Giant dry out-of-plane actuation of PEDOT:PSS thin films

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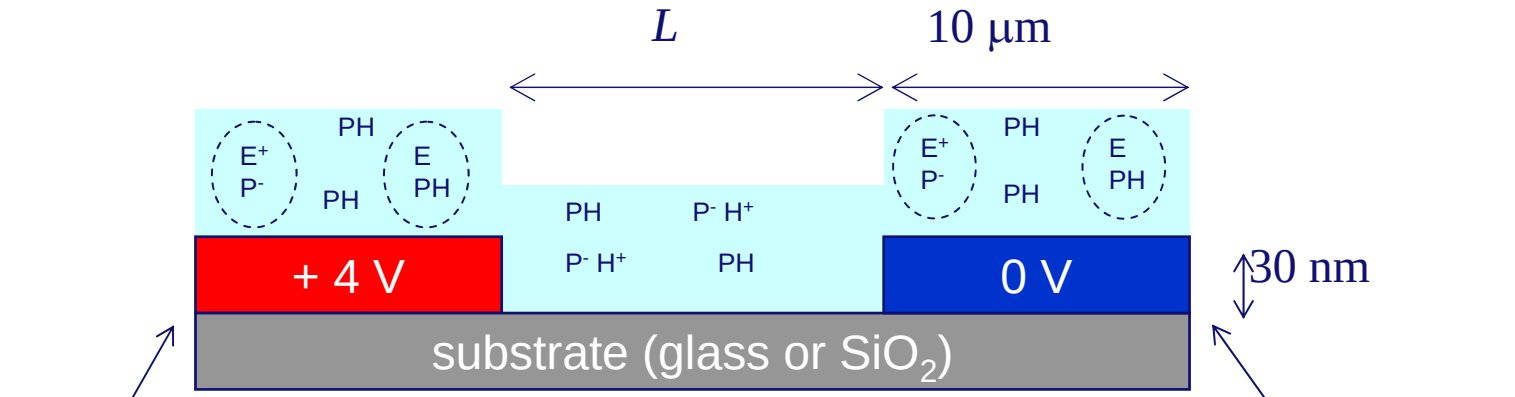
Where innovation starts

Plan

- Sample lay-out + experiment
- Observation: Giant actuation of PEDOT:PSS
  - optical microscopy
  - AFM, STM & Kelvin probe
- Qualitative electrochemical model
- Conclusions

Sample lay-out + dimensions

PEDOT:PSS: oxidatively doped conjugated polymer blend



anode (Au)

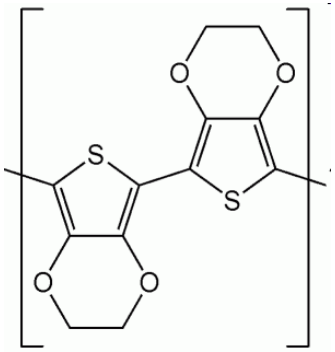
L = 1, 4, 10, 20 μm

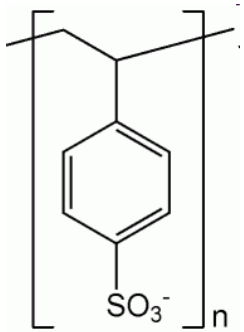
cathode (Au)

E/E$^+$: EDOT monomer (neutral/oxidized)

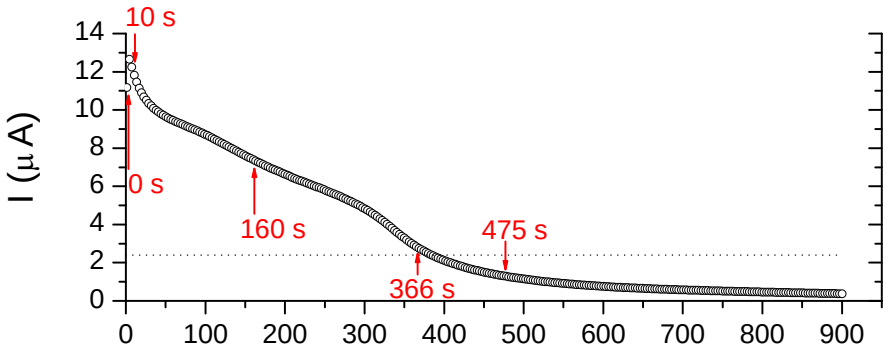
P/P$^-$: PSS monomer (neutral/reduced)

H/H$^+$: hydrogen atom/proton

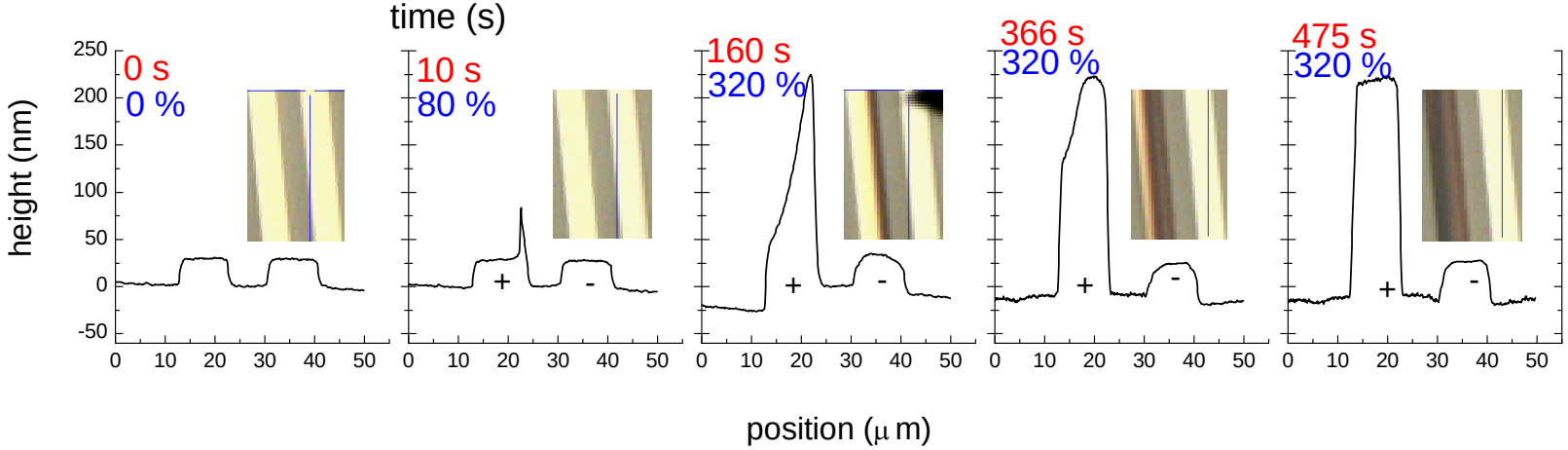




Out-of-plane actuation

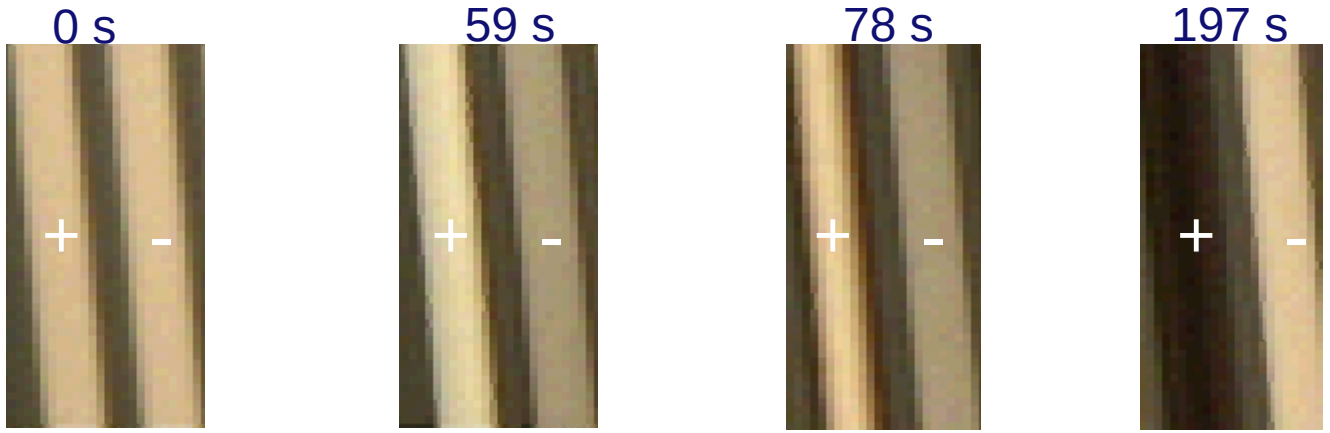


In ambient
RH ≈ 35%

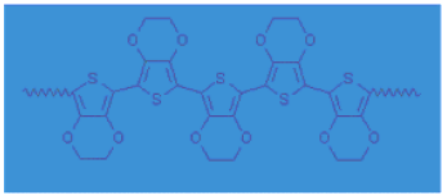


actuation:
- bias = [+4 V;+10 V]
- at the anode (+)
- no volume conservation: osmosis?
- color changes: 2 regimes

Reduction of PEDOT at the cathode

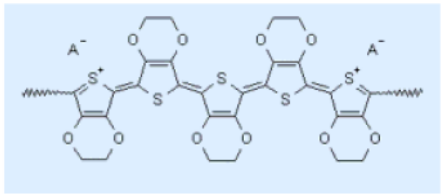


deep blue



(+2 e $^-$) red. ox. (-2 e $^-$)

transparent



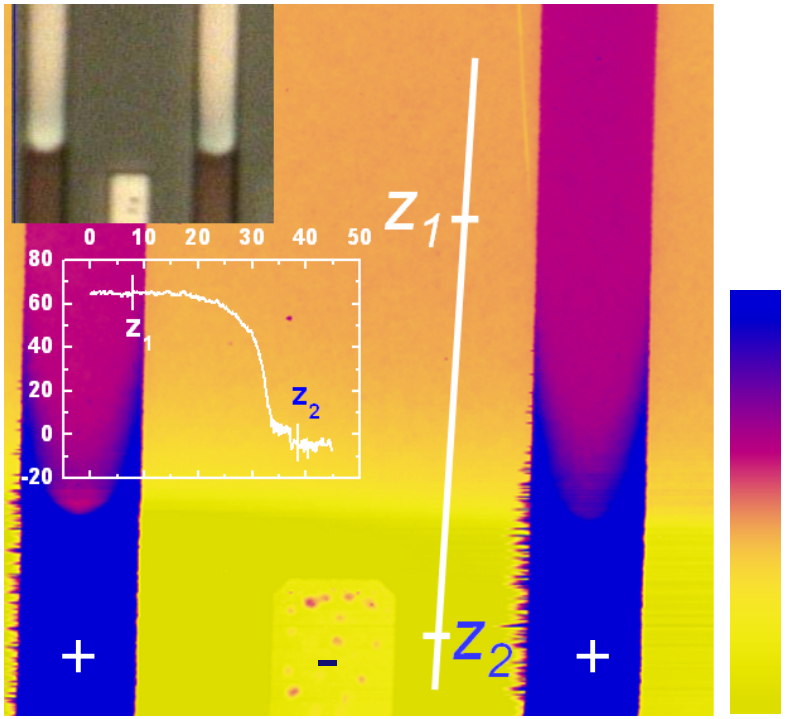
H.W. Heuer *et. al. Adv. Funct. Mater.* **2002**, *12*, 89.

- Bluish at cathode for t < 100 s.
- The disappearance of the bluish color at t > 100 s suggests that the reduced PEDOT is reacted away, e.g. via

$$O_2 + EDOT \rightarrow O_2^- + EDOT^+$$

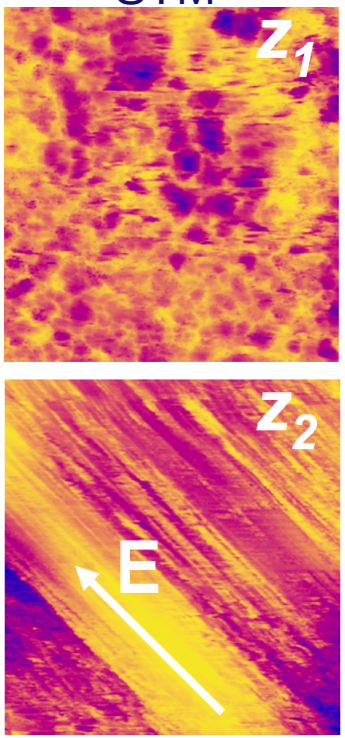
Height and morphology changes in channel

AFM



50 μm x 50 μm
z_{scale} = 150 nm

STM



zero-field area

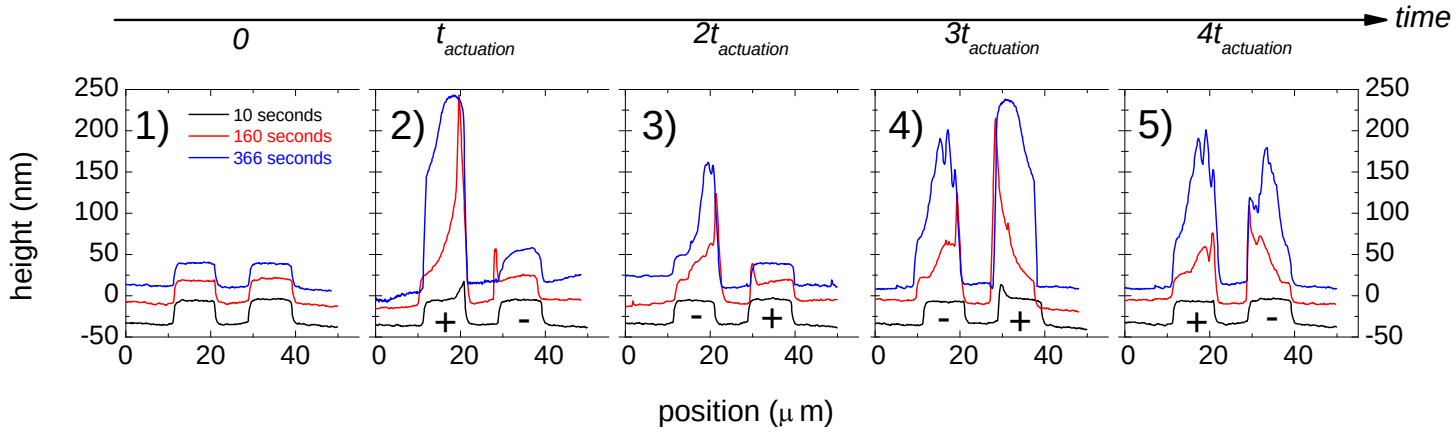
A.M. Nardes *et. al.*
Adv. Mater. **2007**, *19*, 1196.

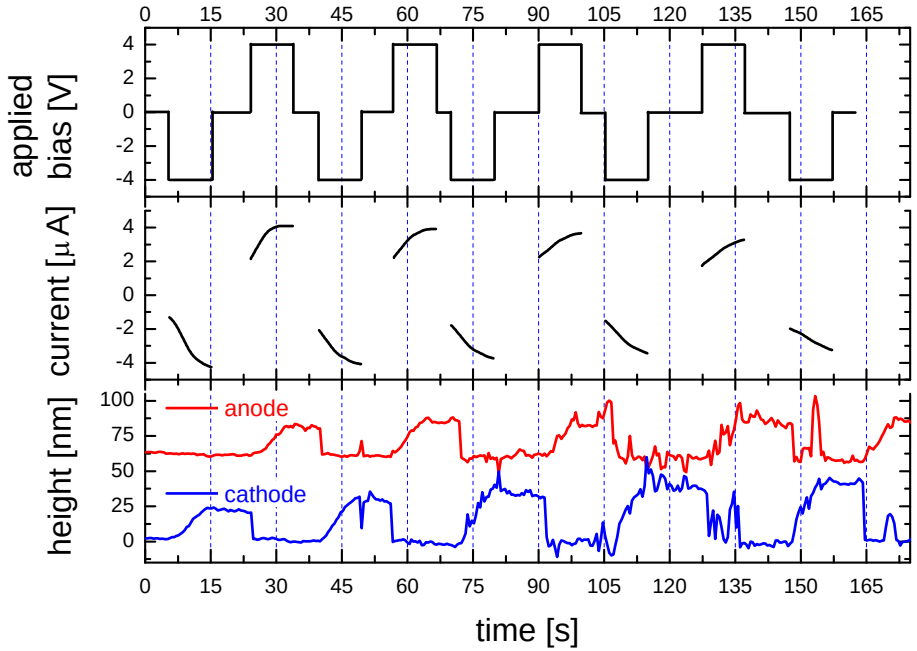
nonzero-field area

400 nm x 400 nm
z_{scale} = 30 nm

•transport of massive entities for longer *t* : PSS^- ?

Reversibility

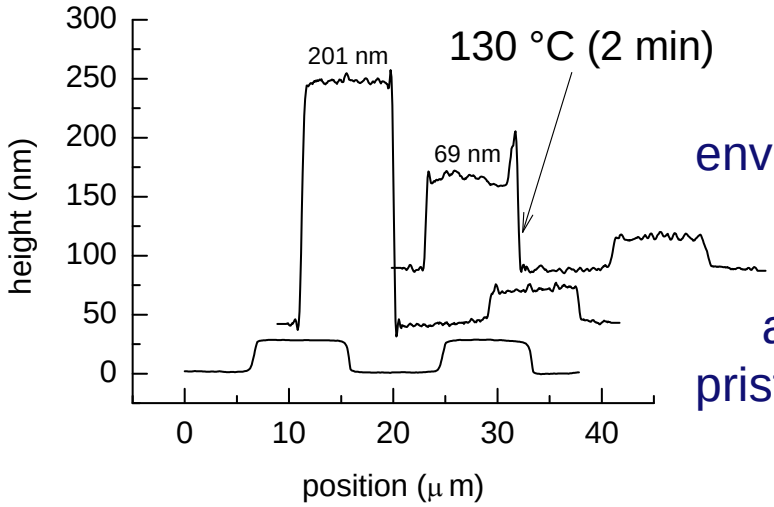




- reversible $t < 100$ s
- hardly reversible $t > 100$ s
- color changes for $t > 100$ s

→ two regimes

Humidity dependence and thermal/temporal stability

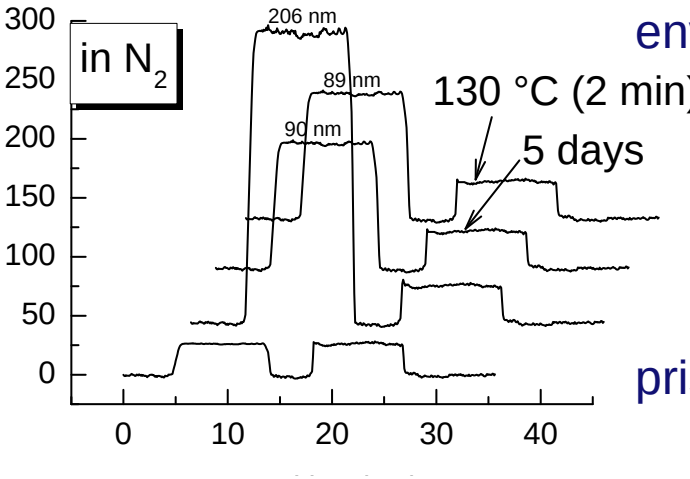


environment I:

annealed (ambient)

actuated (ambient)

pristine



environment II:

annealed (N_2 glove box)

dried (N_2 glove box)

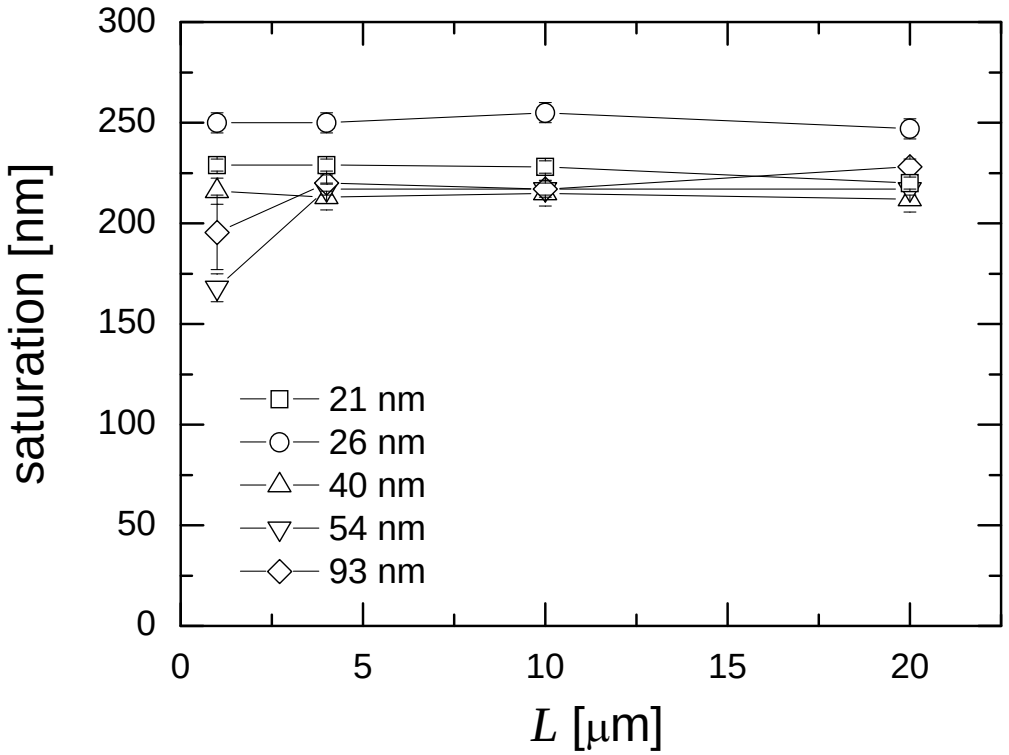
actuated (ambient)

pristine

Volume decreases:

- H_2O evaporation
- Remaining: PSS ?

Maximum attainable actuation



- maximum attainable actuation is independent of geometry!
- limiting factor?

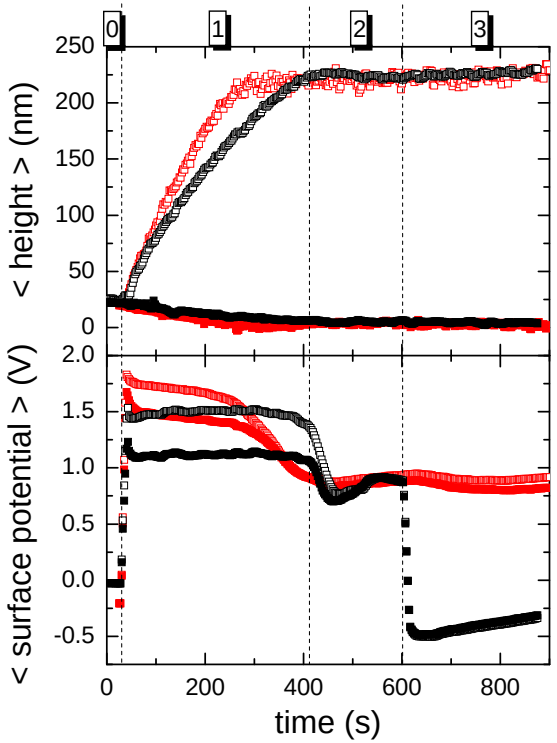
Surface potential screening on 21 nm and 90 nm thick films

■ 21 nm

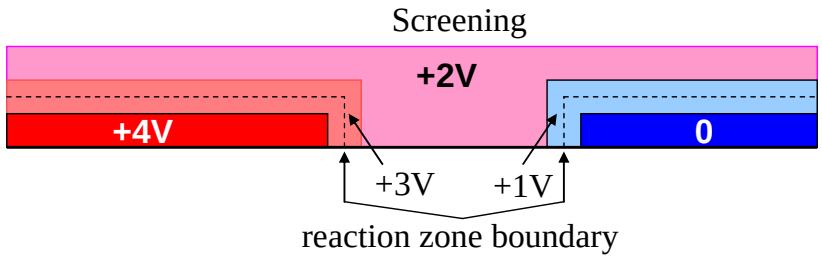
□ 90 nm

0 3 :0 V

1 2 :4 V

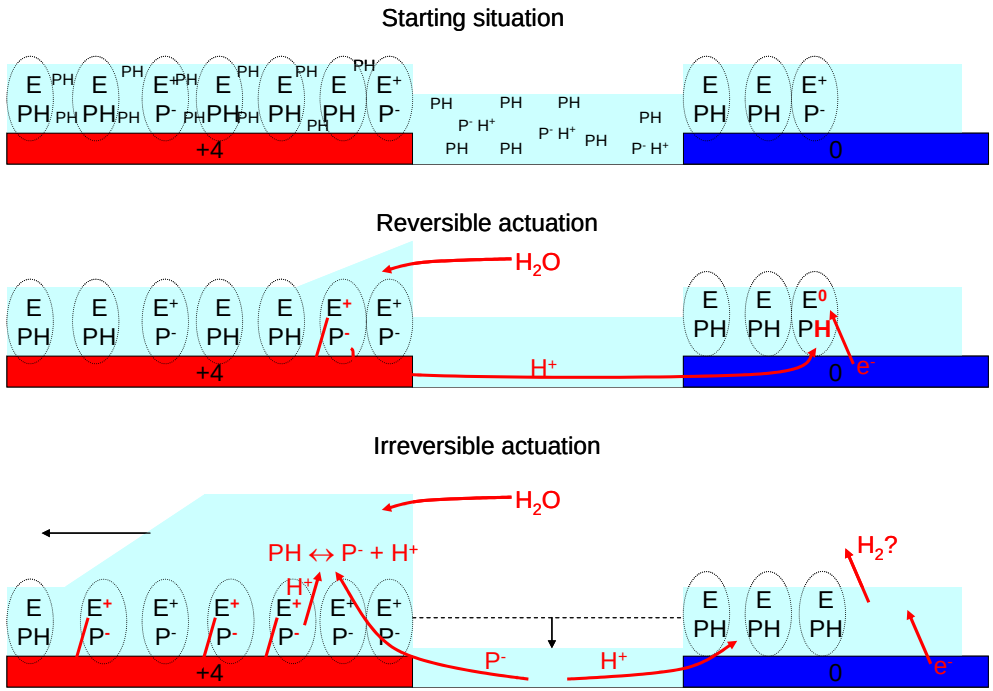


← giant actuation: 990%



- screening by mobile ions ⇒ constant $V_{surface} \approx (0+4)/2$ V
- $\Delta V >> 0$ in thin (≈20 nm) layer only ⇒ limited reaction region
- actuation height independent of film thickness!

electrochemical model



t = 0 s

t > 0 s

$EDOT + PSSH - e^- \rightarrow EDOT^+PSS^- + H^+$

$EDOT^+PSS^- + H^+ + e^- \rightarrow EDOT + PSSH$

bluish

$O_2 + EDOT \rightarrow O_2^- + EDOT^+$

colorless

t > 100 s

$EDOT + PSSH + PSS^- - e^- \rightarrow EDOT^+PSS^- + PSSH$

$H^+ + e^- \rightarrow H\bullet$ (?)

D.S.H. Charrier *et al*, in preparation

Conclusion

- **Combination of observations lead to a qualitative model:**
  - **reversible regime of H^+ (from H_2O osmosis) transport**
  - **irreversible regime of PSS^- transport and side reactions**
  - **ionic screening limits 'reaction region thickness'.**

- **Remaining questions:**
  - **why onset at 4 V**
  - **brownish color on +**
  - **side reactions (over-oxidation?)**
  - **…**

- **Ambient actuation: no need of other ionic reservoir.**

- **Maximum actuation reported so far: 990% at first cycle for a 21 nm thick film.**

Thanks to

nano ned

TU/e

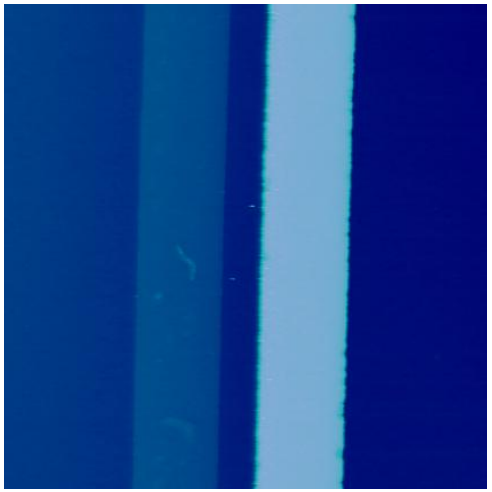
Martijn Kemerink
Réne Janssen
All the M2N group

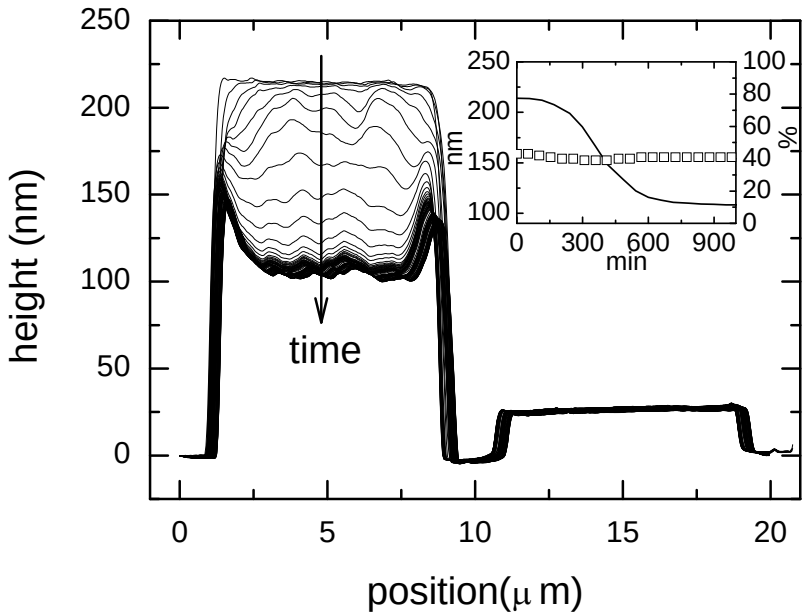
Materials Devices Systems COBRA

Clean room facilities

PHILIPS

For materials supply




height (nm)
position(μm)
time
nm
%
min
0
5
10
15
20
50
100
150
200
250
300
600
900
80
60
40