Area-selective atomic layer deposition of ruthenium using an ABC-type process combined with selective etching

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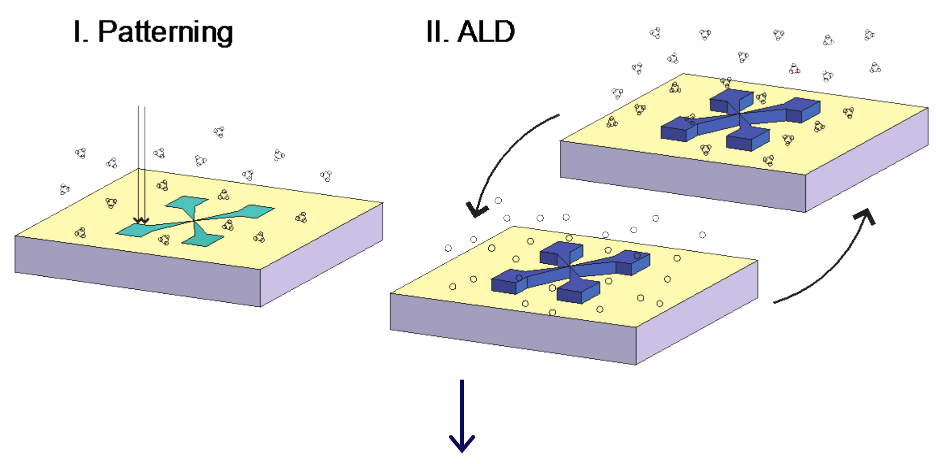
Motivation

- In area-selective atomic layer deposition (AS-ALD) by area-activation, a seed layer deposited by methods such as electron beam induced deposition (EBID) "activates" the surface and catalyzes subsequent ALD growth
- How can we improve the selectivity of this approach and achieve the AS-ALD of Ru?



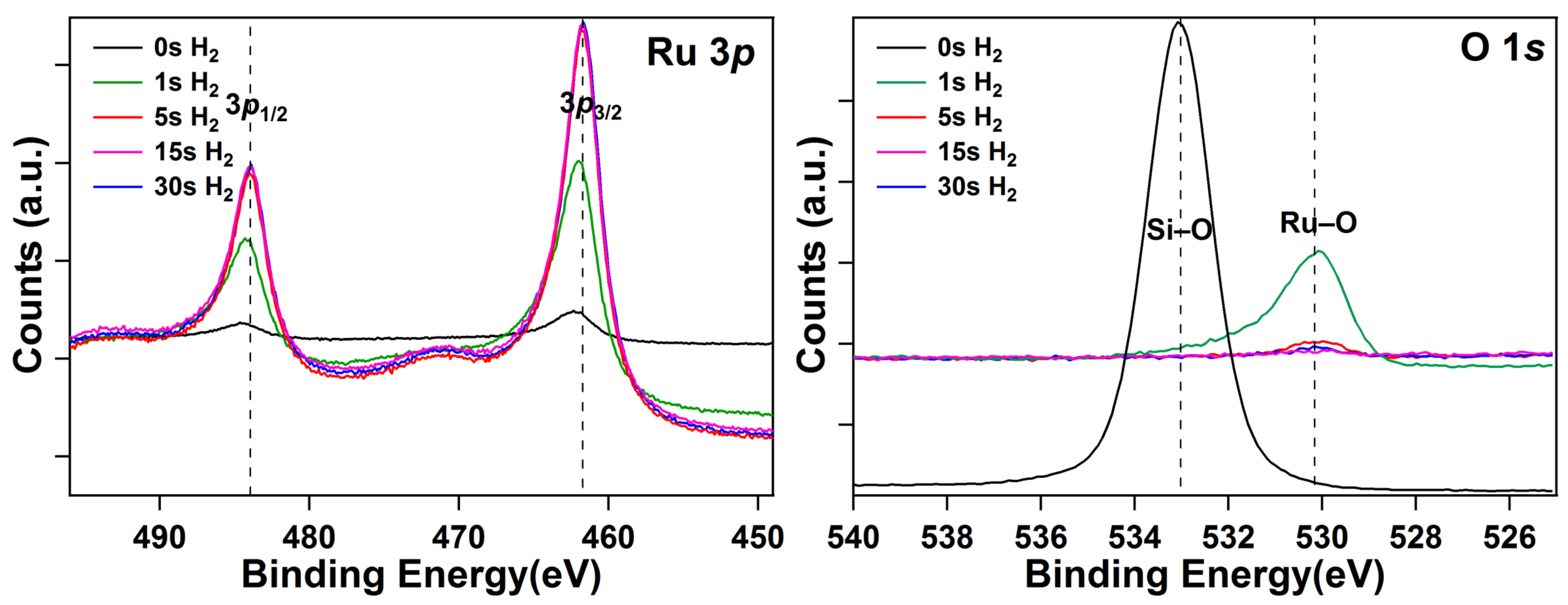
Mackus et al. "Nanopatterning by direct-write atomic layer deposition." *Nanoscale* (2012).

Ruthenium

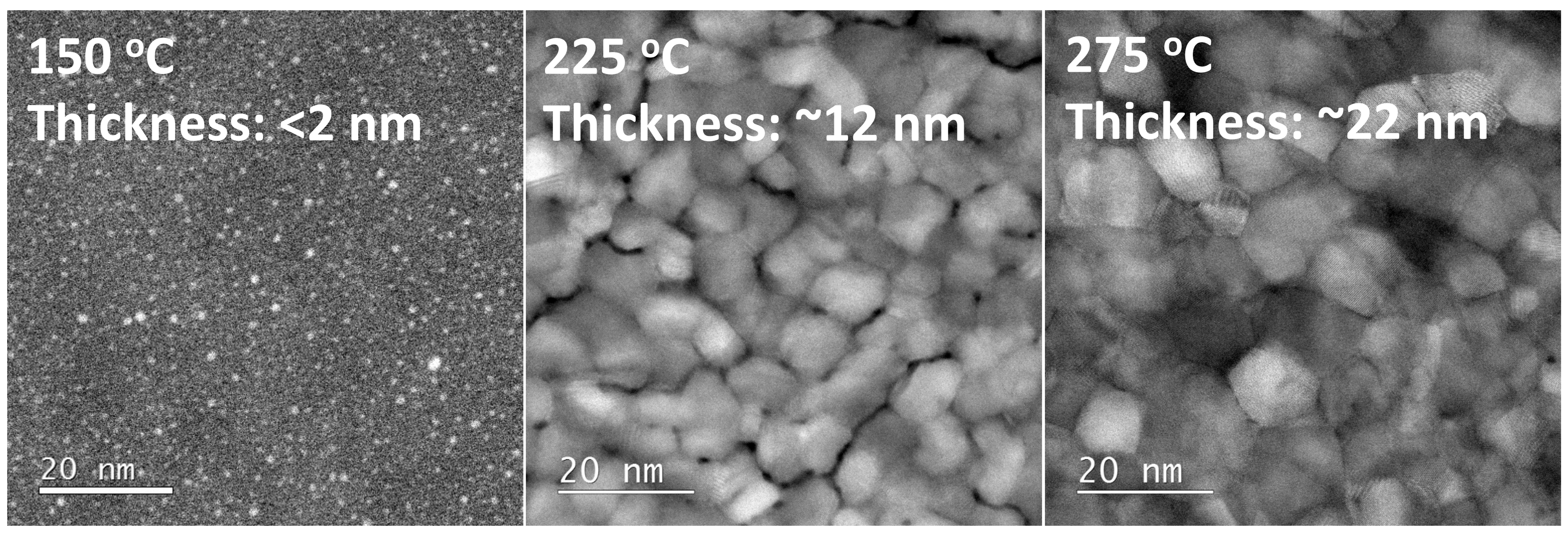
- Good thermal chemical stability, low resistivity (7.1 μΩ for bulk), and a large work function (4.7 eV)
- ALD from ethylbenzen-cyclohexadiene Ru(0) (EBCHDRu) and O_2 gas nucleates with negligible nucleation delay
- Ru can be etched using an O_2 plasma, which forms RuO_4

Ru ALD using an ABC-type process

X-ray photoelectron spectroscopy of 500 cycles 15s EBCHDRu, 15s O_2 gas, and variable H_2 pulses on SiO_2 at 225 °C



Plan-view TEM of 500 cycles 15s EBCHDRu, 15s O_2 gas, 5s H_2 gas pulses on SiO_2 at different temperatures



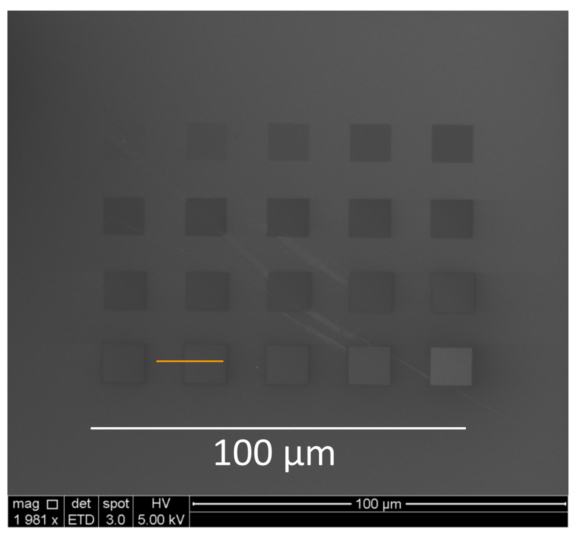
Islands | Nearly closed | Closed

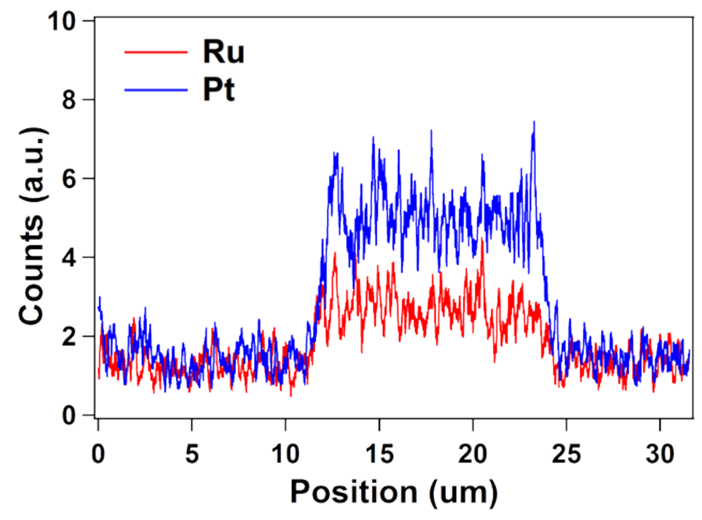
- Addition of H_2 step enables high quality Ru film deposition at low temperatures by reducing RuO_2 every cycle
- Transmission electron microscopy (TEM): Islanded growth observed on SiO_2 at 150 °C

AS-ALD combined with selective etching of Ru using O_2 Plasma

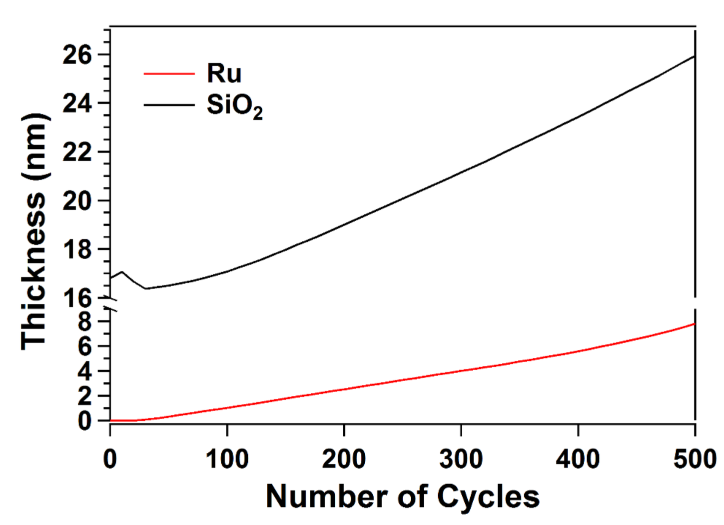
Temperature	Substrate	Growth Rate (nm/cycle)
100	Ru	No growth
	SiO_2	No growth
150	Ru	0.03
	SiO_2	0.002
225	Ru	0.041
	SiO_2	0.035
300	Ru	0.05
	SiO_2	0.05

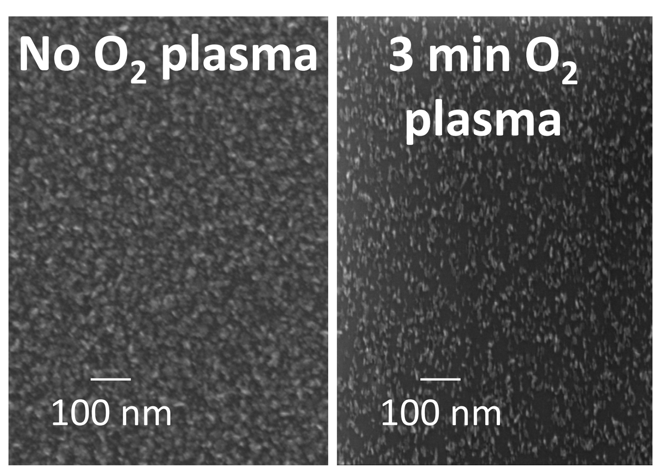
Scanning electron microscopy and energy dispersive X-ray spectroscopy of 200 Ru ABC ALD cycles at 150 °C on EBID-patterned sample



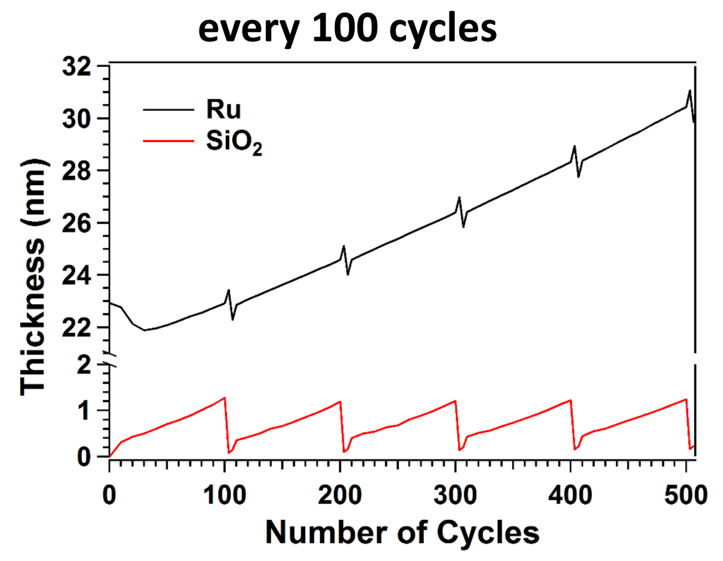


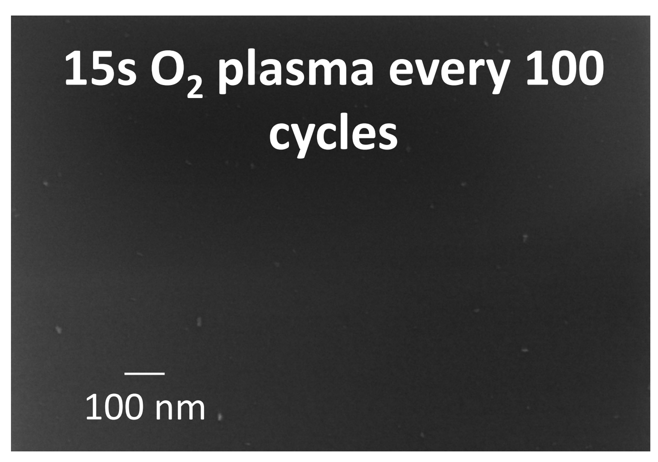
In-situ spectroscopic ellipsometry and scanning electron microscopy of 500 Ru ABC ALD cycles at 150 °C





15s O_2 plasma, 15s H_2 gas pulse every 100 cycles





- Differences in growth rates on Ru and SiO_2 increase as temperature decreases
- Ru ABC ALD grows faster on EBID seed layers at 150 °C than on SiO_2
- O_2 plasma can be used to remove undesirable Ru growth from SiO_2
- O_2 plasma pulses can be integrated into an ALD supercycle to achieve high selectivity onto Ru

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