

Atomic Layer Deposition of Aluminum doped Zinc Oxide

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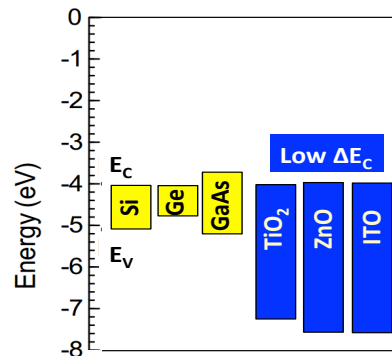
Michelle Rincon (Mentor)

Outline

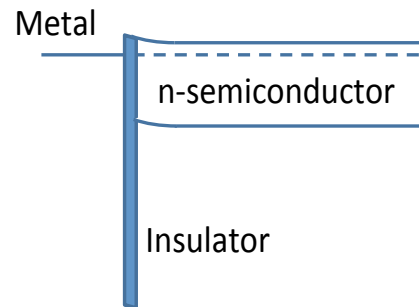
- Motivation of Aluminum Doped Zinc Oxide(AZO)
- Why ALD?
- AZO Fabrication Process
- Growth Characterization: Growth Rate and Pressure
- Characterization: Al. Concentration and Electrical Properties
- Compare to Literatures
- Conclusion

Why Aluminum Doped ZnO?

- Wide-bandgap semiconductor
- Piezoelectric
- Transparent conductive electrode
- Can be very highly doped
 - Oxygen vacancies
 - **Aluminum**
- MIS selective contacts
 - Small barrier for electrons
 - Large barrier for holes



Metal/insulator/ semiconductor



Project objectives

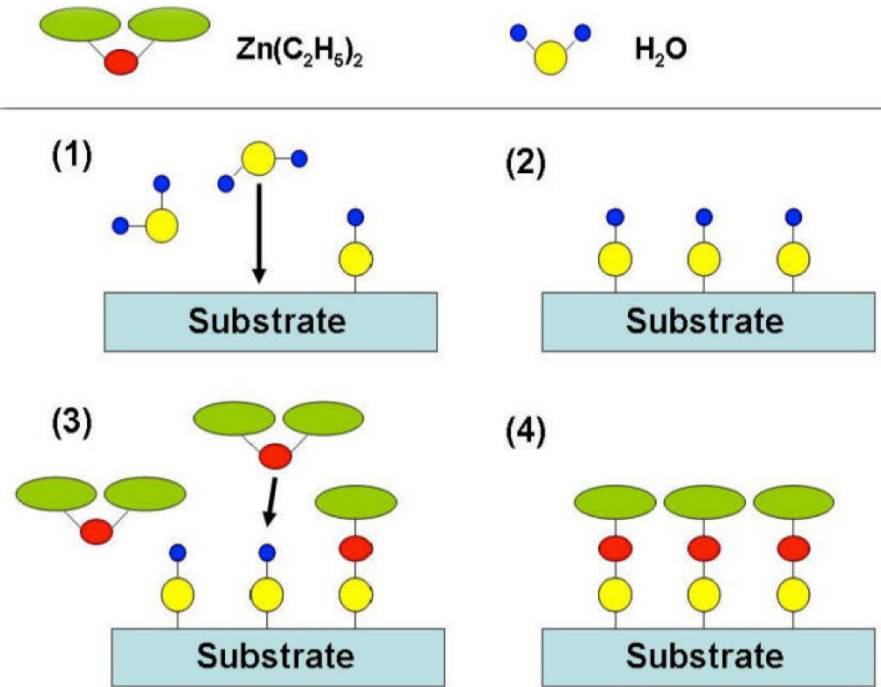
- Reliable and controlled growth of Al doped ZnO using ALD
- Variable film quality by changing ratios between Zn and Al precursors
 - Film stoichiometry
 - Resistivity/Mobility
 - Growth rate

What is ALD?

Atomic layer deposition: a powerful tool for thin film deposition

- Precise thickness control (nanometer scale)
- Pinhole-free
- Totally conformal coating on any shape and geometry
- High repeatability

Flow-through traveling wave setup



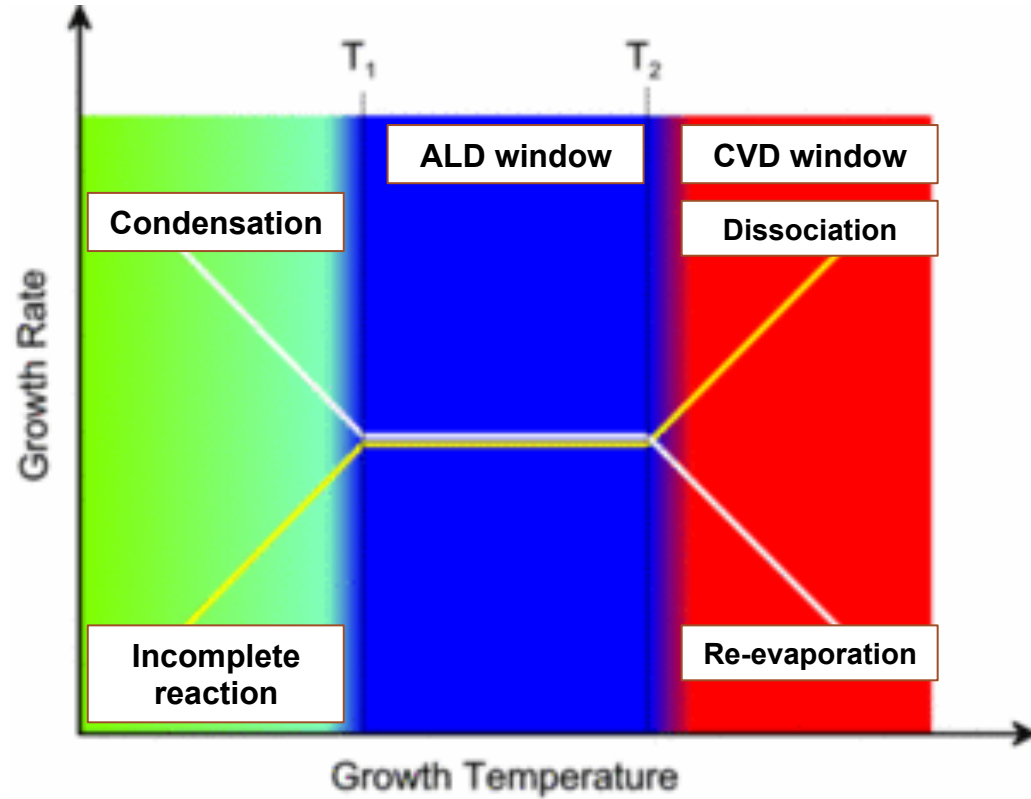
ALD window

Typical process conditions:

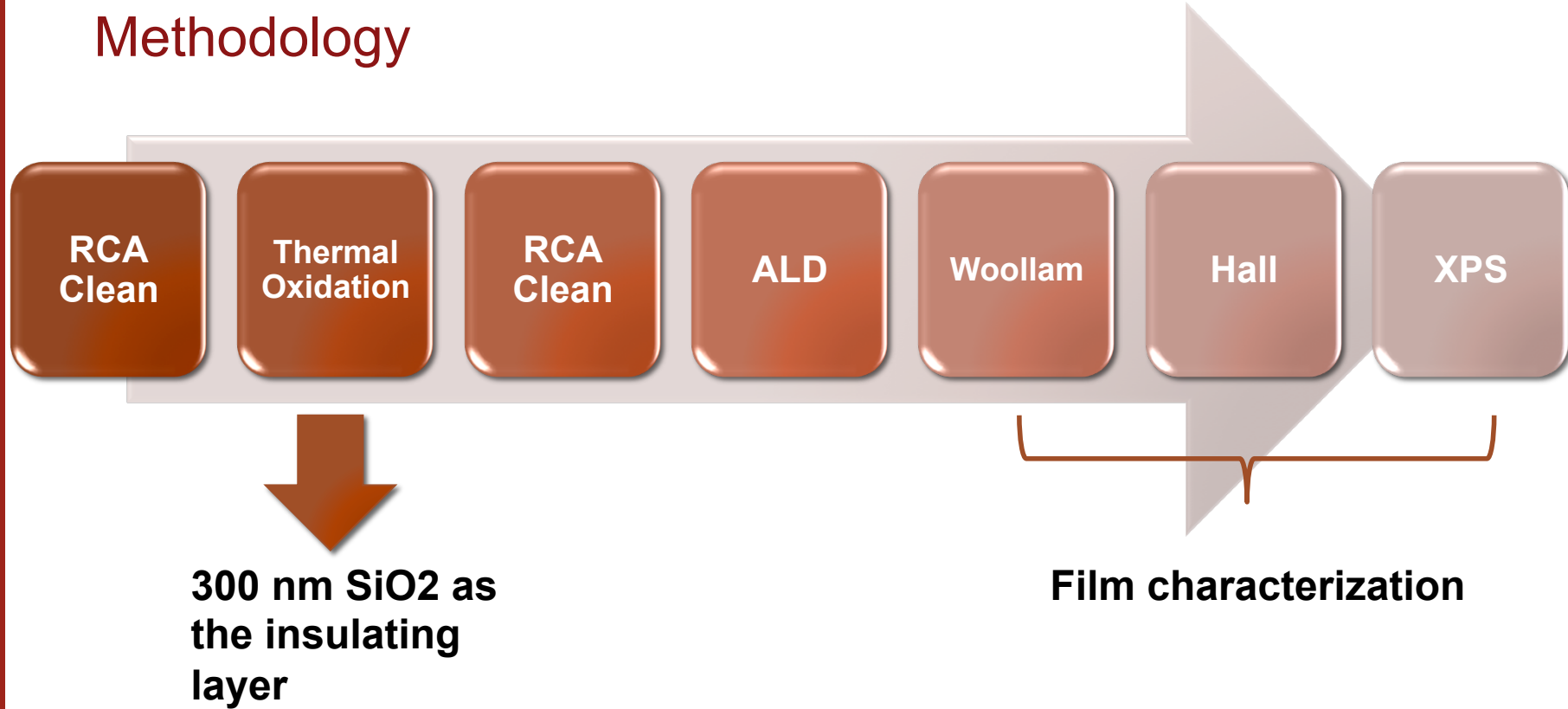
- Pressure range: 0.1-10 mbar
- Temperature: 50-500 °C

ZnO ALD on Si:

- 130-170 °C
- Precursors: $\text{Zn}(\text{C}_2\text{H}_5)_2$ & H_2O



Methodology



Al doped ZnO recipe

Flow & Temperature:

- Previous ZnO recipe by Jiheng and Pranav

Micro cycle 'X' for ZnO:

- Al doping concentration

Macro repeat cycle 'Y' for AZO:

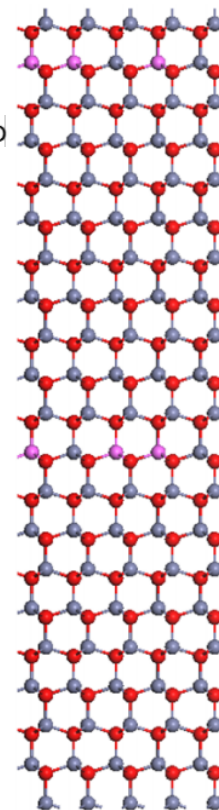
- Film thickness

e.g. Cycle ratio Zn:Al = 10:1 (X)

Total cycle = 154 cycles (Y)

	Instruction	#	Value
0	flow		20
1	heater	9	150
2	heater	8	150
3	heater	10	140
4	heater	7	150
5	stabilize	10	
6	stabilize	8	
7	stabilize	9	
8	wait		300
9	pulse	DEZ, $\text{Zn}(\text{C}_2\text{H}_5)_2$	0.03
10	wait		40
11	pulse	H_2O	0.015
12	wait		45
13	goto	9	10 X
14	pulse	TMA, $\text{Al}(\text{CH}_3)_3$	0.015
15	wait		40
16	goto	9	14 Y
18	wait		300
19	flow		5

Cycle Ratio
Zn:Al|10:1



Characterization – film thickness and growth rate

Film thickness:

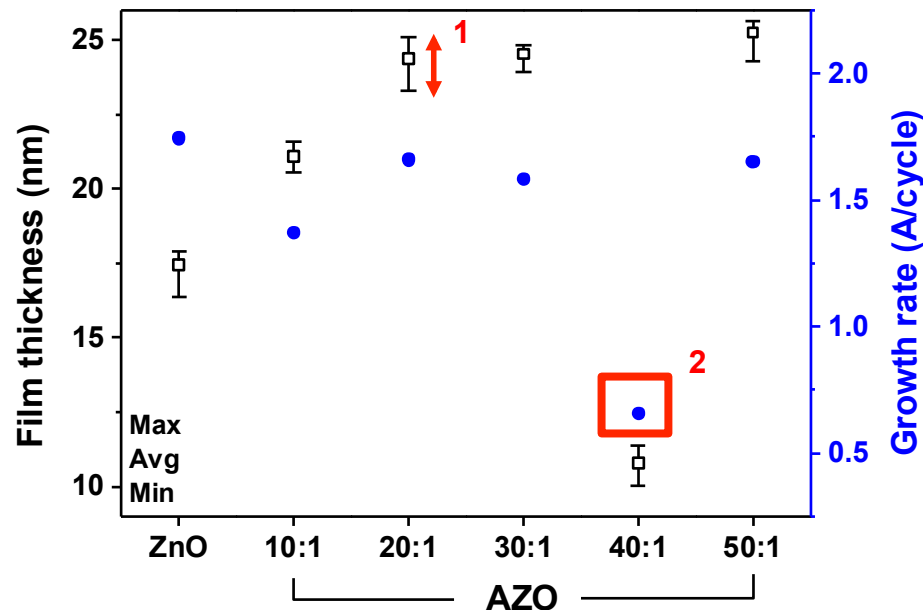
- Avg. from 24.5nm to 10.8nm
- Uniformity(Max-Min) ≤ 1.8 nm

Growth rate:

- Around 1.5 A/cycle except 40:1 AZO (Zn:Al = 40:1)

Expected problems:

- Unstable chamber pressure
- Precursor depletion



Pressure monitoring 1 – Pressure vs. Operation time

Base pressure:

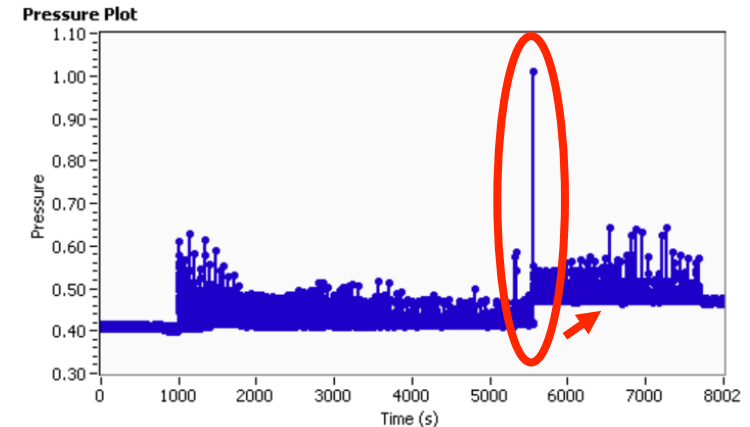
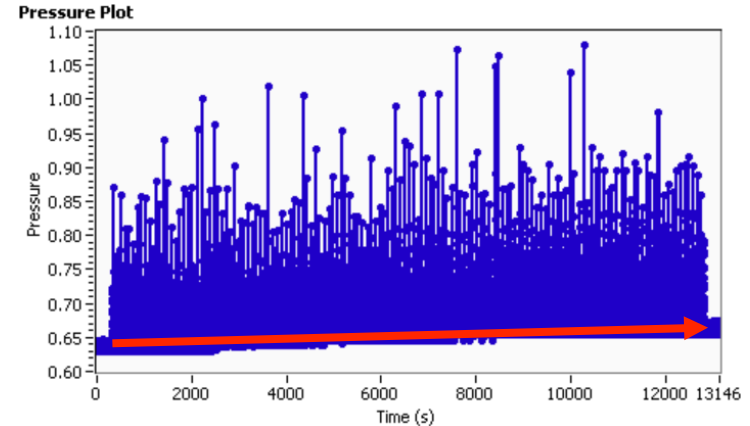
- Unstable and increase

H₂O pressure peak:

- Sudden huge increase followed by base pressure change

Expected problems and solutions:

- H₂O residue → Purge time ↑ ~ 45s,
Clean the gas lines
- Pressure sensor issue → fix or replace



Pressure monitoring 2 – 40:1 AZO, abnormal growth rate

20:1 AZO

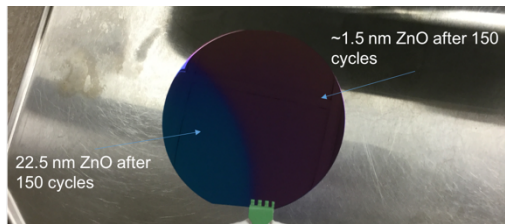
- Normal growth rate ~ 1.66 Å/cycle
- Zn pressure ~ 0.1 Torr

40:1 AZO

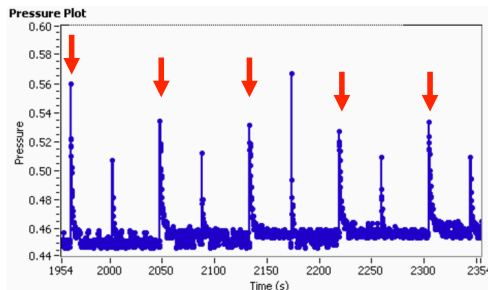
- Abnormal growth rate ~ 0.66 Å/cycle
- Zn pressure ~ 0.01 Torr
- Around 10 times smaller Zn pressure

Expected problem and solution:

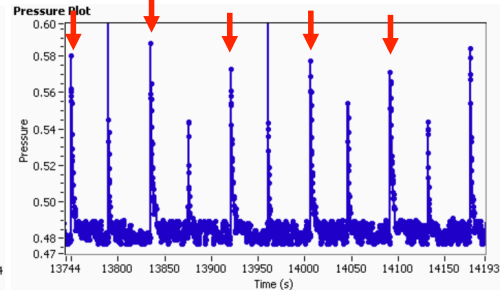
- Zn Precursor depletion $\rightarrow$ replacement



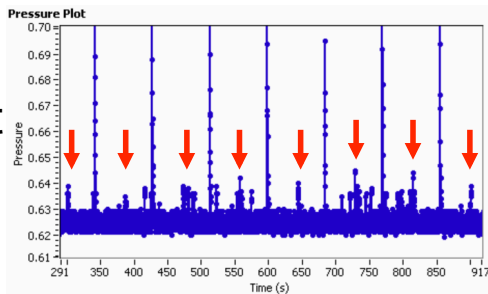
20:1 AZO beginning



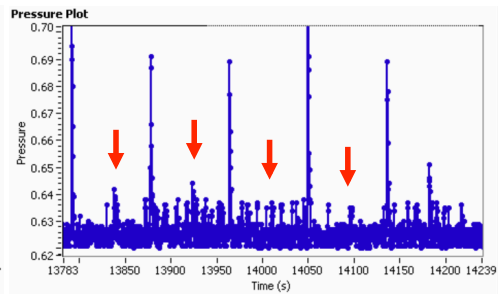
20:1 AZO end



40:1 AZO beginning



40:1 AZO end



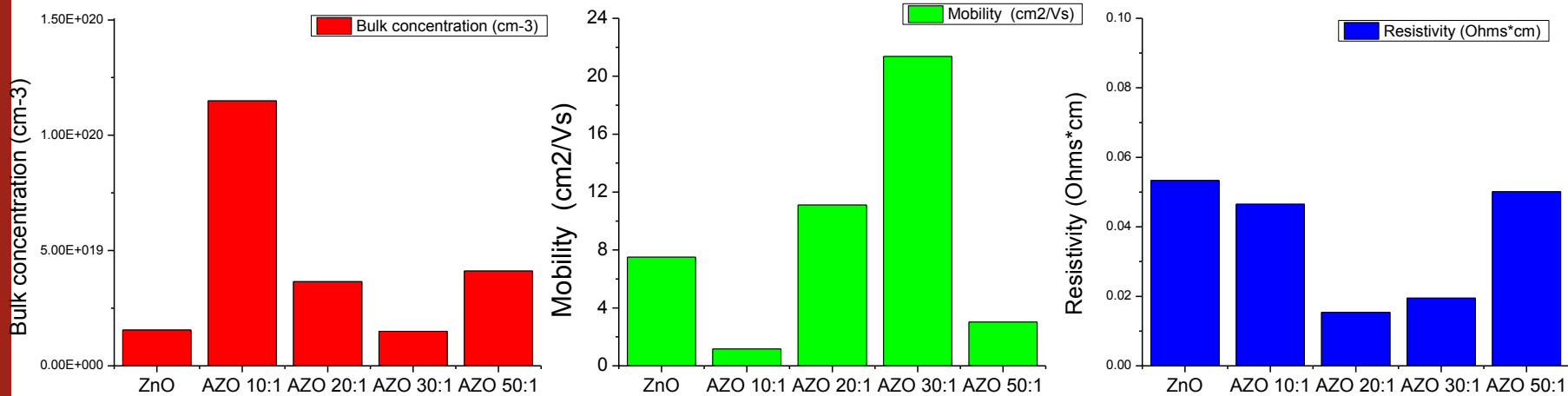
* ↓ : Zn Pressure peak

ZnO Hall Measurement Results

Name	Ratio	Cycles	Thickness (nm)	Bulk concentration	Mobility	Resistivity
ZnO	-	100	17.44	-1.56E+19	-7.5111	0.05333
AZO	10 / 1	154	21.08	-1.15E+20	-1.168	0.04652
AZO	20 / 1	147	24.38	-3.65E+19	-11.109	0.01538
AZO	30 / 1	155	24.53	-1.50E+19	-21.372	0.01947
AZO	40 / 1	164	10.79	N/A	N/A	N/A
AZO	50 / 1	153	25.24	-4.12E+19	-3.0254	0.05012

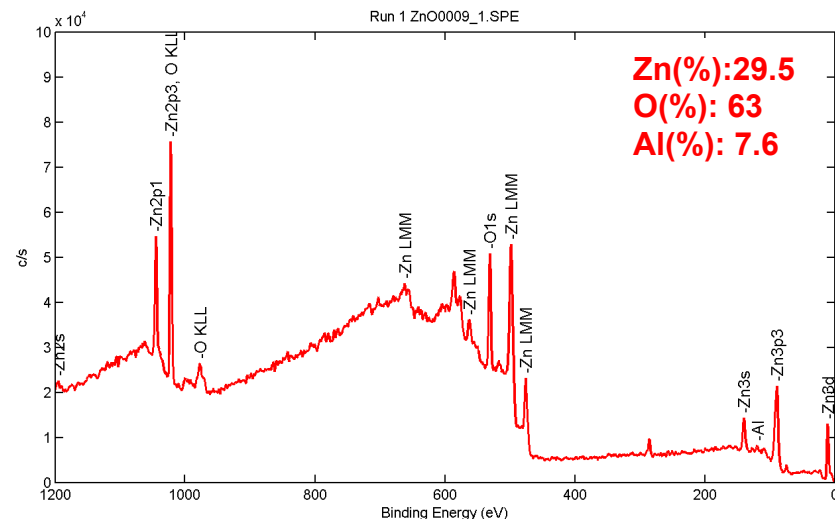
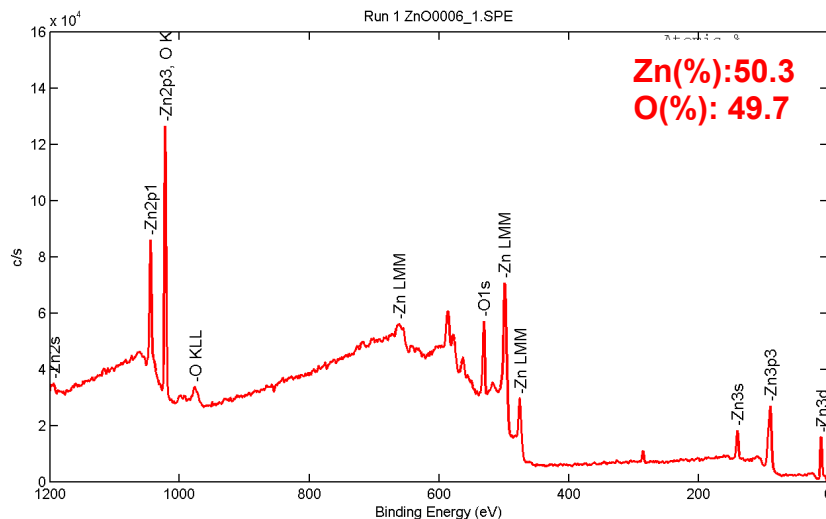
- Variable: Cycle ratio (Zn : Al)
- Results: ALD deposition results in very uniform coating which gives much better Hall measurement results
- In case of Zn:Al = 40:1, the thickness of AZO film is decreased more than half due to the precursor issue

ZnO Hall Measurement Results



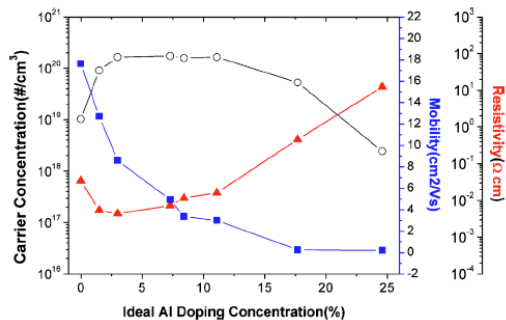
- 10:1 gives highest bulk centration due to high Al doping
- Similarly, mobility drops for AZO due to the high bulk concentration
- AZO 20:1 and 30:1 give the lowest resistivity
- Overall, all sample showed good conductivity

XPS Film Characterization

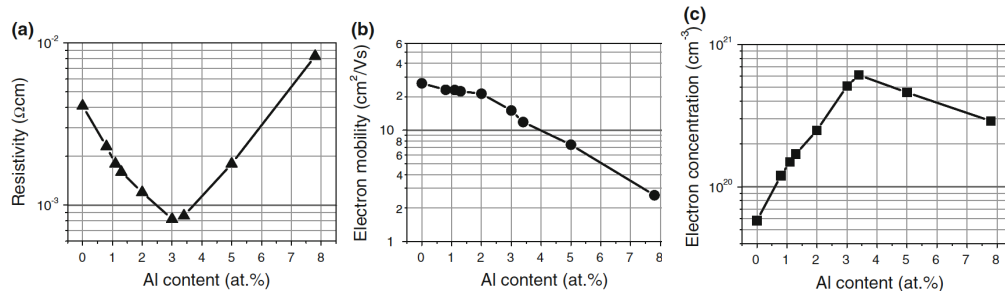


Name	Zn(%)	Al(%)	O(%)
ZnO	50.3	0	49.7
AZO 10:1	29.5	7.6	63
AZO 20:1	37.3	5.5	57.2
AZO 30:1	52.9	4.7	42.4
AZO 50:1	52.2	1.8	46

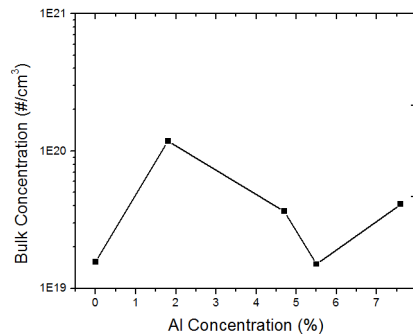
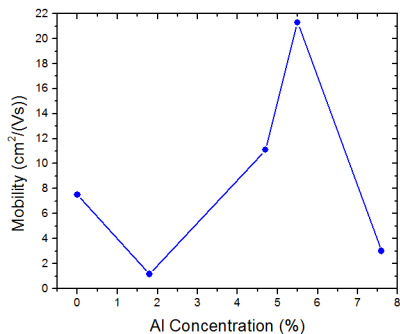
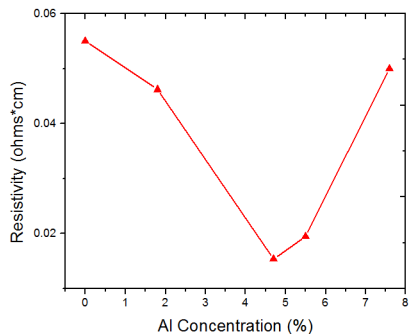
Comparison to Literatures



Parag Banerjee, etc.al



G.Luka, etc.al



Experimental Results

Potential Problems

- Growth
 - Issues with old DEZ precursor
 - Inadvertent precursor heating
 - Pressure fluctuation
 - Inconsistent water precursor injection
- Measurement
 - Contacts for Hall measurements
 - Woollam model and fitting

Conclusion

- Developed standard ALD Al doped ZnO recipe
- ALD window similar to literature
- Controlled growth and good uniformity within ALD window
- Recipe requires further modification
 - Zn:Al ratio does not follow reported trend
 - New precursor bottle will be used
 - Possibly try deposition in Fiji2