Polymer dielectric layers prepared by initiated chemical vapor deposition (iCVD) for flexible electronics on various platforms

NGC 2017
Tomsk, Russia

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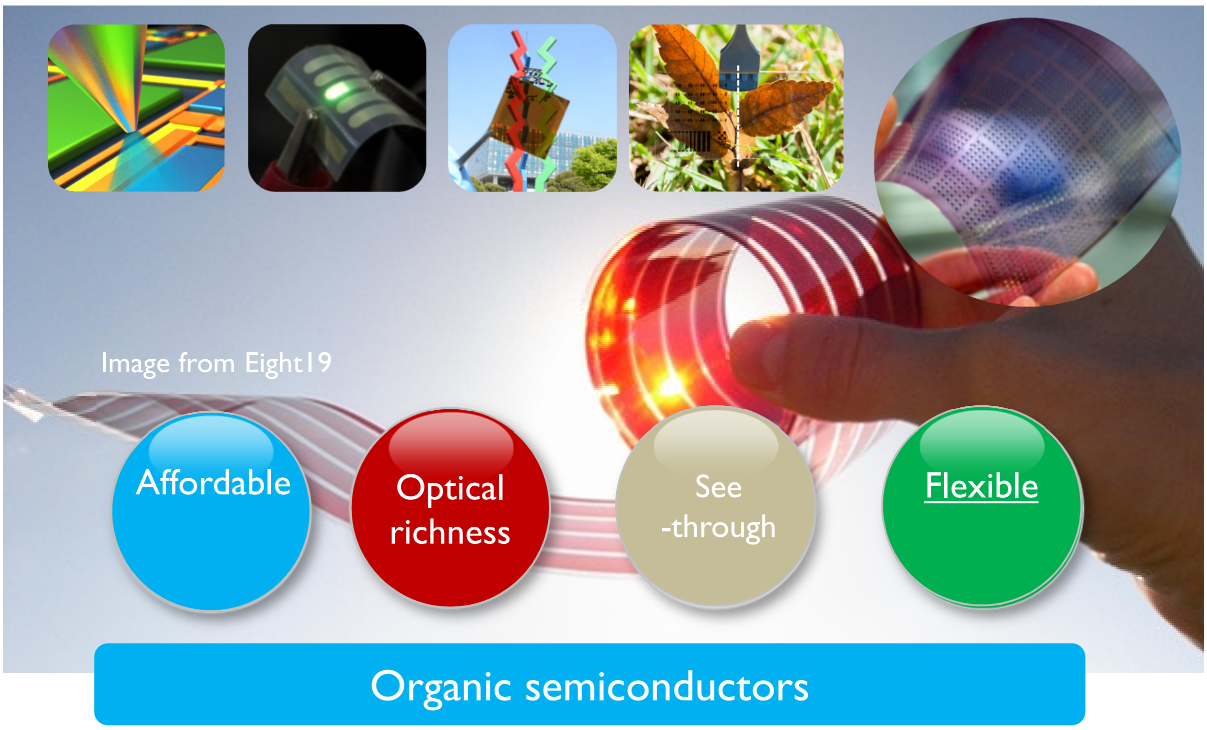
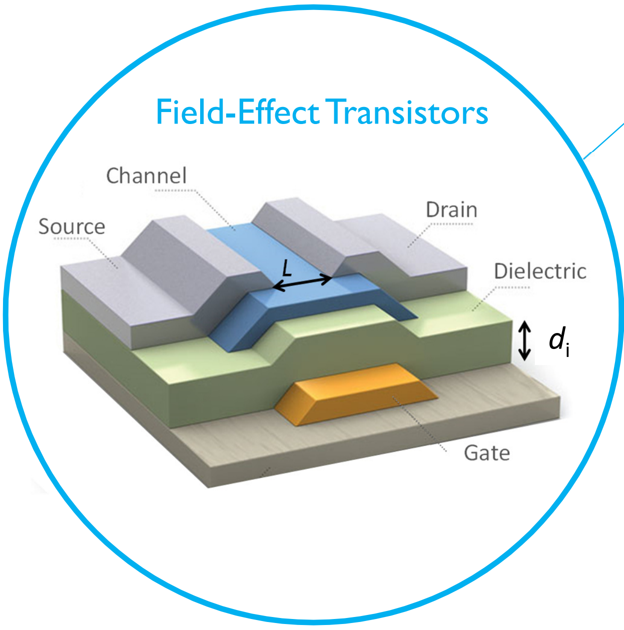
Introduction

Key advantages of organic semiconductors



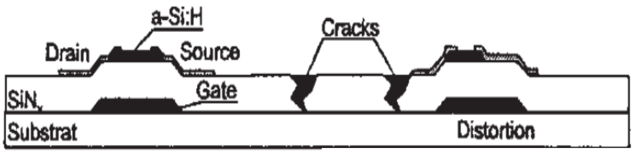
Challenges in flexible electronics: *Importance of ultrathin gate dielectrics*



Ultrathin gate insulators are a key element for :

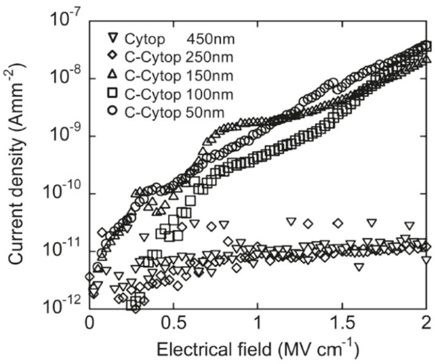
- low-V operation;
- down-scaling of transistors; and
- have been achieved with oxides, etc.

Conventional dielectric layers are prone to crack formation under strain that occurs during fabrication or bending.



Journal of the SID 9/4, 2001 291

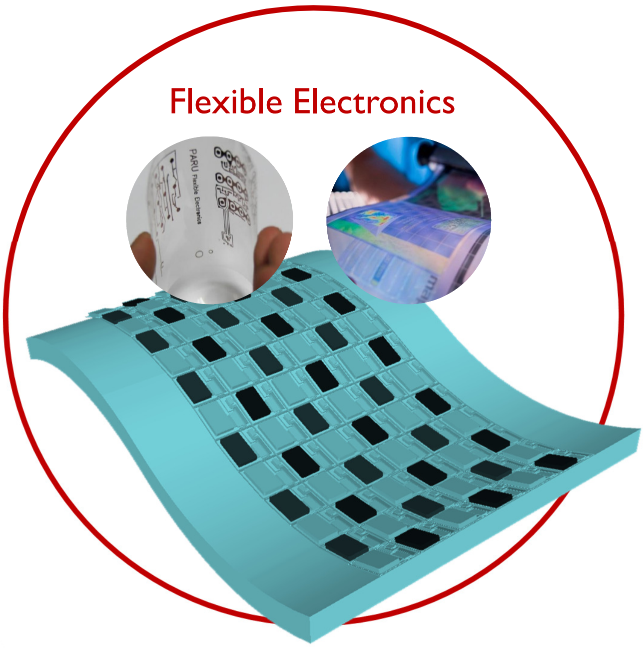
What about polymer dielectrics ?



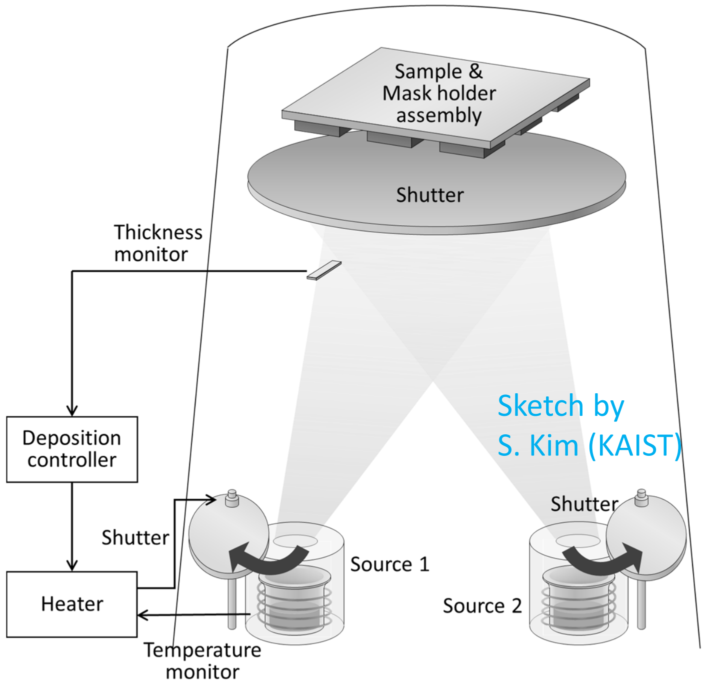
H. Sirringhaus et al. Chem. Mater. 22, 1559 (2010)

Polymer gate insulators are essential for flexible electronics, but

- it has been challenging to make them ultrathin while maintaining low leakage and high breakdown



Lesson from OLEDs: *how to obtain quality ultrathin films ?*

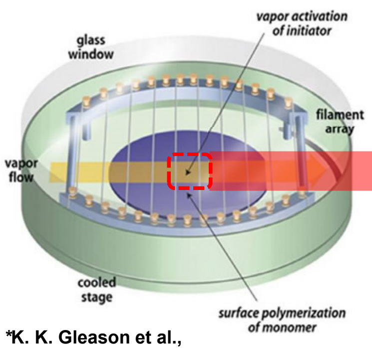


What made OLED TV possible that requires sublayers typically on the order of only a few tens of nm over very large area?

Vapor-based approach and its controllability …. !

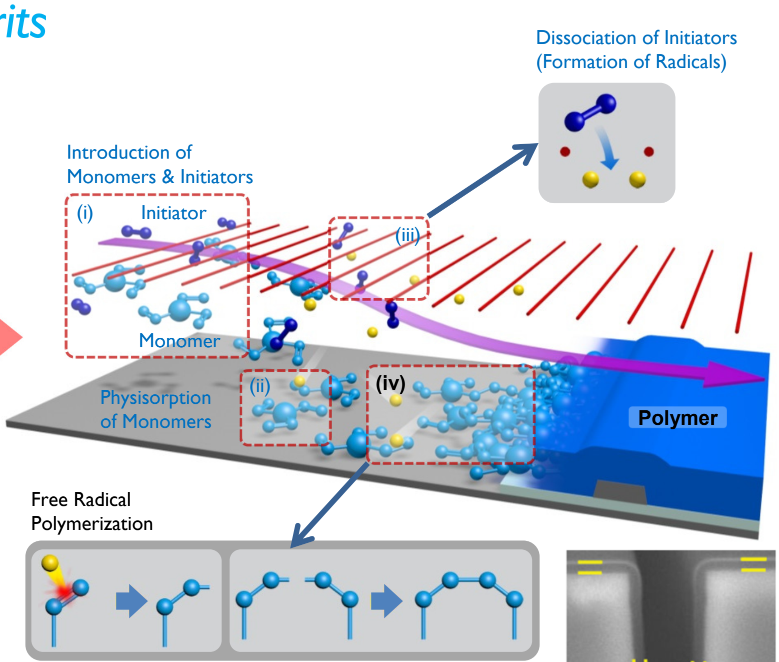
Polymer dielectrics based on iCVD Process: *mechanism & merits*

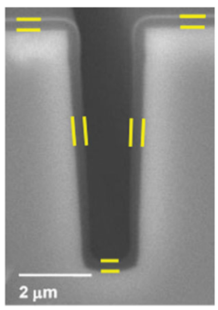
Initiated CVD (iCVD)



K. K. Gleason et al., *Macromolecules 2006, 39, 3688

**www.optics.Rochester.edu*

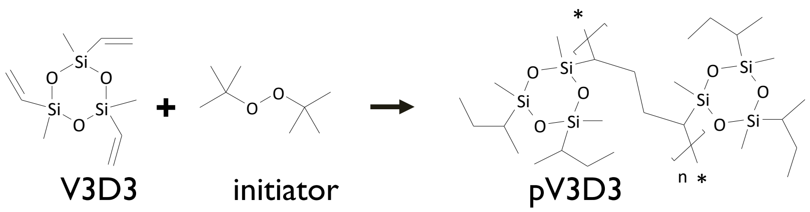




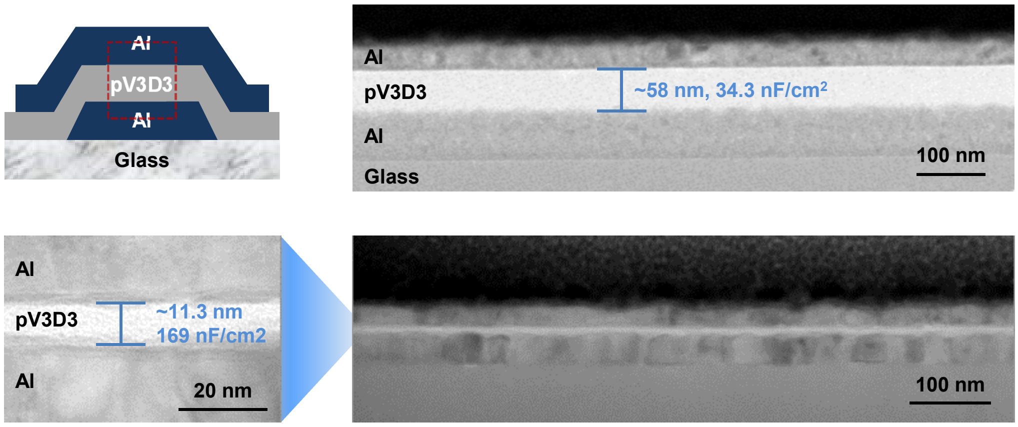
- Advantages of iCVD process
  - ✓ Conformal, uniform coating over large area
  - ✓ Low-temperature (~RT) & solvent-less process
  - ✓ Wide range of material choice/ tunability

K. K. Gleason et al., *Adv. Mater. 2009, 21, 1

pV3D3 for gate insulators

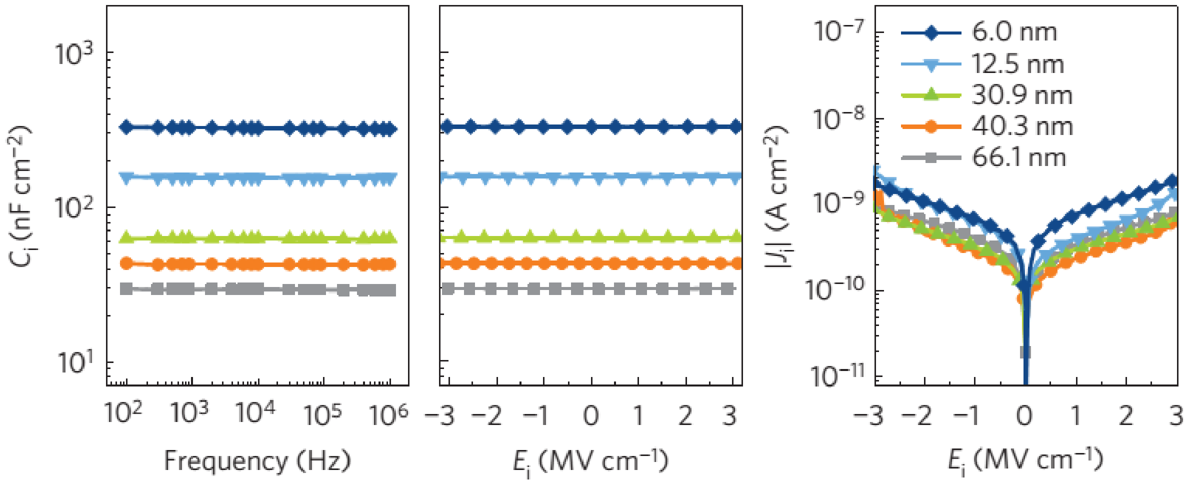


pV3D3: poly(1,3,5-trimethyl-1,3,5-trivinyl cyclotrisiloxane)



pV3D3 insulating layers: *thickness scalability*

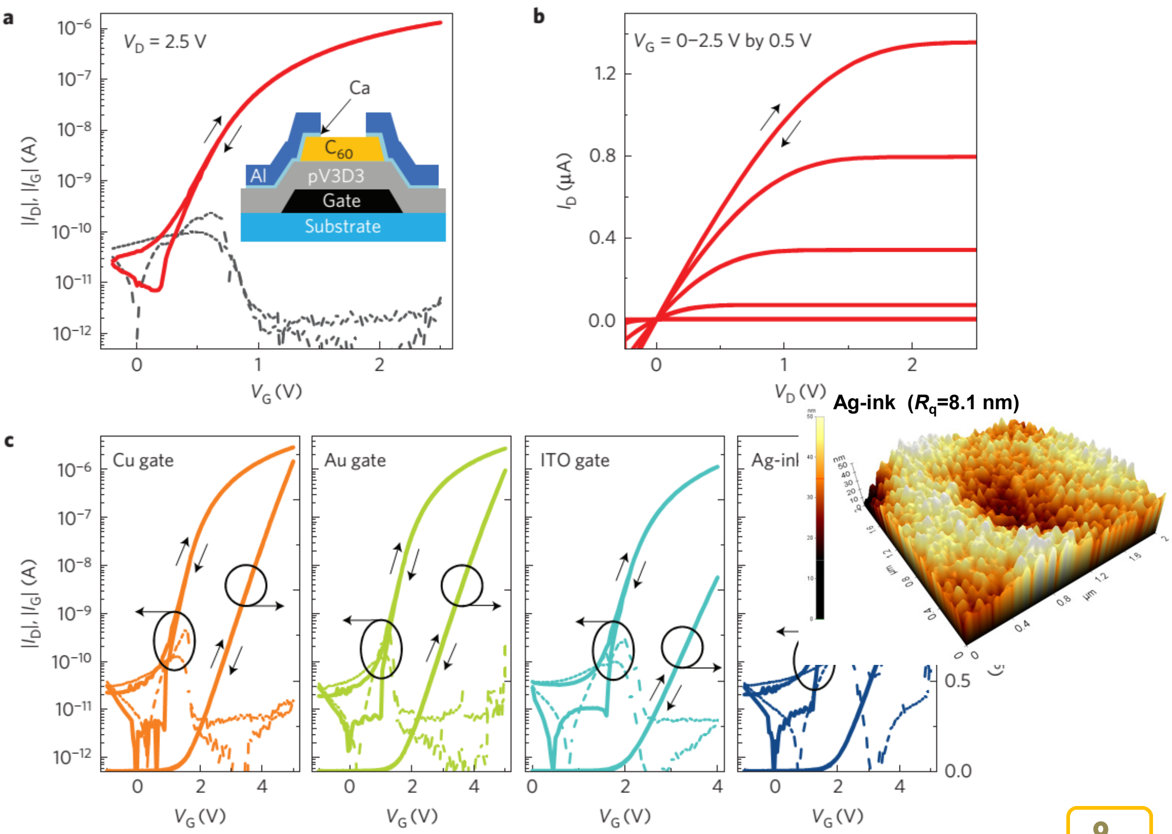
MIM (Al/ pV3D3 (*x* nm)/ Al)



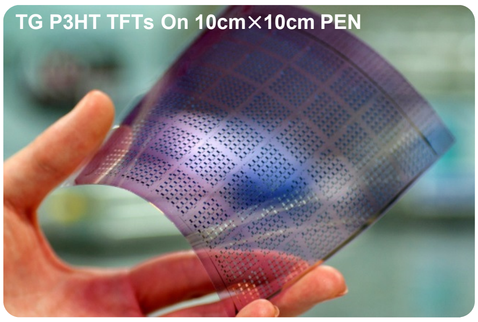
- pV3D3 can be scaled down to ~6 nm with excellent insulating property.
- C_i can be controlled to over 300 nF/cm^2.

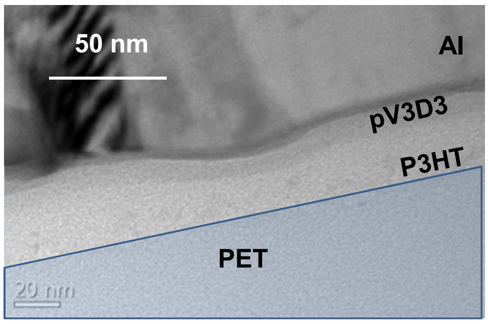
Moon et al., Nature Mater. 14 (6) 628 ('15)

Application to low-V bottom-gated OTFTs



Application to top-gated OTFTs over large area





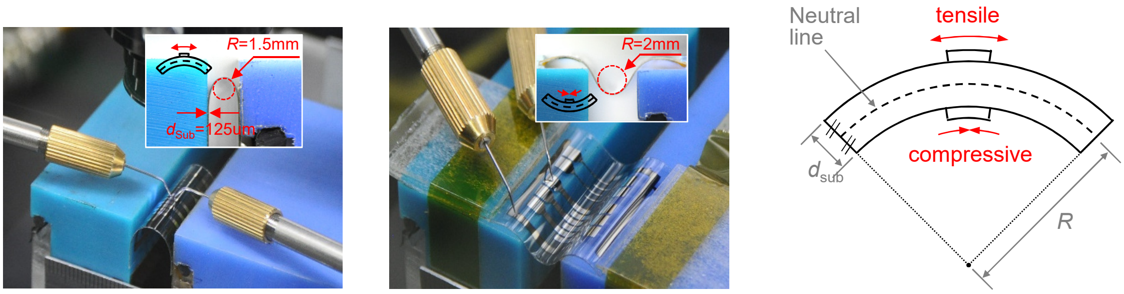
Cowork with Prof. Y.-Y. Noh in Dongguk Univ.

	Active layer	Fabrication method of active/dielectric	μ_{sat} [cm²/Vs]	V_T [V]	μ_{stdev}/μ_{ave} [%]	$V_{T.stdev}/V_{T.ave}$ [%]
This work	P3HT	bar-coating/iCVD	0.069 ±0.011	-1.86 ±0.06	16	3.2
Previous work*	DPPT-TT	spin-coating/spin-coating	0.72 ±0.27	-39 ±4.2	38	11
	DPPT-TT	bar-coating/bar-coating	1.64 ±0.41	-41.6 ±2.5	25	6.0

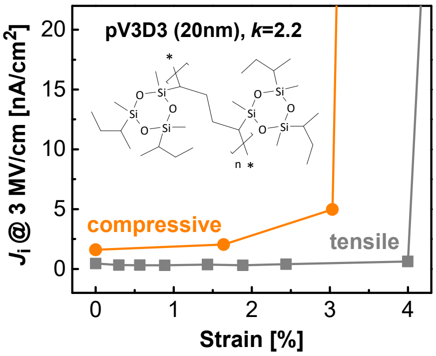
*Y.-Y. Noh et al., Adv. Mater. 2013, 25, 4302

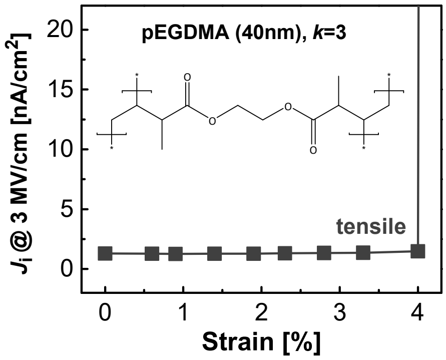
Moon et al., Nature Mater. 14 (6) 628 ('15)

Mechanical flexibility of pV3D3



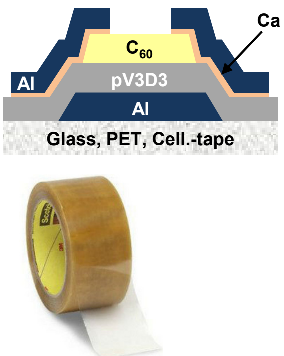
Moon et al., Nature Mater. 14 (6) 628 ('15)

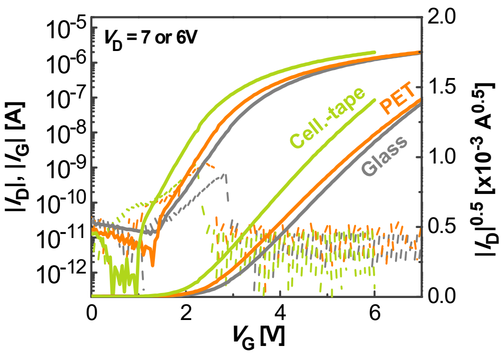


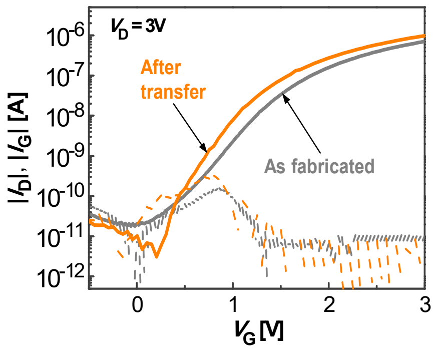


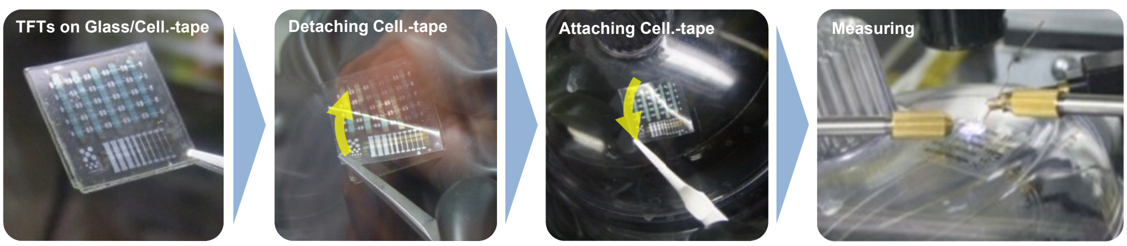
*pEGDMA: Poly(ethylene glycol dimethacrylate)

OTFTs on various flexible substrates







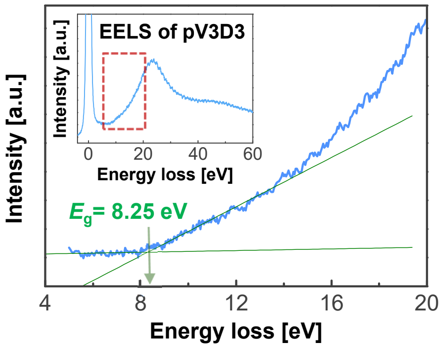


Mild processes (RT & solventless) of iCVD allows one to use virtually any kind of substrate.

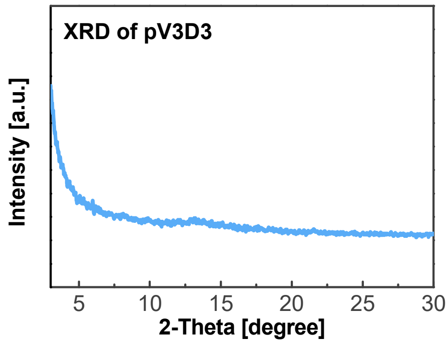
Moon et al., Nature Mater. 14 (6) 628 ('15)

Origin of the excellent insulting property (1)

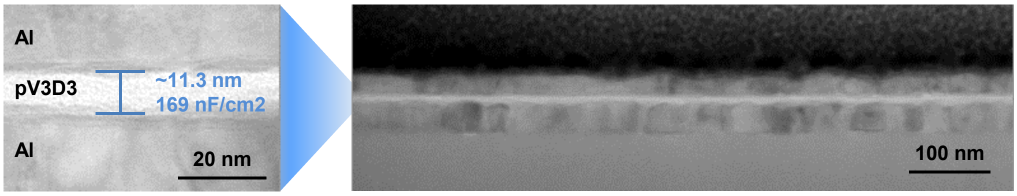
- Wide energy gap



- Amorphous phase



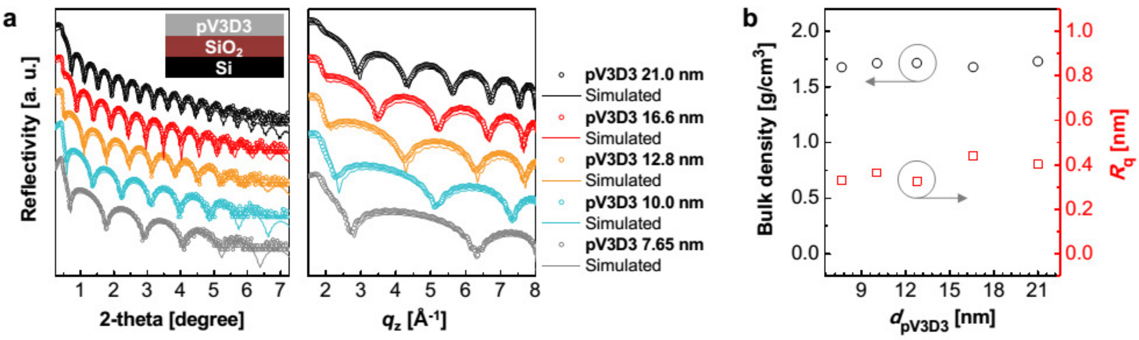
- Uniform film thickness/ conformal deposition



*EELS: electron energy loss spectroscopy
*XRD: L-ray diffraction

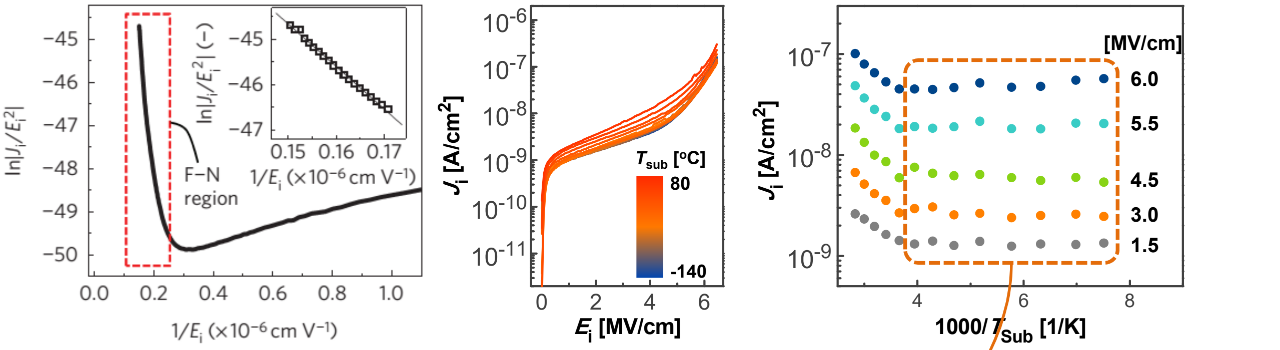
Origin of the excellent insulting property (2)

X-ray reflectivity (XRR) spectra of pV3D3 thin films with various thickness (d_{pV3D3}). a) XRR data and corresponding fits as a function of 2-theta (left) and q_z (right). Inset figure indicates the sample structure used for the analysis. **b)** Bulk density and surface roughness of pV3D3 as a function of d_{pV3D3}. All values were obtained from the XRR data in **a)**.



- Virtually same density down to sub-10-nm thick films
- Higher density than most organosilicone polymers (e.g. PDMS 0.965 g/cm^3)

Origin of the excellent insulting property (3)



Moon et al.,
Nature Mater. 14 (6) 628 ('15)

Conduction mechanism	Simple model	Temperature dependency
Direct tunneling	$J \sim V \exp\left(-\frac{2d\sqrt{2m\phi}}{\hbar}\right)$	None
Fowler-Nordheim tunneling	$J \sim V^2 \exp\left(-\frac{4d\sqrt{2m}(\phi_{FN})^{3/2}}{3\hbar qV}\right)$	None
Hopping conduction	$J \sim V \exp\left(-\frac{\phi}{kT}\right)$	$\ln\left(\frac{J}{V}\right) \sim \frac{1}{T}$
Thermionic emission	$J \sim T^2 \exp\left(-\frac{\phi - q\sqrt{qV/4\pi\varepsilon d}}{kT}\right)$	$\ln\left(\frac{J}{T^2}\right) \sim \frac{1}{T}$

** Cowork with Prof. S.-Y. Choi in KAIST*

- Tunneling limited characteristics
- Indication of low amount of traps

Moon et al., Nature Mater. 14 (6) 628 ('15)

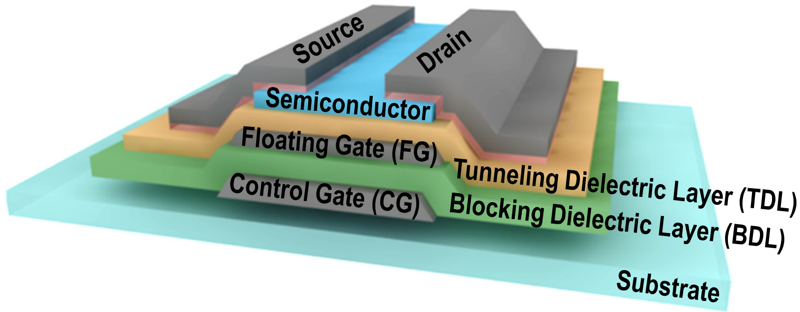
Other applications of iCVD polymers ?

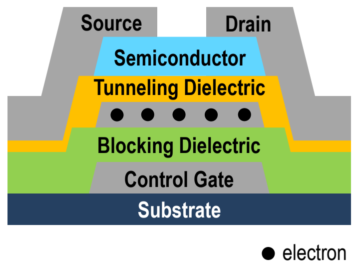
- Flexible non-volatile memory

TFT-based non-volatile memory operation

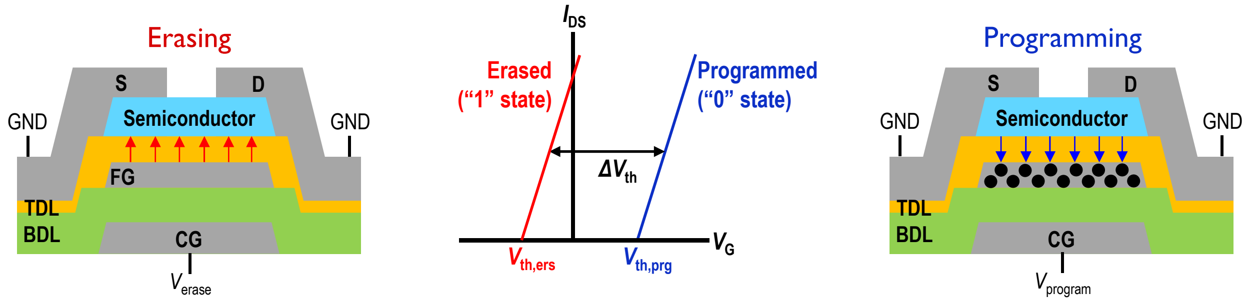
Structure

Thin-film transistor (TFT)-based floating gate flash memory



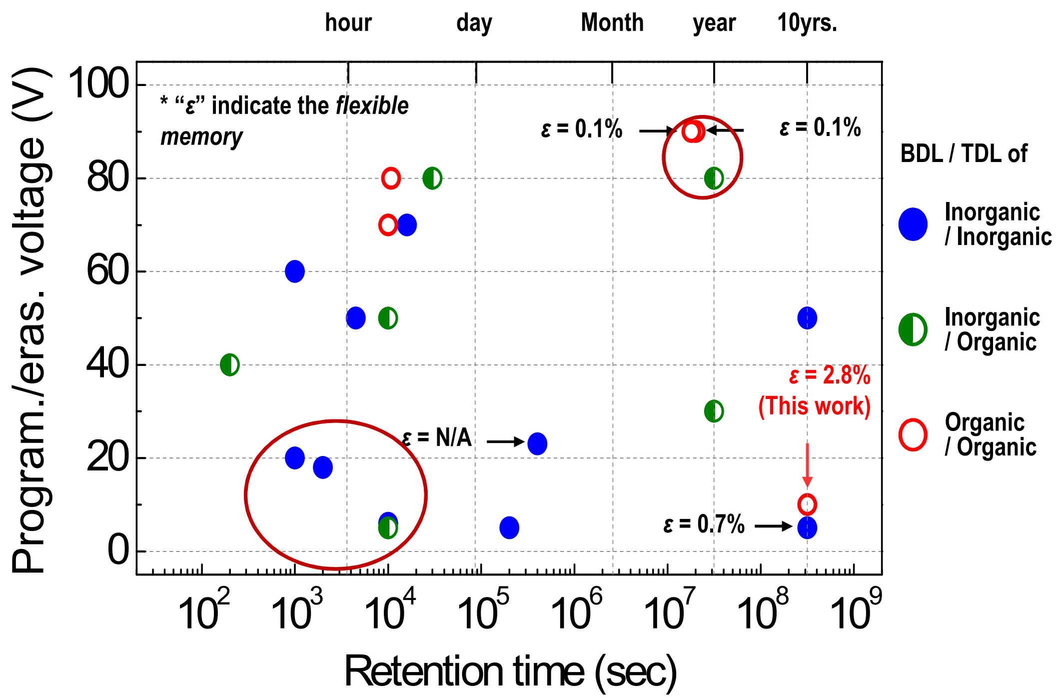


Operation

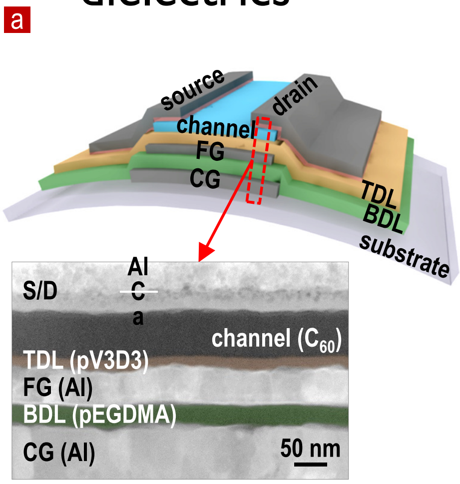


Challenges in TFT memory devices

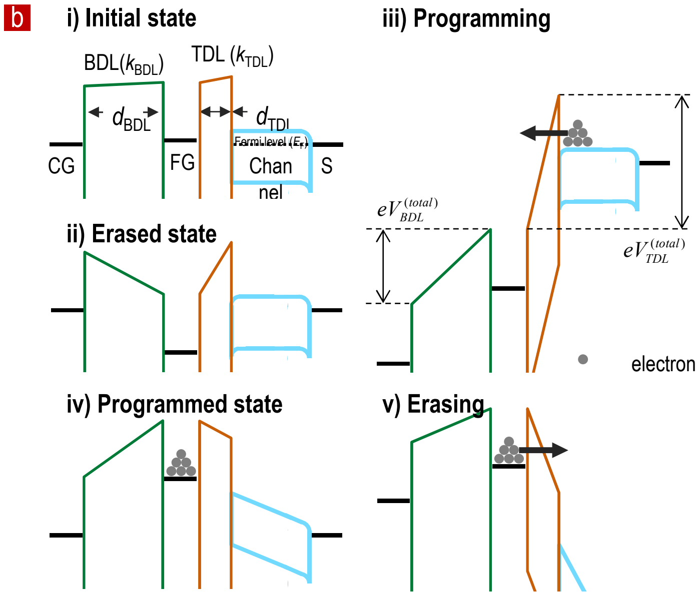
It has been challenging to achieve both long retention and reasonably low prog./erasing voltages at the same time in organic TFT memory devices...

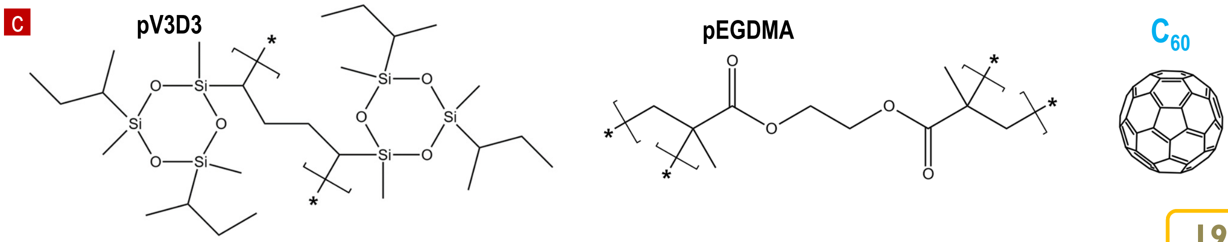


Organic non-volatile memory with iCVD processed dielectrics

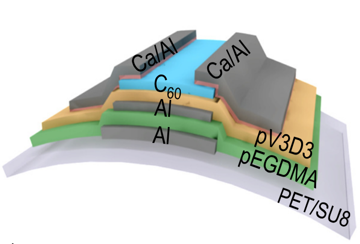


S. Lee et al. Nature Comm. 8, 725 (2017)

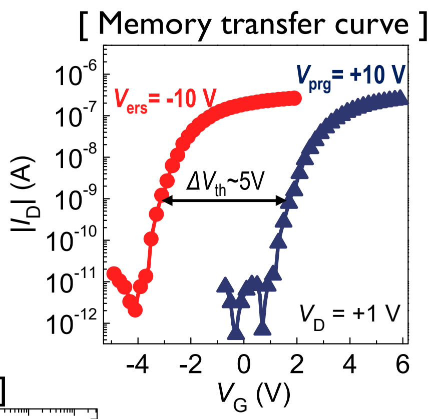


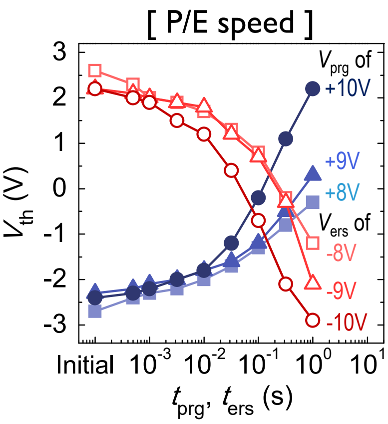


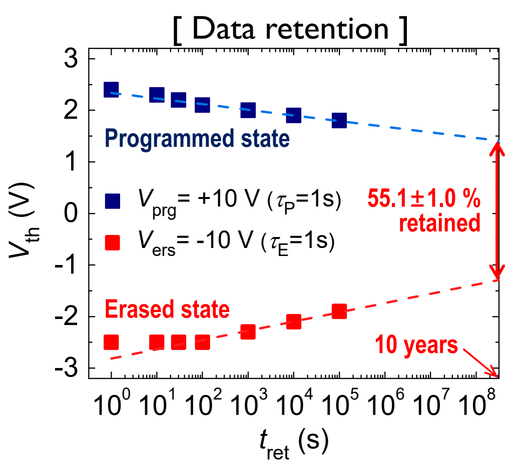
Memory characteristics: Transfer, speed, retention



* W= 980 μm/ L= 200 μm



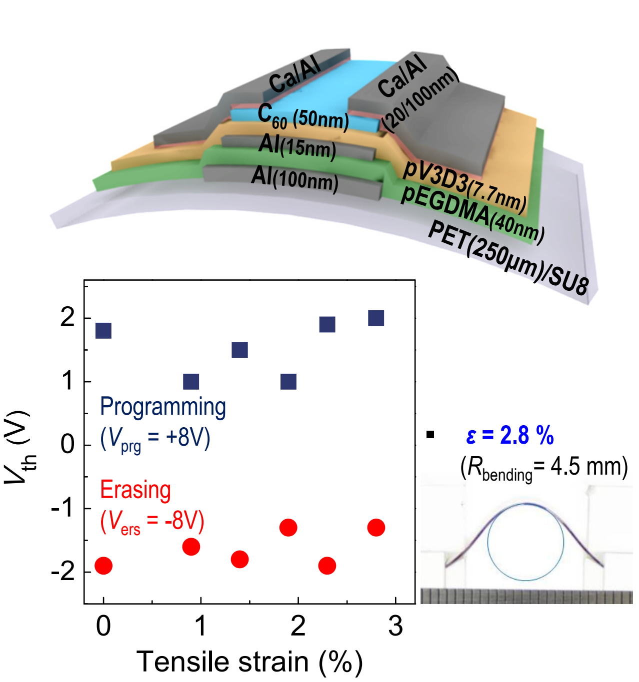


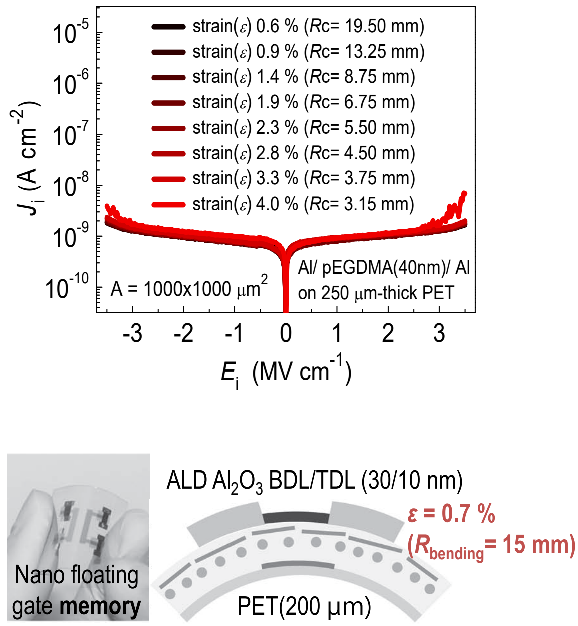


Operates successfully Program/ Erase of ±10 V

S. Lee et al. Nature Comm. 8, 725 (2017)

Highly flexible organic flash memory under the 2.8 % strain

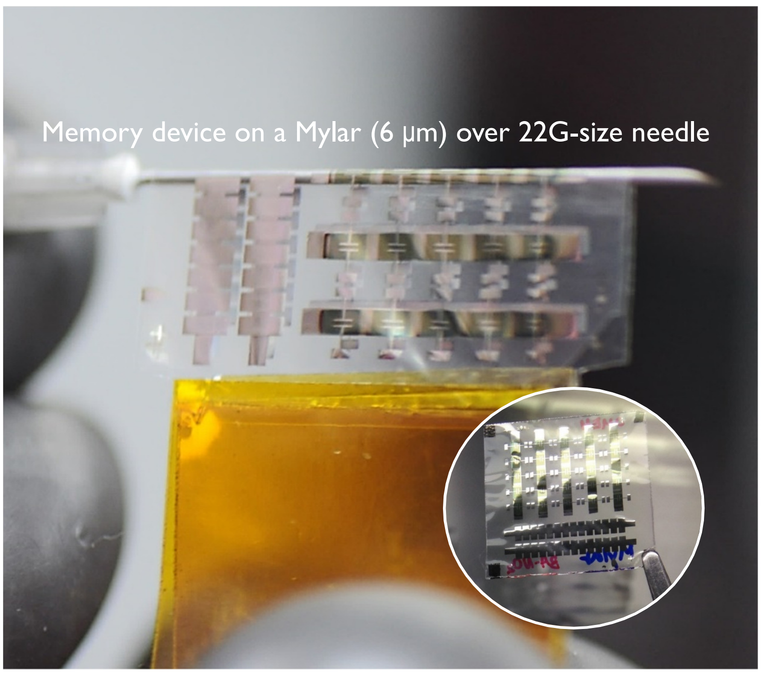


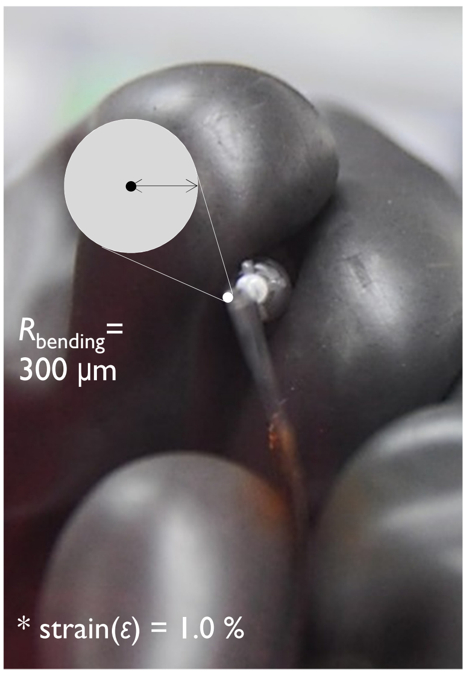


V.A.L.Roy* *et al. Adv. Mater.* 25, 872 (2013)

Operates successfully even after 2.8 % strain

Fabrication of ultra-flexible memory devices





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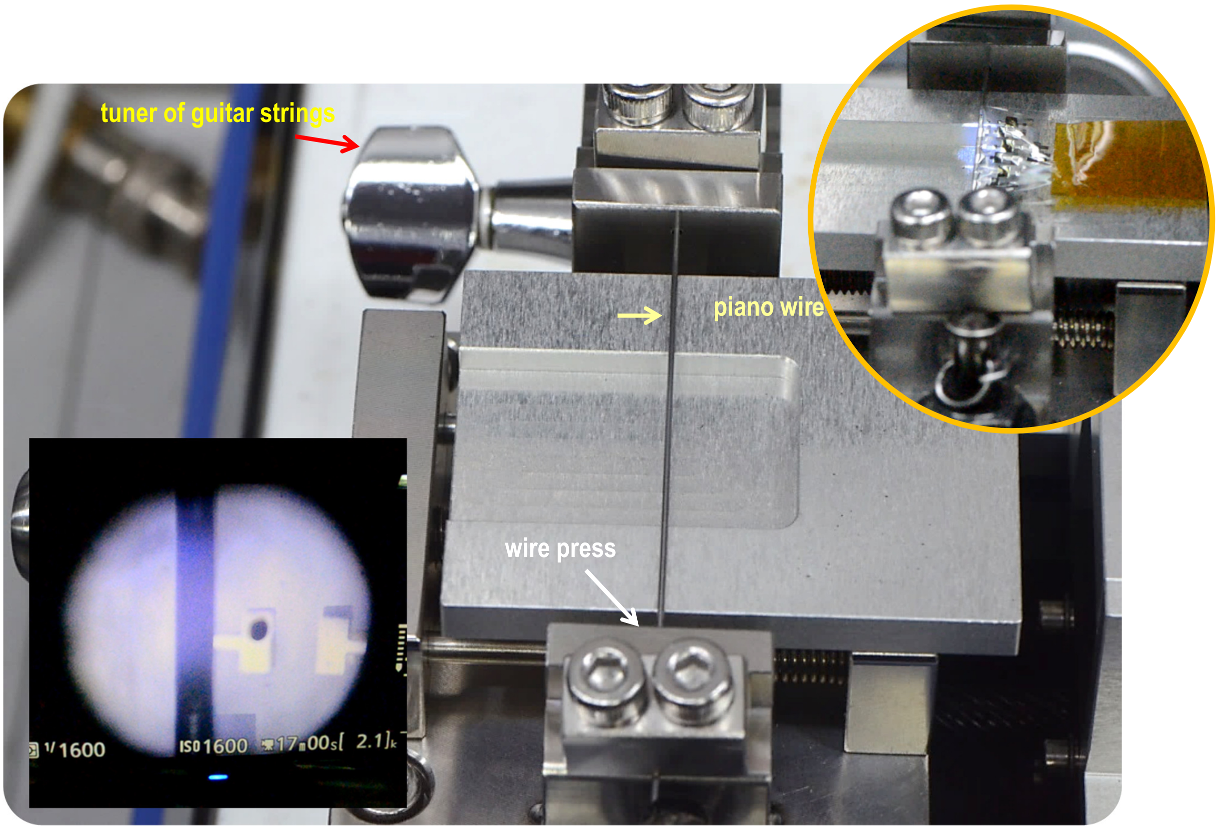
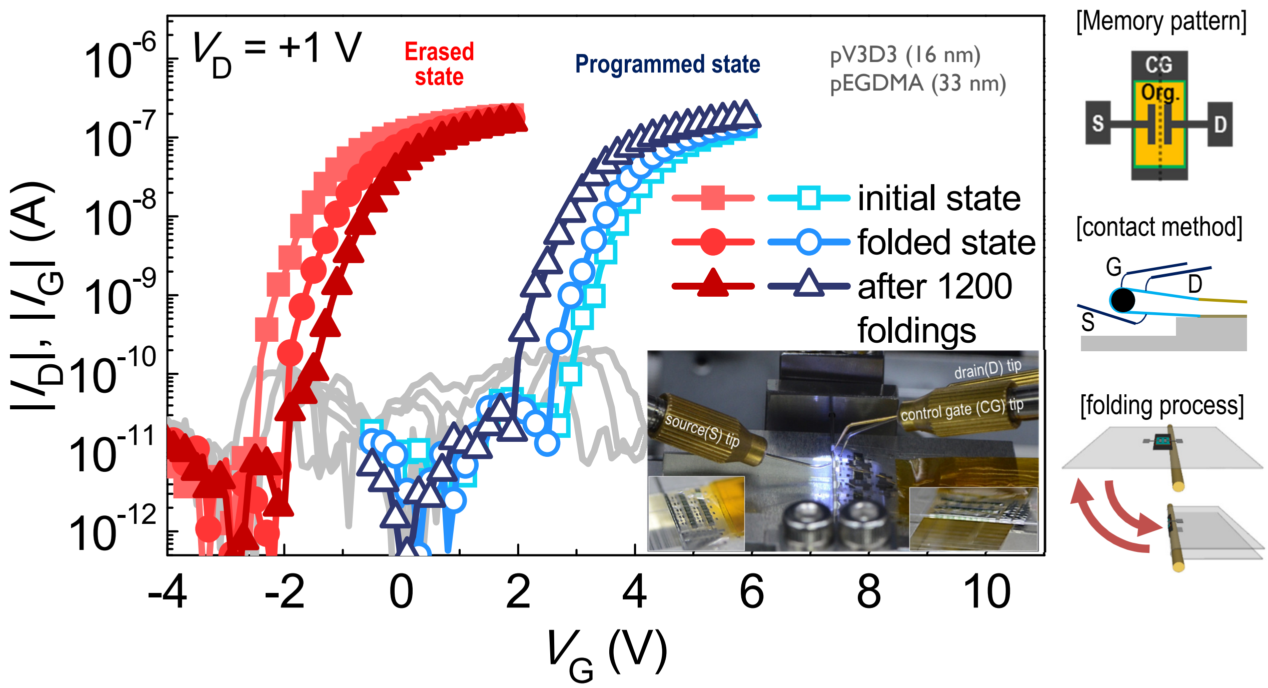
Custom-designed folding endurance test machine



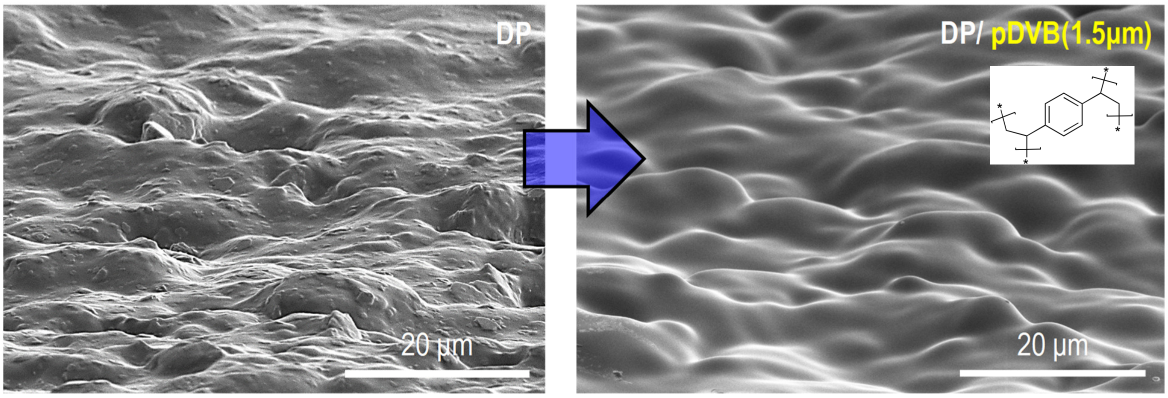
Foldable memory characteristics

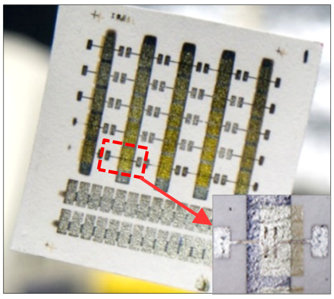
* ε = 1.0 %

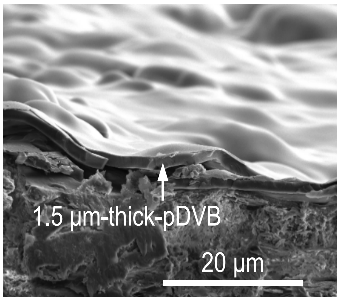


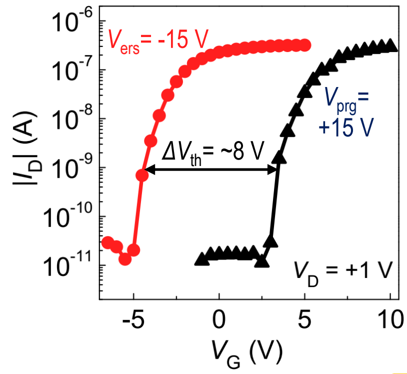
S. Lee et al. Nature Comm. 8, 725 (2017)

Other variations: memory on papers









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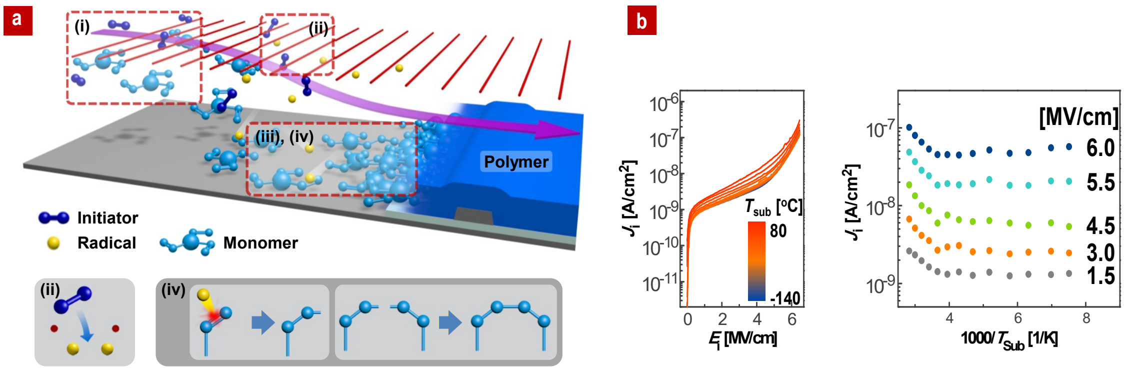
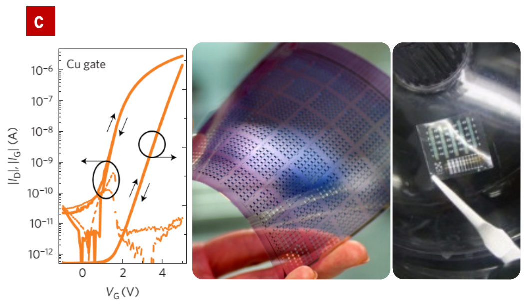
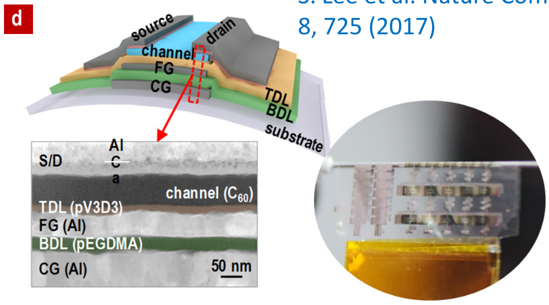
Summary

iCVD*-based polymers for versatile gate dielectrics in flexible electronics





S. Lee et al. Nature Comm. 8, 725 (2017)



Moon et al., Nature Mater. 14 (6) 628 (2015) [collaboration w/ Prof. S.G. Im and B.J. Cho]

Acknowledgement

- The work on TFTs w/iCVD-polymer GI was supported by:
  - the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (MSIP);
  - and the Center for Advanced Soft Electronics funded by MSIP as Global Frontier Project.
- The works on memory and photomemory were funded by Samsung Future Technology Center Program.
- We are grateful to S-Y. Choi at KAIST for allowing us to use a cryogenic vacuum probe station for temperature-dependent measurement of insulator characteristics.
- We also appreciate ETRI for the deposition of IGZO layers.