

**INCREASED VOLATILITY OF BARIUM METAL ORGANICS
BY THE USE OF NITROGEN LEWIS BASES.**

JILLIAN M. BURIK, LINDA K. CHEATHAM, JOHN J. GRAHAM,
ROY G. GORDON and ANDREW R. BARRON*

Department of Chemistry and Materials Research Laboratory,
Harvard University, Cambridge, Massachusetts 02138.

ABSTRACT

Substituted β -diketonate complexes of barium have limited volatility even at reduced pressures. The addition of nitrogen Lewis bases to the CVD carrier gas allows barium β -diketonates, even those with no reported volatility, to be transported in the vapor phase at temperatures as low as 70°C (atmospheric pressure) with no decomposition. No increase in volatility is observed, however, for barium carboxylate complexes.

INTRODUCTION

Metal-organic chemical vapor deposition (MOCVD) is potentially well-suited for the preparation of metal oxide thin films.¹ In principle MOCVD offers the advantage of simple apparatus, mild process conditions, control over microstructure and composition, high deposition rates, and possible large scale processing.

The most extensively studied high T_c oxide superconductor is the 1-2-3 compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, because a single phase superconducting compound can be made reliably and reproducibly.² Attempts to produce thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ by MOCVD have been increasingly successful over the last few years. As with any CVD process, however, the critical factor in the deposition has been the selection of a precursor with suitable transport properties. To date, studies have employed the substituted acetylacetonate complexes of copper, yttrium and barium. Although the commercially available copper and yttrium precursors such as $\text{Cu}(\text{TMHD})_2$ ³ and $\text{Y}(\text{TMHD})_3$ ⁴ (TMHD-H = 2,2,6,6-tetramethylheptane-3,5-dione) are adequate as sources, some discrepancy is

* Author to whom all correspondence should be addressed.

reported for the barium precursor. since high temperatures, $> 250^{\circ}\text{C}$, are required for the sublimation of Ba(TMHD)_2 . In addition, prolonged heating at the temperatures required for sufficient mass transport results in significant decomposition of Ba(TMHD)_2 to non-volatile products. This leads to a change in the concentration of barium in the vapor phase over time, and therefore changes in deposition rate and film composition.

There are two possible solutions to the problem of the general involatility of barium compounds. First, alternative precursor compounds can be developed with higher volatility and stability than those employed at present. Second, new methods of increasing compound volatility can be developed.

In line with the former option several researchers have reported the synthesis and use of fluorinated β -diketonate compounds.⁵ However, thin films grown using these fluorine containing complexes contain significant quantities of BaF_2 , and therefore, require a post-deposition hydrolysis step to remove the fluorine. More recently, Caulton, Chisholm and co-workers⁶ have synthesized a volatile (160°C , 10^{-1} Torr) oxo-alkoxide hydride cluster of barium, $\text{H}_4\text{Ba}_6(\mu_6\text{-O})(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{14}$, although no deposition studies have been reported at this time.

This ever increasing complexity of precursor compound design has prompted us to follow the second route and investigate possible processes for the increased volatilization of commercially available barium, calcium and strontium β -diketonates. Prior to our work in this area Sievers *et. al.*⁷ reported that the addition of vapors of the free ligand TMHD-H to the CVD carrier gas stabilized the vaporization rate of Ba(TMHD)_2 so that its vapor pressure remains constant for several hours. Although premature decomposition of Ba(TMHD)_2 is reduced, high temperatures ($280\text{-}300^{\circ}\text{C}$) are still required to volatilize the precursor. Spee, Mackor and co-workers⁸ have noted that polyether adducts of the fluorinated complex Ba(HFA)_2 (HFA = hexafluoroacetylacetonate) are significantly more volatile (150°C , 0.03 mmHg) than the uncomplexed barium source. Despite this increase in volatility the deposited films contain significant quantities of BaF_2 , and there has been no report that the non-fluorinated Ba(TMHD)_2 can be volatilized by this method.

We report here that the use of nitrogen Lewis bases as a carrier gas, or as an additive to an inert carrier gas, results in the dramatic increase in volatility of Ba(TMHD)_2 and Ba(acac)_2 (acac = acetylacetonate).

EXPERIMENTAL

Ba(TMHD)₂ and Ba(acac)₂ were prepared in aqueous solution by the reaction of Ba(OH)₂ with a slight excess of the β-diketonate. The amines were purchased from commercial sources and used without further purification.

A sample of the barium compound (ca. 1.0 g) was placed in a quartz tube furnace connected at one end to the carrier gas, N₂ or air, which was passed through a glass bubbler containing the appropriate amine before entering the furnace. The bubbler was placed in a constant temperature bath and the gas flow rate maintained at 5 L min⁻¹. NH₃ and NMe₃ were used as the carrier gas without dilution. The effects on the melting and sublimation points of Ba(TMHD)₂ and Ba(acac)₂ with the addition of various nitrogen Lewis bases to the carrier gas are presented in Table 1.

TABLE I. Melting and Sublimation Temperatures of Barium β-Diketonates in the Presence of Amine Lewis Bases.

Barium Compound	Amine	Melting Temperature (°C)	Sublimation Temperature (°C)
Ba(TMHD) ₂	none	150-170 (dec)	
"	NH ₃ ^a	70	150
"	NMe ₃ ^a	62	70
"	NEt ₃ ^b	100	250
"	pyridine ^b	100	230-240
"	H ₂ NC ₂ H ₄ NH ₂ ^b	100	200
"	Me ₂ NC ₂ H ₄ NMe ₂ ^b	150	190-210
Ba(acac) ₂	none	180 (dec)	
"	NEt ₃ ^b	100	180 (dec)

^a neat

^b saturated vapor

RESULTS AND DISCUSSION

In the absence of volatile amines Ba(TMHD)_2 sublimates at reduced pressure (0.05 mmHg) with significant decomposition at 225°C. While at atmospheric pressure decomposition occurs with melting at ca. 170°C. In the presence of amine vapors Ba(TMHD)_2 melts between 70-150°C and sublimates, at atmospheric pressure, with negligible decomposition between 70-240°C (see Table 1). The temperature at which melting and sublimation occur is dependent on not only the amine, but also its partial pressure in the carrier gas. The best results are therefore obtained for NH_3 and NMe_3 when used undiluted. The strontium and calcium TMHD complexes are far more volatile than their barium analogue, both subliming below 150°C (760 mmHg); consequently the addition of amine vapors does little to improve their volatility.

The unsubstituted β -diketonate complex of barium, Ba(acac)_2 , which has no reported volatility, even under reduced pressure, sublimates albeit with some decomposition in the presence of NEt_3 vapors (see Table 1). On the other hand amine vapors have no effect on the carboxylate complexes of barium, $\text{Ba(O}_2\text{CR)}_2$. They remain involatile decomposing at 400-450°C with loss of CO_2 .⁹ The mechanism by which the volatility of the β -diketonate complex is increased is unclear. It should be noted, however, that in direct contrast to the work of Spee and Mackor⁸ with polyethers, we have been unable to isolate amine adducts such as $\text{Ba(TMHD)}_2\text{.(NR}_3)_x$, either *in situ* or by the dissolution of Ba(TMHD)_2 in the appropriate amine. In addition, thin films of barium oxide grown under amine vapors¹⁰ contain no detectable nitrogen and a low carbon content (<5%) suggesting that it is not an amine adduct involved in the deposition.

CONCLUSION

The volatility and thermal stability of Ba(TMHD)_2 is dramatically increased by the addition of amine vapors to the CVD carrier gas. However, the dependence of volatility on the amine partial pressure precludes the use of this process in low pressure CVD systems.

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