ALD of Scandium Oxide from Tris(*N*,*N'*-diisopropylacetamidinato)Scandium and Water

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Scandium oxide is considered to be a high-k dielectric with good leakage properties. In combination with rare earth elements like dysprosium, gadolinium, and lanthanum, scandium produces ternary metal scandates that exhibit promising characteristics. These oxides have dielectric constants of ~22, have large bandgaps and high conduction band offsets with respect to silicon, remain amorphous to high temperatures, and are thermodynamically stable. Using ALD to deposit films for advanced MOSFET and DRAM applications is becoming more prevalent, and as such new ALD precursors and deposition methods are needed to have access to many different materials like the rare-earth scandates. In the first step towards synthesizing scandates it is necessary to have a fully developed scandium oxide ALD process.

Scandium oxide thin films were deposited using ALD from a new scandium precursor $Sc(^iPr_2amd)_3$ and water. The precursor has sufficiently high volatility (0.04 torr at 100°C) and reacts with water to produce Sc_2O_3 with a minimal amount of carbon or nitrogen incorporation in the thin films. The growth rate of the film saturates at 0.7 Å/cycle and the ALD temperature window extends from 225°C to 300°C. The thickness is linear with the number of cycles and has an inhibition of 8-10 cycles on HF last silicon. The composition of the films was determined by Rutherford backscattering (RBS), and the crystallinity was determined by low-angle x-ray diffraction (XRD). The films were amorphous as-deposited, but were polycrystalline upon annealing at 600°C. Other characterization methods used include atomic force microscopy, spectroscopic ellipsometry, and cross-sectional high resolution transmission electron microscopy. Electrical measurements were made using either sputtered Pt contacts or in-situ ALD WN to form MIS and MIM capacitor structures. Capacitance-voltage and current-voltage curves were measured for films with various thicknesses. The dielectric constant was determined to be 13 with a leakage current density of less than 1×10^{-8} A/cm^2 for a film with an EOT of 2.0nm.

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Applications and Characteristics of Sc_2O_3

Scandium Oxide Thin Films:
- Polycrystalline above 400ºC
- Stable in direct contact with silicon
- Relatively high dielectric constant 14-17
- Refractive index of 1.8-1.9
- Optically transparent in the visible

Applications:
- multilayer antireflection and protective coatings
- light-emitting diodes
- thin film interference polarizers
- laser optical coatings

ALD Sc_2O_3 can be used for ternary rare-earth metal oxides such as $GdScO_3$, $DyScO_3$, and <u>$LaScO_3$</u>

→ Excellent properties for use as a gate dielectric or as the insulator in MIM capacitors.

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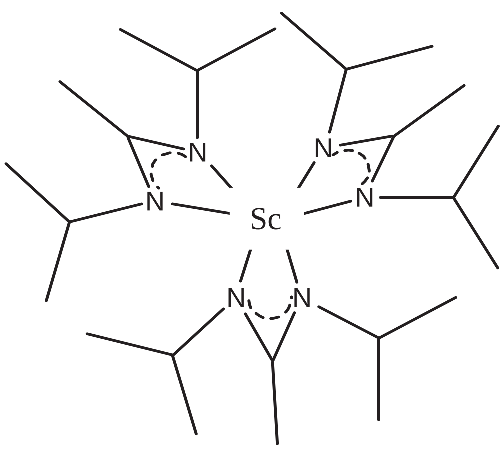
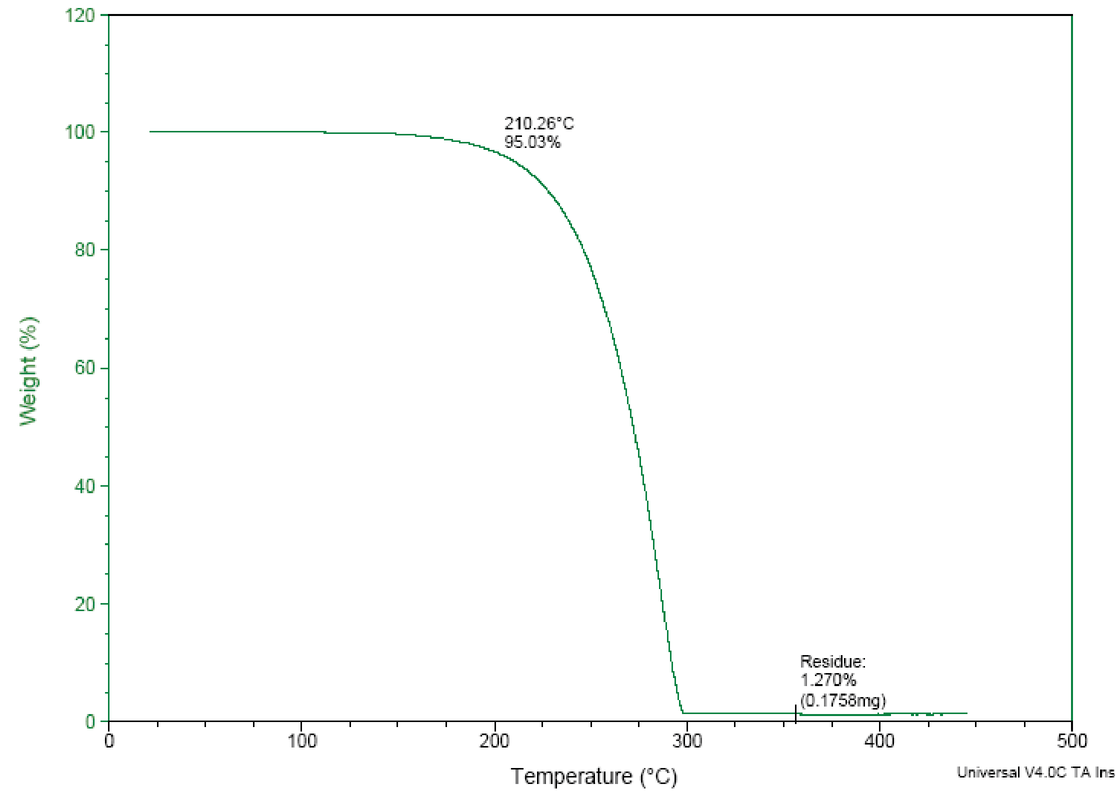
Precursor Characteristics

Crystal structure if we get it in time…





- Precursor: scandium diisopropylacetamidinate $Sc(amd)_3$
- Sublimation: 50mtorr at 125C
- Stability in air > 5 min
- Yield of purified precursor = 71%
- Residue from TG = 1.2%

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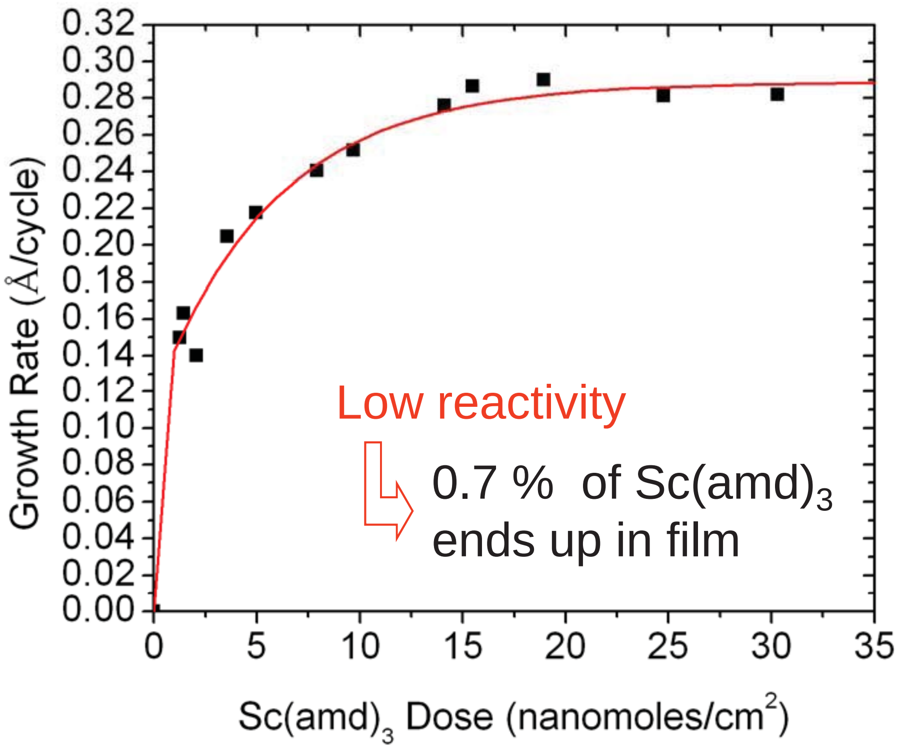
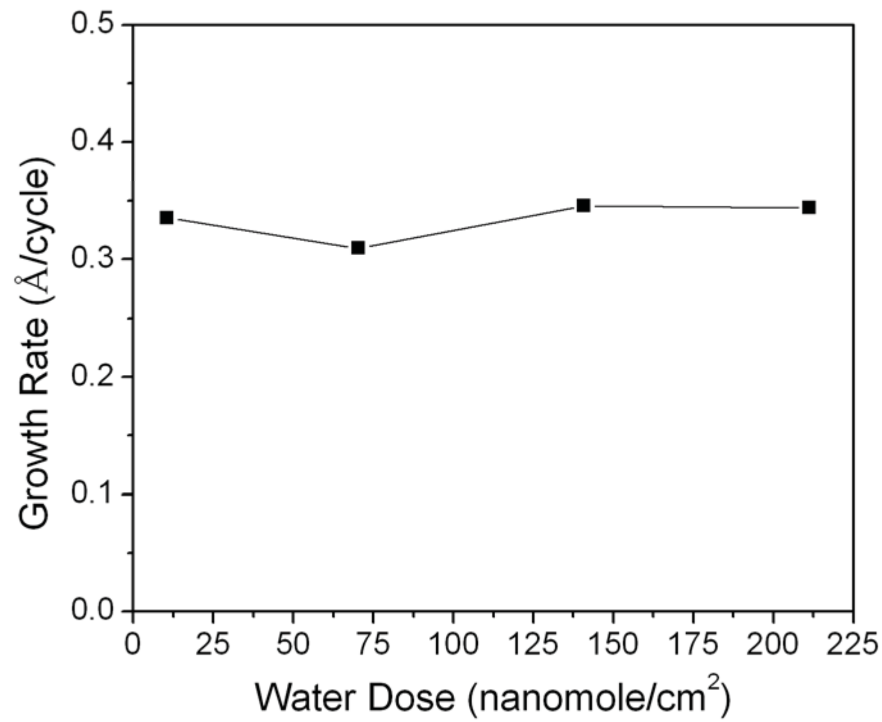
$Sc(amd)_3$ and H_2O Saturation Curves





Growth Temperature of 290°C
HF last (100) Silicon substrates

(At dep. Temp. 290°C, dep. Pres. 0.3 torr)

$Sc(amd)_3$	N_2 purge	H_2O	N_2 purge
[150°C]		[R.T.]	

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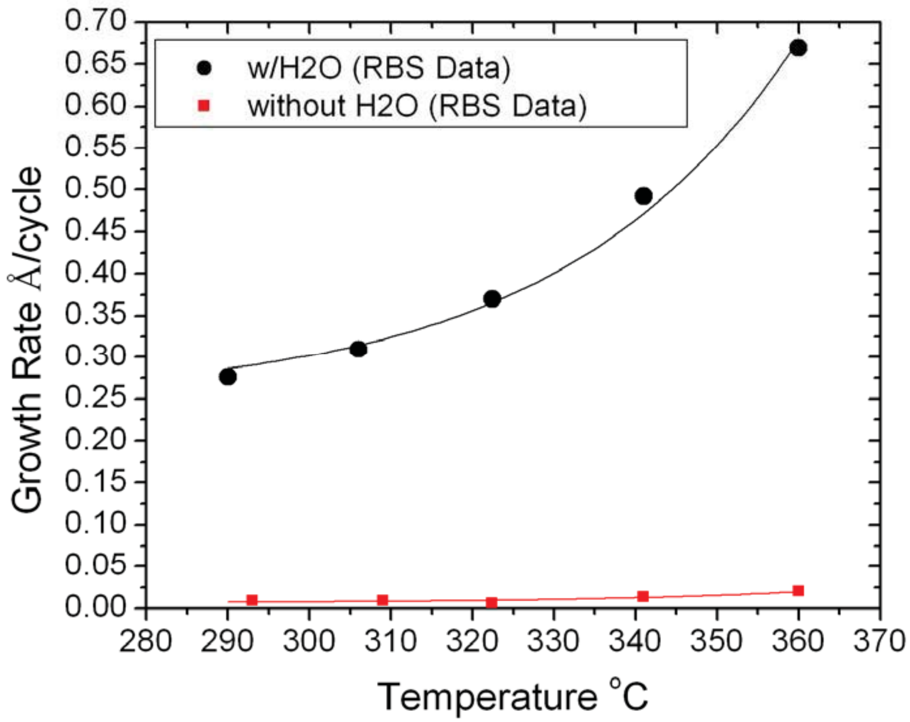


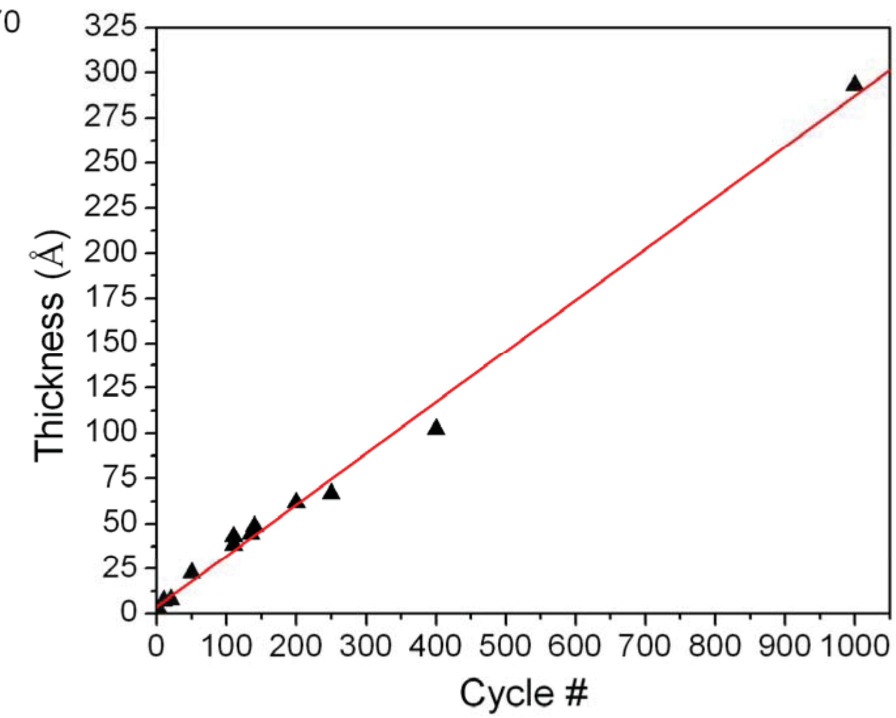
Decomposition is 3% at 360ºC

No decomposition below 330ºC

Reactivity to surface increases with increasing deposition temperature

Linear growth rate of **0.28 Å/cycle**

No significant inhibition on HF-last Si



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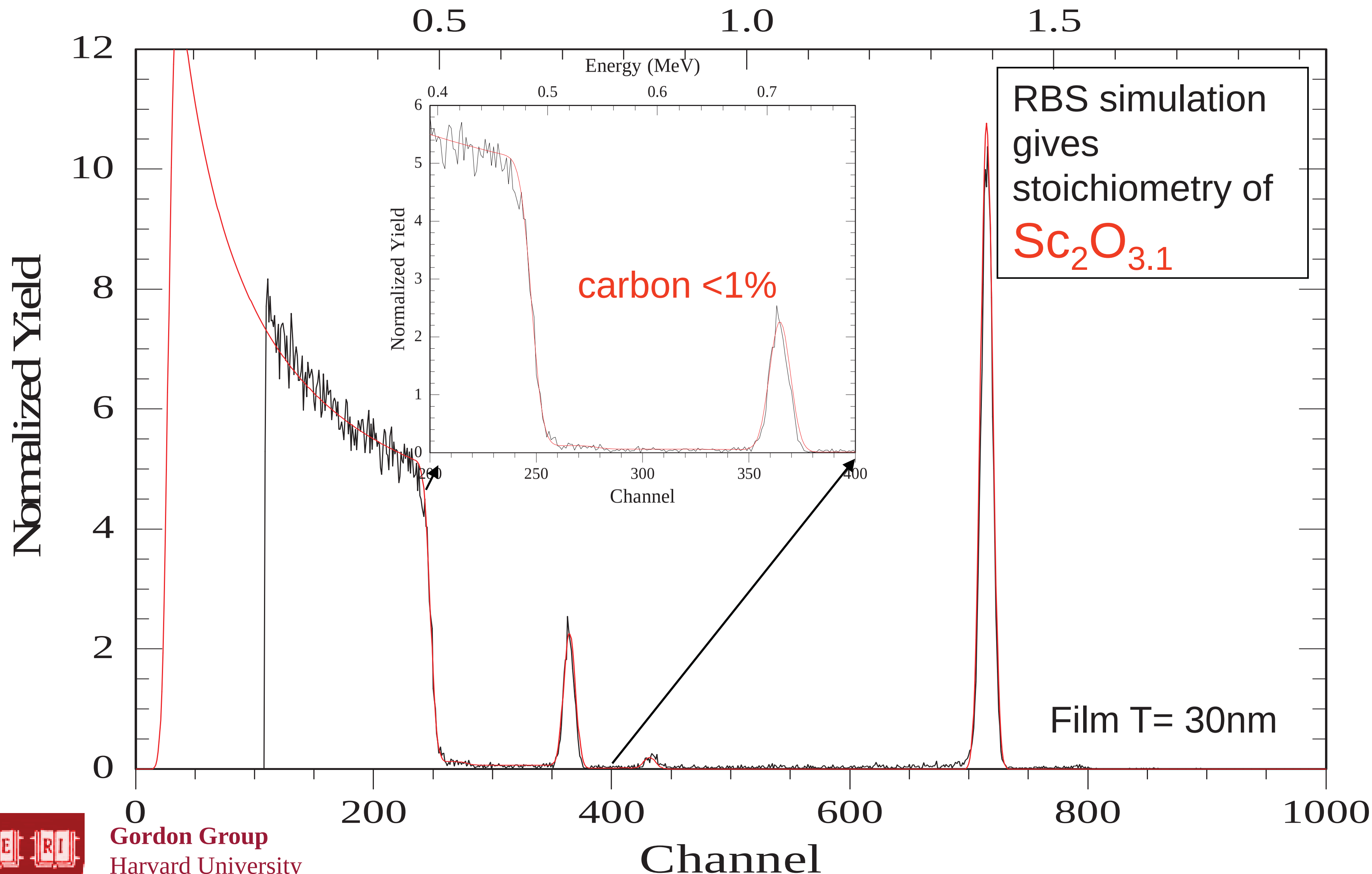
Stoichiometry from RBS



No elements other than Sc and O detected in film.

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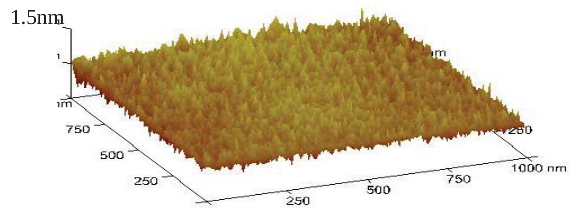
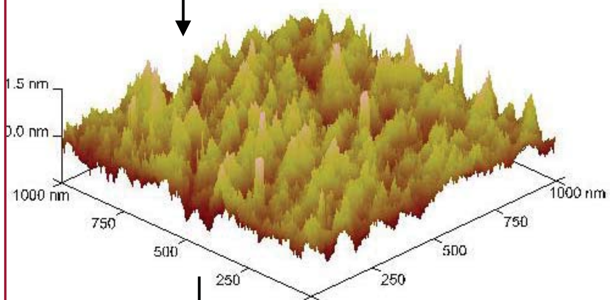
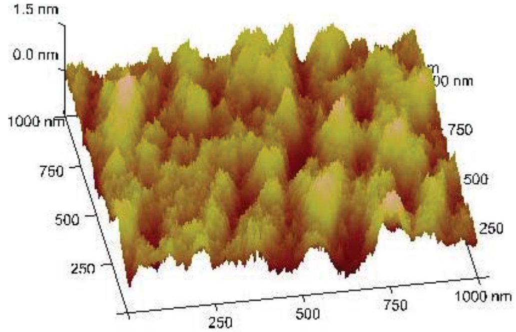
Surface and film morphology



As-Deposited 290°C
RMS = 2.3Å

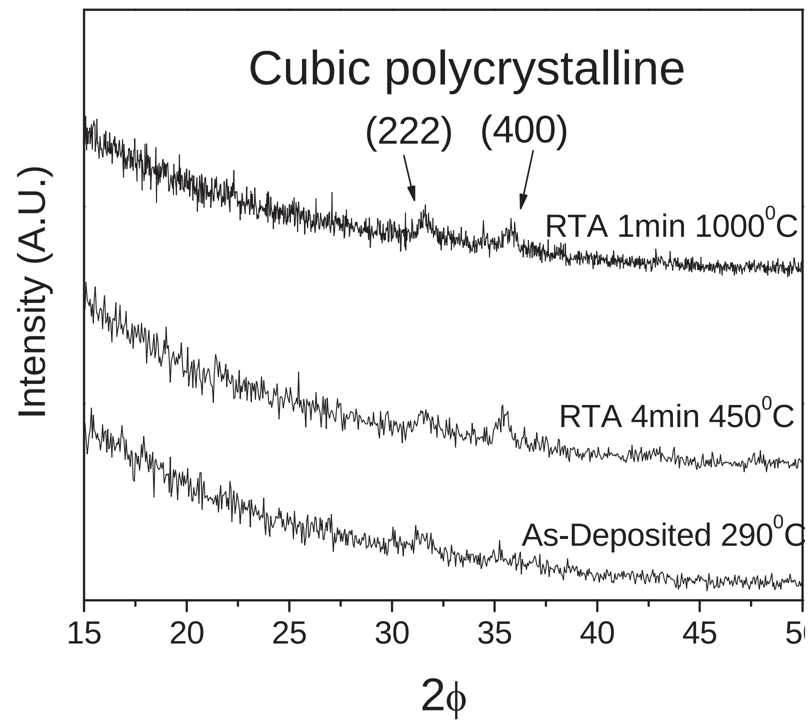


450°C H_2/N_2 anneal (4min)
RMS = 3.3Å



1000°C N_2 anneal (1min)
RMS = 3.6Å

Vertical scale of AFM images is 1.5nm



Crystallization increases with anneal temperature

Roughness increases with anneal temperature

Roughness < 4 Å after 1000°C vacuum anneal

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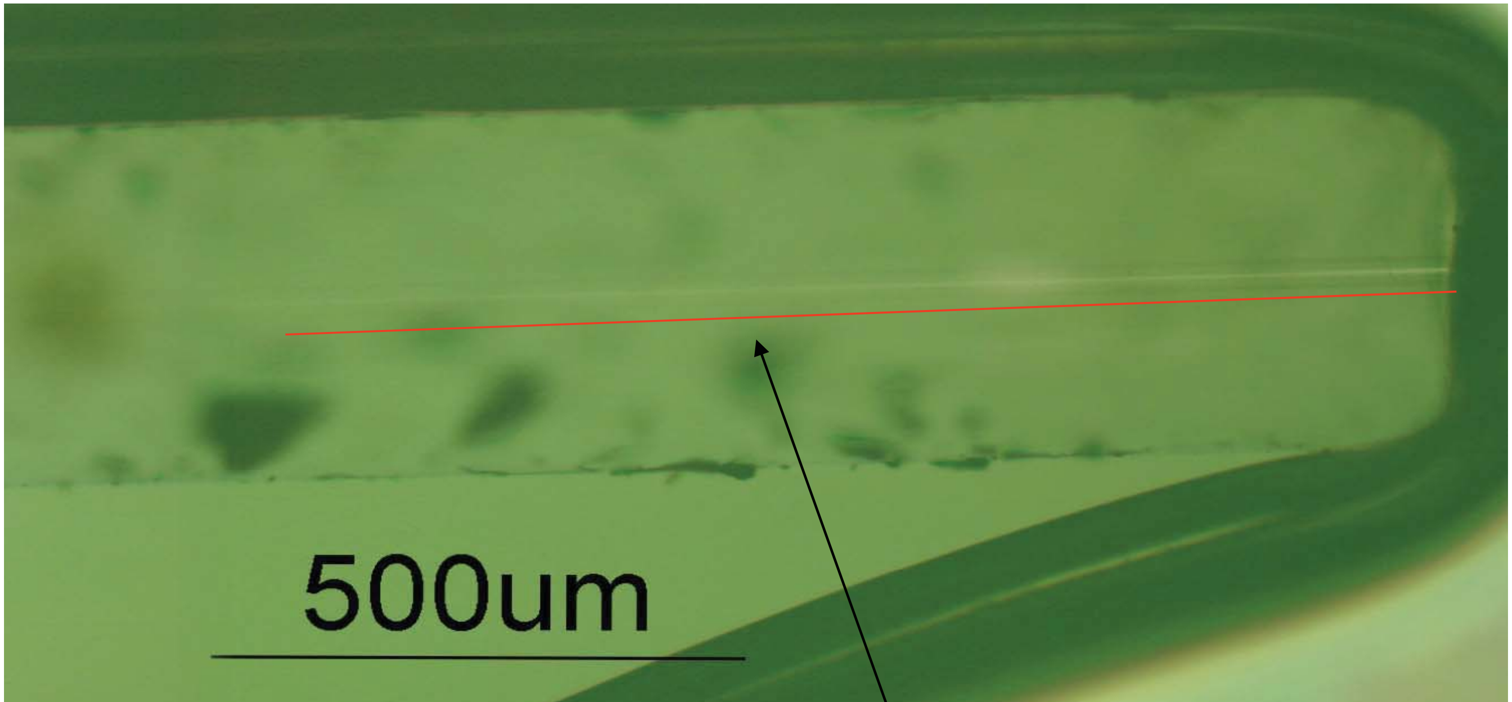
Capillary Tube Penetration:
A Test for ALD Behavior



1130μm penetration of Sc_2O_3 film in a 20 μm diameter fused silica tube

→ Yields an aspect ratio of up to **57**

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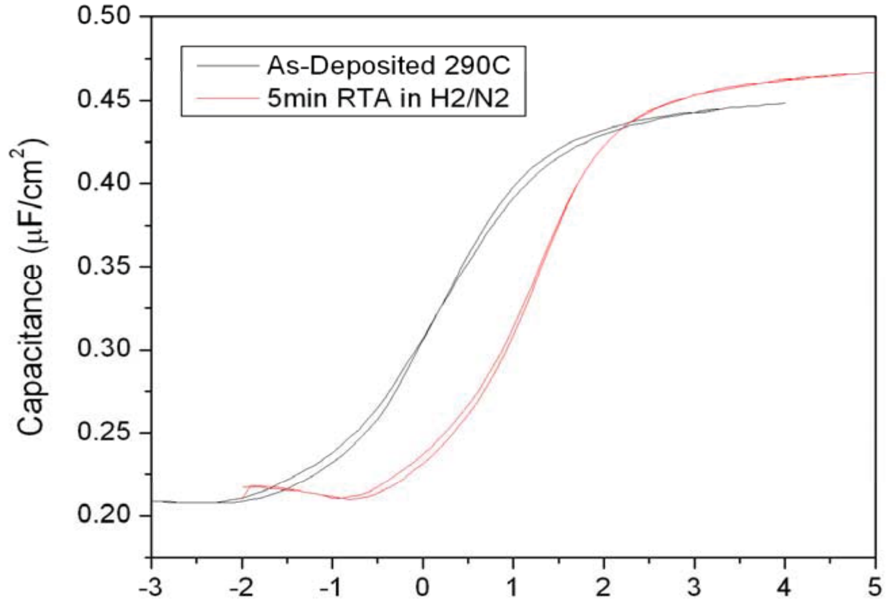
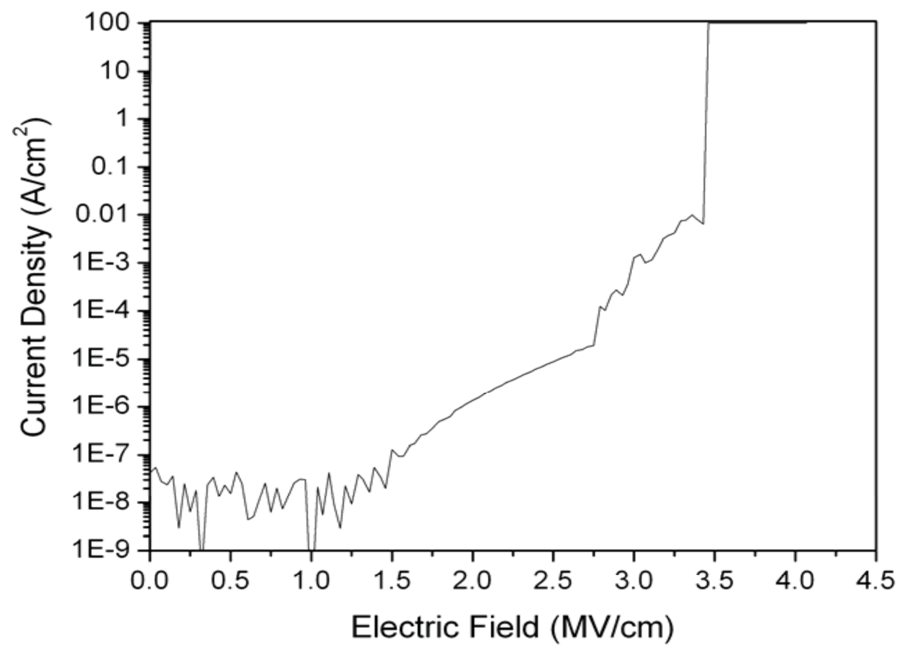
Electrical Properties of a thick Sc_2O_3 Film

- Bubbler temp. = 152°C
- 290°C Deposition Temp
- Thickness = 29nm
- Avg. EOT (annealed) = 6.67nm
- Avg. K = 16.9
- Avg. Breakdown Field (annealed) = 3.50 MV/cm





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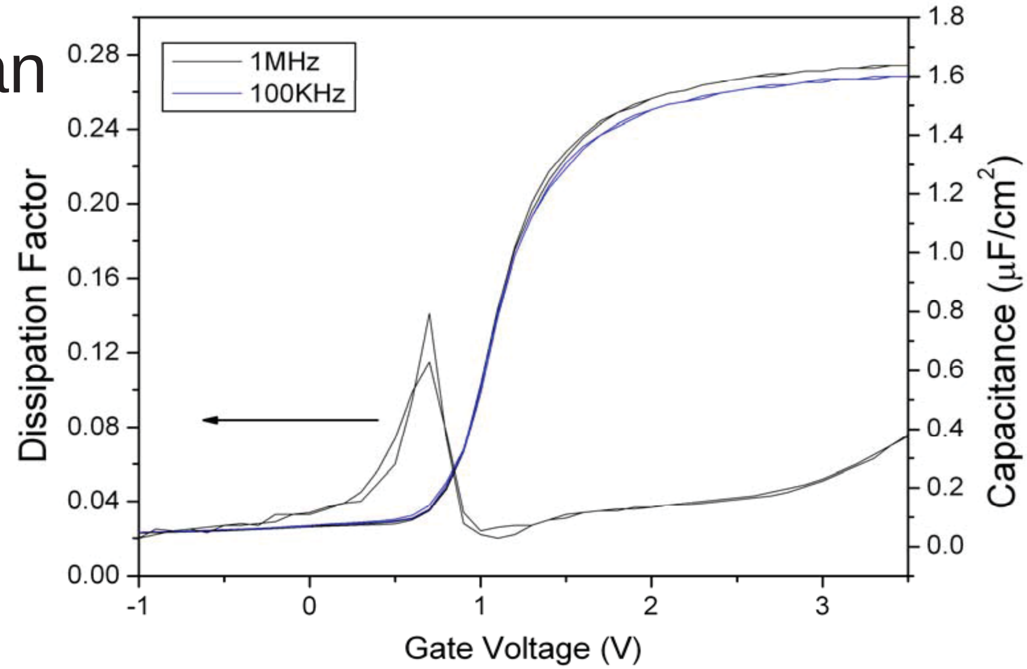
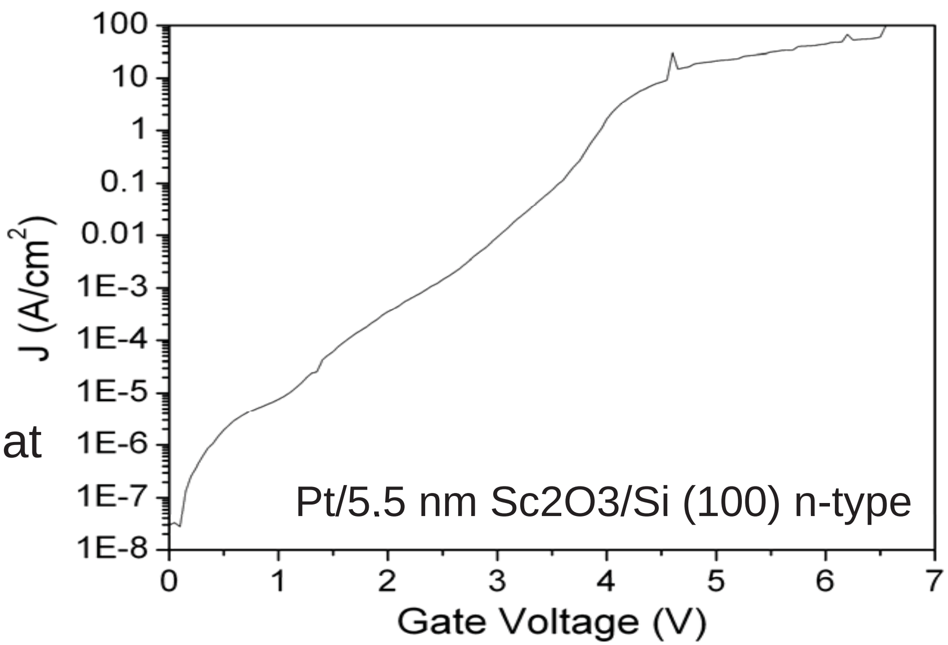
Electrical Properties of an ultrathin Sc_2O_3 film

- EOT = 1.80 nm
- $J = 7.63 \times 10^{-6}$ A/cm^2 at 1V
- Small frequency dispersion
- Ideal CV shape
- Low dissipation and no hysteresis after anneal
- Vfb has a positive shift of 300mV from ideal





RTA 5min at 450ºC

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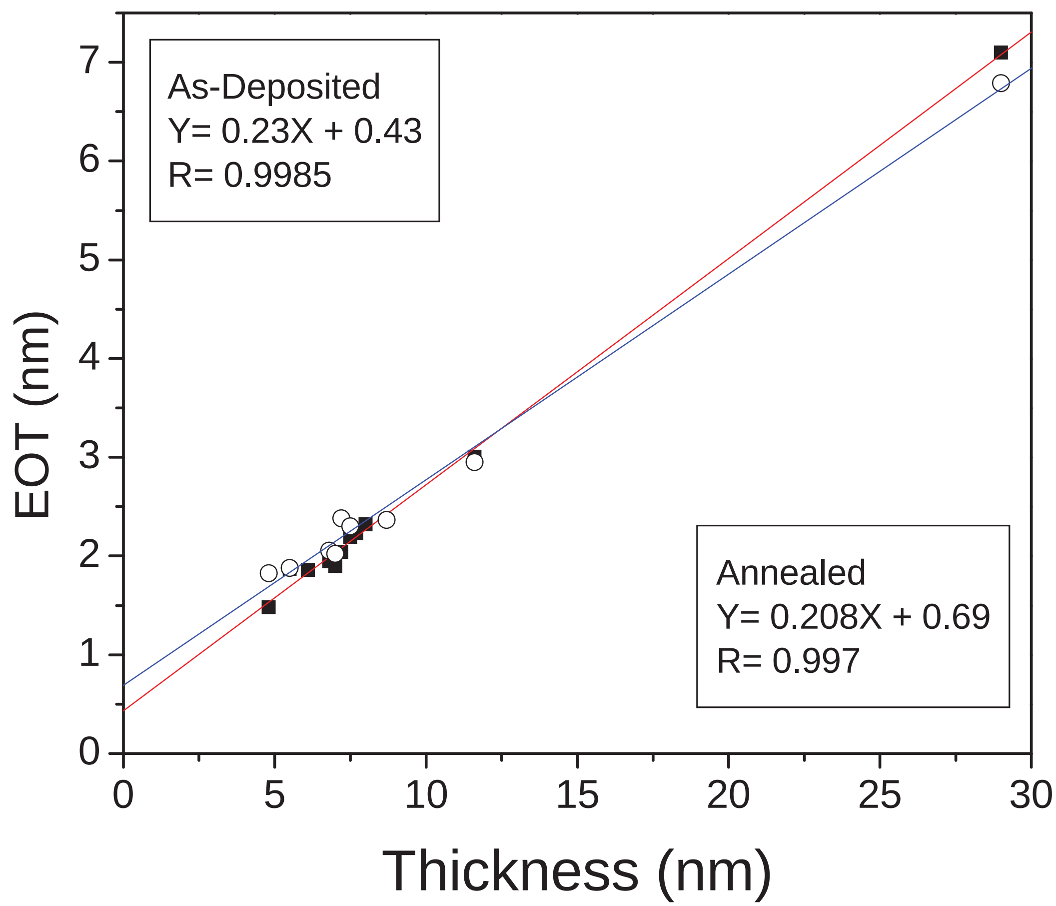
EOT vs. Thickness

As-Deposited at 290C and Annealed in forming gas at 450C



As-Deposited
K = 16.9 ± 0.3
IL = 0.43 ± .05 nm

Annealed
K = 18.7 ± 0.5
IL = 0.69 ± .08 nm

Annealing increases dielectric constant and increases extrapolated interfacial layer.

Dielectric Constant (from slope)
Intercept provides interfacial oxide thickness

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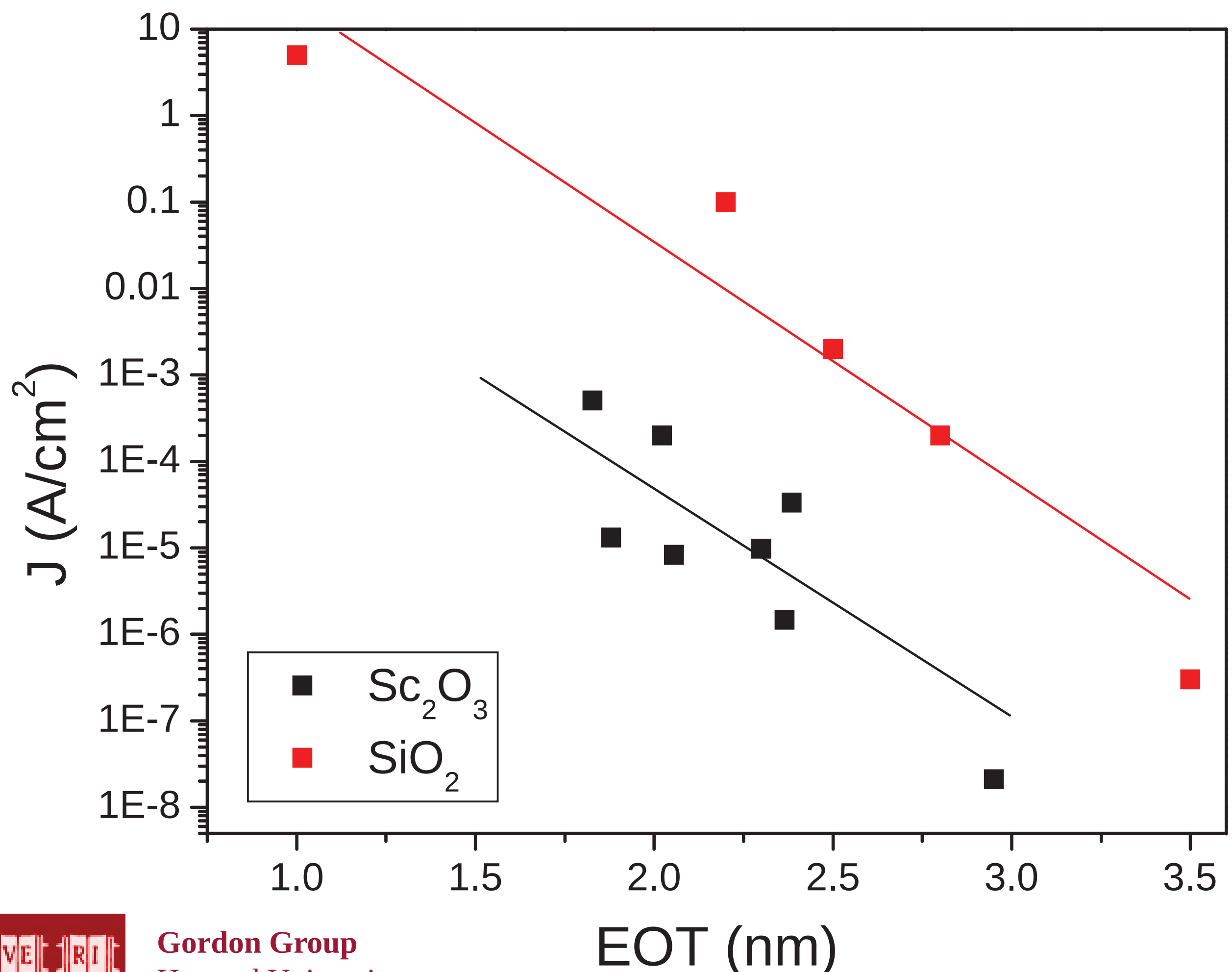
J vs. EOT for annealed Sc_2O_3



- Leakage is lower than equivalent SiO_2 films
- Not as low as many other high-K oxides

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Summary

- Pure, self-limited $Sc_2O_{3.1}$ thin films were grown from a new precursor $Sc(^iPr_2\text{-Me-amd})_3$
- Electrical properties are acceptable, but not ideal.
- Low growth rate.
- Large ALD temperature window <275º-350º with no decomposition.
- No inhibition on HF-last silicon surfaces.
- Use of ALD Sc_2O_3 to deposit more complex ternary oxides and for specialty coatings applications should be feasible with this type of precursor.

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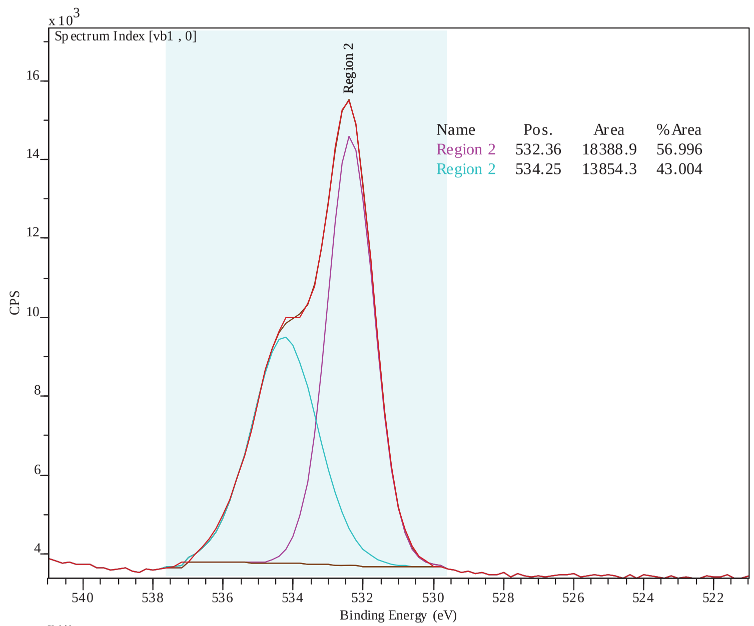
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Region 2 534.25 13854.3 43.004
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536
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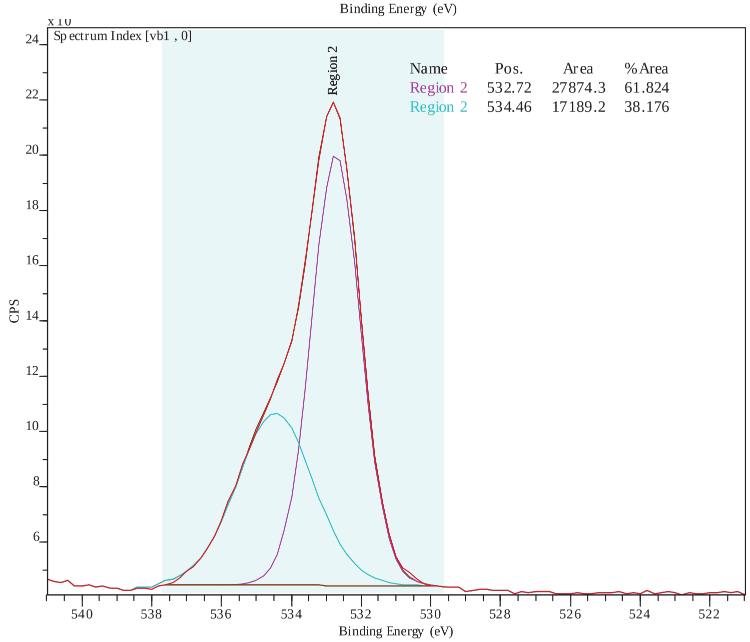
526
524
522
Binding Energy (eV)


Spectrum Index [vb1 , 0]
Region 2
Name Pos. Area %Area
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524
522
Binding Energy (eV)