3742 *Chem. Mater.* **2009,** *21,* 3742–3744
DOI:10.1021/cm902030d

CHEMISTRY OF
MATERIALS
Communication

Atomic Layer Deposition Growth of BaB_2O_4 Thin Films from an Exceptionally Thermally Stable Tris(pyrazolyl)borate-Based Precursor

Mark J. Saly,[†] Frans Munnik,[‡] Ronald J. Baird,[§] and Charles H. Winter*,[†]

[†]*Department of Chemistry, Wayne State University, 5101 Cass Avenue, Detroit, Michigan 48202,* [‡]*Forschungszentrum Dresden-Rossendorf, Postfach 51 01 19, 01314 Dresden, Germany, and* [§]*Institute for Manufacturing Research, Wayne State University, 1129 Engineering, Detroit, Michigan 48202*

Received July 6, 2009

Strontium (Sr) and barium (Ba) are components of many important thin film materials.[1] The widely used film growth techniques chemical vapor deposition[2] (CVD) and atomic layer deposition[3] (ALD) require molecular precursors that volatilize at moderate temperatures without decomposition. In addition, ALD requires precursors that are thermally stable at the substrate temperature to avoid loss of the self-limited growth mechanism.[3] As a result, there has been considerable effort over many years directed toward the development of volatile precursors containing Sr and Ba.[1] The high atomic weights, small charge-to-size ratios, and attendant low Lewis acidities of Sr and Ba afford low volatility, poor thermal stability, and inappropriate reactivity for most existing classes of CVD and ALD precursors. State of the art CVD precursors include fluorinated β-diketonate complexes containing neutral polydentate ether ligands[4] and β-ketoiminato complexes with pendant polyether substituents.[5] The former class sublimes between 120 and 160 °C at low pressures, but fluorine incorporation in the film may lead to changes in materials properties. The β-ketoiminato complexes decompose in the solid state concurrently with sublimation and thus lack thermal stability.[5] Because of the strict precursor thermal stability requirement, only Sr and Ba β-diketonate[6] and metallocene[7] complexes have been demonstrated in ALD growth. $[M(thd)_2]_n$ complexes ($M = Sr$, $n = 3$; $M = Ba$, $n = 4$; thd = 1,1,5,5-tetramethylheptane-3,5-dionate) have very low vapor pressures due to their oligomeric structures[8] and are not reactive enough toward water or dioxygen to allow self-limited metal oxide growth without plasma activation or use of ozone.[6] The metallocenes $Sr(C_5H_2iPr_3)_2$ and $Ba(C_5H_2tBu_3)_2$ or tetrahydrofuran adducts thereof permitted the ALD growth of $SrTiO_3$, $BaTiO_3$, SrS, and BaS thin films.[7] $Ba(C_5H_2tBu_3)_2$ was employed for the ALD growth of $BaTiO_3$ films at substrate temperatures of up to 325 °C.[7d] $Sr(C_5H_2iPr_3)_2$ showed evidence for thermal decomposition at 300 °C in $SrTiO_3$ ALD film growth.[7d]

Herein, we report the ALD growth of BaB_2O_4 films from the precursor bis(tris(3,5-diethylpyrazolyl)borate)-barium ($BaTp^{Et2}{}_2$) and water. This process exhibits self-limited ALD growth up to 375 °C, which demonstrates the exceptional thermal stability of $BaTp^{Et2}{}_2$. ALD precursors with the highest thermal stability permit self-limited growth over the widest possible temperature range, may allow the growth of crystalline materials at higher temperatures, and may deposit higher purity materials because of the absence of decomposition pathways that incorporate undesired elements such as carbon and hydrogen. $BaTp^{Et2}{}_2$ also contains a 2:1 B/Ba ratio, and this precursor stoichiometry is maintained in the BaB_2O_4

---

*Corresponding author. E-mail: chw@chem.wayne.edu.

(1) (a) Wojtczak, W. A.; Fleig, P. F.; Hampden-Smith, M. J. *Adv. Organomet. Chem.* **1996**, *40*, 215–340. (b) Condorelli, G. G.; Malandrino, G.; Fragalà, I. L. *Coord. Chem. Rev.* **2007**, *251*, 1931–1948. (c) Wessels, B. W. *Annu. Rev. Mater. Sci.* **1995**, *25*, 525–546. (d) Matthews, J. S.; Rees, W. S. Jr. *Adv. Inorg. Chem.* **2000**, *50*, 173–192.

(2) (a) Pierson, H. O. *Handbook of Chemical Vapor Depostion* (*CVD*); Noyes Publications/William Andrew Publishing: Norwich, NY, 1999. (b) Hitchman, M. L.; Jenson, K. F. *Chemical Vapor Deposition: Principles and Applications*; Academic Press: London, 1993.

(3) (a) Leskelä, M.; Ritala, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5548–5554. (b) Niinistö, L.; Päiväsaari, J.; Niinistö, J.; Putkonen, M.; Nieminen, M. *Phys. Status Solidi A* **2004**, *201*, 1443–1452. (c) Putkonen, M.; Niinistö, L. *Top. Organomet. Chem.* **2005**, *9*, 125–145.

(4) (a) Belot, J. A.; Neumayer, D. A.; Reedy, C. J.; Studebaker, D. B.; Hinds, B. J.; Stern, C. L.; Marks, T. J. *Chem. Mater.* **1997**, *9*, 1638–1648. (b) Teren, A. R.; Belot, J. A.; Edleman, N. L.; Marks, T. J.; Wessels, B. W. *Chem. Vap. Deposition* **2000**, *6*, 175–177. (c) Marks, T. J.; Belot, J. A.; Reedy, C. J.; McNeely, R. J.; Studebaker, D. B.; Neumayer, D. A.; Stern, C. L. *J. Alloys Compd.* **1997**, *251*, 243–248.

(5) (a) Schulz, D. L.; Hinds, B. J.; Stern, C. L.; Marks, T. J. *Inorg. Chem.* **1993**, *32*, 249–250. (b) Schulz, D. L.; Hinds, B. J.; Neumayer, D. A.; Stern, C. L.; Marks, T. J. *Chem. Mater.* **1993**, *5*, 1605–1617. (c) Neumayer, D. A.; Belot, J. A.; Feezel, R. L.; Reedy, C.; Stern, C. L.; Marks, T. J. *Inorg. Chem.* **1998**, *37*, 5625–5633.

(6) (a) Kosola, A.; Putkonen, M.; Johansson, L.-S.; Niinistö, L. *Appl. Surf. Sci.* **2003**, *211*, 102–112. (b) Vehkamäki, M.; Hatanpää, T.; Hänninen, T.; Ritala, M.; Leskelä, M. *Electrochem. Solid-State Lett.* **1999**, *2*, 504–506. (c) Kwon, O. S.; Kim, S. K.; Hwang, C. S.; Jeong, J. *J. Electrochem. Soc.* **2005**, *152*, C229–C236. (d) Lee, S. W.; Kwon, O. S.; Han, J. H.; Hwang, C. S. *Appl. Phys. Lett.* **2008**, *92*, 222903. (e) Kwon, O. S.; Lee, S. W.; Han, J. H.; Hwang, C. S. *J. Electrochem. Soc.* **2007**, *154*, G127–G133.

(7) (a) Hatanpää, T.; Ritala, M.; Leskelä, M. *J. Organomet. Chem.* **2007**, *692*, 5256–5262. (b) Vehkamäki, M.; Hatanpää, T.; Ritala, M.; Leskelä, M.; Väyrynen, S.; Rauhala, E. *Chem. Vap. Deposition* **2007**, *13*, 239–246. (c) Kukli, K.; Ritala, M.; Sajavaara, T.; Hänninen, T.; Leskelä, M. *Thin Solid Films* **2006**, *500*, 322–329. (d) Hatanpää, T.; Vehkamäki, M.; Mutikainen, I.; Kansikas, J.; Ritala, M.; Leskelä, M. *Dalton Trans.* **2004**, 1181–1190.

(8) (a) Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Otway, D. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2883–2890. (b) Rossetto, G.; Polo, A.; Benetollo, F.; Porcha, M.; Zanella, P. *Polyhedron* **1992**, *11*, 979–985. (c) Drozdov, A. A.; Trojanov, S. I. *Polyhedron* **1992**, *11*, 2877–2882. (d) Brooks, J.; Davies, H. O.; Leedham, T. J.; Jones, A. C.; Steiner, A. *Chem. Vap. Deposition* **2000**, *6*, 66–69.

(9) (a) Likosius, M.; Wenger, C.; Pasko, S.; Costina, I.; Dabrowski, J.; Sorge, R.; Müssig, H.-J.; Lohe, C. *IEEE Trans. Elecron Dev.* **2008**, *55*, 2273–2377. (b) Vehkamäki, M.; Ritala, M.; Leskelä, M.; Jones, A. C.; Davies, H. O.; Sajavaara, T.; Rauhala, E. *J. Electrochem. Soc.* **2004**, *151*, F69–F72. (c) Gaskell, J. M.; Przybylak, S.; Jones, A. C.; Aspinall, H. C.; Chalker, P. R.; Black, K.; Potter, R. J.; Taechakumput, P.; Taylor, S. *Chem. Mater.* **2007**, *19*, 4796–4803. (d) Harjuoja, J.; Hatanpää, T.; Vehkamäki, M.; Väyrynen, S.; Putkonen, M.; Niinistö, L.; Ritala, M.; Leskelä, M.; Rauhala, E. *Chem. Vap. Deposition* **2005**, *11*, 362–367.

films. Use of heterobimetallic precursors to control the ratios of two different elements in thin films is rare in ALD and generally affords poor stoichiometry control.[9] Metal borates are important thin film materials,[10] and there are only a few reports of their growth by CVD.[11] This is the first report of a metal borate film growth by ALD.

ALD growth of BaB_2O_4 on silicon substrates was studied using $BaTp^{Et2}_2$ and water vapor. The synthesis and properties of $BaTp^{Et2}_2$ have been reported by our group.[12] $BaTp^{Et2}_2$ sublimes at 210 °C/0.05 Torr with 0.1% residue and decomposes at ~380 °C in the solid state.[12] The growth behavior was assessed by varying precursor pulse lengths, substrate temperatures, and the number of deposition cycles.[13] Investigation of growth rate as a function of $BaTp^{Et2}_2$ pulse length was performed at 325 °C (Figure 1a). The number of deposition cycles, the water pulse length, and the length of the purge after the water pulse were held constant at 2000, 0.5 s, and 5.0 s, respectively. The $BaTp^{Et2}_2$ reservoir was maintained at 205 °C and the purge length after the $BaTp^{Et2}_2$ pulse was 10.0 s. The growth rate was 0.23 Å/cycle with $BaTp^{Et2}_2$ pulses of ≥1 s, which demonstrates self-limited ALD growth.

The dependence of growth rate on substrate temperature was also investigated (Figure 1b). Depositions were carried out using $BaTp^{Et2}_2$ and water pulse lengths of 3.0 and 0.5 s, respectively, and 2000 deposition cycles. Nitrogen purge lengths of 10.0 and 5.0 s were used after the $BaTp^{Et2}_2$ and water pulses, respectively. A growth rate of 0.23 Å/cycle was observed between 250 and 375 °C. An area of constant growth rate within a specific temperature range is termed the "ALD window," and is characteristic of a robust ALD process.[3] Growth rates of 0.17 and 0.34 Å/cycle were observed at substrate temperatures of 240 and 400 °C, respectively, which are outside of the ALD window.

Elastic-recoil detection analysis (ERDA) was performed on 45−47 nm thick BaB_2O_4 films deposited at 325 and 350 °C to determine the elemental compositions (Table 1). The B/Ba ratios were close to the expected ratio for BaB_2O_4. Hydrogen concentrations for films grown at 325 and 350 °C were 1.2 ± 0.2 and 0.84 ± 0.1 at %, respectively, and the carbon concentrations were 0.3 ± 0.3 and <0.2 at %, respectively. For both samples, the nitrogen concentration was below the detection limit of 0.2 at %.

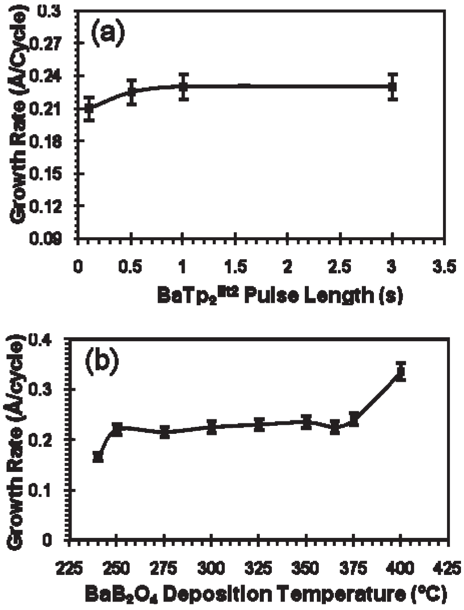

Figure 1. Plots of (a) growth rate versus pulse length of $BaTp_2^{Et2}$ at 325 °C and (b) growth rate versus substrate temperature.

Table 1. Elemental Composition of Thin Films Deposited from $BaTp^{Et2}_2$ and Water, As Determined by ERDA

T (°C)	B:Ba ratio	O:Ba ratio	%H	%C
325	2.1 ± 0.3	3.8 ± 0.4	1.2 ± 0.2	0.3 ± 0.3
350	2.2 ± 0.3	4.7 ± 0.4	0.84 ± 0.1	< 0.2

X-ray photoelectron spectroscopy on a film deposited at 325 °C revealed Ba $3d_{5/2}$ and Ba $3d_{3/2}$ binding energies of 775.5 and 790.9 eV, respectively, with an O 1s ionization at 530.8 eV. The B 1s and Ba $4p_{1/2}$ ionizations were superimposed at 190.7 eV, and thus reliable B concentration data could not be obtained. After argon ion sputtering for 1 min, the carbon and nitrogen ionizations were below the detection limits. All films were amorphous as determined by X-ray diffraction. Annealing of an amorphous film grown at 325 at 550 °C in an oxygen atmosphere afforded crystalline β-BaB_2O_4.

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to probe the surface morphology of the as-deposited films. Micrographs of characteristic film surface features were collected for films deposited at 325 and 350 °C, with thicknesses of 68 and 47 nm, respectively. Films deposited at both temperatures were smooth and featureless. The AFM rms surface roughnesses of typical 2 × 2 μm^2 areas in both films were 0.53 nm. SEM micrographs revealed smooth, pinhole-free films at all magnifications.

The results described herein are significant from several perspectives. Foremost, $BaTp^{Et2}_2$ has high thermal stability, which allows self-limited ALD film growth to occur up to 375 °C. The decomposition temperature of $BaTp^{Et2}_2$ (~380 °C in the solid state[12]) is much higher than those of widely used CVD precursors.[1,4,5] The most thermally stable Ba ALD precursor reported to date is $Ba(C_5H_2tBu_3)_2$, which may be thermally stable up to 350 °C as a solid.[7d] The upper temperature limit of BaB_2O_4 ALD growth described herein exceeds that of

---

(10) (a) Nikogosyan, D. N. *Nonlinear Optical Crystals: A Complete Survey*; Springer: New York; 2005. (b) Chen, C.; Lin, Z.; Wang, Z. *Appl. Phys. B: Laser Opt.* **2005**, *80*, 1–25. (c) Keszler, D. A. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 204–208. (d) Becker, P. *Adv. Mater.* **1998**, *10*, 979–992.

(11) (a) Studebaker, D. B.; Stauf, G. T.; Baum, T. H.; Marks, T. J.; Zhou, H.; Wong, G. K. *Appl. Phys. Lett.* **1997**, *70*, 565–567. (b) Wersand-Quell, S.; Orsal, G.; Thévenin, P.; Bath, A. *Thin Solid Films* **2007**, *515*, 6507–6511. (c) Malandrino, G.; Lo Nigro, R.; Fragalà, I. L. *Chem. Vap. Deposition* **2007**, *13*, 651–655. (d) Malandrino, G.; Lo Nigro, R.; Fragalà, I. L. *Inorg. Chim. Acta* **2007**, *360*, 1138–1142.

(12) Saly, M. J.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **2009**, *48*, 5303–5312.

(13) Details of the film depositions and characterization are presented in the Supporting Information.

$BaTiO_3$ ALD growth from $Ba(C_5H_2tBu_3)_2$, $Ti(OiPr)_4$, and water by 50 °C.[7d] Tris(pyrazolyl)borate ligands have been coordinated to most metals in the periodic table.[14] Ba is one of the most difficult elements in the periodic table for which to prepare volatile and thermally stable compounds, so the present success with $BaTp^{Et2}{}_2$ suggests that many other metal complexes containing tris(pyrazolyl)borate ligands should also combine volatility and high thermal stability. Precursor thermal decomposition destroys self-limited ALD growth and low decomposition temperatures represent a drawback of most existing ALD precursors.[3] Hence, complexes containing tris(pyrazolyl)borate ligands may constitute a general class of thermally stable ALD precursors. Dimeric $[BaTp_2]_2$ (Tp = tris(pyrazolyl)borate) has been used as a CVD precursor for BaB_2O_4 films,[11c] but it undergoes thermal decomposition at 330 °C[12] and does not offer enhanced thermal stability compared to $Ba(C_5H_2tBu_3)_2$.[7d] The higher thermal stability of $BaTp^{Et2}{}_2$, relative to $[BaTp_2]_2$, highlights the importance of careful ALD precursor optimization.[12]

Bimetallic precursors with 1:2 Sr/Ta ratios have been used for the ALD growth of Sr−Ta−O films.[9a,b] Variable Sr/Ta ratios (0.5−1.5) were observed depending upon the deposition conditions, possibly because of loss of volatile tantalum species from the growing film.[9b] ALD growth of $PrAlO_x$ and $NdAlO_x$ films was demonstrated using bimetallic isopropoxide precursors with 1:1 metal ratios, but substoichiometric Pr/Al and Nd/Al ratios (0.30−0.71) were obtained.[9c] $Bi(CH_2SiMe_3)_3$ was employed with ozone for the ALD growth of Bi−Si−O films.[9d] The Si/Bi ratio increased from about 1.5 at 200 °C to about 5 at 450 °C. In the present work, the 2:1 B/Ba stoichiometry of $BaTp^{Et2}{}_2$ is maintained in the BaB_2O_4 thin films, within the uncertainty of the ERDA measurements. Such stoichiometry control implies that two Tp^{Et2} ligands remain coordinated to the surface-bound Ba species, and that hydrolysis of $BaTp^{Et2}{}_2$ is rapid and very efficient. $[BaTp_2]_2$[11c] and $MgTp_2$[11d] have been employed with dioxygen as precursors for the CVD growth of BaB_2O_4 and $Mg_2B_2O_5$ films, respectively, at 750−900 °C. Although the 2:1 B/Ba ratio of $[BaTp_2]_2$ was retained in BaB_2O_4, $Mg_2B_2O_5$ has a 1:1 B/Mg ratio, which differs from the 2:1 ratio in $MgTp_2$. The high CVD growth temperatures probably afford decomposition products that can lead to variable B/metal ratios in the thin films. ALD growth of B_2O_3 and BN films has been reported,[15] as has boron phosphate on silica surfaces.[16]

β-BaB_2O_4 is an important thin film material, and has many applications because of its nonlinear optical properties.[10,11] Thin films of BaB_2O_4 have not been previously grown by ALD, presumably because of the difficulty in controlling the B/Ba ratio with separate precursors. CVD growth of BaB_2O_4 films required a 2.5:1 ratio of B to Ba precursors for optimum depositions.[11a] BaB_2O_4 must possess the crystalline β-phase to exhibit nonlinear optical properties. The present work provides a solution to controlling the B/Ba stoichiometry in BaB_2O_4, but films grown at 375 °C (the upper limit of the ALD window) on silicon remain amorphous. $SrTiO_3$ and $BaTiO_3$ are also important thin film materials that must be crystalline to exhibit the desired ferroelectric properties.[6,7] The ALD growth of $BaTiO_3$ films from $Ba(C_5H_2tBu_3)_2$, $Ti(OiPr)_4$, and water has an upper limit of 325 °C,[7d] but affords amorphous material. It is not clear if $BaTp^{Et2}{}_2$ is an appropriate precursor for $BaTiO_3$ growth, due to the facile B incorporation described herein. An oxygen precursor other than water may avoid B incorporation, and experiments are in progress to probe this issue. Hwang and co-workers showed that use of a 3 nm thick crystalline $SrTiO_3$ seed layer led to the subsequent growth of a crystalline $SrTiO_3$ layer at 370 °C with the desired perovskite structure using an ALD process with $[Sr(thd)_2]_3$, $Ti(OiPr)_2(thd)_2$, and water.[6d] This process may not proceed by a true ALD mechanism, because $[Sr(thd)_2]_3$ lacks sufficient reactivity toward water to form SrO films below its decomposition temperature,[6e,7d] and $Ti(OiPr)_2(thd)_2$ undergoes thermal decomposition at ~230 °C.[17] It is possible that other crystalline substrates may lead to growth of β-BaB_2O_4 at temperatures as low as 375 °C, without having to resort to postdeposition annealing.

In summary, the present work describes a significant enhancement of thermal stability in a Ba ALD precursor, relative to existing Ba ALD and CVD precursors, through use of a tris(pyrazolyl)borate-based ligand. $BaTp^{Et2}{}_2$ also confers a precise 2:1 B/Ba ratio in the BaB_2O_4 films. Precursors containing tris(pyrazolyl)borate ligands should allow the ALD growth of a variety of metal borate films, and similar B/metal stoichiometry control should be possible. Precursor-based composition control, as documented herein, is largely unprecedented in the ALD growth of ternary materials.

Acknowledgment. We are grateful to the Army Research Office (grant nos. W911NF-07-0489 and W911NF-06-1-0102) and SAFC Hitech for generous support of this research. We are grateful to Charles L. Dezelah IV of Picosun USA for helpful discussions.

Supporting Information Available: Film characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

---

(14) Trofimenko, S. *Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London; 1999.

(15) (a) Putkonen, M.; Niinistö, L. *Thin Solid Films* **2006**, *514*, 145–149. (b) Ferguson, J. D.; Weimer, A. W.; George, S. M. *Thin Solid Films* **2002**, *413*, 16–25. (c) Mårlid, B.; Ottosson, M.; Pettersson, U.; Larsson, K.; Carlsson, J.-O. *Thin Solid Films* **2002**, *402*, 167–171.

(16) (a) Brei, V. V.; Kaspersky, V. A.; Gulyanitskaya, N. U. *React. Kinet. Catal. Lett.* **1993**, *50*, 415–421. (b) Gun'ko, V. M. *Kinet. Catal.* **1993**, *34*, 463–466. (c) Puurunen, R. L. *J. Appl. Phys.* **2005**, *97*, 121301.

(17) Turgambaeva, A. E.; Krisyuk, V. V.; Sysoev, S. V.; Igumenov, I. K. *Chem. Vap. Deposition* **2001**, *7*, 121–124.