Atomic Layer Deposition of Ruthenium from $RuCp_2$ and Oxygen: Film Growth and Reaction Mechanism Studies

Titta Aaltonen,[a] Antti Rahtu,[a,b] Mikko Ritala,[a] and Markku Leskelä[a]
[a]Laboratory of Inorganic Chemistry
Department of Chemistry, P.O. Box 55
FIN-00014 University of Helsinki, Finland
[b]Present address: Harvard University
12 Oxford Street, Cambridge, MA 02138, USA

Highly conformal ruthenium thin films have many applications in microelectronics; for example, as capacitor electrodes in new generation dynamic random access memories (DRAMs) (1,2). Atomic layer deposition (ALD) (3) is a suitable method for growing films with excellent conformality and good large area uniformity (4). Metallic ruthenium films have been grown by ALD at a temperature range of 275–400°C from $RuCp_2$ and oxygen (5). The films had low impurity contents (H, C, O <0.5 at %), low resistivities (12–15 μΩcm), and excellent conformality. The film growth rate increased with increasing deposition temperature; at 350°C the film growth rate stabilized to 0.45 Å/cycle. The film thickness depended linearly on the number of applied reaction cycles (Fig. 1), which enables simple and accurate thickness control of the films.

The process is based on oxidative decomposition of the Cp ligands of the ruthenium precursor. The reaction mechanism of the process was studied *in situ* with a quadrupole mass spectrometer (QMS) and a quartz crystal microbalance (QCM) at 350°C. The two main gaseous reaction by-products were H_2O and CO_2 and they were detected during both the $RuCp_2$ and the O_2 pulses. The signal obtained from CO_2 (m/z = 44) during the pulsing sequence is shown in Fig. 2. The QMS study thus reveals that the adsorbed oxygen layer, which has formed on the ruthenium surface during the preceding oxygen pulse, oxidizes part of the Cp ligands during the $RuCp_2$ pulse. The remaining species become oxidized and a new layer of adsorbed oxygen forms on the surface during the following oxygen pulse. The QCM analysis showed a mass decrease during the $RuCp_2$ pulse and a mass increase during the O_2 pulse (Fig. 3). The reacting oxygen atoms that leave the surface give rise to the mass decrease detected during the $RuCp_2$ pulse and the adsorbing oxygen atoms give rise to the mass increase detected during the oxygen pulse.

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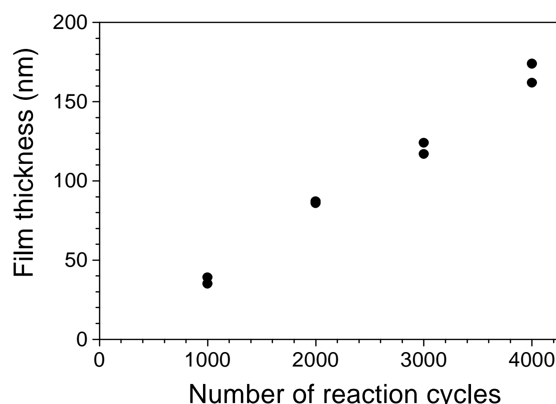

Fig. 1. Film thickness *vs.* number of the applied reaction cycles at 350°C.

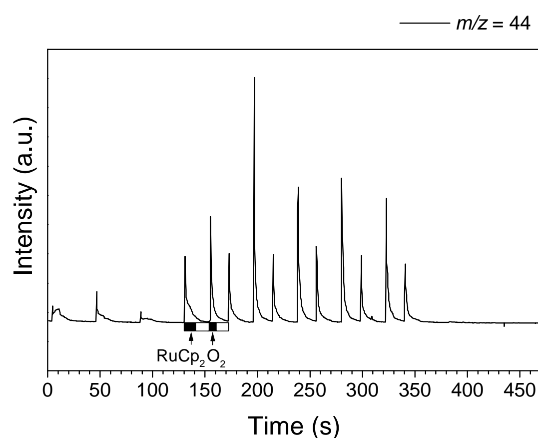

Fig. 2. QMS signal from CO_2 (m/z = 44) during the pulsing sequence.

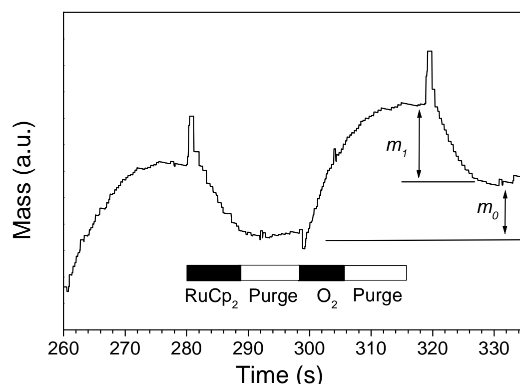

Fig. 3. QCM data measured during the reaction cycles. m_0 denotes the total mass change during one complete reaction cycle and m_1 denotes the mass change during the $RuCp_2$ pulse.