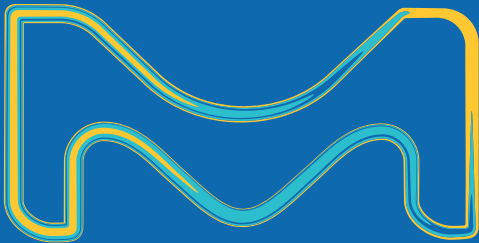


Leakage variation with Aspect Ratio in ALD High- κ ZrO_2 Dielectrics

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AA-TuP70 Abstract 2231

2020-06-30
ALD 2020

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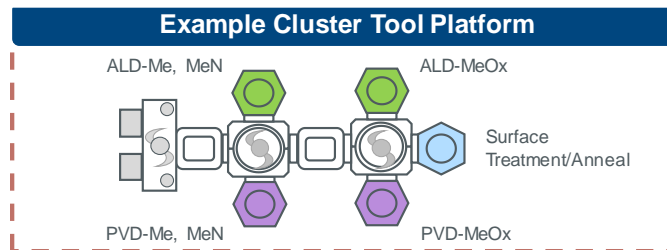
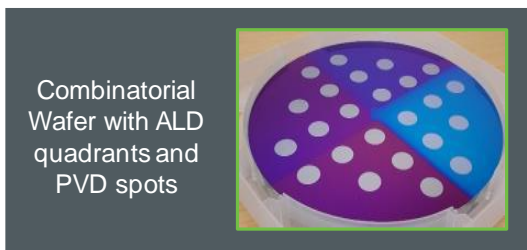
**EMD
PERFORMANCE
MATERIALS**

high-throughput experimentation and expertise for faster MEMORY innovation at intermolecular

World's largest high-throughput thin-film facility



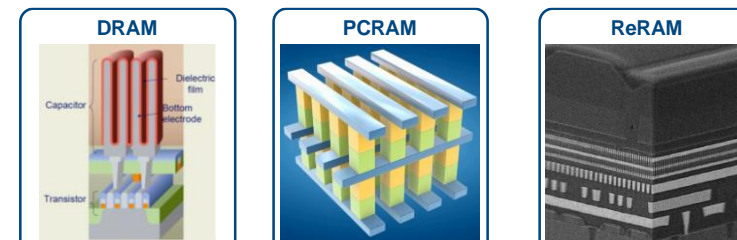
- Facility highlights
- (1) 45,000 sf lab space
 - (2) 11 cluster tool platforms
 - (3) 19 PVD chambers
 - (4) 15 ALD chamber
 - (5) 85 people
 - (6) ~1/2 with advanced degree



Advanced film characterization (XRF, XRR, XRD, XPS, VASE, etc.) and world-class etest capabilities

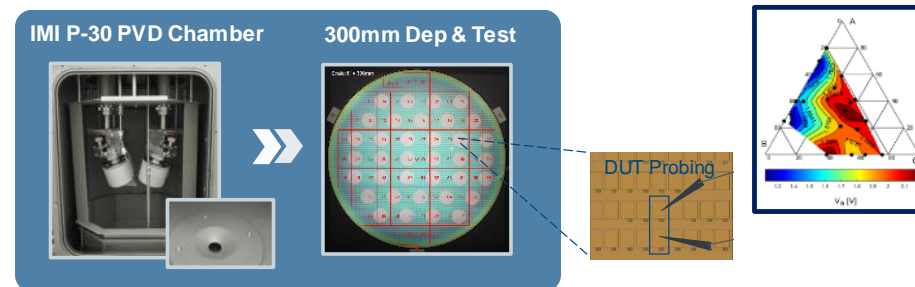


10+ years experience in memory



Focus	Capacitor	OTS Selector	ReRAM cell
Materials	High-K & High WF	Chalcogenides	Switching, Enabler, Contacts
Processes	ALD, PVD, anneal	ALD, PVD, anneal	ALD, PVD, anneal
Device	MIMCAP, customer	MIMCAP, customer	MIMCAP, customer
Main Metrics	Cap: J - EOT	OTS: J, V_{th} , V_{hold}	R_{On}/R_{Off} , V_{sw} , I_{sw}

Successfully screened 1000's of OTS, MSM, MIEC and TMO selector compositions

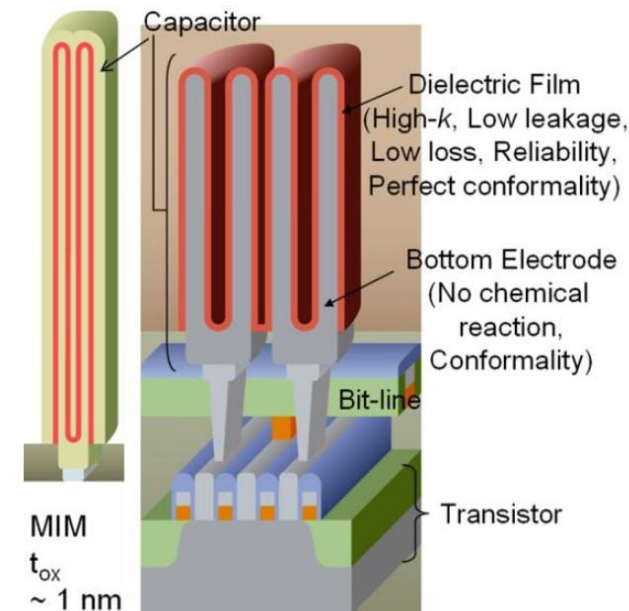


Denser Memory Enabled by ALD

Challenge: Scaling DRAM capacitors

- Denser packing of memory elements → higher storage density, lower voltage operation
- Large capacitor areas by “folded up” 3D geometry
 - Ultrathin dielectric sandwiched between electrodes

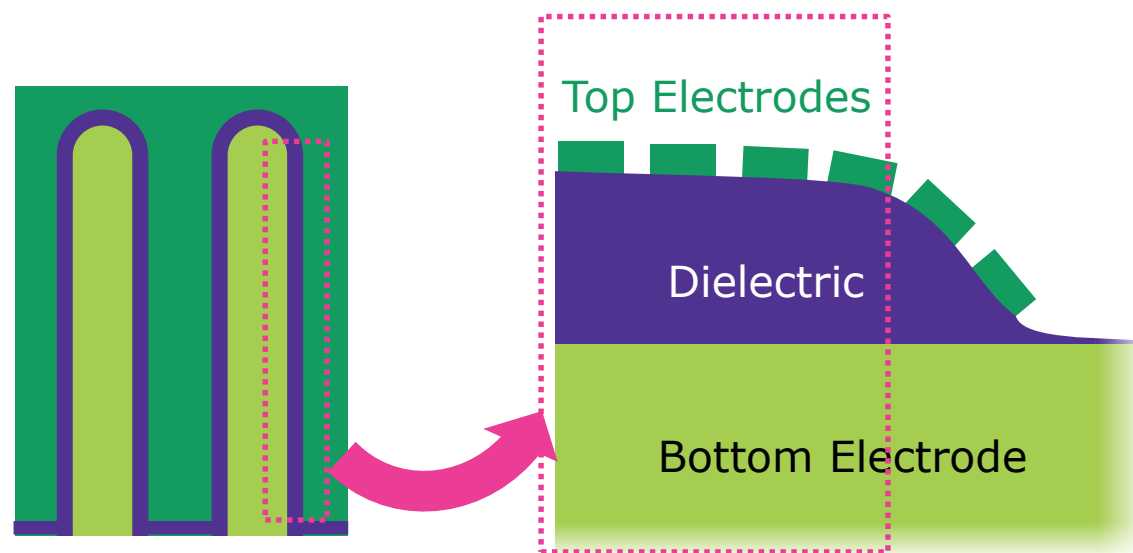
$$C = \kappa \epsilon_0 \frac{A}{d}$$



Conformal ALD high- κ dielectrics with low leakage

- High aspect ratio (HAR) ALD
- Conformality limits device density
- *Changes in material properties with trench depth?*

Our approach to investigating HAR-ALD:

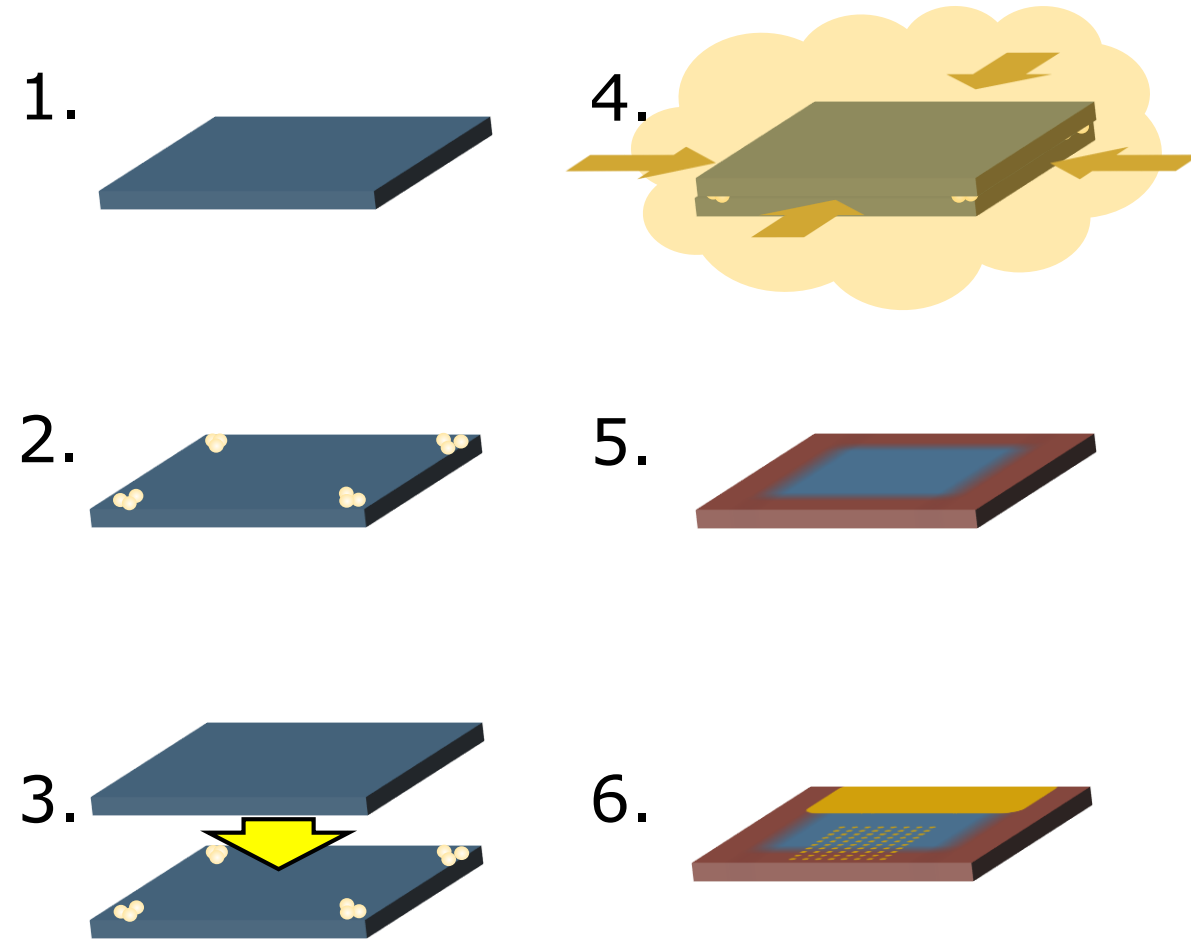


HAR Test Vehicle by Intermolecular

U.S. patent application 16/714,934

Projects nanoscale HAR phenomena onto the >100 μm scale for study by standard metrology.

1. Start with a flat coupon (typically 44mm).
2. Apply monodisperse micro-beads to corners.
3. Place a flat cover coupon.
4. Load into reactor and perform ALD.
5. Remove cover and beads. Perform metrology along film gradient.
6. Perform post-processing and deposit any additional layers. Add top contacts for electrical testing.



Trench geometry can be related to circular vias using the **equivalent aspect ratio** (EAR):*

*Cremers *et al.*, *Appl. Phys. Rev.* **6** (2019) 021302

$$AR_{trench} = L/w \quad L : \text{Distance from edge of coupon}$$

$$EAR_{via} = L/(2w) \quad w : \text{Spacing between coupons}$$

Test vehicle useful for EAR_{via} up to ~400

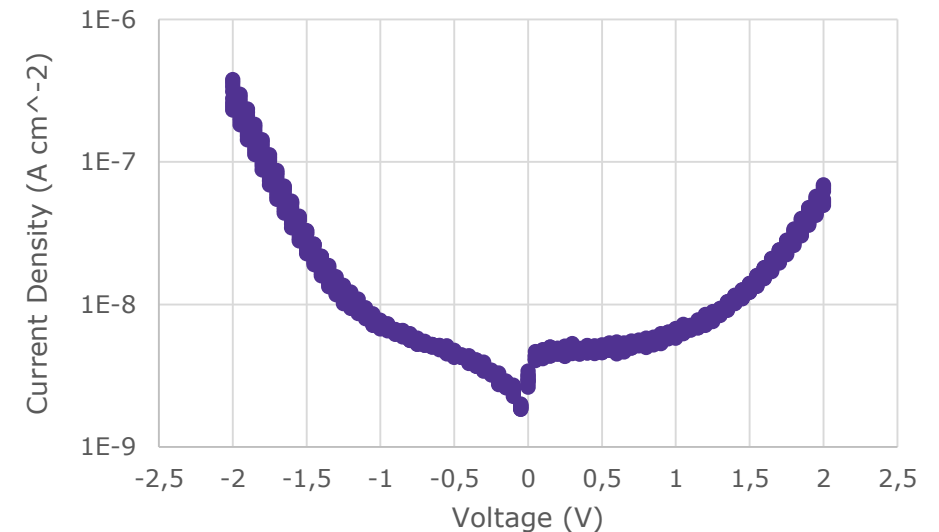


MIMcap Model Capacitor

- Blanket PVD TiN (bottom electrode)
- ALD ZrO₂ (dielectric)
 - *80 cycles amide-type Zr precursor / 4% O₃*
 - *250 °C, 1 Torr*
- Shadow masked PVD TiN (top electrodes)
 - *254 μm dia.*
- Post-metal anneal (450 °C in N₂, 5 min.)

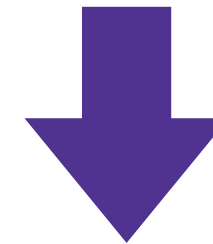
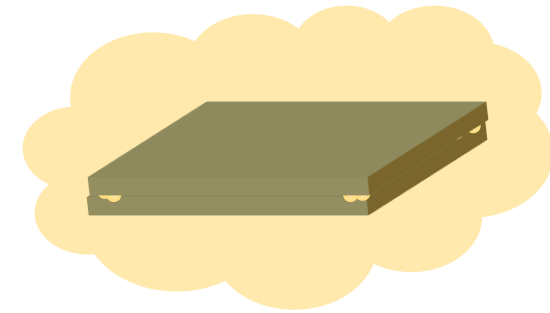
Good capacitor performance

- Low leakage current
- $k = 24.5(4)$ (0 V capacitance measurement)



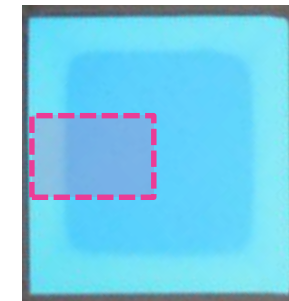
MIMcap Model DRAM Capacitors by HAR-ALD

- Blanket PVD TiN (bottom electrode)
- HAR-ALD ZrO₂ (dielectric)
 - 80 cycles amide-type Zr precursor / 4% O₃
 - 250 °C, 1 Torr
 - SiO₂ microbead spacer diameter: $w = 50 \mu\text{m}$
 - Reactant Knudsen number: $\lambda/w \approx 0.7$
 - *Transitional flow (not molecular flow)*
- Shadow masked PVD TiN (top electrodes)
 - 203 μm dia.
- Post-metal anneal (450 °C in N₂, 5 min.)



*Representative
HAR-ALD sample
appearance*

*Top contact array
will be deposited in
dashed region*

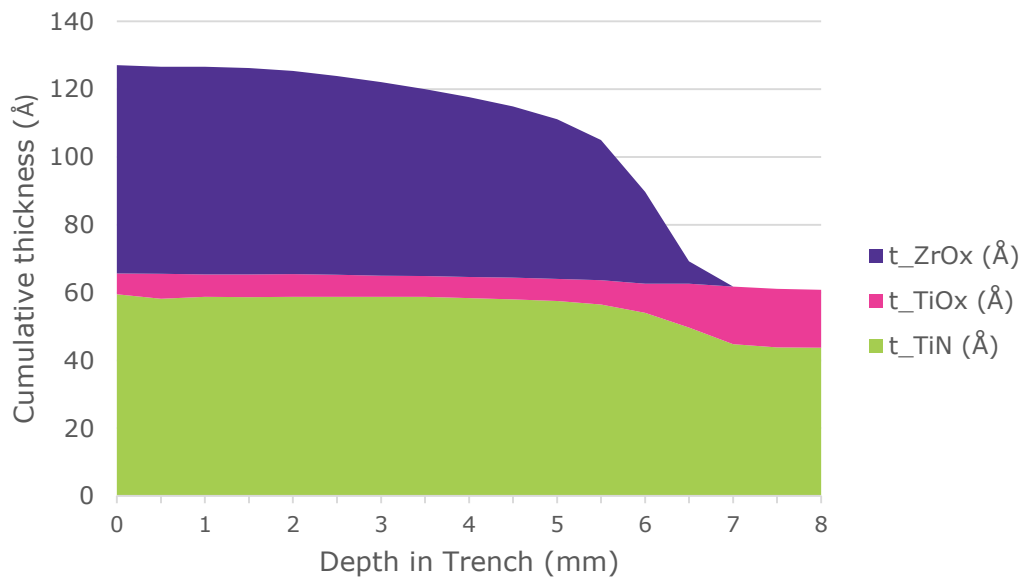
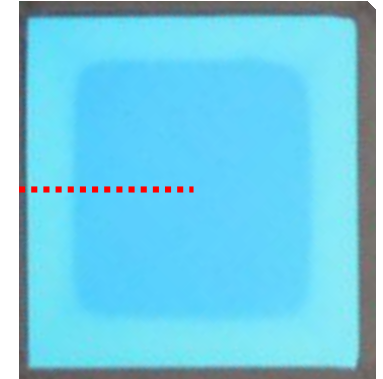


MIMcap Model DRAM Capacitors by HAR-ALD

Film thickness profile measured by ellipsometry

- Poor fit when assuming a $\text{SiO}_x/\text{TiN}/\text{ZrO}_x$ stack
- Better fits when assuming the TiN electrode surface oxidizes to TiO_x
 - Few-Å TiO_x layer below ZrO_2
 - Thickens toward end of the ZrO_2 film as ozone migrates deeper into the HAR trench

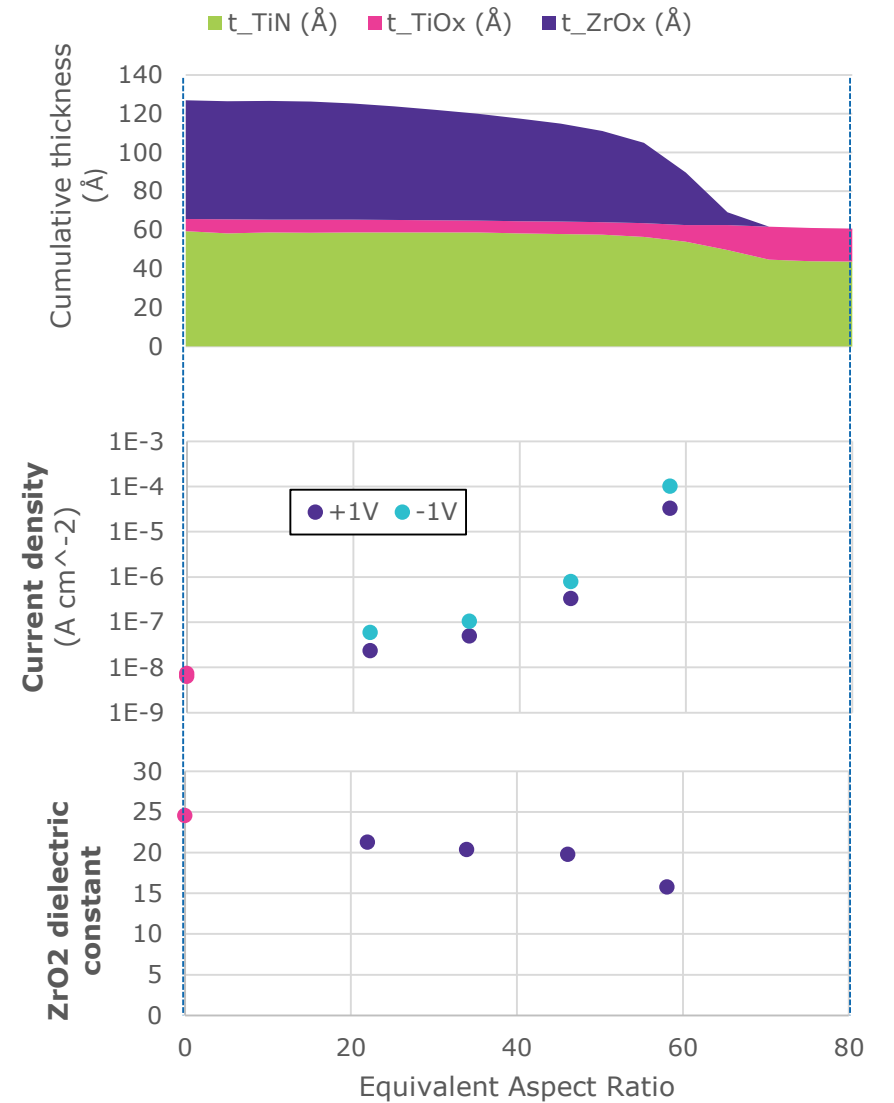
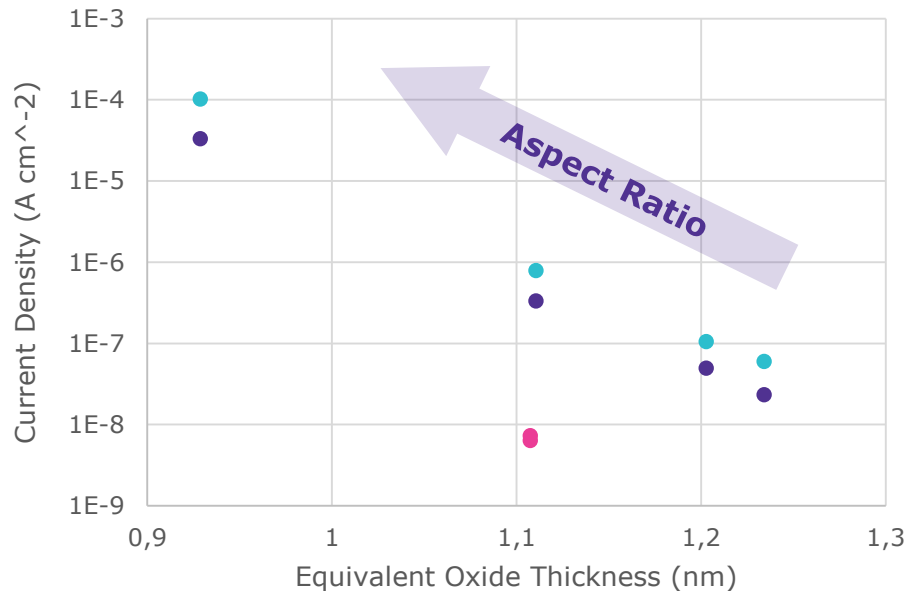
Representative HAR-ALD sample appearance and ellipsometer line scan location:



MIMcap Performance vs. Aspect Ratio

- Electrical testing shows changes in electrical properties with equivalent aspect ratio:
 - Higher leakage with depth, as expected for a thinning film
 - Lower ZrO_2 dielectric constant with depth

→ Significantly worse performance of HAR-ALD ZrO_2 vs. blanket ALD ZrO_2



HAR-ALD Platform for Mechanism Understanding

Remaining Questions:

- What causes higher leakage for HAR-ALD ZrO_2 vs. blanket ZrO_2 ?
- How does reaction chemistry change with depth into the trench?
 - Macroscale HAR-ALD platform enables metrology (XPS, XRD, synchrotron techniques)
- How can the process be modified for more consistent performance?

Further Applications for HAR-ALD:

- 3D NAND Flash memory is the leading non-volatile memory
 - Memory cells are stacked: bit density grows by adding layers/tiers
- Phase-change memory (PCM) density will improve with 3D architectures enabled by ALD*

*Cheng *et al.*, *JVSTA* **37** (2019) 020907

*Adinolfi *et al.*, *ACS Nano* **13** (2019) 10440

James and Choe, "TechInsights memory technology update", *IEDM 2018*



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