

## NEW LIQUID PRECURSORS FOR CHEMICAL VAPOR DEPOSITION

ROY G. GORDON, FENG CHEN, NICHOLAS J. DICEGLIE JR., AMOS KENIGSBURG,  
XINYE LIU, DANIEL J. TEFF AND JOHN THORNTON  
Harvard University Chemical Laboratories, Cambridge, Massachusetts 02138

### ABSTRACT

New precursors have been found for chemical vapor deposition (CVD) of many metal oxides. Each precursor is a mixture formed by randomly attaching a selected set of organic groups, such as the isomers of the butyl group, to a metal 2,4-pentanedionate (also known as acetylacetonate) in place of the methyl groups of the 2,4-pentanedionate ligand. Most of these new mixed metal beta-diketonates are liquids at room temperature, whereas the corresponding metal 2,4-pentanedionates are solids. In the cases where they were solids or viscous liquids, small amounts of organic solvents were added to reduce the viscosity. We have so far prepared mixed beta-diketonate precursors for barium, strontium, calcium, magnesium, aluminum, indium, tin, lead, bismuth, titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum, manganese, iron, ruthenium, cobalt, nickel, copper, zinc, yttrium, lanthanum and cerium.

Liquid sources are much more convenient for CVD than solid sources. These liquid mixtures or solutions were vaporized by ultrasonically nebulizing the liquid into a flow of hot nitrogen carrier gas preheated to 150-250 °C. These vapor mixtures were mixed with air or oxygen and flowed over substrates heated typically to 350-450 °C. Films of the corresponding metal oxide (or carbonate, in the case of barium, strontium and calcium) were deposited on substrates of silicon or glass. Gas pressures from 20-760 Torr were used.

Because a common set of ligands is used for each of these metal precursors, they can be mixed as liquids or vapors without any precipitation due to ligand exchange reactions. To demonstrate their use in forming mixed metal oxides, we have prepared films of ferroelectric barium titanate. This method should be applicable to other mixed metal oxides of current interest, such as high dielectric constant strontium titanate, ferroelectric bismuth strontium tantalate, superconducting yttrium barium copper oxide, refractory yttrium zirconium oxide, second-harmonic generating barium borate, metallic lanthanum strontium cobalt oxide and magnetoresistive lanthanum strontium manganate.

### INTRODUCTION

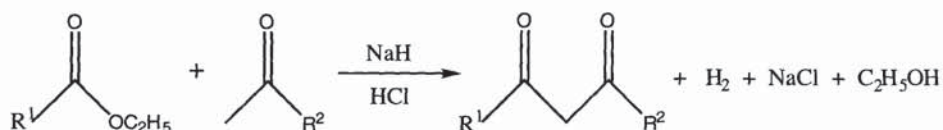
Chemical vapor deposition (CVD) is a versatile method for preparing a wide variety of materials. An effective CVD process needs to have a reproducible supply of a gas containing the elements to be deposited. If the reactant chemicals are gases, they can be directly metered into the apparatus. Liquid reactants can generally be vaporized reproducibly. Sufficiently volatile and thermally stable liquids can be vaporized by bubbling a carrier gas through the liquid. Even liquids with relatively low vapor pressures and limited thermal stability can be successfully vaporized by direct liquid injection or by nebulization into a heated carrier gas.

Solid materials are not so easily used to generate reactant vapors. The rates of sublimation from solid surfaces are often low and not very reproducible. Sintering and evaporation can change the available surface area, and decomposition or contamination of the solid surface can change the rate of evaporation. Unfortunately, many potentially useful CVD precursors are solids. In particular, the beta-diketonates of many metals have been tried as CVD precursors, despite the difficulties inherent in the fact that they are solids.

We have now found that liquid beta-diketonates can be prepared for the majority of metals, by combining them with a mixture of beta-diketonate ligands which prevents their crystallization. The ligands in the mixture may be considered to be derived from 2,4-pentanedione by substituting various isomeric butyl and propyl groups for terminal hydrogens. The disorder introduced by the different shapes and sizes of these alkyl groups prevents crystallization, so that the resulting mixture of metal beta-diketonates remains either as a liquid or a solid glass at room temperature. Those that are glasses are extremely soluble in organic solvents, so in these cases highly concentrated liquid solutions can be formed by adding a small proportion of solvent. Then the liquid or solution can be vaporized by direct liquid injection or by nebulization, and used in a CVD process. In this way, we have so far prepared 21 liquid mixtures and 7 solutions of glasses, and used each of them for the CVD of metal oxides.

#### PREPARATION OF LIQUID METAL BETA-DIKETONATES

The beta-diketone ligands were prepared by the Claisen condensation of an ethyl ester and a methyl ketone in the presence of a strong base, such as sodium hydride, followed by acid hydrolysis and distillation of the crude product.



The alkyl groups  $\text{R}^1$  and  $\text{R}^2$  are randomly selected from *tert*-butyl, *sec*-butyl, *iso*-butyl and isopropyl. The exact proportions do not appear to be critical, and we have generally used equal molar proportions of the alkyl groups. The individual beta-diketones may be prepared separately and then mixed before combining them with the metal. A simpler procedure is to condense simultaneously a mixture of methyl ketones, such as *tert*-butyl methyl ketone, *sec*-butyl methyl ketone, isobutyl methyl ketone and methyl isopropyl ketone, along with a mixture of ethyl esters, such as ethyl isobutyrate, ethyl isovalerate, ethyl 2-methylbutyrate and ethyl trimethylacetate.

Compounds can be formed between these ligands and most metals. Many different reactions can be used to bind beta-diketonate ligands to metals.[1] Additional ligands, besides the beta-diketonate mixtures, may also be bound to the metal. For example, the barium, strontium and calcium mixed beta-diketonates may be complexed with donor solvents, such as ethers or amines. Metals in higher oxidation states, such as titanium(IV) or tantalum(V), may contain other ligands, such as alkoxides or halides, in addition to the mixed beta-diketonate ligands.

#### Synthetic Techniques and Reagents.

All manipulations were carried out using standard Schlenk techniques under dry nitrogen either in a drybox or on a Schlenk line unless otherwise stated. Hexane, EtOH, MeOH, benzene,  $\text{N,N,N',N',N''}$ -pentamethyldiethylenetriamine (pmdeta) and THF were distilled from appropriate drying agents and stored under nitrogen over molecular sieves prior to use.  $\text{Et}_3\text{N}$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$  and  $\text{Zn}(\text{OAc})_2$  were purchased from Aldrich and used as received.  $\text{YCl}_3$ ,  $\text{LaCl}_3$ , Ba and Sr were purchased from Cerac and used as received.  $\text{Zr}(\text{acac})_4$ ,  $\text{Ta}(\text{OEt})_5$ ,  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$



and  $\text{TiO}(\text{acac})_2$  were purchased from Alfa and used as received.  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  was purchased from Strem and used as received.

#### Synthesis of the Beta-Diketonate Ligand Mixture.

The ketone mixture was added slowly and steadily over 3 hours to a rapidly-stirred mixture of the esters, sodium hydride and toluene heated to 90 °C, using a syringe pump. After cooling and stirring overnight, the mixture was neutralized with aqueous hydrochloric acid and the organic layer was separated. The product mixture was distilled from the crude organic layer at 30 mbar from about 70-110 °C, and dried over molecular sieves.

Yields were around 80%. By proton-decoupled carbon-13 NMR analysis in deuteriochloroform, the resulting reaction product was found to be a mixture containing ten of the beta-diketone ligands. Table 1 gives the chemical shifts of the central carbon between ketone groups, in the major (enol) forms of these compounds, as identified by separate syntheses of the pure compounds. This single resonance line is easily resolved for each compound in this mixture, making it useful for analysis, whereas other lines in the proton and C-13 NMR spectra are badly overlapped. Table 1 also gives the numbers assigned by Chemical Abstracts to eight previously known compounds in this mixture. The general formula is written  $\text{R}^1\text{C}(=\text{O})\text{CHR}^3\text{C}(=\text{O})\text{R}^2$ , where  $\text{R}^3 = \text{H}$  in all these examples.

Table 1. NMR data for the beta-diketone ligands

Name	R <sup>1</sup>	R <sup>2</sup>	Chemical Shift C13 NMR, ppm	Chemical Abstracts No.
2,6-dimethyl-3,5-heptanedione	iso-Pr	iso-Pr	94.9	57733-60-5
2,7-dimethyl-3,5-octanedione	iso-Pr	iso-Bu	97.8	7307-07-5
2,6-dimethyl-3,5-octanedione	iso-Pr	sec-Bu	96.0	not reported
2,2,6-trimethyl-3,5-heptanedione	iso-Pr	tert-Bu	92.9	7333-23-5
2,8-dimethyl-4,6-nonanedione	iso-Bu	iso-Bu	100.6	7307-08-6
2,7-dimethyl-4,6-nonanedione	iso-Bu	sec-Bu	98.8	not reported
2,2,7-trimethyl-3,5-octanedione	iso-Bu	tert-Bu	95.7	69725-37-7
3,7-dimethyl-4,6-nonanedione	sec-Bu	sec-Bu	97.0	43865-74-2
2,2,6-trimethyl-3,5-octanedione	sec-Bu	tert-Bu	94.0	34865-71-9
2,2,6,6-tetramethyl-3,5-heptanedione	tert-Bu	tert-Bu	90.6	1118-71-4

#### Synthesis of Metal $\beta$ -diketonates

Synthesis of  $\text{Ba}(\text{beta-diketonate})_2$ . Ba (0.878 g, 6.39 mmol) and pmdeta (2.22 g, 12.8 mmol) were placed together in a flask and 7 mL of THF was added. Bubbles were evolved slowly upon addition of a beta -diketone mixture (2.26 g, 12.8 mmol) diluted with 7 mL of THF. The reaction, more intense after passing  $\text{NH}_3$  through the solution for 5 minutes, continued for 20 minutes until there was very little metal. The  $\text{NH}_3$  flow was continued for another 5 minutes followed by 15 minutes of stirring until only flecks of metal remained. On addition of  $\text{NH}_3$  to the solution the second time, a light green gel, perhaps  $\text{Ba}(\text{beta-diketonate})_2(\text{NH}_3)_x$ , formed but slowly disappeared on stirring under flowing  $\text{N}_2$ . The solution was then filtered through celite and the solvent was removed *in vacuo* to leave a light yellow liquid (4.16 g, 78%). On exposing this liquid to air, a white solid material formed. A similar preparation was used for strontium.

Synthesis of  $\text{Ti}(\text{O}^i\text{Pr})_2(\beta\text{-diketonate})_2$ . A  $\beta$ -diketone mixture (6.84 g, 38.8 mmol) diluted with 10 mL of THF was added to  $\text{Ti}(\text{O}^i\text{Pr})_4$  (5.50 g, 19.4 mmol) in 10 mL of THF. This gave an amber solution which was stirred for 2 hr. The solvent was removed *in vacuo* and the resulting brown, viscous liquid was pumped on for 2 hr at 40 °C (9.25 g, 93%). Due to the presence of  $\text{O}^i\text{Pr}$  groups, this species is air sensitive.

Synthesis of  $\text{TiO}(\beta\text{-diketonate})_2$ . A  $\beta$ -diketone mixture (8.51 g, 48.2 mmol) diluted with 10 mL of  $\text{Et}_2\text{O}$  was cannula-transferred to  $\text{Ti}(\text{O}^i\text{Pr})_4$  (6.85 g, 24.1 mmol) diluted with 10 mL of  $\text{Et}_2\text{O}$ . The reaction produced heat and resulted in an amber-colored solution. After complete addition, the solvent was removed *in vacuo* leaving an orange-brown liquid. This was heated to 90 °C for 1 min under static vacuum and then stirred under dynamic vacuum for 5 min. The process was repeated twice resulting in a very dark brown liquid. Then, 50 mL of THF was added and the reaction was stirred under air for 5 min. The solution gradually began to turn red upon dropwise addition of  $\text{H}_2\text{O}$  (0.66 mL, 36.7 mmol) and was very dark red after stirring 12 hr. After heating to 50 °C for 30 min, the solvent was removed *in vacuo* and the resulting viscous liquid was pumped on for 4 hr (both done at 50 °C). On cooling, the liquid eventually became a solid, very dark brown glass (9.47 g, 94%).

Synthesis of  $\text{Zr}(\beta\text{-diketonate})_4$ .  $\text{Zr}(\text{acac})_4$  (7.50 g, 15.4 mmol) and a beta-diketone mixture (13.5 g, 76.9 mmol) were added together to a flask neat. The flask was fitted with a reflux column and the yellow mixture was heated to 130 °C when a colorless liquid (acacH) began to reflux. After heating for 12 hours and the solution had become clear, the acacH and excess  $\beta$ -diketones were removed *in vacuo* at 130 °C leaving a slightly viscous yellow liquid (11.43 g, 94%). Exposure to air resulted in formation of crystalline plates.

Synthesis of  $\text{Ru}(\beta\text{-diketonate})_3$ .  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  (1.81 g, 8.01 mmol) was suspended in 15 mL of EtOH and a beta-diketone mixture (4.23 g, 24.1 mmol) diluted with 7 mL of EtOH was added. Smoke was evolved upon dropwise addition of  $\text{Et}_3\text{N}$  (2.45 g, 24.2 mmol) diluted with 15 mL of EtOH. The solution was refluxed at 98 °C for 26 hours, the solvent was removed *in vacuo* and 30 mL of hexane was added. After filtration, the solvent was removed leaving a very dark red/brown, viscous liquid (4.07 g, 81.4%). This liquid was taken up in 3.20 g of mesitylene giving a 56% w/w solution. The product did not show any appreciable change on exposure to air.

Synthesis of  $\text{Zn}(\beta\text{-diketonate})_2$ .  $\text{Zn}(\text{OAc})_2$  (10.52 g, 57.4 mmol) was suspended in 25 mL of EtOH and a  $\beta$ -diketone mixture (24.98 g, 142.3 mmol) was added. The solution was refluxed at 110 °C for 12 hours giving a slightly turbid solution. The solution was filtered and the solvent was removed *in vacuo* giving a viscous, yellow liquid (18.96 g, 80%). This liquid formed some white solid on exposure to air.

Synthesis of  $\text{Y}(\beta\text{-diketonate})_3$ . A beta-diketone mixture (16.85 g, 96.0 mmol) was diluted in 30 mL of EtOH and added to  $\text{YCl}_3$  (5.01 g, 25.7 mmol) dissolved in 75 mL of EtOH. Some smoke was evolved upon dropwise addition of  $\text{Et}_3\text{N}$  (7.80 g, 77.1 mmol) diluted with 15 mL of EtOH and the solution eventually became yellow and cloudy. After stirring for hours, the EtOH was removed *in vacuo* at ambient temperature to leave white solid suspended in a yellow oil. To this was added 60 mL of hexane. After filtration, removal of the solvent *in vacuo* and further evacuation at 90 °C to remove excess  $\beta$ -diketone, a viscous yellow liquid (11.19 g, 71%) remained. This product formed some white solid upon exposure to air.

Synthesis of  $\text{La}(\beta\text{-diketonate})_3$ . A beta-diketone mixture (13.51 g, 77.0 mmol) was diluted in 30 mL of EtOH and added to  $\text{LaCl}_3$  (5.00 g, 20.4 mmol) dissolved in 100 mL of EtOH. Some smoke was evolved upon dropwise addition of  $\text{Et}_3\text{N}$  (6.19 g, 61.2 mmol) diluted with 20 mL of

EtOH and the solution eventually became yellow. After stirring 12 hours, the EtOH was removed *in vacuo* at ambient temperature to leave white solid suspended in a yellow oil. To this was added 50 mL of hexane. After filtration, removal of the solvent *in vacuo* and further evacuation at 90 °C to remove excess  $\beta$ -diketone, a very viscous yellow liquid (8.22 g, 61%) remained. This was dissolved in 12.58 g of pmdeta to give a 40% w/w solution. This solution formed some white solid upon exposure to air.

#### CVD USING THE NEW LIQUID PRECURSORS

The liquid mixtures were vaporized in a well-controlled, reproducible manner by ultrasonic nebulization. The liquids were pumped at the desired rate (typically about 0.05 cc/min) by a syringe pump onto the surface of a horizontal quartz plate driven by a piezoelectric transducer at 1.44 Mhz.[2] This quartz plate formed the bottom of a home-made stainless steel housing, through which the mist was carried upward by a low flow (0.2 to 1 L/m) of nitrogen carrier gas. During this upward flow, all large droplets having a terminal velocity faster than the upward gas flow velocity fell back to the quartz plate, where they were broken down again into smaller droplets. In this way, the mist reaching the top of the housing consisted of droplets all of which are smaller than a predetermined size, typically set to 20 microns. These small droplets met preheated (typically to 250 C) nitrogen carrier gas and were vaporized very quickly as they were carried into the reactor. Pressures from 20 Torr to atmospheric pressure were used.

Silicon and glass substrates were used. Film composition and thickness were determined by Rutherford Backscattering Spectroscopy (RBS). Sheet resistance was measured by 4-point probe.

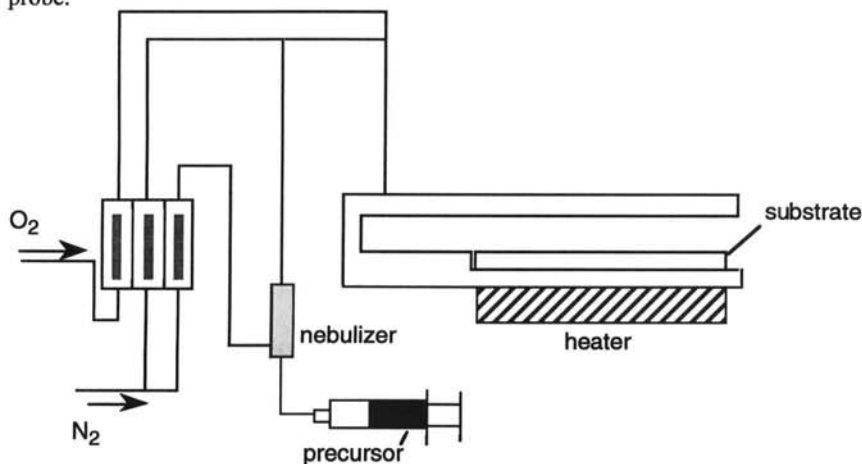


Figure 1. Schematic cross section of the CVD reactor.

#### RESULTS OF THE CVD EXPERIMENTS

Deposition of films from the barium liquid precursor yielded barium carbonate films. Addition of oxygen or nitrous oxide to the deposition atmosphere did not reduce the carbon content. Similar results were obtained from the strontium and calcium precursors. The



magnesium precursor yielded carbon-free magnesium oxide films. Deposition from both of the titanium precursors yielded carbon-free titanium dioxide films.

Mixed solutions of titanium and barium precursors in the absence of added oxygen gas yielded films with Ba/Ti ratios constant along the gas flow direction, but with considerable carbon contamination, about 30 atomic per cent. Adding nitrous oxide did not decrease the carbon content. Adding oxygen reduced the carbon content considerably, to below 10 atomic per cent, but then the Ba/Ti ratio decreased along gas flow direction. The mixed titanium/barium precursor solutions are stable in the absence of moisture, and have been stored for months with no change or precipitation.

In the presence of oxygen, the ruthenium precursor yielded metallic ruthenium dioxide films with resistivities about  $1.4 \times 10^{-4}$  ohm-cm. In the absence of oxygen, the films had a composition  $\text{RuO}_{0.5}$ . Carbon was not detected in the ruthenium oxide films.

The copper beta-diketonate was a solid glass at room temperature. It is highly soluble in organic solvents. For example, a diglyme solution with concentration of 1.6 mole/liter was prepared. This solubility is 17 times larger than the solubility of commonly used precursor copper(thd)<sub>2</sub> (Hthd=2,2,6,6-tetramethylheptanedione).[3] A mesitylene solution of the copper beta-diketonate mixture was used for CVD of copper oxide films. The stoichiometry of the films depended on the oxygen content of the deposition atmosphere, varying from  $\text{Cu}_2\text{O}$  with no oxygen to  $\text{CuO}$  for 20% oxygen.

Oxide films were also prepared from the liquid beta-diketonate precursors for aluminum, indium, tin, bismuth, zirconium, niobium, tantalum, molybdenum, iron, zinc, yttrium, lanthanum and cerium, and from solutions of the glassy beta-diketonate precursors for lead, vanadium, chromium, manganese, cobalt and nickel.

## CONCLUSIONS

Liquid precursors were prepared for all types of metals, including main group, transition and lanthanide metals. They have been vaporized by ultrasonic nebulization and used for the CVD of metal oxides and mixed metal oxides, such as barium strontium titanate. Because the same ligand mixture can be used for all of the metals, the different metal precursors can be mixed, either in the liquid or vapor states, without the precipitation of non-volatile products of ligand exchange, that are often observed when attempts are made for CVD of mixed metal oxides.

## ACKNOWLEDGMENTS

This work was supported in part by the U. S. National Science Foundation, and the National Renewable Energy Laboratory under a subcontract from the U. S. Department of Energy.

## REFERENCES

1. Specific examples of preparative procedures for similar ligands are given in *Inorganic Syntheses*, for chromium(III) in **5**, pp. 130-131 (1957) and **24**, pp. 183-184 (1986); for cobalt(III) in **5**, pp. 188-189 (1957); for rare earth metals in **11**, pp. 94-98 (1968); for cerium(IV) in **12**, pp. 77-78 (1970) and **23**, pp. 147-8 (1985); for manganese(III) in **23**, pp. 148-149 (1985); for iron(II) in **31**, pp. 267-269 (1997); for copper(II) in **23**, pp. 146-147 (1985); for beryllium in **2**, pp. 17-20 (1946); and for calcium, strontium and barium in **31**, pp. 1-7 (1997).
2. The power supply and transducer were manufactured by Cetac, Inc., Omaha, NE.
3. L. G. Hubert-Pfalzgraf, *Electrochem. Soc. Proc.* **97-25**, 824 (1997).