Atomic Layer Deposition of Ru-containing materials using RuO_4 as both the co-reactant and the metal source

Ruthenium-containing materials often display interesting physical and chemical properties, making them relevant to a wide variety of applications. For example, a range of Ru-based ternary oxides are promising electrocatalysts with excellent chemical stability for the oxygen evolution reaction (OER).[1] In addition, their electronic properties make them interesting electrode materials, and some even show superconductivity.[2,3] Ru-based bimetallic nanomaterials are also investigated for applications in electrocatalysis.[4]

As ruthenium is a rare element, it is advisable to use such materials not in their bulk form, but as thin films or nanoparticles on high surface area substrates. Therefore, ALD would be an appropriate method of synthesis. In ALD, the most common way of making ternary oxides or binary alloys is to alternate two different metal oxide or single metal ALD processes in sequence. The metal source is typically a metalorganic precursor, in which the metallic center is in a certain oxidation state, and a co-reactant is used to achieve the desired oxidation state in the target material.[5] In this work we report a low temperature ALD route towards Ru-containing materials, in which the inorganic RuO_4-precursor is used as both the Ru-source and the oxidizing co-reactant. If the target material is a Ru-containing ternary oxide, the RuO_4-precursor can be directly combined with a metalorganic precursor in a 2-step process.

As a proof of concept, we first show that an ALD process for aluminum ruthenate can be obtained by combining $Al(CH_3)_3$ with RuO_4 in a 2-step process at sample temperatures 50°C-125°C. Similarly, Pt-doped ruthenium oxide can be obtained by reaction of the classical Pt precursor, $PtMe_3CpMe$, with RuO_4 at sample temperatures 40°C-120°C. Both processes display good ALD-behavior, as is evident from the saturation of the half-reactions and the linearity of growth (shown in Figure 1 and 2 for the TMA/RuO_4 process). As a general reaction mechanism for the 2-step process, we propose that the RuO_4-precursor combusts the organic ligands of the chemisorbed metalorganic precursors, while simultaneously binding RuO_2 to the surface. Both films are amorphous as-deposited, and the elemental composition is shown in Table 1. Finally, we show that a crystalline Ru-rich Pt-Ru alloy can be obtained by introducing an additional reduction step after the RuO_4 exposure, making it a 3-step process (Table 1).

[1] Kim et al. *J. Am. Chem. Soc.,* **2017**, 139, 12076.

[2] Koster et al. *Rev. Mod. Phys.,* **2012**, 84, 253.

[3] Maeno et al. *Nature* **1994**, 372, 532.

[4] Li et al. *Energy Environ. Sci.*, **2018**, 11, 1232.

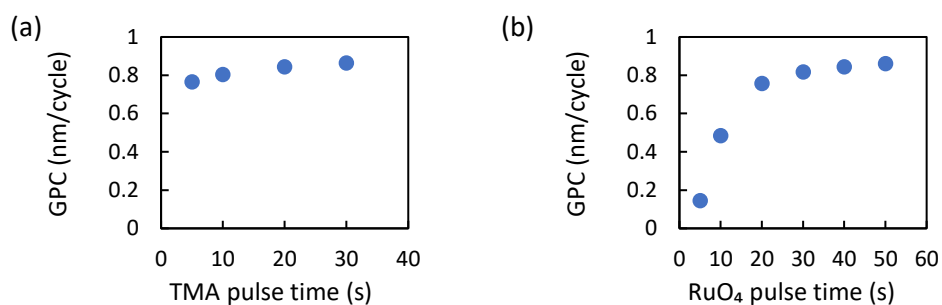[5] Han et al., *Chem. Mater.* **2012**, 24, 4686.

(a)

GPC (nm/cycle)

TMA pulse time (s)

(b)

GPC (nm/cycle)

RuO$_4$ pulse time (s)

Figure 1. Saturation curves of the growth rate for the 2-step aluminum ruthenate process as a function of the (a) TMA and (b) RuO$_4$ pulse times. The thickness of the films was determined by X-ray reflectivity (XRR) measurements.
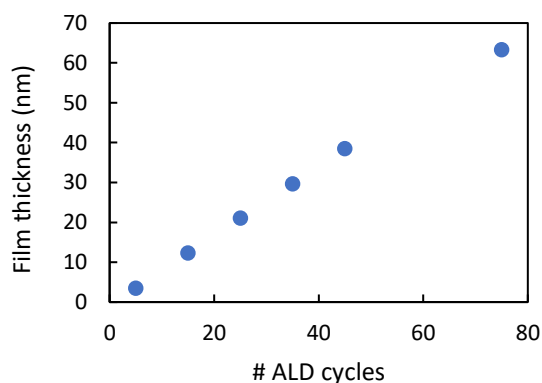

Film thickness (nm)

ALD cycles

Figure 2. Linearity of growth for the 2-step aluminum ruthenate process. The thickness of the films was determined by XRR.

Table 1. Relative atomic concentrations of the elements detected in the bulk of the films by XPS depth profiling, for the three different ALD processes. Note that the overlap of the C1s peak with the Ru3d$^{5/2}$ peak in the XPS spectrum makes it difficult to quantify the carbon content of the films, additional chemical analysis is ongoing.

	[Ru] at%	[Al] or [Pt] at%	[O] at%
TMA/RuO$_4$	24	38	38
MeCpPtMe$_3$/RuO$_4$	54	10	36
MeCpPtMe$_3$/RuO$_4$/H$_2$	83	12	5