A Cobalt Layer Deposition Study: Dicobaltatetrahedranes as Convenient MOCVD Precursor Systems

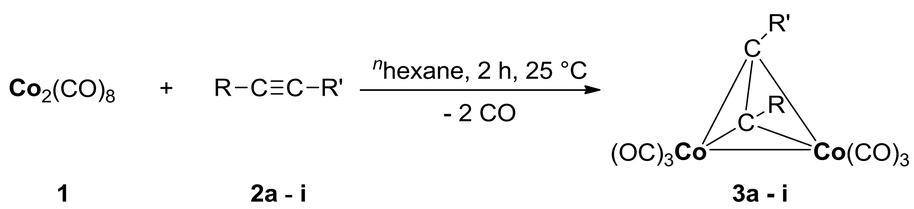
***Colin Georgi*, Heinrich Lang** *

Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry, Inorganic Chemistry, 09107 CHEMNITZ, GERMANY.
E-mail: heinrich.lang@chemie.tu-chemnitz.de

Introduction

Herein, we present the application of a series of dicobaltatetrahedranes of general composition $[Co_2(CO)_6(\mu^2\text{-}RC{\equiv}CR')]$ (R = H, R' = $(CH_3)_3Si$, $^nC_4H_9$, $^nC_5H_{11}$, $^nC_6H_{13}$, $^nC_7H_{15}$; R = $^nC_3H_7$, R' = $(CH_3)_3Si$, CH_3; R = R' = C_2H_5, $(CH_3)_3Si$) as CVD precursors for the deposition of thin cobalt layers in a home-built CVD cold-wall reactor. These organometalic compounds are low melting precursors which don't require any addition of reactive gases during the deposition process. Within the series of compounds, the substituents R and R′ have systematically been varied to investigate the influence on the physical properties, including melting point, vapor pressure or combustion process. Cobalt layers were formed in the temperature range between 225 and 380 °C with nitrogen as carrier gas. The produced layers were characterized by SEM, EDX and XPS measurements.

Synthesis



1 **2a - i** **3a - i**

a	R = R' = $(CH_3)_3Si$	**d**	R = R' = C_2H_5	**g**	R = H; R' = $^nC_5H_{11}$
b	R = $(CH_3)_3Si$; R' = H	**e**	R = CH_3; R' = $^nC_3H_7$	**h**	R = H; R' = $^nC_6H_{13}$
c	R = $(CH_3)_3Si$; R' = $^nC_3H_7$	**f**	R = H; R' = $^nC_4H_9$	**i**	R = H; R' = $^nC_7H_{15}$

Fig. 1: Synthesis of **3a** – **i**.

For the synthesis of CVD precursors **3a** – **i**, $Co_2(CO)_8$ and the respective alkyne were reacted at room temperature in *n*-hexane (*Fig.* 1) within 2 h. Under elimination of two equivalents of CO, a tetrahedral structure consisting of two carbon and two cobalt atoms is formed. The compounds were produced in virtually quantitative yields and they are insensitive to oxygen and humidity. The substituents R and R' influence the melting points and the vapor pressure of the appropriate dicobaltatetrahedranes.

Vapor pressure measurements

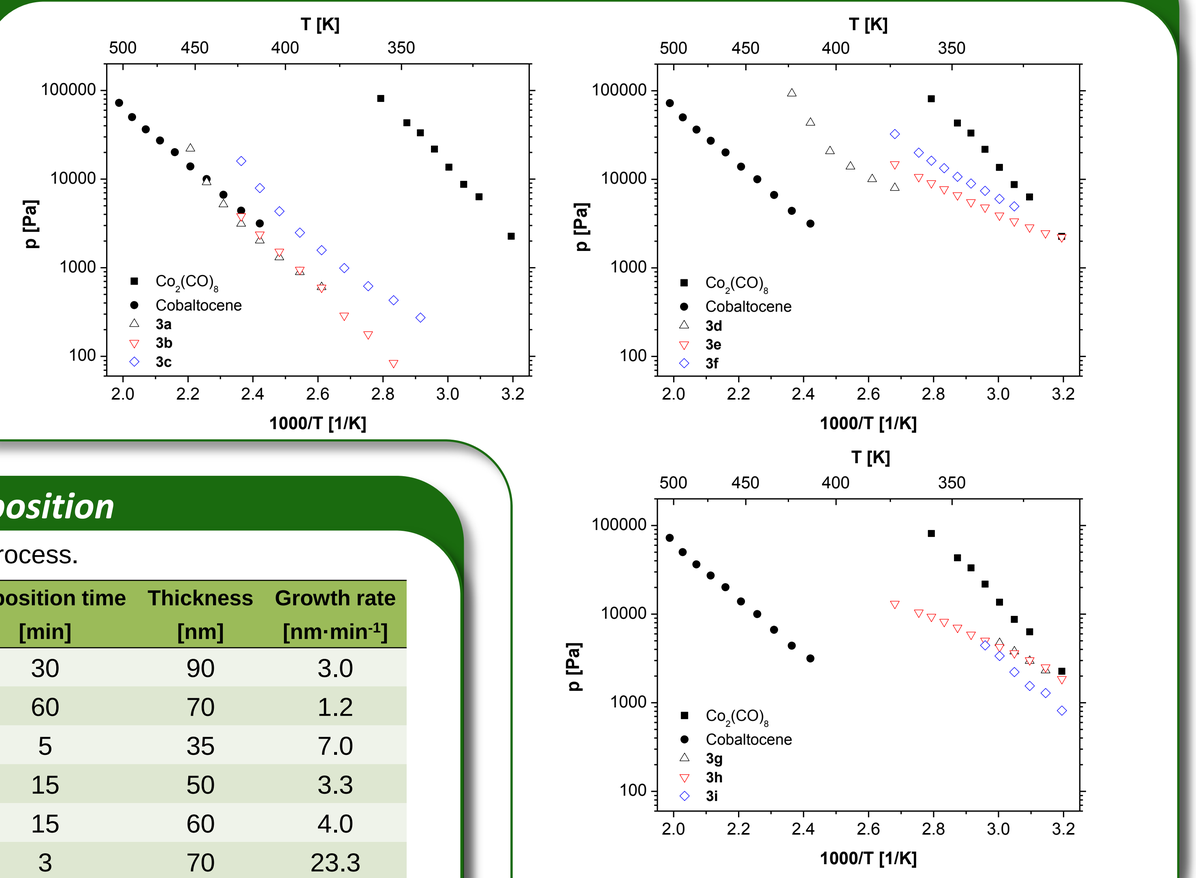


Fig. 5: Vapor pressure traces of **3a** – **i** compared with cobaltocene and $Co_2(CO)_8$, respectively.

Chemical Vapor Deposition

Tab. 2. Deposition parameters of **3a** – **i** for MOCVD process.

Compd.	$\vartheta_{precursor}$ [°C]	$\vartheta_{deposition}$ [°C]	Gasflow N_2 [mL·min^{-1}]	Pressure [mbar]	Deposition time [min]	Thickness [nm]	Growth rate [nm·min^{-1}]
3a	25	250	50	0.25	30	90	3.0
3b	25	350	50	0.45	60	70	1.2
3c	25	380	50	10	5	35	7.0
3d	25	380	50	50	15	50	3.3
3e	25	380	50	50	15	60	4.0
3f	25	225	50	50	3	70	23.3
3g	25	250	50	50	5	50	10.0
3h	25	250	50	50	5	50	10.0
3i	25	250	50	50	5	50	10.0

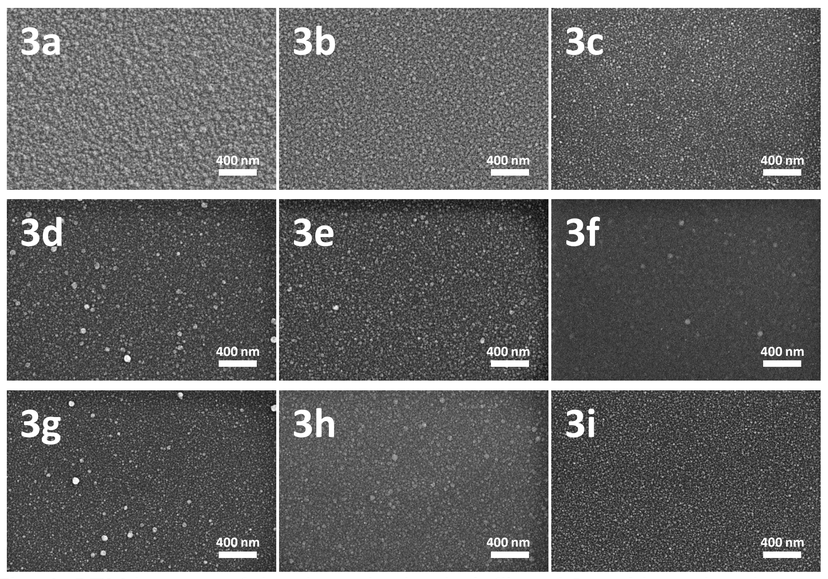


Fig. 4. SEM images of the deposited cobalt film of **3a** – **i** by using the parameters given in *Tab. 2.*

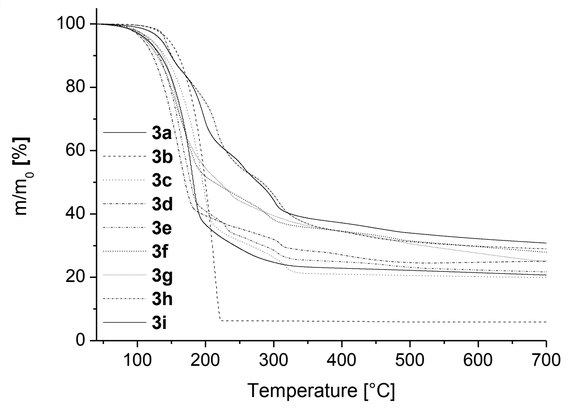


Fig. 2: TG traces of **3a** – **i**; Ar 60 mL·min^{-1}, heating rate 10 K·min^{-1}**.**

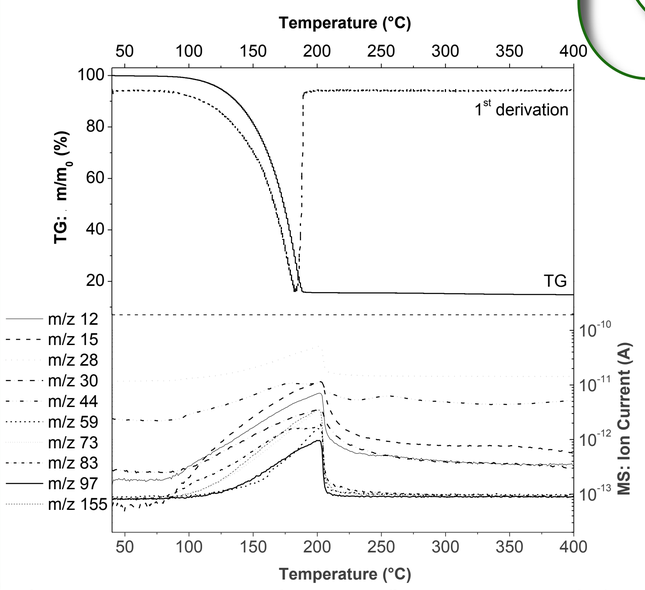


Fig. 3: TG-MS traces of **3a**; gas flow Ar 60 mL·min^{-1}, heating rate 5 K·min^{-1}**.**

Tab. 1: Mass fragments observed during the TG-MS measurement of **3a**.

m/z	Fragment
12	C^+
15	CH_3^+
28	CO^+, Si^+
30	CH_2O^+, $C_2H_6^+$
44	CO_2^+, $C_3H_7^+$
59	Co^+, $HSi(CH_3)_2^+$
73	$Si(CH_3)_3^+$
83	CoC_2^+, $C_2HSi(CH_3)_2^+$
97	$C_2HSi(CH_3)_3^+$
155	$CCo(CO)_3^+$, $C_2Co_2(CO)_6^+$

Thermal behavior and decomposition process

Since XPS is a surface sensitive measurement method for the determination of the elemental composition, contaminations on the film surface may be overestimated; therefore, the measurements have additionally been performed after removing a layer of the film by argon ion sputtering (Table 3). For all deposited films it was observed that the surface contains a noteworthy amount of carbon, oxygen and silicon (**3a** – **3c**) impurities, while inside the layer the cobalt content is much higher. For **3a** – **3c** within the layer almost no silicon is found, which leads to the assumption that the $(CH_3)_3Si$ groups decompose to volatile follow up products and are not involved in the film formation. The introduction of alkyl chains to the precursor systems in all cases led to an increased carbon content. Within the films generated with **3d** – **f** relatively high oxygen contents were found, which decrease with the asymmetry of the precursor, whereby the carbon content increases. The cobalt amount is almost constant at ca. 60 % for the deposition with alkyl substituted **3d** – **i**. The deposition using precursors **3g** – **i** leads to cobalt layers containing carbon as the main impurity.

Tab. 3: XPS results of thin films deposited using **3a** – **i** as precursor.

Compd.	Surface composition				Layer composition			
	C1s	O1s	Si2s	Co2p	C1s	O1s	Si2s	Co2p
3a	34.5	26.0	5.6	33.9	2.5	0.8	0.0	96.7
3b	46.7	34.0	12.2	7.1	4.1	26.6	0.8	68.5
3c	51.9	32.1	11.1	4.9	23.9	3.3	0.4	72.4
3d	34.5	41.1		24.4	4.2	34.4		61.4
3e	34.6	38.8		26.6	4.4	33.2		62.4
3f	47.7	40.4		11.9	13.6	25.5		60.9
3g	17.3	28.6		54.1	35.2	5.7		59.1
3h	44.5	15.3		40.2	32.3	9.3		58.4
3i	44.6	14.3		41.1	36.5	6.5		57.0

Film characterization

Trimethylsilyl- and alkyl- substituted dicobaltatetrahedranes **3a** – **i** were synthesized and used as potential precursors for MOCVD of cobalt. TG and vapor pressure measurements were carried out showing high volatility of the complexes and a decomposition below 400 °C. The deposition of about 100 nm thin cobalt films were carried out in a vertical home build cold wall CVD-reactor. The characterization of these layers with SEM, EDX and XPS indicate that without the addition of any reactive gas continuous and homogeneous films were formed, of pure cobalt for **3a**. Precursor **3b**, **3d** and **3e** produced a mixture of cobalt and cobalt oxide with minor impurities of carbon. The layers obtained with **3c** and **3g** – **i** consist of cobalt, carbon and minor cobalt oxide impurities. The film formation using **3f** as cobalt source contains a mixture of cobalt, cobalt oxide and carbon.

Conclusion

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References & Acknowledgement