Redox-gated Molecular Memory Devices based on Dynamic Doping of Polythiophene

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University of Alberta
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Canada Foundation for Innovation

Today's solid state memory (>$100 billion annually):

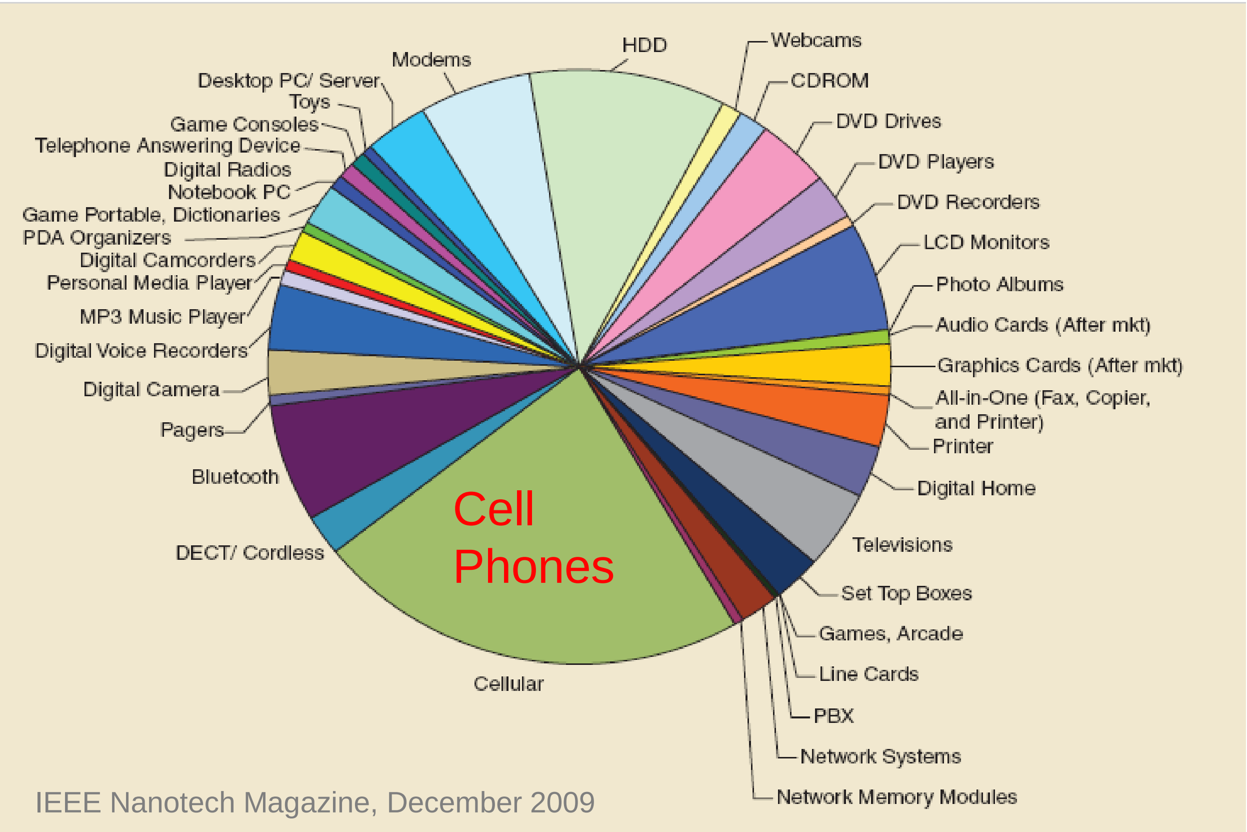
	write/erase speed	cell size	retention	cycle life
Dynamic Random Access Memory (DRAM)	< 10 nsec	1T1C*	65 msec	$>10^{15}$
Static RAM	< 1 nsec	6T	long with power on	$>10^{15}$
Flash (cameras, USB stick)	1 µsec- 10 msec	1T	> 10 yrs	10^{3} - 10^{5}

No "universal" memory- we need different types for different needs

* T = transistor, C = capacitor

Nonvolatile solid state Memory Devices:

- enabled mobile electronics (cell phones, MP3 players, etc)
- ~$65 billion/year (not counting disk drives)
- 16 billion units (i.e. chips) sold in 2009



IEEE Nanotech Magazine, December 2009

“Alternative” nonvolatile memory in ITRS roadmap:

Phase Change RAM

Magnetic RAM

Polymer memory

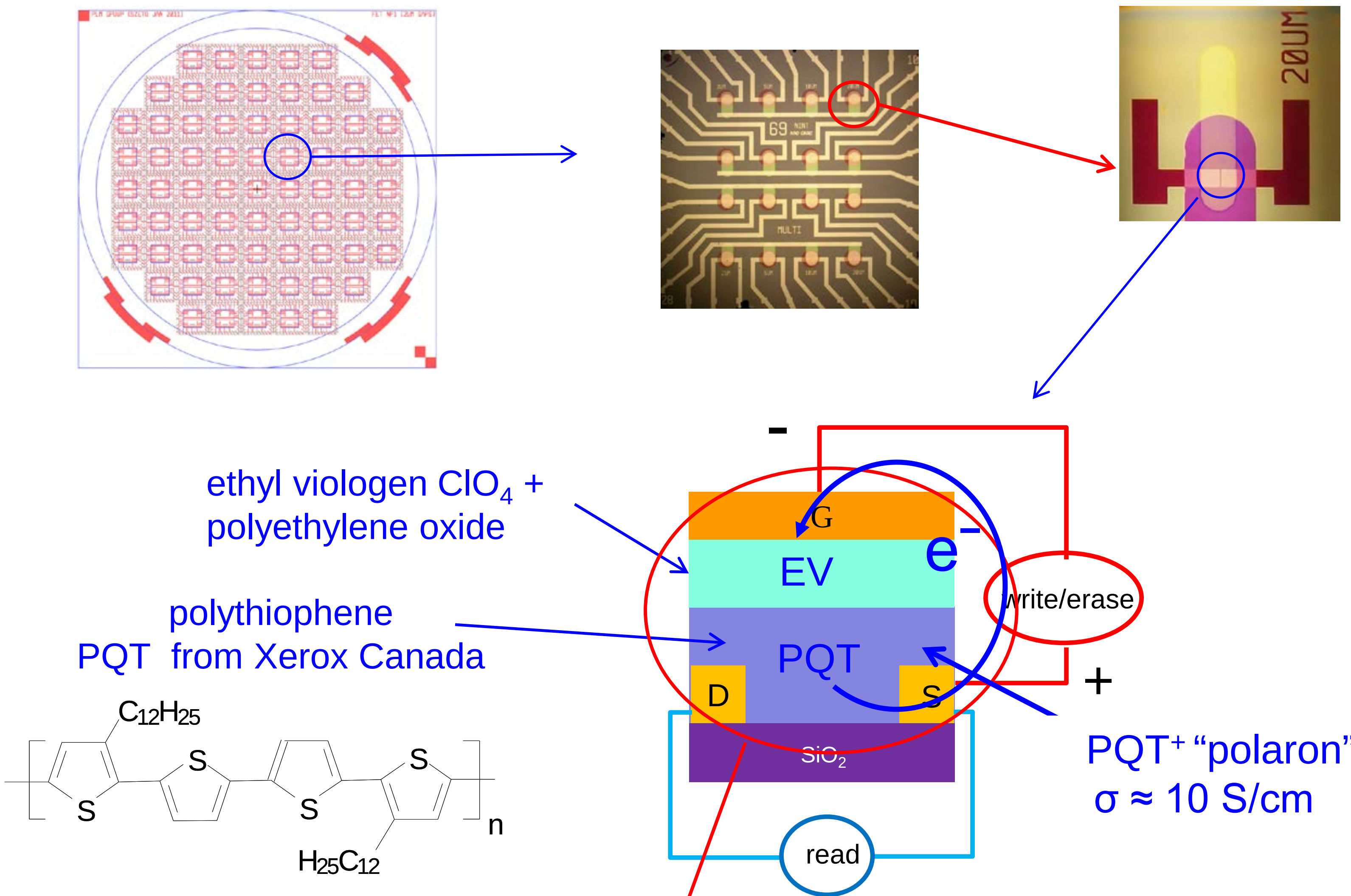
Fuse/antifuse

Molecular memory

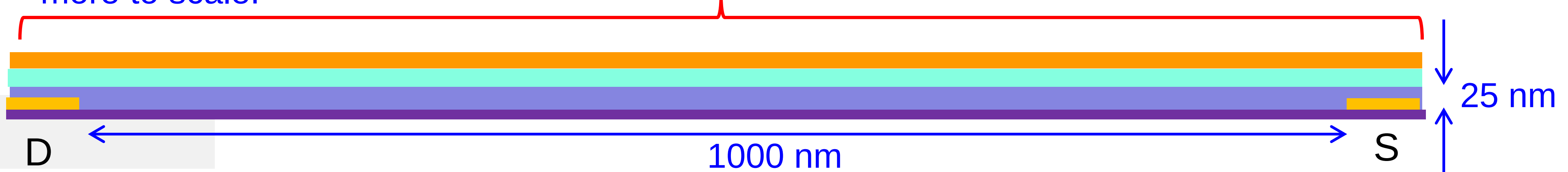
Nanomechanical

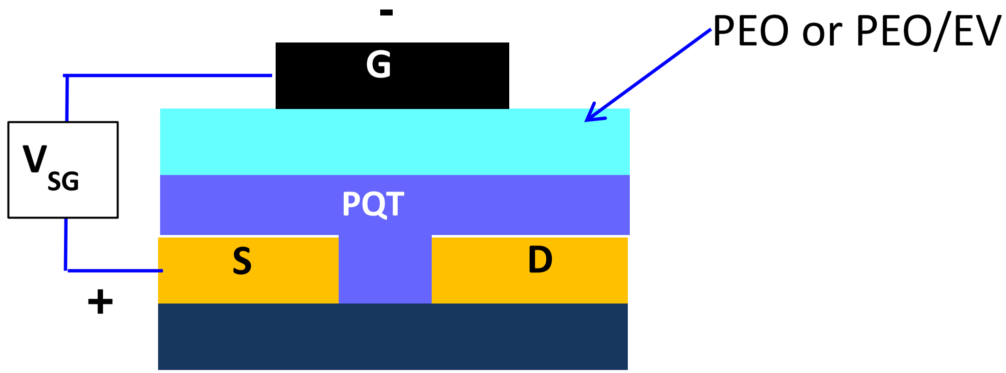
Scifinder hits:	“nonvolatile memory”:	31,800
	“resistance memory”:	9,900
	“conductance switching”:	10,560

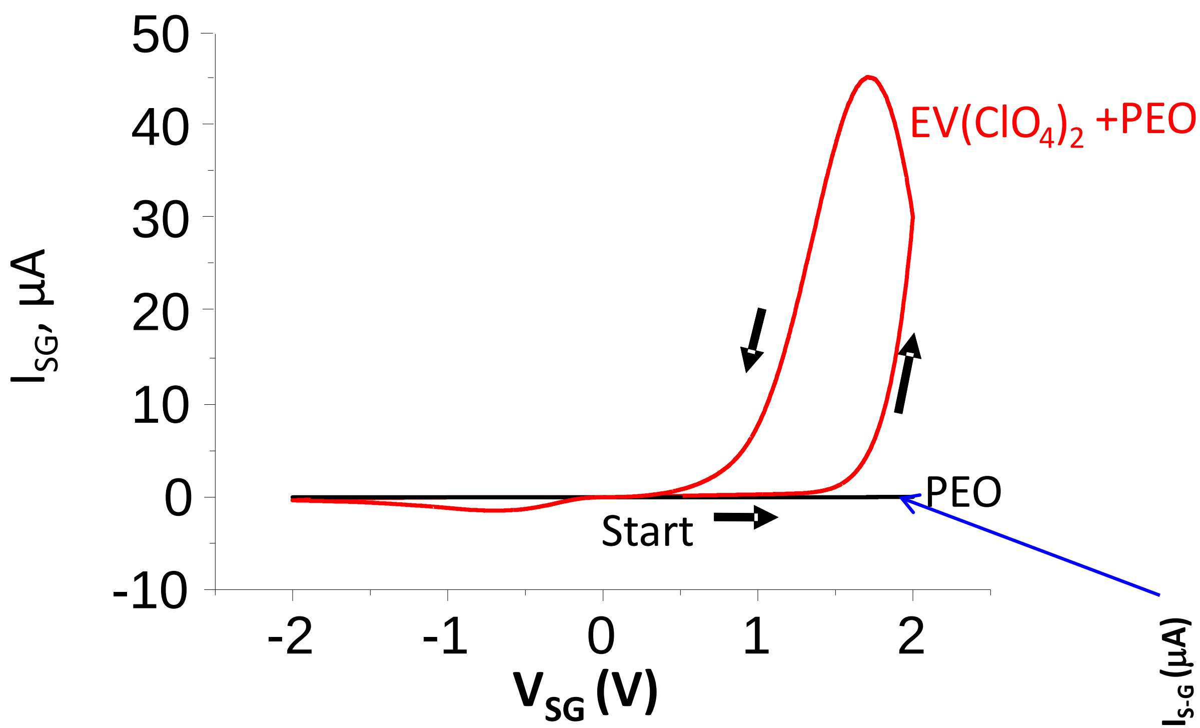
“Redox gated” molecular memory:

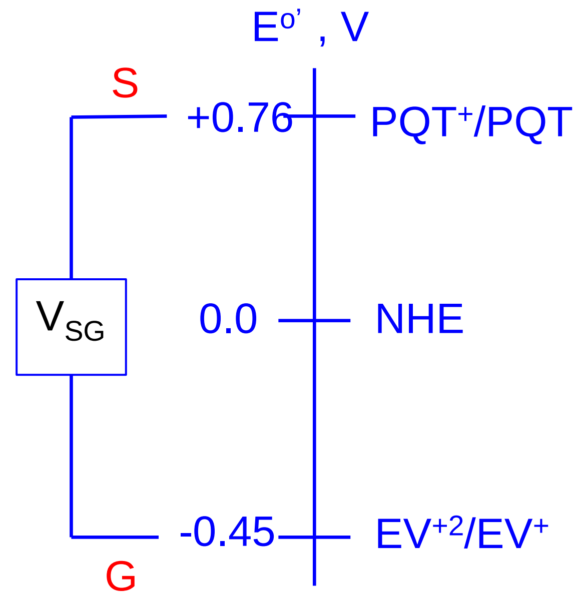


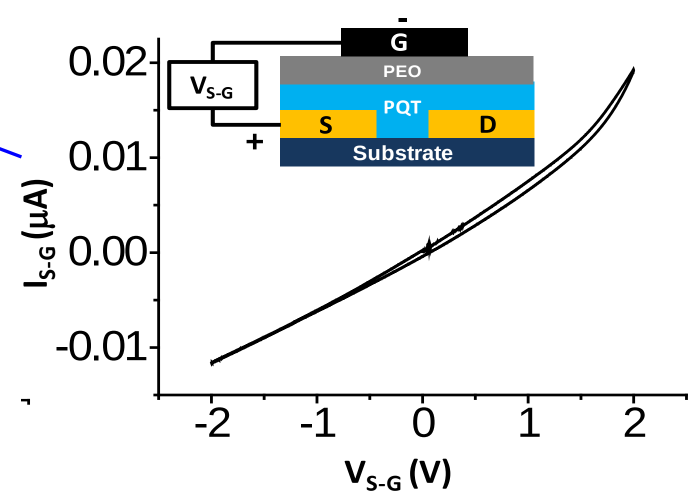
more to scale:









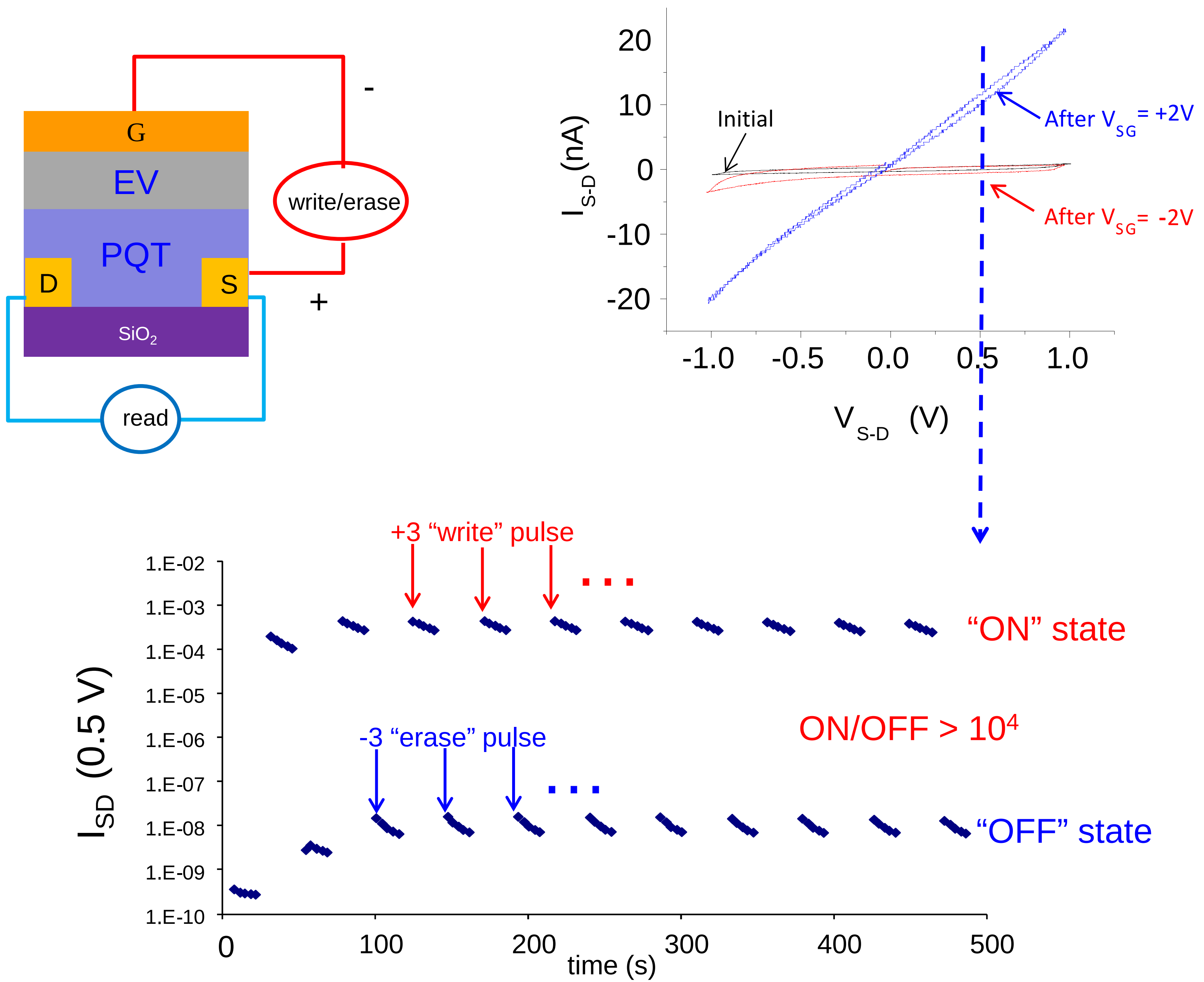


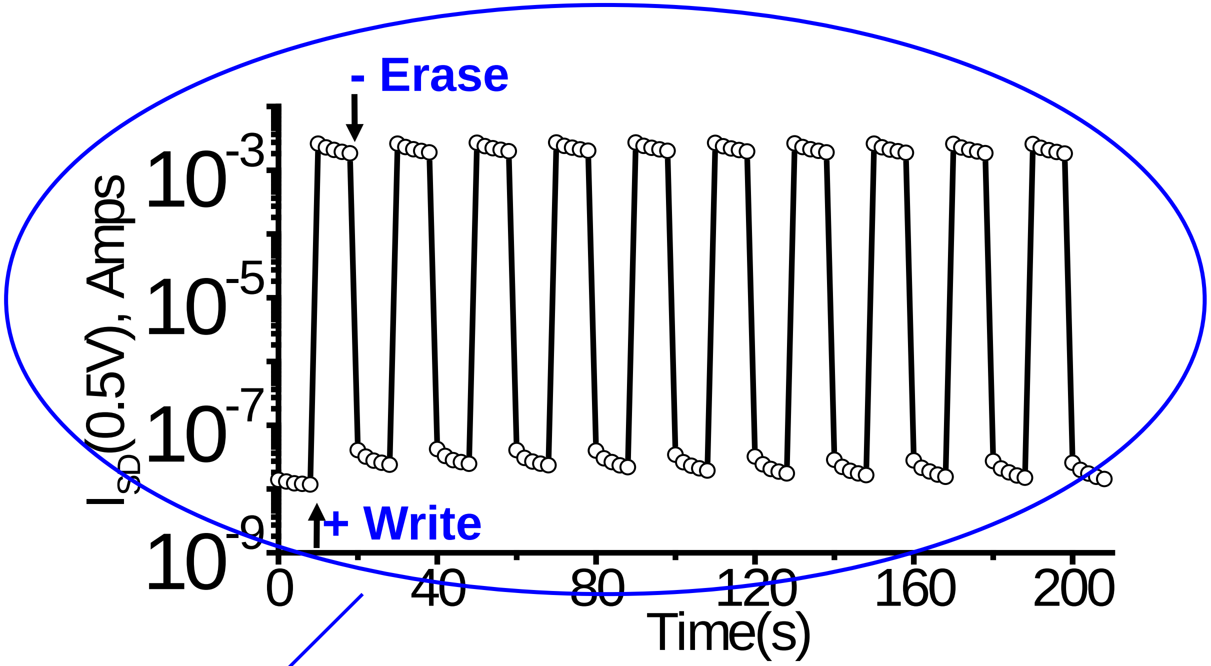
V_{SG} drives a redox reaction:

"write" →

$$PQT + EV^{+2} \rightarrow PQT^{+} + EV^{+}$$

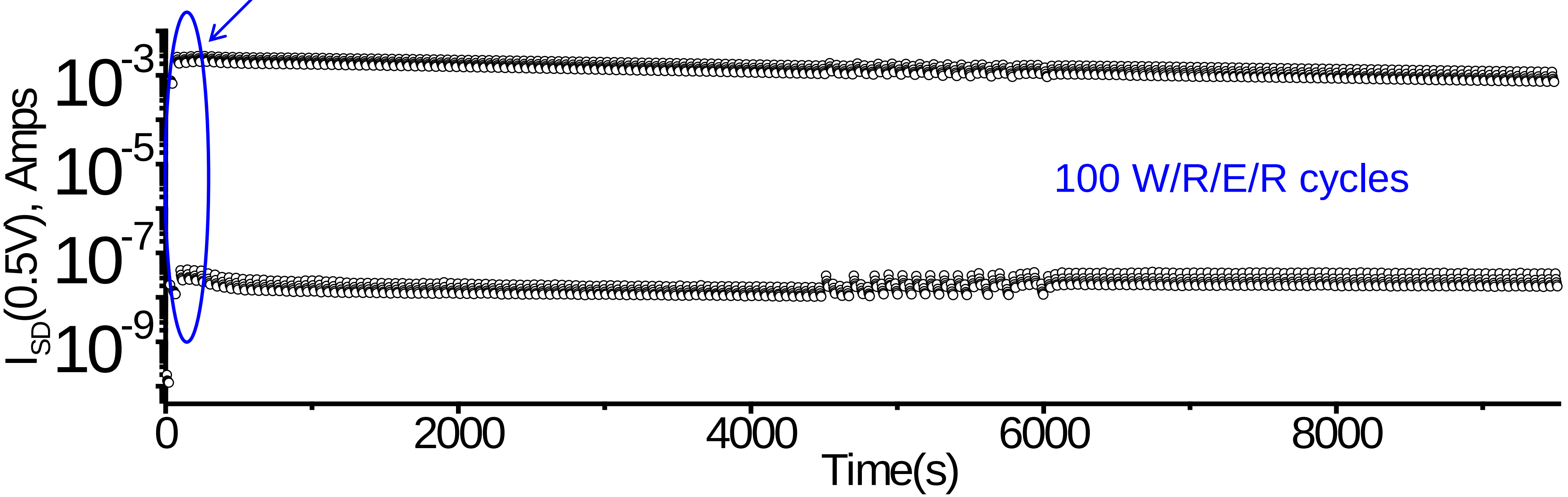
← "erase"


G
EV
PQT
D
S
SiO_2
write/erase
-
+
read
Initial
After V_{SG} = +2V
After V_{SG} = -2V
I_{S-D} (nA)
V_{S-D} (V)
20
10
0
-10
-20
-1.0
-0.5
0.0
0.5
1.0
+3 "write" pulse
-3 "erase" pulse
"ON" state
"OFF" state
ON/OFF > 10^4
I_{SD} (0.5 V)
time (s)
1.E-02
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
0
100
200
300
400
500



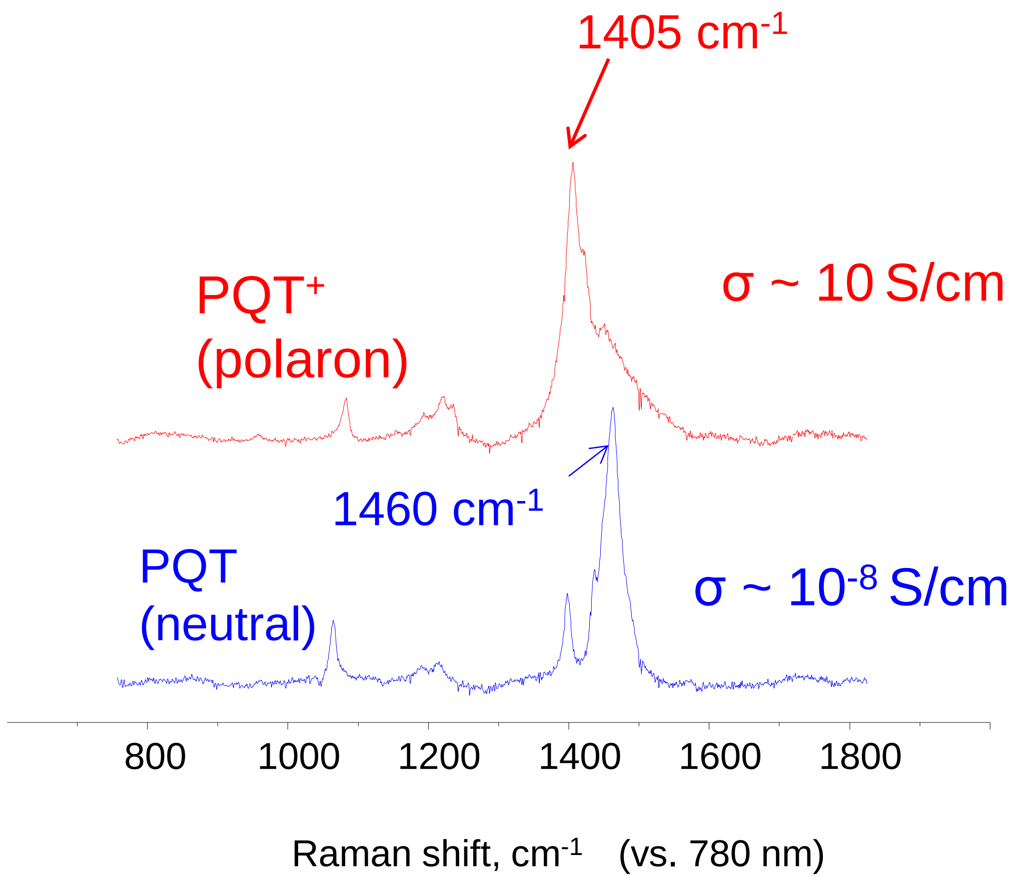
Note:

- resistance readout
- low energy W/E
- nondestructive “read”
- should scale well
- potentially longer cycle life than “flash”



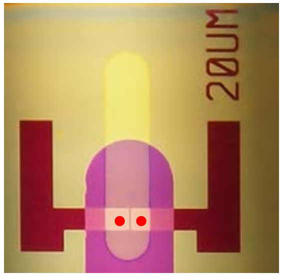
ACS Appl. Mater. Interfaces ***2013, 5, 11052.***

Raman spectroelectrochemistry of PQT:

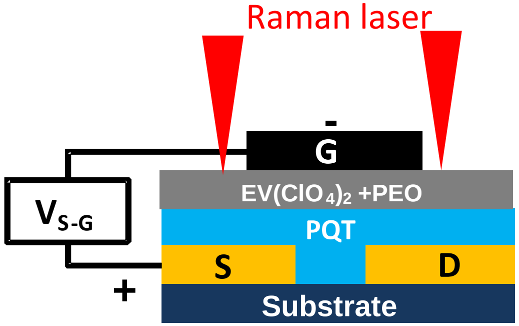


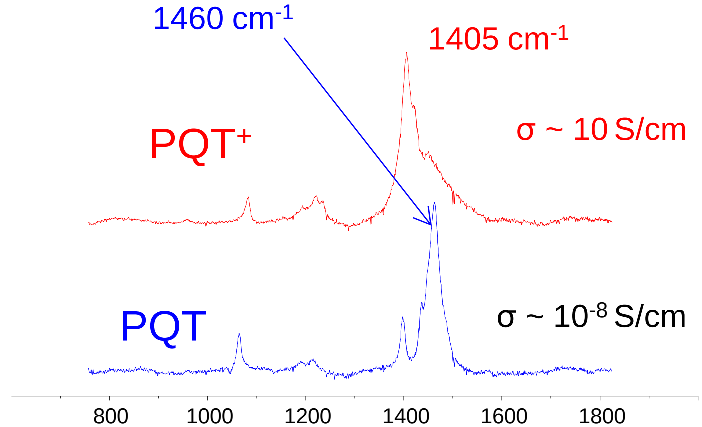
Raman permits monitoring of PQT^+ formation in *working* memory device

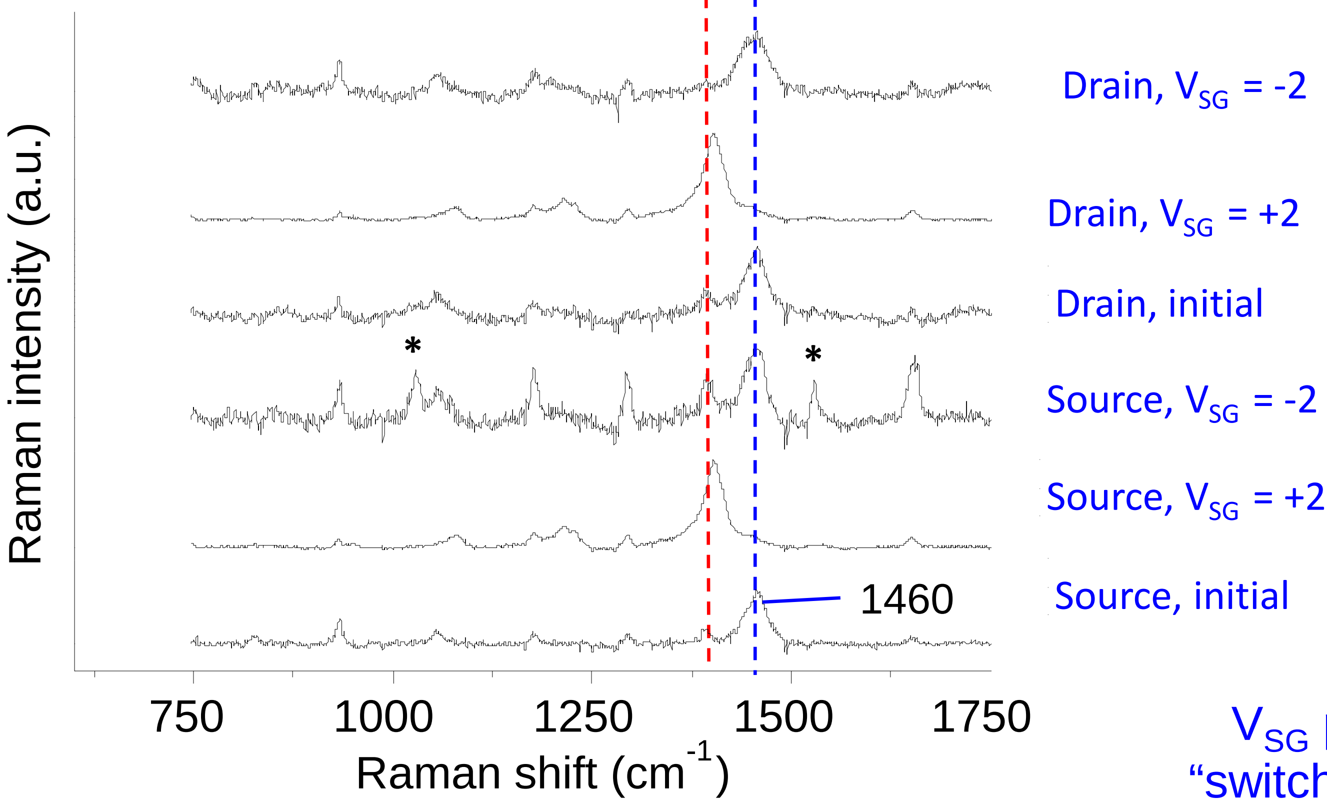
Solid state spectroelectrochemistry:



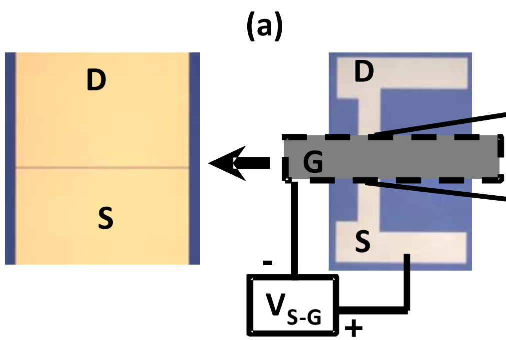
top view







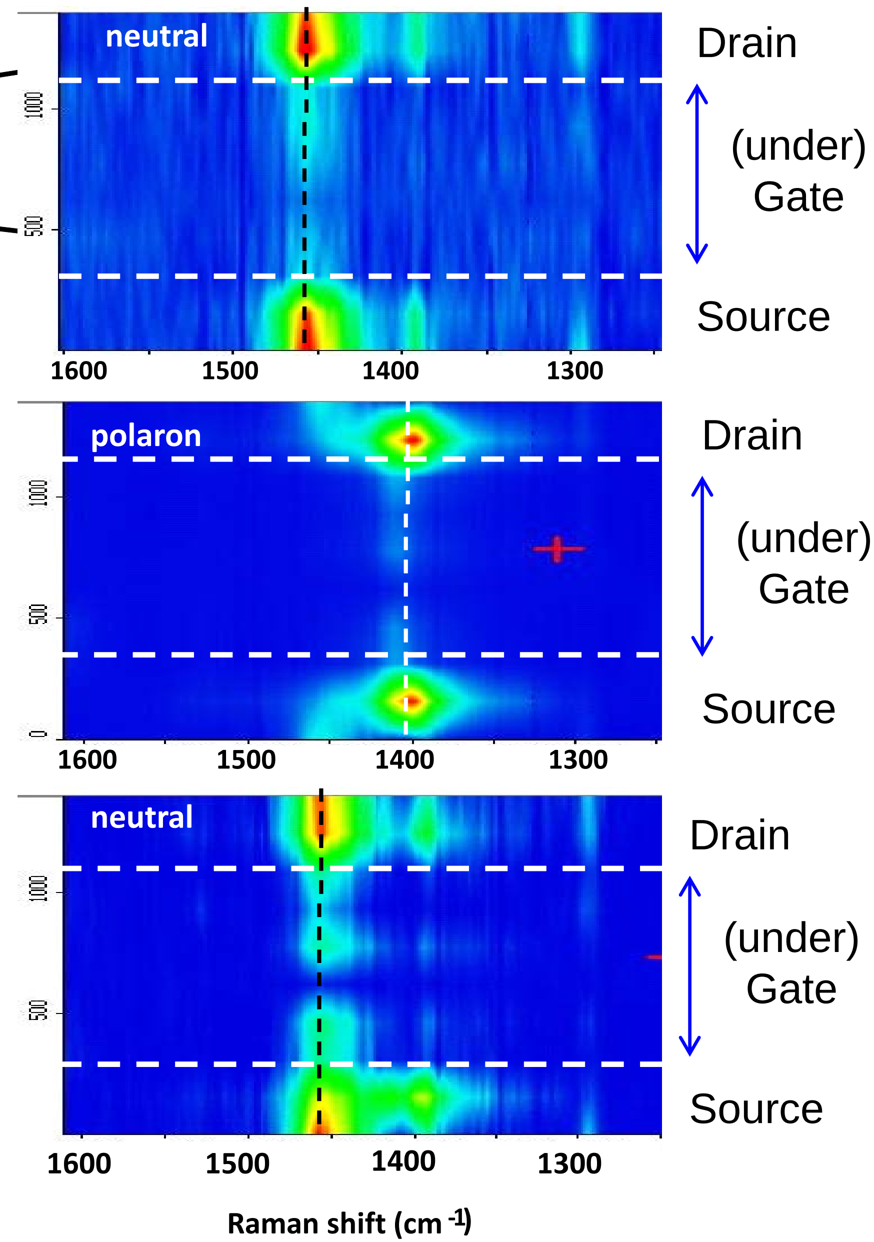
V_{SG} pulses are "switching" polymer between high and low conductance states



Initial

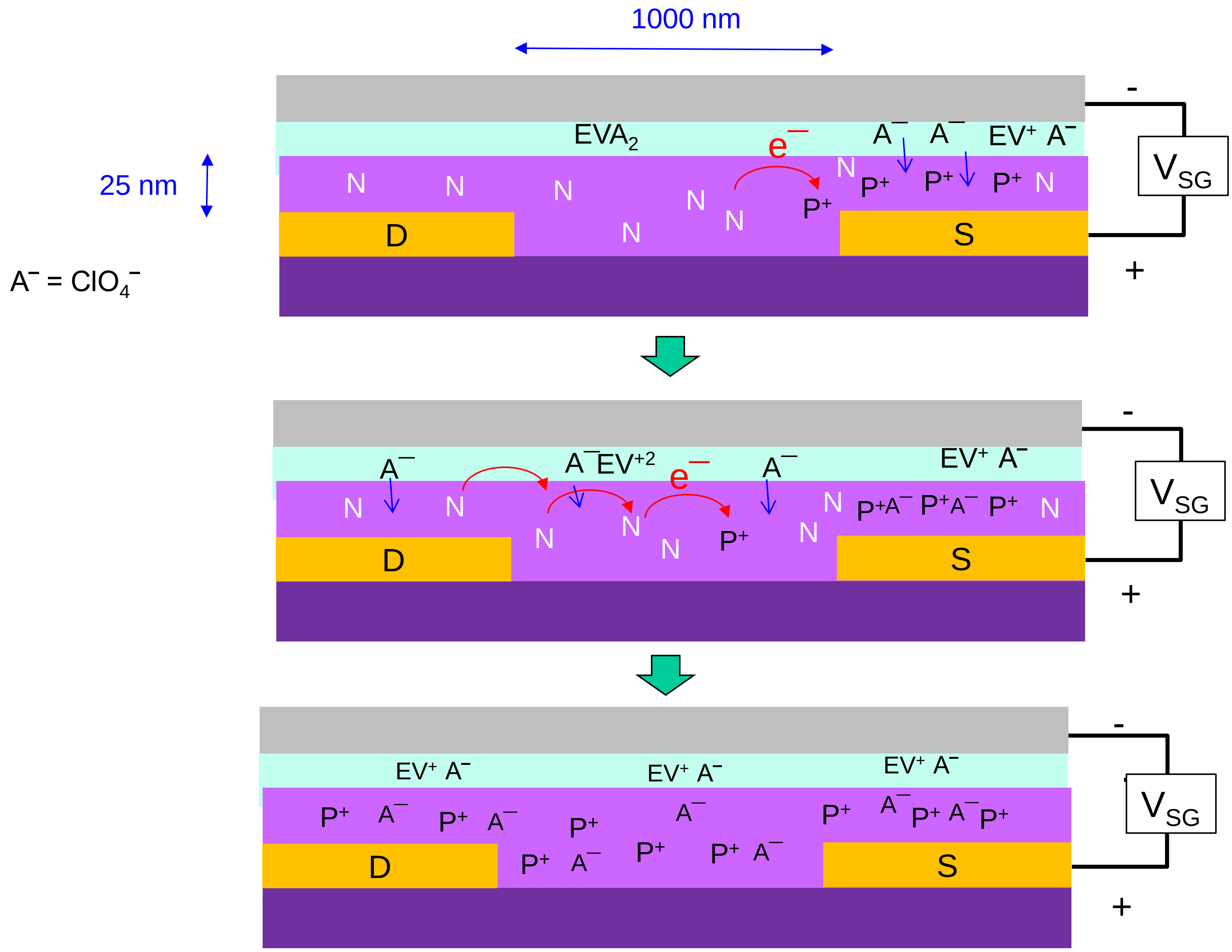
$V_{SG} = +2V$

$V_{SD} = -2V$



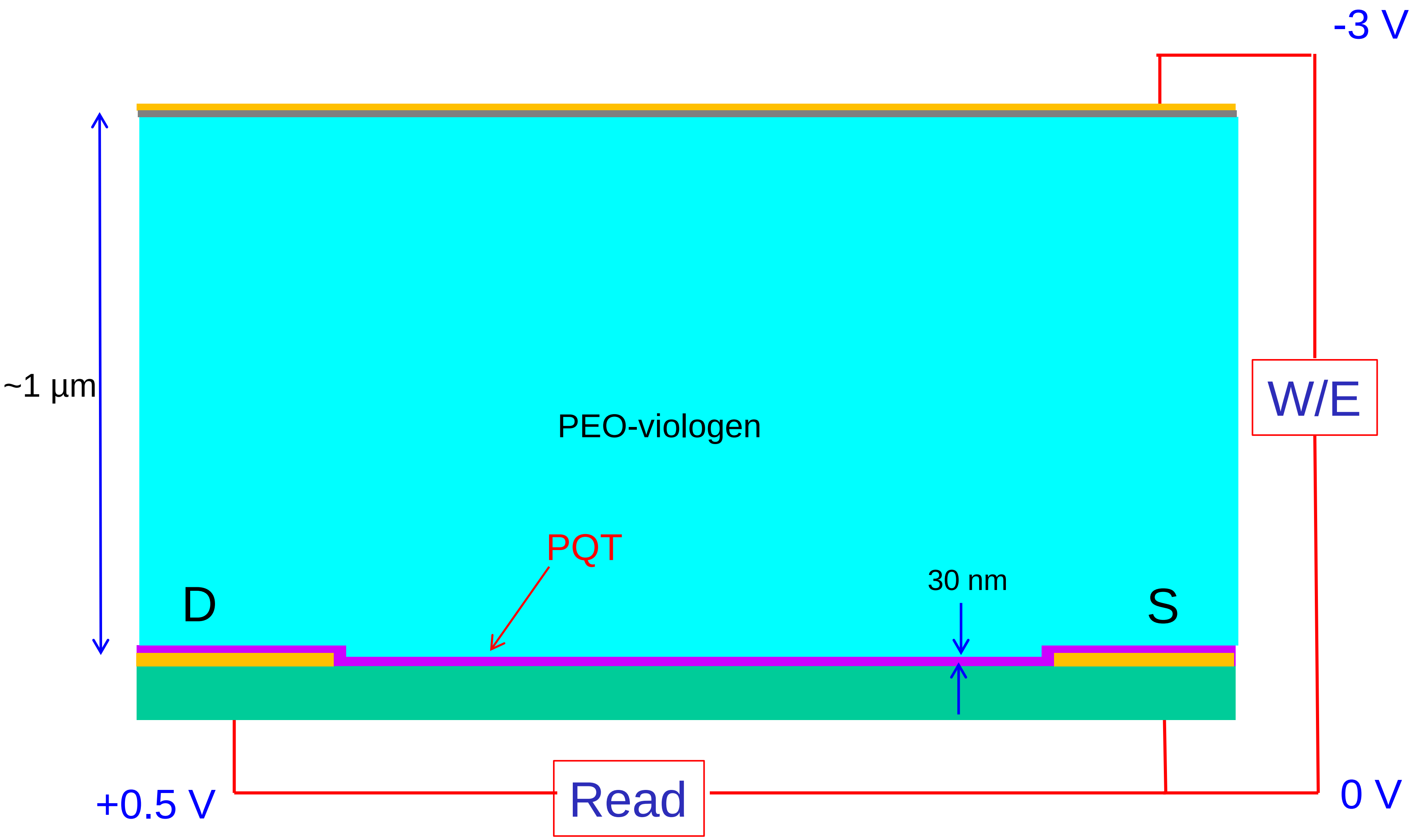
- polaron generation mediates conductance and "memory"
- polaron is produced in *entire* source/channel/drain region

J. Am. Chem Soc. 2012, 134, 14869

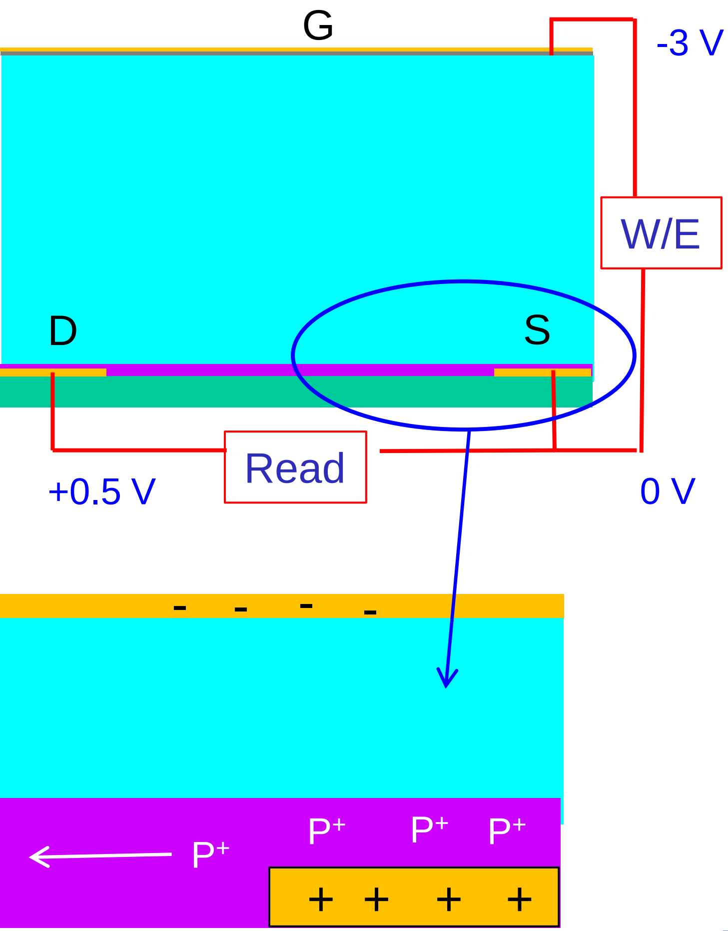


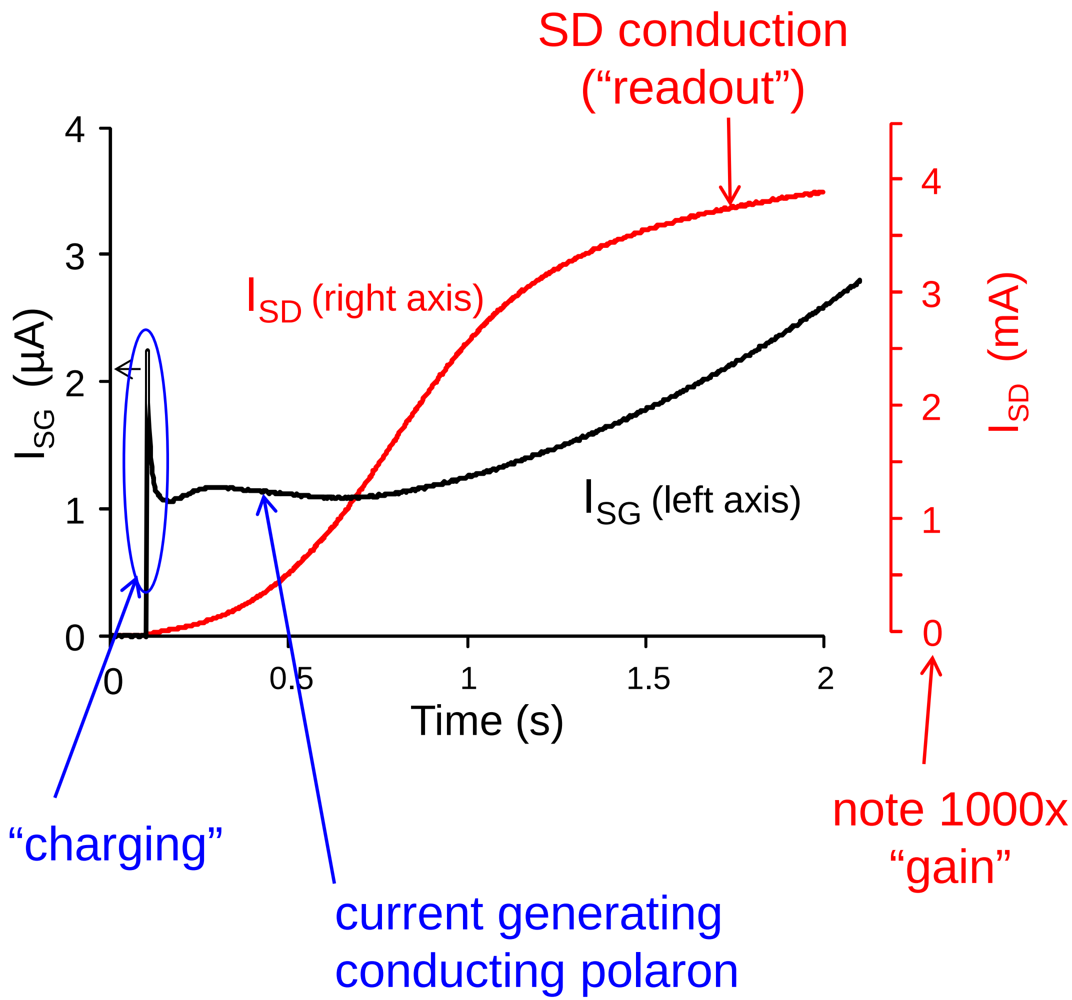
Polythiophene is not only a redox polymer but also a conducting polymer, so electron transport “laterally” is quite efficient.

A closer look at dynamics, using a circuit equivalent to a bi-potentiostat:



Now, monitor S-D current *during* +3 V S-G “write” pulse

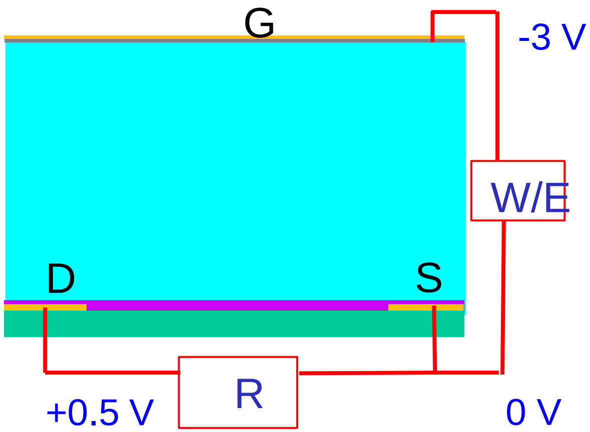




- charging (RC)
- P^+ generation
- P^+ propagation

Which one(s) control speed?

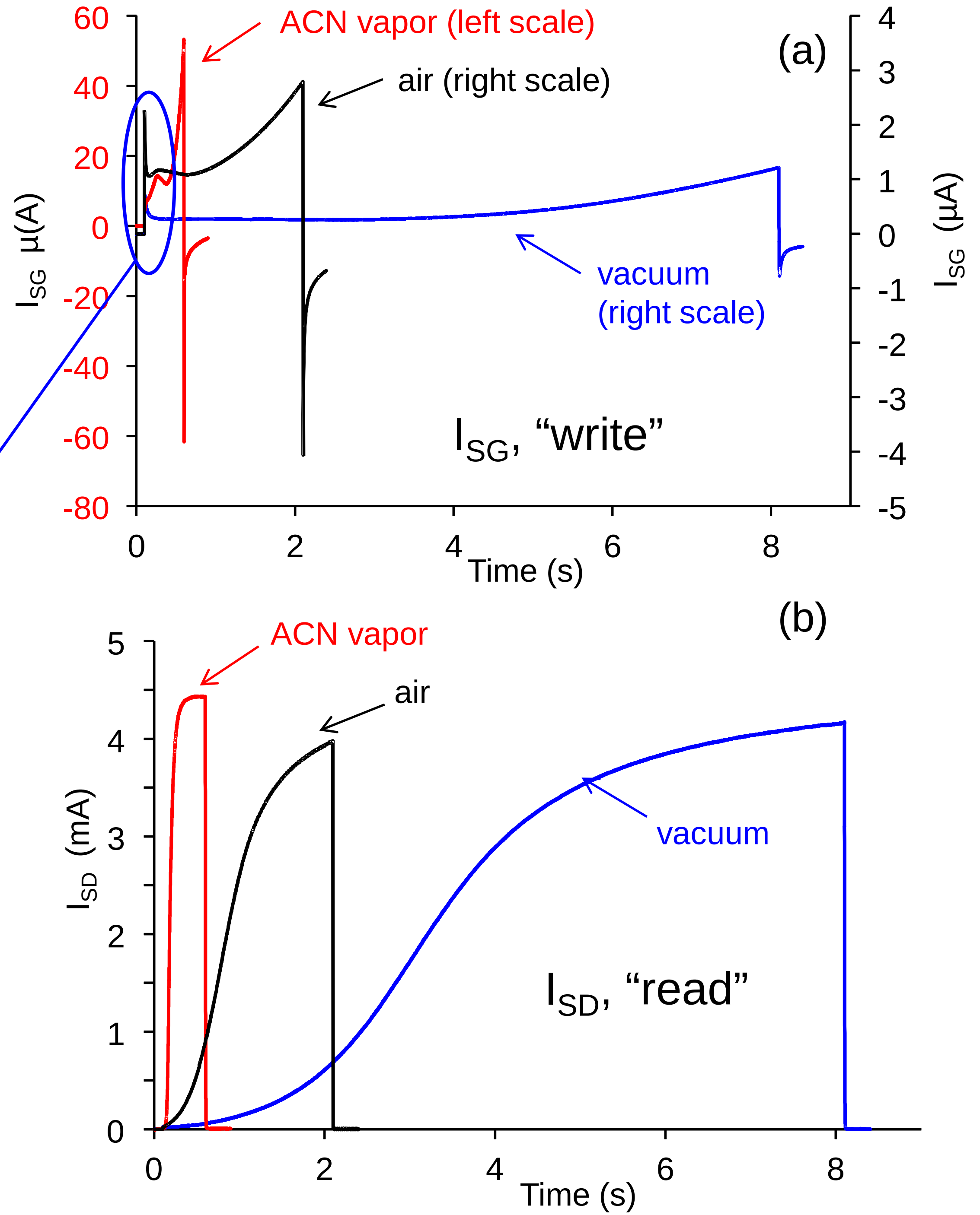
An interesting effect of atmosphere:



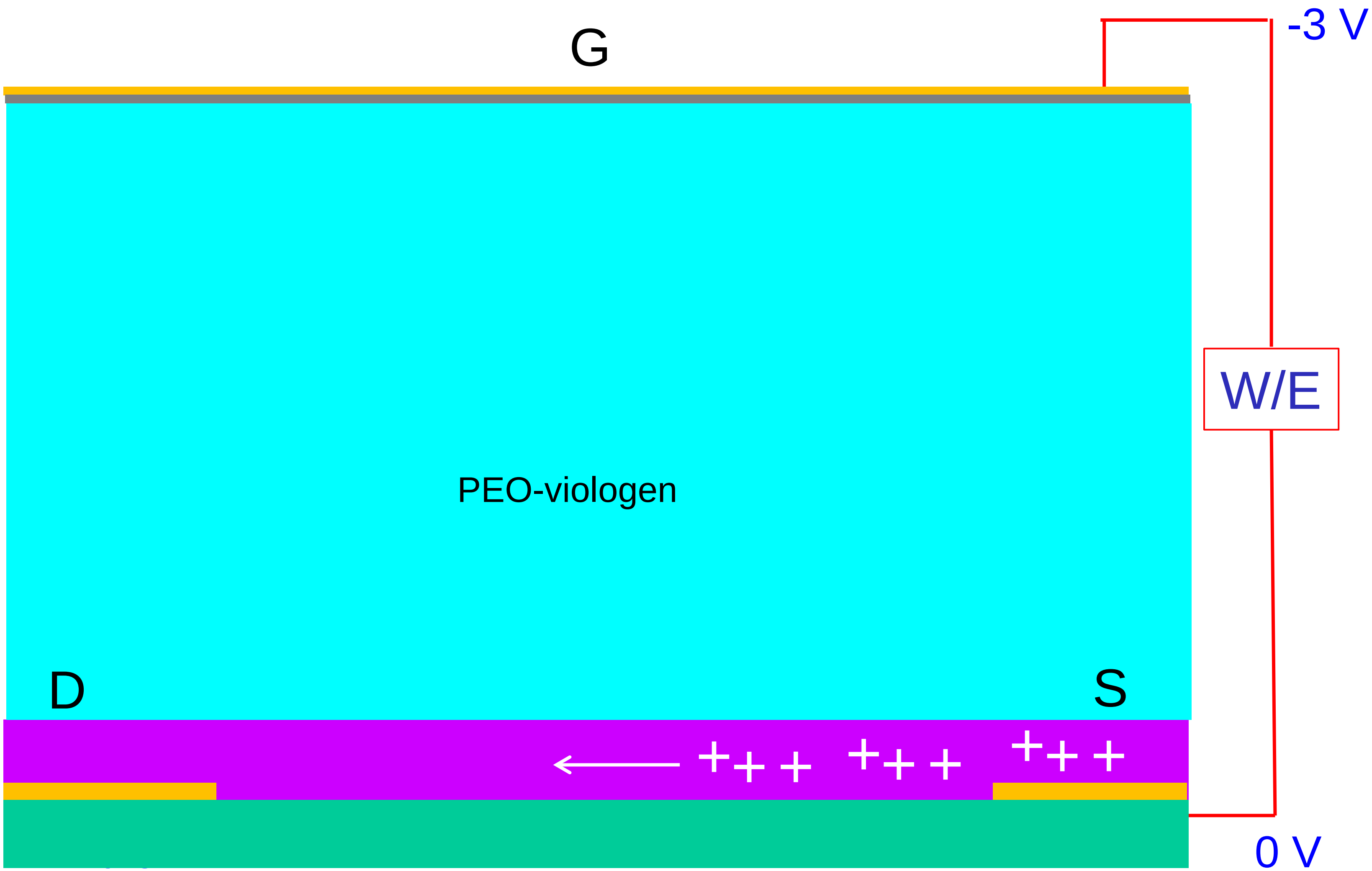
RC charging?
ionic mobility?
propagation speed?

	RC (msec)
Ambient	0.18
Vacuum	0.037
ACN vapor	0.081

all < 1 msec, can't be the problem

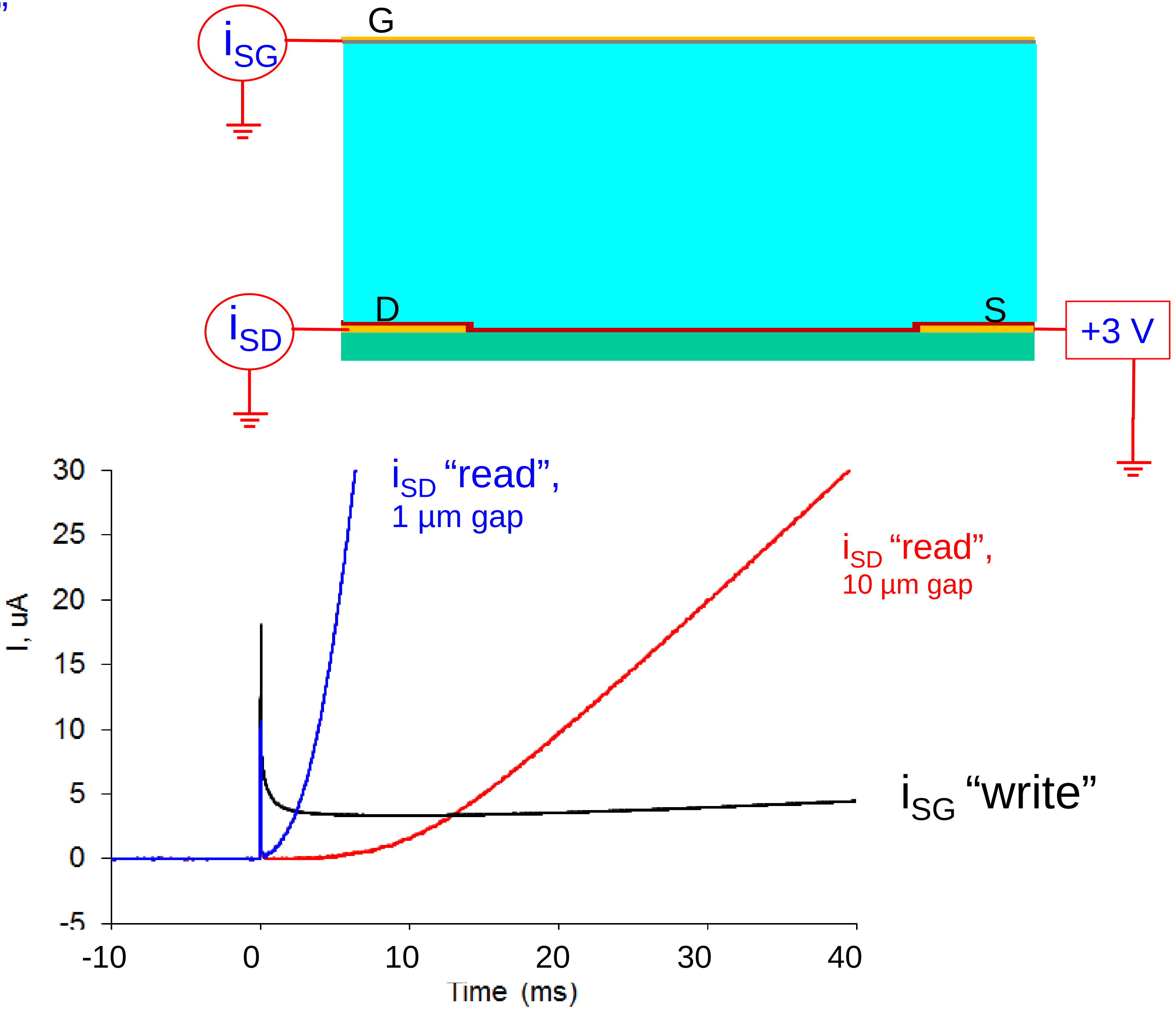


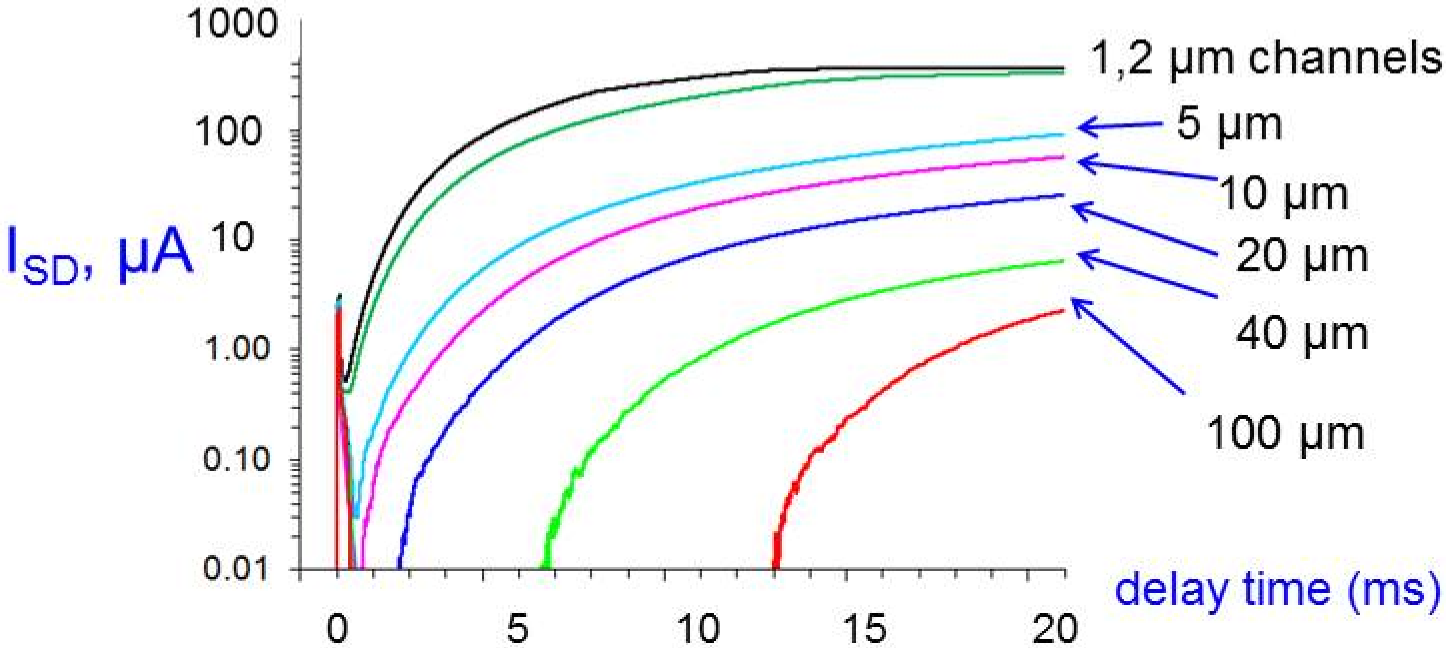
Propagation of polarons into channel:

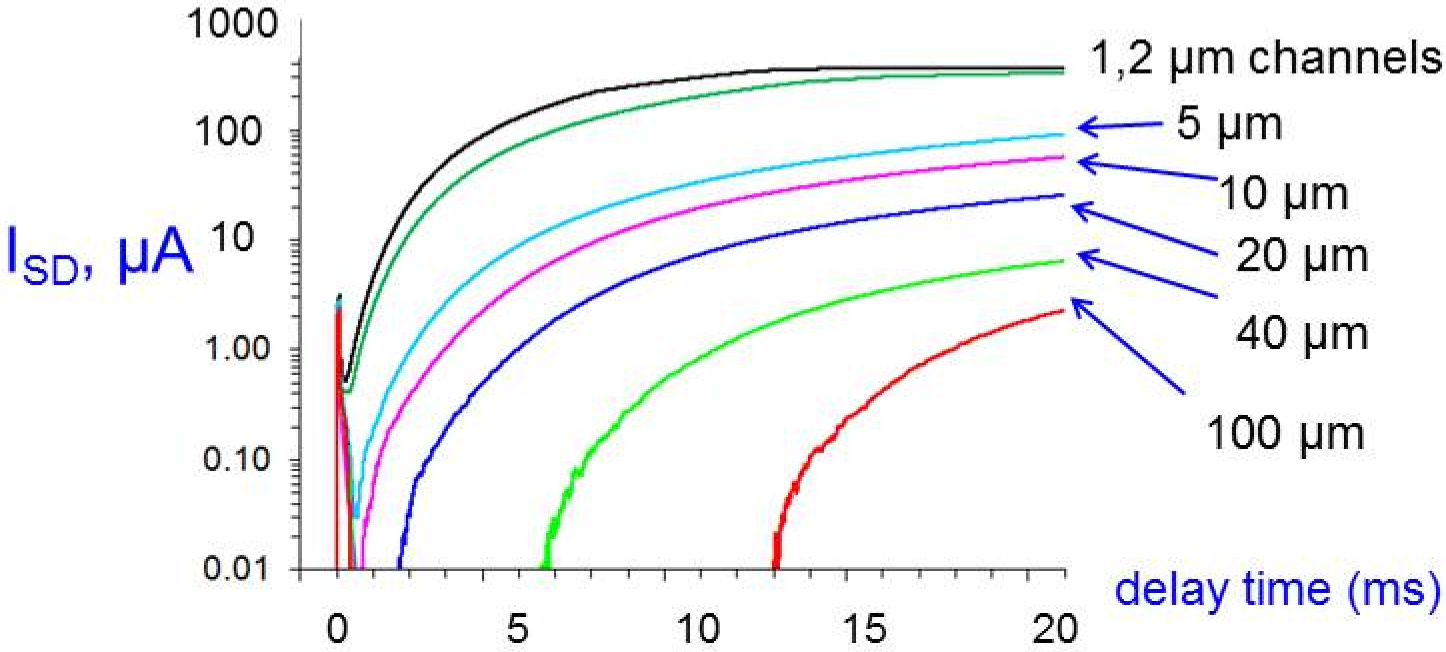


Propagation is essential, could it be the slow step?

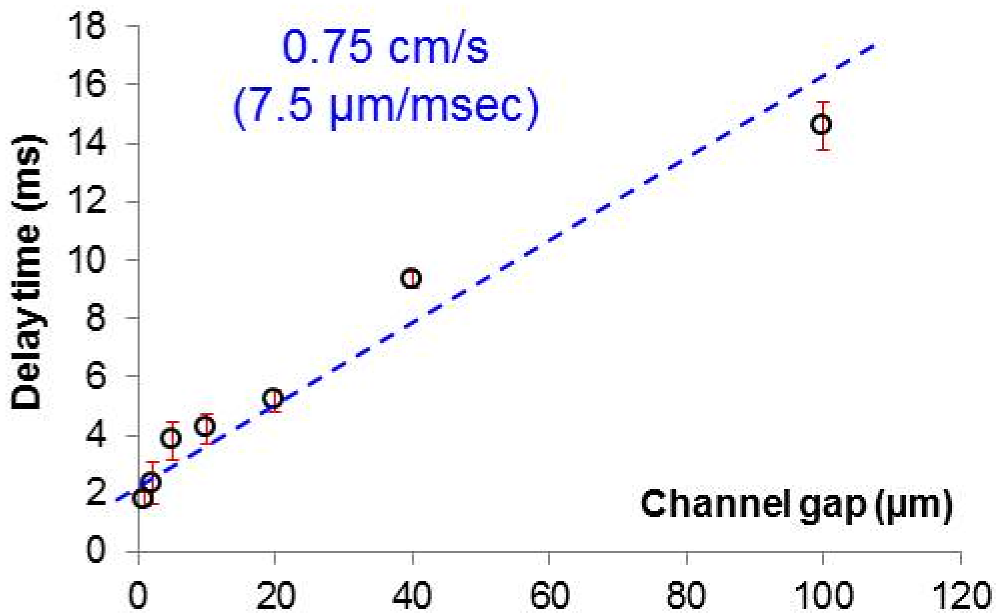
“Propagation” experiment:



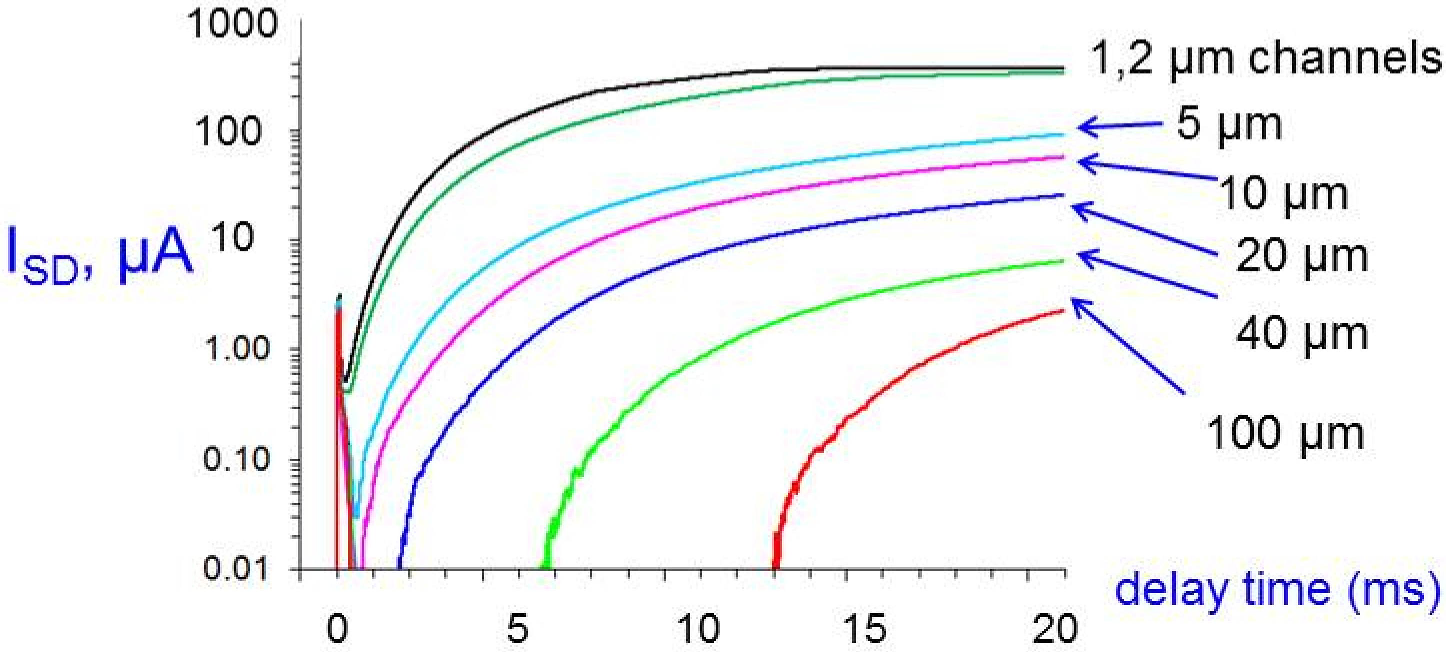

1000
100
10
1.00
0.10
0.01
I_{SD}, µA
0
5
10
15
20
delay time (ms)
1,2 µm channels
5 µm
10 µm
20 µm
40 µm
100 µm



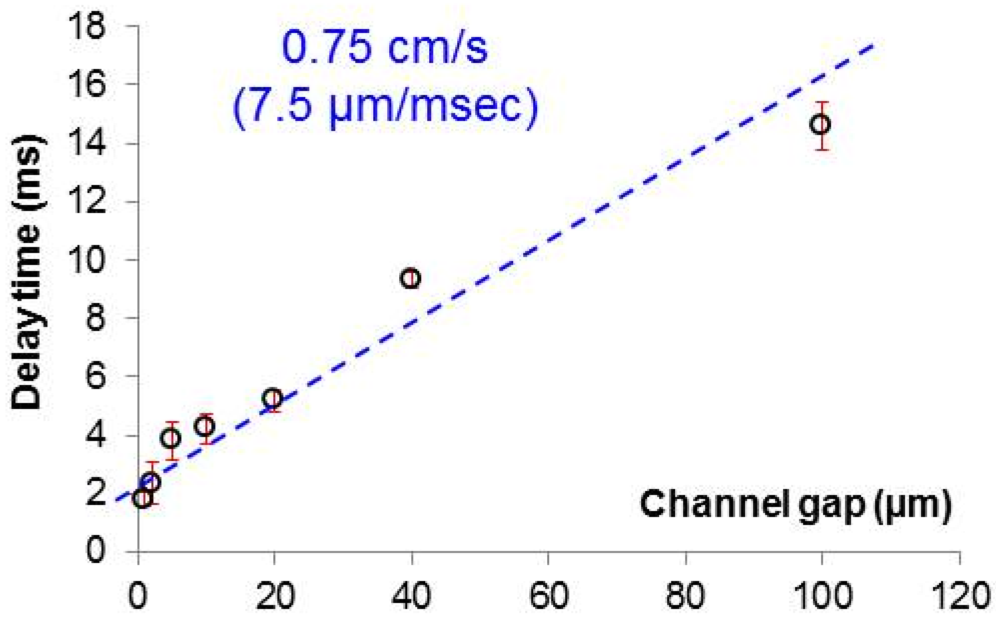
1000
100
10
1.00
0.10
0.01
I_{SD}, μA
0
5
10
15
20
delay time (ms)
1,2 μm channels
5 μm
10 μm
20 μm
40 μm
100 μm



0.75 cm/s
(7.5 μm/msec)
Delay time (ms)
Channel gap (μm)
0
2
4
6
8
10
12
14
16
18
0
20
40
60
80
100
120

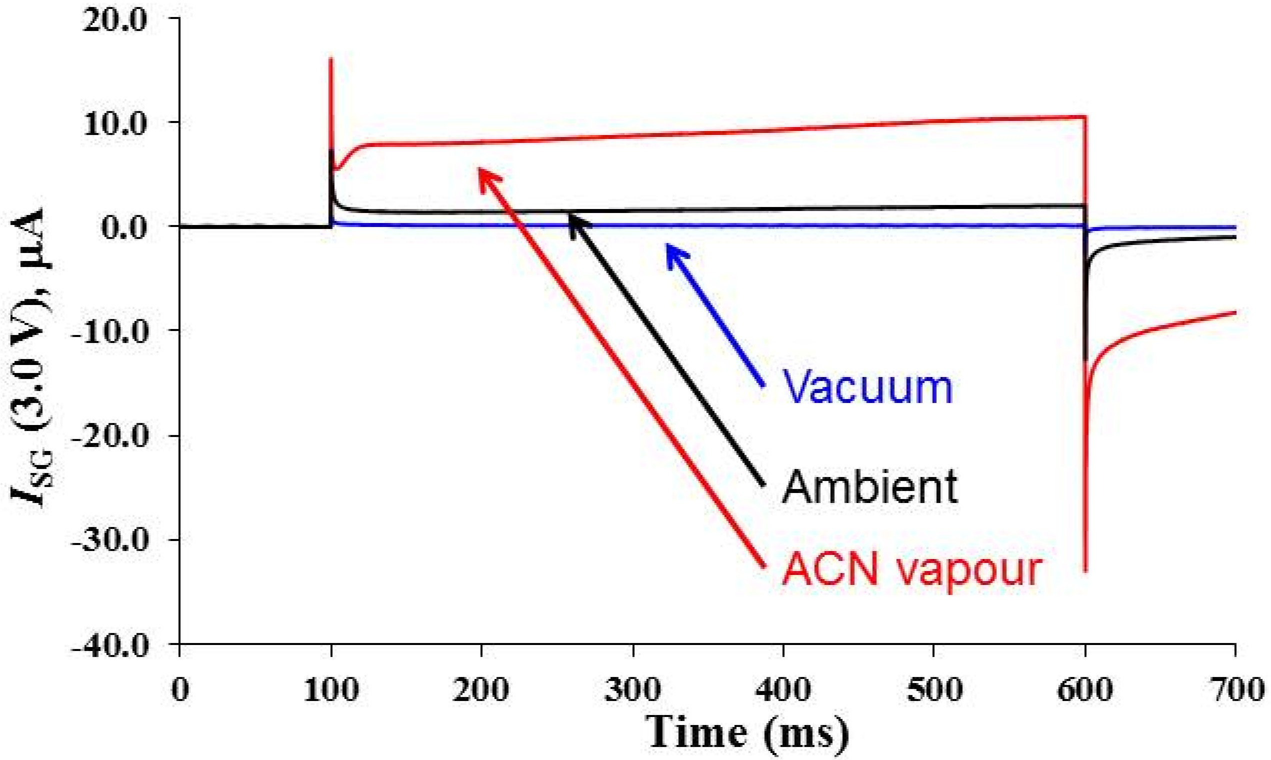


for our 1-5 µm channels, propagation delay is only a few msec. Cannot explain "write" times of ~ 1 sec



I_{SG} "write" current:

	RC (msec)	R (Ω)
Ambient	0.18	250 k
Vacuum	0.037	240 k
ACN vapor	0.081	60 k



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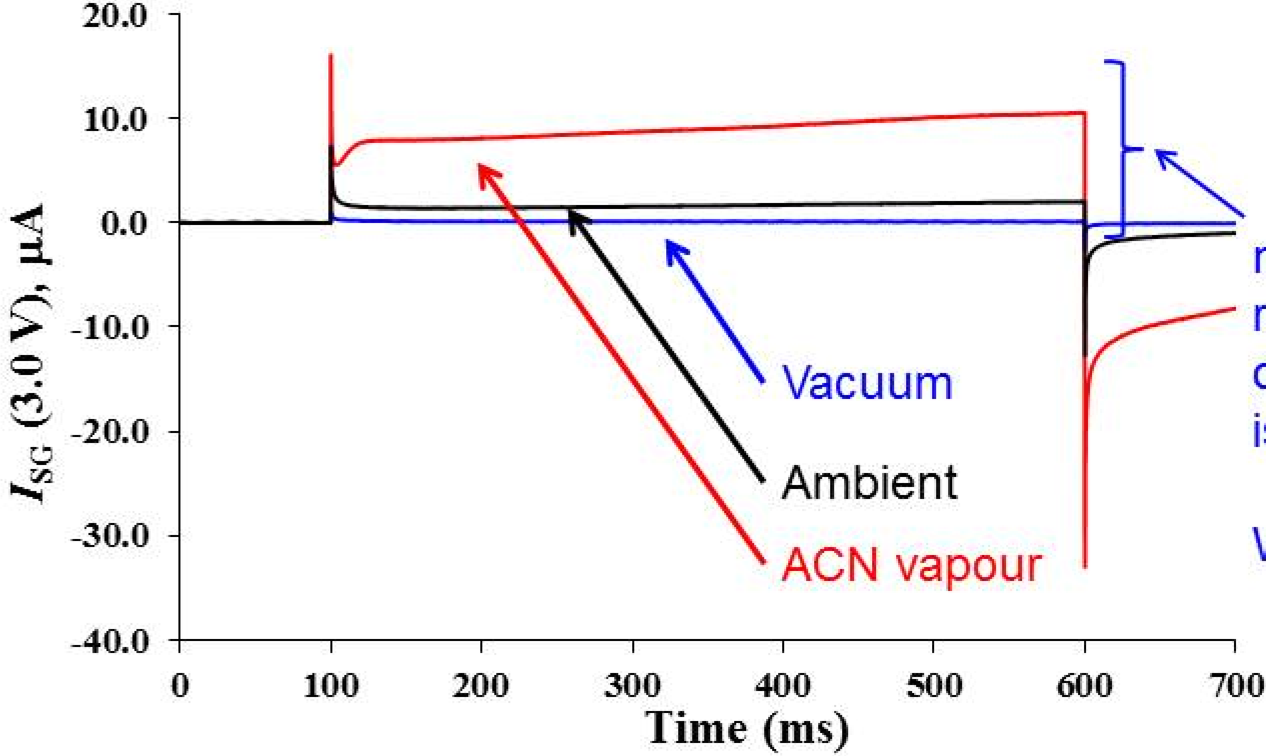
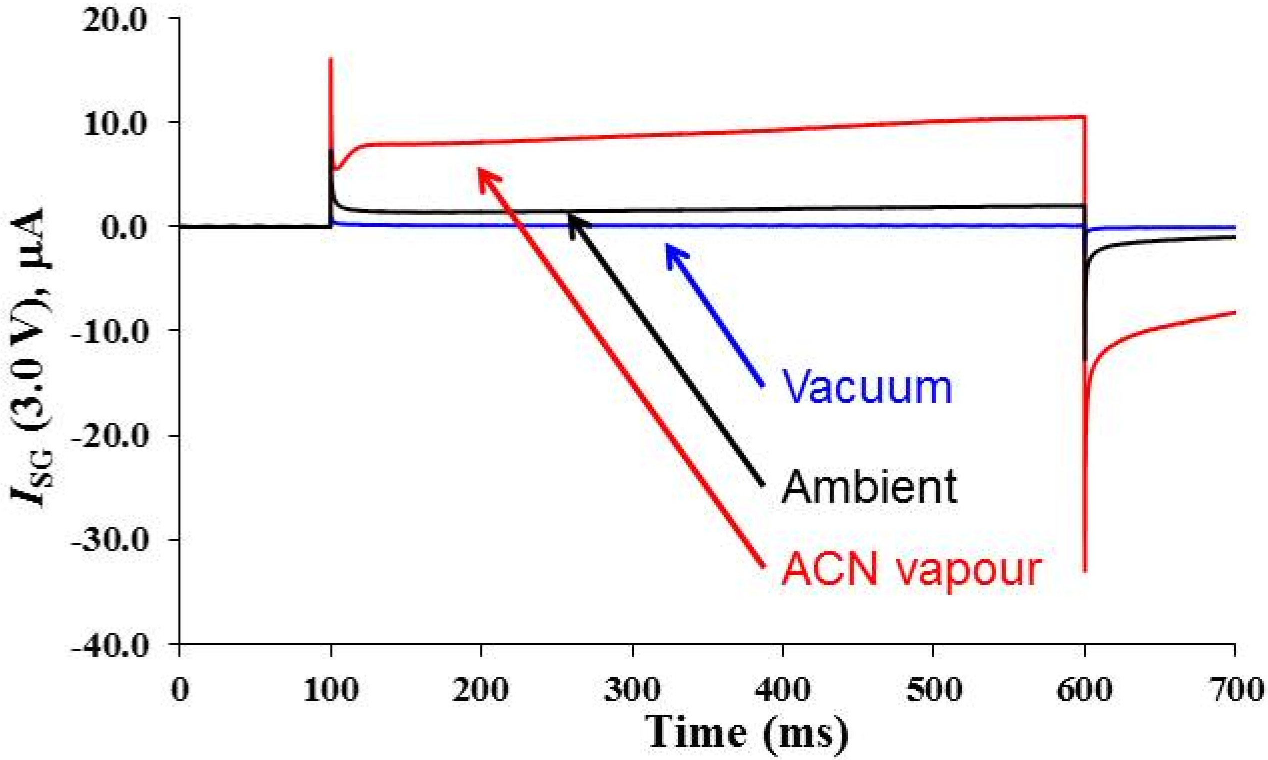


note that P^+ generation rate strongly depends on atmosphere, and is nearly t-independent.

Why?

	RC (msec)	R	iR for i= 5 uA
Ambient	0.18	250 kΩ	1.25 V
Vacuum	0.037	240 kΩ	1.21 V
ACN vapor	0.081	60 kΩ	0.30 V

} major ohmic losses in electrolyte ! (Ambient, Vacuum)



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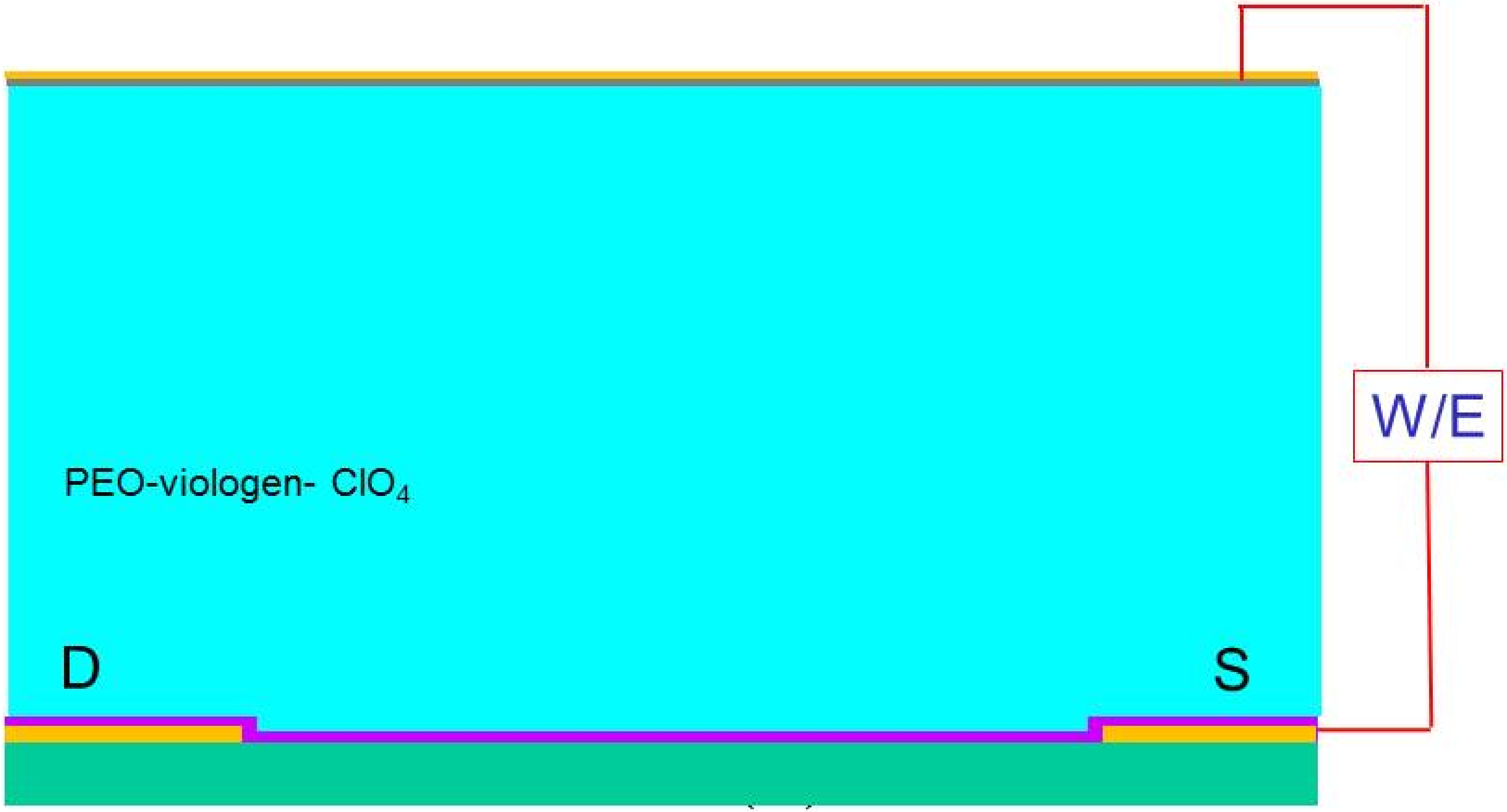

	RC (msec)	R	iR for i= 5 uA	
Ambient	0.18	250 kΩ	1.25 V	major ohmic losses in electrolyte !
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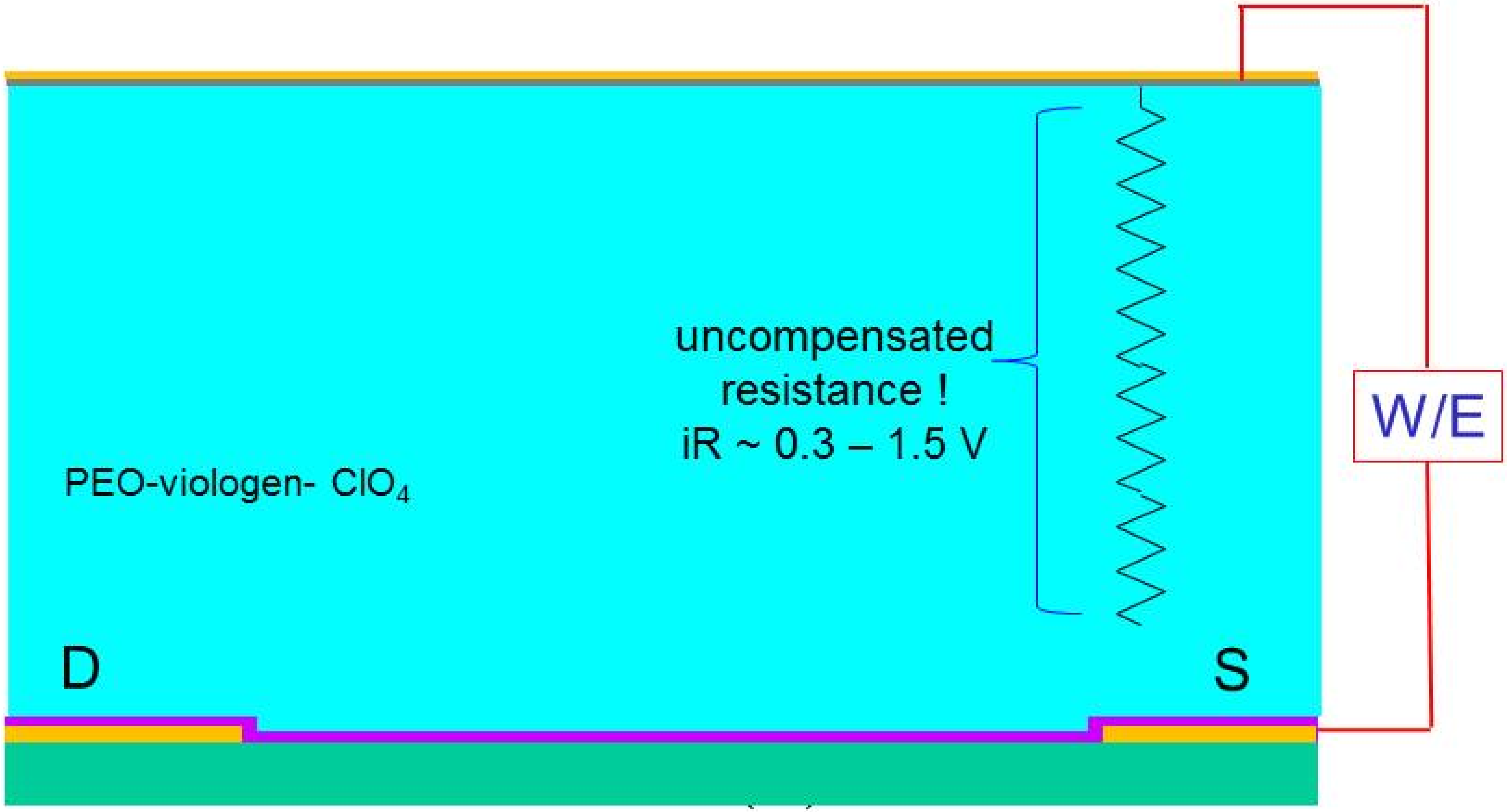
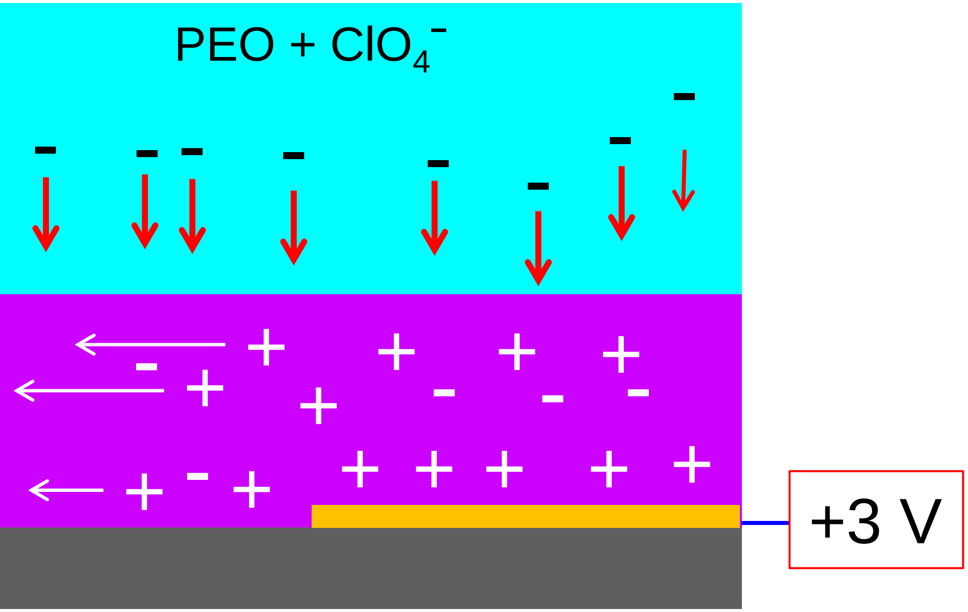


close-up of S electrode:

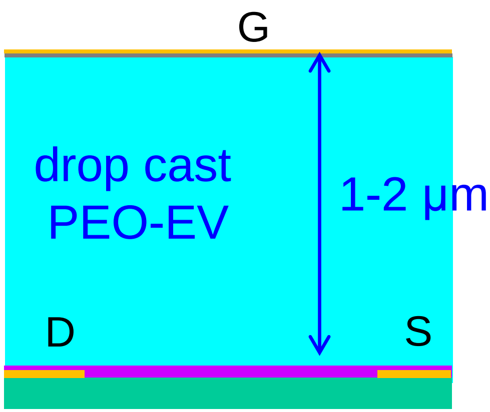


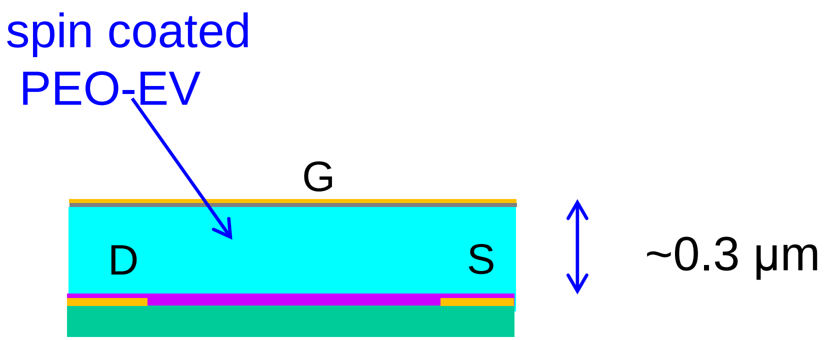
- "W" pulse generates polarons
- anions move toward polarons, compensate + charge
- polarons "fill" the Source region
- polarons propagate throughout PQT layer, anions continue to migrate from PEO

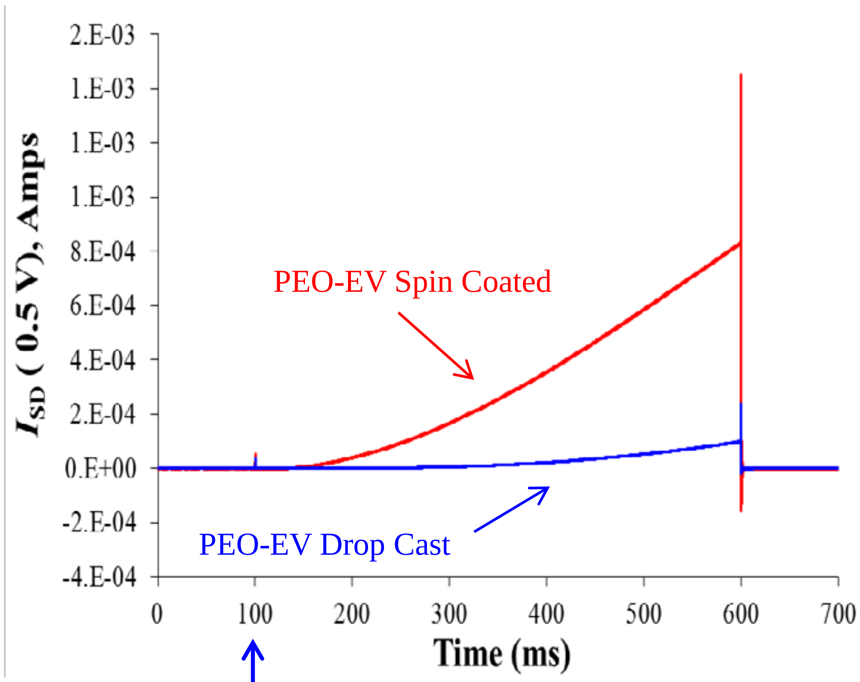
the bad news: iR losses in PEO layer reduce "write" current, thus requiring ~ 500 msec to "fill" source region.

the good news: there are solid electrolytes with conductivity >1000x higher than PEO-ClO_4, which should reduce "write" time to 10 - 100 μsec. We can also make the electrolyte at least 10x thinner

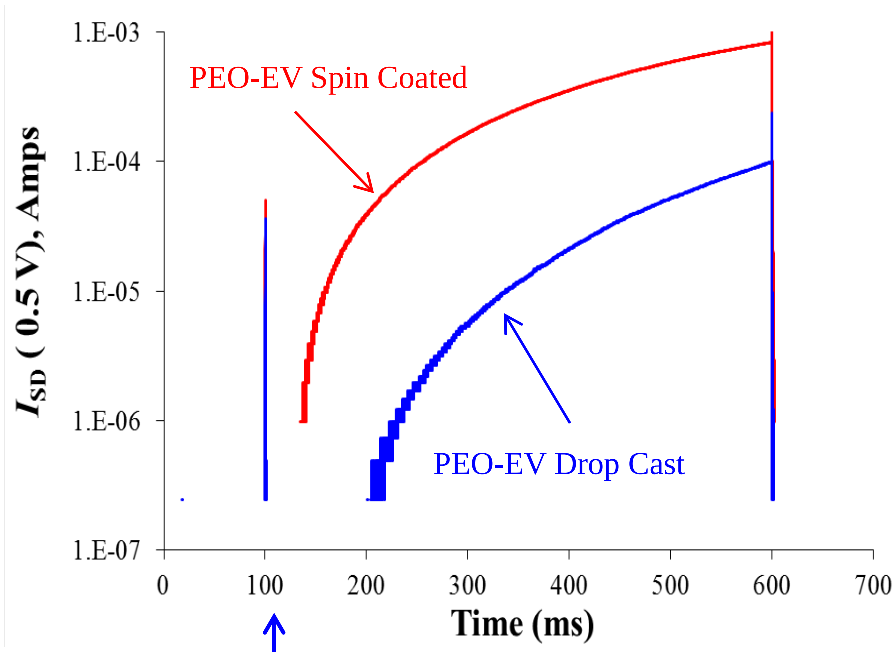
Some progress:





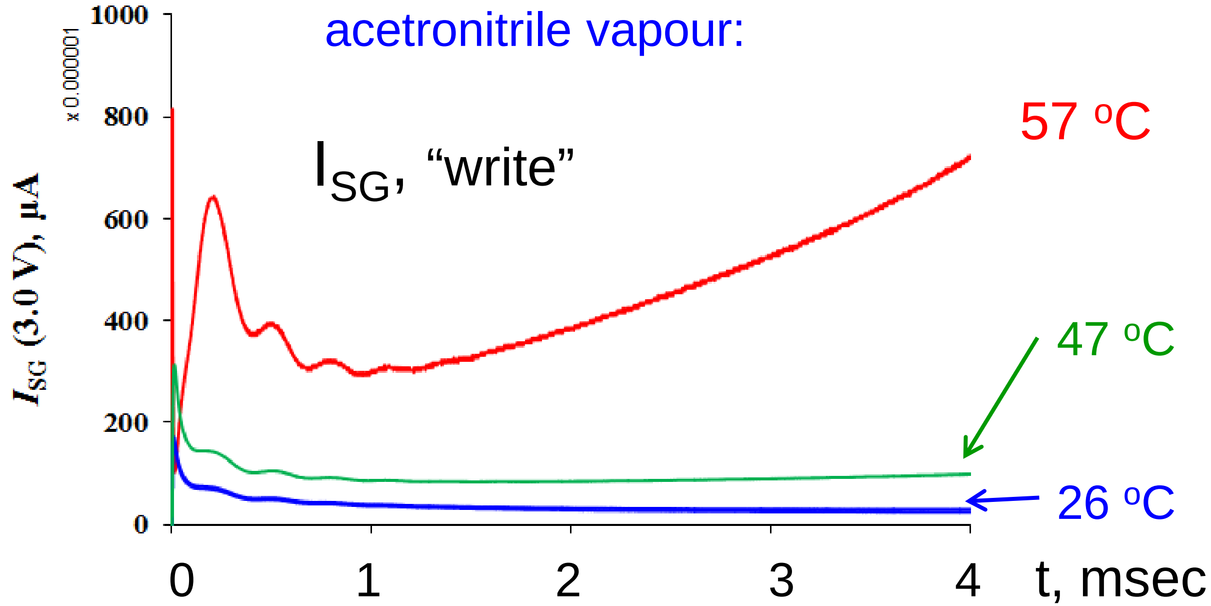


"write" pulse

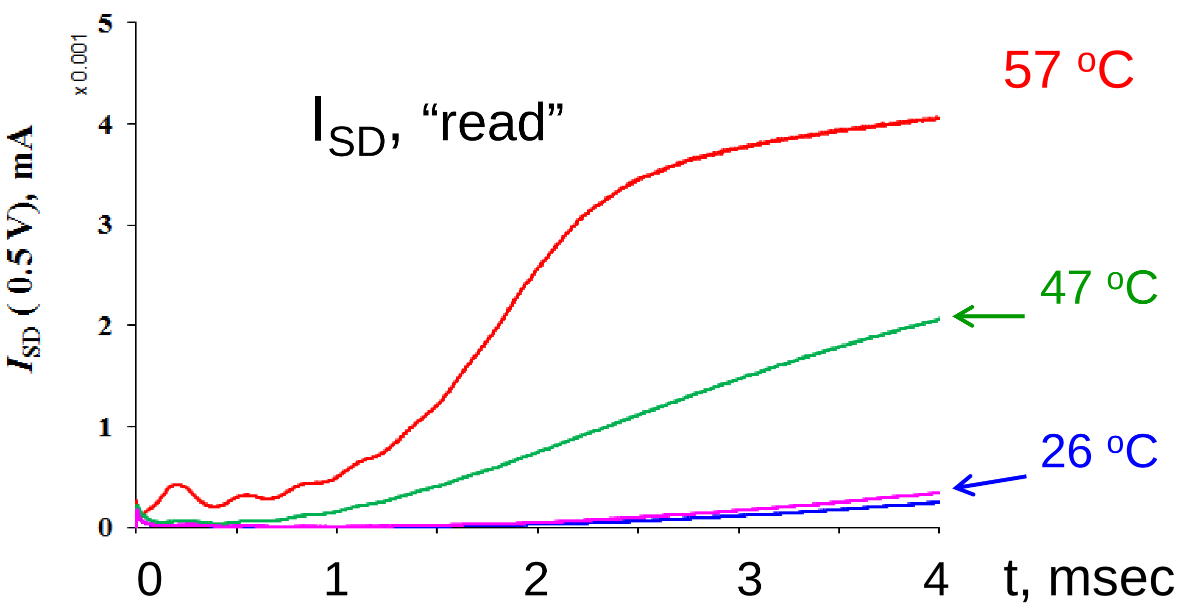


"write" pulse

acetronitrile vapour:



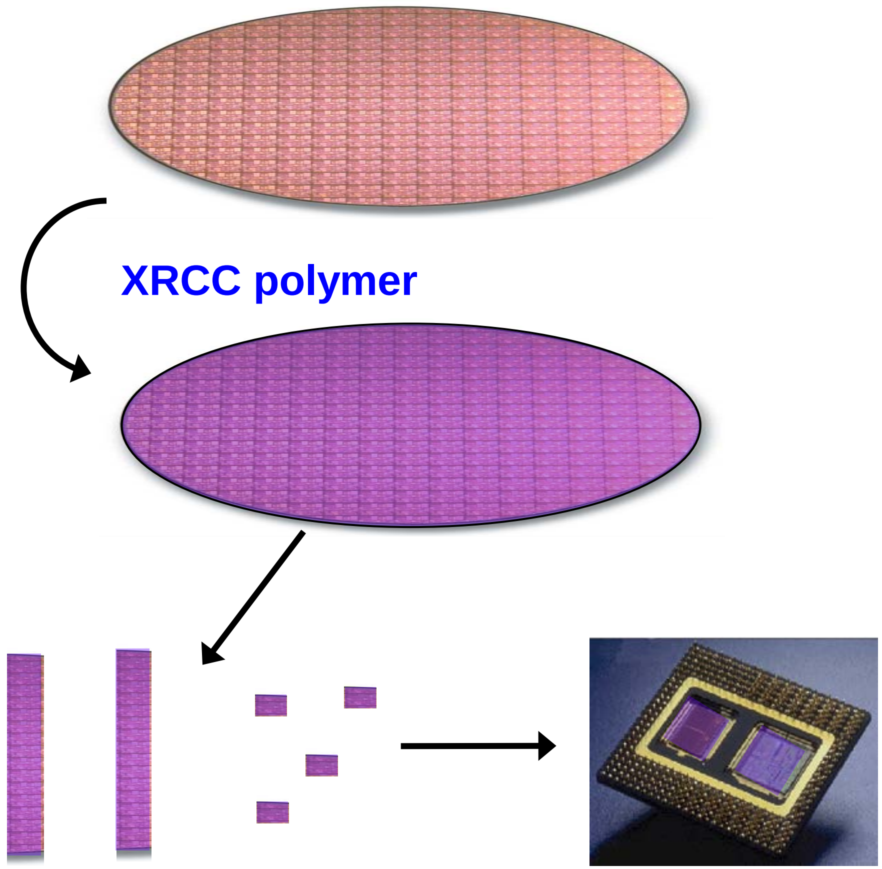
~100 X higher "write" current than drop cast, ambient



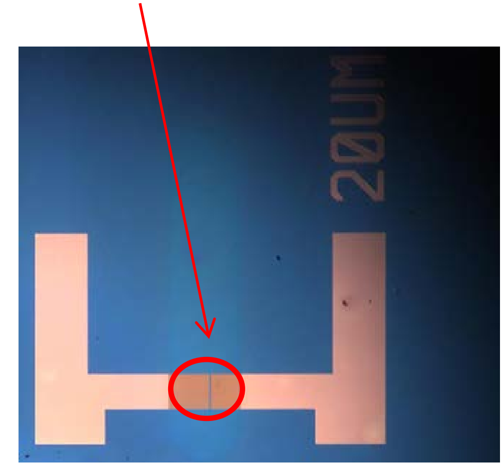
Note:
effective "write" speed of ~2 msec instead of ~500 msec

CMOS with support electronics

XRCC polymer

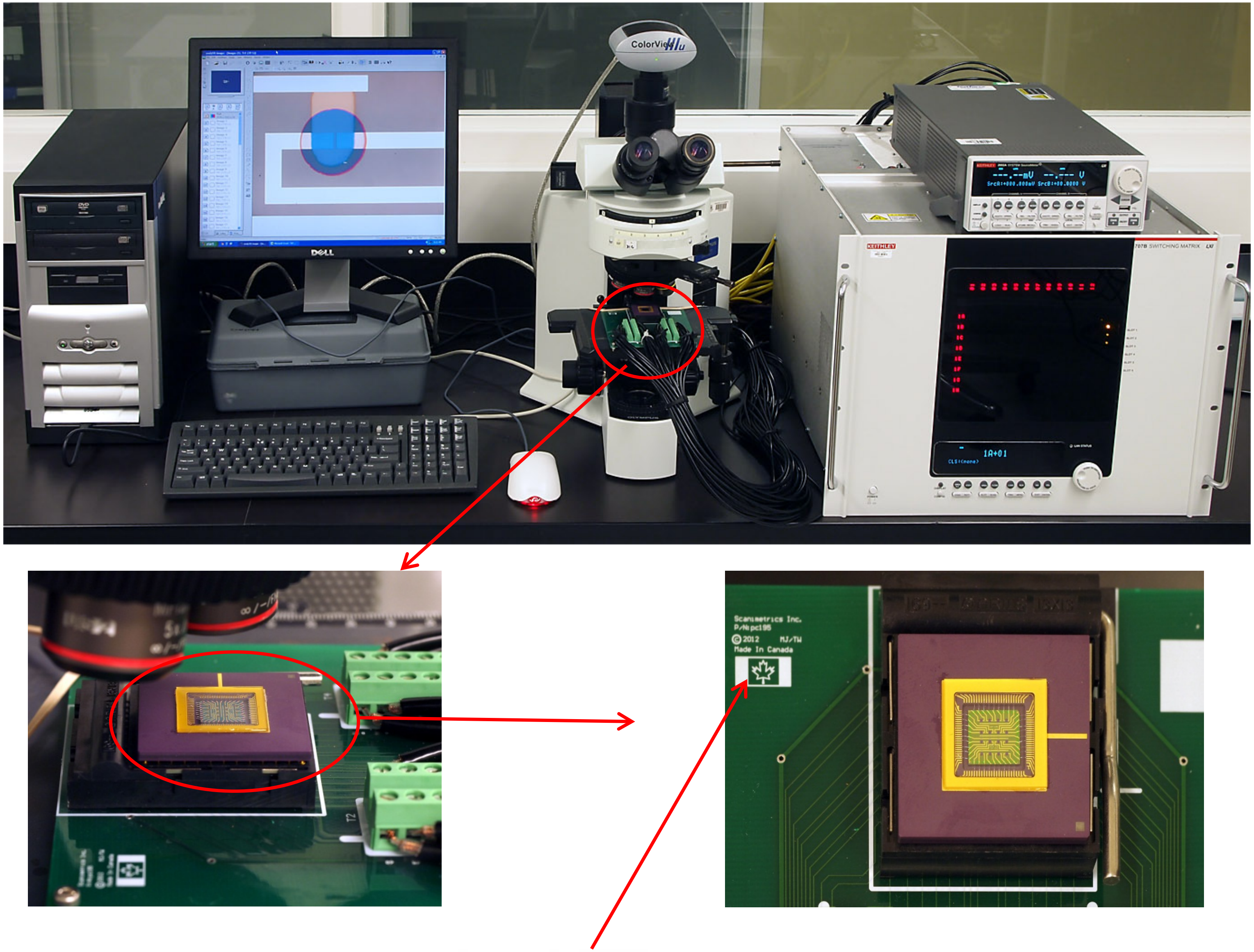


Thin film transistor substrate



Target: high “value added” to CMOS by integrating molecular nonvolatile memory

Low density prototype tester:



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