

HEMICAL APOR EPOSITION

6/98

CVD

Chemical vapor deposition :
CVD
S&E Current Journals
UC San Diego
Received on: 01-20-99

Halide CVD of Bismuth Titanate
Surface Quality of Epitaxial CeO₂
Effect of HCl on Silicon Carbide CVD
Ti-N-Si Coatings
Synthesis of Composite Films

E
rrent
urnals

42
4
6

ISSN 0948-1907 - Vol.6 (1998) - CVDEFX - December 1998


WILEY-
VCH

Contents <http://www.wiley-vch.de>

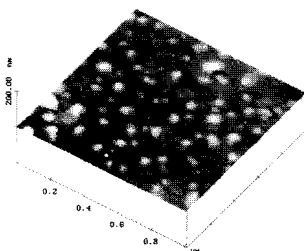
Communication: Bismuth titanate is an interesting ferroelectric material whose properties suggest applications in FETs and in displays. CVD has several advantages in preparing such materials, but a major issue is the selection of precursors. Commonly organometallics are used, but here halide precursors are used, the main advantage being that they yield clean and well-defined grain boundaries. The results show that halogen-free and phase-pure bismuth titanate films with a pronounced *c*-axis orientation can be deposited.

M. Schuisky, A. Hårsta*

Chem. Vap. Deposition **1998, 4, 213 ... 216**

Halide Chemical Vapor Deposition of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

Communication: Cerium oxide has potential as an excellent material for buffer layers in high-temperature superconductor thin films. Here a low pressure aerosol MOCVD process is used for preparing high quality (001) epitaxial ceria films on oriented sapphire substrates. By controlling the maximum temperature for the volatilization of the precursor, a smooth surface with a roughness $R_q = 0.56 \text{ nm}$ is obtained (see Figure).



K. Fröhlich,* J. Šouc, D. Machajdík,
M. Jergel, J. Snauwaert, L. Hellemans

Chem. Vap. Deposition **1998, 4, 216 ... 220**

Surface Quality of Epitaxial CeO_2 Thin
Films Grown on Sapphire by Aerosol
MOCVD

Communication: Anhydrous metal nitrates are useful as single source precursors for CVD of metal oxide films. MOCVD of such films can lead to incorporation of carbon or hydrogen into the films, so single source precursors that cleave directly to metal oxide films with highly volatile byproducts are desirable. In this communication it is shown that, with relatively little optimization, anhydrous metal nitrates exhibit the necessary volatility and reactivity for CVD applications.

D. G. Colombo, D. C. Gilmer,
V. G. Young, Jr., S. A. Campbell,
W. L. Gladfelter*

Chem. Vap. Deposition **1998, 4, 220 ... 222**

Anhydrous Metal Nitrates as Volatile
Single Source Precursors for the CVD of
Metal Oxide Films

Communication: Atmospheric pressure CVD is an attractive method of coating glass substrates since it can be directly integrated with commercial float glass manufacturing lines. Tin sulfide materials are important and of interest for a range of applications by CVD, and here the first APCVD of SnS and SnS_2 from the reaction of tin chloride and H_2S is described. The Figure shows an example of single-phase crystalline SnS_2 .



L. S. Price, I. P. Parkin,* T. G. Hibbert,
K. C. Molloy

Chem. Vap. Deposition **1998, 4, 222 ... 225**

Atmospheric Pressure CVD of SnS and
 SnS_2 on Glass

Full Paper: Barium is a constituent of some technologically important thin film materials, such as high-temperature superconductors and ferroelectrics. Barium sulfide is also potentially important as a phosphor host material for thin film electroluminescent displays. In this work, these sulfide films have been grown by atomic layer epitaxy from a precursor synthesized in situ during film growth by gas-solid reaction. In situ synthesis avoids problems relating to aging of precursor sources. In photoluminescence the films gave a broad emission spectrum.

V. Saanila, J. Ihanus, M. Ritala,*
M. Leskelä

Chem. Vap. Deposition **1998**, *4*, **227** ... 233

Atomic Layer Epitaxy Growth of BaS and BaS:Ce Thin Films from In Situ Synthesized Ba(thd)₂

Full Paper: Silicon carbide is an important material and this has motivated many CVD studies, but there is still a lack of agreement on some kinetic aspects of the process. In this paper a comprehensive investigation is reported with kinetic modeling of the effects of HCl on growth rate, stoichiometry, and surface morphology of SiC films produced by the decomposition of MTS. The Figure shows the faceted polycrystalline form of β -SiC.



G. D. Papasouliotis, S. V. Sotirchos*

Chem. Vap. Deposition **1998**, *4*, **235** ... 246

Hydrogen Chloride Effects on the CVD of Silicon Carbide from Methyltrichlorosilane

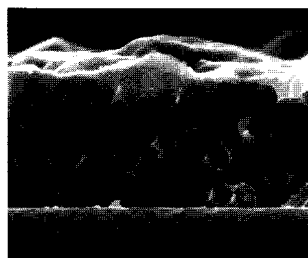
Full Paper: Ti-N-Si coatings offer a promising alternative to Ti-N coatings, which suffer from brittleness. This paper reports on the silicon alloying of Ti-N by CVD with NH₃ or N₂ as the nitrogen source; with N₂, incorporation of Ti-N-Si in a Ti-N matrix is achieved. The influence of precursors and experimental parameters on the phase composition of the coating is reported. It is shown that co-deposits have an improved oxidation resistance in comparison to Ti-N coatings, especially below 950 °C.

G. Llauro, R. Hillel,* F. Sibieude

Chem. Vap. Deposition **1998**, *4*, **247** ... 252

Elaboration and Properties of CVD Ti-N-Si Coatings

Full Paper: Composite materials have widespread applications in the aircraft, automobile, and electronics industries. A new method for the synthesis of composite films has been developed and used to synthesize ZnO-SiO₂ and Cu-SiO₂ composites with a range of silica particle sizes. The morphology of the composite films can be controlled and an example of a dense composite film of SiO₂-Cu is shown in the Figure.



S. Jain, S. Gu, M. Hampden-Smith,*
T. T. Kodas*

Chem. Vap. Deposition **1998**, *4*, **253** ... 257

Synthesis of Composite Films

DIERCK RAABE

COMPUTATIONAL MATERIALS SCIENCE

THE SIMULATION OF MATERIALS MICROSTRUCTURES AND PROPERTIES

1998. XX, 379 pages with 116 figures and 13 tables. Hardcover.

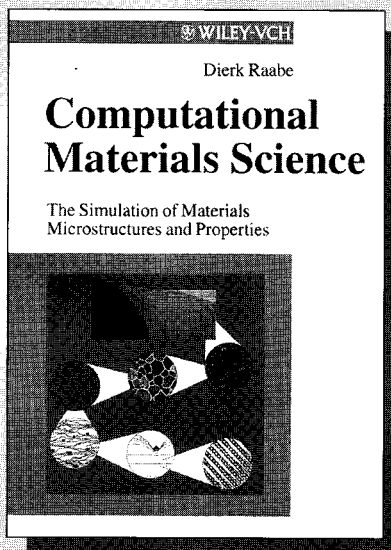
DM 248.-/öS 1810.-/sFr 220.-

ISBN 3-527-29541-0

Modeling and simulation play an ever increasing role in the development and optimization of materials.

Computational Materials Science presents the most important approaches in this new interdisciplinary field of materials science and engineering.

This book addresses graduate students and professionals in materials science and engineering as well as materials-oriented physicists and mechanical engineers.



From the Contents:

- Introduction
- Modeling and Simulation
- Solving Partial Differential Equations
- Computer Architecture
- Software Design
- Simulations at the Macro-Meso Level
- Simulations at the Meso-Micro Level
- Simulations at the Micro-Nano Level
- Integrated Modeling and Simulation

WILEY-VCH • P.O. Box 10 11 61 • 69451 Weinheim, Germany
Fax: +49 (0) 62 01-60 61 84 • e-mail: sales-books@wiley-vch.de
<http://www.wiley-vch.de/>

 WILEY-VCH

Chemical Vapor Deposition

ISSN 0948-1907

Editors: Michael L. Hitchman, Peter Gregory

Associate Editors: Jörn Ritterbusch, Deborah Marik

Administration: Roslyn Main

News Editor: Richard Dixon

Production: Agnes Petersen

Marketing: Angelika Böhrnsen

Editorial Office:

Chemical Vapor Deposition
Department of Pure and Applied Chemistry
University of Strathclyde
295 Cathedral Street, Glasgow G1 1XL, UK
Tel.: (+44) 141 553 4189
Fax: (+44) 141 548 4822
e-mail: m.l.hitchman@strath.ac.uk

Advertising: Richard Dixon

WILEY-VCH, Advertising, Boschstrasse 12, D-69469 Weinheim
Tel.: (+49) 6201 60 65 61, Fax: (+49) 6201 60 65 50
e-mail: adsales@wiley-vch.de

Editorial Advisory Board:

S. E. Alexandrov, St. Petersburg
M. Allendorf, Sandia Natl. Labs.
G. A. Battiston, Padua
C. Bernard, Grenoble
T. M. Besmann, Oak Ridge Natl. Lab.
W. G. Breiland, Sandia Natl. Labs.
J.-O. Carlsson, Uppsala
K. H. Dahmen, Tallahassee
J. G. Eden, Illinois
A. Figueras, Barcelona
R. A. Fischer, Bochum
W. L. Gladfelter, Minnesota
M. Hammond, SI Diamond Inc.
M. J. Hampden-Smith, New Mexico

H. E. Hintermann, Ins
P. John, Heriot Watt
H. Jürgensen, AIXTRON
B. Lux, Vienna
T. Mäntylä, Tampere
T. Marks, Northwestern
B. S. Meyerson, IBM
R. L. Moon, Hewlett Packard
S. Oda, Tokyo
W. Richter, Berlin
G. B. Stringfellow, Utah
G. Verspui, Philips
G. Wahl, Braunschweig
J. O. Williams, N. E. Wales Institute

Published six times per year as a part of *Advanced Materials* by
WILEY-VCH Verlag GmbH, D-69469 Weinheim (Germany).
For ordering information see the current *Advanced Materials* masthead.

Laue oscillations) appear close to the high-angle reflections. The film thickness can then be evaluated as:

$$d \approx \frac{1}{2\sin w_i \sin w_{i-1}} \quad (4)$$

where w_i and w_{i-1} are positions of adjacent satellite maxima.

Received: April 3, 1998
Final version: July 1, 1998

- [1] F. Weiss, K. Fröhlich, R. Haase, M. Labeau, D. Selbmann, J. P. Senateur, O. Thomas, *J. de Phys. IV C3* **1993**, 3, 321.
- [2] K. Fröhlich, D. Machajdik, F. Weiss, B. Bochu, *Mater. Lett.* **1994**, 21, 377.
- [3] K. Fröhlich, J. Šouc, D. Machajdik, A. P. Kobzev, F. Weiss, J. P. Senateur, K. H. Dahmen, *J. de Phys. IV C5* **1995**, 5, 533.
- [4] I. E. Graboy, N. V. Markov, V. V. Maleev, A. R. Kaul, S. N. Polyakov, V. L. Svetchnikov, H. W. Zanderbergen, K. H. Dahmen, *J. Alloys Compd.* **1997**, 151, 318.
- [5] M. Becht, T. Morishita, *J. Alloys Compd.* **1997**, 151, 310.

Anhydrous Metal Nitrates as Volatile Single Source Precursors for the CVD of Metal Oxide Films**

By Daniel G. Colombo, David C. Gilmer,
Victor G. Young, Jr., Stephen A. Campbell, and
Wayne L. Gladfelter*

The most common precursors for the chemical vapor deposition (CVD) of metal oxide films are metal alkoxides and acetylacetonates.^[1] Thermal decomposition of these hydrocarbon-containing precursors can lead to incorporation of carbon and/or hydrogen into the film. In many instances, the depositions of metal oxide films using these precursors are significantly improved by the addition of water, or some other oxygen source such as O_2 , O_3 or N_2O . The presence of these reactive oxygen sources oxidize silicon substrates forming an SiO_2 layer at the interface, which can be a serious problem in certain applications such as the use of high k dielectrics in field effect transistors.^[2] We have sought to develop single source precursors that cleave directly to metal oxide films, and gaseous byproducts that can be easily removed from the CVD reactor. Recently, we reported the low temperature deposition of crystalline titanium dioxide thin films using tetranitratotitanium(IV), $Ti(NO_3)_4$.^[3] We now report that many of the anhydrous metal nitrates are sufficiently volatile, and suitably reactive for the CVD of metal oxide thin films.

The anhydrous metal nitrates of zirconium,^[4] tin,^[5] cobalt,^[6] and gallium,^[7] and the oxo-nitrates of vanadium and chromium^[8] were synthesized using procedures adapted from the literature. As with $Ti(NO_3)_4$,^[9] the metals in $Sn(NO_3)_4$ ^[10] and $Zr(NO_3)_4$ ^[11] are surrounded by a dodecahedral arrangement of eight oxygens from bidentate nitrate ligands (Fig. 1). Both are white, microcrystalline solids that readily sublime at 40 °C (Sn) and 100 °C (Zr) under a static vacuum of 0.05 torr. Both compounds are fairly thermally robust; $Sn(NO_3)_4$ decomposes with evolution of brown fumes around 100 °C, and $Zr(NO_3)_4$ is stable to 140 °C. Dark green $Co(NO_3)_3$ has three bidentate nitrate ligands that form an octahedral arrangement of oxygens around the metal (Fig. 1). It is extremely air- and water-sensitive and readily sublimates in a static vacuum of 0.05 torr at 35 °C. Both $VO(NO_3)_3$ and $CrO_2(NO_3)_2$ are liquids at room temperature; $VO(NO_3)_3$ is pale yellow and moderately light sensitive (boiling point of 65 °C at 0.7 torr), while $CrO_2(NO_3)_2$ is dark red and is both thermally and light sensitive (boiling point of 65 °C at 0.7 torr). White, microcrystalline gallium nitrate exists as the N_2O_5 adduct,^[7] sublimates as low as 80 °C at 0.05 torr, and exhibits a novel structure (see below). All of these anhydrous metal nitrates are powerful oxidizing and nitrating agents, capable of reacting vigorously with organic substrates, and they are readily hydrolyzed in the presence of water.^[12] The oxo-nitrates should be stored at 0 °C and out of direct light when not in use.

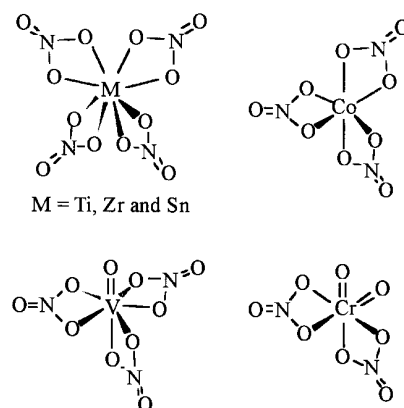


Fig. 1. Structures of the molecular precursors. The proposed structures of the vanadium and chromium oxo complexes are based on related compounds.

Using $Zr(NO_3)_4$, typical ZrO_2 film deposition rates at a reactor temperature of 400 °C ranged from 40 Å/min (precursor $T = 85$ °C) to 130 Å/min (precursor $T = 100$ °C). Rutherford backscattering spectrometry (RBS) indicated an oxygen:metal ratio ranging from 2.0 to 2.2 for as-deposited films. The X-ray diffraction pattern shown in Figure 2a exhibits reflections characteristic of the cubic phase of ZrO_2 . The relative intensities of the reflections indicates a preferred orientation of the polycrystalline film with the (100) plane parallel to the substrate surface. This result is

[*] Prof. W. L. Gladfelter, Dr. D. G. Colombo, Dr. D. C. Gilmer,
Dr. V. G. Young Jr.
Department of Chemistry, University of Minnesota
Minneapolis, MN 55455 (USA)

Prof. S. A. Campbell
Department of Electrical Engineering, University of Minnesota
Minneapolis, MN 55455 (USA)

[**] The authors gratefully acknowledge support from the Semiconductor Research Corporation and the National Science Foundation (CHE-9616501).

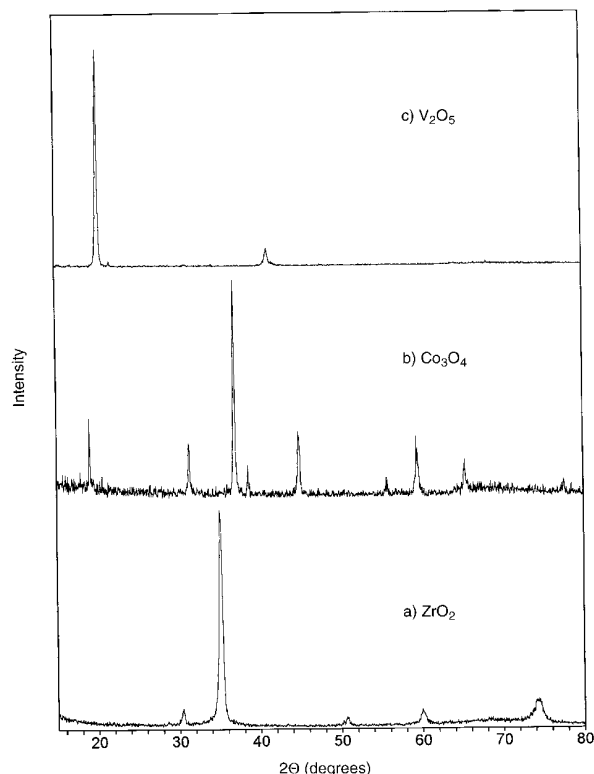


Fig. 2. a) Cubic ZrO_2 deposited using $\text{Zr}(\text{NO}_3)_4$ on $\text{Si}(100)$ at 400°C . Reflections at 30.5° , 35.1° , 50.7° , 60.0° and 74.4° correspond to the 111, 200, 220, 311, and 400 reflections. b) Co_3O_4 deposited using $\text{Co}(\text{NO}_3)_3$ on $\text{Si}(100)$ at 400°C . Reflections at 19.1° , 31.4° , 37.0° , 38.7° , 44.9° , 55.7° , 59.5° , 65.4° , and 77.3° correspond to the 111, 220, 311, 222, 400, 422, 511, 440, and 533 reflections. c) Oriented, crystalline films of V_2O_5 deposited using $\text{VO}(\text{NO}_3)_3$ on $\text{Si}(100)$ at 500°C . Reflections at 20.3° and 41.2° correspond to the 001 and 002 reflections of V_2O_5 .

interesting, given that this is the highest temperature phase of ZrO_2 . While the cause of this is not known, it is interesting to note that the lattice mismatch between cubic ZrO_2 ($a = 5.09 \text{ \AA}$) and Si ($a = 5.4307 \text{ \AA}$) is 6.3 %.

When the precursor vessel containing cobalt(III) nitrate was maintained at ambient temperature, deposition rates reached nearly $300 \text{ \AA}/\text{min}$ at a reactor temperature of 500°C . The XRD of the polycrystalline films exhibited reflections characteristic of the spinel phase of Co_3O_4 (Fig. 2b), and the oxygen-to-metal ratio, as measured by RBS, was 1.3.

The high volatility of the oxo-nitrate precursors was immediately evident upon opening the valve to the precursor vessel. In the case of $\text{VO}(\text{NO}_3)_3$, the entire reaction tube was filled with an orange gas, which deposited V_2O_5 at $210 \text{ \AA}/\text{min}$ when the reactor was maintained at 300°C . A substantial amount of the unreacted precursor was collected in a liquid nitrogen cooled trap, located between the reactor tube and the vacuum pump. When the precursor vessel was cooled to 0°C or 15°C , the deposition rate decreased to 40 or $100 \text{ \AA}/\text{min}$, respectively. Although RBS indicated an oxygen-to-metal ratio that ranged from 2.5 to

2.7 for films deposited as low as 300°C , only those films deposited at 500°C were crystalline (Fig. 2c). Reflections at 20.3° and 41.2° corresponded to the 001 and 002 reflections of V_2O_5 . At 300°C , $\text{CrO}_2(\text{NO}_3)_2$ deposited a red powdery film which rapidly decomposed to a water-soluble solid upon exposure to the atmosphere. This chemical behavior is characteristic of CrO_3 which reacts with atmospheric moisture to form water-soluble hydrous oxides of $\text{Cr}(\text{III})$. Upon raising the reactor temperature to 500°C , no deposition was observed within the hot zone. Instead, a film formed at the cooler exit and entrance regions. This behavior is also consistent with the conversion of $\text{CrO}_2(\text{NO}_3)_2$ into CrO_3 ; the latter is known to sublime under vacuum at temperatures greater than 200°C .

Glassy oxide films of SnO_2 deposited using $\text{Sn}(\text{NO}_3)_4$ were somewhat oxygen rich. RBS indicated that as-deposited films had oxygen-to-metal ratios ranging from 2.1 to 2.7. Films deposited at 500°C were polycrystalline. Annealing all films in air at 700°C for 2 h reduced the O:M ratio, and in the case of crystalline films an O:M ratio of 2.0 was achieved.

Previous studies had suggested that solid $\text{Ga}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_5$ was an ionic compound formulated as $[\text{NO}_2][\text{Ga}(\text{NO}_3)_4]$.^[7] Single crystal X-ray crystallography has verified that assignment (Fig. 3). Four monodentate nitrate ligands are bound to the gallium in a slightly distorted tetrahedron. The Ga–O bond length of $1.888(2) \text{ \AA}$ is within the sum of the covalent radii of Ga and O. At $1.320(3) \text{ \AA}$, $\text{N}(1)–\text{O}(1)$ is lengthened relative to $\text{N}(1)–\text{O}(3)$ and $\text{N}(1)–\text{O}(2)$ ($1.214(3) \text{ \AA}$ and $1.210(3) \text{ \AA}$, respectively). It is also slightly longer than the N–O bond length ($1.22 \text{ \AA}$) for a typical ionic nitrate.^[13] The nitronium ion sits on a special position and extends along channels parallel to the crystallographic c -axis. The equivalent N–O bond lengths are $1.112(9) \text{ \AA}$, and the distance between nonbonded oxygens of neighboring $[\text{NO}_2]^+$ cations is $3.89(1) \text{ \AA}$. The FTIR spectrum of

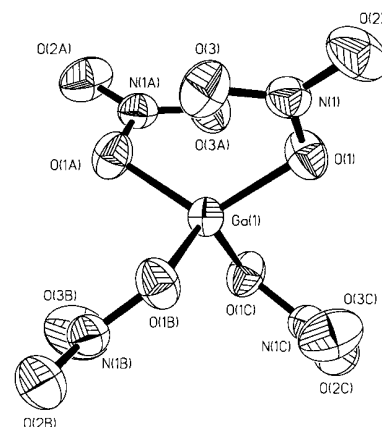
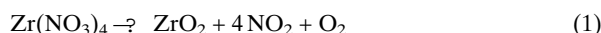


Fig. 3. Structure of the anion of $[\text{NO}_2][\text{Ga}(\text{NO}_3)_4]$. All of the nitrate ligands are symmetry related. Selected distances [$\text{\AA}$] and angles [$^\circ$]: $\text{Ga}(1)–\text{O}(1) = 1.888(2)$, $\text{O}(1)–\text{N}(1) = 1.320(3)$, $\text{N}(1)–\text{O}(2) = 1.210(3)$; $\text{O}(1)–\text{Ga}(1)–\text{O}(1\text{A}) = 104.84(6)$, $\text{O}(1)–\text{Ga}(1)–\text{O}(1\text{B}) = 119.21(13)$, $\text{N}(1)–\text{O}(1)–\text{Ga}(1) = 111.59(14)$, $\text{O}(2)–\text{N}(1)–\text{O}(3) = 126.6(3)$, $\text{O}(2)–\text{N}(1)–\text{O}(1) = 116.2(2)$, $\text{O}(3)–\text{N}(1)–\text{O}(1) = 117.2(2)$.

[NO₂][Ga(NO₃)₄] in a fluorolube mull revealed bands at 2369 and 2351 cm⁻¹, consistent with the values reported earlier.^[7]

Upon heating a precursor vessel containing [NO₂][Ga(NO₃)₄] to 78 °C, deposition rates in the range of 13–400 Å/min were achieved. The higher deposition rates occurred for runs where the precursor had sublimed over much of the inner surface of the precursor vessel. This created a higher surface area, which improved the sublimation efficiency and subsequent delivery of the precursor to the reactor. All films grown using [NO₂][Ga(NO₃)₄] were amorphous, and the oxygen-to-metal ratios (2.0–2.6) obtained by RBS indicated the presence of excess oxygen.

None of the films contained detectable (approximately 2 at.-% by RBS) amounts of nitrogen; an observation attesting to the efficiency of cleavage of at least one N–O bond of each nitrate. Based only on the stoichiometry of the metal-containing products, some M–O bond cleavage is also required. A possible stoichiometry for the thermolysis of zirconium nitrate is shown in Equation 1.



In previous studies, NO₃⁻, preadsorbed on TiO₂ powders from aqueous solutions, produced NO, NO₂ and O₂ upon heating under vacuum using temperature programmed desorption methods.^[14] The relevance of these results to the current study must be considered with some caution because the depositions reported in the current study were conducted under strictly anhydrous conditions. Preliminary infrared spectral evidence obtained for the corresponding titanium reaction^[3] suggested NO₂ was produced. It is possible that either the unstable molecule, NO₃, or NO could be directly formed during the deposition. Unfortunately, the gas-phase reactions of NO₃ (dissociates to NO + O₂) and NO (reacts with O₂ to form NO₂) could conceal their appearance as primary products in the deposition. Efforts to determine the kinetics and mechanisms of these depositions are under way.

With relatively little optimization, we have demonstrated that anhydrous metal nitrates exhibit the volatility and reactivity necessary for CVD applications. Given the obvious absence of any carbon and hydrogen, and the presence of an intrinsic oxidant in the form of the nitrate ligand, we believe that anhydrous metal nitrates represent a useful class of single-source precursors for the CVD of metal oxide films.

Experimental

A quartz, hot-wall reactor (2.6 cm × 35.0 cm) was equipped with a precursor vessel and a mechanical vacuum pump. Nitrogen carrier gas flow (30 mL/min) was monitored using flowmeters, and pressure was measured with a mercury manometer. The pressure of the CVD reactor during a deposition ranged from 1.2 to 2.3 torr. The temperature reported for the de-

position was determined using a thermocouple, positioned between the reactor tube and the heating coils in the center of the furnace. The substrate was p-doped Si(100), and each wafer was degreased and passivated prior to use by immersion in the following baths for 10 min each: methylene chloride; 70 % H₂SO₄:30 % H₂O₂ solution at 80 °C; distilled water; 10 % (v/v) HF solution; and distilled water. The substrates were placed parallel to the gas flow at 2, 4, and 6 cm from the reactor inlet. Table 1 summarizes the film deposition conditions and their characterization. Unless otherwise noted, all films were visually smooth and adhered strongly to the substrates.

Received: April 28, 1998
Final version: July 7, 1998

Table 1. Typical results of CVD using anhydrous metal nitrates.

Precursor	Precursor T [°C]	Deposition T [°C]	Deposition Time [min]	Deposition Rate [Å/min]	RBS [O/M]	XRD [a]
Zr(NO ₃) ₄	90	400	85.0	56	2.1	P
Co(NO ₃) ₂	25	500	5.0	290	1.3	P
VO(NO ₃) ₃	0	500	15.3	98	2.5	P
[NO ₂][Ga(NO ₃) ₄]	78	400	20.0	430	2.1	A
annealed	-	700 [b]	-	-	2.0	A
Sn(NO ₃) ₄	25	400	30.0	150	2.4	A
annealed	-	700 [b]	-	-	2.0	P

[a] P = polycrystalline; A = amorphous. [b] Annealed for 2 h under air.

- [1] H. Treichel, A. Mitwalsky, G. Tempel, G. Zorn, D. A. Bohling, K. R. Coyle, B. S. Felker, M. George, W. Kern, A. P. Lane, N. P. Sandler, *Adv. Mater. Opt. Electron.* **1995**, 5, 163.
- [2] S. A. Campbell, D. C. Gilmer, X.-C. Wang, M.-T. Hsieh, H.-S. Kim, W. L. Gladfelter, J. Yan, *IEEE Trans. Electron. Dev.* **1997**, 44, 104.
- [3] D. C. Gilmer, D. G. Colombo, C. J. Taylor, J. Roberts, G. Haugstad, S. A. Campbell, H.-S. Kim, G. D. Wilk, M. A. Gribelyuk, W. L. Gladfelter, *Chem. Vap. Deposition* **1998**, 4, 9.
- [4] B. O. Field, C. J. Hardy, *Proc. Chem. Soc.* **1962**, 76–77.
- [5] C. C. Addison, W. B. Simpson, *J. Chem. Soc.* **1965**, 598.
- [6] R. J. Fereday, N. Logan, D. Sutton, *J. Chem. Soc.* **1969**, 2699.
- [7] D. Bowler, N. Logan, *J. Chem. Soc., Chem. Commun.* **1971**, 582.
- [8] A. D. Harris, J. C. Trebellas, H. B. Jonassen, *Inorg. Synth.* **1967**, 9, 83.
- [9] C. D. Garner, S. C. Wallwork, *J. Chem. Soc.* **1966**, 1496.
- [10] C. D. Garner, D. Sutton, S. C. Wallwork, *J. Chem. Soc.* **1967**, 1949.
- [11] J. Weidlein, U. Müller, K. Dehnicke, *Spectrochimica Acta* **1968**, 24A, 253.
- [12] C. C. Addison, N. Logan, *Adv. Inorg. Chem. Radiochem.* **1964**, 6, 71.
- [13] J. Laane, J. R. Ohlsen, *Prog. Inorg. Chem.* **1980**, 27, 465.
- [14] R. I. Bickley, R. K. M. Jayanty, J. A. Navio, C. Real, M. Macias, *Surf. Sci.* **1991**, 251/252, 1052.

Atmospheric Pressure CVD of SnS and SnS₂ on Glass**

By Louise S. Price, Ivan P. Parkin,* Thomas G. Hibbert, and Kieran C. Molloy

Tin forms a range of sulfides.^[1] The two most widely studied are SnS^[2] and SnS₂,^[3] both materials are semiconductors with band gaps of 1.3 and 2.18 eV respectively^[4,5]

[*] Dr. I. P. Parkin, L. S. Price
Department of Chemistry, University College London
20 Gordon Street, London WC1H 0AJ (UK)
Dr. T. G. Hibbert, Dr. K. C. Molloy
Department of Chemistry, University of Bath
Claverton Down, Bath, BA2 7AY (UK)

[**] Dr. D. Sheel and Dr. K. Sanderson of Pilkington Glass PLC are thanked for useful discussions and for providing the reactor coater. Mr. D. Knapp and Mr. D. Morphet are thanked for help with construction of the APCVD rig. Mr. G. Elwin is thanked for assistance with rig design and initial testing. The EPSRC are acknowledged for grants to KCM (GR/L54721) and IPP (GR/L56442).