ALD of Ruthenium at 100°C using the ToRuS-precursor

Matthias Minjauw[1], Boris Capon[1], Jolien Dendooven[1], Marc Schaekers[2], Christophe Detavernier[1]

1 Dept. of Solid-state Sciences, Ghent University, Belgium (Matthias.Minjauw@ugent.be)
2 IMEC, Belgium

Due to its high work function (>4.7 eV), high chemical and thermal stability, low bulk resistivity (7 μΩ.cm), broad range of oxidation states and conductive oxide, Ru is a material with various applications, e.g. in microelectronics and catalysis. Over the last decade, several ALD processes for Ru have been reported based on metalorganic precursors, typically with ALD-windows lying well above 200°C [1]. RuO_4 is a potential inorganic precursor for ALD which was reported to thermally decompose above 150°C. The ToRuS-blend (Air Liquide) has been used in a pulsed-CVD process at temperatures above 190°C [2], where in the first half-cycle a layer of RuO_2 is CVD-deposited (by the combined thermal and catalytic decomposition of RuO_4), which is then reduced to Ru by exposure to H_2 during the second (self-terminating) half-cycle.

In this abstract we report a low temperature (100°C) ALD process for Ru using the ToRuS-precursor, leading to films with an unexpected degree of purity. The thermal decomposition behavior of the precursor for temperatures below 150°C was investigated and it was found that the decomposition starts at a sample temperature of 125°C. The ToRuS/H_2-process (0.0045 mbar/4 mbar) was attempted at temperatures below this decomposition limit and it was found that ALD growth of pure Ru is possible in a very narrow temperature window near 100°C. The saturation behavior of both half-cycles was verified at 100°C (Figure 1). The growth on different substrates (ALD Al_2O_3 and TiN, H-terminated Si and PVD Pt and Ru) was followed using in-situ ellipsometry (ISE), and the linearity of the process was confirmed with a GPC of 1.2 Å/cycle during steady state growth, which is higher than typical growth rates for Ru ALD [1]. The incubation times on all substrates were found to be quite low (Figure 1). Though the films are grown at a low temperature, they are considerably pure and are of good quality as evidenced by a resistivity of 17.8 μΩ.cm for an 18 nm thick Ru layer. In contrast to films grown at lower or higher temperatures, XPS indicated the presence of only little oxygen in the films ALD-grown at 100 °C, with a relative atomic concentration <5% (Figure 1). It is hypothesized that the catalytic activity of the Ru-surface for dissociation of RuO_4 to RuO_2 is the mechanism behind the first half-reaction during steady state growth, which is probable as the deposited RuO_2 itself does not catalyze this dissociation [3], and hence the reaction is self-terminating.

[1] J. Hamäläinen, M. Ritala, M. Leskelä, Chem. Mater. 26 (2014) 786–801
[2] J. Han, S. Lee, G.-J. Choi, S. Lee, C. Hwang et. al., Chem. Mater. 21 (2009) 207–209
[3] U. Backman, M. Lipponen, A. Auvinen, U. Tapper et. al., Radiochim. Acta 93 (2005) 297–304

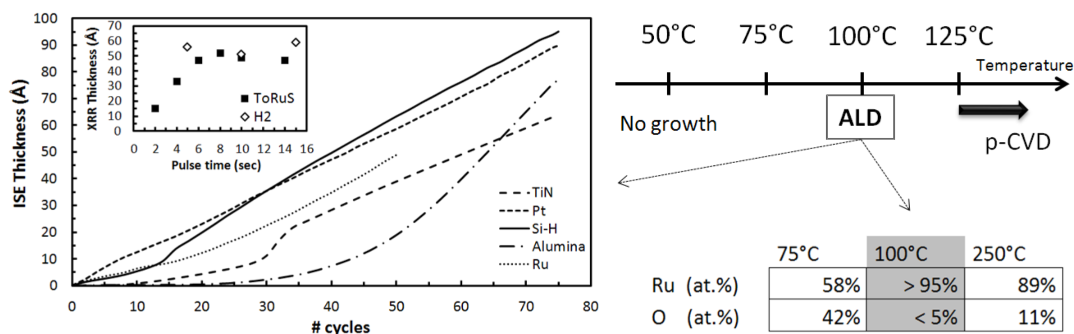

Figure 1. Illustration of ALD-characteristics and purity for the process at 100°C. Left: growth-curves on different substrates as determined by ISE, the inset shows the saturation behavior of the process; Right: table with relative atomic concentrations of films grown at different temperatures as determined by XPS.