

ALD Capabilities at MRC UT Austin

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ALD reactors at MRC – Savannah-100

Savannah-100 Cambridge ALD (2007)

- Precursors – as Nov 2012

0= water 1= trimethyl Al (TMA). RT

2= MgO- amidinate (2-28-10) 3= BeO (Liquid 2-6-12) Patent 4= tetrakis(dimethylamino) Hf TDMHf. 115C. - 0.97A/cycle

5= ammonia gas

- N₂ carrier



ALD reactors at MRC – Savannah-xxx

Savannah Cambridge ALD (2009)

0= water 1= Al –

0.92A/cycle 2= Hf 3= La -150C

Pure La_2O_3 absorbs moisture quickly, so LaAlO is preferred.

4= Zr. 73C - 0.9A/cycle ZrO_2 did not form good interface with III-V. ZrAlO was preferred instead.

5= ammonia

- N_2 carrier



ALD reactors at MRC - Fiji

Fiji ALD Cambridge (2010)

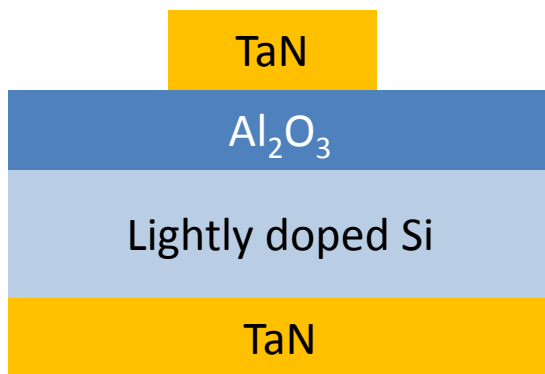
- Precursors:
0= water 1= Al 2= Ti (TDMAT) - 75C
3= Hafnium (TDMHf) -115C
4= Empty. (Set up for low vapor pressure precursor, w/ extra carrier gas input)
- ICP RF plasma assisted source gases: Ar, N₂, H₂, NH₃, O₂
- Ozone generator
- Ar carrier



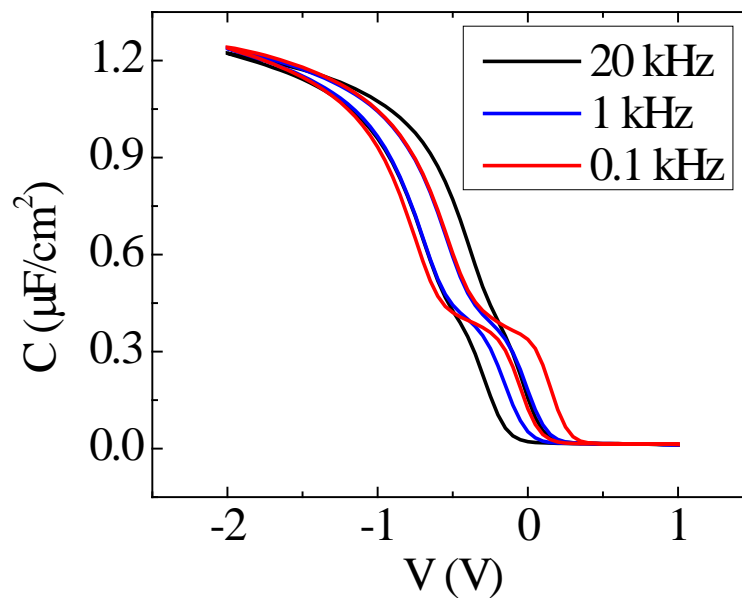
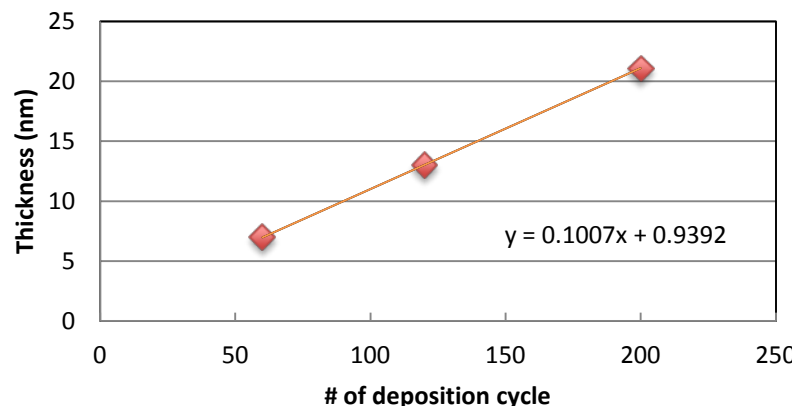
Al₂O₃ on Si

- Precursors : H₂O/TMA
- Chamber temperature: 250/200 °C
- Substrate: lightly doped p-Si (10-20 Ω·cm). HF cleaned

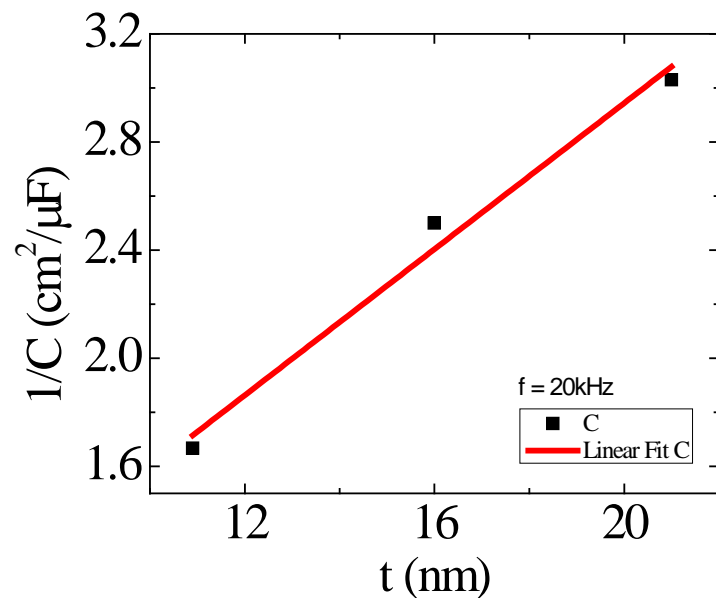
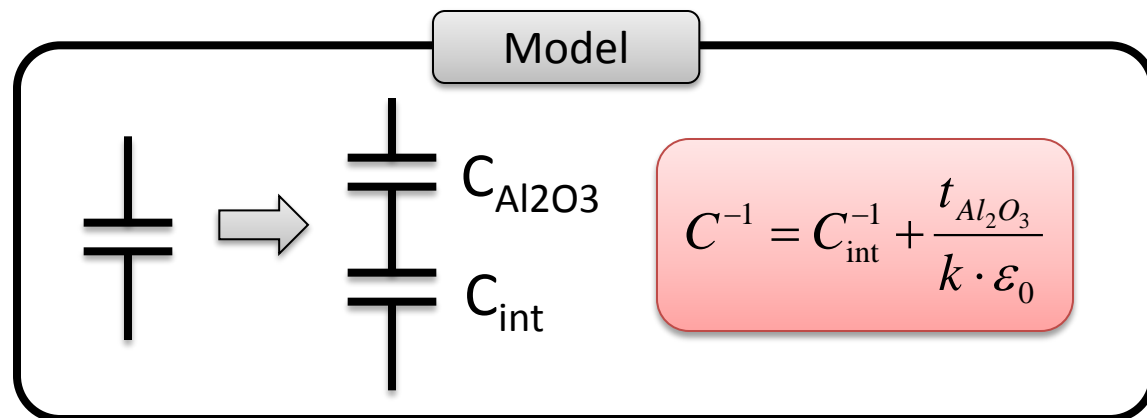
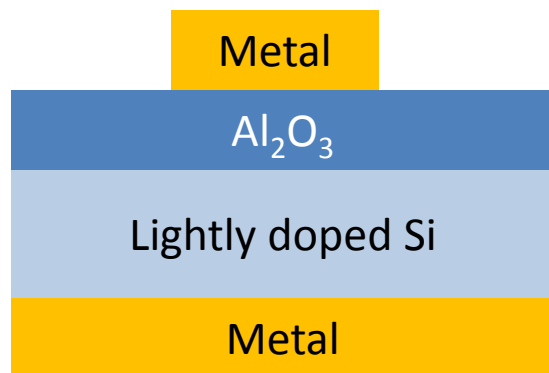
MOS test structure to characterize the Al₂O₃ deposited by ALD



ALD Savannah 250C - Al₂O₃

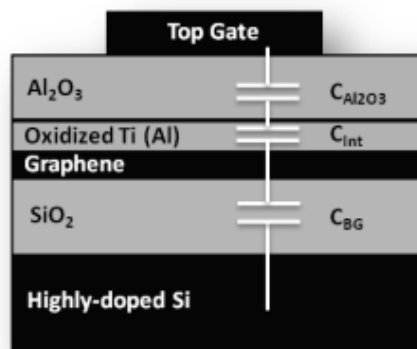
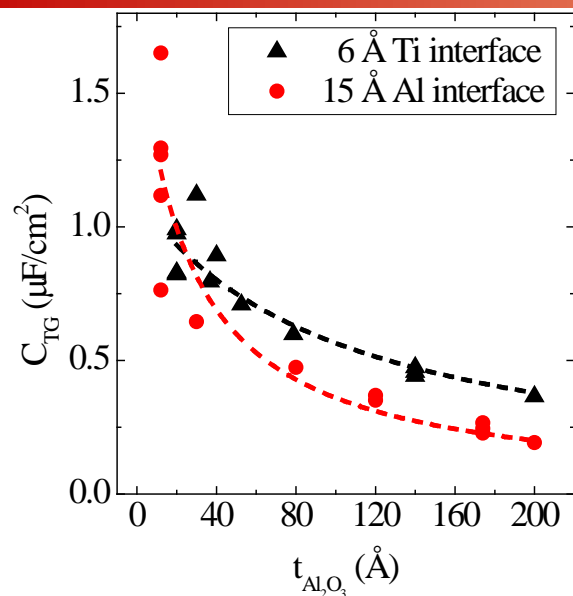


Al₂O₃ on Si: Dielectric Constant (k)

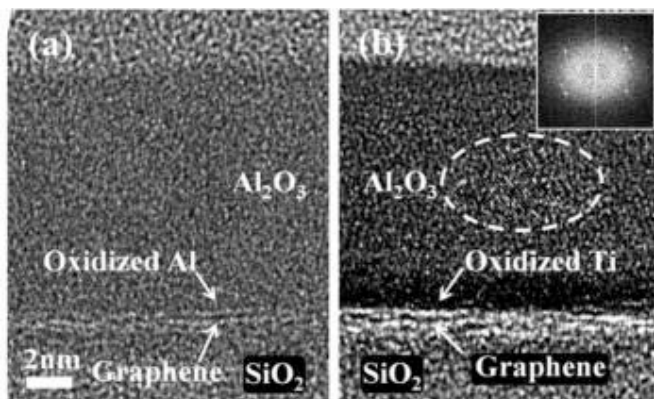
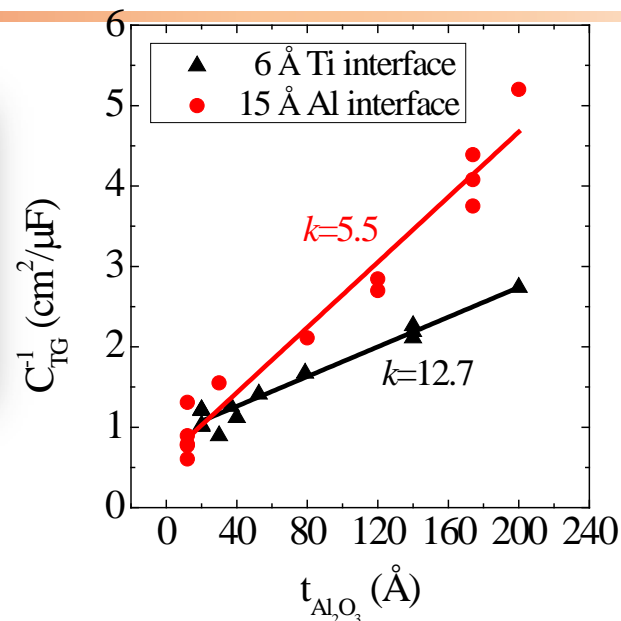


Parameter	Value
Dielectric constant (k)	8.4
$C_{\text{it}} \text{ (}\mu\text{F/cm}^2\text{)}$	4.14

Al₂O₃ on Graphene



$$C_{TG}^{-1} = C_{int}^{-1} + \frac{t_{Al_2O_3}}{k \cdot \epsilon_0}$$



B. Fallahazad *et al*, Appl. Phys. Lett. **100**, 093112 (2012);

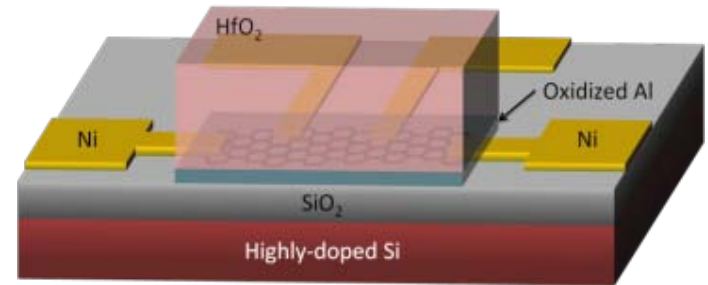
- A nucleation layer is required for ALD of dielectrics on graphene
- The nucleation layer has a significant impact on the dielectric constant and morphology of the subsequently grown ALD dielectric

HfO₂ on Graphene

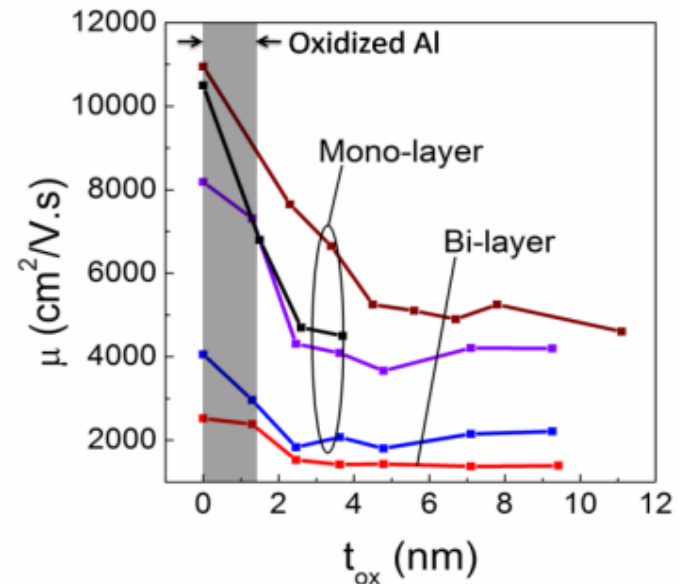
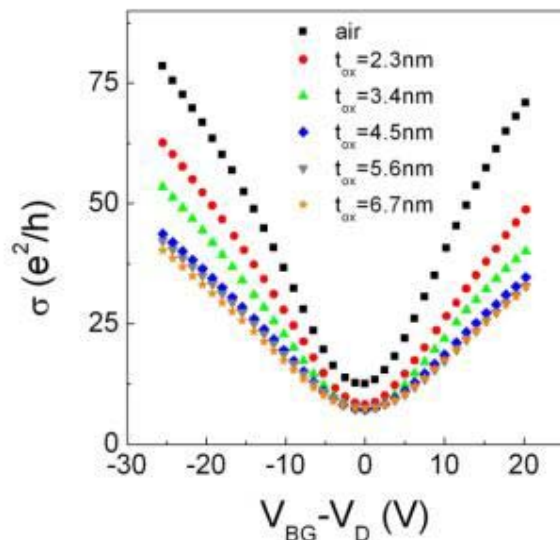
TEMAH: Tetrakis(EthylMethylamino)Hafnium

- Top dielectric stack

- Interface: Oxidized Al (15Å)
- Precursor: H₂O/TEMAH
- Chamber Temperature: 200/200 °C



Dielectric Constant (k): 16

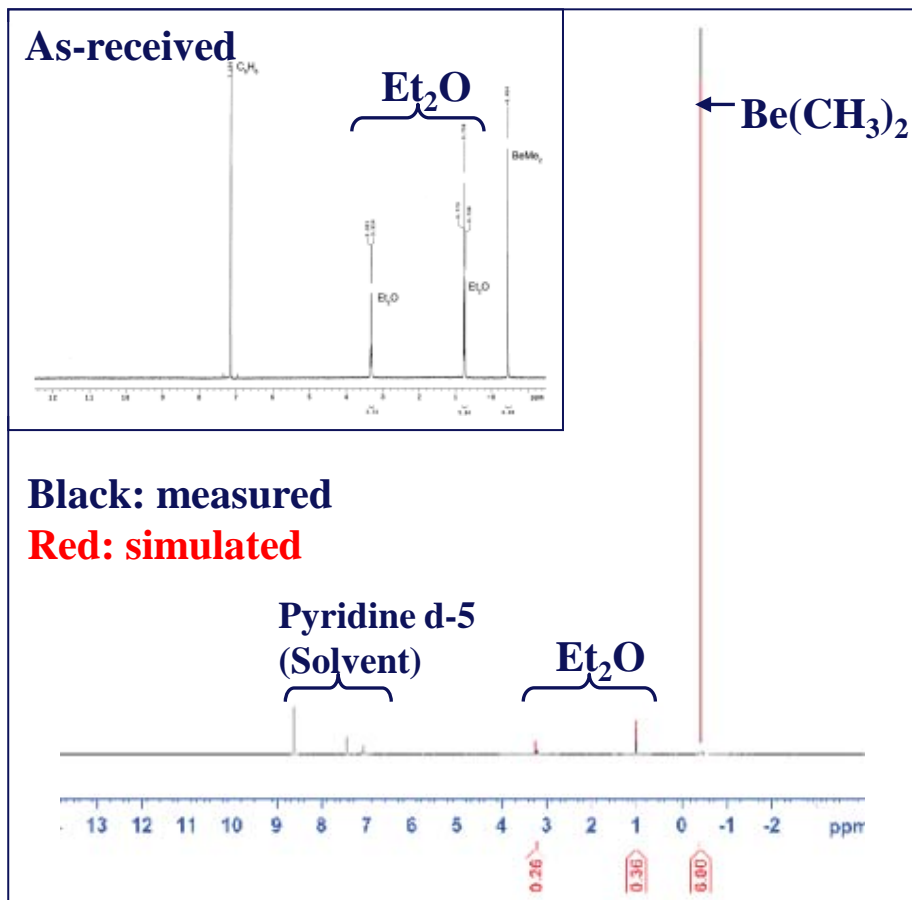


ALD of AlN?

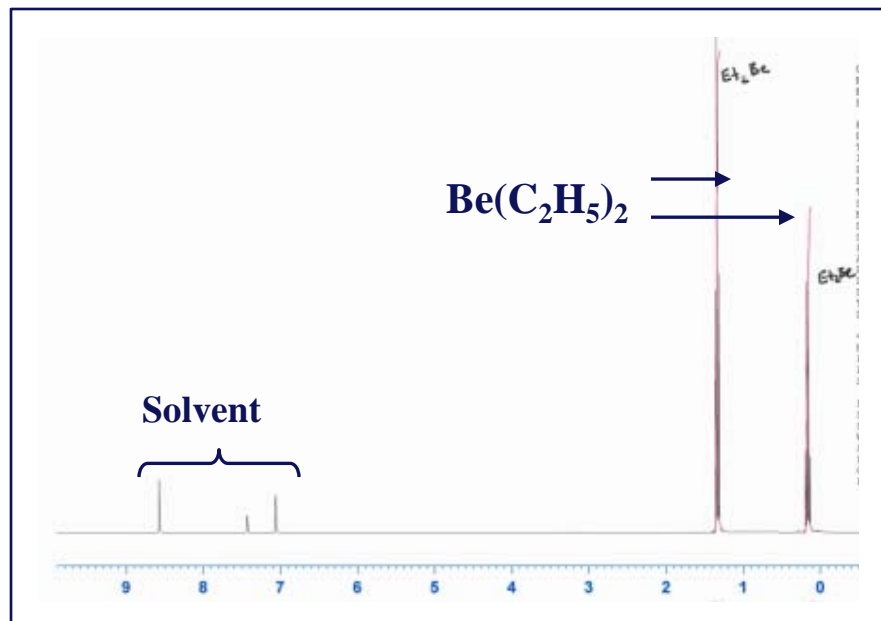
- Precursors: TDMAA/Ammonia
- Temperature: 200-300 C
- Deposition rate: very low (less than 0.1Å /cycle)
- Deposited film very leaky

TDMAA: Tris(DimEthylAmido)Aluminum

Dimethylberyllium (solid)



Diethylberyllium (liquid)

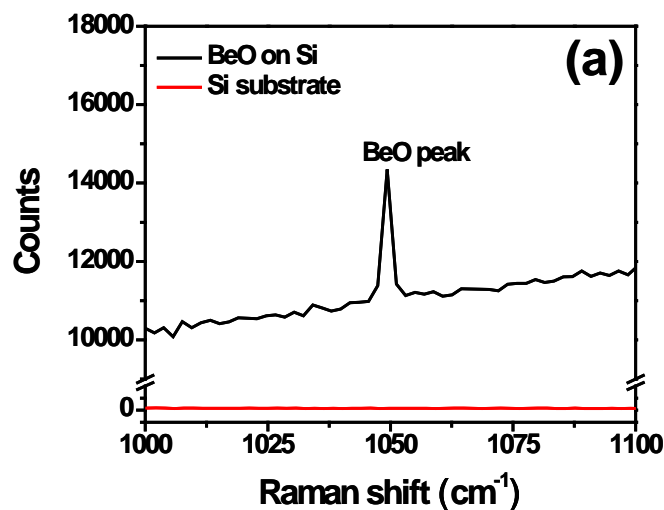


Grignard metathesis:



Ether (solvent): $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
(very stable liquid)

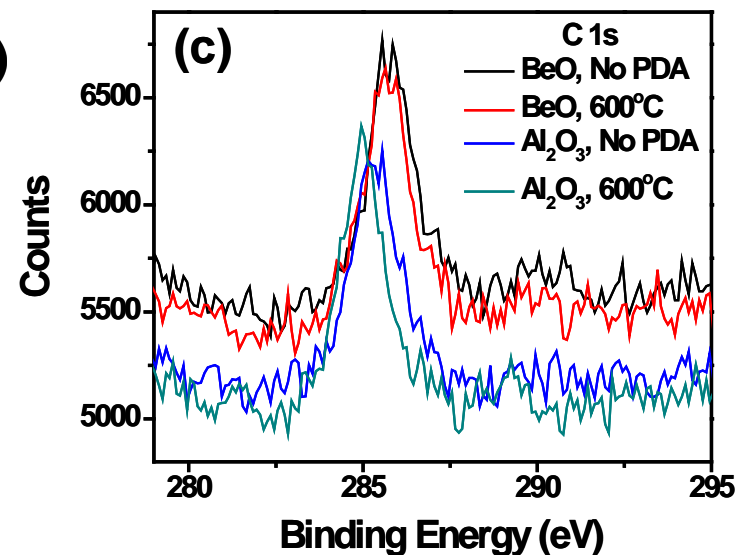
- ❑ ALD BeO precursors were successfully synthesized.
- ❑ After multiple rounds of sublimation, ether impurities were much reduced.



Be 1s

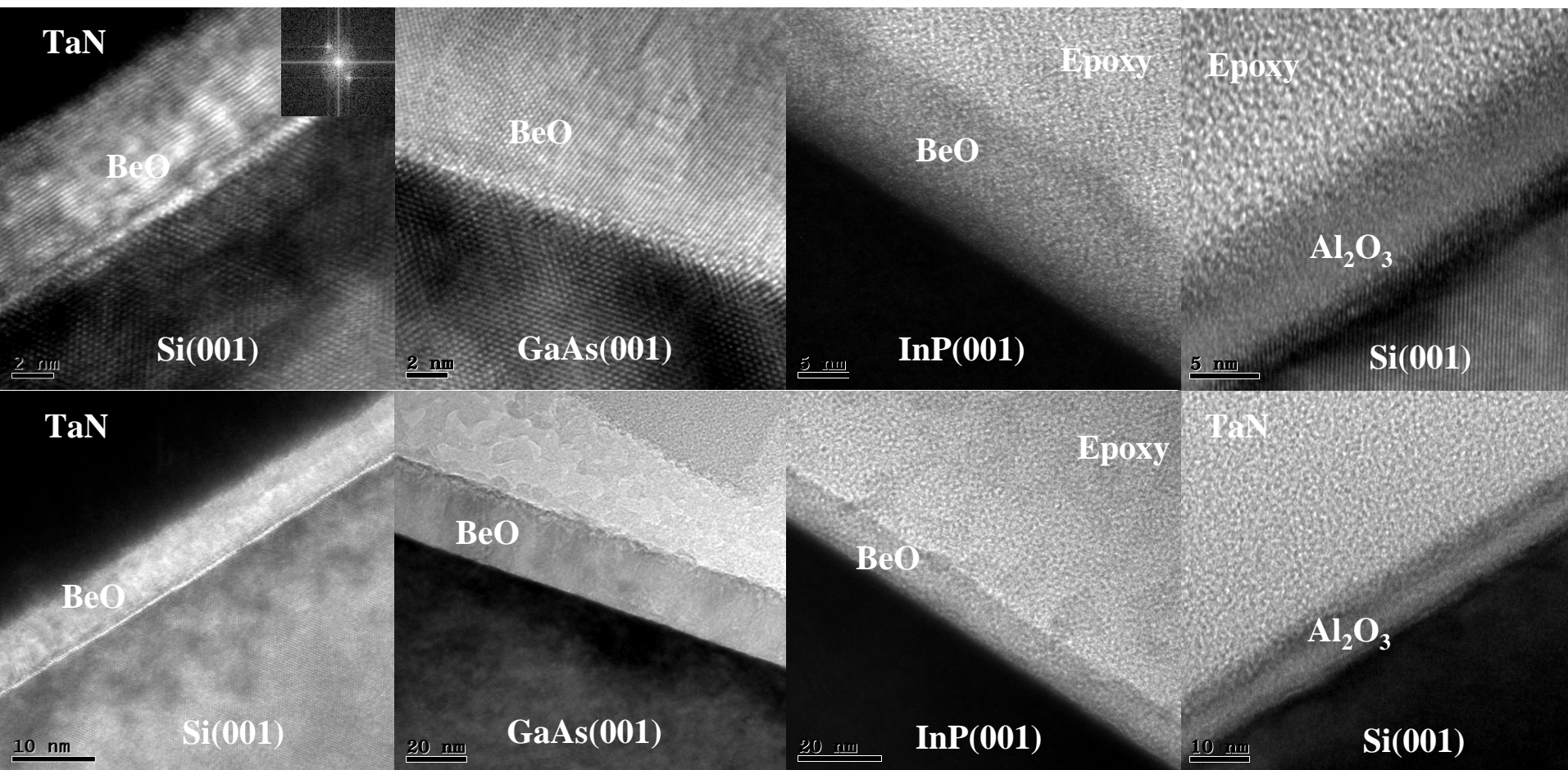
Be-O →

(b)



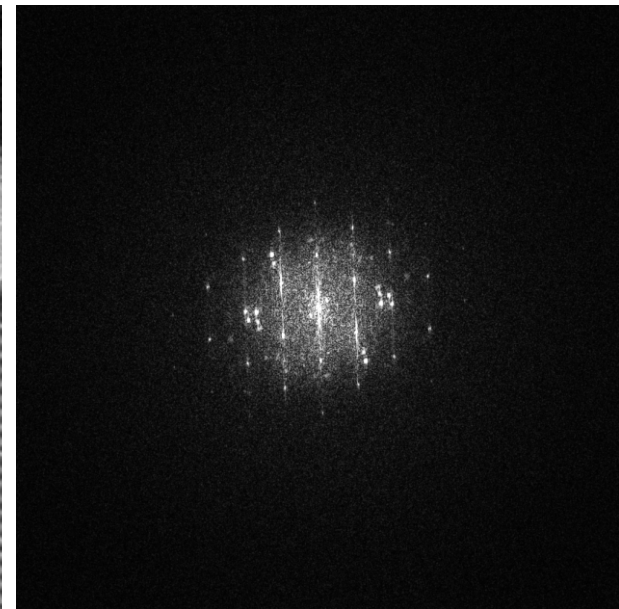
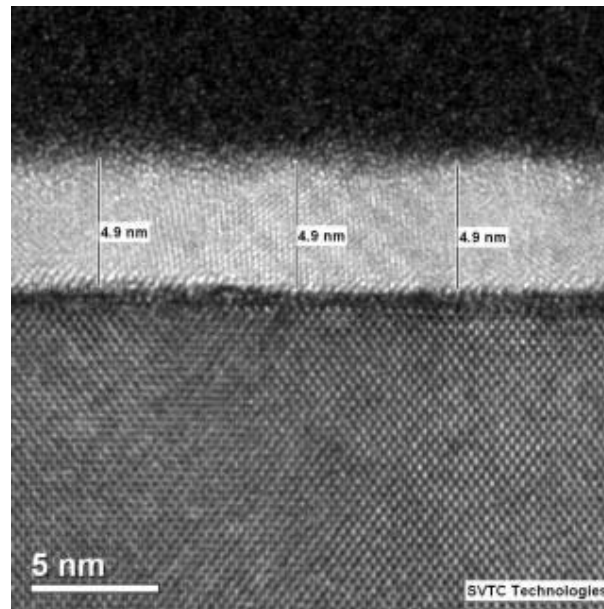
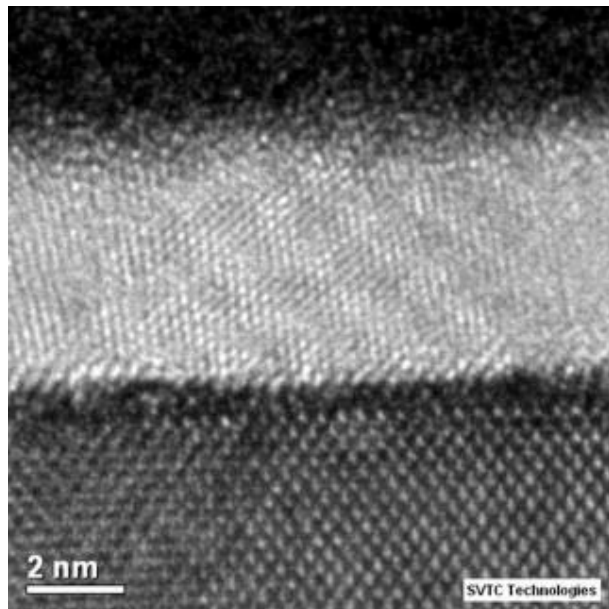
(a) Raman spectrum, (b) XPS of Be 1s, (c) XPS of C 1s.

- ❑ From Raman and XPS, ALD BeO film is successfully deposited.
- ❑ ALD BeO shows slightly higher carbon impurities due to low quality of synthesis.



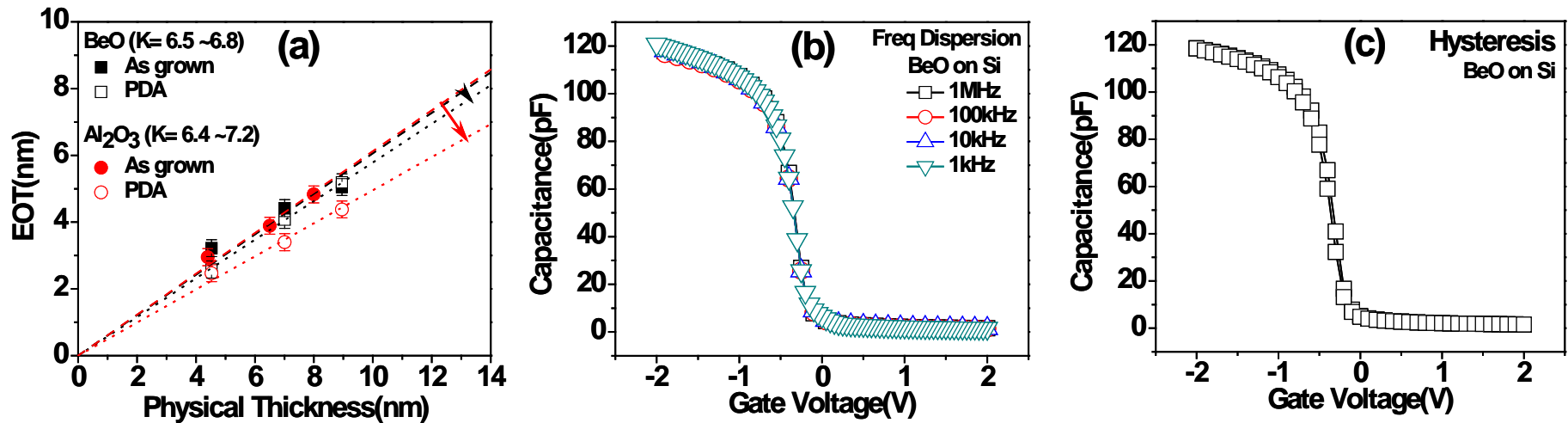
- ❑ As-grown ALD BeO on Si and GaAs shows high crystallinity.
- ❑ ALD BeO shows a relatively distinct interface.

ALD BeO on Ge substrate



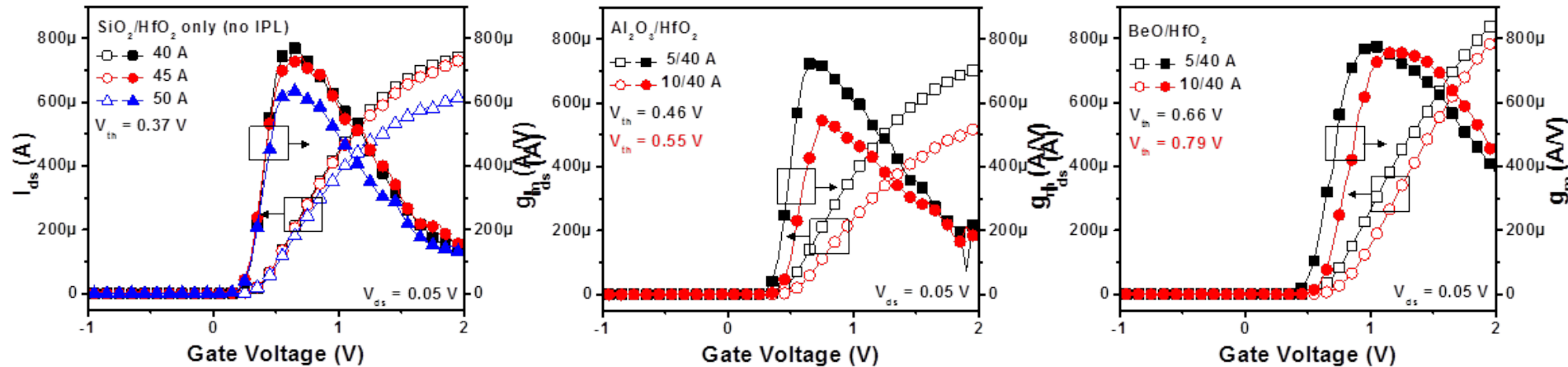
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TaN/BeO/p-Si (MOS) structure



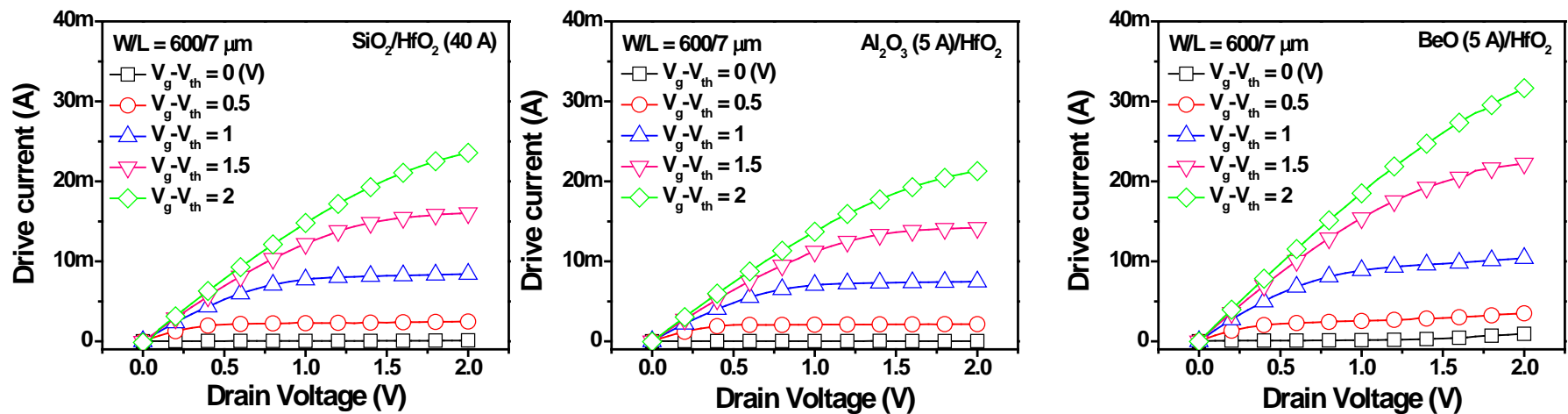
(a) Physical thickness versus EOT without/with PDA, (b) Frequency dispersion and (c) Hysteresis.

- ALD BeO shows negligible frequency dispersion and hysteresis.
- The dielectric constants of the BeO film are $k = 6.5$ before annealing and $k = 6.8$ after annealing.
- The Al₂O₃ dielectric constant changes significantly by annealing, from $k = 6.4$ to 7.2 .



NMOSFETs I_d - V_g characteristics of SiO₂/HfO₂, Al₂O₃/HfO₂, and BeO/HfO₂ gate stacks.

- ❑ With the slightly lower EOT, the BeO/HfO₂ stack exhibits more positive V_{th} (0.66 V), higher drive current at $V_g = 2$ V
- ❑ From literature, interface charge (including interface trapped charge and interface fixed charge) is “+” value. So BeO IPL may reduce the interface charge and result in a higher threshold voltage.



I_d - V_d characteristics of SiO₂/HfO₂, Al₂O₃/HfO₂ and BeO/HfO₂ gate stacks.

□ BeO/HfO₂ gate stack shows significant increased drive current compared to SiO₂/HfO₂ and Al₂O₃/HfO₂ gate stacks.

Conclusions

BeO vs Al₂O₃ vs HfO₂

	BeO	Al ₂ O ₃	HfO ₂
1. Thermal stability	Better	Middle	Poor
2. E _g & ΔE _c	Larger (10.6eV, 2.3eV)	(8.5eV, <1.9eV)	Lower
3. Diffusion barrier	Better	Middle	Poor
4. Self-cleaning effect	Better	Middle	Poor
5. Structural defects	lower	middle	Larger
6. Orbitals	No filled “P” orbital	“P” orbital	“d” orbital
7. Thermal conductivity	High	Poor	Poor

Energy bandgap↑ → Quantum tunneling current↓ → Defect generation↓
 Cation and Anion similar → Stacking fault energy↓ → Intrinsic defects↓
 Temperature ↑ → Phonon scattering ↑ → Thermal conductivity ↓
 Bonding distance ↓ → Orbital splitting ↑ → Energy bandgap↑(10.6eV)
 Bonding distance ↓ → Binding energy ↑ → High melting point