Atomic Layer Deposition of Ruthenium Dioxide Thin Films Using RuO_4 and Alcohols as Reactants

Nithin Poonkottil[1], Matthias Minjauw[1], Andreas Werbrouck[1], Christophe Detavernier[1] and Jolien Dendooven[1]

[1]CoCooN research group, Dept. Solid State Sciences, Ghent University, Belgium

Ruthenium dioxide (RuO_2) is the most stable oxide of Ru and has attracted tremendous attention in different applications such as supercapacitors, catalysis, and electrochemical devices. The high conductivity, good chemical stability, a work function value that is even higher than metallic Ru are few properties that make this material so demanding[1]. Although RuO_2 is such an interesting material, atomic layer deposition (ALD) literature reports on this material are scarce. The existing ALD processes based on metalorganic Ru precursors necessitate careful tuning of the O_2 partial pressure in order to deposit RuO_2 films, as Ru metal is produced at lower O_2 partial pressures. Furthermore, reported processes often require high temperature (>180°C) depositions and suffer from high nucleation delays, up to several hundred cycles in some cases.[2]

In this scenario, we present a novel ALD strategy solely for the synthesis of RuO_2 films that takes advantage of the reaction between various alcohols and ruthenium tetroxide (RuO_4) without any significant nucleation delay. The process, which uses methanol and RuO_4 as reactants, exhibits a growth per cycle (GPC) of 1 angstrom (Å) per cycle (**Figure 1a and 1b**) at a substrate temperature as low as 60 °C. A constant GPC of 1Å is obtained in the temperature window of 60 °C-120 °C, while the RuO_4 precursor is known to decompose above 125 °C.[3] The depositions result in amorphous RuO_2 films, as confirmed with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements. The films can be transformed into crystalline rutile RuO_2 by annealing in helium or air at around 400 °C (**Figure 1c**). The films are conductive, as is evident from the resistivity value of 230 μΩ.cm for a 20 nm film, and the conductivity improved slightly after the anneal.

Interestingly, the reaction of other alcohol molecules such as ethanol, 1-propanol, and 2-propanol with RuO_4 results in a higher GPC compared to the methanol-based process and it is concluded that the GPC can be increased by increasing the number of carbon atoms in the alcohol chain (**Figure 1d**). However, all these processes employing different alcohols display typical self-saturating ALD properties. The reaction mechanism of the developed ALD approach was studied in depth using *in situ* mass spectrometry and *in vacuo* XPS studies. A reaction mechanism is proposed based on these learnings, wherein during the first half-cycle, alcohol molecules are oxidized into aldehyde and H_2O on a RuO_2 surface. This in turn causes the partial reduction of the surface RuO_2 layer into RuO_x or Ru. During the next half-cycle RuO_4 oxidizes the surface back to RuO_2 and additional RuO_2 is deposited on the surface.

References

1. Ryden, W.; Lawson, A.; Sartain, C. C., Electrical Transport Properties of Ir O 2 and Ru O 2. *Physical Review B* **1970,** *1* (4), 1494.

2. Austin, D. Z.; Jenkins, M. A.; Allman, D.; Hose, S.; Price, D.; Dezelah, C. L.; Conley Jr, J. F., Atomic layer deposition of ruthenium and ruthenium oxide using a zero-oxidation state precursor. *Chemistry of Materials* **2017,** *29* (3), 1107-1115.

3. Minjauw, M. M.; Dendooven, J.; Capon, B.; Schaekers, M.; Detavernier, C., Atomic layer deposition of ruthenium at 100° C using the RuO 4-precursor and H 2. *Journal of Materials Chemistry C* **2015,** *3* (1), 132-137.

This work is funded by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No.765378.