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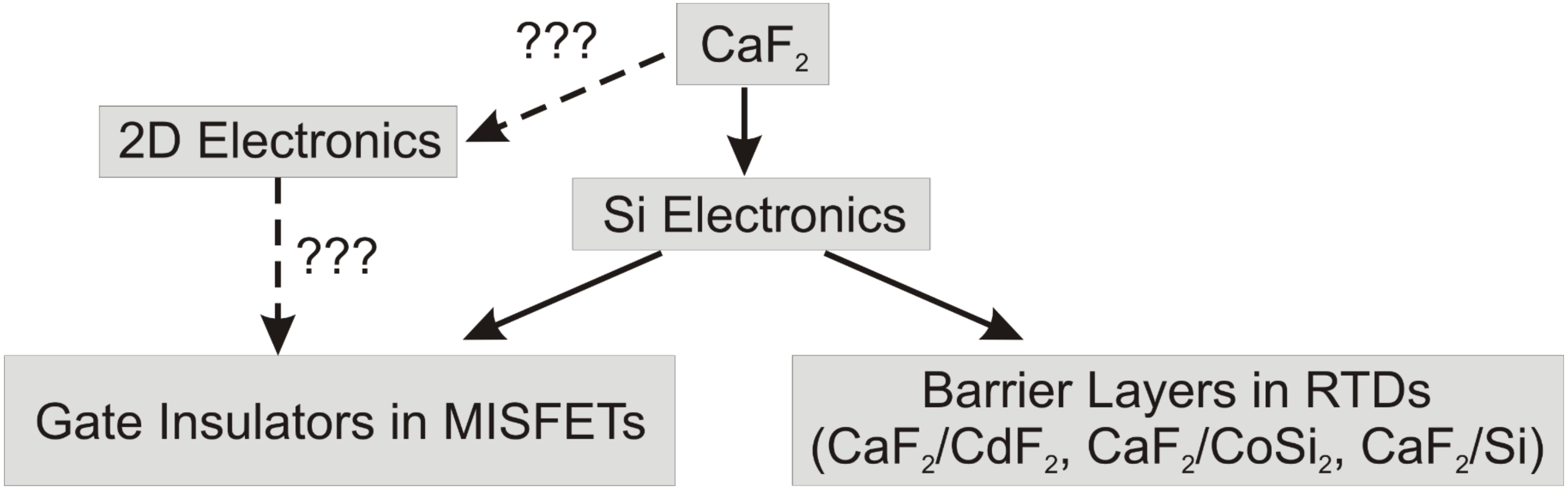
Crystalline Calcium Fluoride: A Record-Thi
Insulator fo ... lectr

Ioffe Institute

Outline

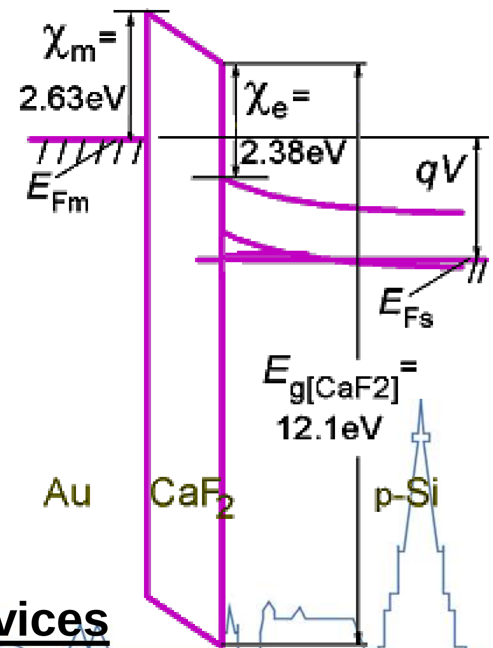
- Introduction: what is CaF_2?
- Growth, Structure and Insulating Properties of Tunnel-Thin (1-2nm) CaF_2 Films
- Ultrathin CaF_2 Films in MoS_2 FETs
- Conclusions
- Outlook

Introduction: What is CaF_2?



Main parameters of CaF_2

- Bandgap width: 12.1 eV
- Conduction band offset with Si: 2.38 eV
- Electron effective mass: $1.0m_0$
- Dielectric constant: 8.43
- Lattice constant: 0.546 nm (0.543 nm for Si) → MBE on Si



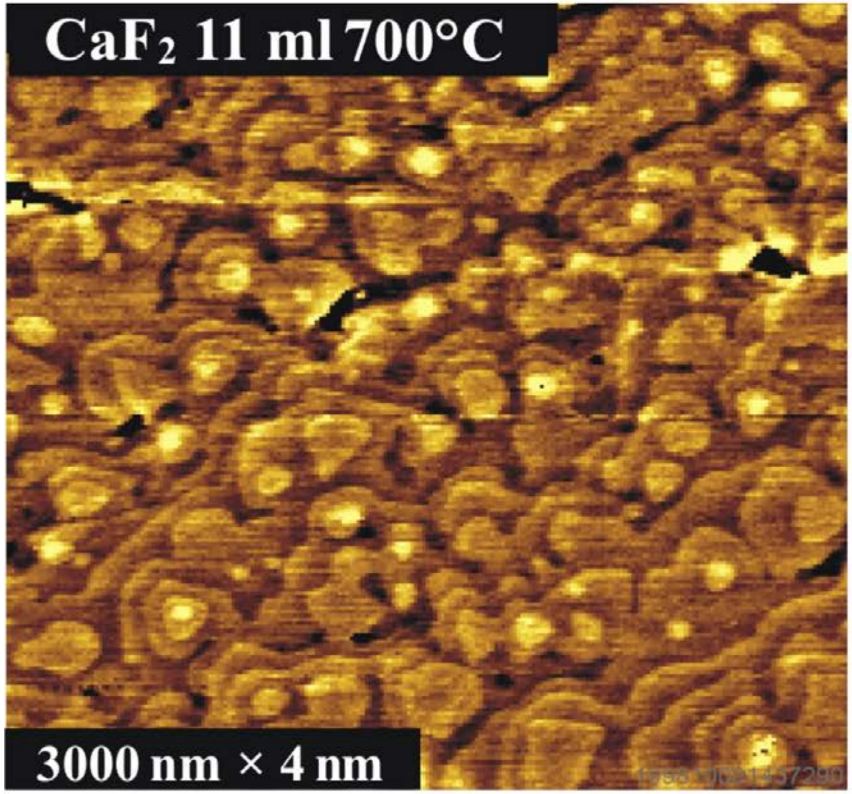
CaF_2 is high-k crystalline material for new electronic devices

Growth, Structure and Insulating Properties of Tunnel-Thin (1-2nm) CaF_2 Films

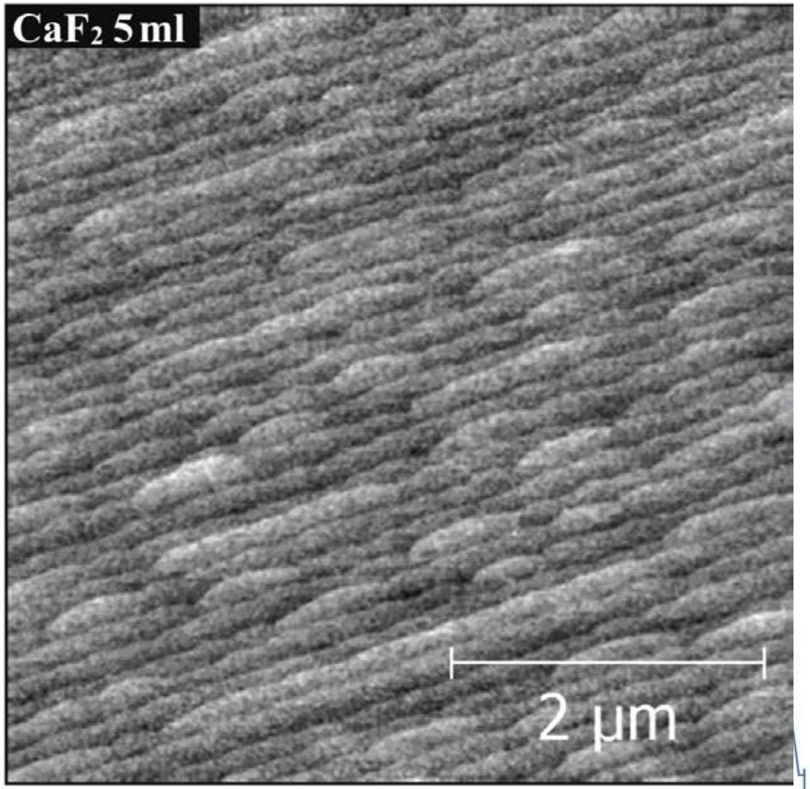
Surface of MBE-Grown CaF_2 Films

- Homogeneous CaF_2 can be grown only on Si(111) with < 10’ misorientation

T = 700°C

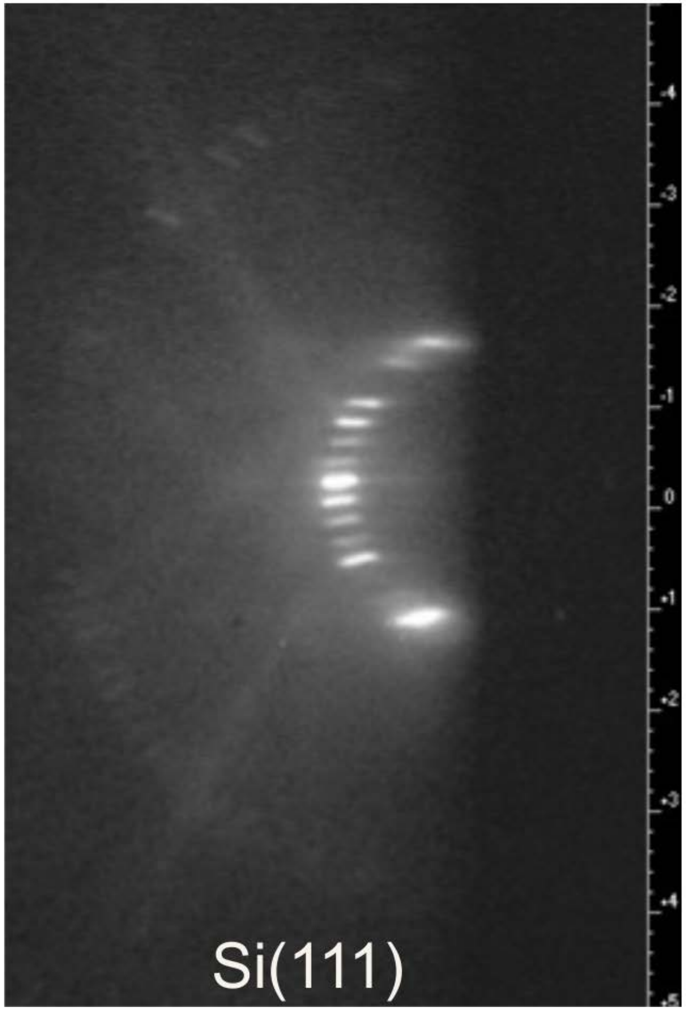


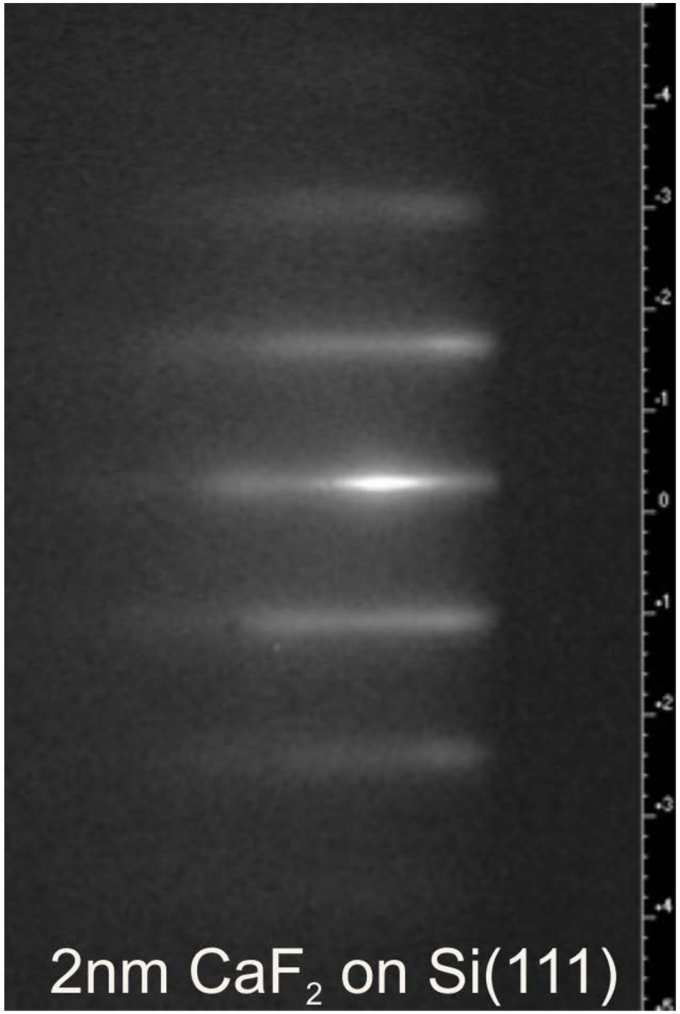
T = 250°C



<u>Low growth temperature of 250°C is the key feature of our MBE method</u>

Homogeneity and Crystallinity of CaF_2 Films

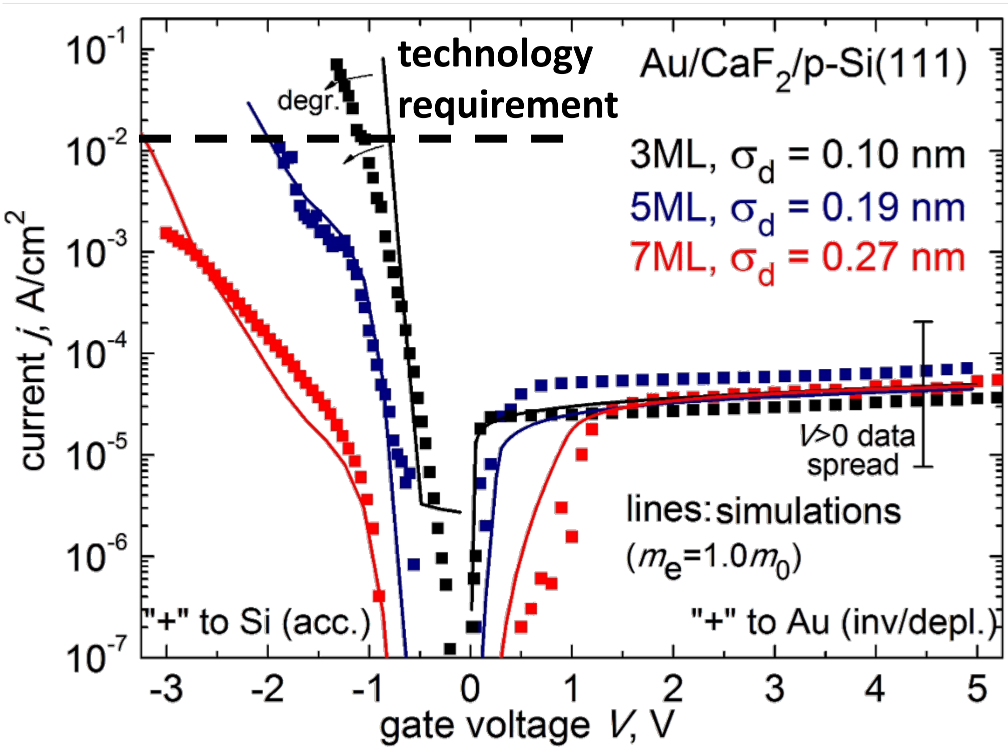


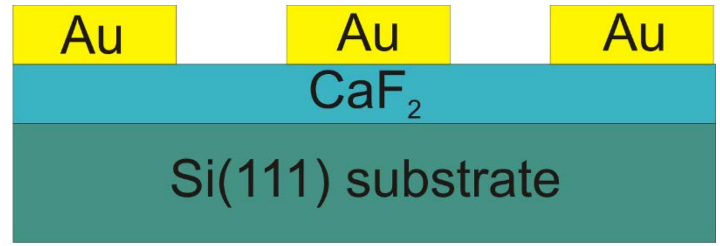


- Homogeneous 2nm CaF_2 film consists of F-Ca-F monolayers (1ML=0.315nm)
- Distinct streaks in RHEED patterns indicate high crystallinity of our CaF_2 films

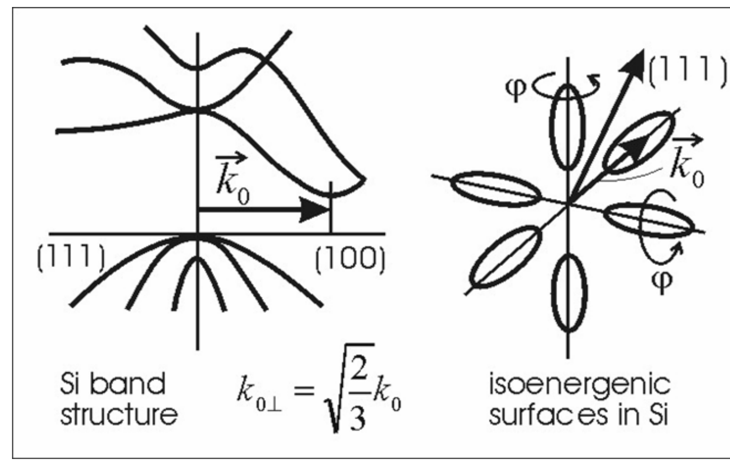
Tunnel Leakage Currents through CaF_2 Films

Au/CaF_2[3-7ML]/Si(111) structures on p- and n-Si substrates





1ML = 0.315 nm



M. Vexler and Yu. Illarionov, Phys. Sol. State 2010;
Yu. Illarionov *et al*, Microel. Eng. 2011

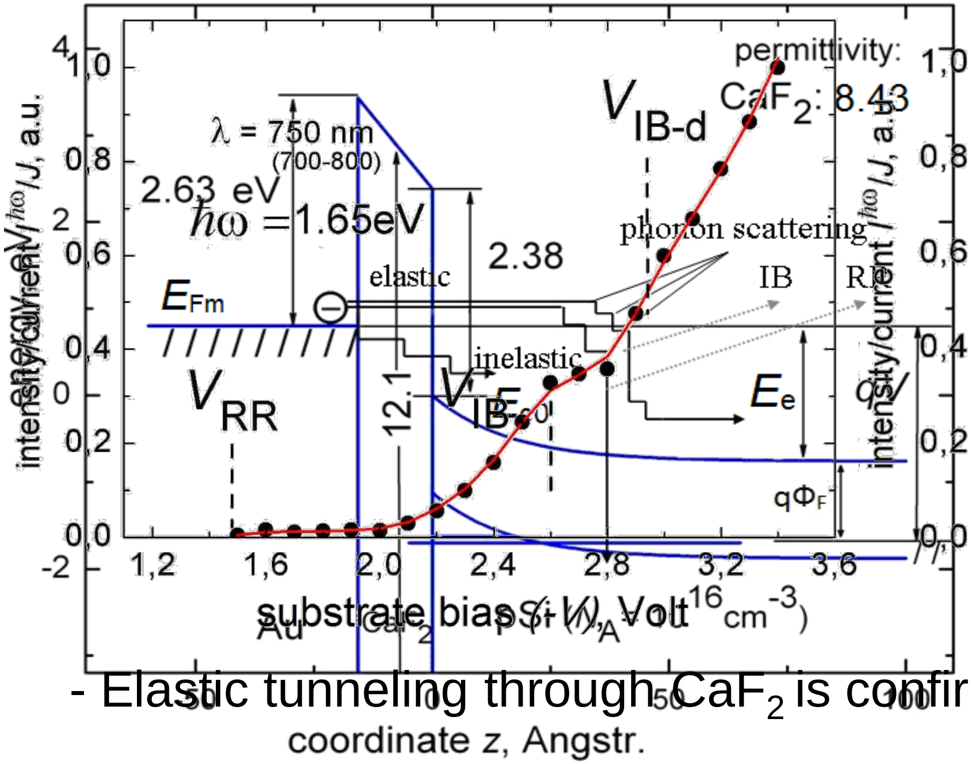
$$T(E,k_\perp^2) = C_R \cdot \exp\left(-\frac{2\sqrt{2m_e}}{\hbar}\int\sqrt{E_{ci}(z) - E + \frac{\hbar^2 k_\perp^2}{2m_e}}dz\right) \quad \& \quad T^*(E,E_\perp) = \left\langle T\left(E,k_\perp^2(E,E_\perp,\varphi)\right)\right\rangle_\varphi$$

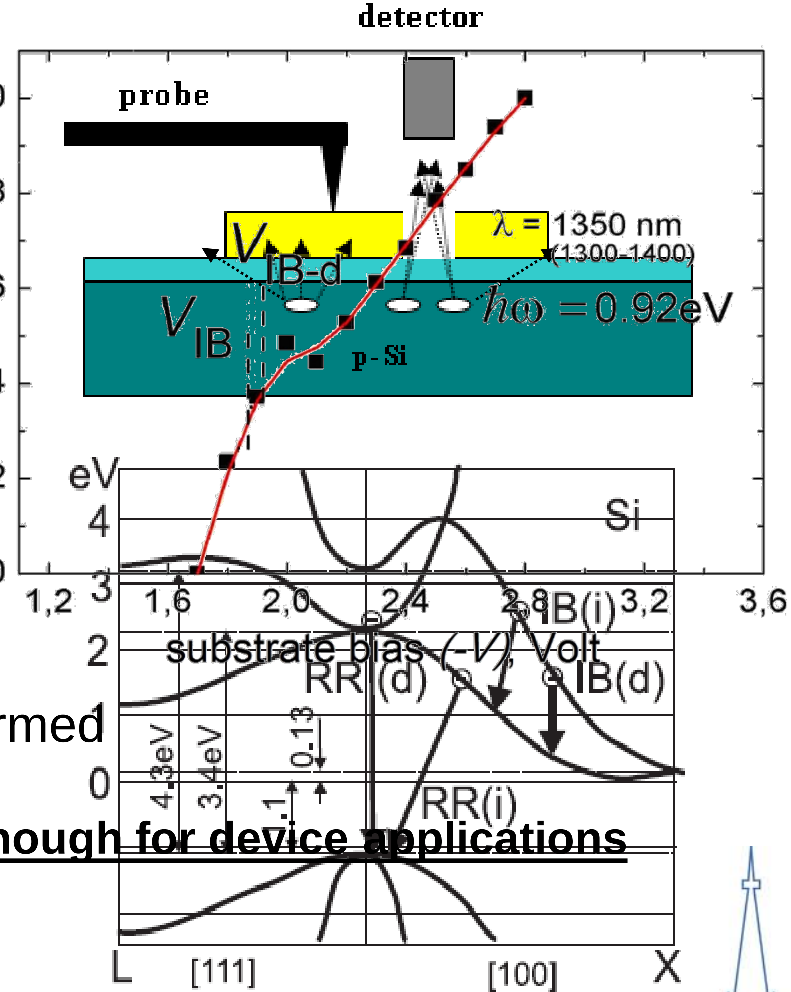
High-quality 1-2nm thick CaF_2 layers have been achieved

Yu. Illarionov *et al*, Thin Solid Films 2013 Yu. Illarionov *et al*, J. Appl. Phys. 2014

Injection Properties of CaF_2 Layers

Tunnel injection of electrons into p-Si substrate





- Elastic tunneling through CaF_2 is confirmed

$q|V| = qV_{RR} = \hbar\omega + q\Phi_F$, E_g ($\hbar\omega \approx E_g$)

Quality of 1-2nm thick CaF_2 layers is high enough for device applications

$q|V| = qV_{IB} = \hbar\omega + q\Phi_F$

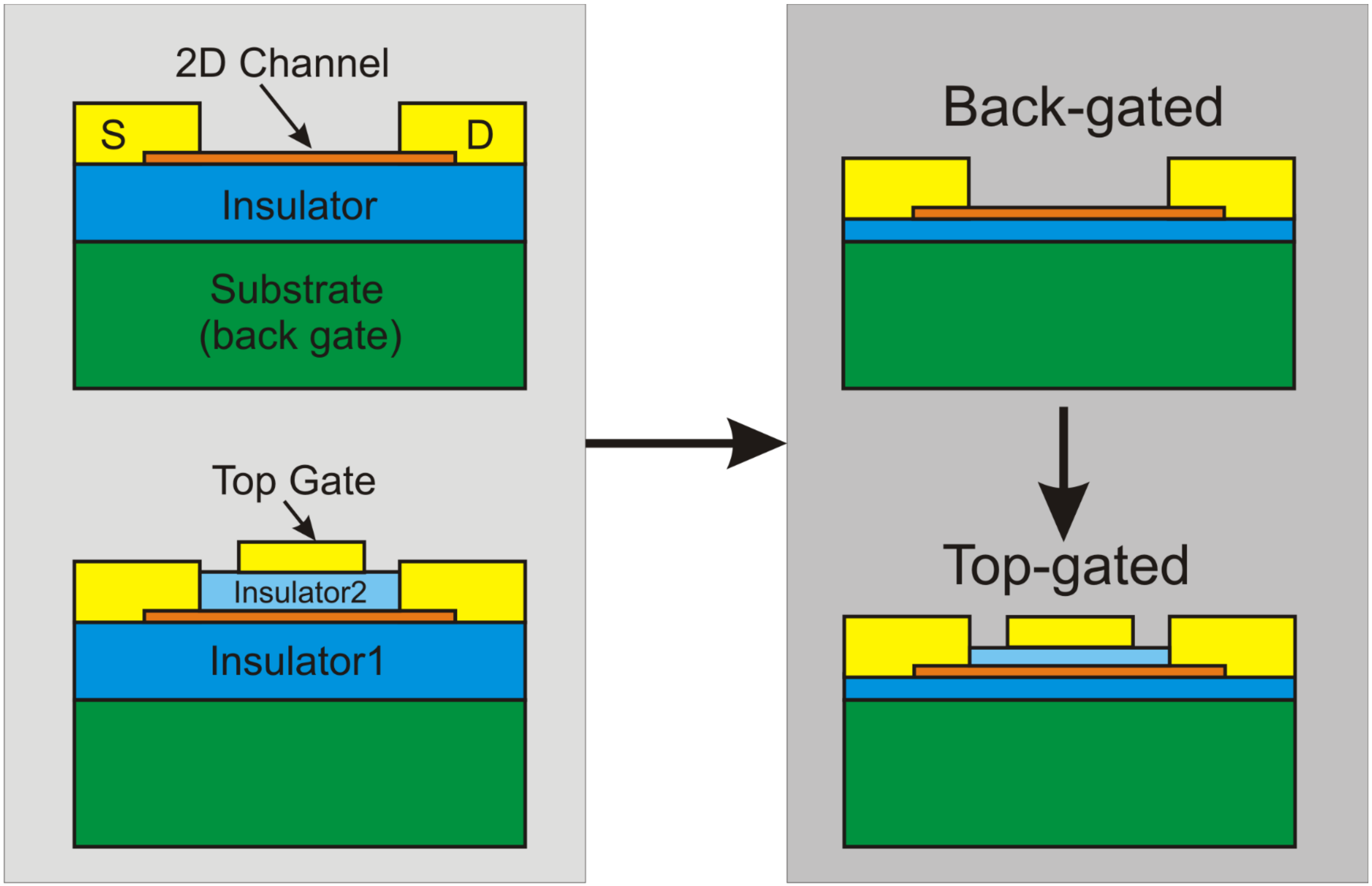
$q|V| = qV_{IB-d} = E_e|_{Edir(Ee)=\hbar\omega} + q\Phi_F$

Yu. Illarionov *et al*, Thin Solid Films 2013
Yu. Illarionov *et al*, J. Appl. Phys. 2014

Ultrathin CaF_2 Films in MoS_2 FETs

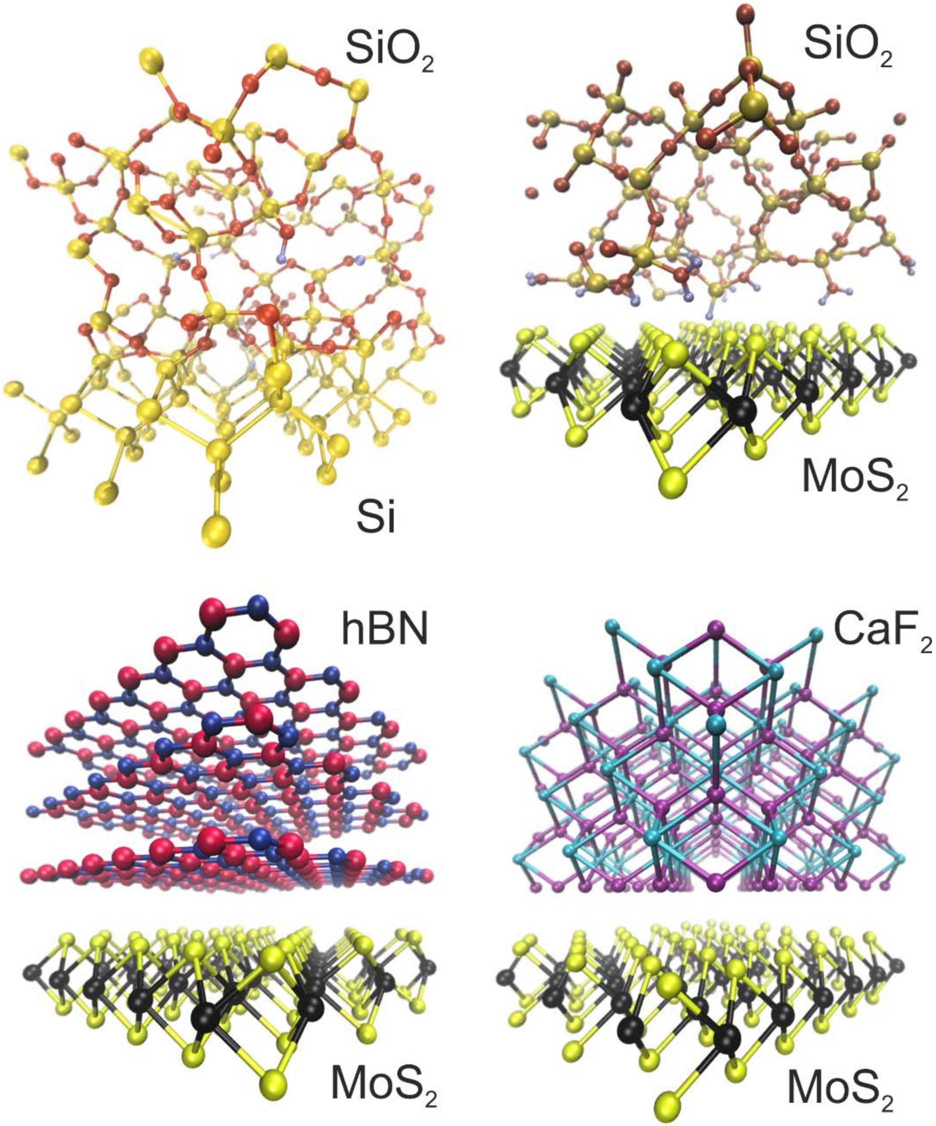
Introduction: State of the Art

Prototypes: d_{ins}>25nm　　Commercial FETs: d_{ins}<5nm



- Modern device technologies require scaling down to sub-1nm EOT

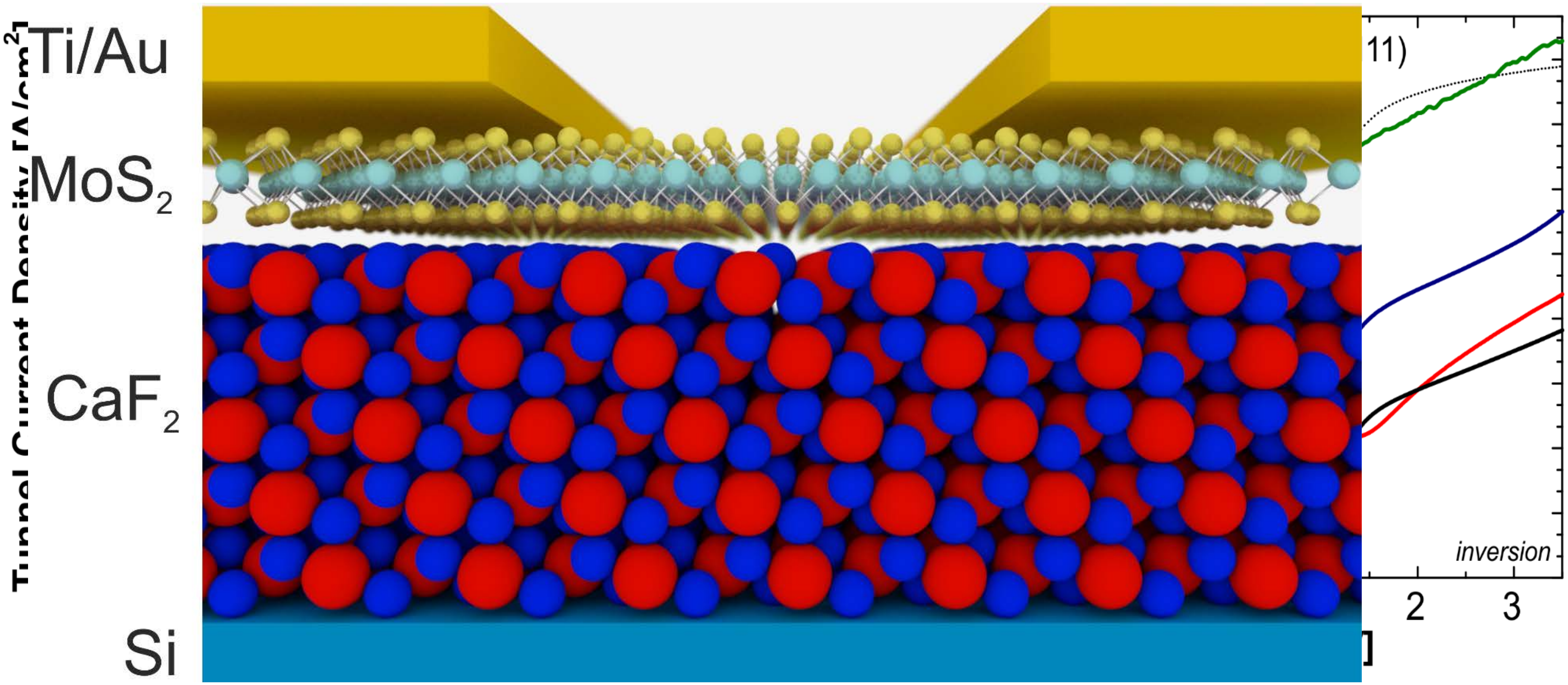
Selection of the Best Insulator for Scaling



- High-quality interface is required

Selection of the Best Insulator for Scaling

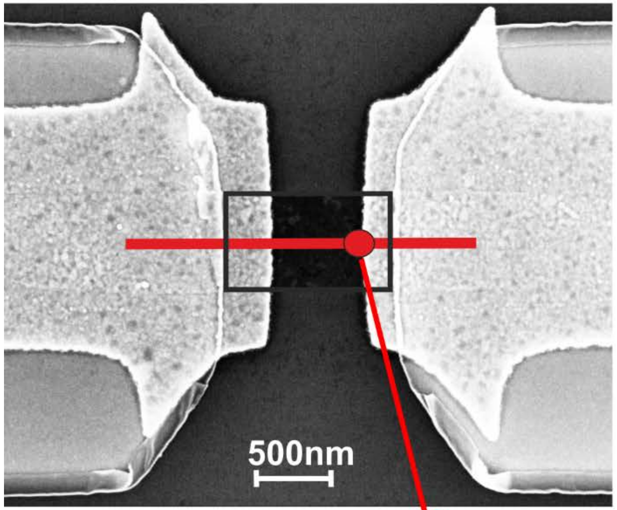
Main Requirements: Low Leakages and High Interface Quality

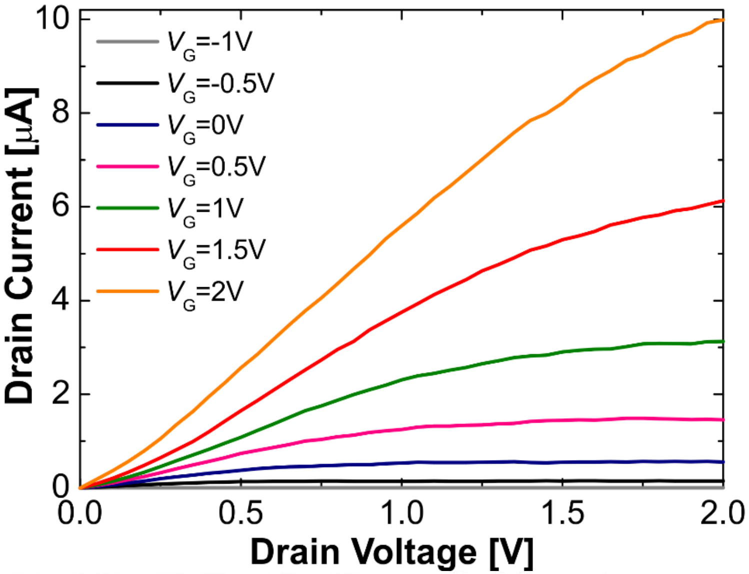


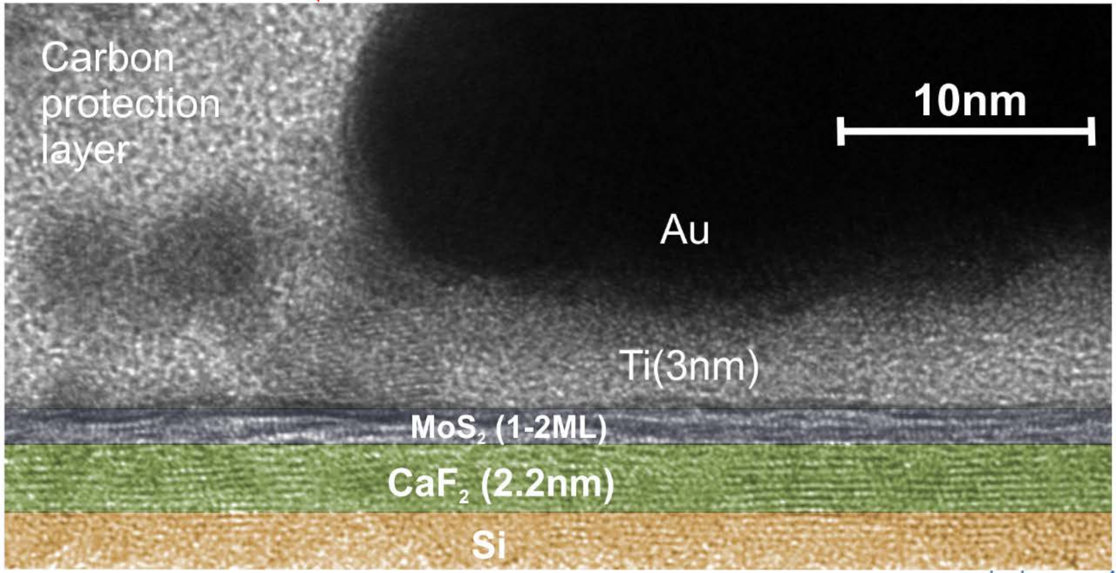
- Thin layers of high-k oxides are amorphous → poor interface quality
- hBN exhibits excessive gate leakages

Crystalline CaF_2 forms <u>quasi van der Waals interface with 2D materials</u> and exhibits <u>low tunnel leakages for sub-1nm EOT</u>

CaF_2(2nm)/MoS_2 FETs: Device Performance



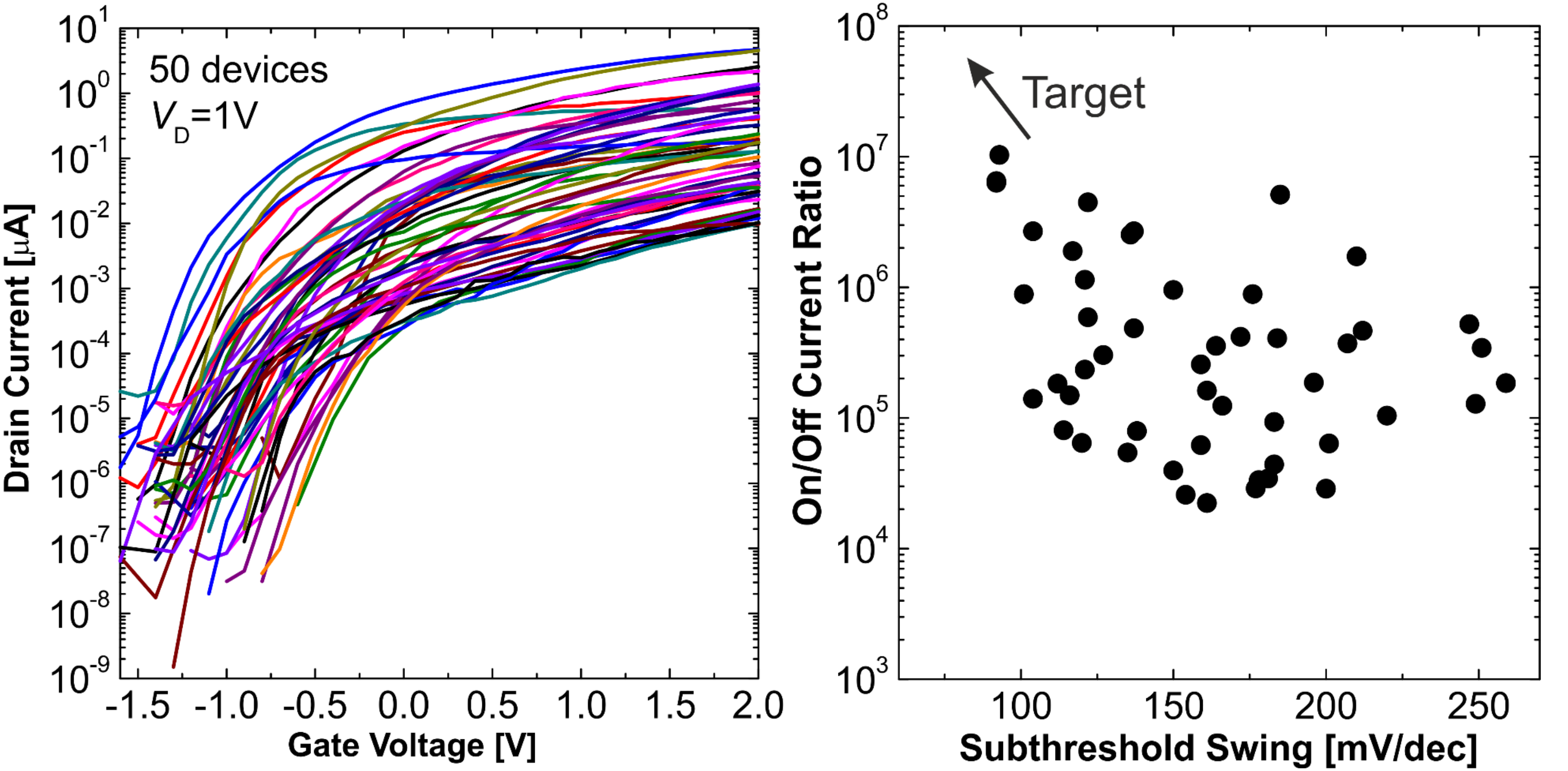




Yu.Yu. Illarionov *et al*, Nature Electron. 2019

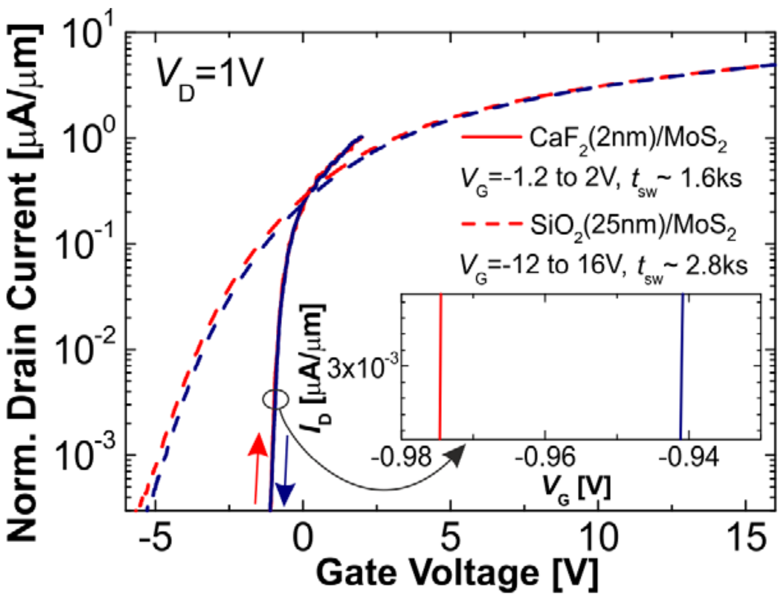
Crystalline CaF_2 insulator of only 2nm thickness (EOT about 0.9nm)

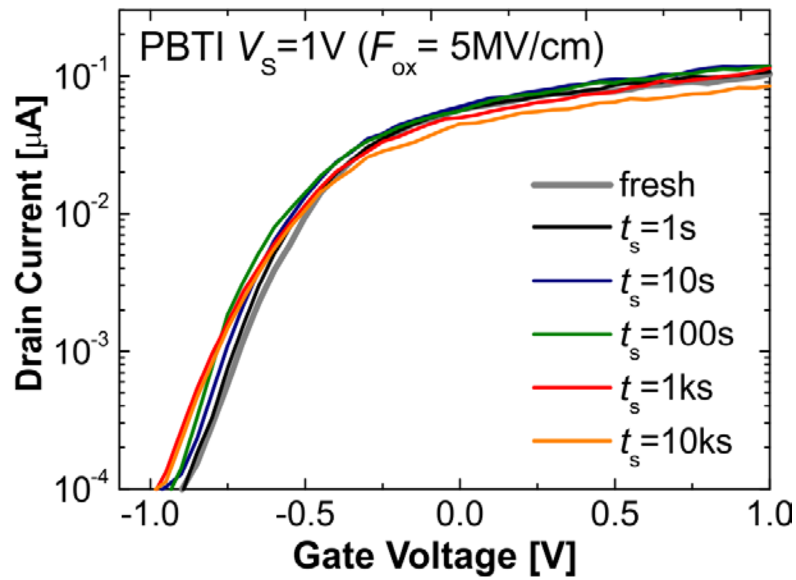
CaF_2(2nm)/MoS_2 FETs: Variability

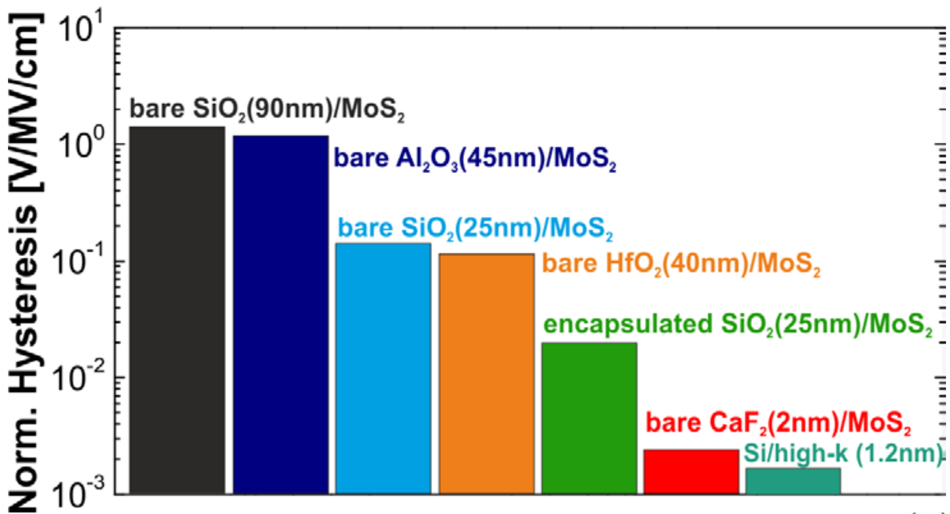


- Numerous functional devices with SS down to 90mV/dec and on/off current ratio up to 10^7

CaF_2(2nm)/MoS_2 FETs: Stability



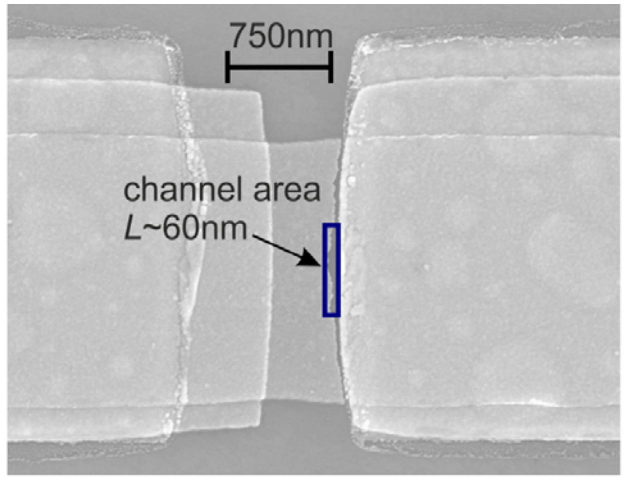


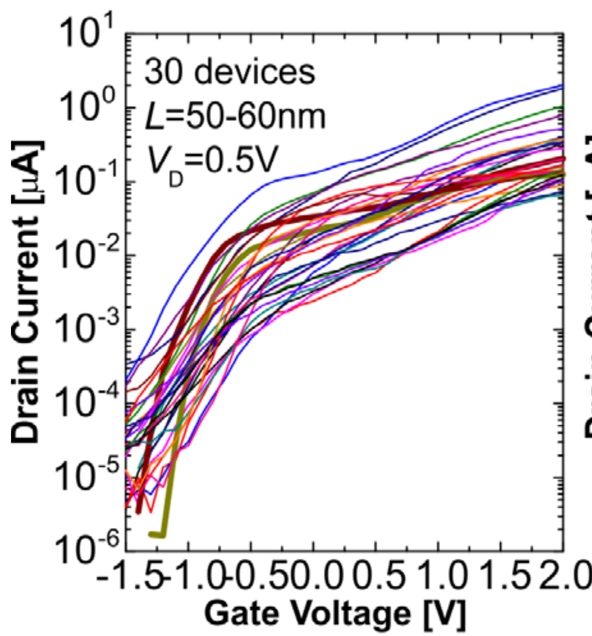


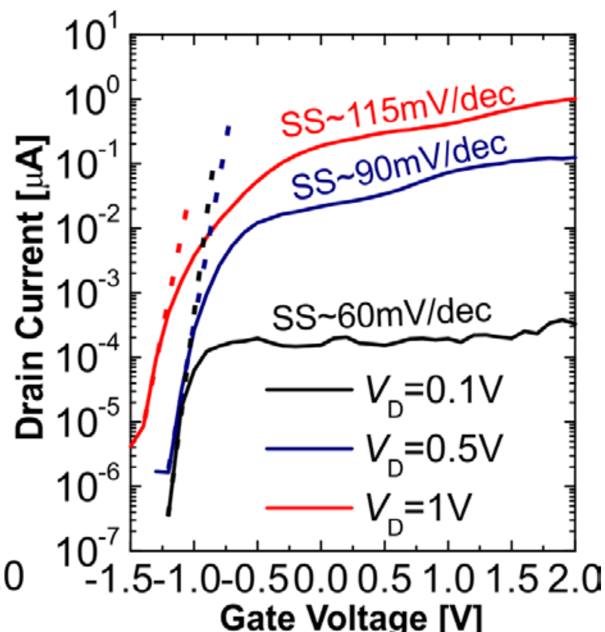
Yu.Yu. Illarionov *et al*, Nature Electron. 2019

Small hysteresis and BTI shifts are observed for these devices

Nanoscale MoS_2 FETs with 2nm CaF_2







CaF_2/MoS_2 FETs with L=50-60nm exhibit SS down to 60mV/dec

Conclusions

- We developed low-temperature MBE growth techniques of CaF_2 on Si(111)
- We achieved device-level quality of ultrathin (1-2nm) CaF_2 films
- For the first time we fabricated MoS_2 FETs with simultaneously sub-100nm

Outlook…

Epitaxial Fluorides: Many Materials with Fascinating Properties

Compound	Crystal structure	Lattice constant (Å)	Linear thermal expansion coefficient ($\times 10^{-6}$ K^{-1})	Lattice mismatch with Si (GaAs) at RT(%)	Melting point (°C)	Band gap (eV)	Reference
KF	cubic NaCl	5.348	31	−1.5 (−5.4)	858	~11	7
RbF	cubic NaCl	5.652	27	+4.1 (−0.3)	795	~10	7
CdF_2	cubic fluorite	5.388	19	−0.8 (−4.7)	1100	8	7
CaF_2	cubic fluorite	5.4629	19	+0.7 (−3.4)	1360	12.1	1, 7, 9
SrF_2	cubic fluorite	5.7996	18	+6.8 (+2.6)	1190	11.25	1, 7, 9
BaF_2	cubic fluorite	6.2001	18	+14.2 (+9.7)	1280	11.0	1, 7, 9
LaF_3	hexagonal	$a_{sup}/(P6_{3cm}) = 7.187$, $c = 7.350$	$\alpha_{11} = 10.7$	+7.4 (+3.6)	1493	—	9
CeF_3	hexagonal	$a_{sup}/(P6_{3cm}) = 7.112$, $c = 7.279$	$\alpha_{11} = 16.5$	+6.7 (+2.8)	1430	—	9
NdF_3	hexagonal	$a_{sup}/(P6_{3cm}) = 7.030$, $c = 7.199$	$\alpha_{11} = 14.7$	+5.4 (+1.5)	1374	—	9
GaF_3	rhombohedral	$a = 5.2$, $\alpha = 57.5°$	—	—	~950	9.6	22
$BaMgF_4$	orthorhombic	$a = 5.81$, $b = 14.51$, $c = 4.13$	—	—	—	—	19

M. Sugiyama *et al*, Microelectron. J. 1996

Standard Insulators: CaF_2, CdF_2, SrF_2, LaF_3, …

Antiferromagnets: NiF_2, MnF_2, …

Diamagnets: ZrF_2, …

Ferroelectrics: $BaMgF_4$, …