Selective Deposition:
A Materials Supplier's Perspective

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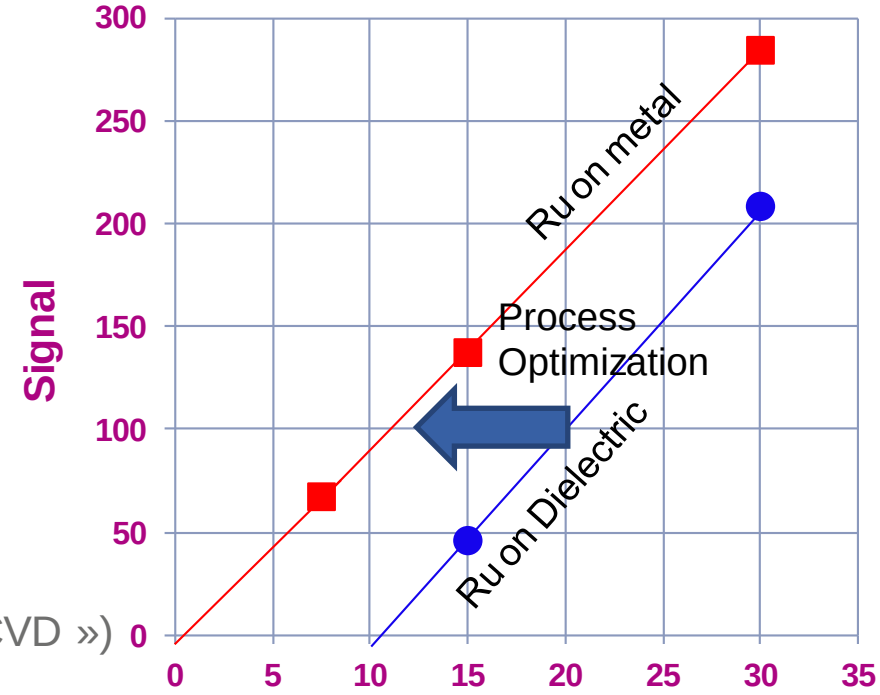
Outline

- **Diversity of ASD**
- **A Materials Supplier Perspective:**

  The balancing act of Innovation vs Manufacturability
- **Illustrative examples of contributions**
- **Highlights**

Diversity of ASD

- **Selective CVD/ALD**
  - Selective Epi
  - Selective W / Mo (~ 1980) on Si, TiN, Al
  - Salicide / selective surface reactions
  - « Induction time » in metal CVD
  - SAM-based methods
- **Topography based methods**
  - Super conformal catalysed or inhibited CVD
  - Flowable
  - Dep / Etch / Dep / Etch (« sequential HDP CVD »)



➔ **Some may need an (partial) etchback**

A Materials Supplier Perspective: Contribution

Design small.
Think big

➔ **Pathfinding / tool kit building**

- **Precursor design / tuning & rework**
  - H_2O-based process
  - high GPC
  - Higher thermal stability precursors (metal CVD)
  - Low T precursors (SAM-based ALD)
  - Etch / Dep controllable precursors.
- **SAM Design & Combinatorial screening**

Manufacturability Constraints (not ASD specific)

- **Safety**
  - High pace of molecule introduction + extreme property materials

    ➔ 2 major accident / years on average in the last 7 years at precursor suppliers

- **Regulatory**
  - TSCA, REACH, K-REACH, TW-REACH, RoHS, IMDG…
  - No self decomposition at 65°C for ~ 1 week with no P buildup / self heating
  - Customer specific « banned substance lists »
  - Cost of implementation / entry barriers of new substances

Manufacturability Constraints

Design small.
Think big

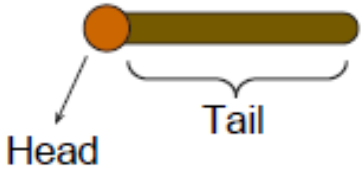
- **Affordability (lower precursor efficiency in selective CVD)**
  - Reuse of molecules « available » from other industries
  - # of synthesis steps from closest commodity materials (think of the LIGAND!)
  - Yield of each steps
- **Defect Free Manufacturing**
  - No « usual suspects » in precursor/SAM impurity effects
  - No standard metrology for blocking layer efficiency at early stage
  - Acute sensitivity to impurities in intrinsic selective CVD processes

Illustrative examples

- **SAM design (HT, coverage%,…) for DoM**
  - Monopodal SAM screening for DoM ALD
  - Chemistry consideration for HT SAMs
- **Ru CVD growth selective inhibition**
- **Metal oxide etch back (selective etch, etch back)**

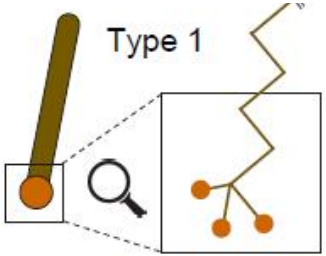
Area Selective ALD (-OH protection based)

Design small.
Think big

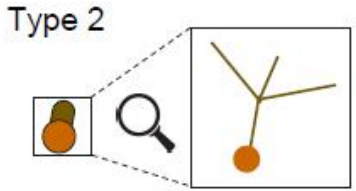


- Nb of attachment legs (1/2/3) & chemical function
- R chain length / backbone structure
- R chain functionality (-CF2-, -CH2-, …)
- More exotic pods (di-pods for HT applications)

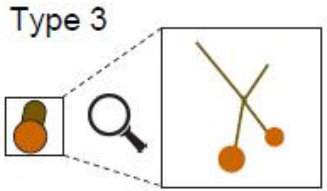
➔ **Highly combinatorial problem ➔ need a screening tool**



- Long and narrow tail
- 3 bonding sites



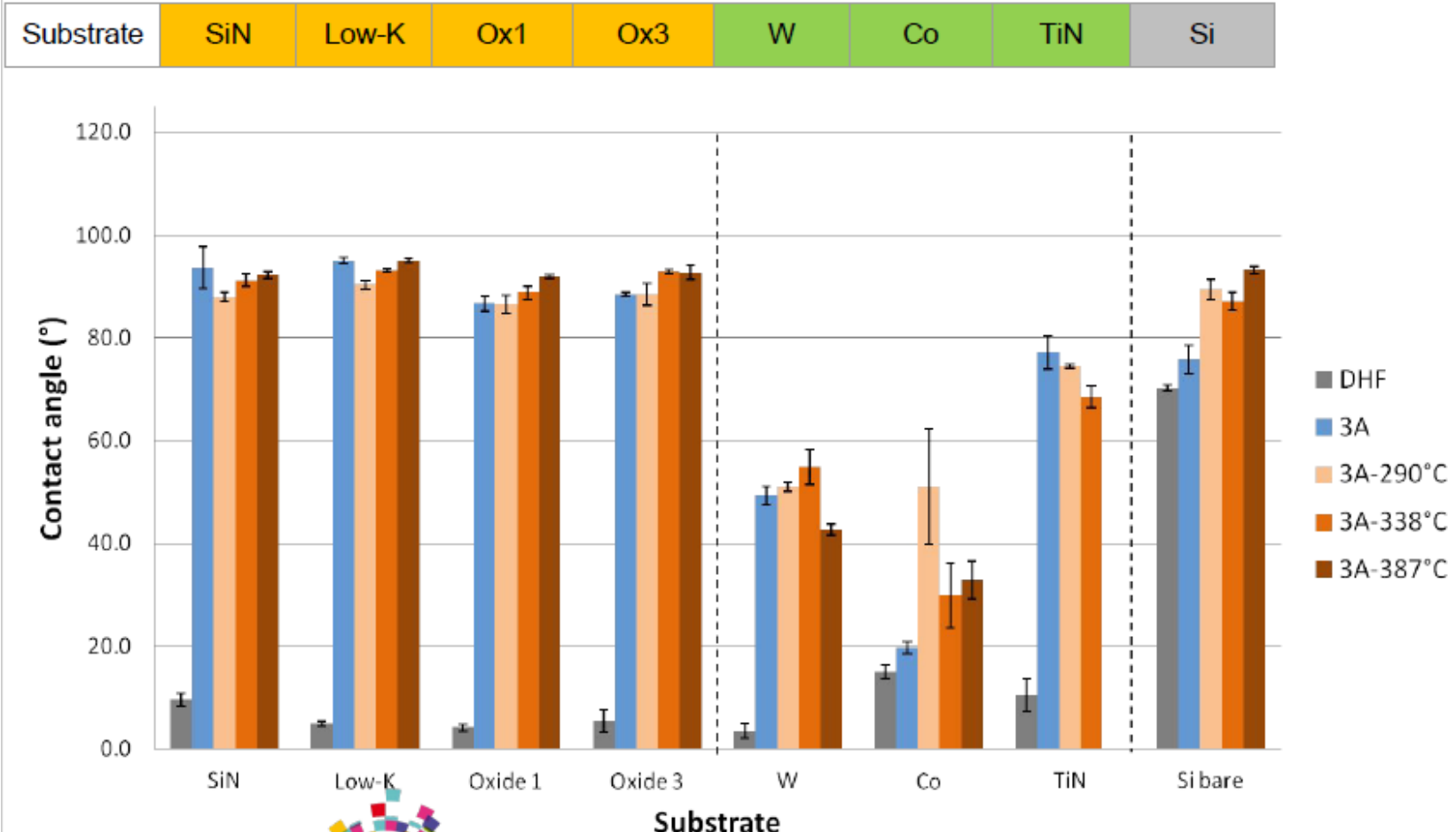
- Short and wide tail
- 1 bonding site



- Short and narrow tail
- 2 bonding sites

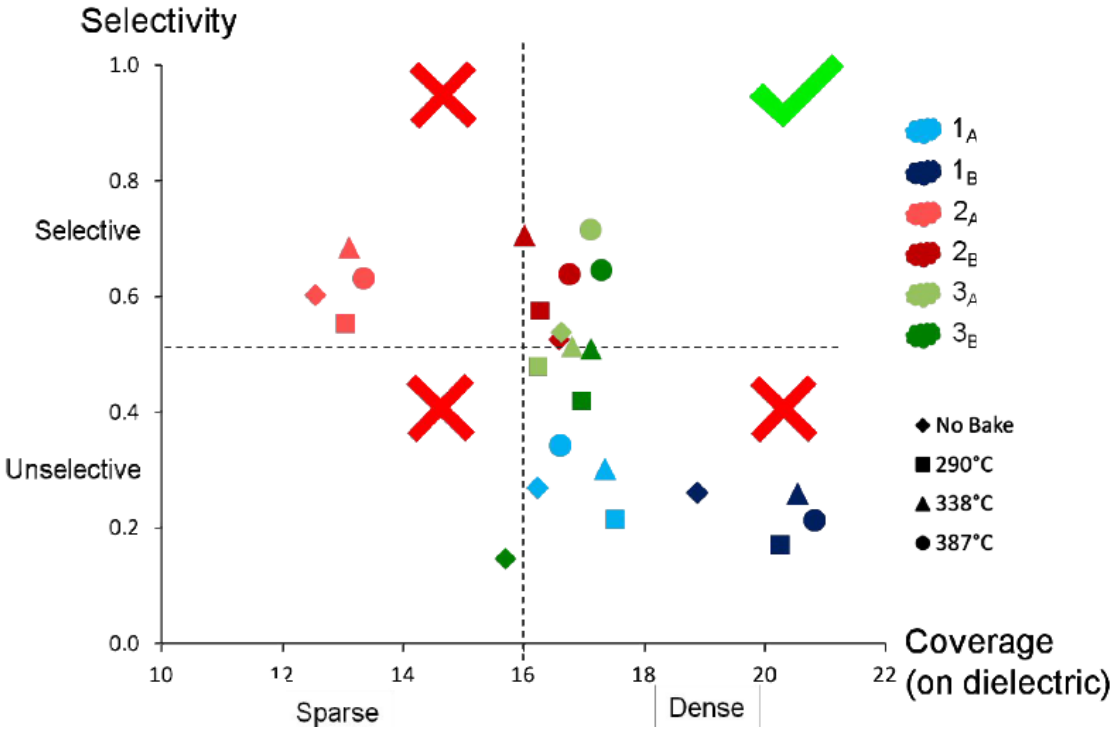
Screening Results example

Design small.
Think big



Screening Results

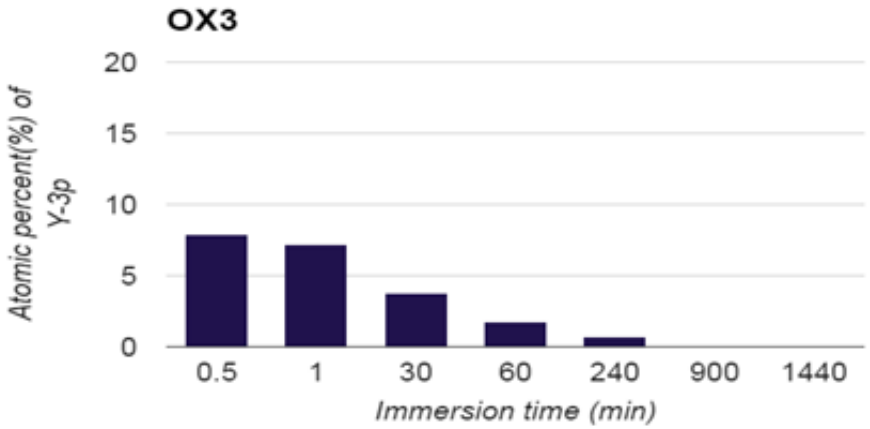
Design small.
Think big



CREATING CUSTOMER VALUE

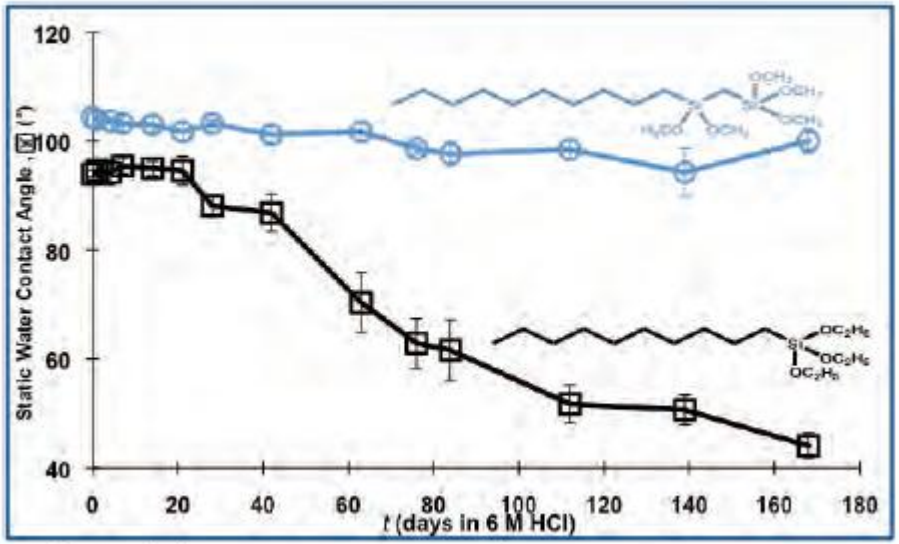
Challenges

- **Metrology of early « nucleation » (<< DL of XPS)**
- **Preferential appearance of defects at sharp edges**
- **Effect of SAM dispense method and exposure (additional variable)**



Chemistry for Dipodal SAMs

Dipodal Silane Hydrolutic Stability compared to conventional silane

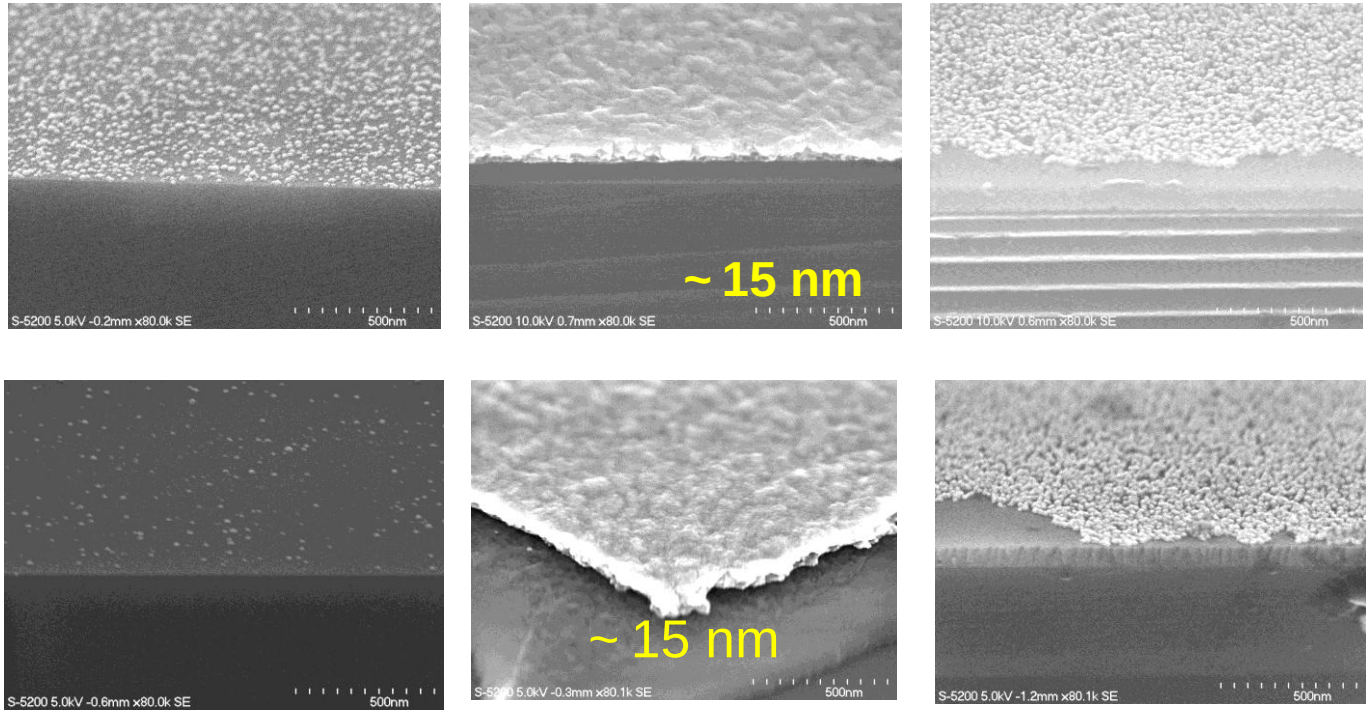


B. Arkles, et al. Chemistry - A European Journal, 2014, 20, 9442.

Enhanced selectivity CVD: RuCVD

Design small.
Think big

Si | **Pt** | **SiO2**



CREATING CUSTOMER VALUE

Metal Oxide Dry Etch Back (Thermal, continuous)

Design small.
Think big

(A/sec)

F-based	150◦C	200◦C	300◦C	350◦C	400◦C	425◦C
Nb_2O_5	13.5	90.0	185	>330	>330	>330
Ta_2O_5	0	67.7	247	>283	>283	>287
ZrO_2	0	0	0.46	7.5	~370	>370
HfO_2	0	0	0	1.9	14.7	E/D
TiO_2	0	1.7	153	>315	>315	>315
Al_2O_3	0	0	0	0	0	0
SiO_2	0	0	0	0	0	0
TiN	0	Etched	Etched	Etched	Etched	Etched
TaN	0	0	Etched/Changed	Etched/Changed	Etched/Changed	Etched/Changed
SiN	-	-	0.46	3.8	5.1	12.8

Highlights

- **Energetic & Toxic materials – Stay safe**
- **Don’t stop material innovation, but consider scaleability early**
- **Revisit old data / « failed experiments »**
- **Defectivity & impurity effects : just the beginning**

THANK YOU