Synthesis, Characterization and Application of Novel Ruthenium Precursors for MOCVD by a Single Source Approach

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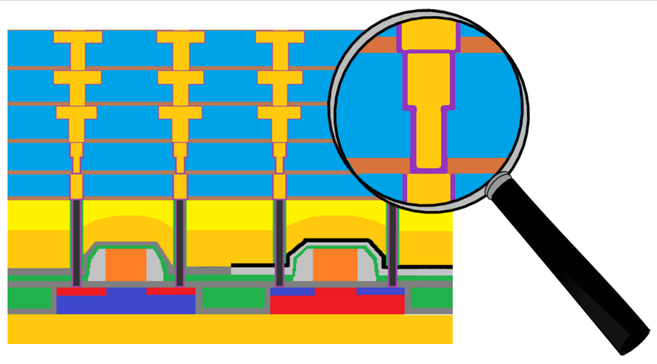
Motivation

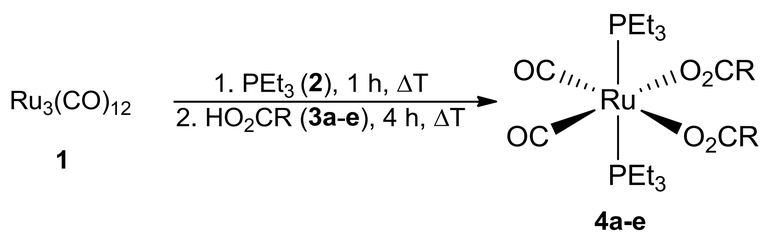
Thin ruthenium layers are promising candidates for many applications in semiconductor industry. [1] However, their use as diffusion barrier for copper interconnects in integrated circuits is limited, due to grain boundaries of a polycrystalline structure allowing copper diffusion at unacceptable low temperatures. [2] Amorphous ruthenium-based films, *e.g*. obtained by incorporation of phosphorus, have been shown to provide better copper diffusion barrier properties than pure polycrystalline ruthenium deposits. [3] We herein present the synthesis and characterization of ruthenium precursors of general type $Ru(CO)_2(PEt_3)_2(O_2CR)_2$ (R = Me, Et, ^{i}Pr, ^{t}Bu, CH_2OCH_3) and their use as *single-source* CVD precursors for the preparation of thin and conformal phosphorus-doped ruthenium layers. Variation of the phosphine and carboxylate ligands allowed influencing the thermal behavior and vapor pressure of the respective precursor. [4]



Precursor Synthesis & Characterization

Synthesis

For the synthesis of CVD precursors **4a–e**, $Ru_3(CO)_{12}$ (**1**), PEt_3 and the respective carboxylic acid were reacted under reflux. Compounds **4a–e** are stable to air and moisture and possess low melting points in a range between 92–143 °C.



4a: R = Me
4b: R = Et
4c: R = ^{i}Pr
4d: R = ^{t}Bu
4e: R = CH_2OCH_3

Single Crystal X-Ray Diffraction

The structures of **4a–4e** in the solid state were determined by single crystal X-ray diffraction studies. Suitable crystal were obtained from a concentrated mixture of a diethyl-ether/*n*-hexane solution at 5 °C. The complexes consist of slightly distorted octahedral coordinated ruthenium atoms with two *trans*-positioned triethylphosphines (P1 and P2), two *cis*-oriented carbonyls and two-monodentate O-bonded carboxylates in the equatorial plane (Fig. 1).

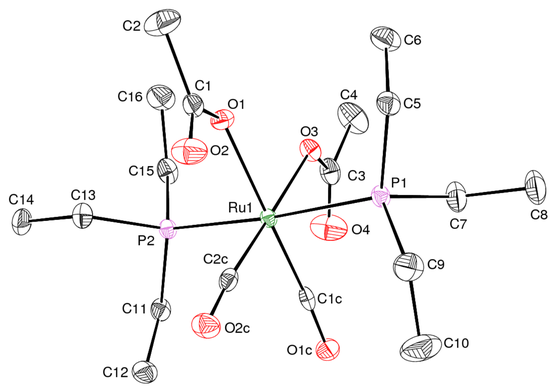


Fig. 1 ORTEP diagram (50 % probability level) of the molecular structure of **4a** with the atom numbering scheme. All hydrogen atoms have been omitted for clarity.

Thermal Behavior

TG measurements were carried out in a temperature range from 40 to 600 °C with a heating rate of 10 K · min^{-1} under a N_2 carrier gas flow of 60 mL · min^{-1}. The decomposition processes of **4a–e** take place in similar temperature ranges from 250 to 280 °C (Fig. 2).

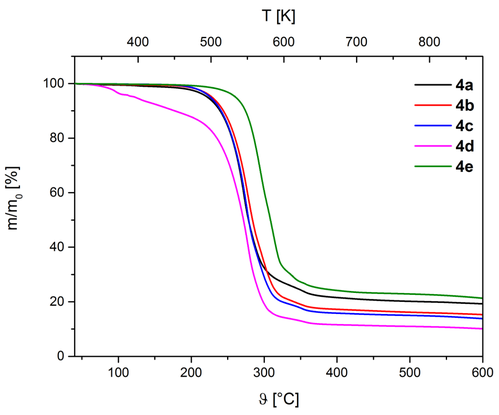


Fig. 2 TG traces of **4a–4e**, gas flow N_2 60 mL min^{-1}, heating rate 10 K min^{-1}.

Chemical Vapor Deposition & Layer Characterization

CVD Deposition Parameters

Chemical vapor deposition experiments were carried out with a home-built vertical cold-wall reactor equipped with a continuous evaporation system at a deposition temperature of 350 °C using nitrogen as carrier gas (60 mL · min^{-1}). As substrate a silicon wafer featuring a 100 nm thick SiO_2 layer was applied.

	4b	**4c**
ϑ (Precursor) [°C]	135	145
ϑ (Deposition) [°C]	350	350
Gas flow (N_2) [mL·min^{-1}]	60	60
Pressure [mbar]	0.9	0.9
Deposition time [min]	45	45
Layer thickness[a] [nm]	50	100
Deposition rate [nm min^{-1}]	1.1	2.2

[a]Determined by cross-sectional SEM images.

Layer Characterization

The SEM images confirm the formation of dense and conformal layers. The film composition was analyzed by EDX showing the characteristic patterns of ruthenium as well as phosphorus for all samples.

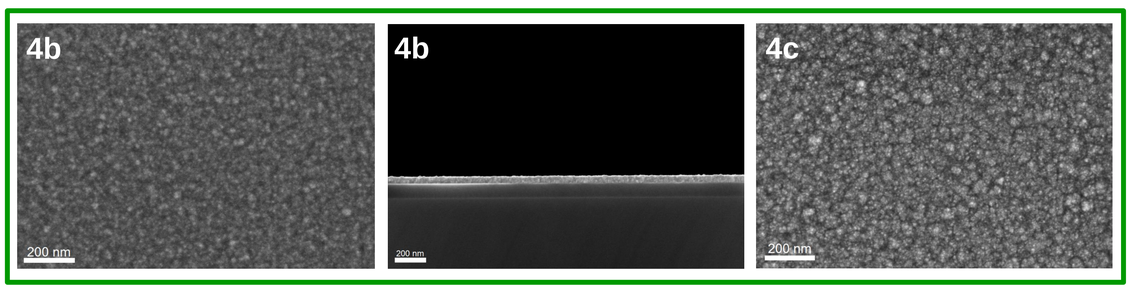


Fig. 3 SEM images of ruthenium films deposited on SiO_2 using complexes **4b** and **4c**.

Elements	**4b** Norm. C [%]		**4c** Norm. C [%]	
	6 keV	3 keV	6 keV	3 keV
C	7.1	10.3	7.7	12.0
O	17.6	10.1	10.2	6.7
Si	49.4	2.4	21.9	0.3
P	2.1	62.6	6.0	62.4
Ru	23.8	14.6	54.2	18.6

Tab. 1 EDX data of ruthenium films deposited on SiO_2 using complexes **4b** and **4c**.

Summary

- ✓ Preparation of air-stable ruthenium CVD precursors **4a–e**
- ✓ Complexes **4a–e** are characterized by low melting points (92–143 °C)
- ✓ Complexes **4a–e** possess low decomposition points (< 280 °C)
- ✓ 50–100 nm thin amorphous Ru(P) layers were deposited by CVD
- ✓ *Single-Source Approach*: no reactive gas or additional P source is needed
- ✓ SEM images show that conformal, homogeneous films were formed
- ✓ EXD measurements show that the films are composed of Ru and P
- ○ XPS measurements are under investigation

References

[1] For example: A. Tuchscherer, C. Georgi, N. Roth, D. Schaarschmidt, T. Rüffer, T. Wächtler, S. E. Schulz, S. Oswald, T. Gessner, H. Lang, *Eur. J. Inorg. Chem.* (2012), 4867–4876.
[2] L. B. Henderson, J. G. Ekerdt, *Thin Solid Films* **517**, (2009), 1645–1649.
[3] J.-H. Shin, H.-W. Kim, K. Agapiou, *et al*., *J. Vac. Sci. Technol. A* **26**, (2008), 974–979.
[4] J. Jeschke, S. Möckel, M. Korb, T. Rüffer, K. Assim, M. Melzer, G. Herwig, C. Georgi, S. E. Schulz, H. Lang, *J. Mater. Chem. C*, (2016), 2319-2328.

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