SYNTHESIS, CHARACTERIZATION AND APPLICATION OF NOVEL RUTHENIUM PRECURSORS FOR MOCVD BY A SINGLE SOURCE APPROACH

Andrea Preuß, Janine Jeschke, Tobias Rüffer and 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

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(II)(PEt₃)₃(alkyl) (R = Me, Et, Pr, Bu, CH₂CO₂H) 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]

Synthesis

For the synthesis of CVD precursors 4a–e, Ru₂(II)(CO)₁₂(1), PEt₃ 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.

Single Crystal X-Ray Diffraction

The structures of 4a–e in the solid state were determined by single crystal X-ray diffraction studies. Suitable crystals 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 carbyls and two monodentate O-bonded carboxylates in the equatorial plane (Fig. 1).

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 N₂ 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).

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 thick 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


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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 SiO₂ layer was applied.

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 SiO₂ using complexes 4b and 4c.

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.

Fig. 2 TG traces of 4a–e, gas flow N₂, 60 mL min⁻¹, heating rate 10 K min⁻¹.

Tab. 1 EDX data of ruthenium films deposited on SiO₂ using complexes 4b and 4c.