Synthesis of New ALD Ruthenium Precursors and Thin Film Growth

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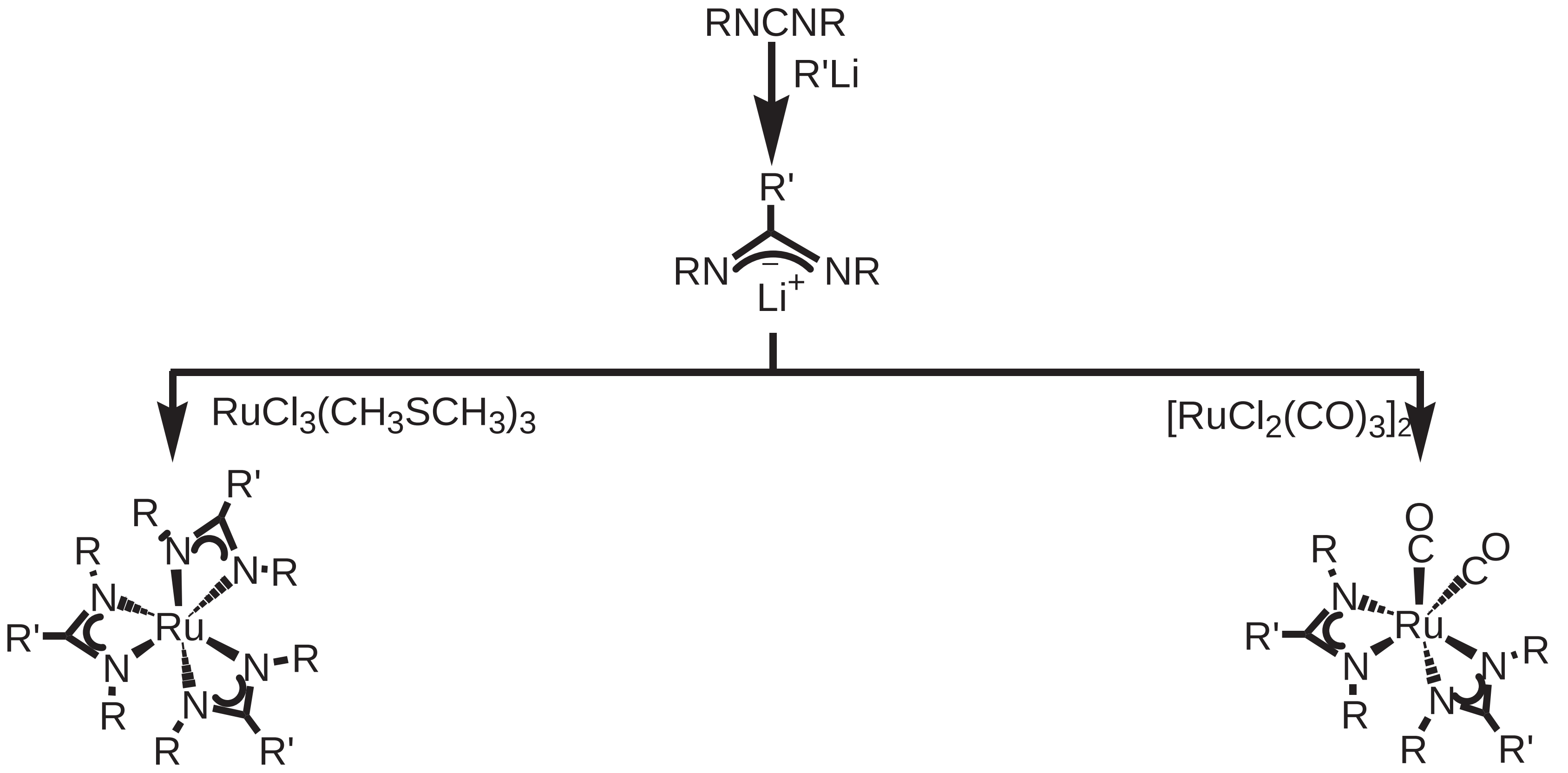
Applications of Ru Thin Films

- Adhesive layer for Cu
  --- Suppression of C-F layer formation
  --- Reduction of residual stress of Cu layer
  --- Good interfacial adhesion with TiN, TaN
  --- Low solubility with Cu film
- Capacitor electrode
  --- Low resistivity (bulk Ru: 7.1 μΩ•cm)
- Gate electrode
  --- work function close to desired value
  for PMOS gate electrode (~ 5 eV)

Synthesis of Ruthenium Amidinates



1 (R = ^{i}Pr, R' = Me)
2 (R = ^{s}Bu, R' = Me)
3 (R = ^{n}Bu, R' = Me)
4 (R = ^{i}Bu, R' = Me)
5 (R = ^{i}Pr, ^{s}Bu, R' = Me)

6 (R = ^{i}Pr, R' = Me)
7 (R = ^{t}Bu, R' = Me)

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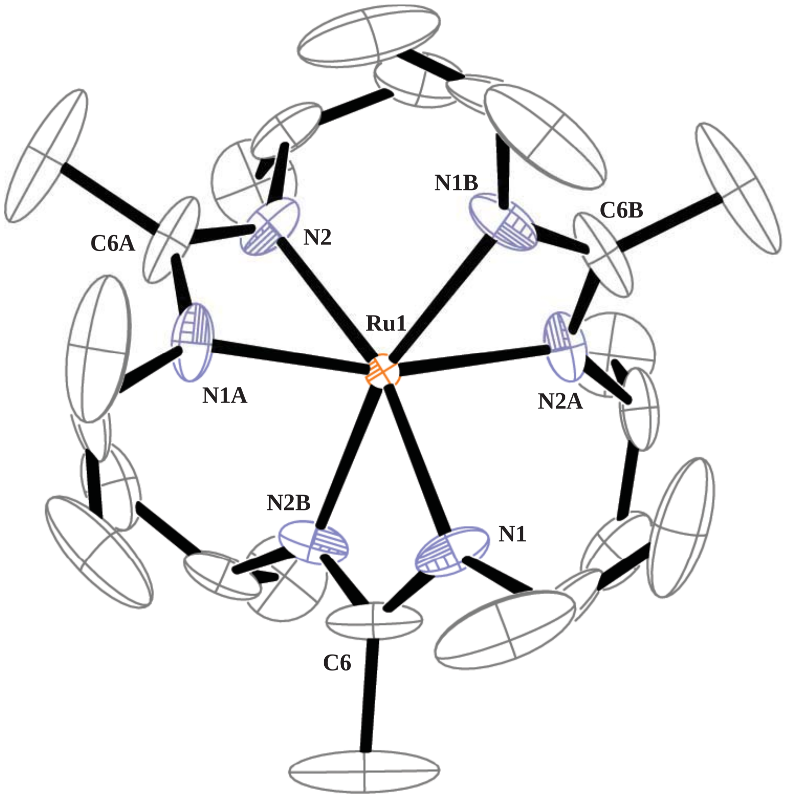
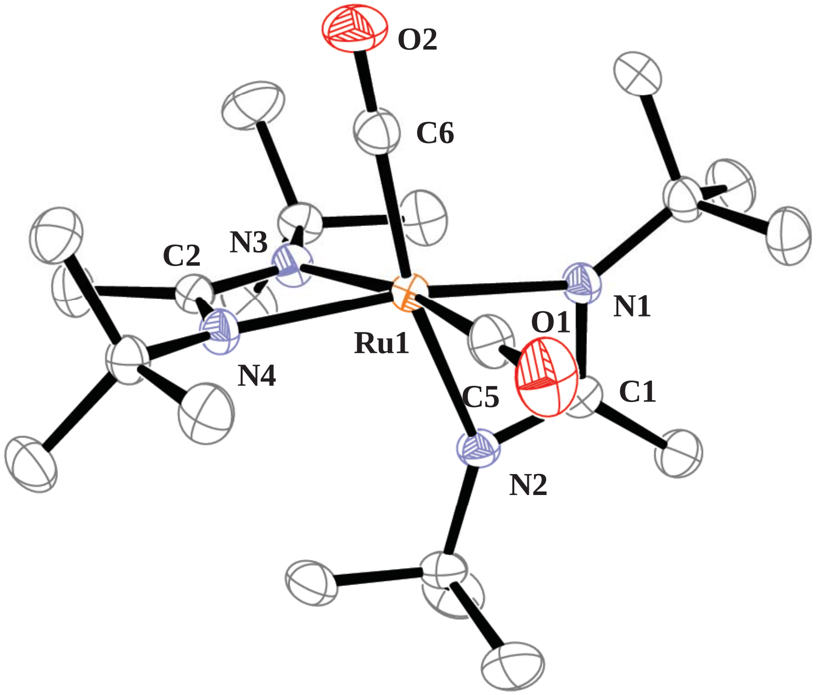
X-ray Structures of Ruthenium Precursors



Ru(iPr-amd)$_3$



Ru(tBu-amd)$_2$(CO)$_2$

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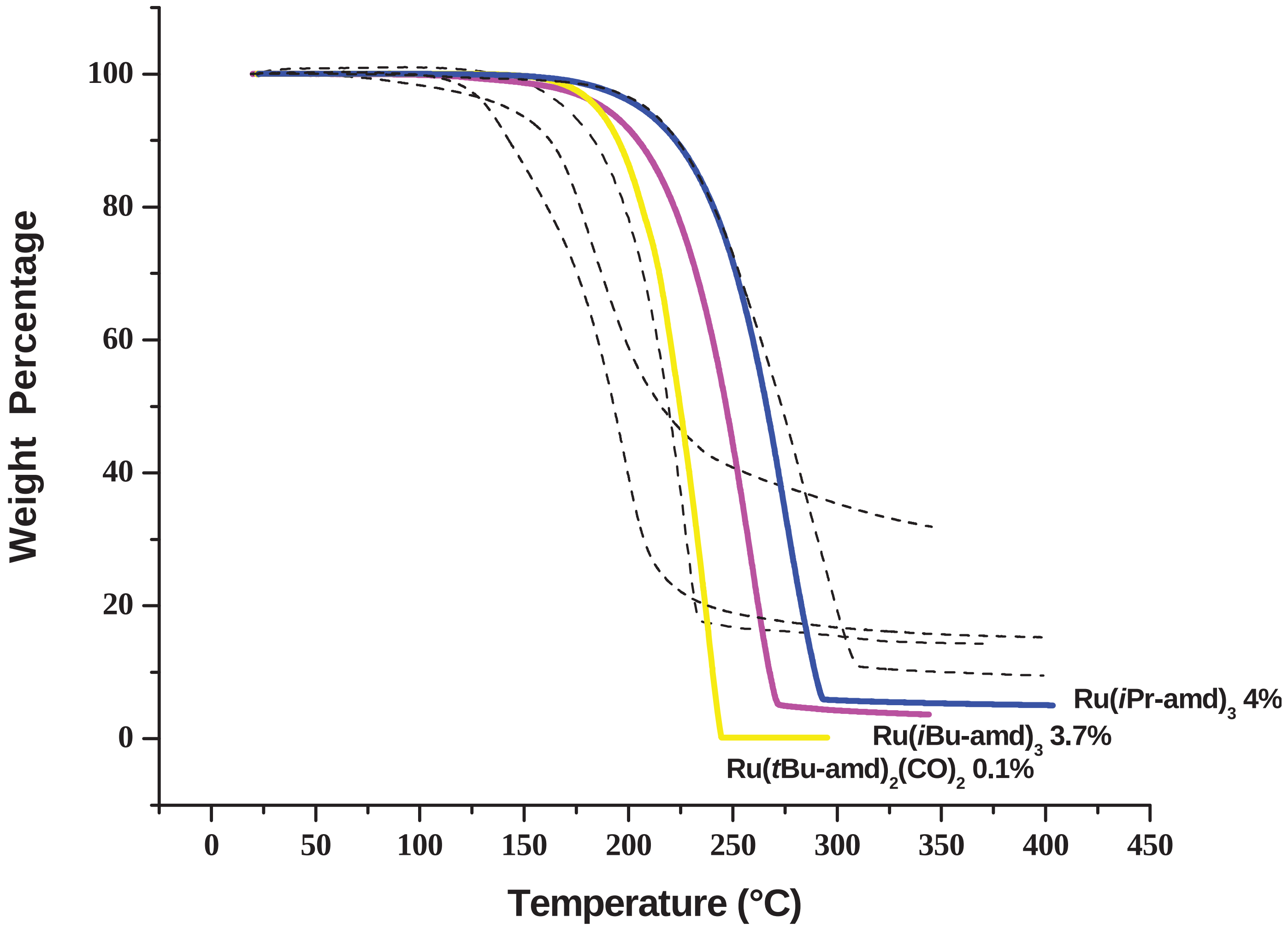
Physical Properties of Ruthenium Amidinates

Compounds	V. P.(^{o}C/Torr)	Yield(%)	m.p.(^{o}C)
$\mathrm{Ru}(i\mathrm{Pr\text{-}amd})_3$	85/0.05	35	--
$\mathrm{Ru}(s\mathrm{Bu\text{-}amd})_3$	85/0.04	40	195
$\mathrm{Ru}(i\mathrm{Bu\text{-}amd})_3$	65/0.04	15	181 - 184
$\mathrm{Ru}(i\mathrm{Pr},\ s\mathrm{Bu\text{-}amd})_3$	90/0.05	30	--
$\mathrm{Ru}(n\mathrm{Pr\text{-}amd})_3$	70/0.1	25	92 - 95
$\mathrm{Ru}(i\mathrm{Pr\text{-}amd})_2(\mathrm{CO})_2$	50/0.045	40	122
$\mathrm{Ru}(t\mathrm{Bu\text{-}amd})_2(\mathrm{CO})_2$	95/0.02	50	203 - 205

Thermal Stability by Thermal Gravimetric Analysis



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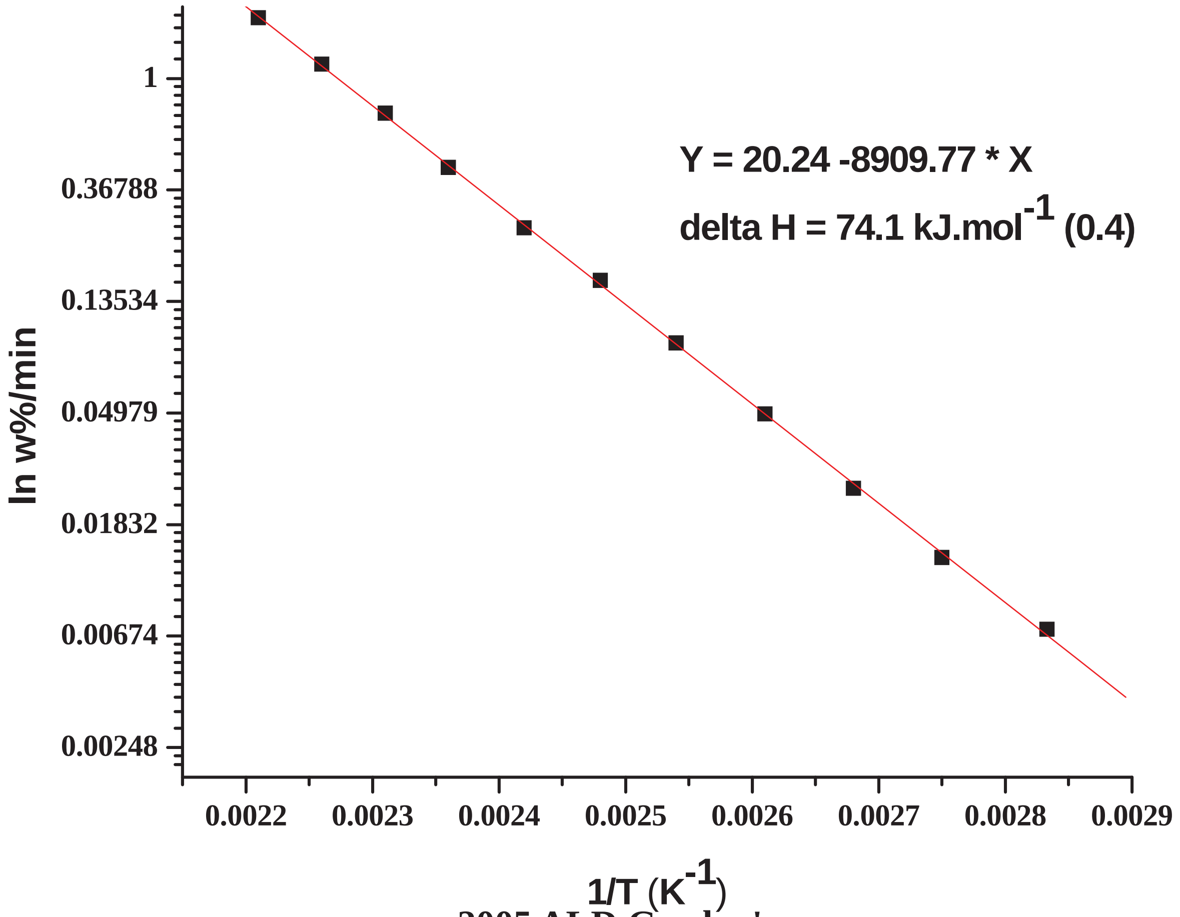
Thermal Studies of Ruthenium Amidinates

Compounds	$t_{1/2}$ (hr, 175 ºC, C_6D_6)	TG Residue
Ru(*i*Pr-amd)$_3$	15	4.0%
Ru(*s*Bu-amd)$_3$	1	15.7%
Ru(*i*Bu-amd)$_3$	0.9	3.7%
Ru(*i*Pr, *s*Bu-amd)$_3$	1.5	8.7%
Ru(*n*Pr-amd)$_3$	0.36	31.9%
Ru(*i*Pr-amd)$_2$(CO)$_2$	---	14.3%
Ru(*t*Bu-amd)$_2$(CO)$_2$	---	0.14%

Conclusion: Ru(*i*Pr-amd)$_3$ is the best choice considering volatility and thermal stability

Evaporation Kinetics of Ru(*i*Pr-amd)$_3$ by Isothermal TG



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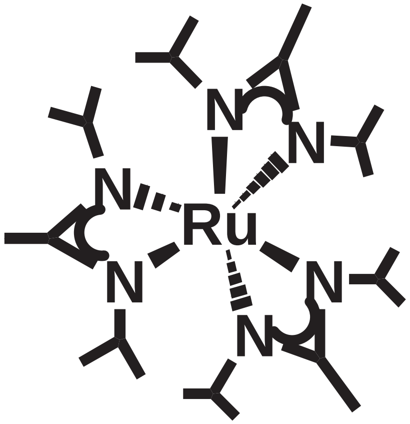
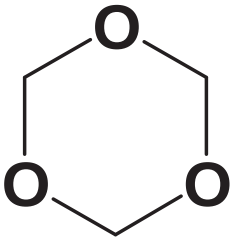
Precursor for ALD Ru Film



Ru(*i*Pr-amd)$_3$

- 85 ^{o}C/0.05 Torr
- Low residue 4%
- Air and moisture stable



trioxane

- 25 ^{o}C/9.5 Torr, m.p. 59 – 62 ^{o}C
- Totally sublimable
- Decomposed to formaldehyde at high T

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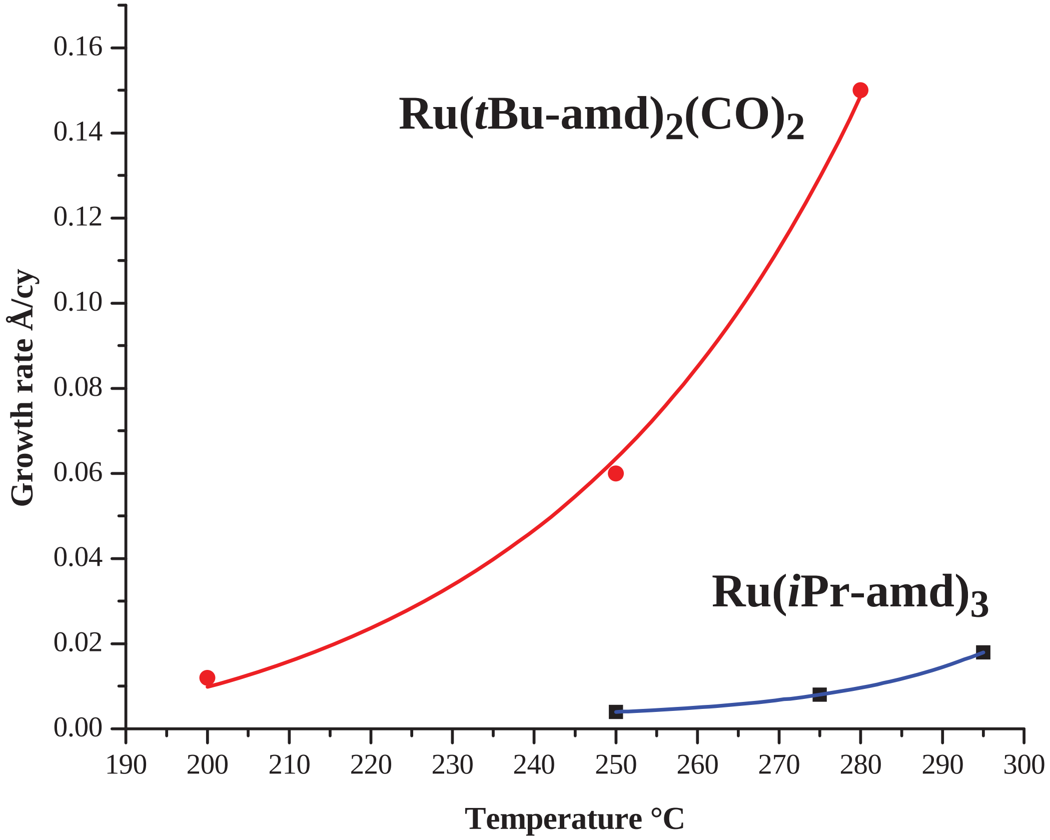
ALD Decomposition Test



ALD sequence:

Ru	Ru	Ru	purge

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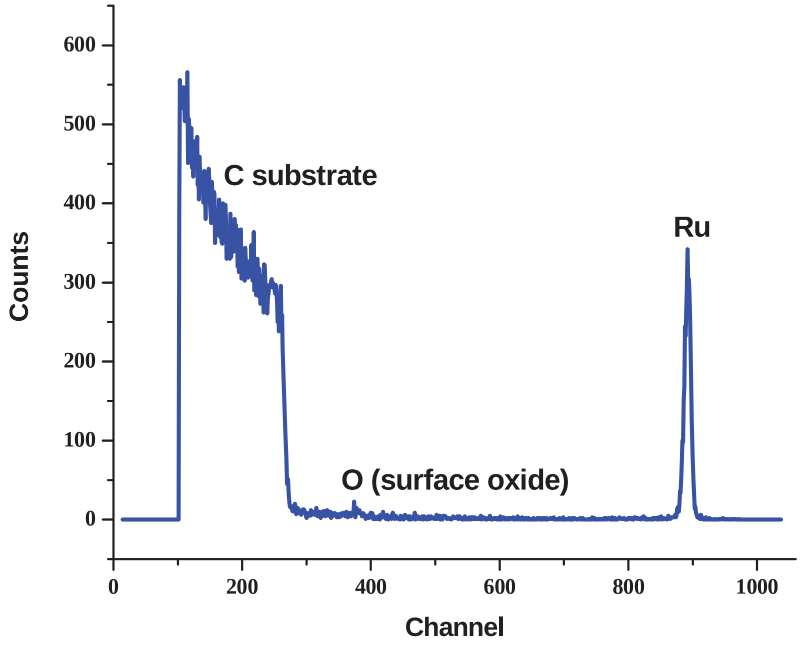
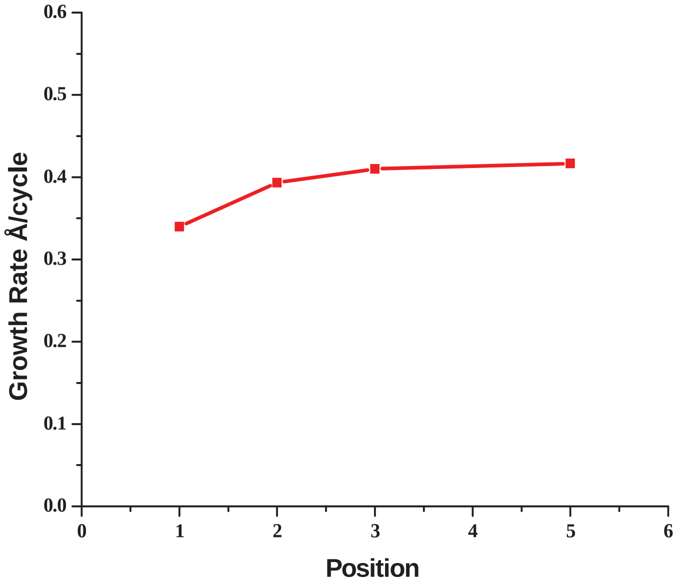
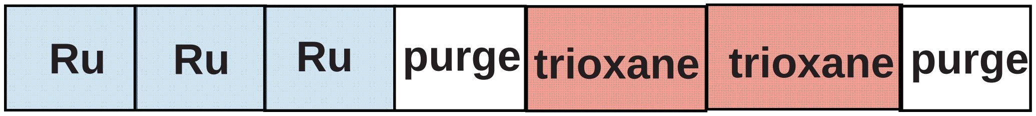
Pure Ru Metal Films





ALD sequence:



Ru	Ru	Ru	purge	trioxane	trioxane	purge

- Thickness: 120 Å/300cycles
- Sheet resistivity: 43 μΩ.cm

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Liquid Injection ALD Ru Based on Nebulization

Delivery Problem: we found trace decomposition particles covering the surface of precursor, which greatly reduced the vaporization rate and the saturation dose could not be reached.

↓

Solution: liquid injection ALD Ru based on nebulization can avoid the trace decomposition at the bubbler stage.

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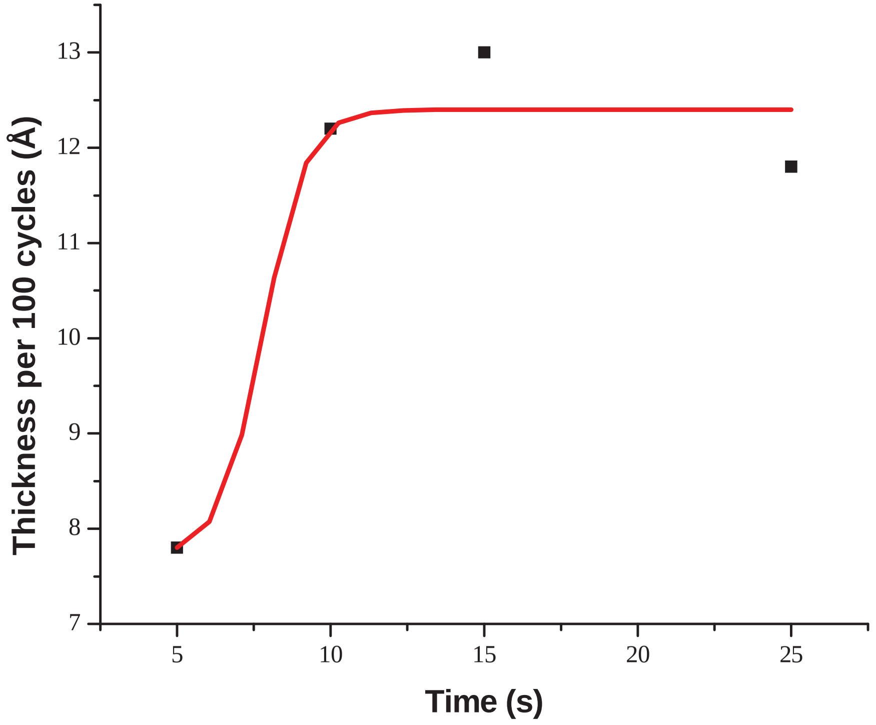
Saturation curve of Ru precursor

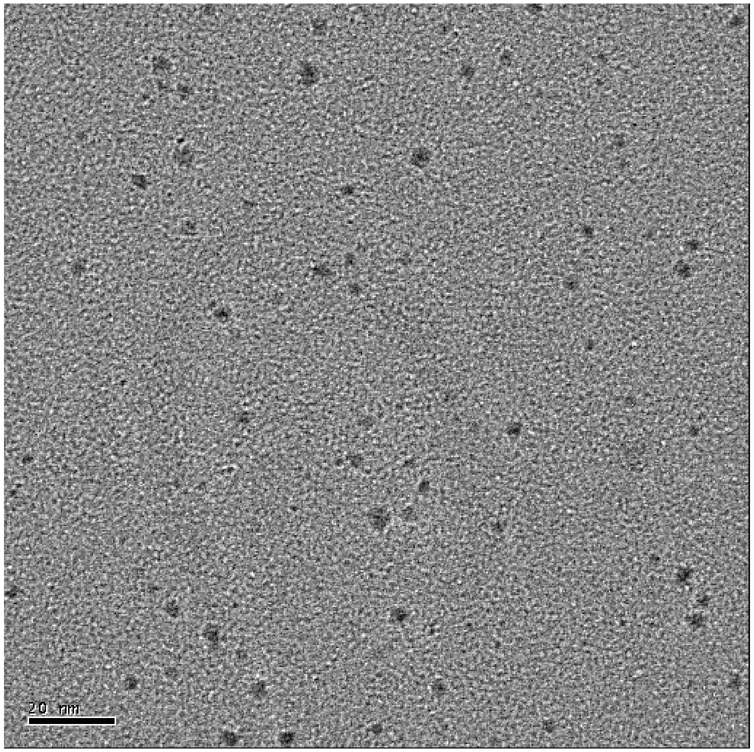


- 1g/25 mL in dodecane
- Growth rate: 0.12 Å/cy

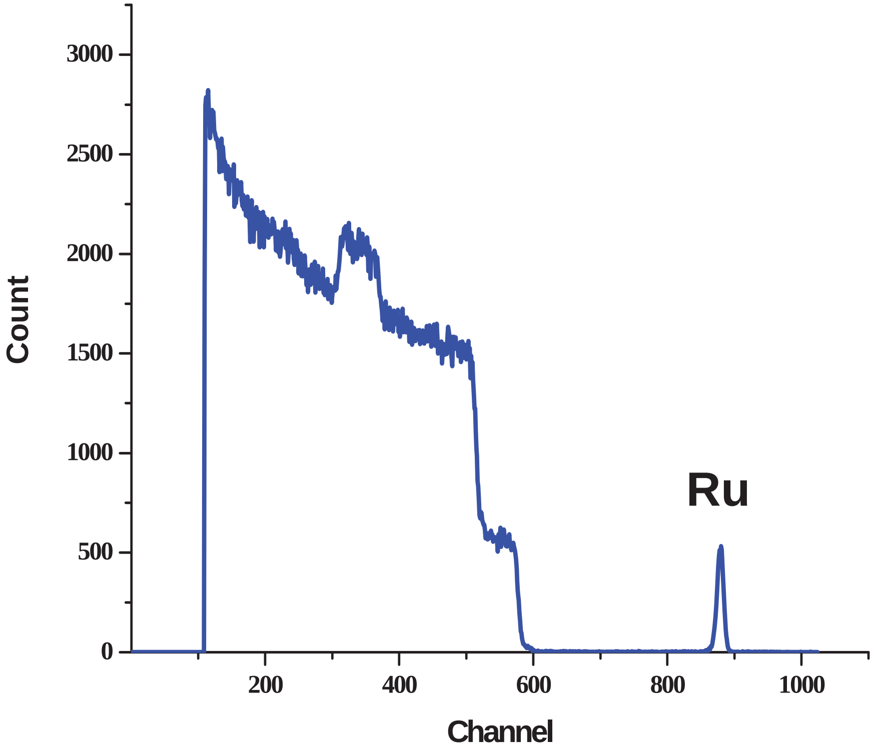
ALD sequence:

Ru	purge	trioxane	purge

Nucleation of Ru on SiO_2: TEM



12 Å



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Summary

- A new Ru precursor --- $Ru(^{iPr}amd)_3$ was synthesized, which is volatile and thermally stable enough for ALD.

- Pure ruthenium film was achieved by ALD process of $Ru(^{iPr}amd)_3$ and trioxane.

- TEM study showed low nucleation spot density at the early stage of Ru film growth.

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