternary oxide films, low impurity contents in the films. Disadvantages are: a few of them are commercially available and they have to be synthesized starting from ligand synthesis, air and moisture sensitivity which however is not so high as generally expected. Best behaving complexes were those containing three alkyl substituents (^{i}Pr, ^{t}Bu) in the Cp ring (Fig. 1). Also those complexes having N and O donor functionalities in the Cp ring showed usable precursor behaviour. According to TG and MS measurements the attempts to use additional multidentate Lewis bases to stabilize the Cp complexes were not very successful. SrS and BaS films showed similar properties as films grown from other precursors by ALD. Cp precursors are the only ones allowing ALD of $SrTiO_3$ and $BaTiO_3$ films by thermally activated processes at reasonable temperatures of 250-350 ^oC. Cp complexes are suitable precursors for preparing sulfide and oxide films by the ALD method where the different precursors are introduced to the substrate one at the time. However, because of their high reactivity towards H_2O and H_2S in conventional CVD other oxygen and sulfur precursors have to be looked for.

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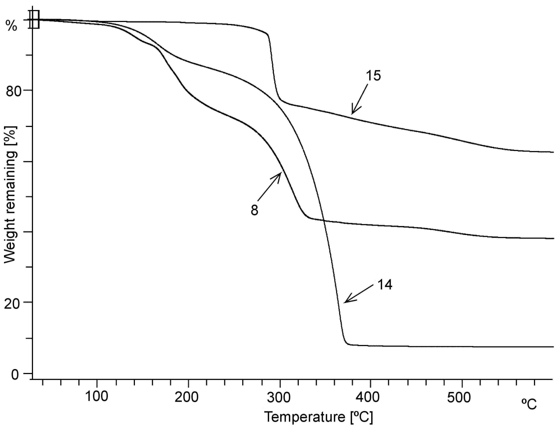

Figure 1. TG curves for complexes $Ba(C_5Me_5)_2(THF)_x$ (8), $Ba(tBu_3C_5H_2)_2(THF)$ (14), $Ba(Me_2NC_2H_4C_5Me_4)_2$ (15).