Growth and Properties of Ultrathin Metal Films for ULSI Interconnects

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Cu-Diffusion Barriers for ULSI Interconnect

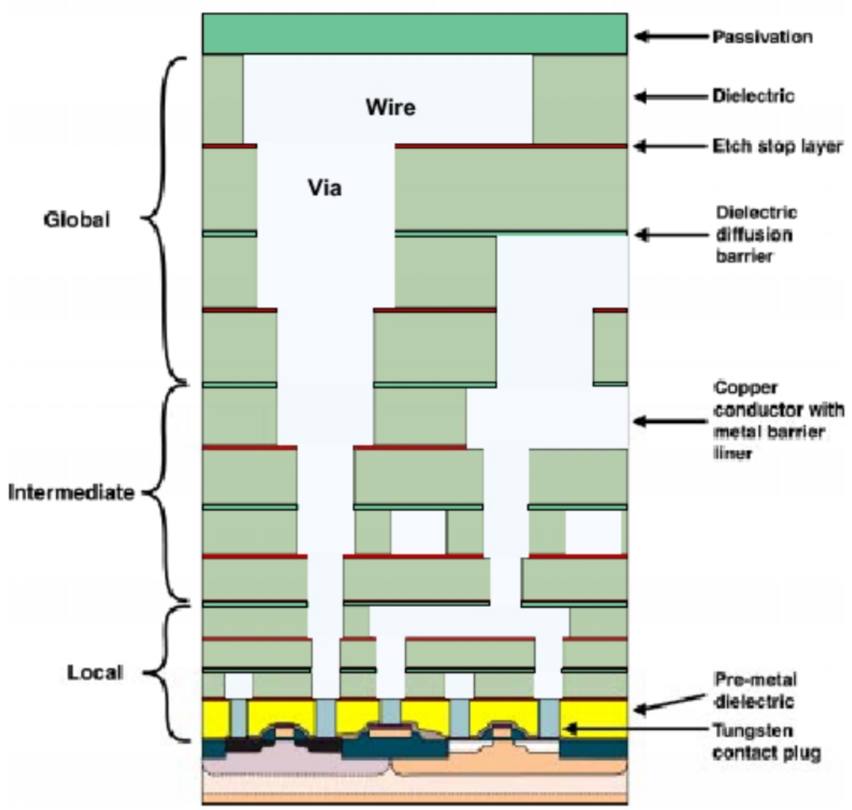
ULSI Interconnect

A barrier layer (generally refractory metals and metal nitrides) must be employed to separate Cu from physical contact with other interconnect materials.

Metal Via Barrier Requirements

- ❖Diffusion and electromigration resistance
- ❖Good adhesion
- ❖Low electrical resistivity (~100 μΩ•cm)
- ❖ Good step coverage

Production year	2010	2013	2016
MPU 1/2 pitch (nm)	45	35	22
Barrier thickness (nm)	5	3.5	2.5 [1]



Manufacturable Solutions:

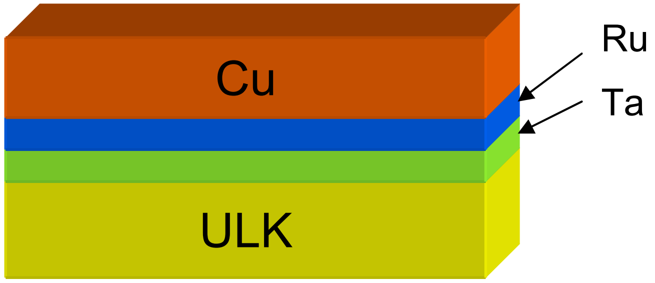
Known

NOT Known

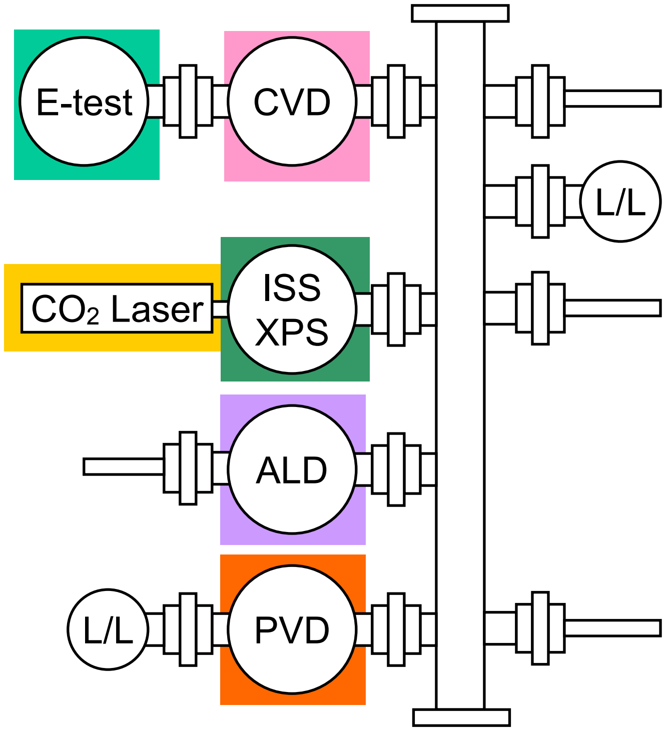
[1] International Technology Roadmap for Semiconductors 2003 Update, http://pubic.itrs.net/, (2003).

Motivation for Ru Barriers

- Challenges on future diffusion barriers
  - Prevent Cu diffusion at a thickness of only 3~5 nm
  - Adhere well to ILD layer and to Cu
  - Seedless Cu plating in high aspect ratio of via holes
- A composite barrier structure is under study.
  - A Ta film serving as the primary diffusion barrier
  - A Ru film in contact with Cu
- Ru is a noble metal and Cu is insoluble in it
- Ru oxide is also conductive and has a favorable reduction potential
- Ru is expected to improve wetting and adhesion properties between Ta and Cu
- Ru could enable direct copper plating on barrier surface without first coating a Cu seed layer.

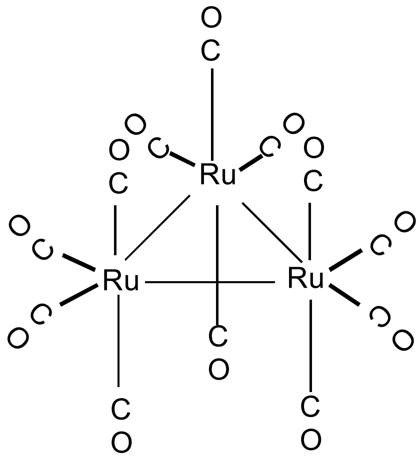


In-situ Film Deposition and Characterization System



- Ultra-thin film deposition systems
  - Physical vapor deposition (PVD)
  - Chemical vapor deposition (CVD)
  - Atomic layer deposition (ALD)
- Barrier characterization systems
  - Real time XPS and ISS analysis with CO_2 laser annealing
  - Electrical measurement
- Annealing facilities
  - CO_2 infrared laser
  - Halogen lamp
- *In-situ* sample transfer system

Chemical Vapor Deposition of Ruthenium Using Ruthenium Carbonyl



- Ruthenium carbonyl $[Ru_3(CO)_{12}]$ is a solid precursor.
- It is stable in air and moisture at room temperature.
- It begins to evaporate at ~80 ^{o}C.
- It decomposes at 150 ^{o}C.

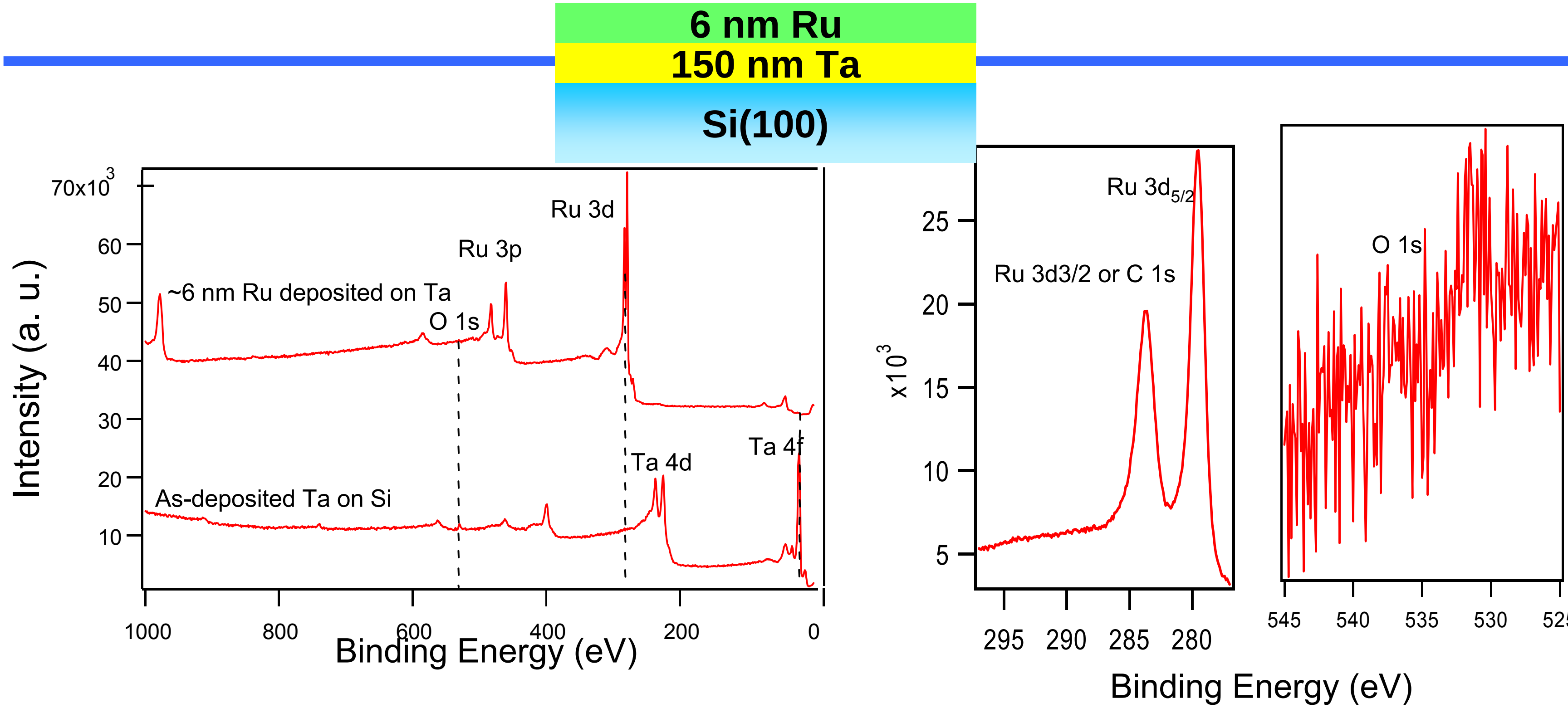
➢ *Why ruthenium carbonyl?*

- A pure Ru film with minimal carbon and oxygen residues can be deposited!
- The compound can be decomposed as low as 150 ^{o}C.
- No reactive gas is needed! (Substrate can be protected!)

➢ *But wait* – the carbonyl gives poor step coverage so it is not feasible for manufacturing. It does show Ru's potential.

Q. Wang, *et al.*, APL 84 (2004) 1380.

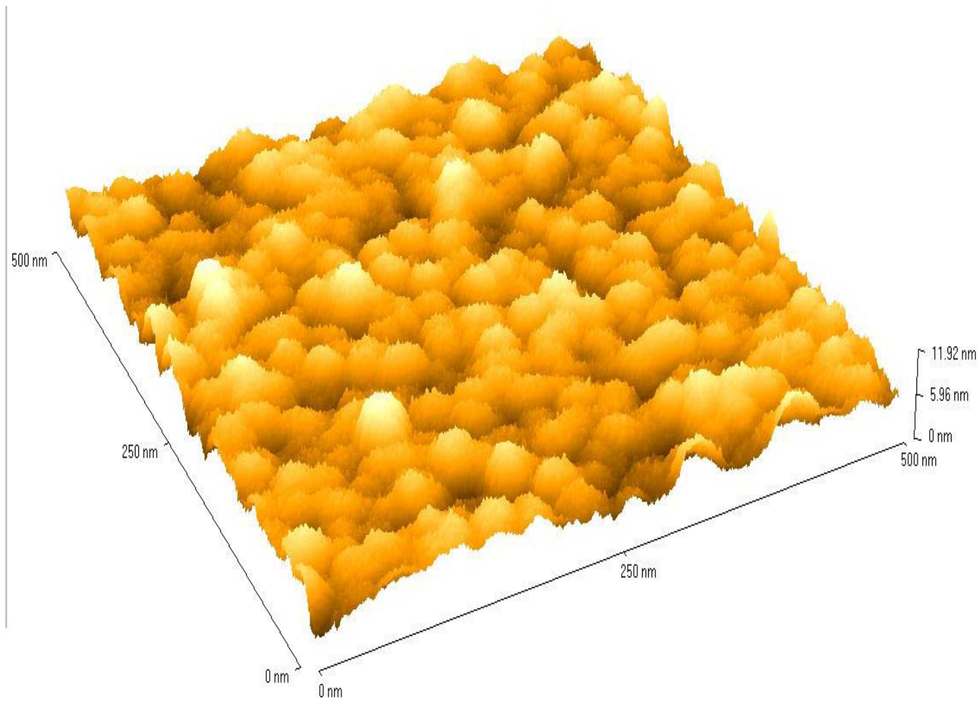
Low Temperature Thermal CVD Ru on Ta

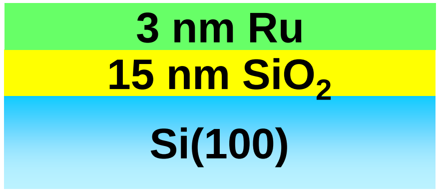


- A 150 nm Ta film was deposited on the Si substrate using PVD.
- A 6 nm Ru film was deposited on Ta surface without any reactive gas at the temperature as low as 150 °C.
- XP spectra indicated a pure Ru film with low C and O contents (<1 %) was deposited at this low temperature.

Q. Wang, *et al.*, APL 84 (2004) 1380.

Ultrathin Ru Film Roughness on SiO_2

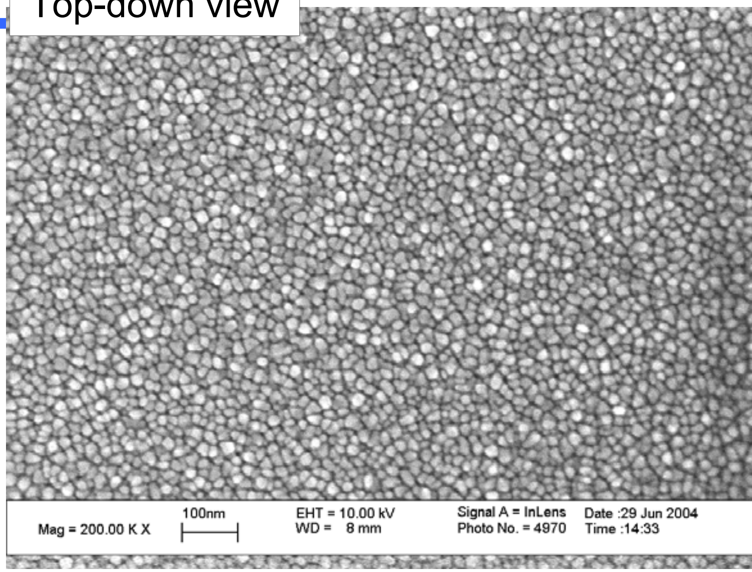




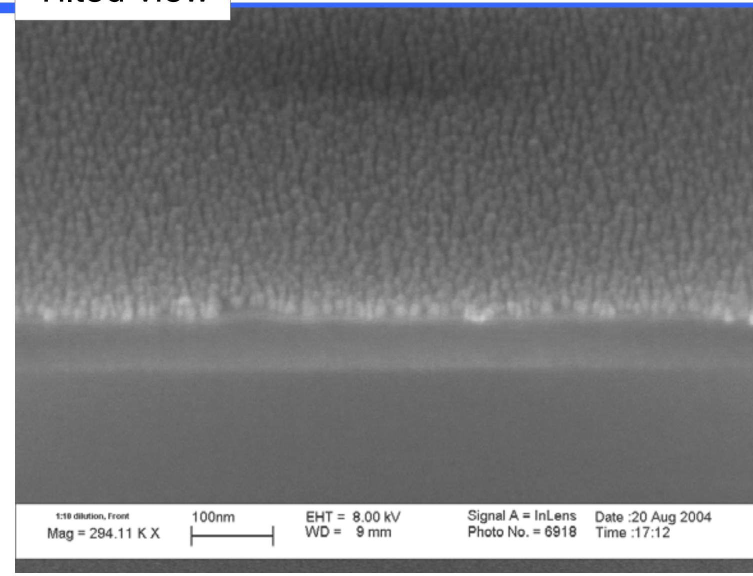
- A 3 nm Ru film was deposited on the SiO_2 substrate.
- The Ru film roughness was ~1.4 nm, measured by AFM.
- The SiO_2 substrate roughness was 0.2 nm.

Ru Film Properties – Microstructure of 30 min film

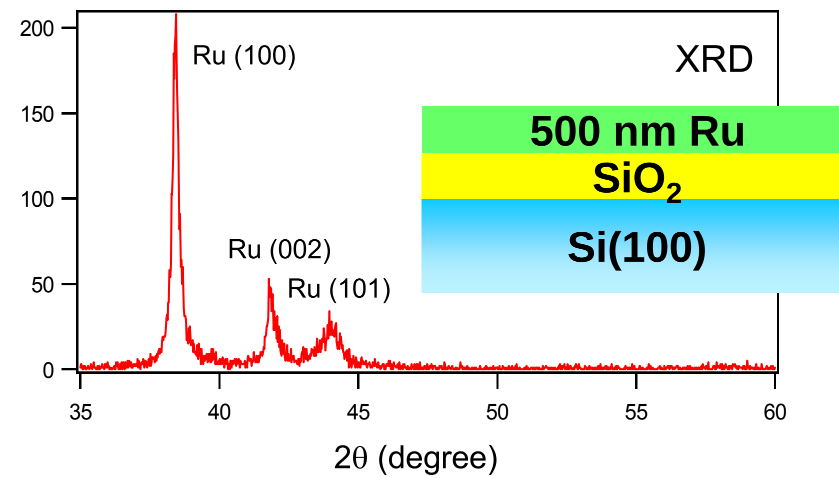
Top-down view



Tilted view

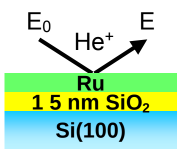


- Polycrystalline and columnar structure
- Average grain size was ~ 20nm.
- Grains are granular → Reveals limitations of Ru-carbonyl precursor; need a different precursor to increase the nucleation density.
- XRD shows crystalline & hexagonal structure of the film.

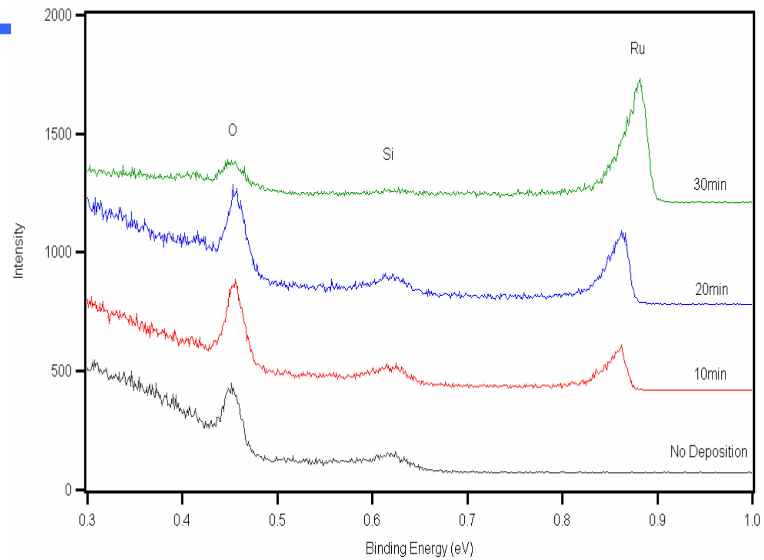


Ru Film Properties – ISS/XPS

ISS

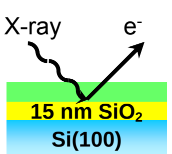


$E/E_0 = f(m_2/m_1)$

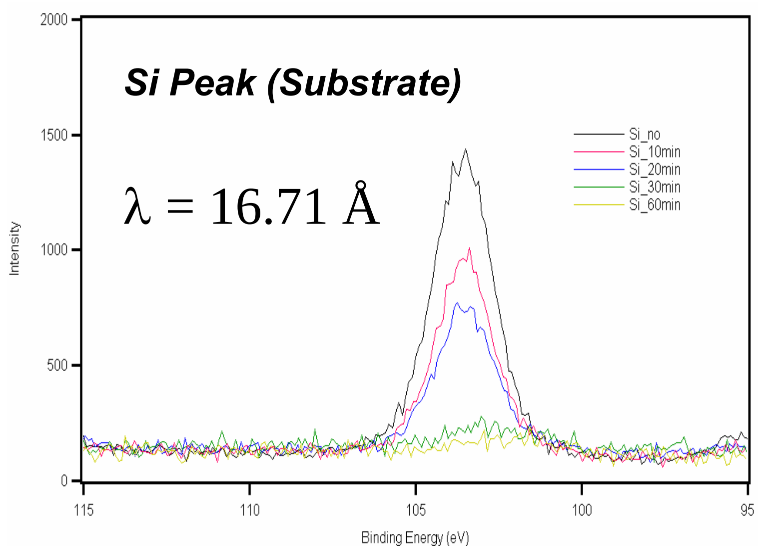


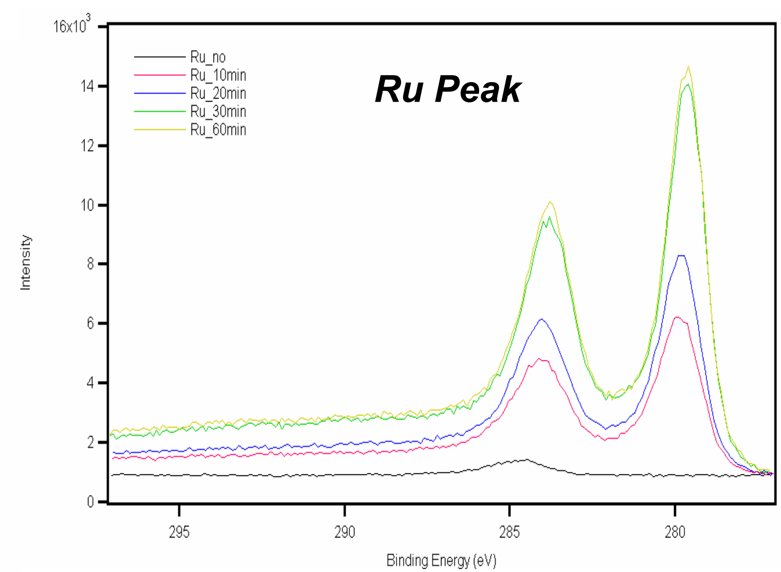
- LEISS → Surface coverage
- Substrate Si peak is attenuated by overlaying Ru film. The Si peak intensity is function of film thickness and mean free path. $I/I_0 = \exp(-d/\lambda\cos\theta)$
- Calculated minimum thickness of continuous Ru film → ~ 3nm

XPS

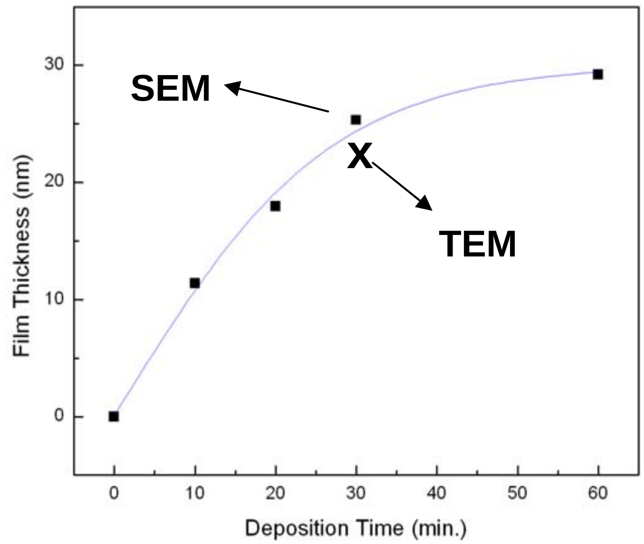


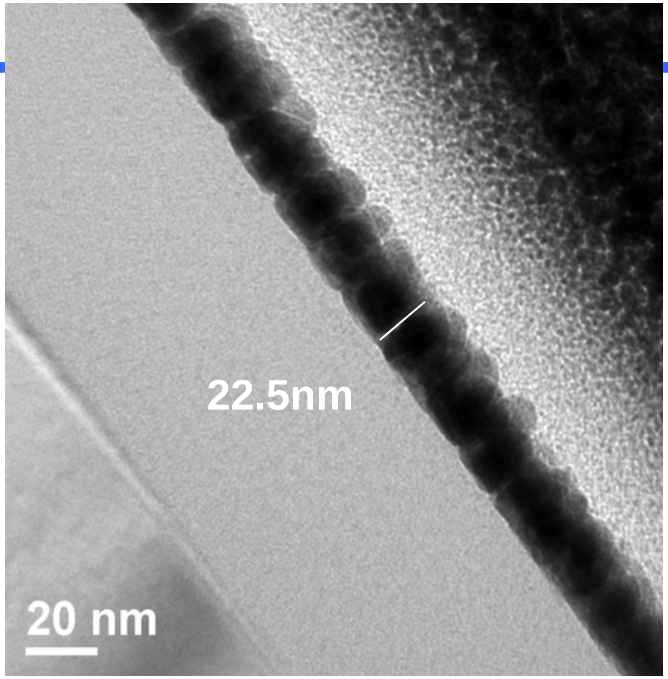
$I / I_0 = f(\lambda / t)$

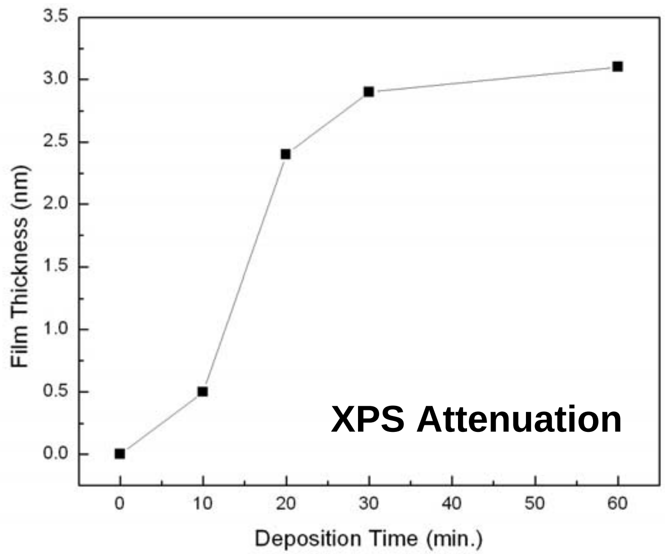




Film thickness measurement



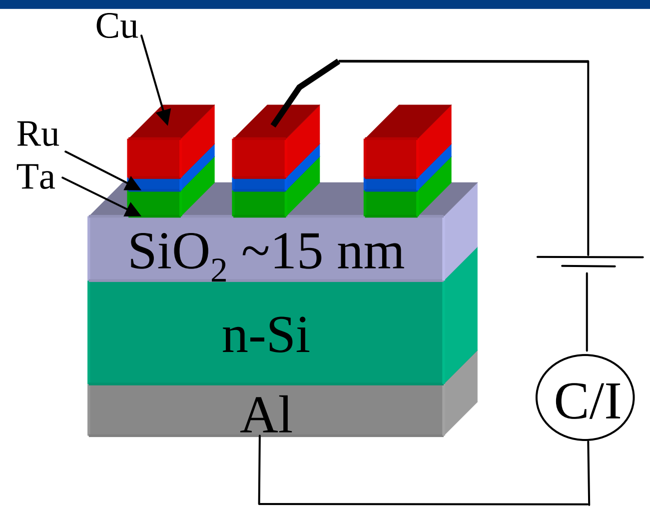


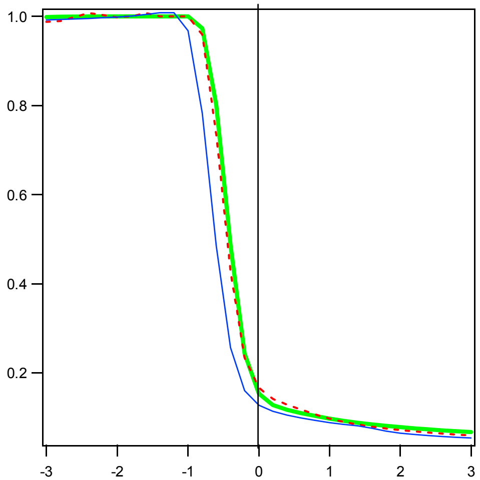


- **Min. thickness of continuous Ru film was ~ 3nm.**
- **However, SEM/TEM shows a much thicker film; ~25nm for the 30-min sample.**
- The error seems to be caused by film roughness or film discontinuity. ISS overestimates surface coverage due to a shadowing effect, and XPS can detect the substrate Si peak due to surface roughness or film discontinuity.

Ru Film Properties – Electrical Test

Barrier electrical test structure





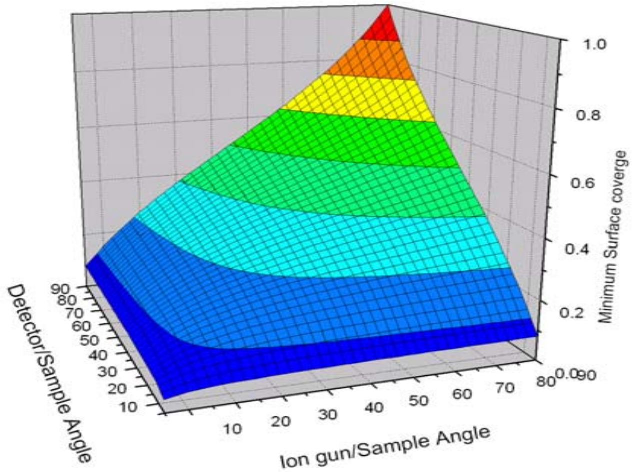
- ***2.5nm / 4nm Ru Barrier (XPS Thickness Basis)***
  - As-deposited
  - 2.5 nm Ru after annealing
  - 4 nm Ru after annealing

- Cu/Ru/Ta MOS capacitor was built, and the flat band voltage shift of a C-V curve (ΔV_{FB}) was used to characterize barrier effectiveness against Cu diffusion.
- Samples need to be prepared carefully to obtain reproducible C-V curves.
  - Annealing for 90 min at 350 °C in high vacuum to neutralize interface trapped charges.
  - *In situ* deposition of Cu dots on the top of Ru dots with shadow mask.
  - To minimize device damages caused by sputter deposition, two-step Cu deposition was applied.
  - A 20 nm Cu film was first deposited using 10 W DC power.
  - A 200 nm Cu film was then deposited using 50 W DC power.
  - Subsequent anneal for 60 min at 350 ºC in 110 mTorr H_2/N_2 forming gas (after ambient exposure) and test *ex situ*

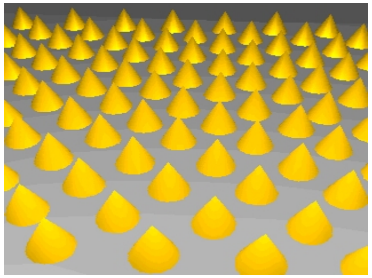
Challenges of Characterizing Ultra-thin Films

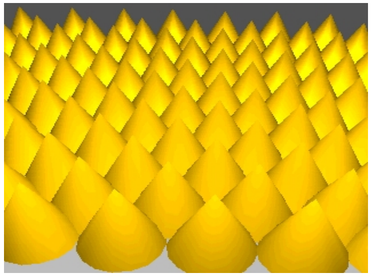
Immediate Challenges:

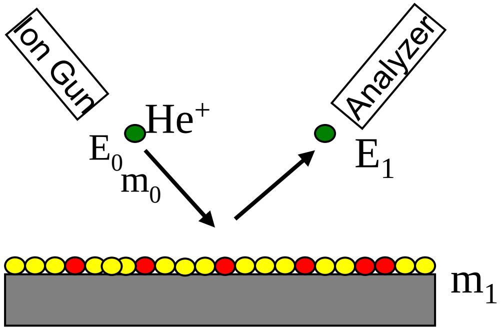
- Description of the thin films and the true barrier
- Ion and electron spectroscopies best suited for flat surfaces



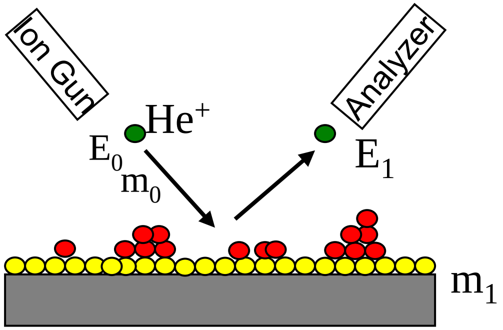
Shadowing effect of ISS
- Effect of ion gun & analyzer angles





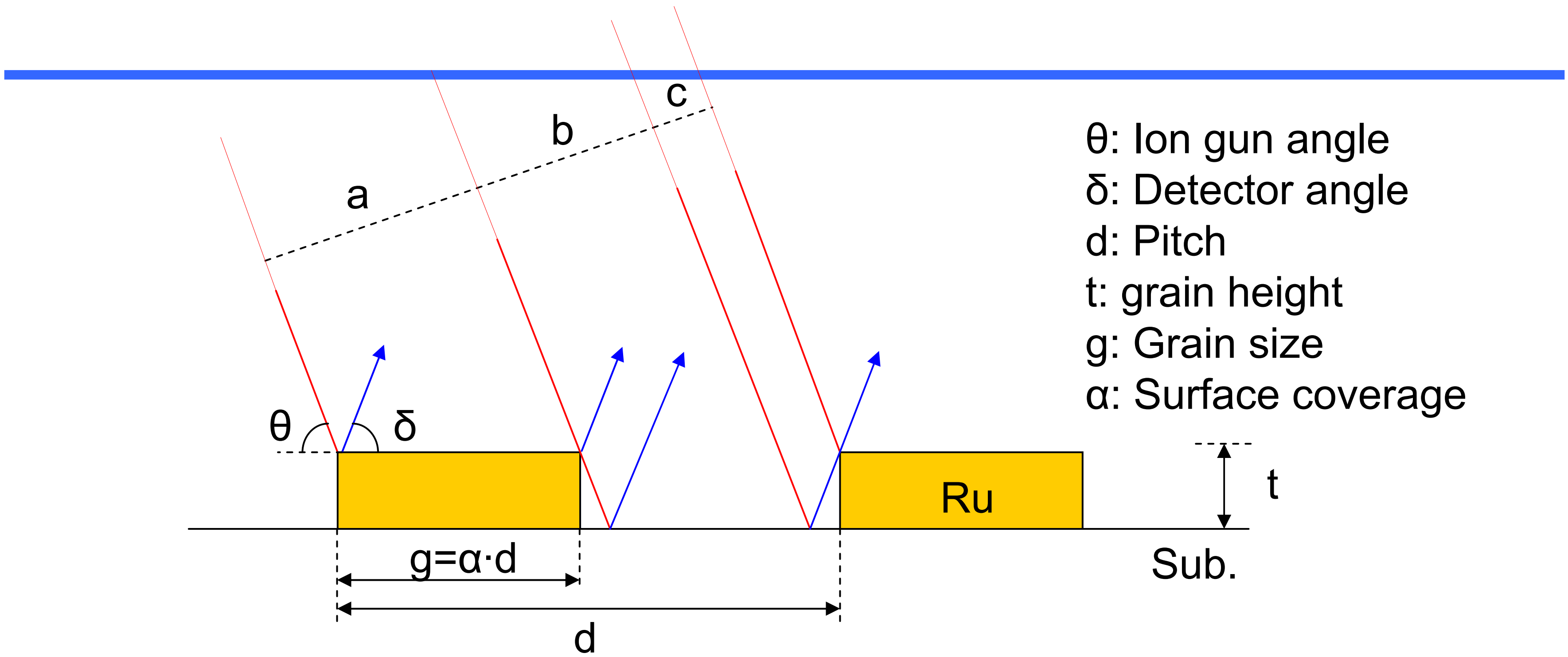


$E_1/E_0=f(m_1/m_0)$



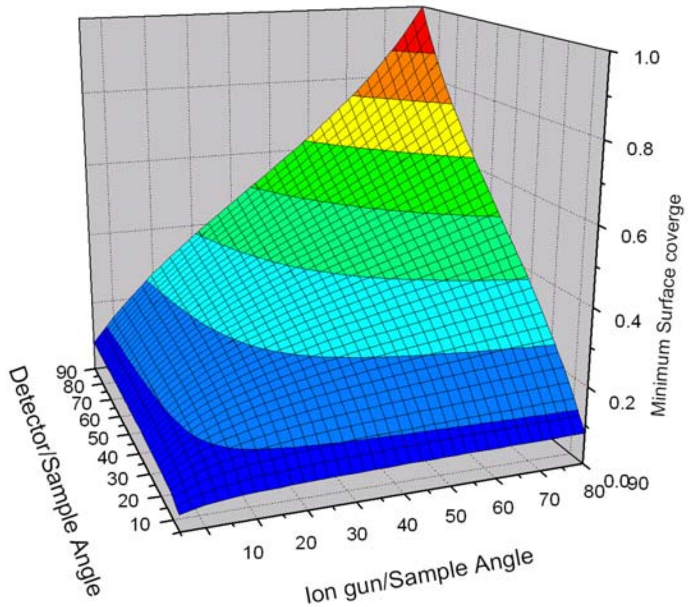
$E_1/E_0=f(m_1/m_0)$

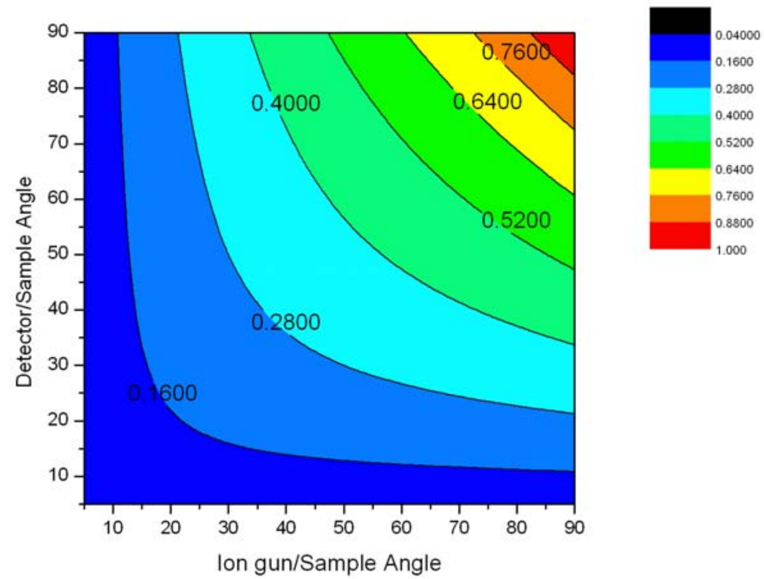
Shadowing Effect - ISS



- ***Assumption: Ru grains are equally sized and spaced.***
- Fraction of sub. peak : $I_{sub}/I_{tot} = b/(a+b+c)$
- $I_{sub} \propto b$, since $I_{tot}/(a+b+c) = \text{const.}$
- $b = \{ (1-\alpha)\cdot d - (1/\tan\theta + 1/\tan\delta)\cdot t \} \cdot \sin\theta$
- ***Minimum α that sub. peak disappears: $1/\alpha_{min} = 1 + (1/\tan\theta + 1/\tan\delta)\cdot(t/g)$***

Shadowing Effect - ISS

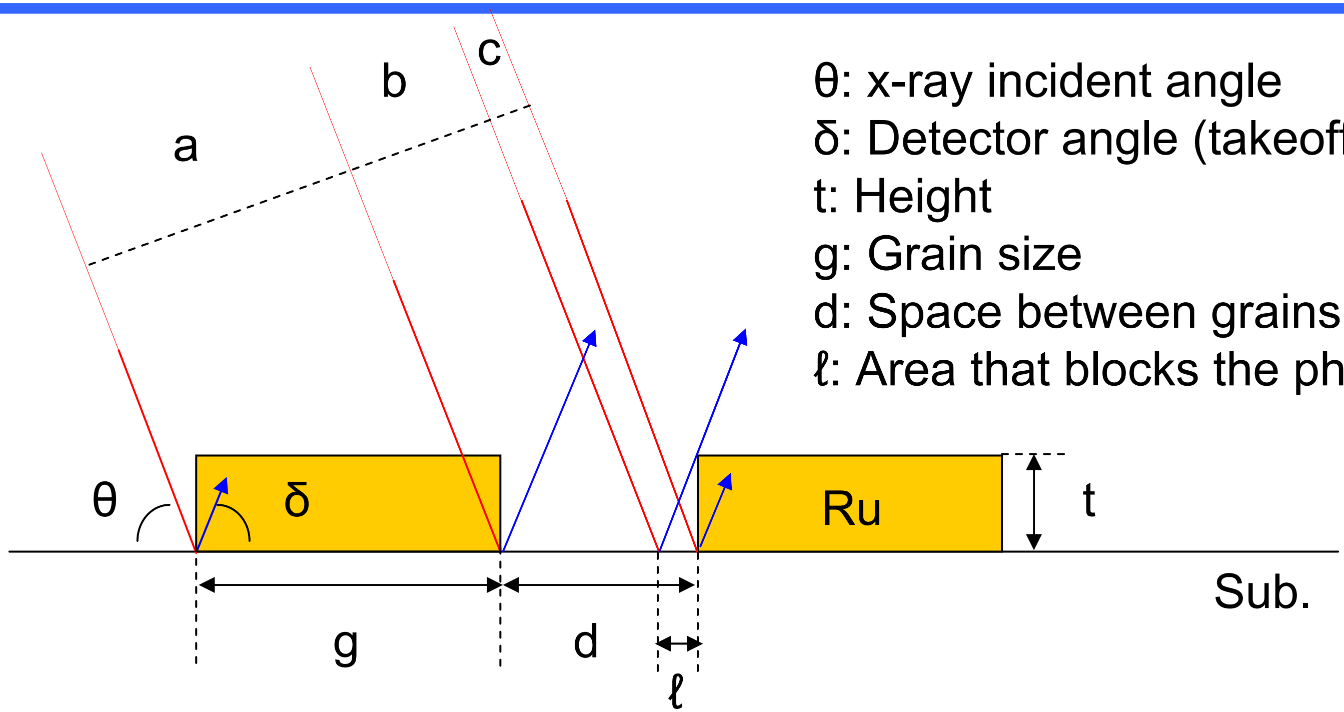




- Grain height & size ratio was assumed to be one, d=g.
- As angles decrease, α_{min} decrease.

  → Sub. peak disappears with lower surface coverage.
- ***Shadowing effect will be gone with θ=δ=90º.***
- ***With θ=δ=60º and d=g, substrate peak disappears with only 47% of surface coverage.***

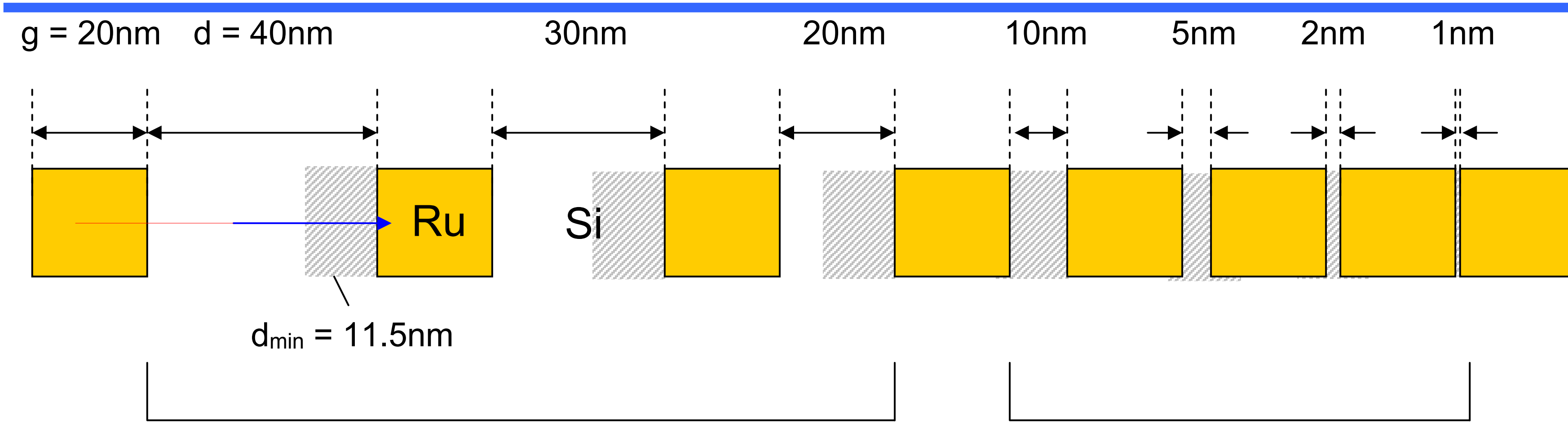
Shadowing in XPS



θ: x-ray incident angle
δ: Detector angle (takeoff angle)
t: Height
g: Grain size
d: Space between grains
ℓ: Area that blocks the photoelectron

- Assumption: X-rays can penetrate Ru and reach the substrate.
  Ru film is discontinuous and thick enough to completely attenuate Si peak under Ru.
- $d_{min} = \ell$: Minimum space that detector can see Si peak.
- With 60º of takeoff angle and 20 nm of Ru film, d_{min} = 11.5 nm.

Why is there a Si XPS Signal for the 30-min film?

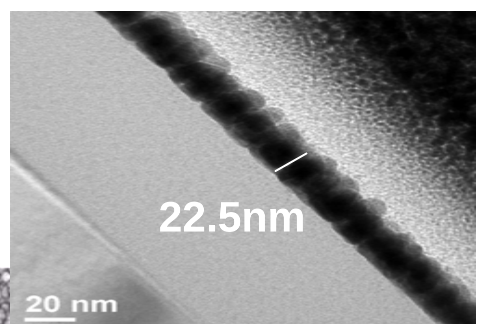


Si peak

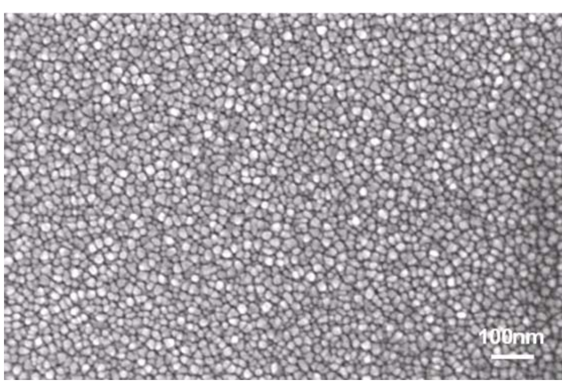
No Si peak

30 min

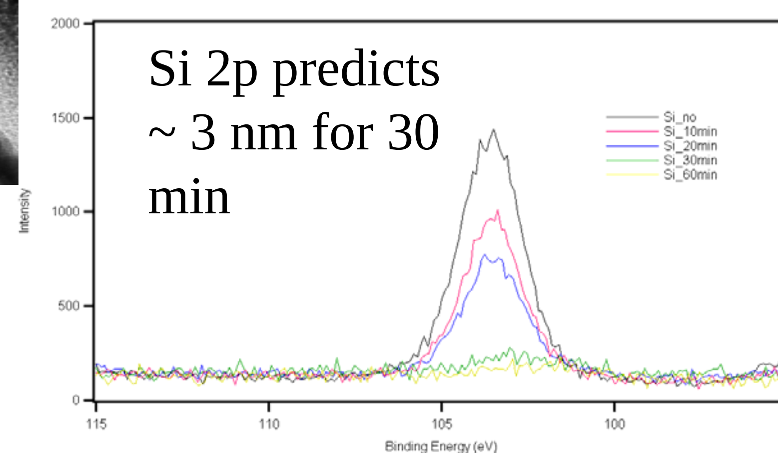
TEM



SEM

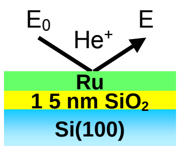


Avg grain size ~ 20 nm

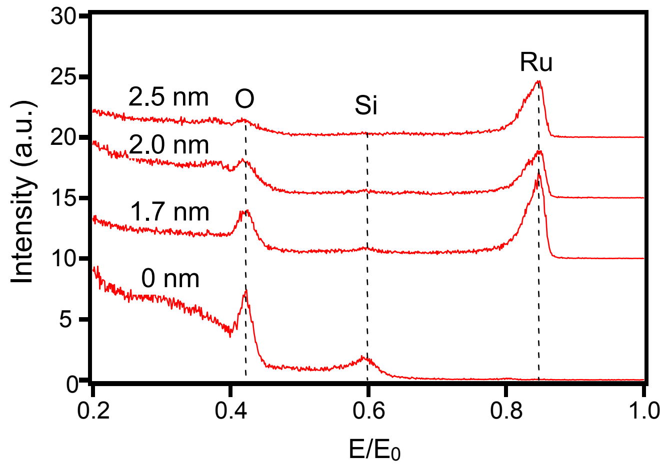


CVD Film Continuity versus Thickness

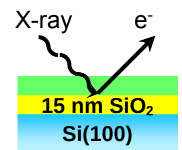
ISS



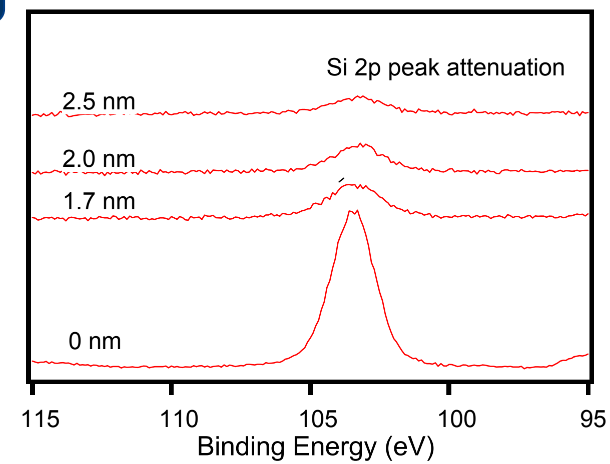
$E/E_0 = f(m_2/m_1)$



XPS



$I / I_0 = f(\lambda / t)$

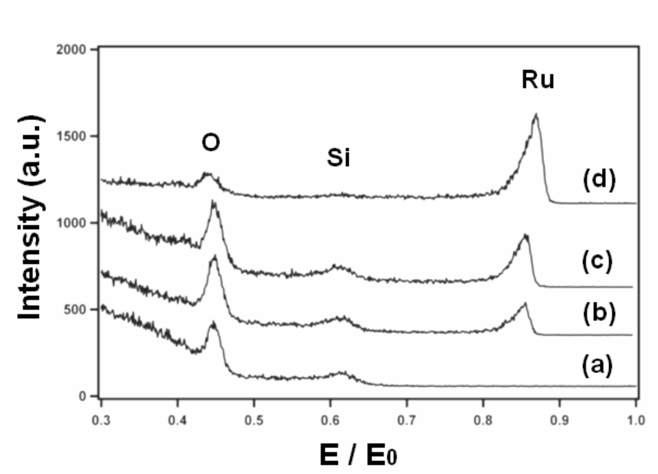


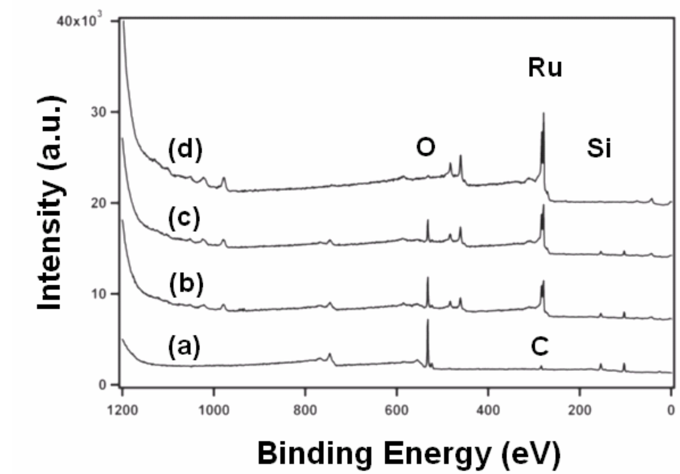
(a) 0 min

(b) 10 min

(c) 20 min

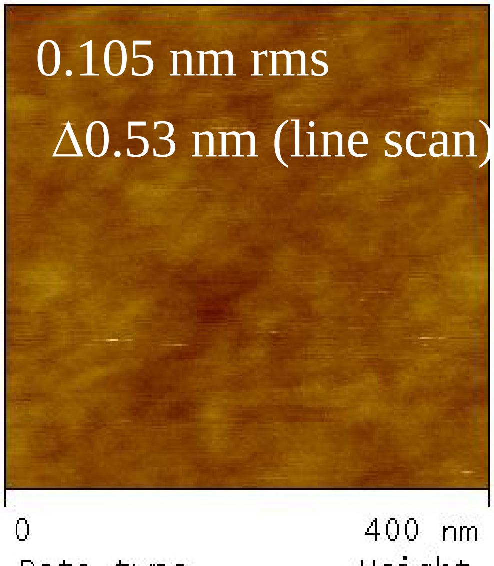
(d) 30 min



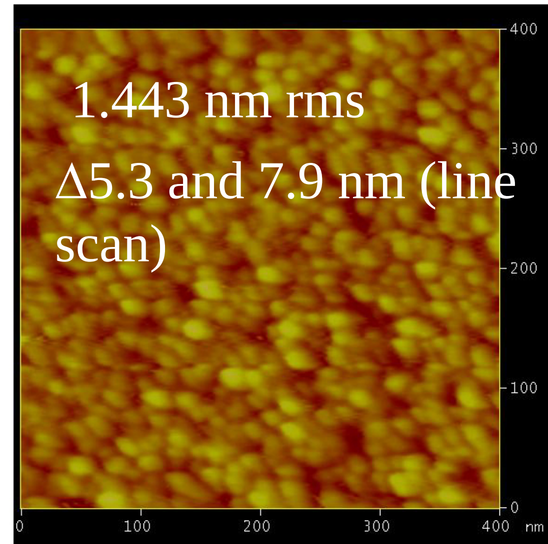


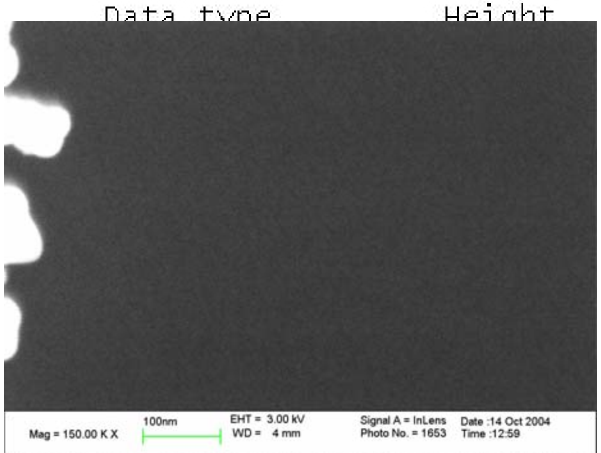
Comparison of PVD and CVD Film Structures

~3.5 nm PVD (quartz balance and XPS) Ru

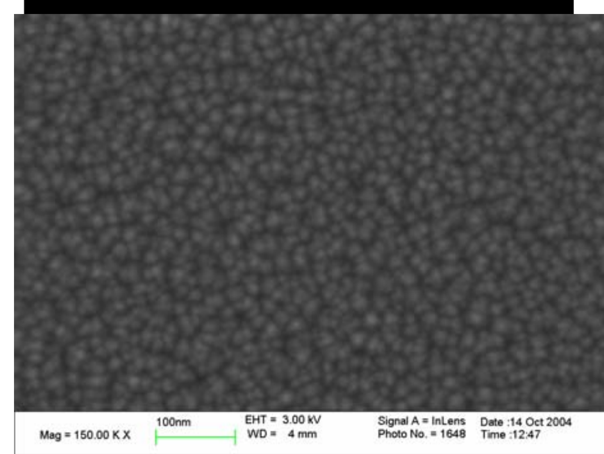


~3.5 nm CVD - XPS



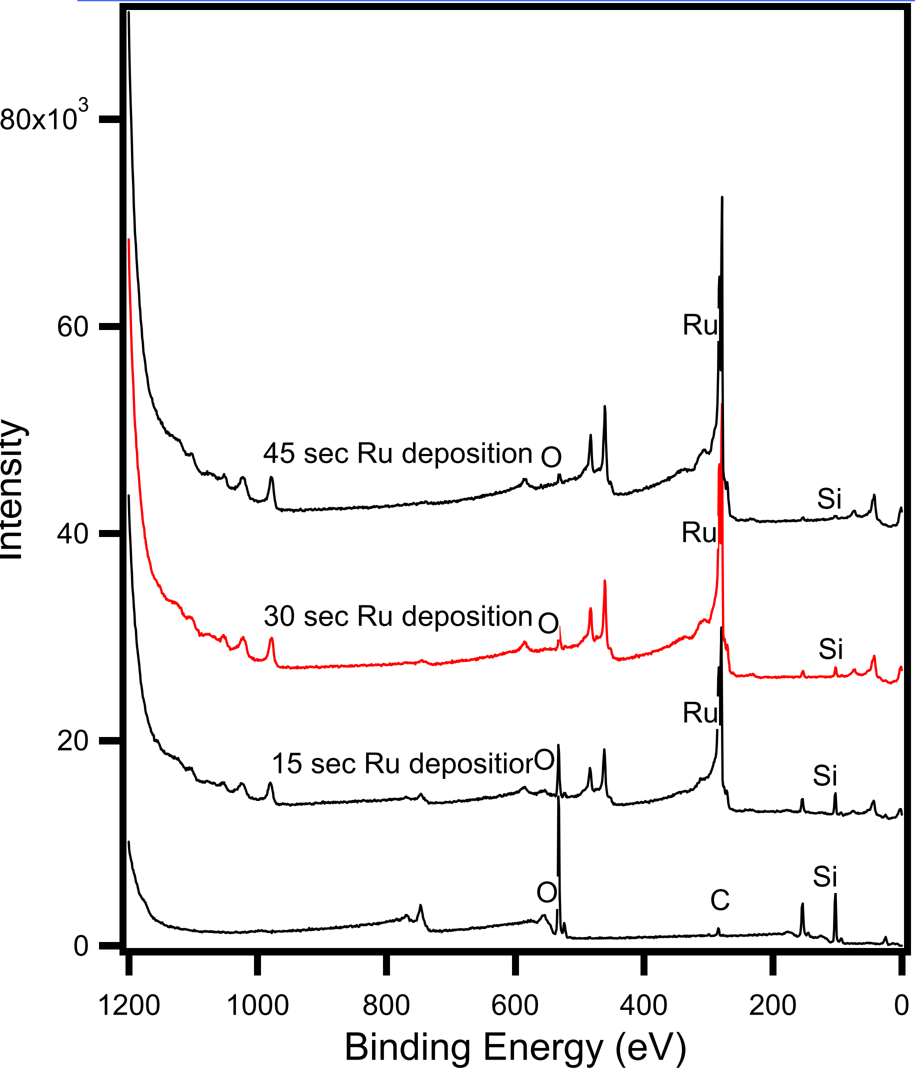


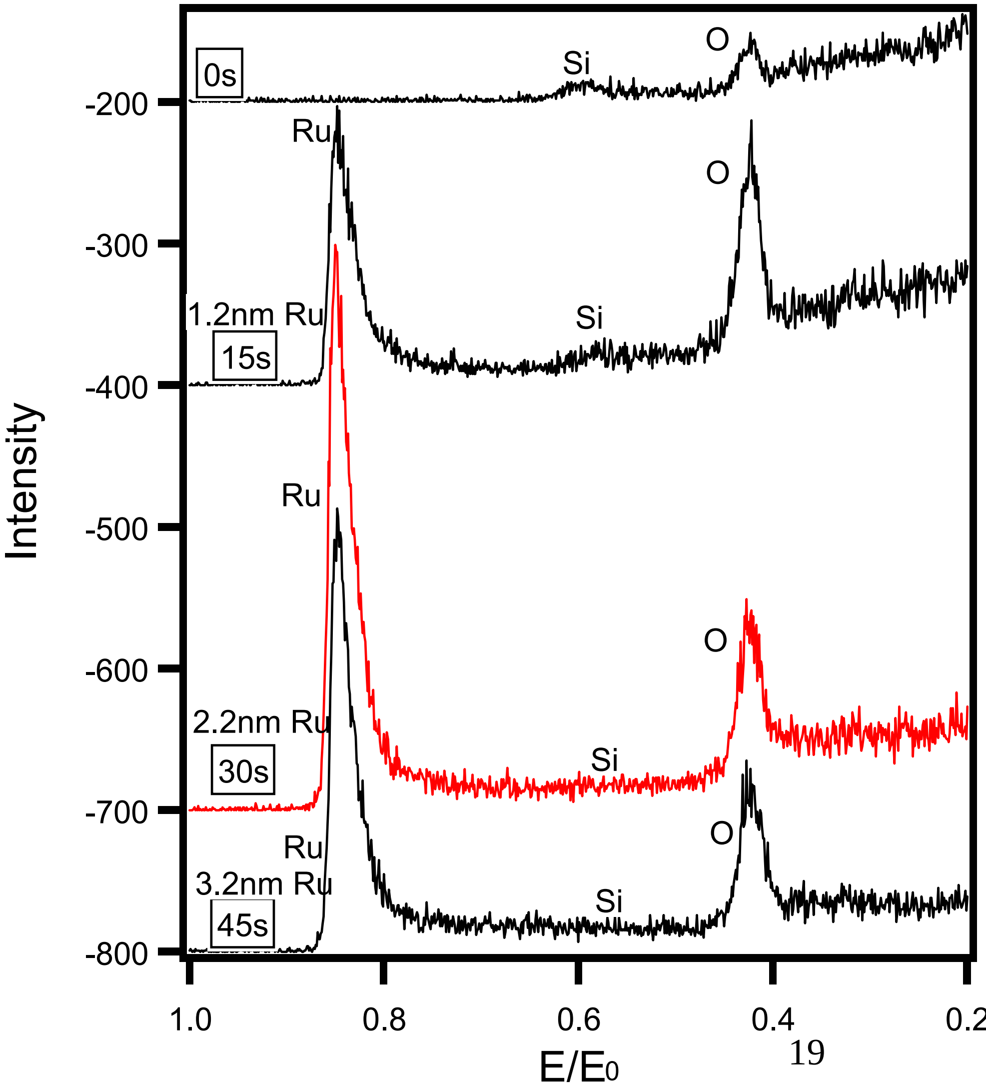
SEM Images of Ru



XPS and ISS measurements for PVD Ru film

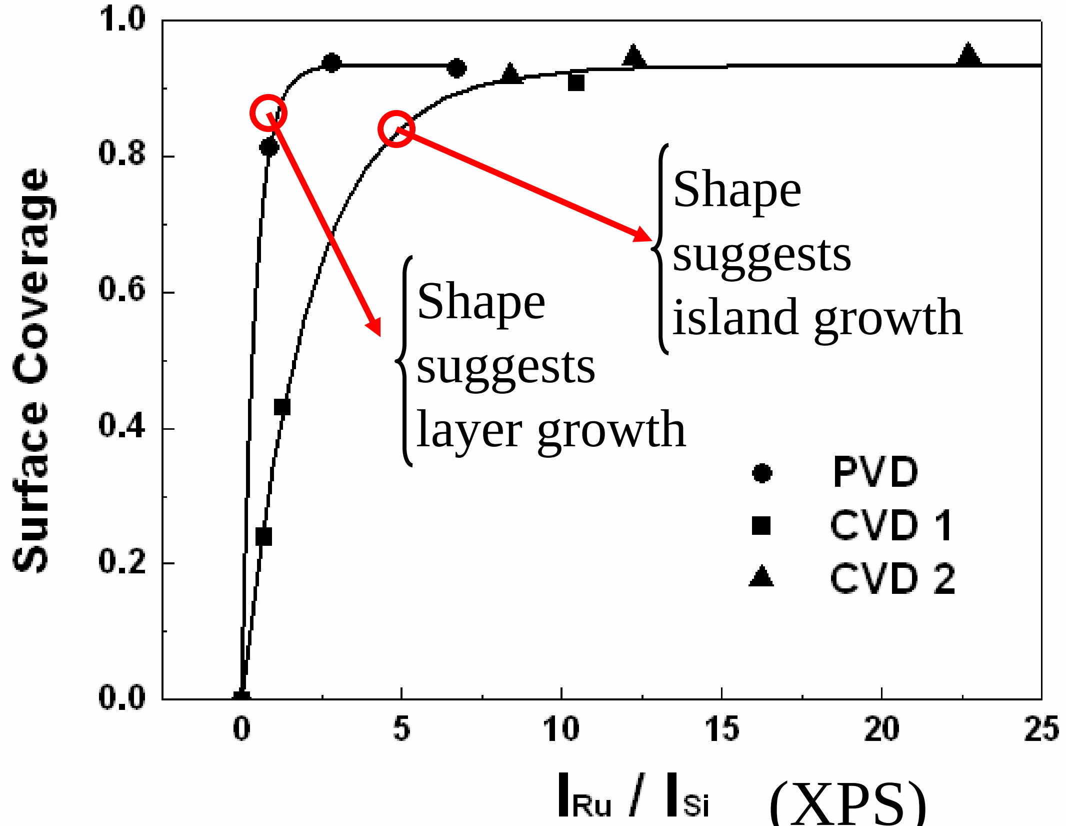
The thickness for fully covering Si substrate is between 1.2 to 2.2 nm





Determining Film Growth Mechanism by Combined Use of ISS and XPS

$$\Theta_i = \frac{A_{Ru,i}/A_{Ru,o}}{A_{Ru,i}/A_{Ru,o} + A_{Si,i}/A_{Si,o}}$$

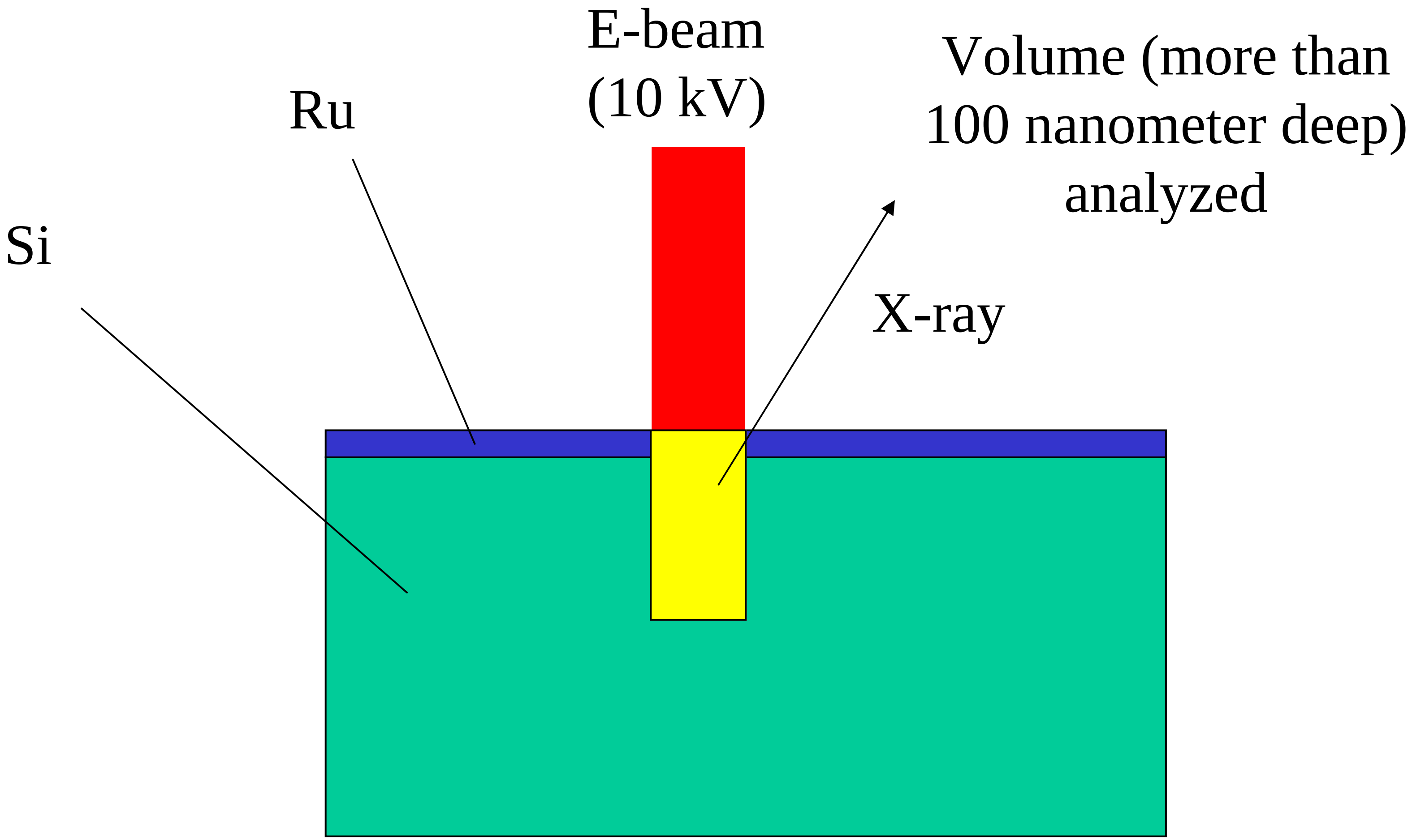


(XPS)

Jiménez *et al*., Appl. Surf. Sci. <u>141</u> (**1999**) 186.

Yubero *et al*., Surf. Sci. <u>457</u> (**2000**) 24.

Energy Dispersive Spectroscopy (EDS) Approach



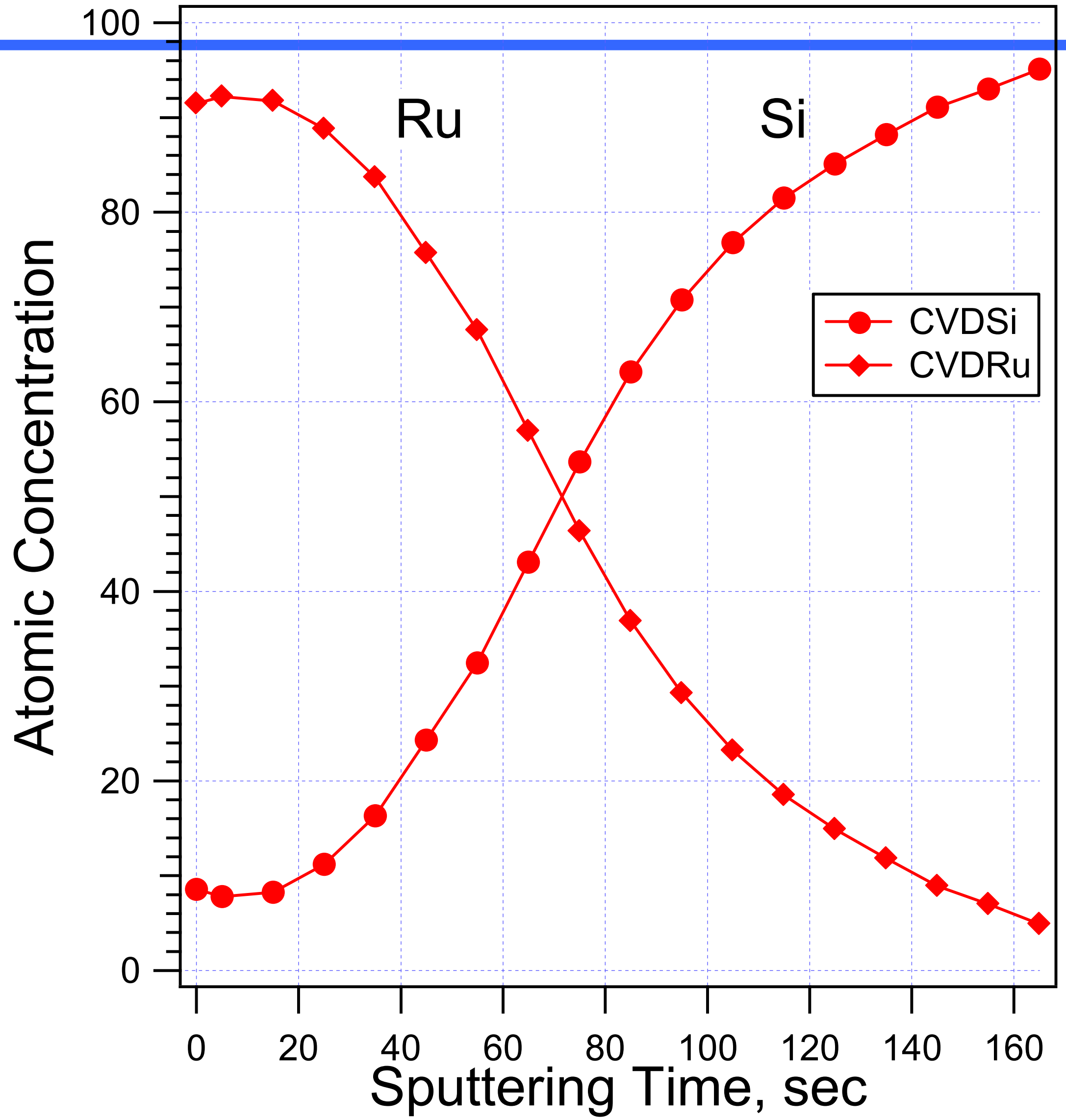
The detection depth of EDS is much larger than XPS, so it is not sensitive to the surface morphology

EDS Measurement for PVD and CVD Ru Films

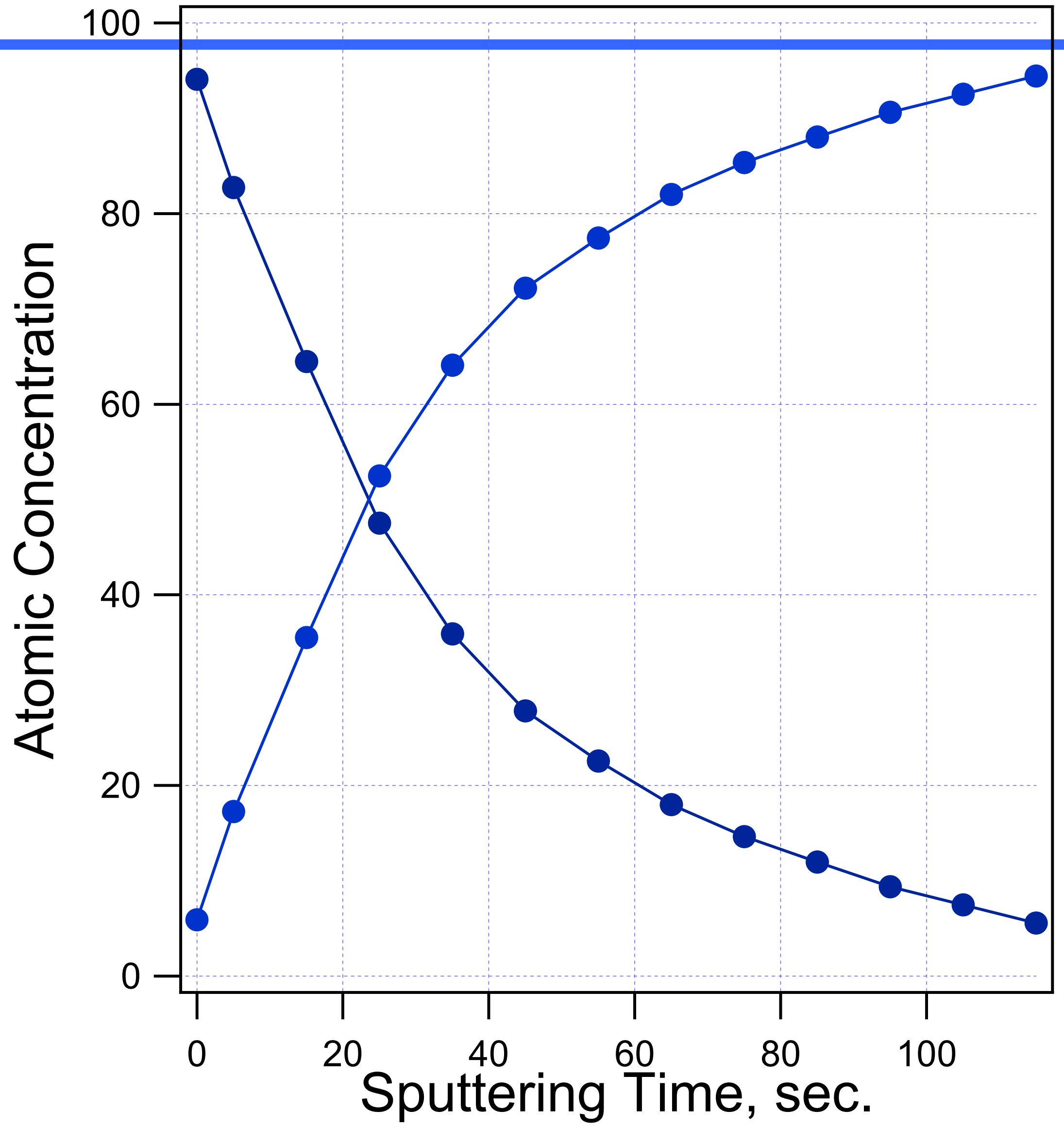
Ru Film	EDS counts
3.5 nm PVD Film	81.6
12 nm PVD Film	284.4
3.5 nm CVD Film	201.6

CVD Film thickness = 7.8 to 8.6 nm

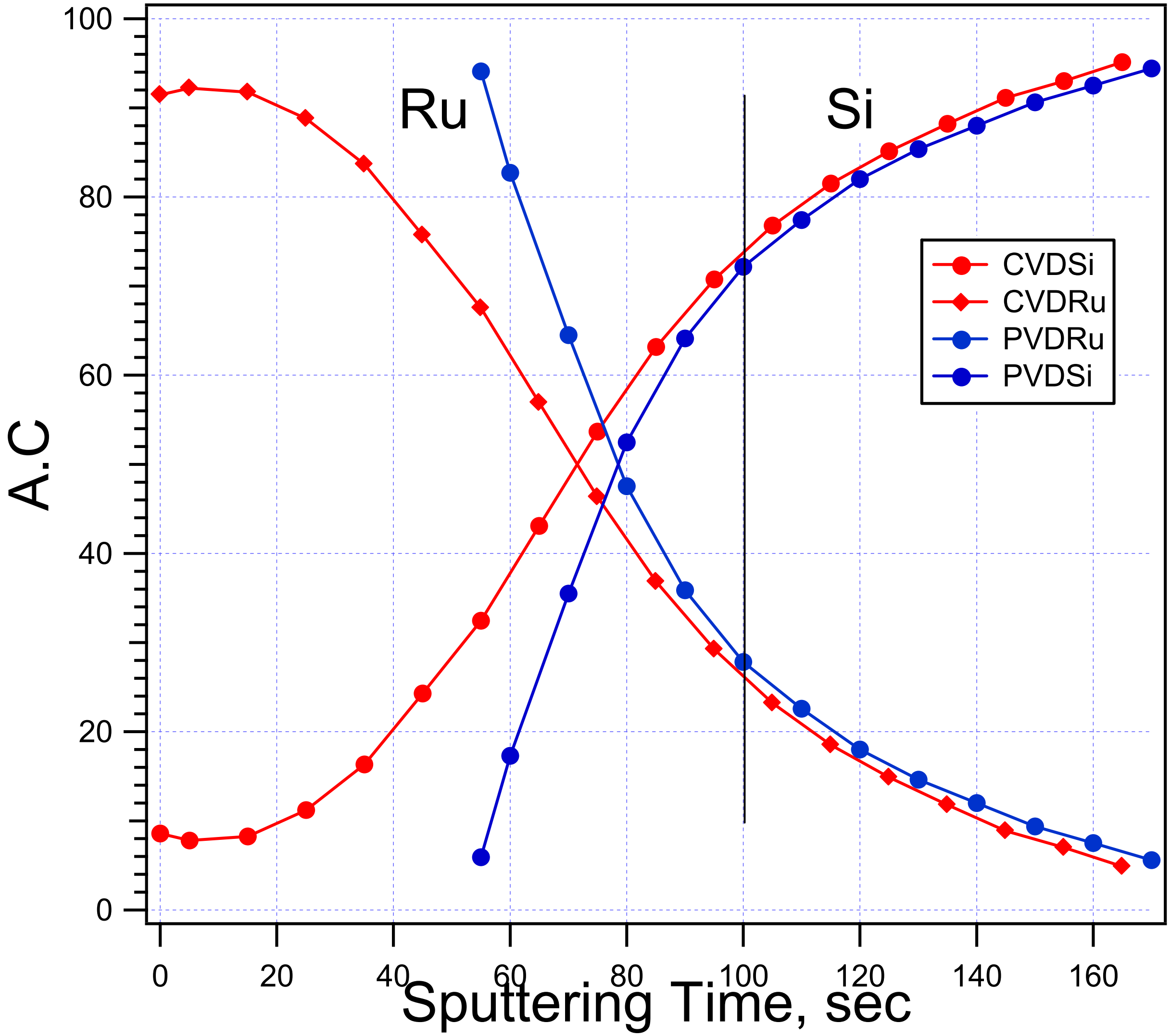
XPS Depth Profile for CVD Ru film (~ 4 nm thick)



XPS Depth Profile for 3.5 nm PVD Ru Film



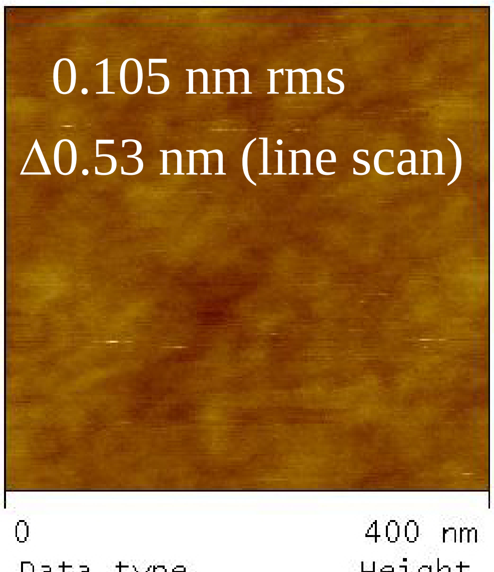
Comparison of Depth Profile for CVD and PVD Films

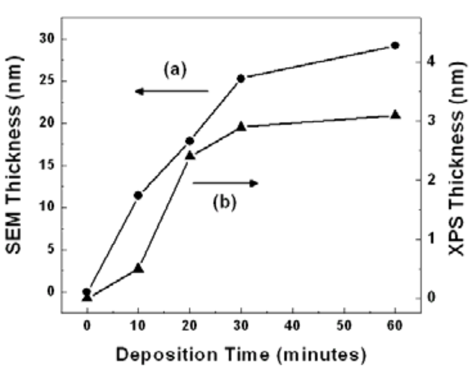


If we assume after the line is the interface, then the thickness of CVD film is 7.8 nm, calculated from from the sputtering time

Comparison of PVD and CVD Film Structures Equivalent Thickness is ~(2-3 ×) or ~ (8 ×)

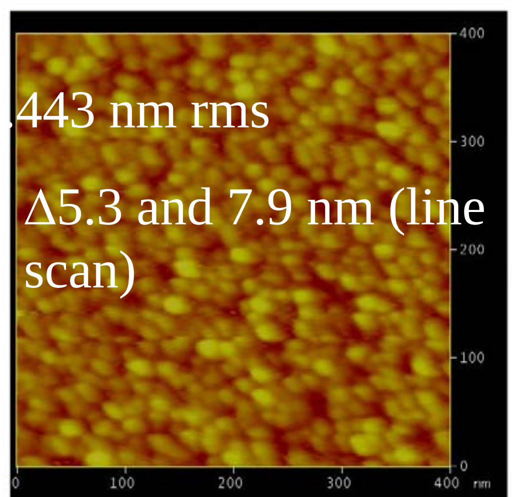
~3.5 nm PVD (quartz balance and XPS) Ru





EDS of 3.5 and 11 nm PVD films and the "3.5" nm CVD film suggests a 7.8 to 8.6 nm CVD film

~3.5 nm CVD - XPS



XPS depth profiling suggests the "3.5" nm CVD film is 7.8 nm

Understanding the True Barrier

- Barrier likely to be much thinner than the physical thickness of the metal film and just when this continuous layer is formed remains an experimental challenge.
- More extensive studies with 2D (PVD) films needed to establish the barrier properties and interfaces that form with the substrate layer.
- New precursors and growth processes (ALD) under study are leading to smoother films than the $Ru_3(CO)_{12}$ system presented.
- Island nucleation is the key to thinner films.
- As film roughness increases we need a way to relate *in situ* measures to film thickness – the equivalent film thickness.