Chemical Vapor Deposition of Conformal Phosphorus-doped Ruthenium Layers

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Motivation

The ongoing miniaturization of devices in semiconductor industry causes new manufacturing and materials challenges. One key destination is the development of a single material liner for future copper interconnects in integrated circuits.[1] A prospect which has been considered is ruthenium, as it possesses a negligible solid solubility with Cu, a high thermal and chemical stability and a low electrical resistance.[2] Unfortunately, its use as sole diffusion barrier for Cu is limited, as the grain boundaries of the polycrystalline structures allow Cu diffusion at unacceptable low temperatures.[3] For this reason the need of the development of amorphous ruthenium-based films arises, *e.g.* obtained by incorporation of phosphorus. This kind of layers have shown to provide better Cu diffusion barrier properties than pure polycrystalline ruthenium coatings.[4]

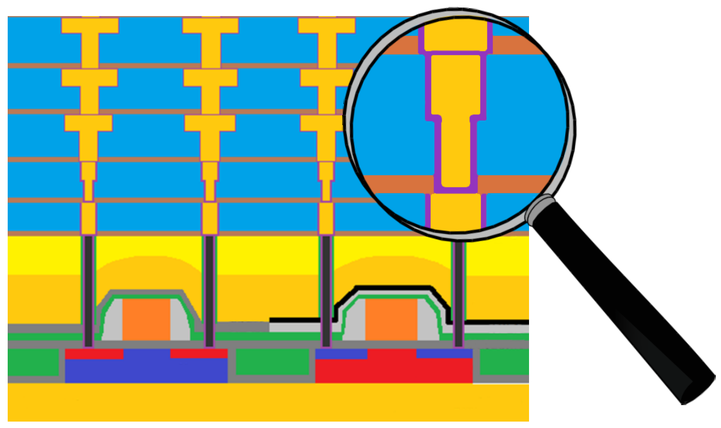

Fig. 1: Schematic structure of an integrated circuit. The magnification shows the diffusion barrier of the Cu interconnect.

Precursor Synthesis & Characterization

For the synthesis of CVD precursors **2a** – **f**, $Ru_3(CO)_{12}$ (**1**), P^nBu_3 and the respective carboxylic acid were reacted under reflux (Fig. 2). Compounds **2a** – **f** are stable to oxygen and moisture.

2a: R = Me
2b: R = Et
2c: R = ^{i}Pr
2d: R = ^{t}Bu
2e: R = CH_2OCH_3
2f: R = CF_3

Fig 2: Synthesis of ruthenium complexes **2a** – **f**.

Tab. 1: Melting points of compounds **2a** – **f**.

	2a	2b	2c	2d	2e	2f
M.p [°C]	108	93	74	48	96	100

The substituents R in complexes **2a** – **f** influence the melting points (*Tab. 1*). In complexes **2a** – **d** the melting points are decreased with increasing chain length and branching of the substituent R.
The single crystal X-ray analysis of **2e** reveals the molecular structure in the solid state (*Fig. 3*). Typical molecular features are the *cis*-arranged carbonyls and the monodentate carboxylates.

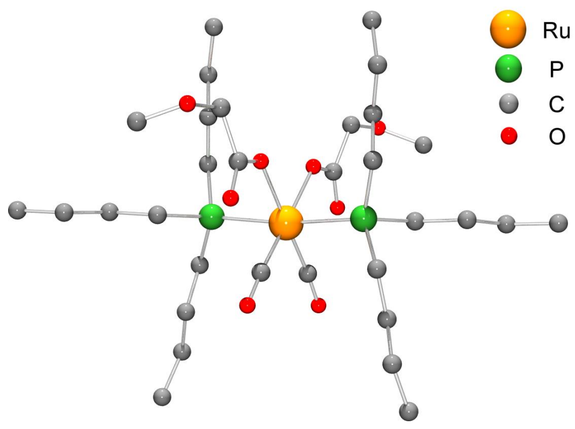

Fig. 3: Molecular structure of **2e** in the solid state.

Thermogravimetric measurements (= TG) were carried out in a temperature range from 40 – 700 °C with a heating rate of 10 K · min^{-1} in a nitrogen carrier gas flow of 60 mL · min^{-1}.

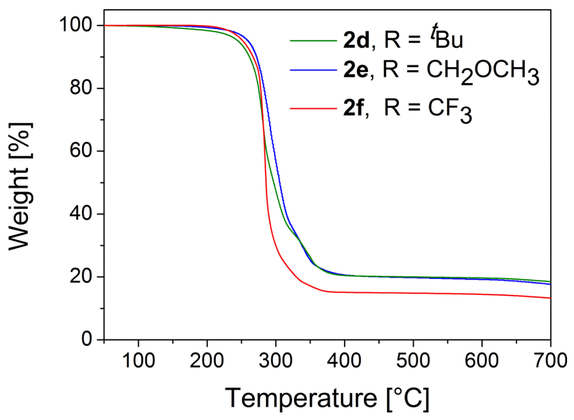

Fig. 4: TG traces of complexes **2d** – **f**.

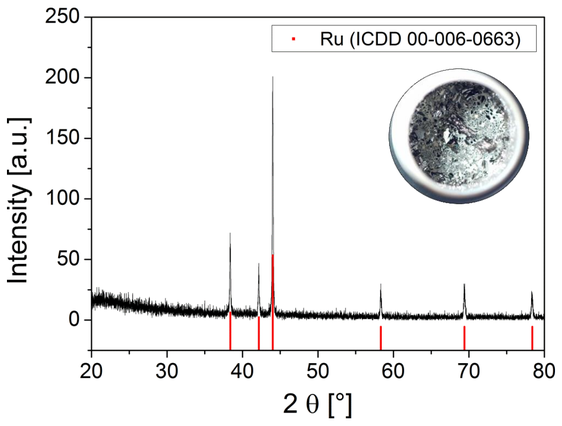

Fig. 5: XRPD pattern of the TG residue of **2e**.

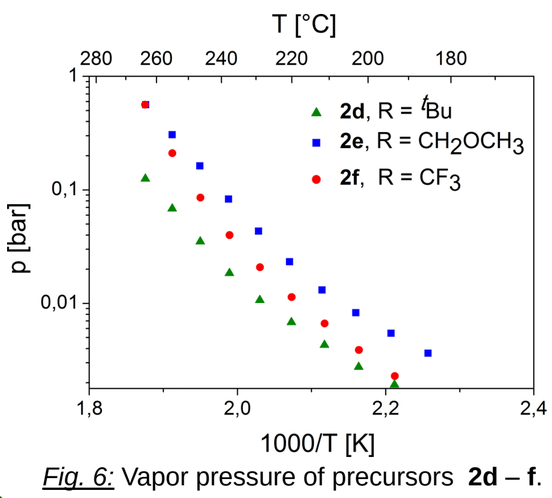

Fig. 6: Vapor pressure of precursors **2d** – **f**.

The TG traces in *Fig. 4* show a decomposition process in the temperature range of 220 – 350 °C. The TG residues were characterized by X-ray powder diffraction (= XRPD) and show for **2e** the reflexes of metallic ruthenium (*Fig. 5*).
Vapor pressure measurements were carried out to get first information of the volatility of the respective precursor (*Fig. 6*). The substituents R influence the vapor pressure, whereat the CH_2OCH_3 substituent in **2e** results in the highest volatility of analyzed compounds.

Chemical Vapor Deposition & Layer Characterization

Tab. 2: Deposition parameters of **2d** – **f**.

	2d	2e	2f
ϑ (Precursor) [°C]	125	135	130
ϑ (Deposition) [°C]	400	400	400
Gasflow (N_2) [mL·min^{-1}]	50	50	50
Pressure [mbar]	0.8	0.8	0.8
Deposition time [min]	60	60	60
Layer thickness [nm]	30	55	65

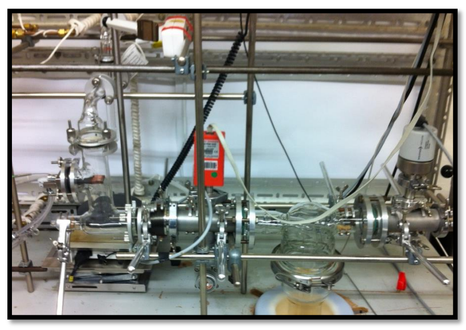

Fig. 7: Home-build vertical cold-wall CVD-reactor.

Chemical vapor deposition experiments were carried out with a home built vertical cold-wall reactor equipped with a continuous evaporation system (*Fig. 7*) at a deposition temperature of 400 °C using nitrogen as carrier gas (50 mL · min^{-1}). As substrate a silicon wafer featuring a 100 nm thick SiO_2 layer was applied.

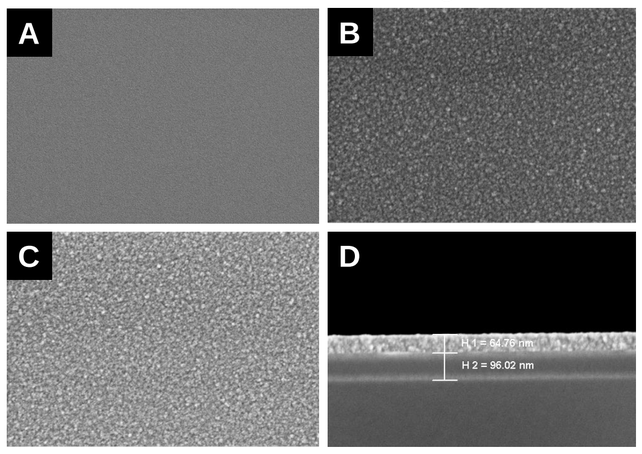

Fig. 8: SEM images of the ruthenium films deposited on SiO_2 using the parameters given in *Tab. 2*. A: **2d**, 10000x; B: **2e**, 80000x; C: **2f**, 80000x; D: **2f**, 50000x.

The SEM images of the films deposited from precursors **2d** – **f** evidence the formation of dense and conformal layers (*Fig. 8*). The film composition was analyzed by EDX (*Fig. 9*). For all samples the presence of the characteristic pattern of ruthenium was found. In addition phosphorus, silicon, oxygen and carbon were found.
To evaluate the crystallinity of the deposited films we performed XRPD. As no reflexes could be determined the layers are amorphous or at least nano-crystalline.

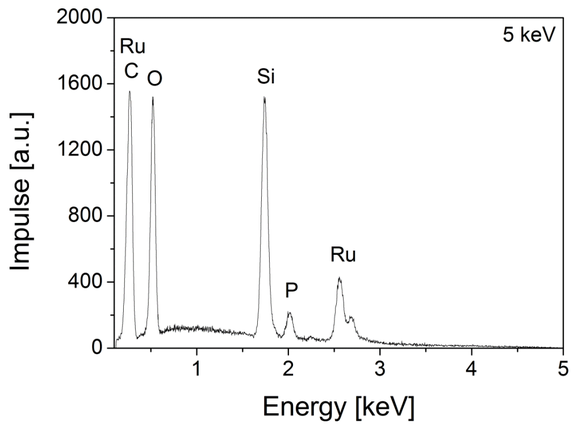

Fig. 9: EDX trace of a Ru(P) layer deposited from **2e**.

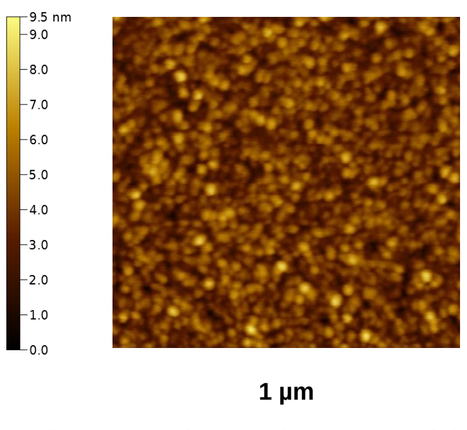

Fig. 10: AFM image of a 55 nm Ru(P) film deposited from **2e**.

Tab. 3: Surface roughness determined by AFM.

Precursor	RMS Roughness [nm]
2d	0.8
2e	1.0
2f	0.8

In order to study the surface roughness of the deposited Ru(P) films AFM images were acquired. A typical AFM image of a Ru(P) film obtained from complex **2e** is depicted in *Fig. 10*. In all investigated cases, the resulting layer topography is characterized by well-interconnected globular grains.
The RMS (= root mean square) roughness values are in the range of 1 nm (*Tab. 3*), which correspond to fairly smooth films.[5]

Conclusion

Ruthenium complexes **2a** – **f** were synthesized and successfully applied as precursors in MOCVD process. Compounds **2a** – **f** are characterized by low melting (< 108 °C) and decomposition points (< 350 °C). The chemical vapor deposition of about 30 – 60 nm thin ruthenium films was carried out in a vertical home-build cold-wall reactor without the addition of any reactive gas. As the precursors already contain a phosphorus source, the deposition of **2a** – **f** led to the formation of amorphous, phosphorus-containing ruthenium layers. The SEM and AFM images indicate that continuous and homogeneous films were formed. The RMS roughness values of 1 nm correspond to fairly smooth films.

References

[1] J. Jeschke, C. Georgi, H. Lang, *patent application*, **2014**, DE10 2014 205 342.0. [2] A. Tuchscherer, C. Georgi, N. Roth, D. Schaarschmidt, T. Rüffer, T. Waechtler, S. E. Schulz, S. Oswald, T. Geßner, H. Lang, *Eur. J. Inorg. Chem.* **2012**, 4867–4876. [3] L. B. Henderson, J. G. Ekerdt, *Thin Solid Films* **2009**, *517*, 1645–1649. [4] J.-H. Shin, H.-W. Kim, K. Agapiou, *et al*., *J. Vac. Sci. Technol. A* ***2008,*** 26, 974–979. [5] J. J. Kim, M. S. Kim, D. Y. Yoon, *Chem. Vap. Deposition*, **2003**, *9*, 105–109.

Acknowledgement

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