Deposition of Phosphorus-Doped Ruthenium Layers by the Single-Source Approach

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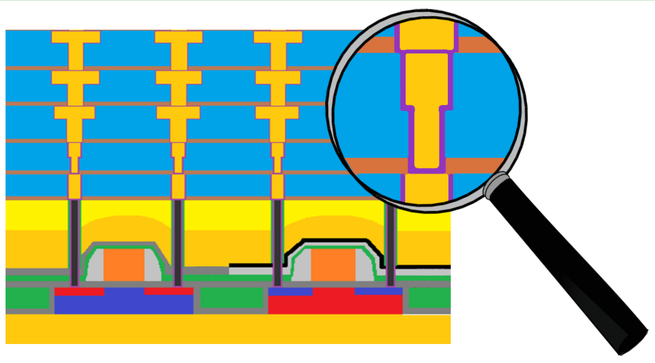
Motivation

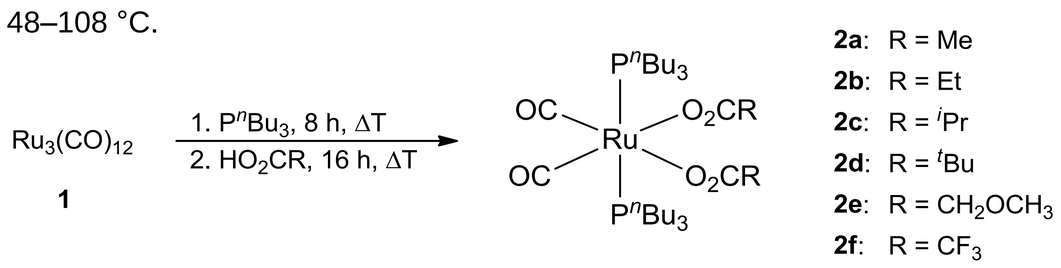
The ongoing miniaturization of devices in semiconductor industry causes new manufacturing and materials challenges. One key destination is the development of a single material liner for future copper interconnects in integrated circuits.[1] A prospect which has been considered is ruthenium, as it possesses 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. Such layers have shown to provide better Cu diffusion barrier properties than pure polycrystalline ruthenium coatings.[4]



Precursor Synthesis & Characterization

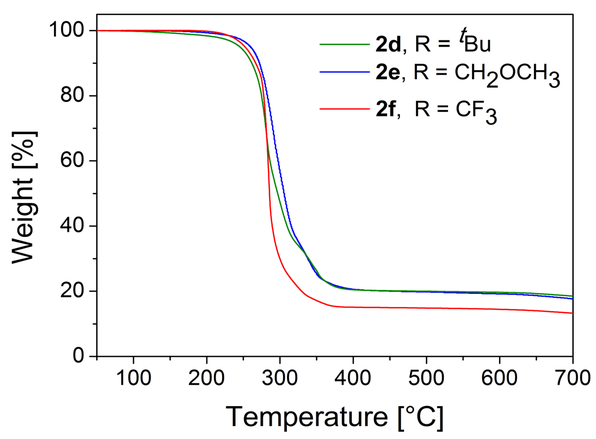
Synthesis

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. Compounds **2a–f** are stable to air and moisture and possess low melting points in a range between 48–108 °C.



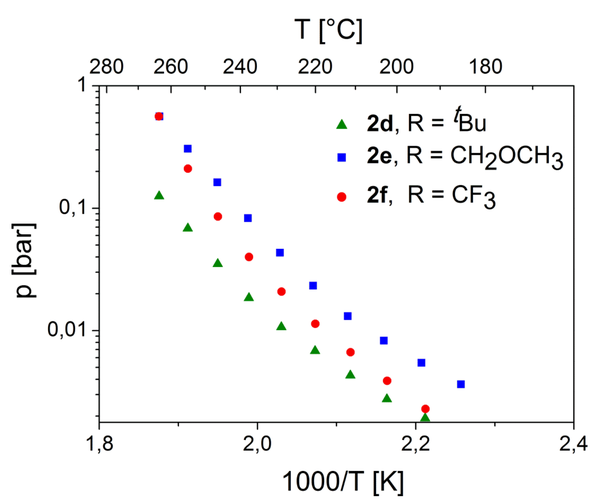
Thermal Behavior

TG measurements were carried out in a temperature range from 40 to 700 °C with a heating rate of 10 K · min^{-1} in a N_2 carrier gas flow of 60 mL · min^{-1}.
The decomposition processes of **2e–f** take place in similar temperature ranges from 220 to 350 °C.



Vapor Pressure

Vapor pressure measurements were carried out to get first information of the volatility of the respective precursors.[2] The substituents R influence the vapor pressure, whereat the CH_2OCH_3 substituent in **2e** results in the highest volatility of analyzed compounds.



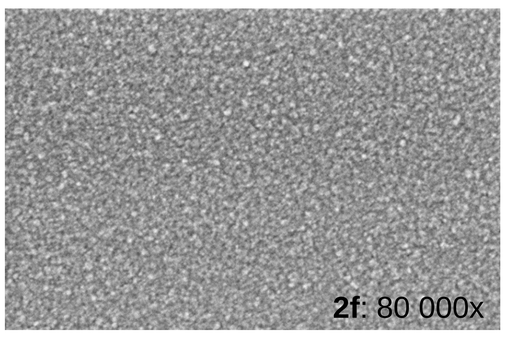
Chemical Vapor Deposition & Layer Characterization

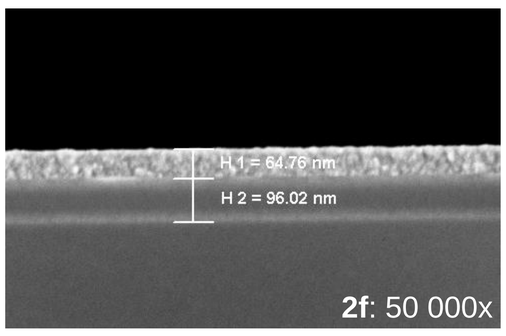
CVD Deposition Parameters

	2d	2e	2f
ϑ (Precursor) [°C]	125	135	130
ϑ (Deposition) [°C]	400	400	400
Gas flow (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

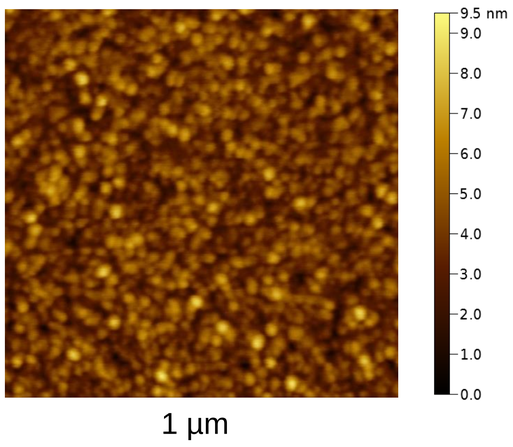
Layer Characterization

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





Surface Roughness



The surface roughness of the deposited Ru(P) films was studies by AFM. 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, which correspond to fairly smooth films.[5]

Summary

- ✓ Preparation of novel, air-stable ruthenium CVD-precursors **2a–f**
- ✓ Compounds **2a–f** are characterized by low melting points (48–108 °C)
- ✓ Compounds **2a–f** possess low decomposition points (< 350 °C)
- ✓ 30–65 nm thin amorphous Ru(P)-layers were deposited by CVD
- ✓ *Single-Source Approach*: no reactive gas or additional P source is needed
- ✓ SEM and AFM images show that conformal, homogeneous films were formed
- ✓ Roughness values correspond to fairly smooth films (RMS = 1.0 ± 0.5 nm)
- ✓ XPS and EXD measurements show that the films are composed of Ru and P

References

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[2] A. Tuchscherer, C. Georgi, N. Roth, D. Schaarschmidt, T. Rüffer *et al.*, *Eur. J. Inorg. Chem.* **2012**, 4867–4876.
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Acknowledgement

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