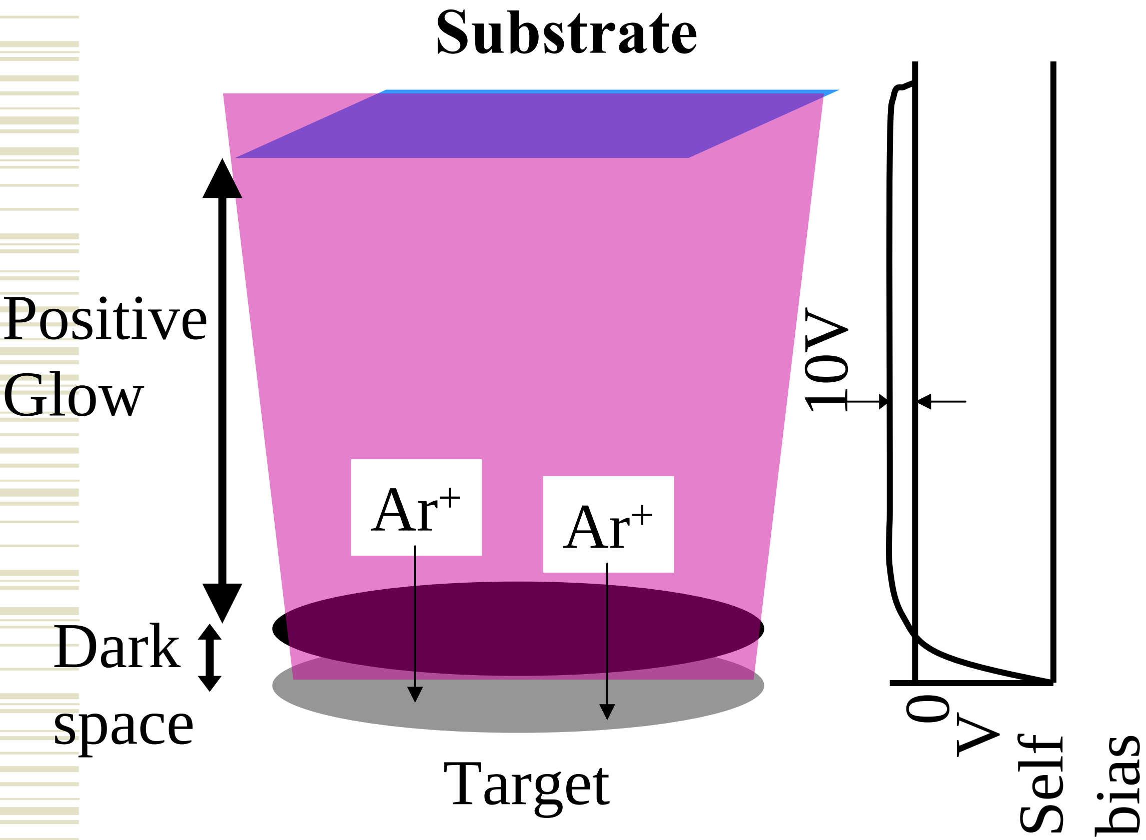
Combinatorial RF Magnetron Sputtering for Rapid Materials Discovery: Methodology and Applications

Philip D. Rack, Jason D. Fowlkes, and Yuepeng Deng
Department of Materials Science and Engineering
University of Tennessee
prack@utk.edu

Outline

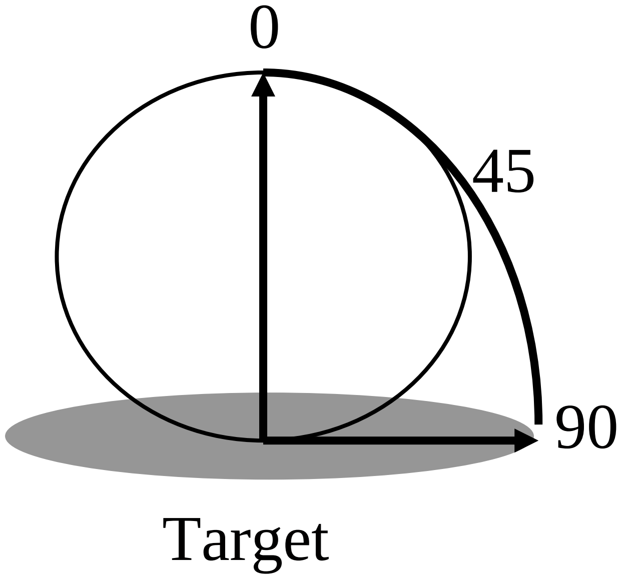
- Sputter Deposition
- Combinatorial Thin Film Sputtering System
- Process Model
- Combinatorial Applications
    - Cr-Fe-Ni Phase Diagram Determination
    - Cu-Ni Carbon Nanofiber Catalysts for PECVD
    - Bulk Metallic Glass Alloy Development
    - YAG:Gd Solid State UV Emitters
- Summary

Sputtering

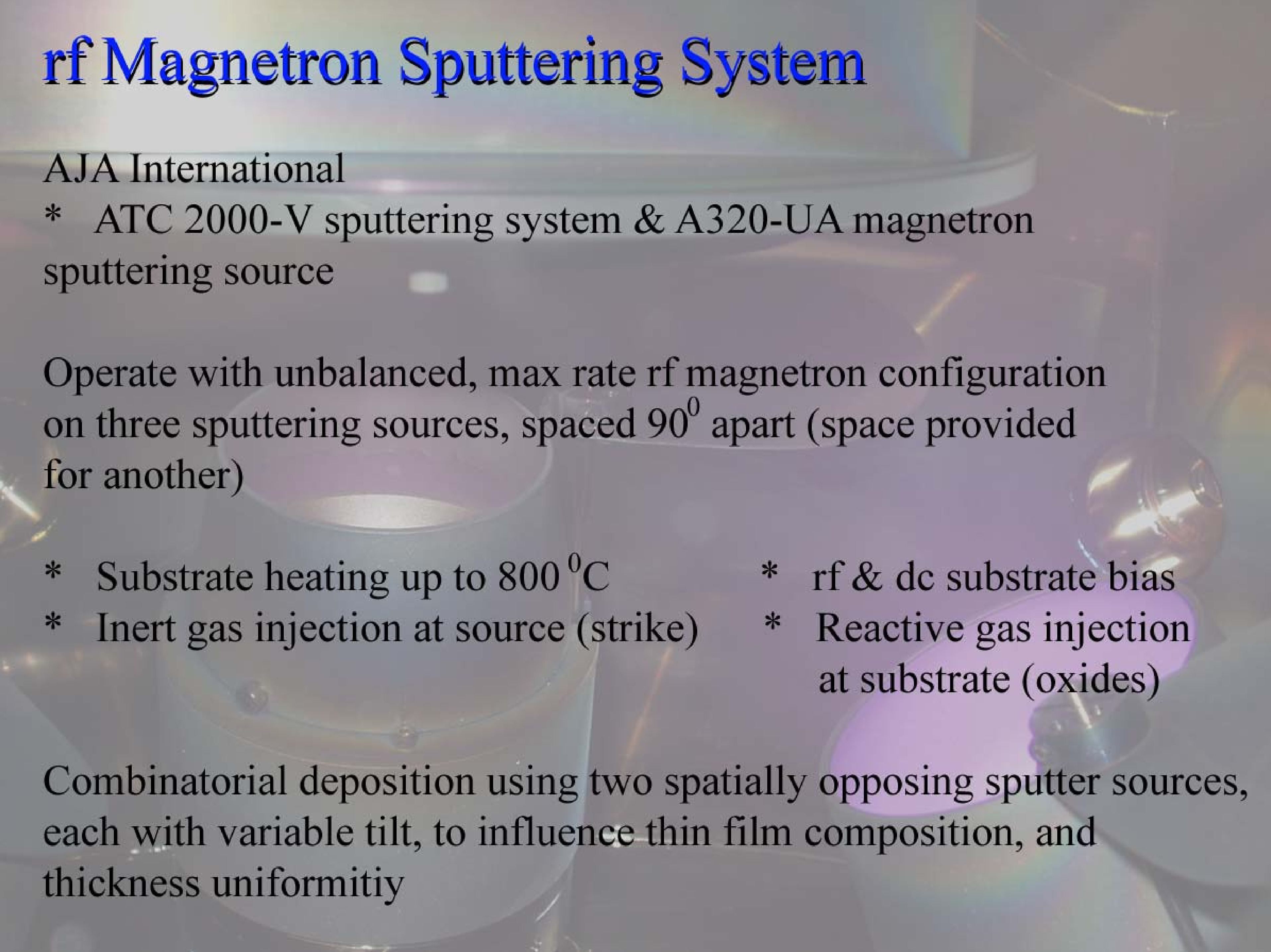


Angular Distribution

$$I(\theta) = I\cos(\theta)$$



rf Magnetron Sputtering System



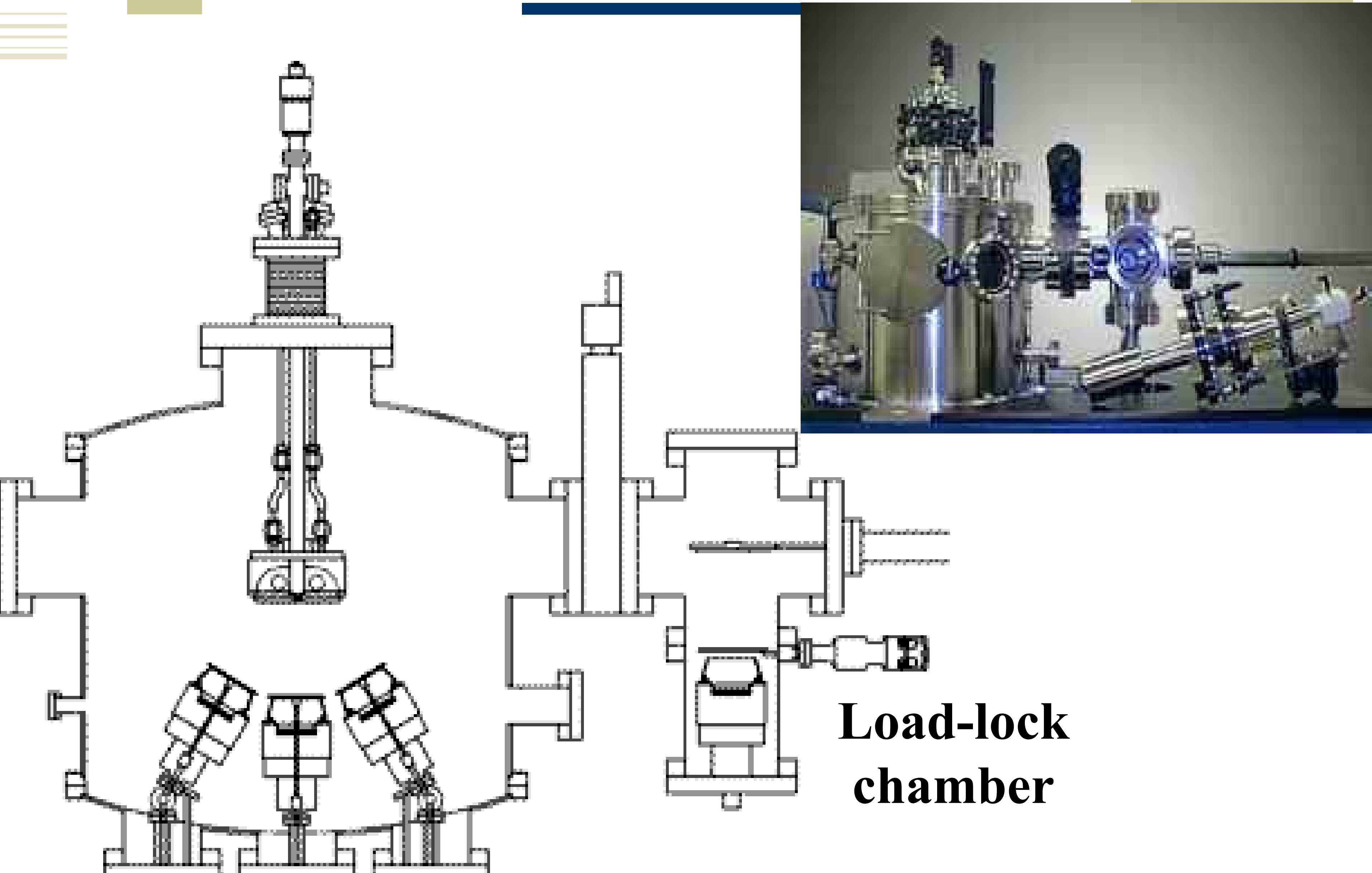
AJA International
*   ATC 2000-V sputtering system & A320-UA magnetron sputtering source

Operate with unbalanced, max rate rf magnetron configuration on three sputtering sources, spaced 90^0 apart (space provided for another)

*   Substrate heating up to $800\,^0$C
*   Inert gas injection at source (strike)
*   rf & dc substrate bias
*   Reactive gas injection at substrate (oxides)

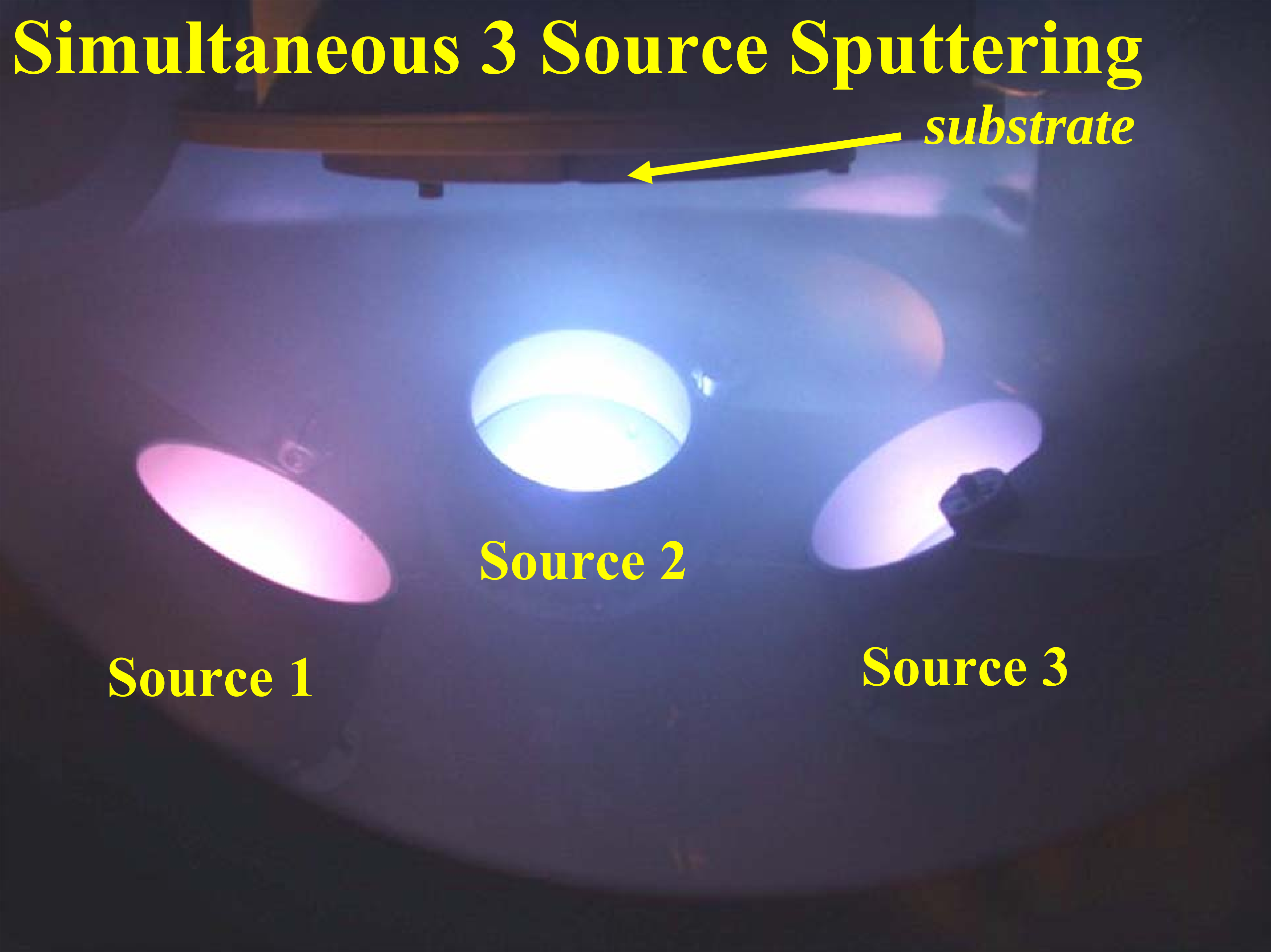
Combinatorial deposition using two spatially opposing sputter sources, each with variable tilt, to influence thin film composition, and thickness uniformitiy

Rf Magnetron Sputtering System



Load-lock chamber

Simultaneous 3 Source Sputtering

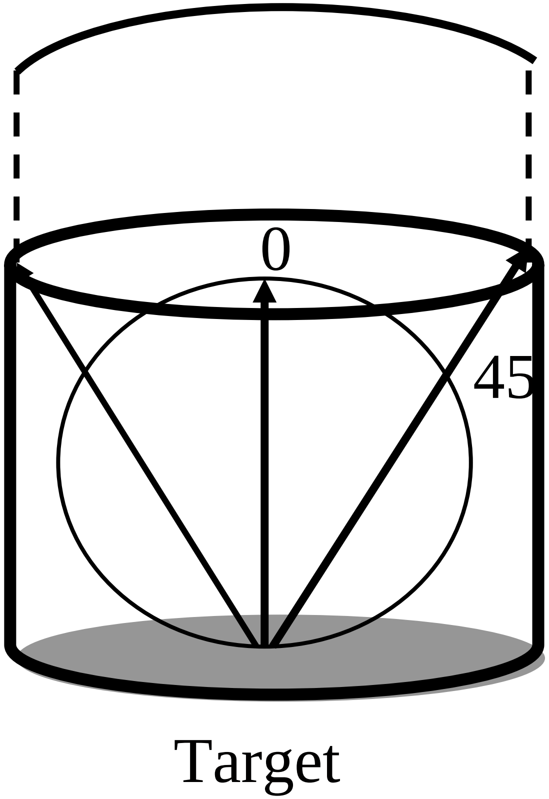


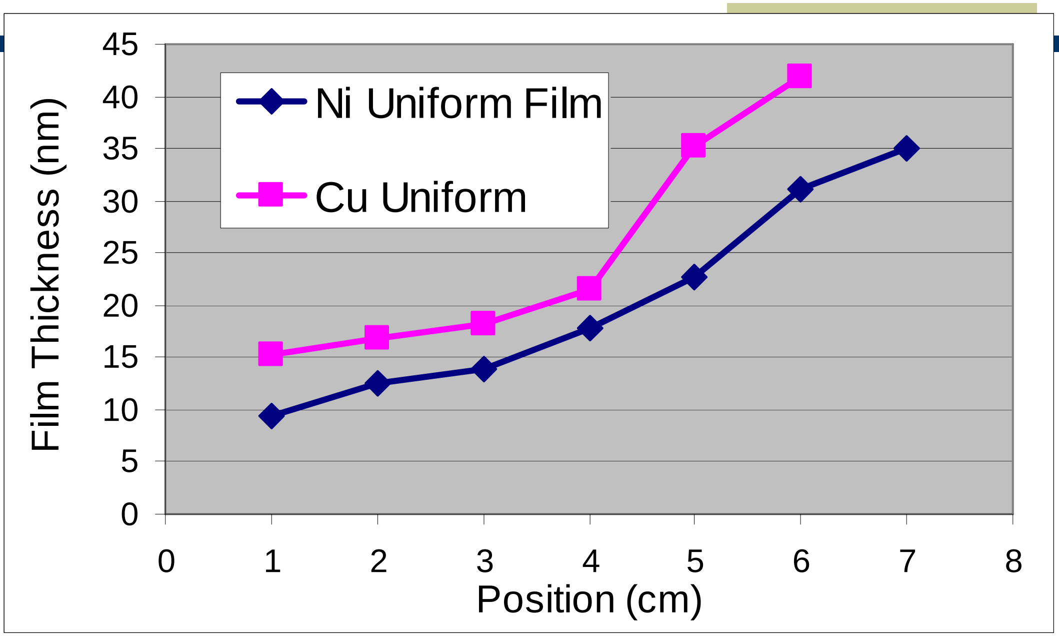
Angular Distribution

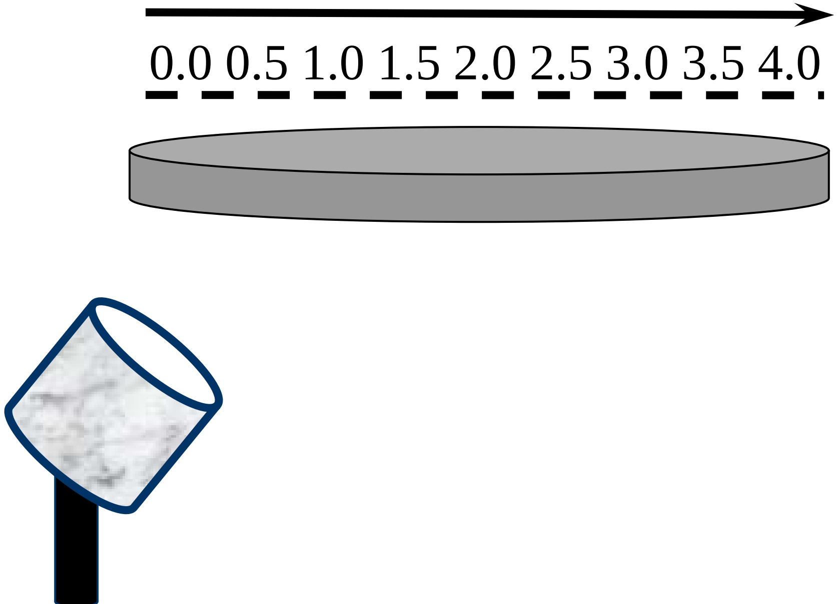
Modified Cosine Distribution

$$I(\theta) = I\cos^{n}(\theta)$$

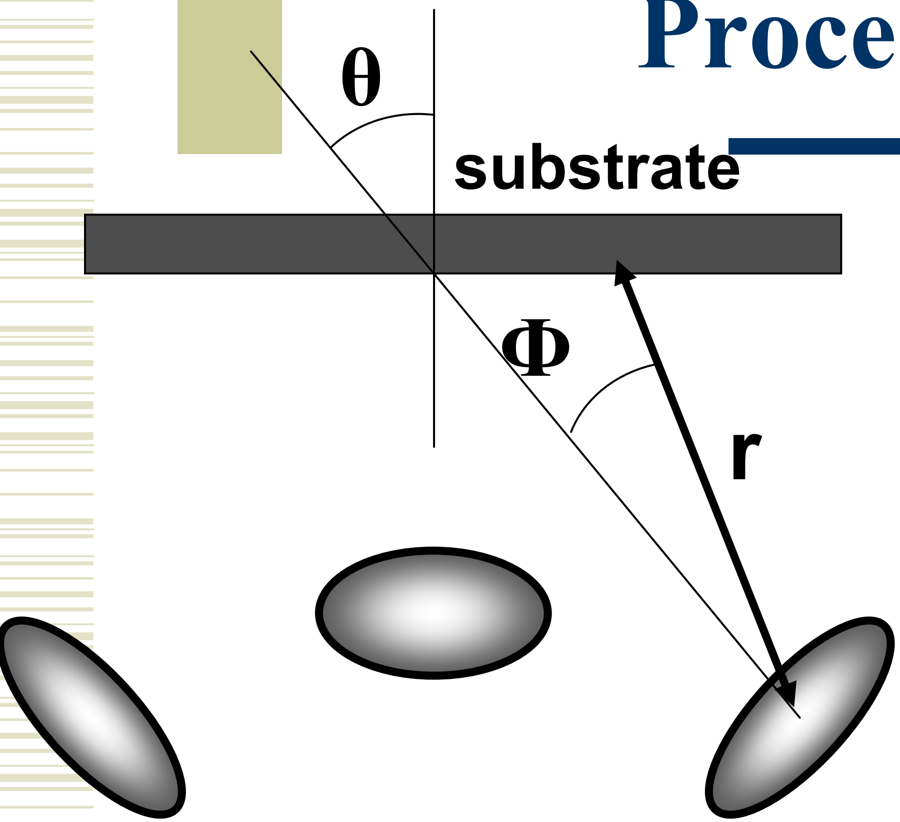
n~10







Process Modeling



Input variables:

Source power, voltage, current

Material sputter yield

Source tilt angle

Substrate position

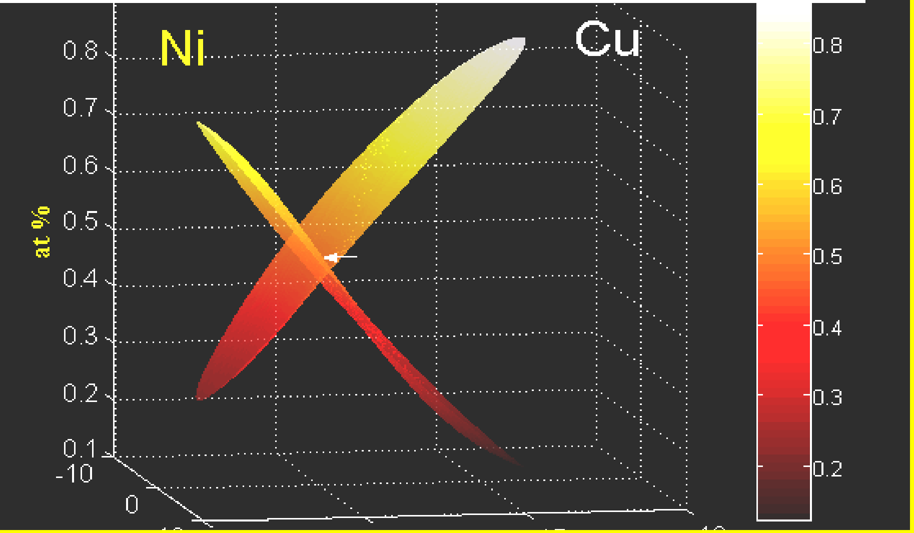
Source time

Determines substrate composition as a function of position

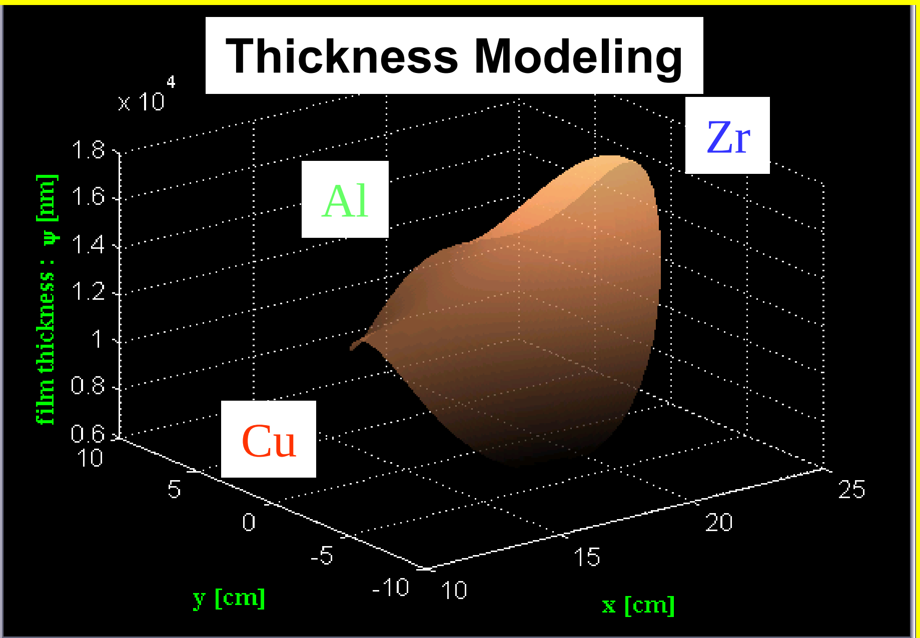
$$n_{total} = \sum_{j=1}^{j=k}\left[\sum_{i=1}^{i=3} n_i\right]_j = \sum_{j=1}^{j=k}\left[\sum_{i=1}^{i=3}\left[\frac{\left\{C_{1[P]}\right\}\left\{\dfrac{\int_0^{360}\int_0^{32.7}\cos\theta\sin\theta\, d\phi\, d\theta}{\int_0^{360}\int_0^{90}\sin\theta\, d\phi\, d\theta}\right\}\left\{\dfrac{PtS}{Vq}\right\}(n+1)\cos^n\phi\cos\theta}{2\pi r^2}\Delta r\Delta\theta\right]_i\right]_j$$

MATLab Process Model

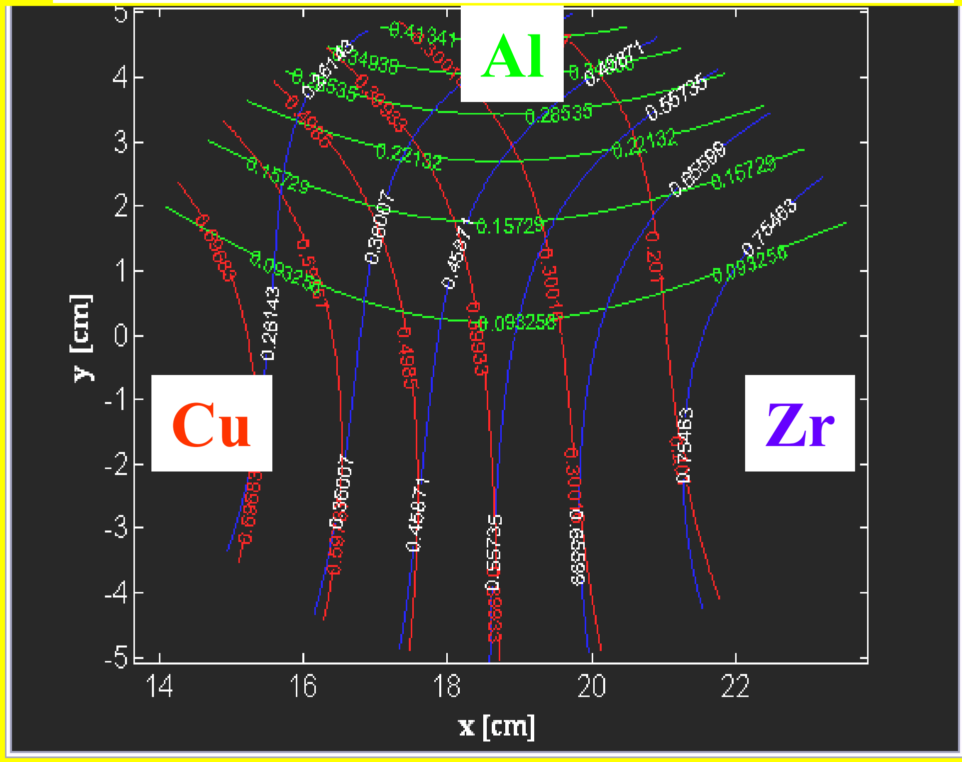
Binary Composition Profile



Thickness Modeling



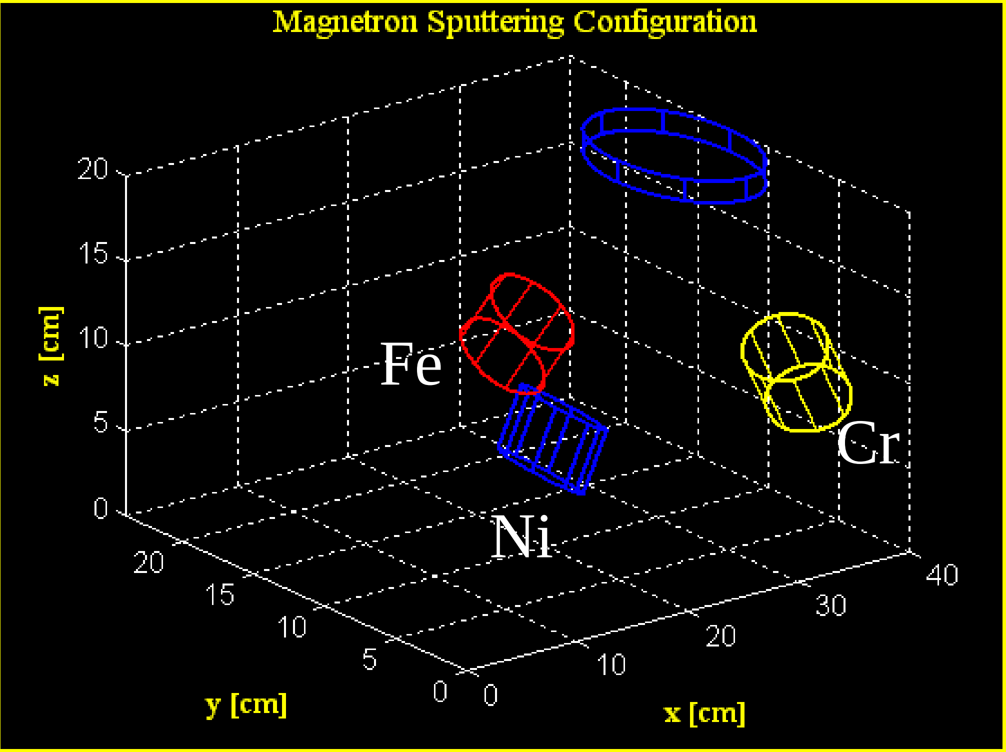
Ternary Composition Profile

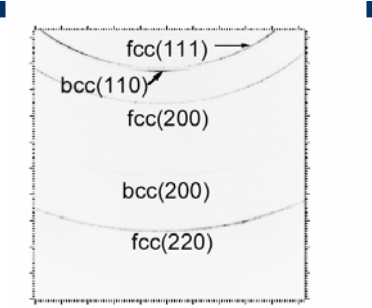


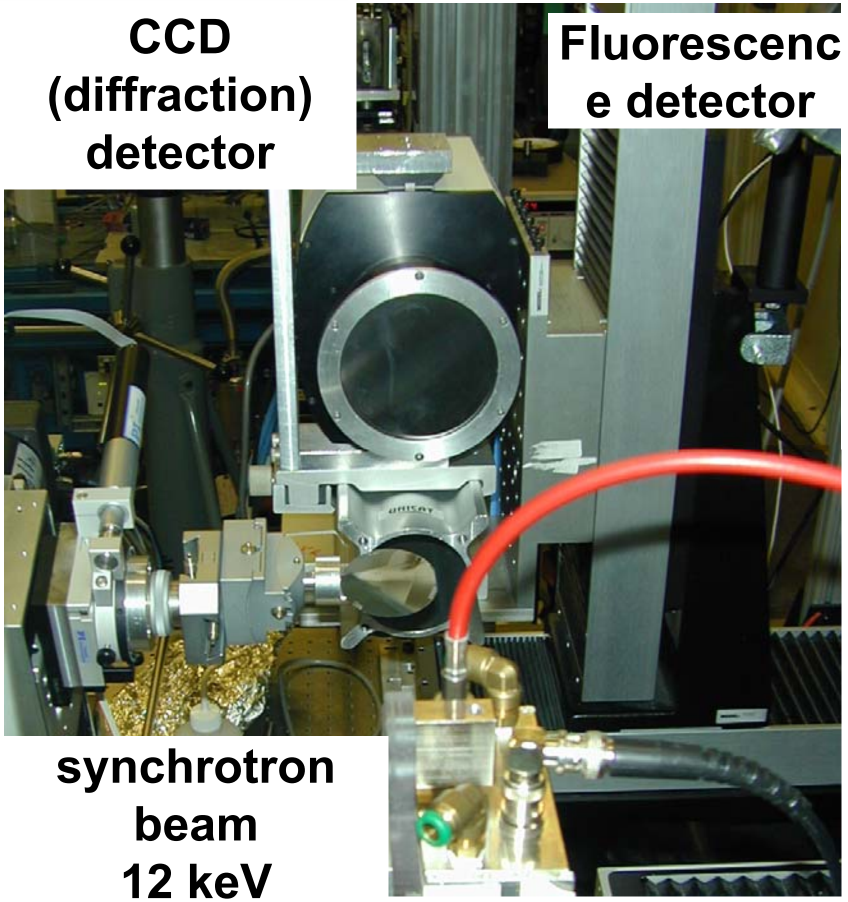
Fe-Ni-Cr Ternary Phase Diagrams

- Co-sputter Fe (160W), Cr (60W), Ni (60W) onto (1 –1 0 2) single crystal sapphire substrates
- Anneal 200, 400, 600, 800 °C for 2 hours
- Rapid synchrotron fluorescence and XRD measurements
- Future Work: Nano-indentation

Non-Equilibrium Ternary Phase Diagrams (Fe-Ni-Cr)







CCD (diffraction) detector

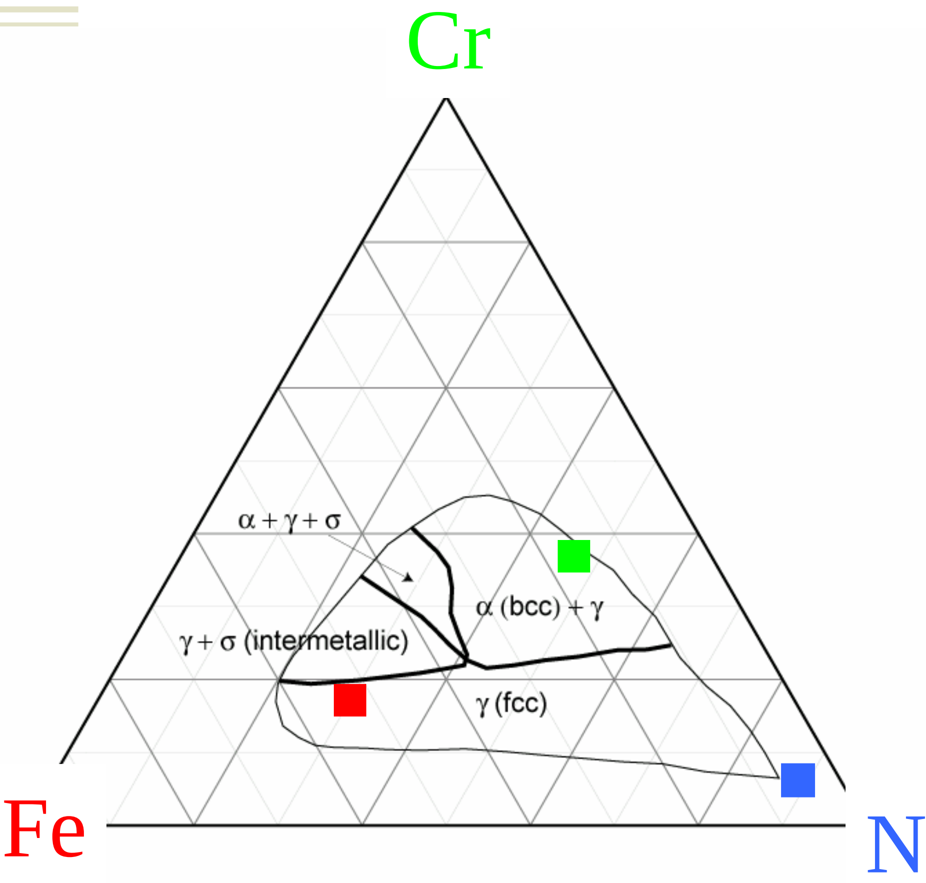
Fluorescenc e detector

synchrotron beam 12 keV

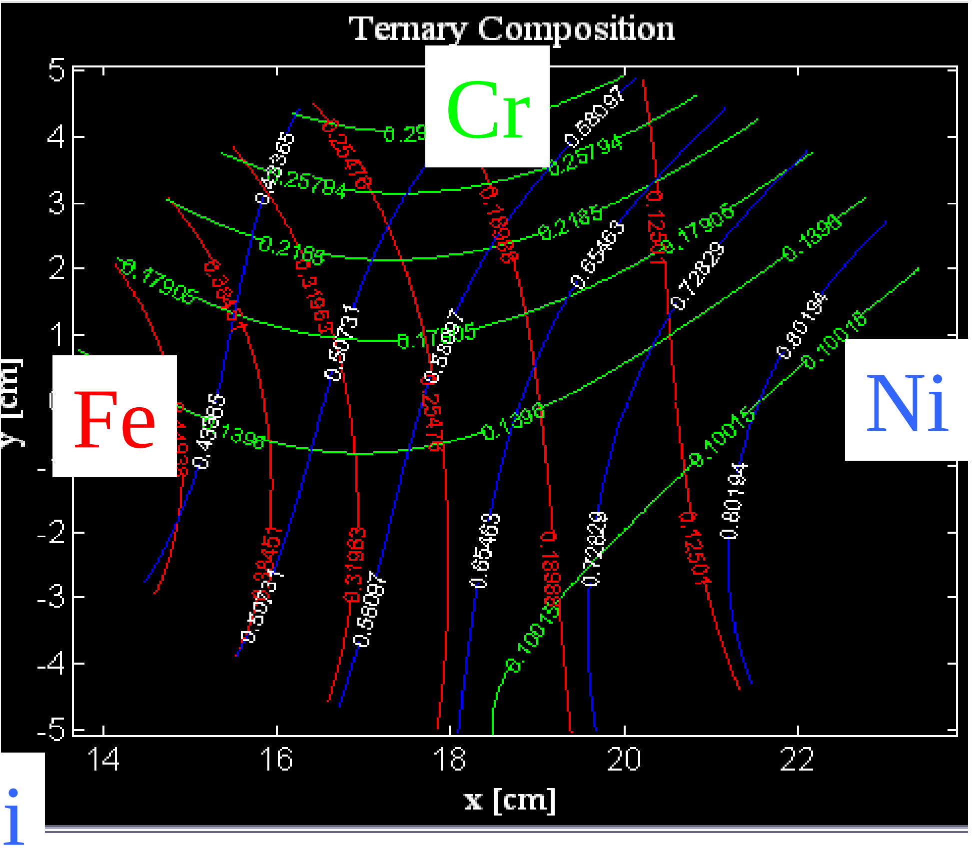
With Pharr et al.

Modeled versus Measured Composition

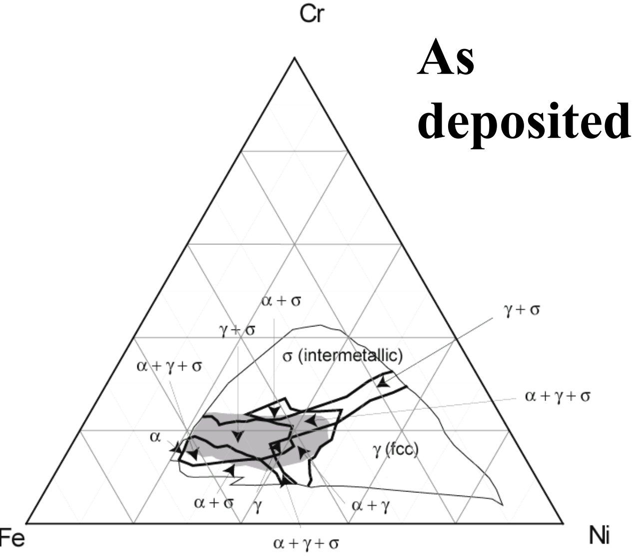
Measured Composition Space

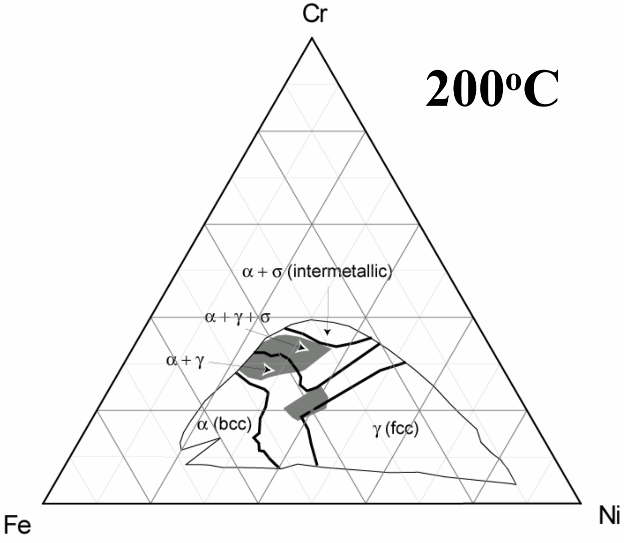


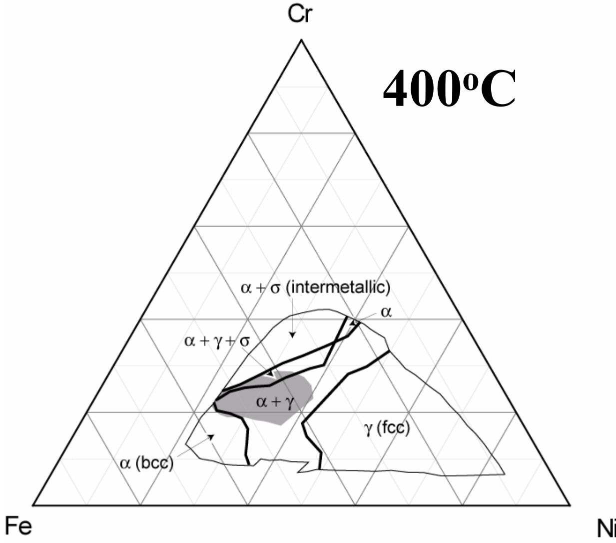
Modeled Composition Space

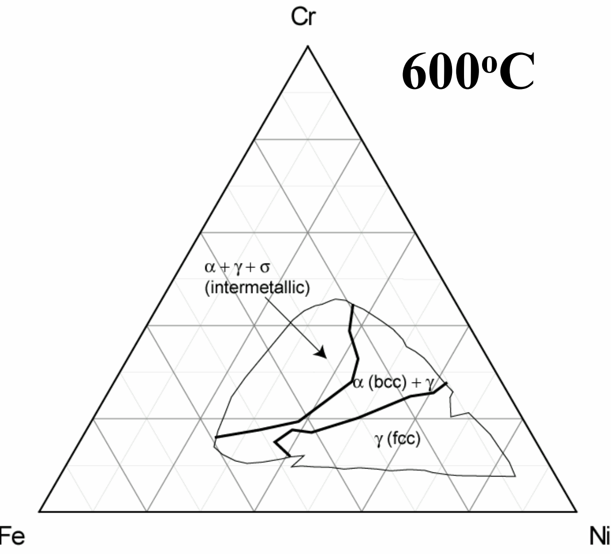


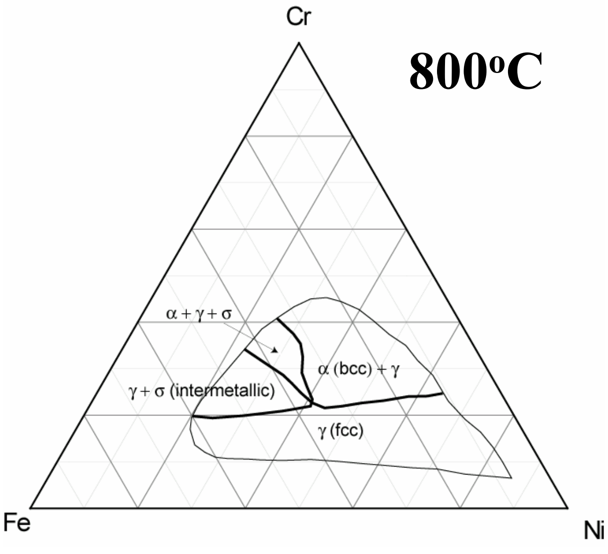
Phase Diagram Temperature Evolution

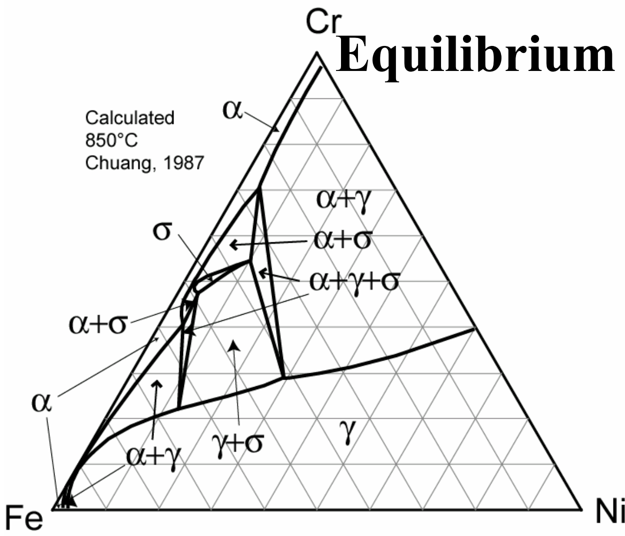

As deposited


200°C


400°C

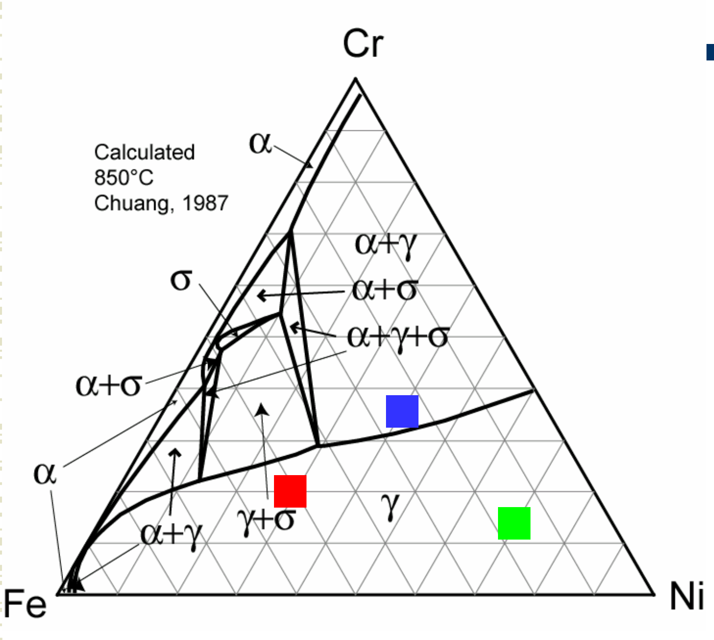

600°C

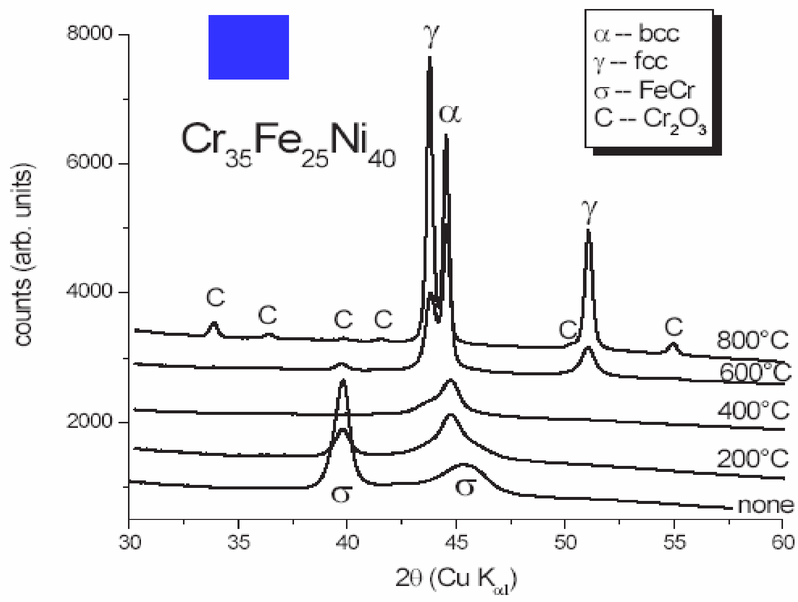

800°C

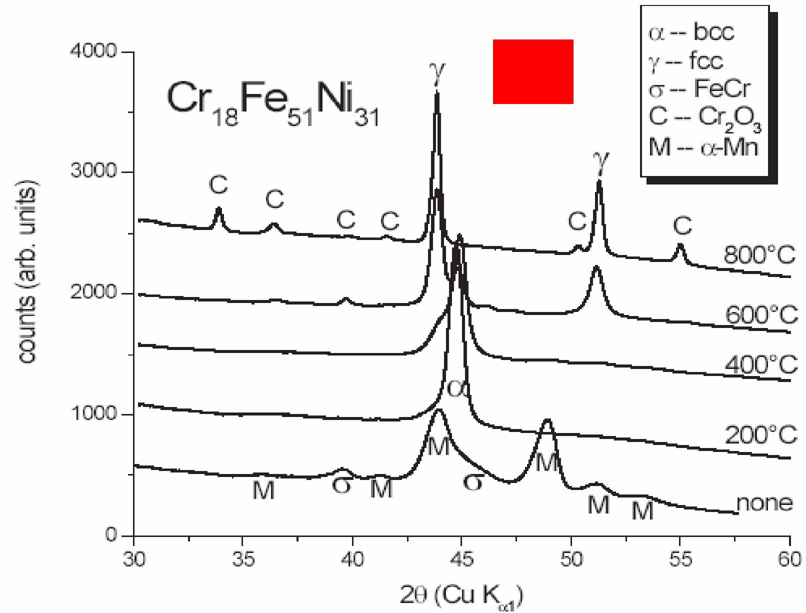

Equilibrium

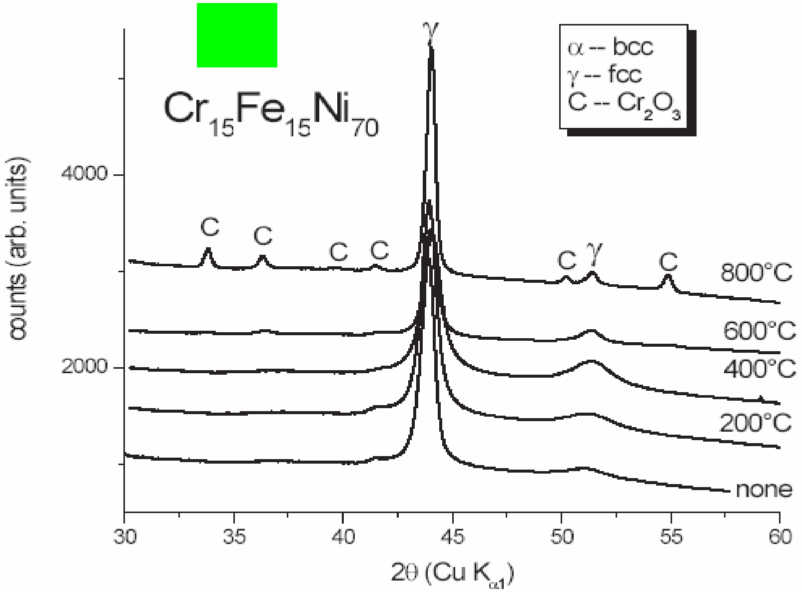
Calculated
850°C
Chuang, 1987

Phase Analysis versus Temperature



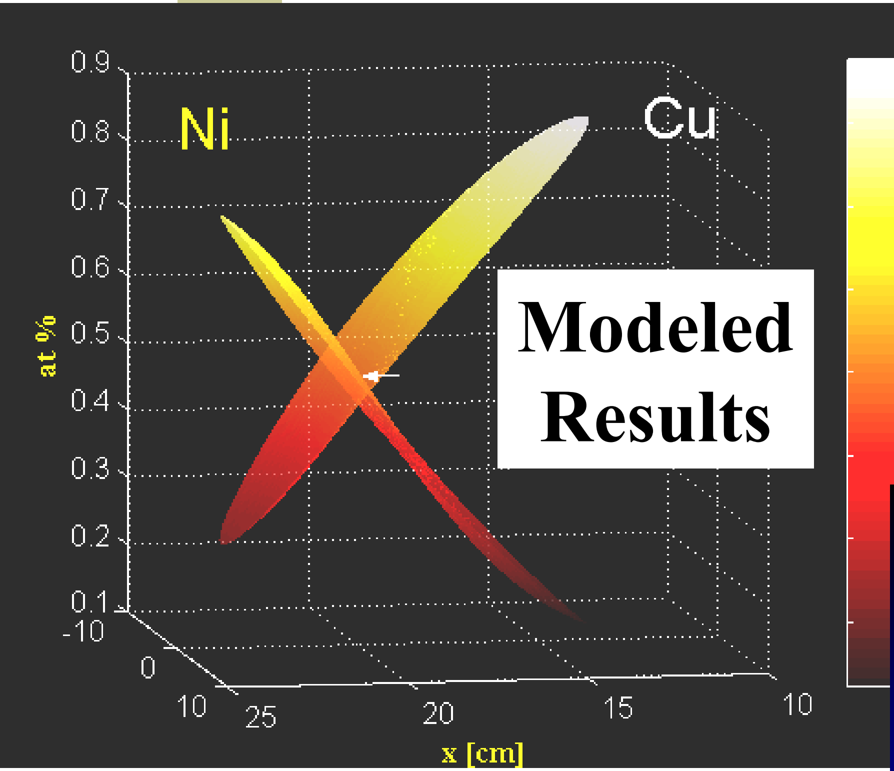






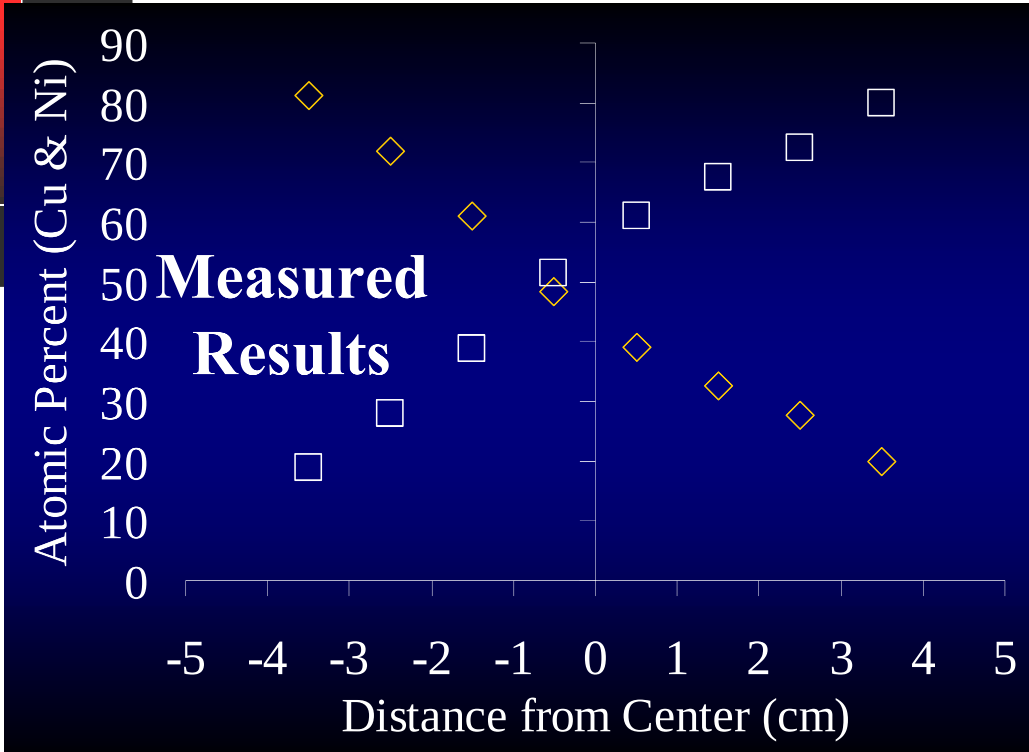
Carbon Nanofiber Catalyst

Cu-Ni Alloy



Modeled Results

Alloy Strip Deposited on Si

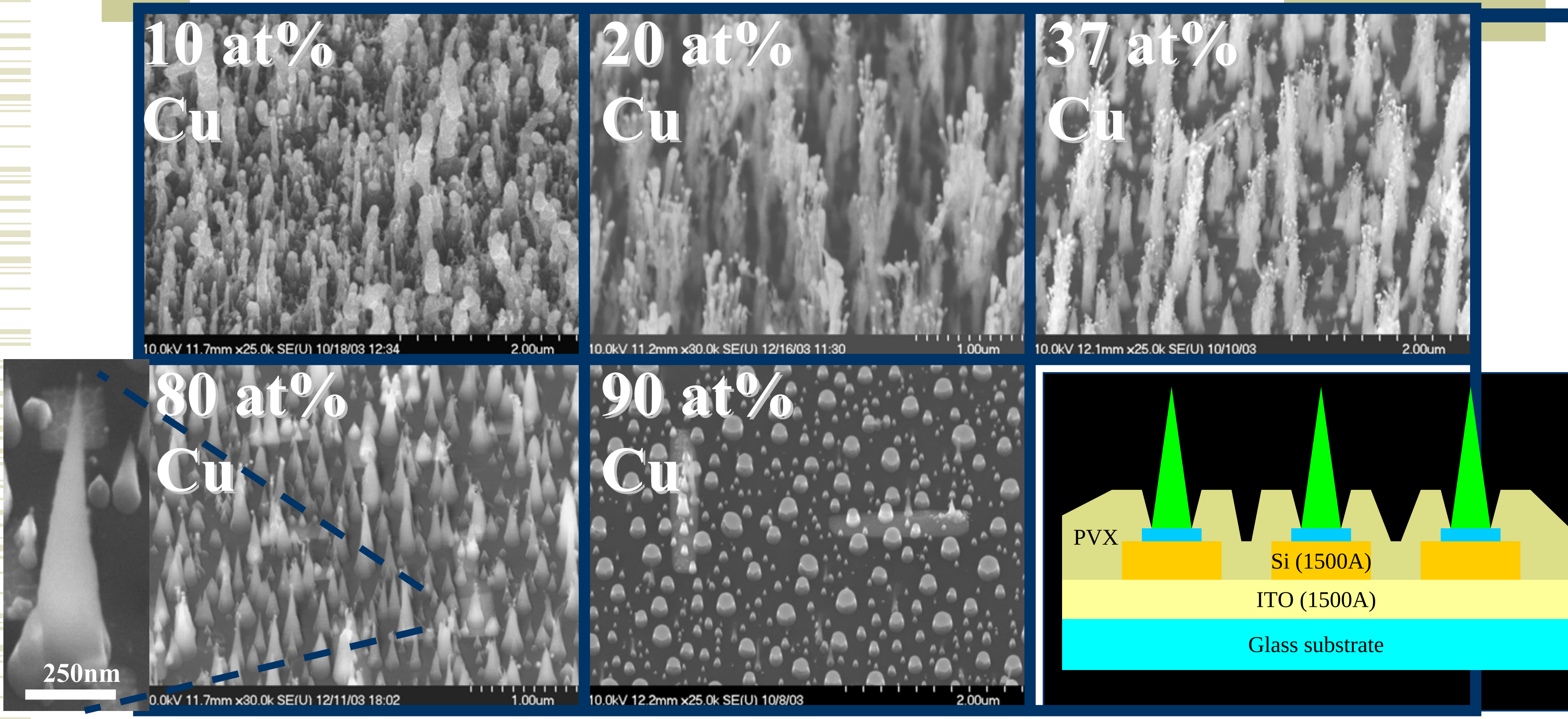


Measured Results

With Klien et al.

Carbon Nanofiber Catalyst

Cu-Ni Alloy



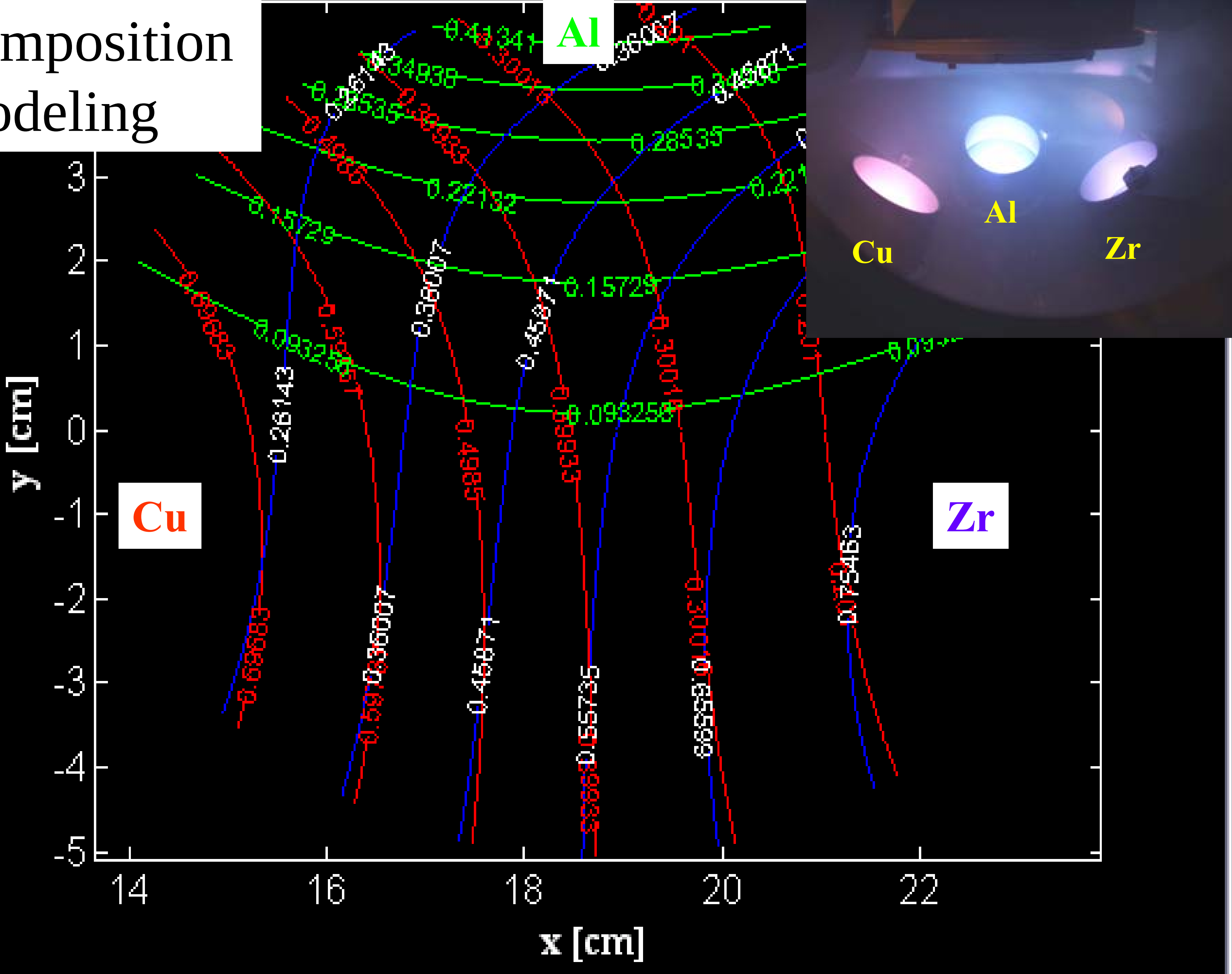
The morphology and shape of vertically–aligned carbon nanofibers are a strong function of the composition of the Cu–Ni catalyst particle that acts as the nucleation site for individual fiber growth. An optimum fiber geometry is realized at 80% Cu.

With Klien et al.

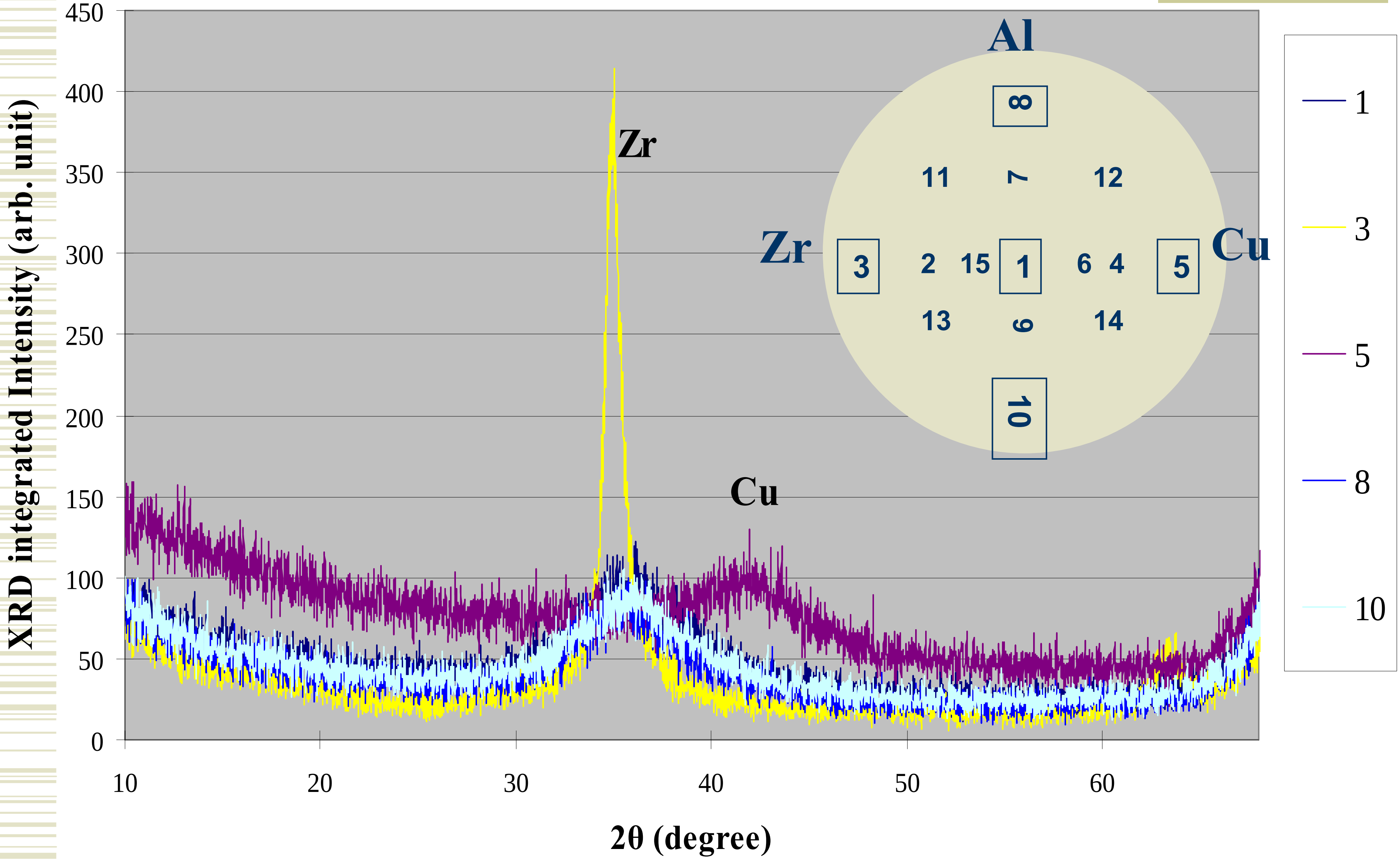
Experimental Procedure

- Sputtering Conditions
  - Base Pressure 1.1x10^{-6} Torr
  - Sputtering pressure: 3mTorr Argon
  - Zirconium power: 225 W, Sputter yield: 0.7
  - Copper power: 50 W, Sputter yield: 2.3
  - Aluminum power: 26 W, Sputter yield: 1.2
  - Time: 2 hours
- Vacuum Anneal 100, 200, 300, 400, 500°C for 10 minutes, 800°C for 30 minutes
- XRD after each anneal

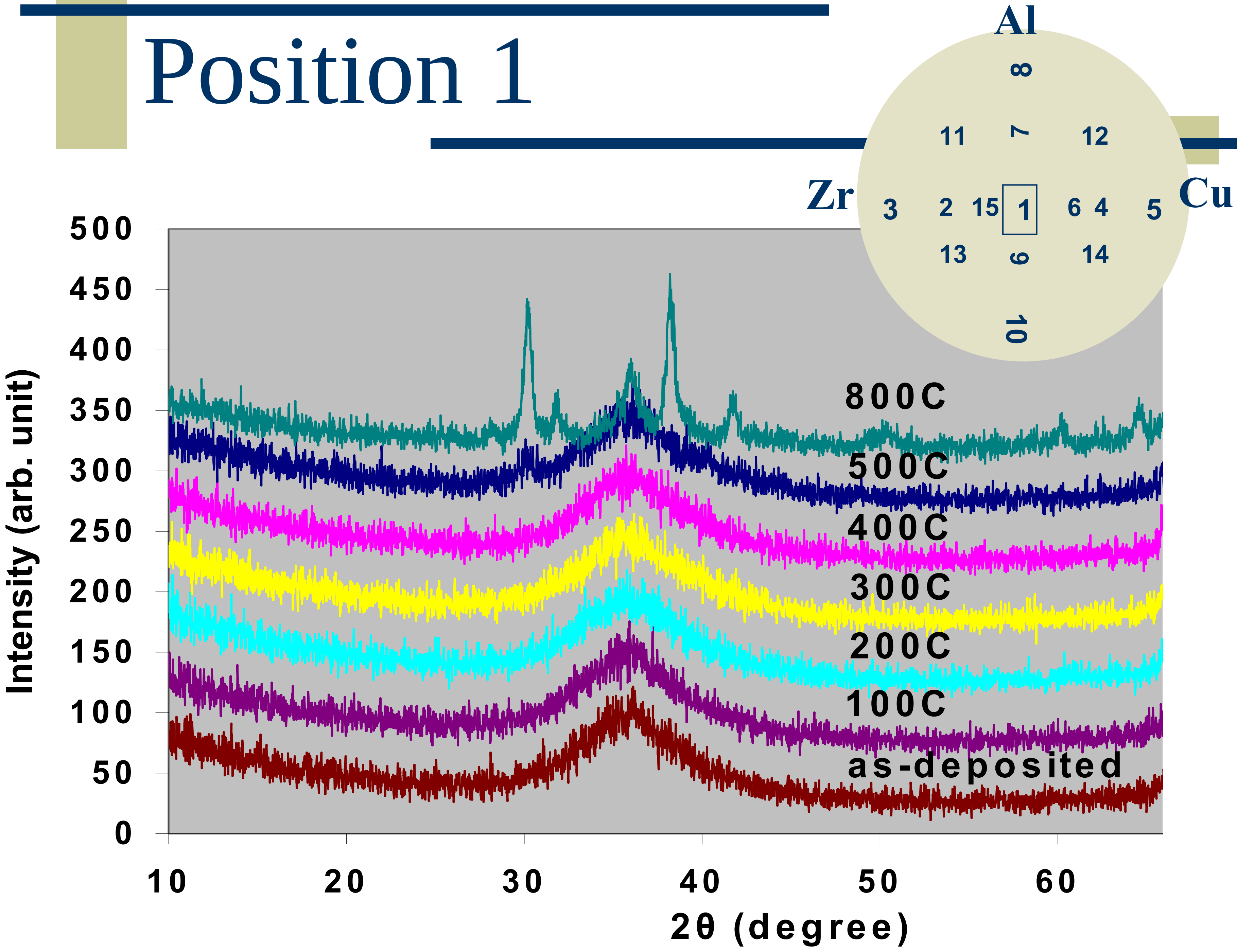
Composition Modeling



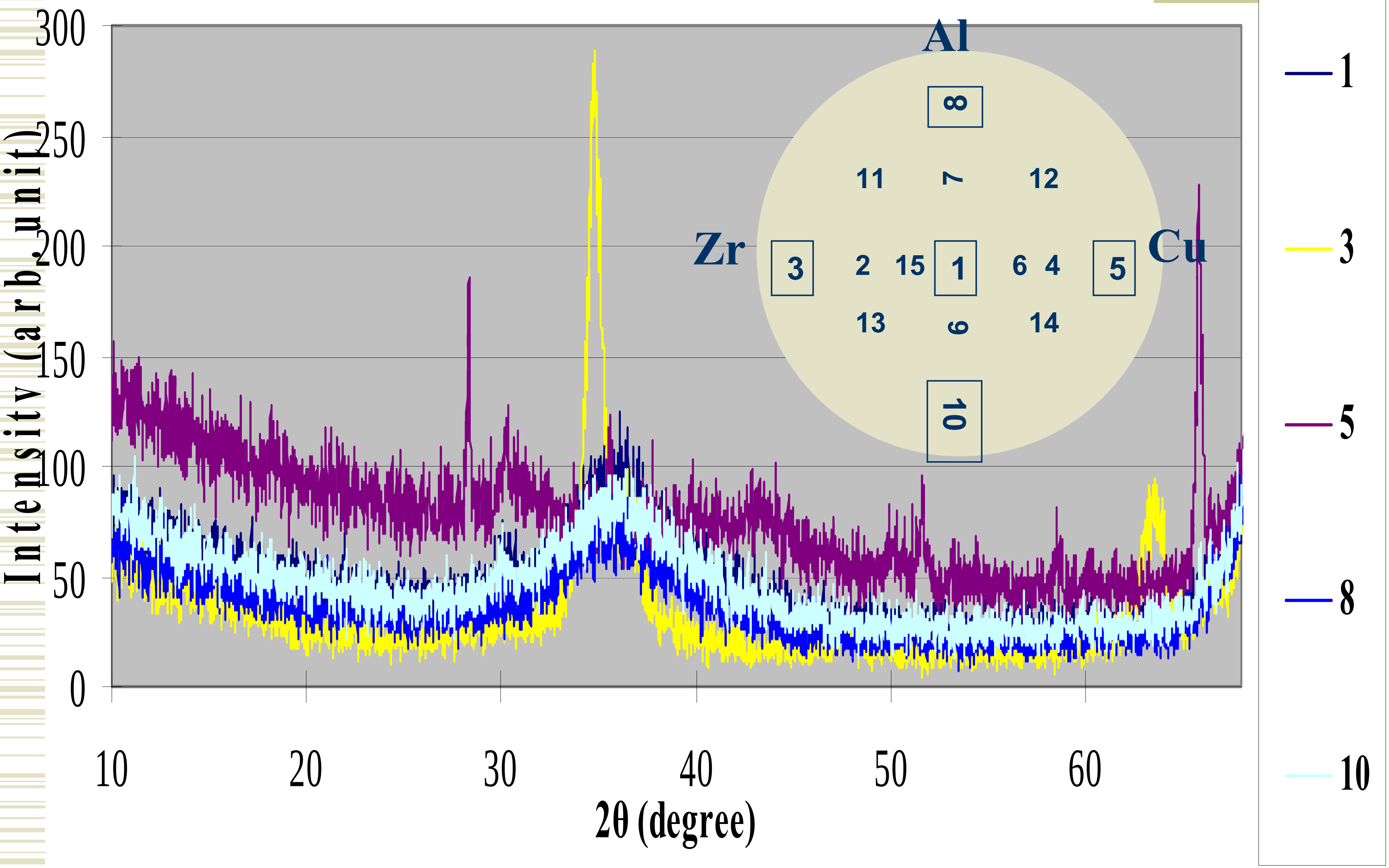
XRD Pattern of As-deposited Film



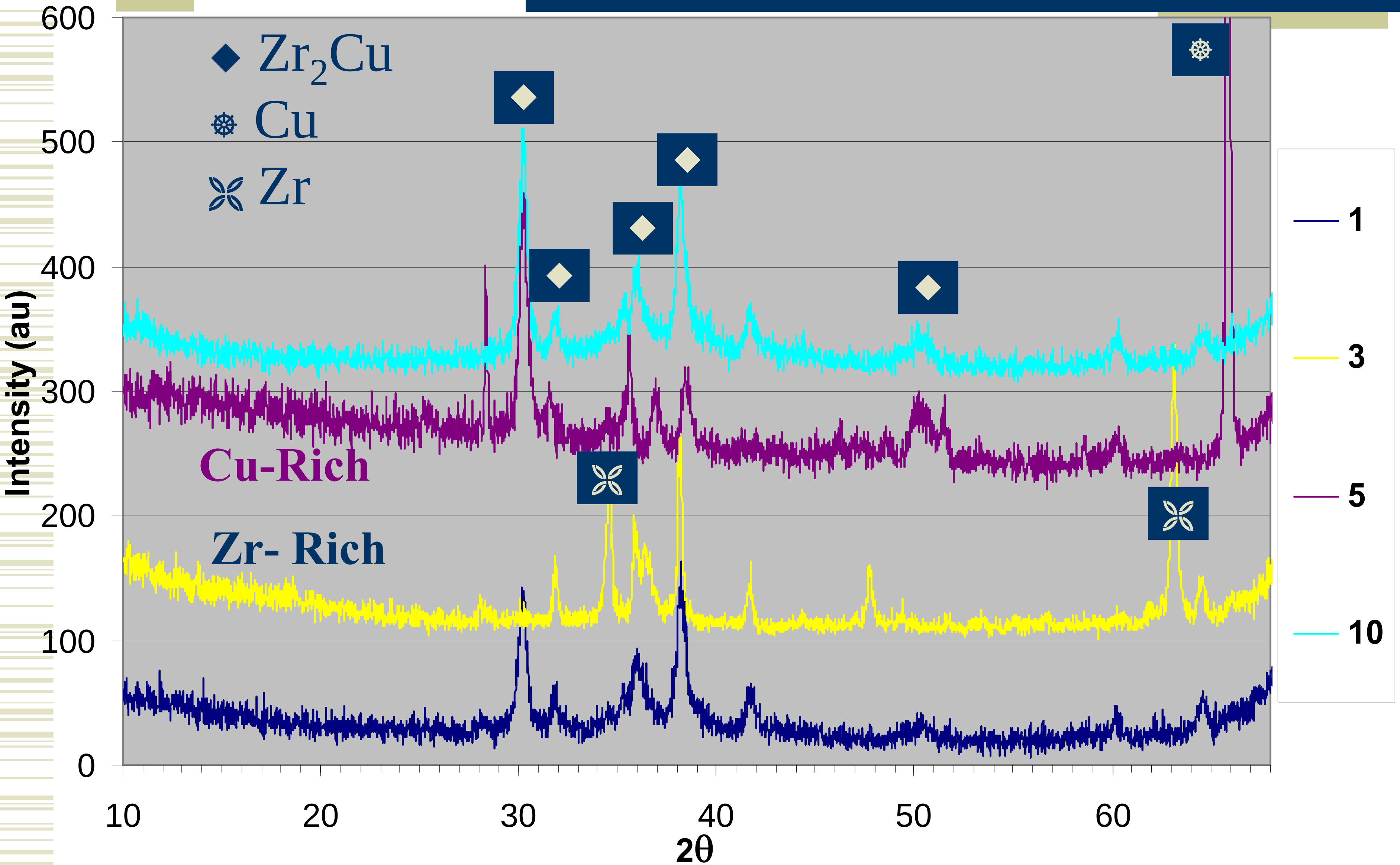
Position 1


Al
Zr
Cu
8
11
7
12
3
2
15
1
6
4
5
13
9
14
10
Intensity (arb. unit)
500
450
400
350
300
250
200
150
100
50
0
800C
500C
400C
300C
200C
100C
as-deposited
10
20
30
40
50
60
2θ (degree)

XRD after 500ºC Anneal



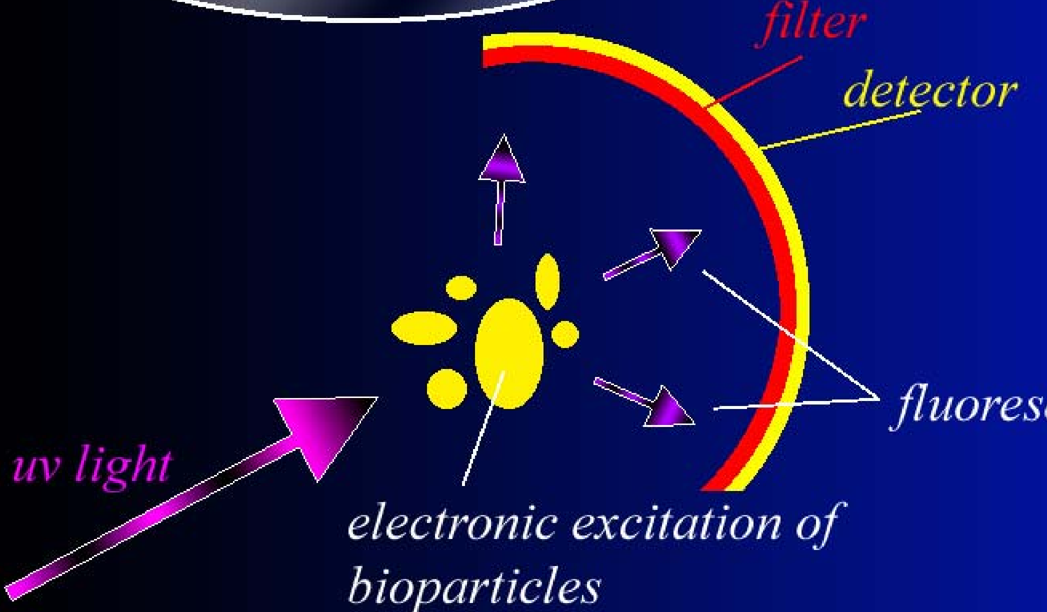
XRD after 800ºC Anneal



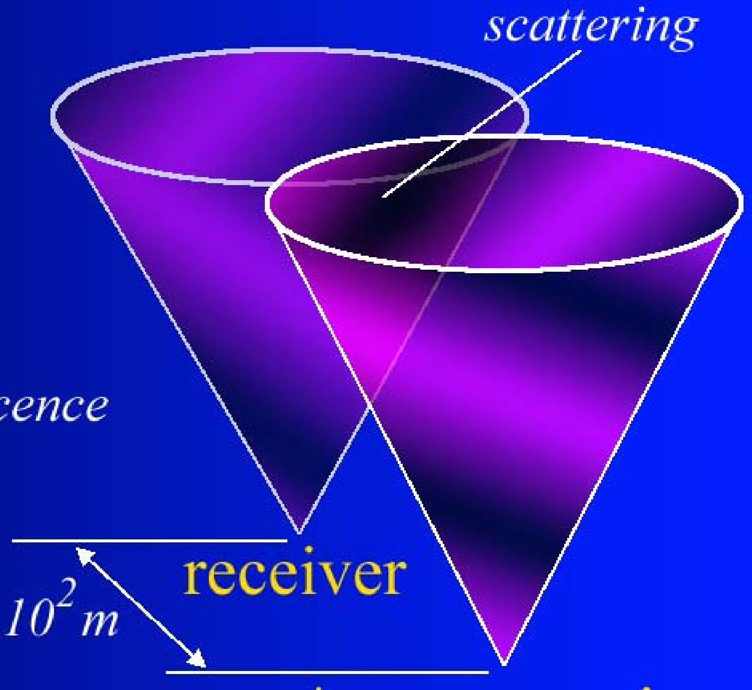
UV light source applications

non-line of sight communications

bioparticle detection



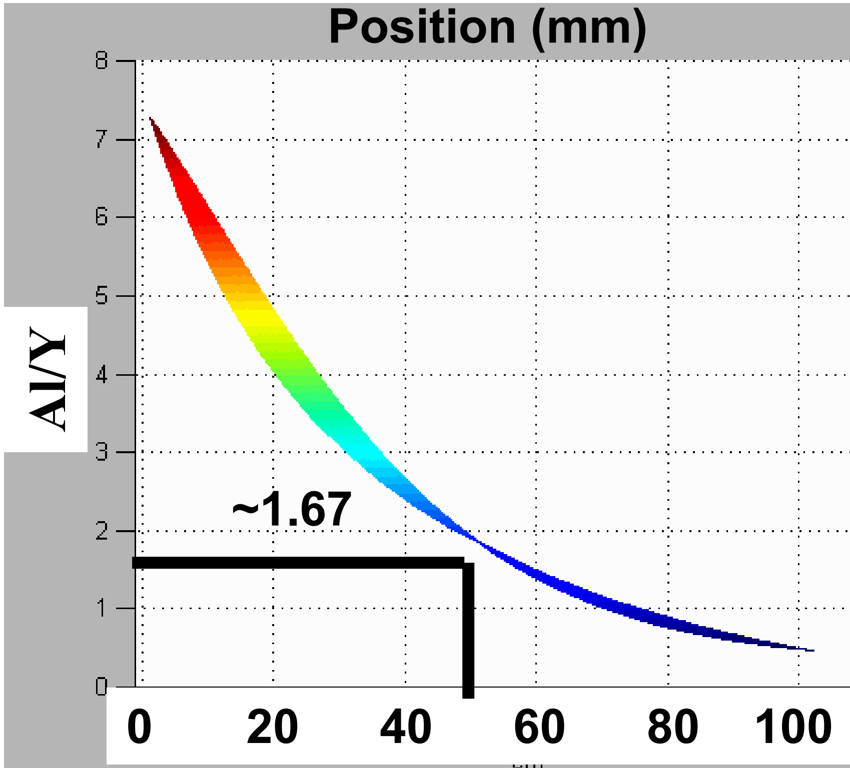
* tunable frequency source (250 - 350 nm)



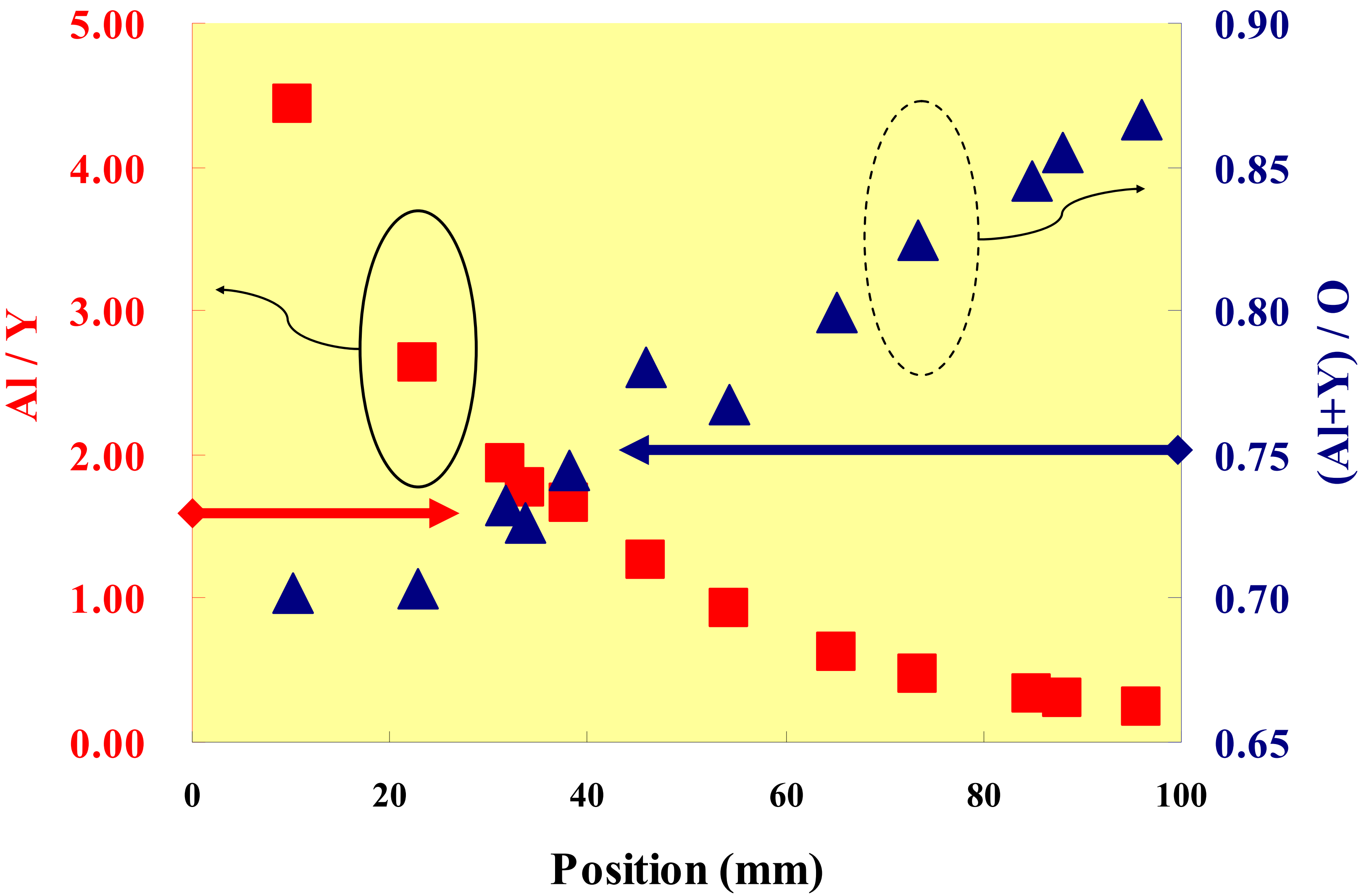
* uv transceiver

$Y_3Al_5O_{12}$ (YAG) Sputter Deposition

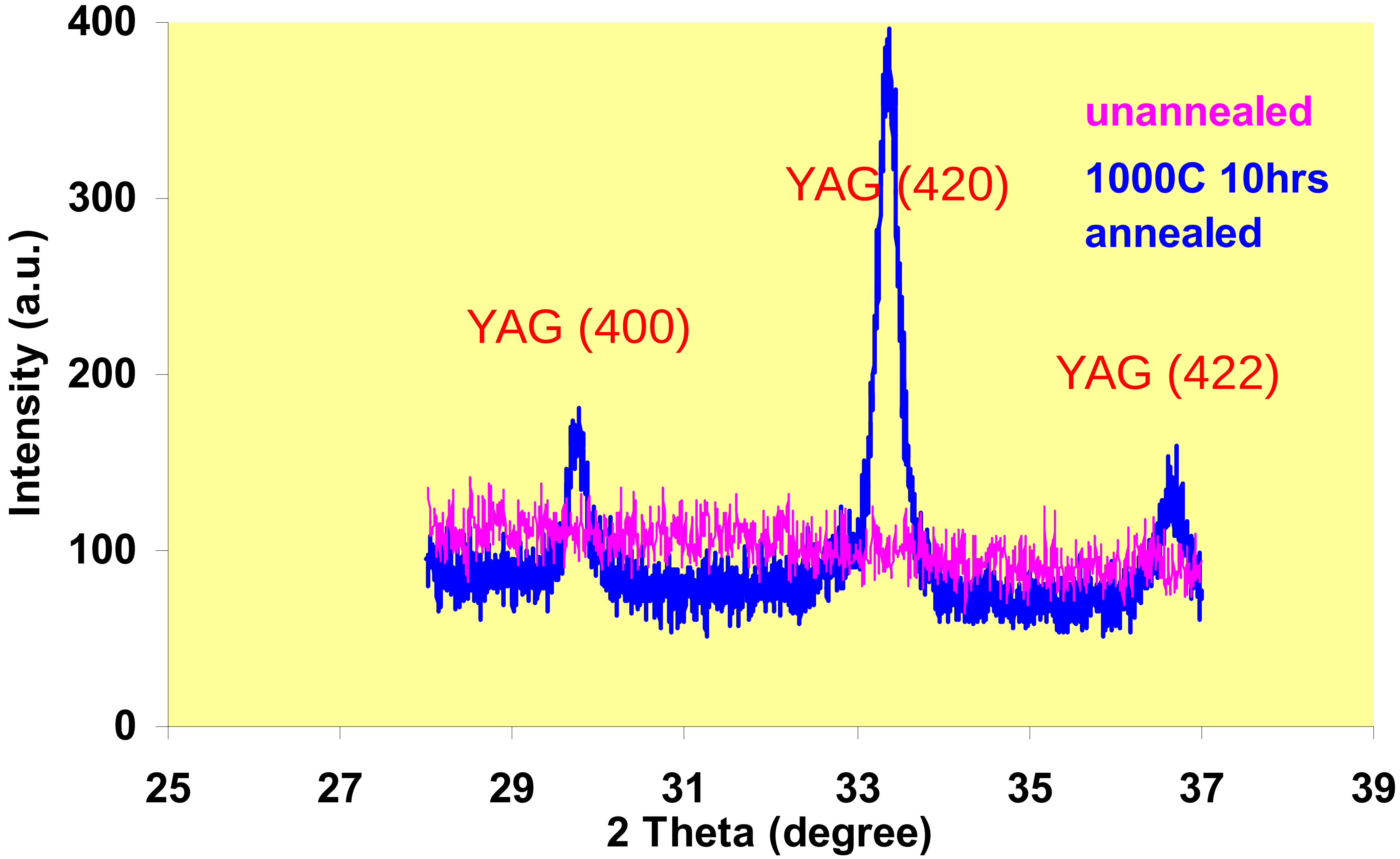
- Initial sputtering conditions:
  - Yttrium Aluminum Oxide gradient:
  - Reactive Sputtering (metallic mode)
  - Power (Y)= 80W; Power (Al)=120W
  - Flow rate (Ar) = 25sccm; (O_2) = 1.4sccm
  - Total pressure = 3mTorr
  - Time = 30min



Al/Y ratio and (Al+Y)/O ratio vs. position on gradient Yttrium Aluminum Oxide films



X-ray Diffraction Intensity of YAG Thin Films



Sputtering YAG:Gd

- Yttrium Aluminum Garnet (×4 layer): Reactive mode

  Power (Y) = 80W; Power (Al) = 130W;

  Flow rate (Ar)=25sccm; Flow rate (O_2)=1.4 sccm;

  Total pressure = 3mTorr; Time = 12.5min
- Gadolinium (×3 layer): Metallic mode

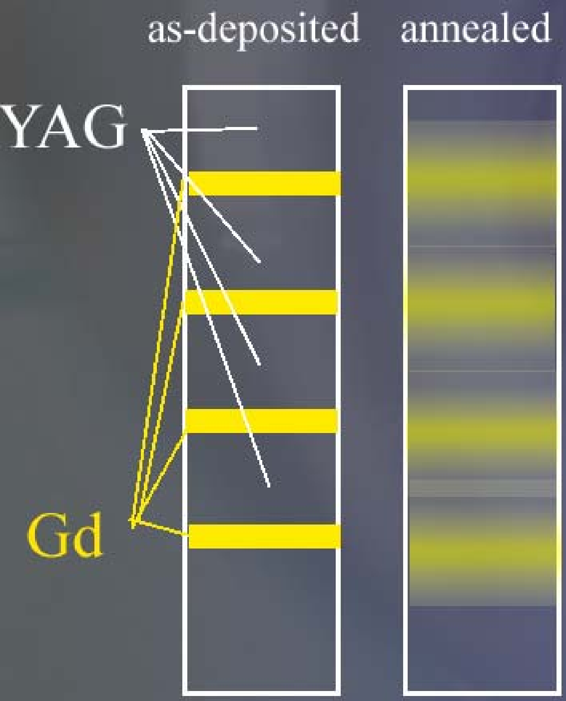
  Power (Gd) = 60W;

  Flow rate (Ar) = 20sccm;

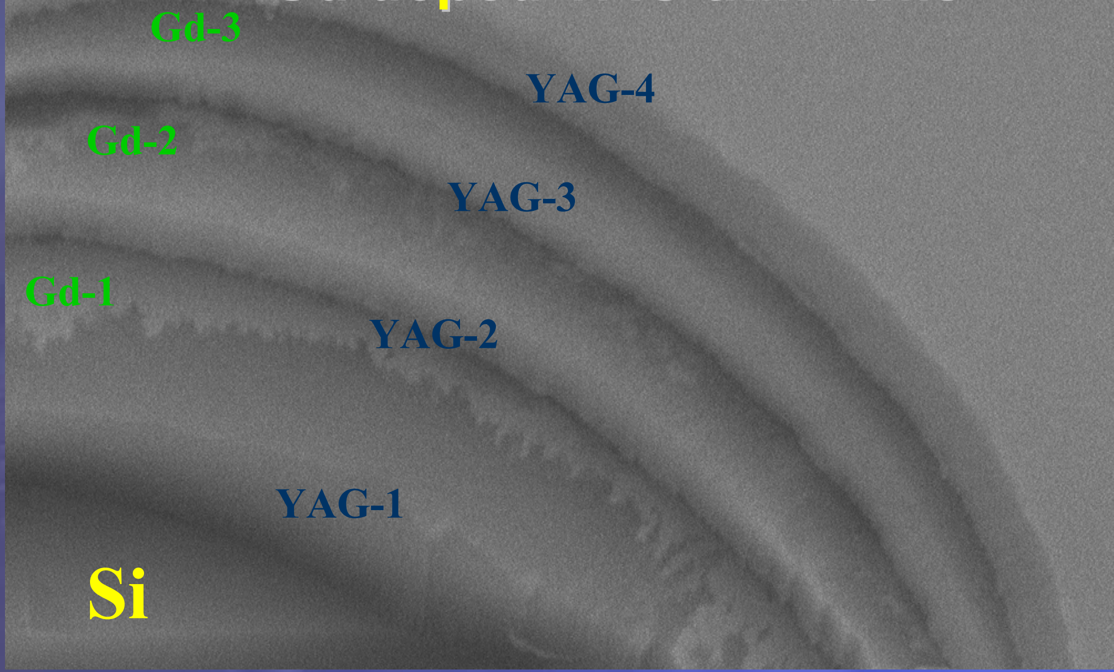
  Total pressure = 3mTorr; Time = 4min or 8min

Furnace Anneal

1000 °C : 10 hrs. : air



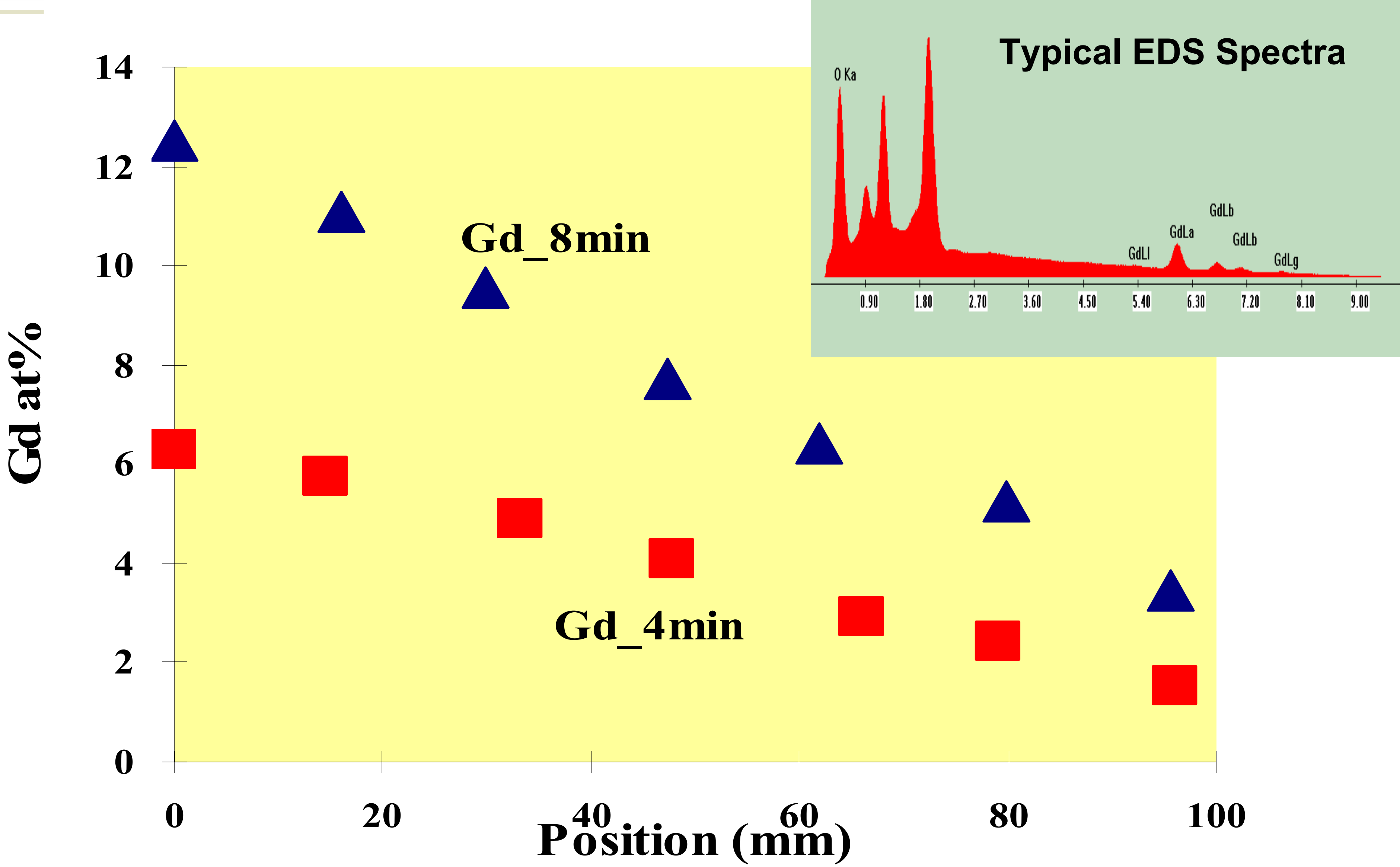
SEM micrograph of multilayer Gd doped YAG thin films



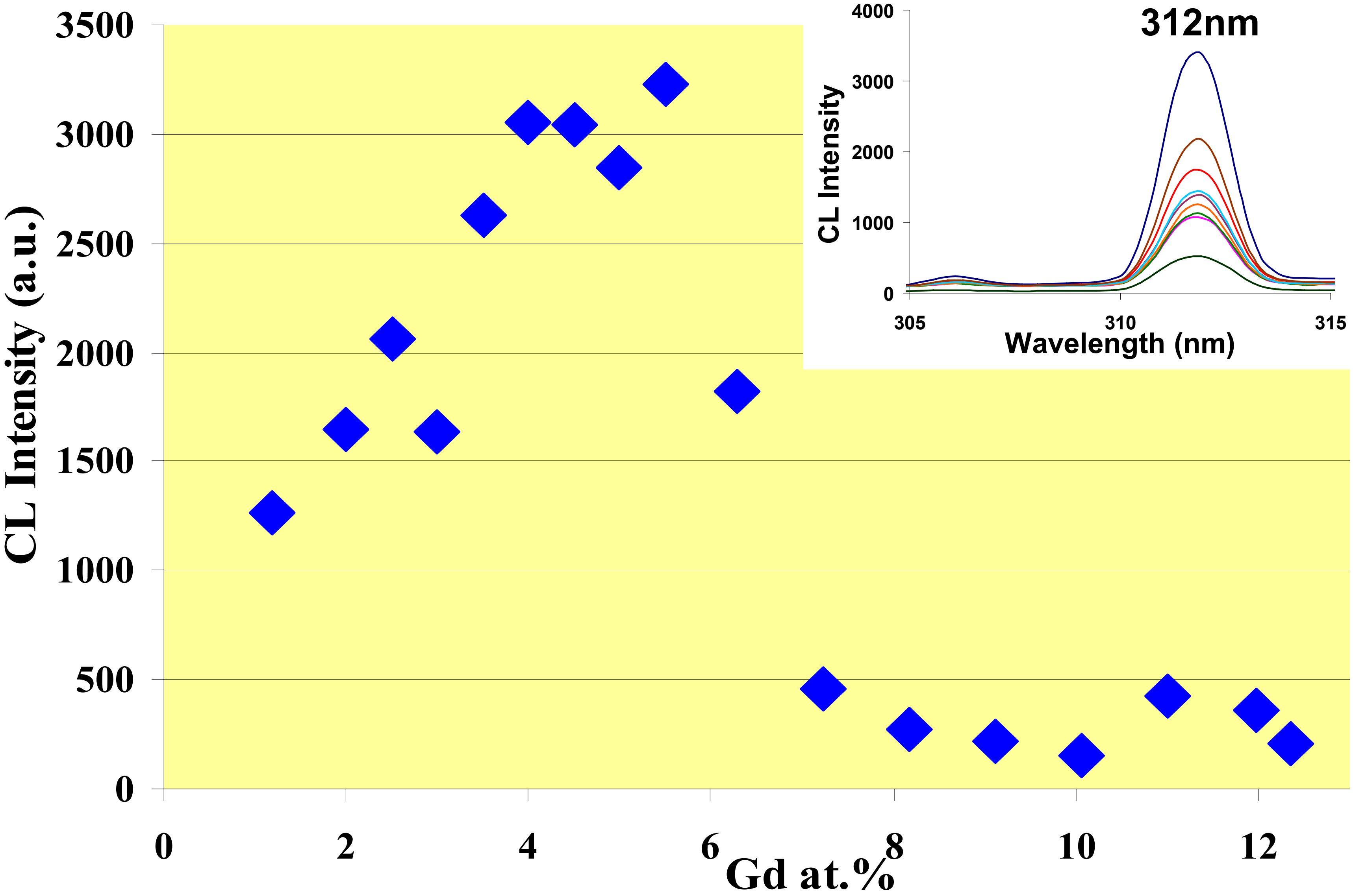
* *in-situ heating cannot be used for combinatorial thin films (substrate must be rotated when heated at high temperature*

* *stacked layers reduces the time required to approach homogenized composition*

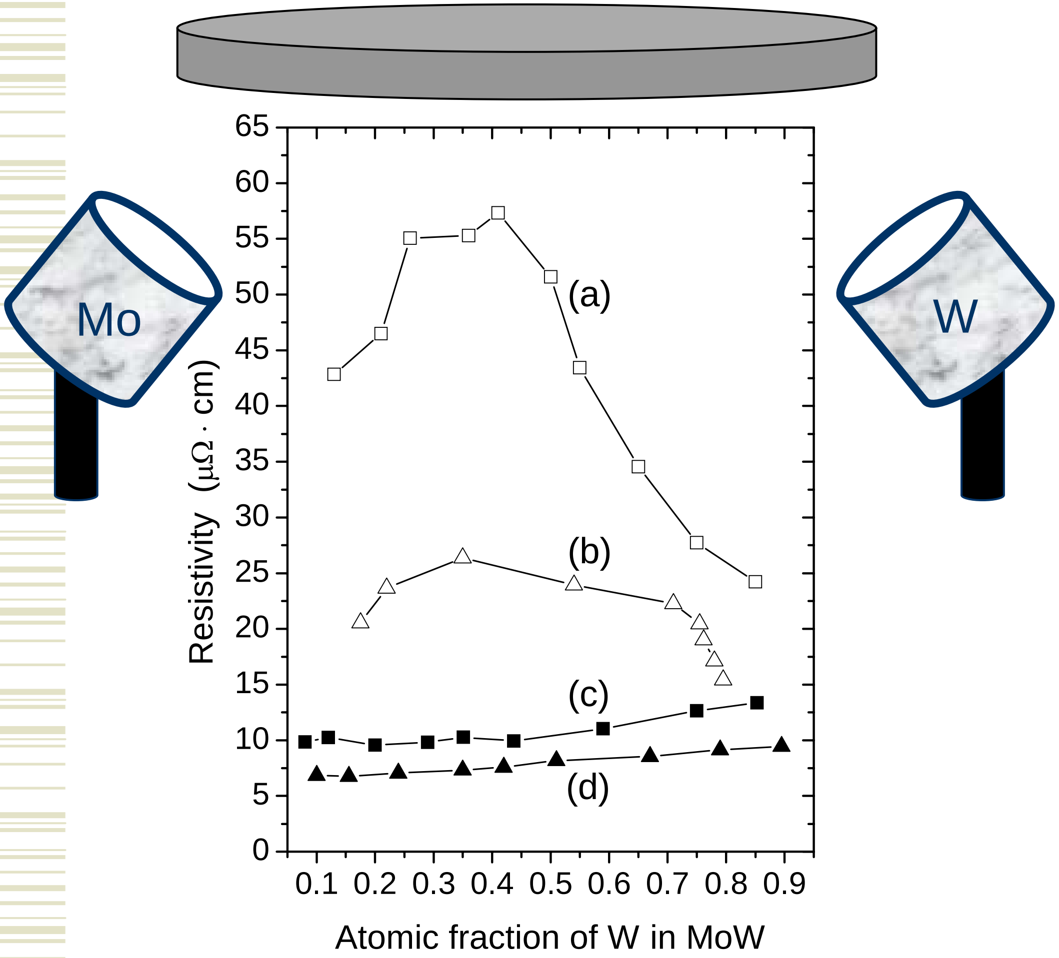
Gadolinium concentration vs. position for Gd doped $Y_3Al_5O_{12}$ films



CL intensity vs. Gd concentration



Binary Mo-W Electrodes



(a)