Atomic Layer Deposition of Palladium Films on Al_2O_3 Surfaces

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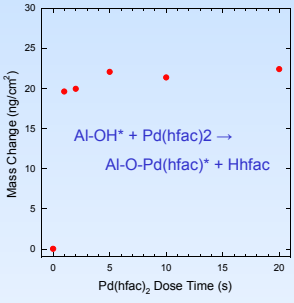
Abstract

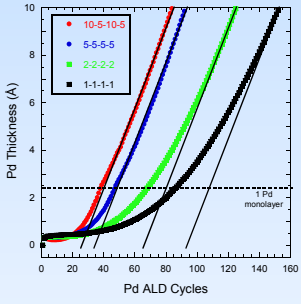
ALD Pd films were deposited at 200 °C on ALD Al_2O_3 surfaces using sequential exposures to Pd(II) hexafluoroacetylacetonate ($Pd(hfac)_2$) and formaldehyde. This technique allows Pd films to be deposited with atomic layer precision on any surface by first depositing a thin ALD Al_2O_3 seed layer. *In situ* quartz crystal microbalance measurements revealed that the Pd nucleation is hampered by the relatively slow reduction of the adsorbed $Pd(hfac)_2$ species, but is accelerated using larger initial reactant exposures. Pd films were deposited on silicon, glass and mesoporous anodic alumina (AAO) following the ALD of a 1-2 nm Al_2O_3 seed layer. These samples yielded a Pd ALD growth rate of 0.2 Å/cycle following a nucleation period of slower growth. The films are pure, cubic phase Pd and are relatively rough and highly conductive. ALD Pd films deposited on the inside walls of very high aspect ratio AAO membranes show promise for hydrogen sensors.

Pd Nucleation on Al_2O_3 using QCM

➢ Many potential reducing and oxidizing agents were screened (H_2, alcohols, acetone, TMA , O_3, H_2O_2 etc). Only formaldehyde (HCOH) enabled nucleation of Pd on Al_2O_3.

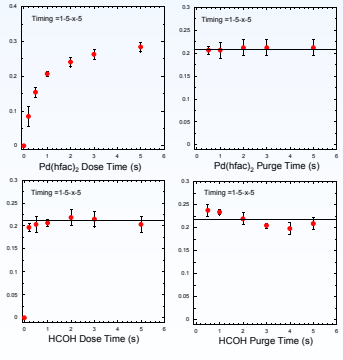


• $Pd(hfac)_2$ reaction saturates rapidly, but reduction after first exposure is slow

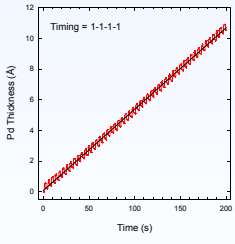


• Longer exposures yield faster nucleation

Growth of Pd using QCM

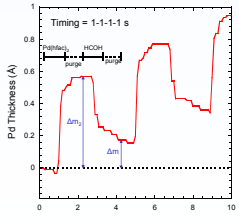


• "Soft saturation" of $Pd(hfac)_2$
• Optimal timing sequence = 1-1-1-1



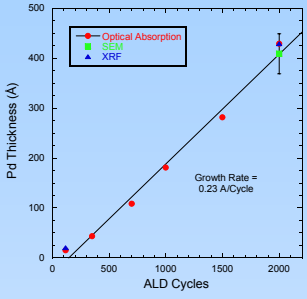
• Linear growth, G=0.21 Å/cycle

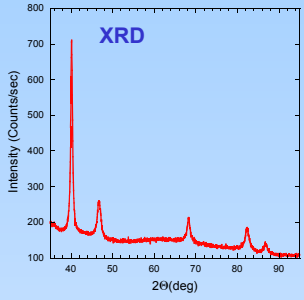
• Step shape analysis ($\Delta m_2/\Delta m$) reveals ~1 hfac ligand remains following $Pd(hfac)_2$ exposure



Growth and Analysis of Pd Films

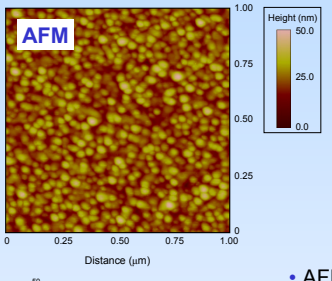
➢ ALD Pd films deposited on glass and Si(111) following 2-nm Al_2O_3 buffer layer

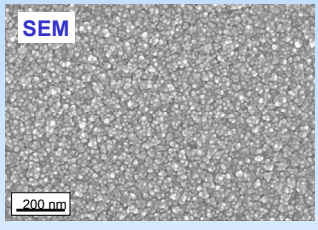


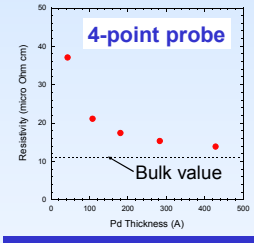


• Nucleation and growth confirm QCM results

• Cubic Pd, 111-oriented







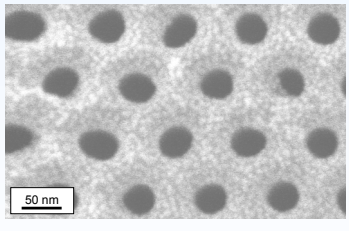
• AFM shows nanocrystalline surface, RMS roughness=4.2 nm for 42 nm thick film

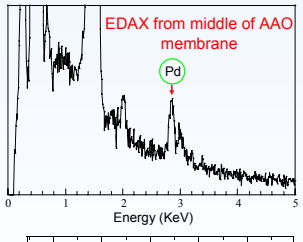
• SEM shows nanocrystalline surface

• 4-point probe resistivity=14 μΩ cm for 42 nm thick film

Pd ALD in AAO for Hydrogen Sensing

➢ AAO membrane: pore diameter d=40 nm, pore length L=60 μm, aspect ratio L/d=1500
➢ Coat AAO with ~2 nm ALD Pd, measure resistance change upon H_2 exposure





• SEM shows nanocrystalline surface

• EDAX shows infiltration of Pd into center of AAO membrane

• Fast resistance increase during H_2 exposures due to Pd-hydride formation