Willkommen
Welcome
Bienvenue

Strategic Focus Area
Advanced Manufacturing

FOXIP - Functional Oxides Printed on Polymers and Paper

Laboratory for Thin Films and Photovoltaics (Empa-TFPV)
Laboratory of Functional Polymers (Empa)
Soft Transducers Lab (LMTS-EPFL)
Polymer Nanotechnology Group (PSI)

Empa
Materials Science and Technology

EPFL

PAUL SCHERRER INSTITUT
PSI

Project duration: July 2017 - October 2021

SFA-AM annual review meeting, 17/18 March 2022

Motivation: Printed Electronics

- Printed electronic devices and circuits for the **Internet-of-Things:** interactive, secure, smart documents / packaging / product authentification

ECB

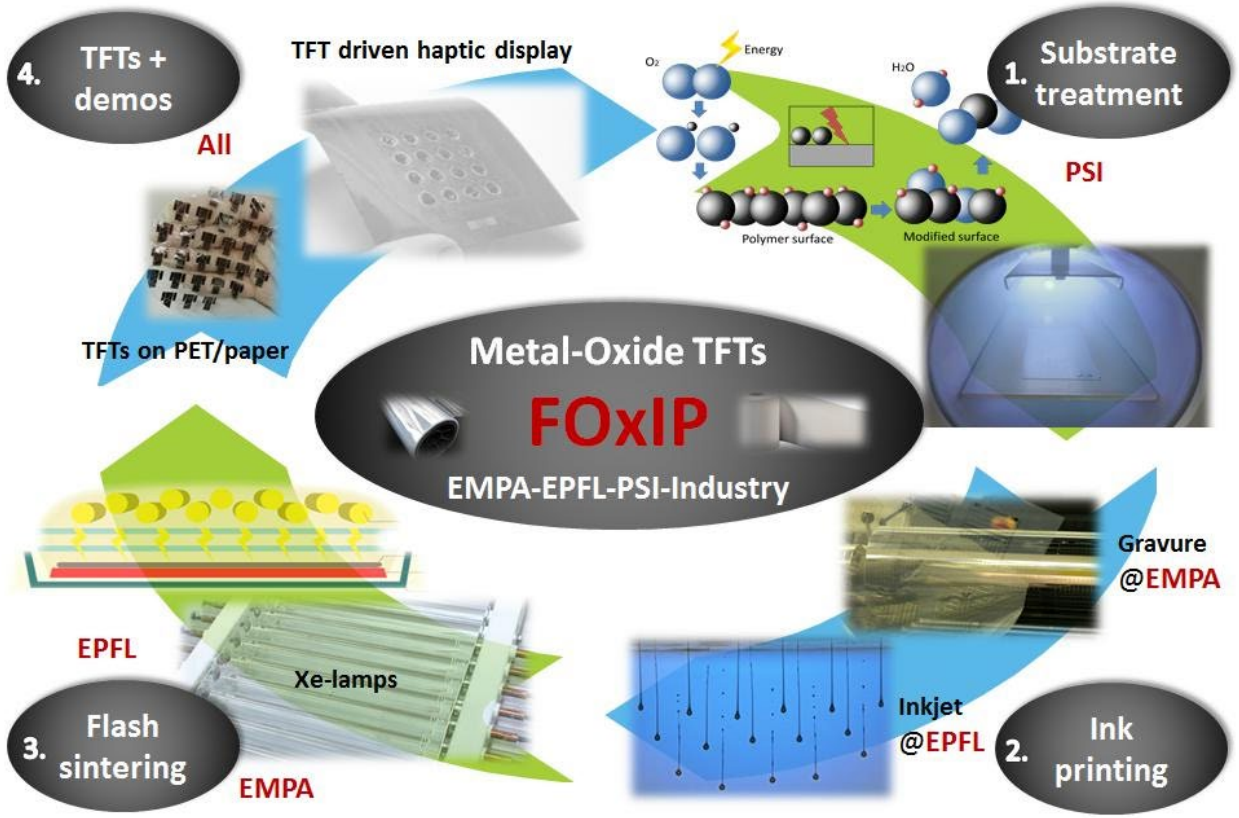
IMEC

Post

Tetrapak

Key challenge addressed in FOXIP

- How to print inorganic oxides (semiconductor, conductor and dielectric) without applying high temperature sintering, on temperature sensitive flexible substrates like polymers and paper?

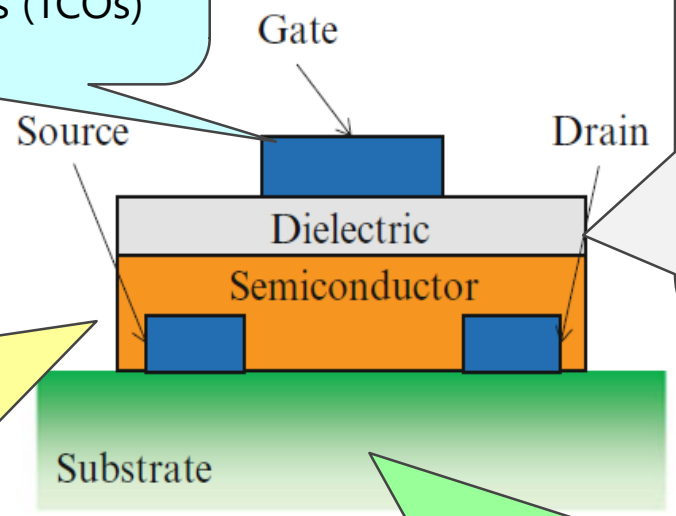


Metal-Oxide Thin Film Transistor (TFT)

as driving, logic or sensing element

Source, drain & gate:

- metal inks
- transparent conductors (TCOs)
- graphene



$$C_G = \frac{\varepsilon_r \varepsilon_0}{d}$$

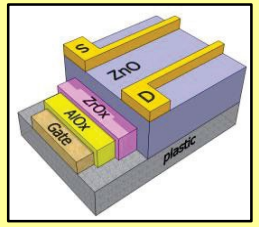
Dielectric:

- Al_2O_3 (ε = 9)
- YAlOx

Semiconductor:

Aim max. channel mobility >10 cm^2/Vs

- In-Zn-O
- Zn-Sn-O
- In-Ga-Zn-O



Flexible substrates:

- PI (T_g=450°C)
- PEI (T_g=200°C)
- PET (T_g=78°C)
- paper (T_g ~ 150°C)
- Biodegradable PLA

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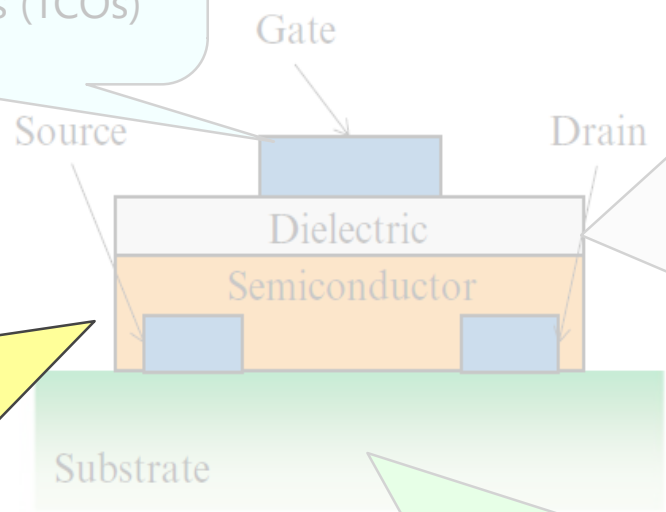

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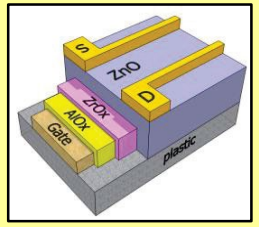

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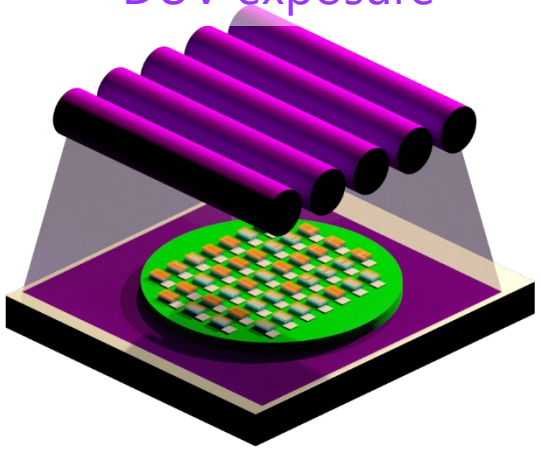
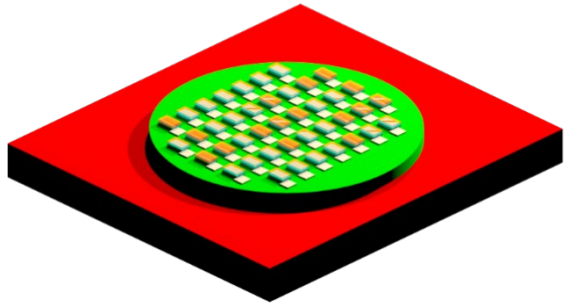
- Biodegradable PLA

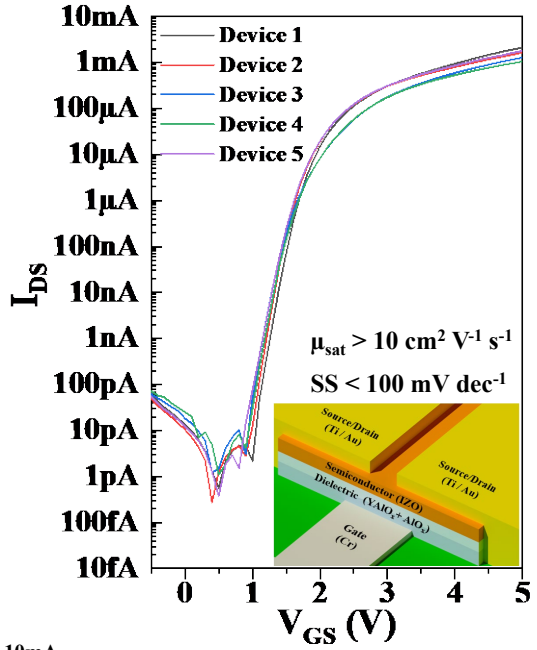
DUV-enhanced curing for solution-processed IZO semiconductor

DUV exposure

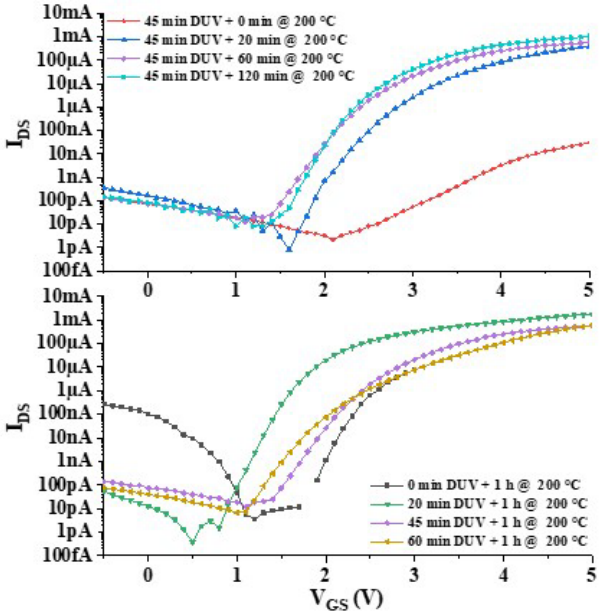


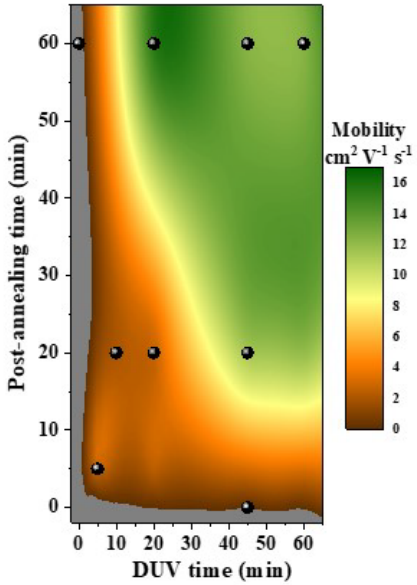
Post- annealing @ 200°C

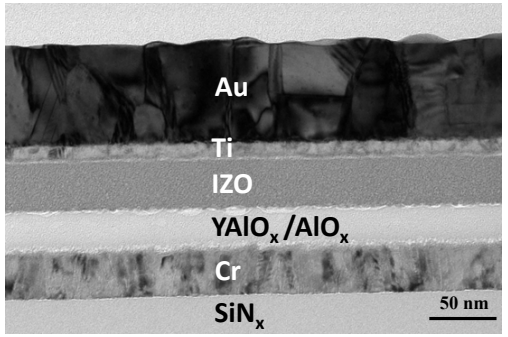


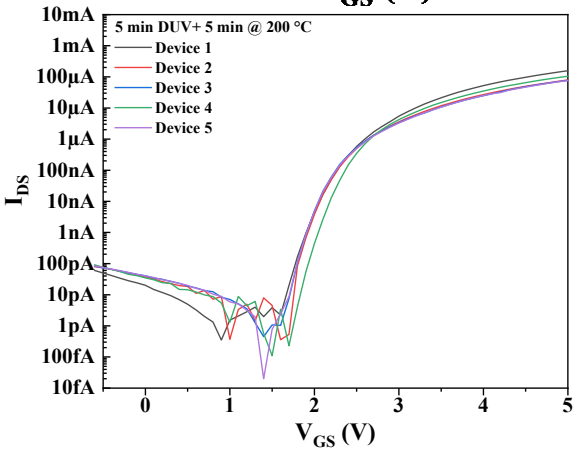


Minimization of thermal budget via a parametric study







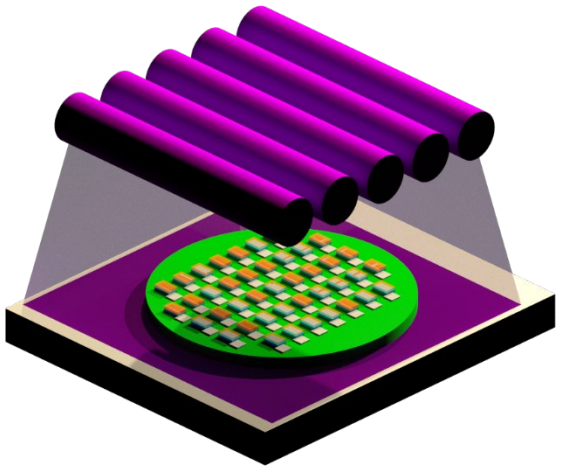


- Semiconductor annealing shortened to 10 min @ 200 °C

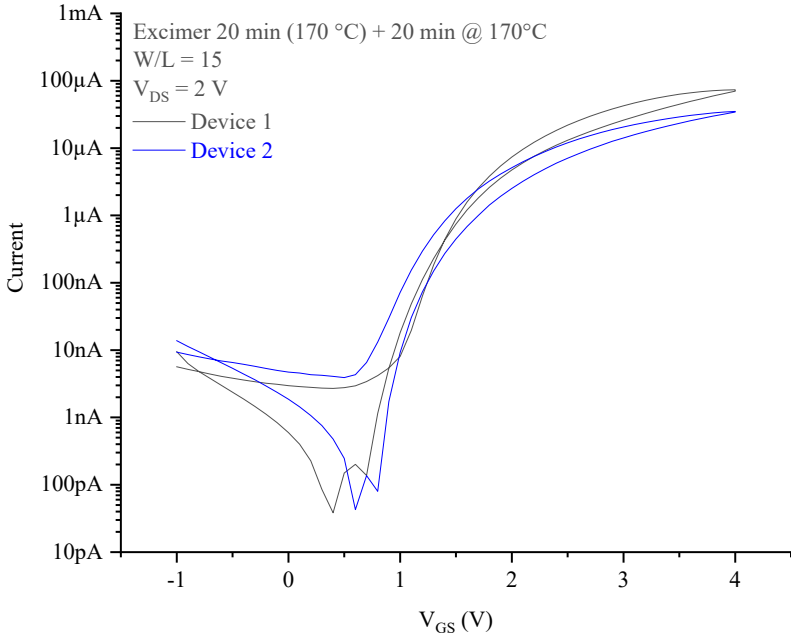
Mancinelli et. al, *ACS App. Electron. Mater. 2020, 2, 10*

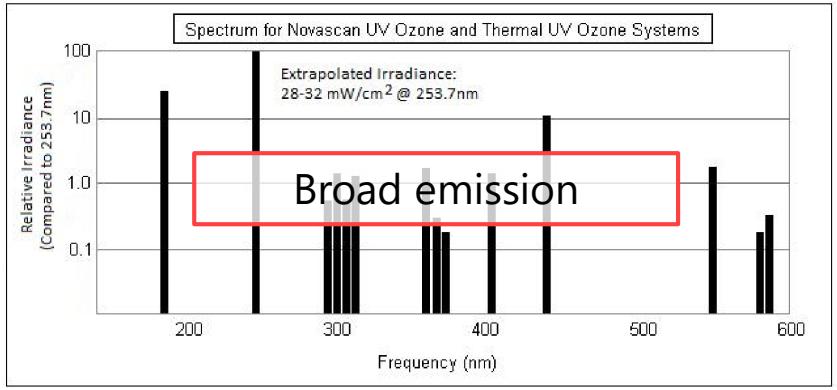
Excimer curing for reduced annealing temperatures

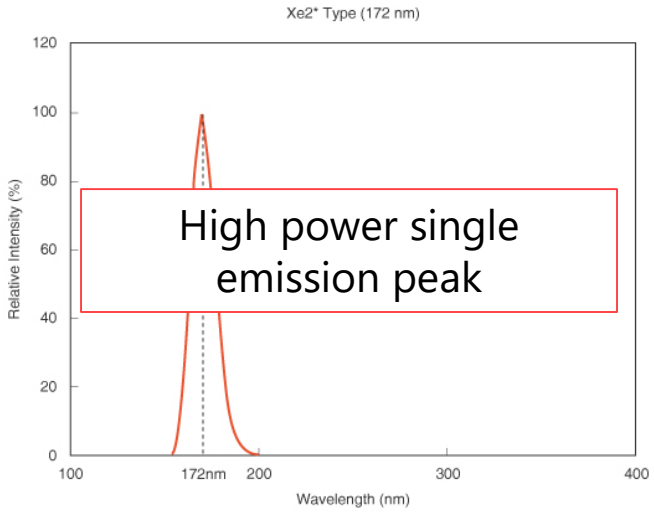
DUV



Excimer lamp







- IZO annealing temperature reduced to 170 °C:

  - too high for PET/paper
  - but PEI foil possible (Tg=200°C)

Metal-Oxide Thin Film Transistor (TFT)

as driving, logic or sensing element

Source, drain & gate:

- metal inks
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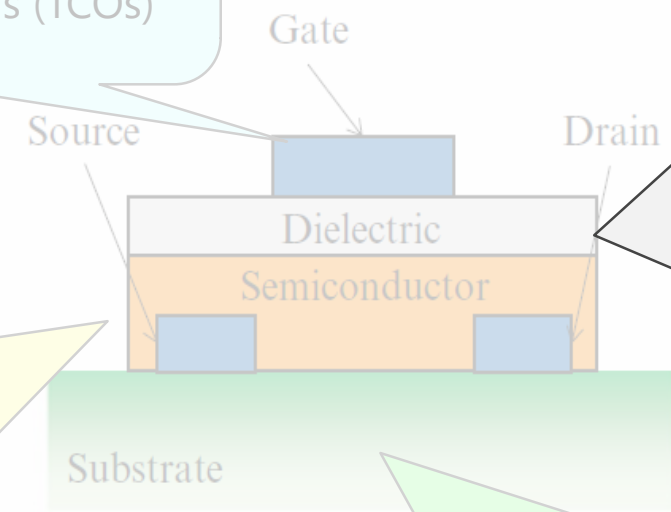
- graphene



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Semiconductor:

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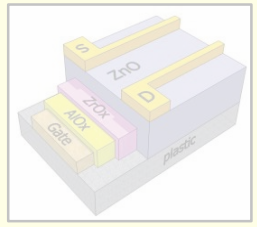
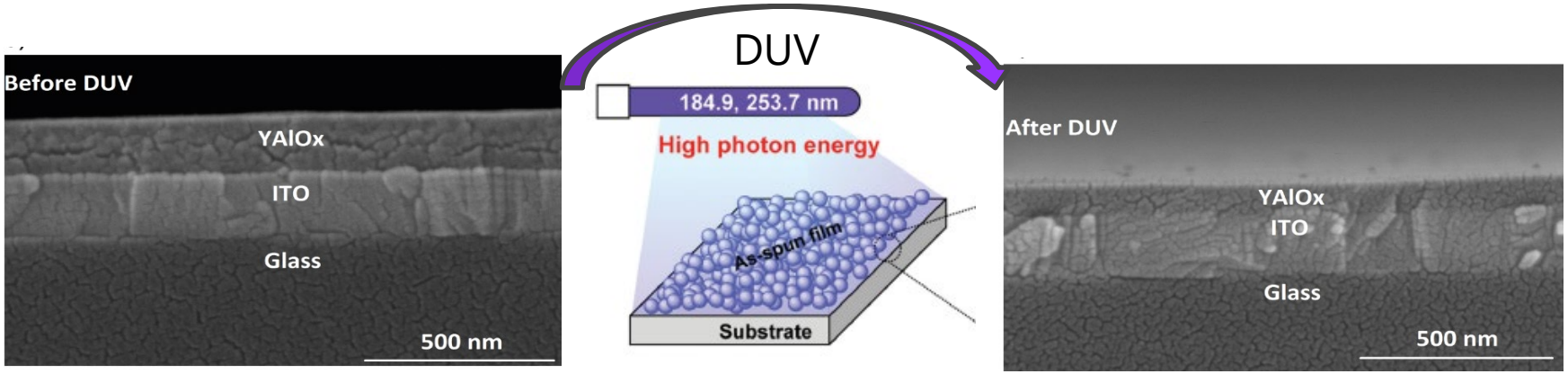
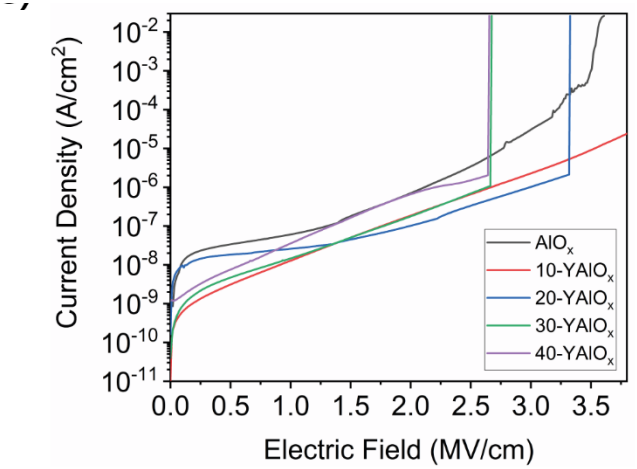


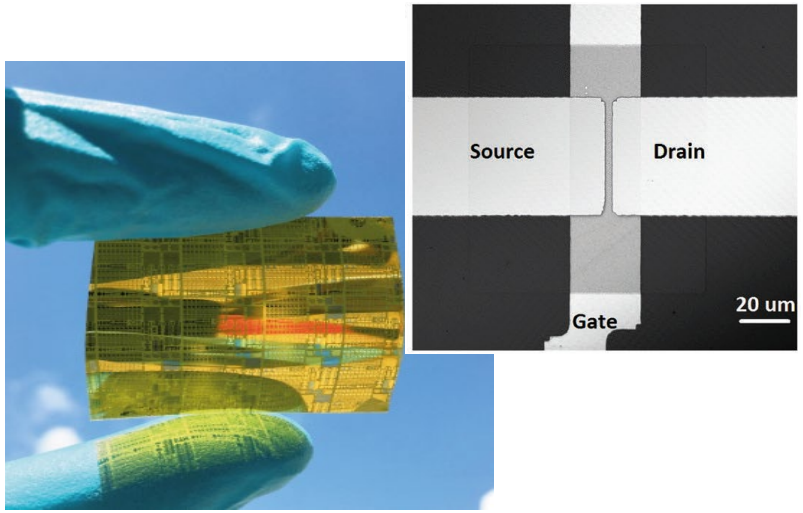
Flexible substrates:

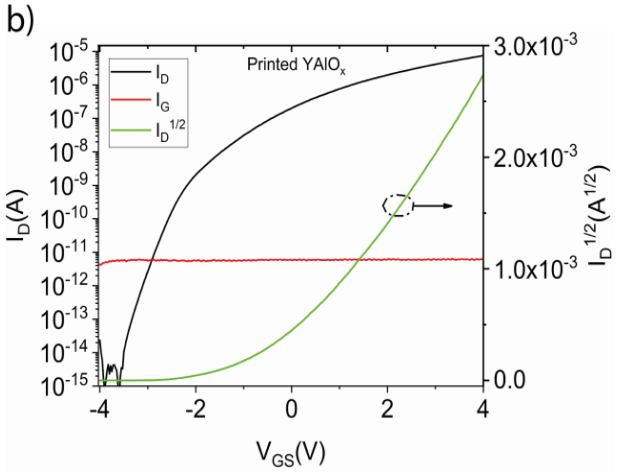
- PI (T_g=450°C)
- PEI (T_g=200°C)
- PET (T_g=78°C)
- paper (T_g ~ 150°C)
- Biodegradable PLA

Printed oxide dielectric





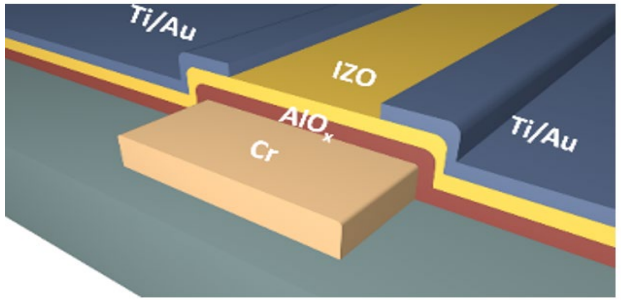




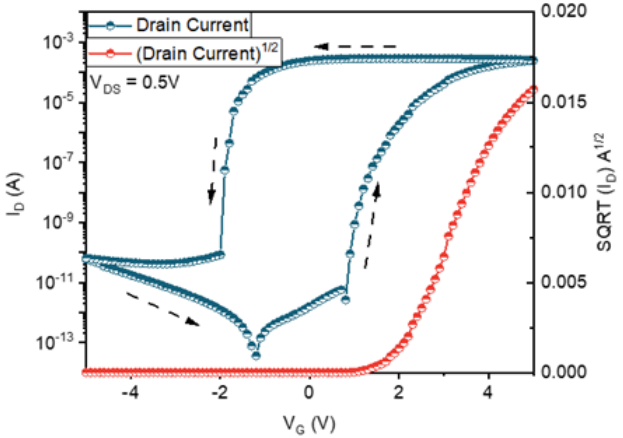
- Ink-jet printed YAlOx dielectric obtained by DUV annealing with maximum process temperature 150 °C

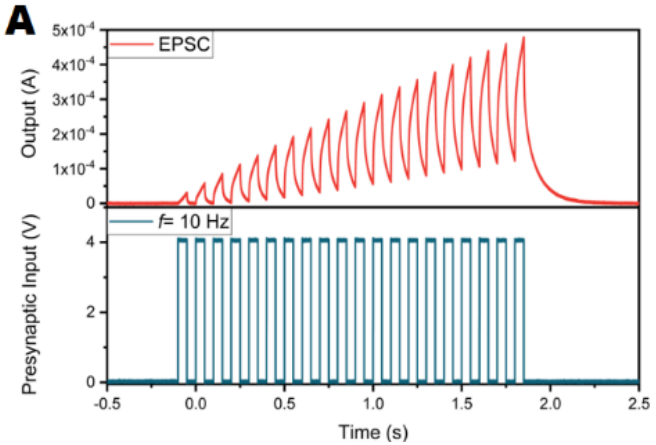
Bolat et. al, *Adv. Electron Mater.* (2019) 1800843

Printed TFT…. with synaptic function!

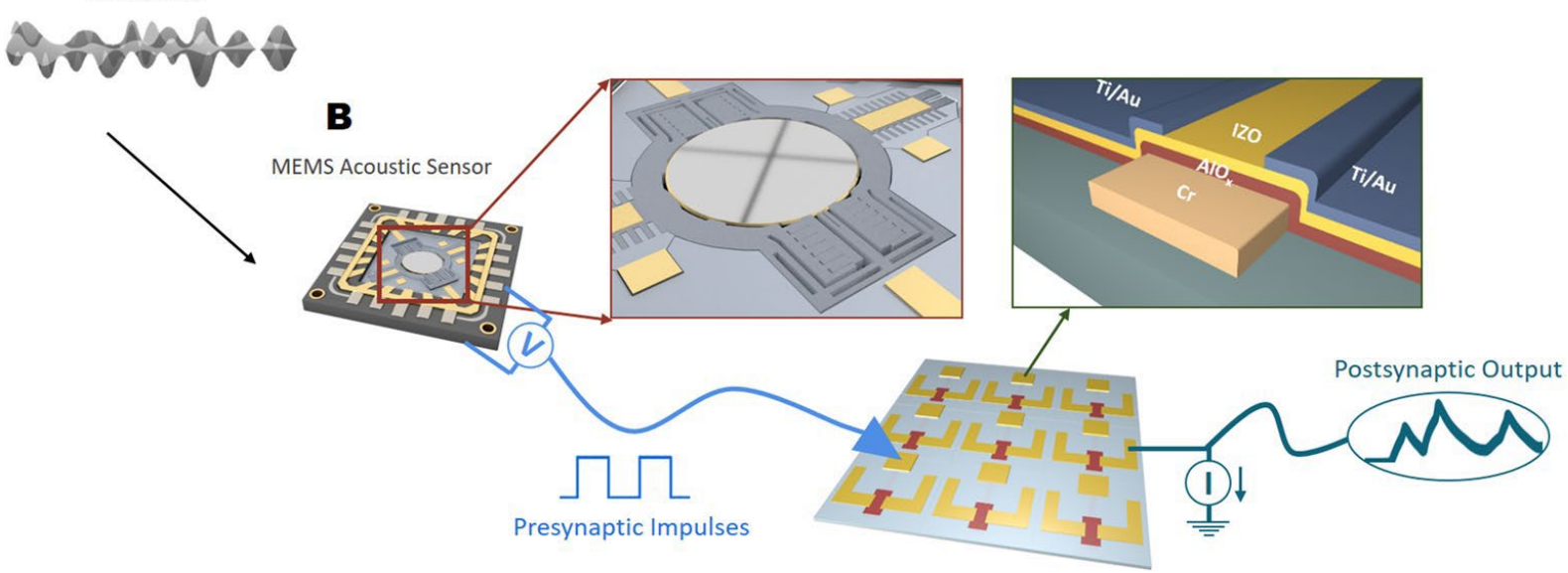


Printed AlOx dielectric + In-Zn-O semic.





Unexpected hysteresis **=> memory element => synaptic function**



- Demonstrator: acoustic response system with synaptic TFTs sensitive to the whole audio-range (20 Hz to 20 kHz)

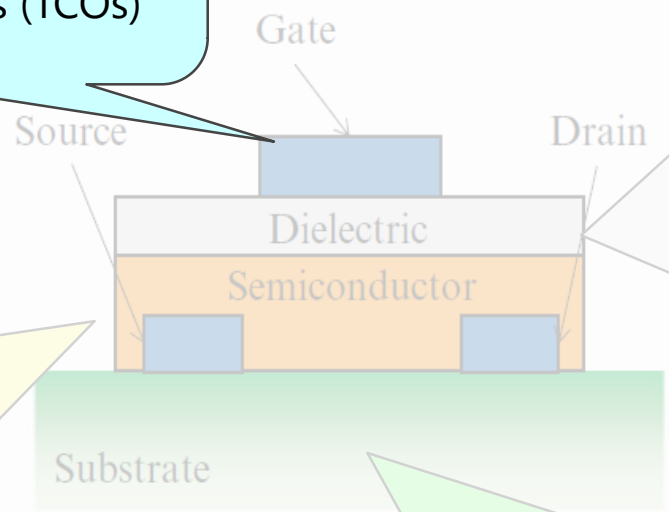
Bolat et al., *Sci. Rep.* **10,** 16664 (2020)

Metal-Oxide Thin Film Transistor (TFT)

as driving, logic or sensing element

Source, drain & gate:

- metal inks
- transparent conductors (TCOs)
- Graphene, MXenes



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Dielectric:

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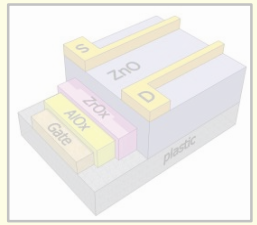

Flexible substrates:

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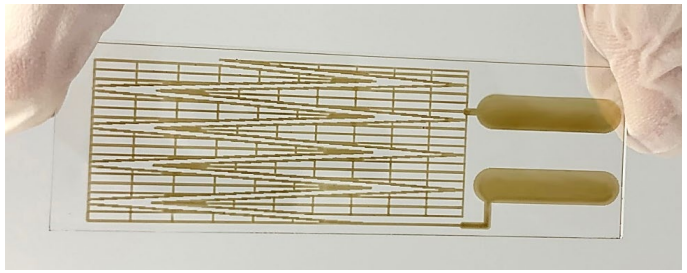
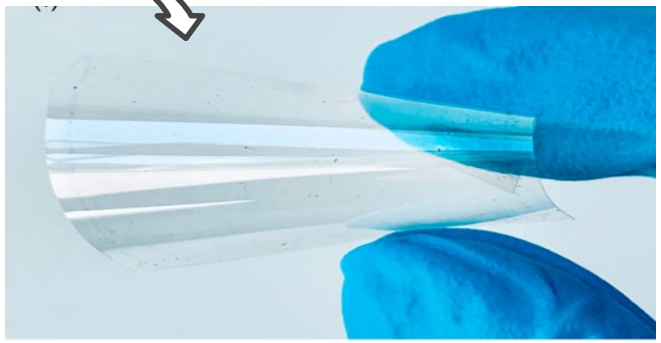
- paper (T_g ~ 150°C)
- Biodegradable PLA

Printed ITO transparent security systems

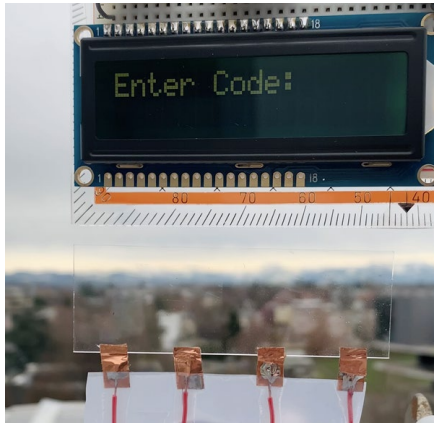


Ink-jet printed ITO ink

After drying @ 250°C + photonic curing

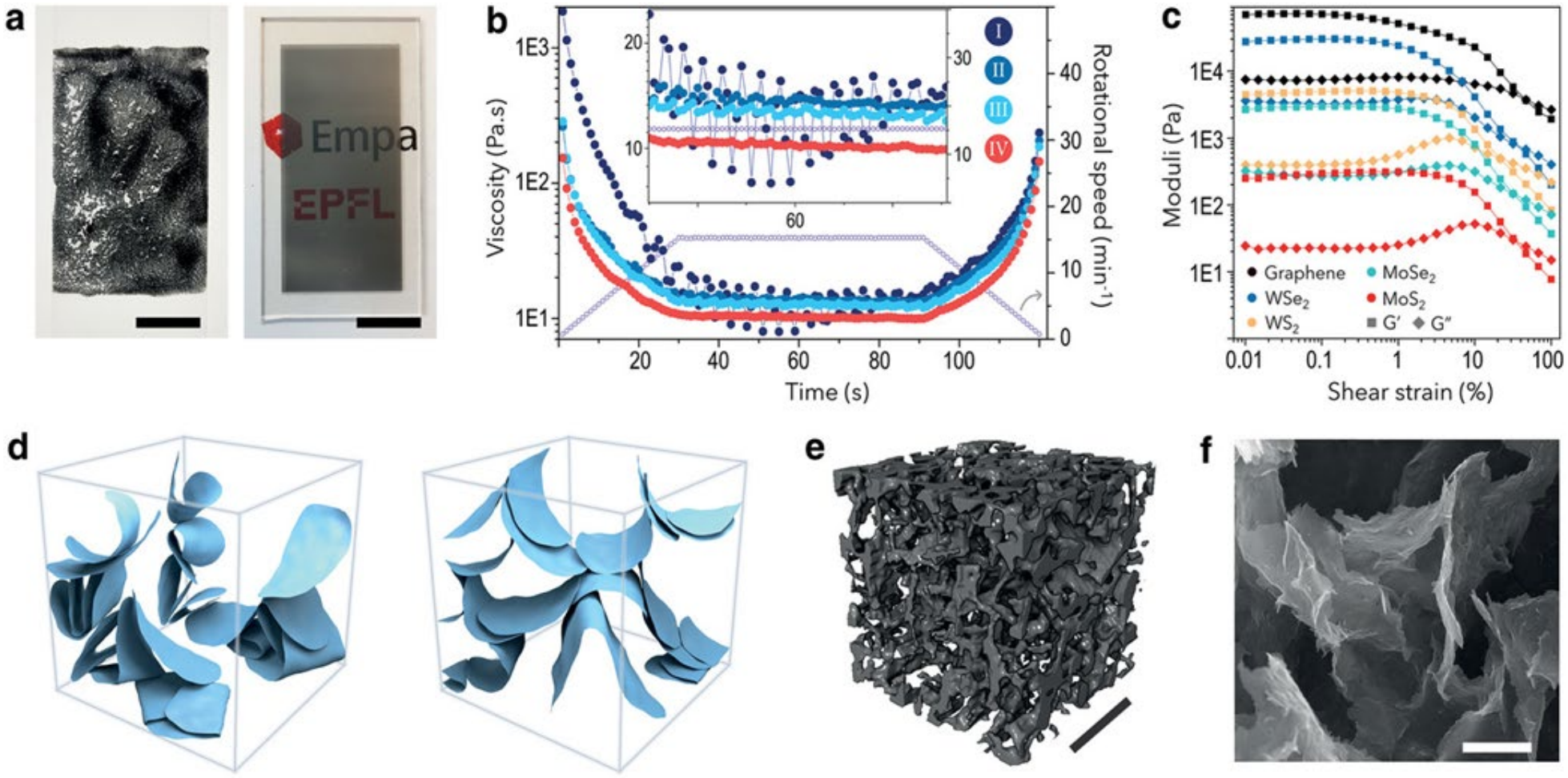


on flexible polyimide foil



Gilshtein et al., *Adv. Mater. Technol.* **5,** 2000369 (2020)

Additive-free inks of 2D materials = “vdW inks”



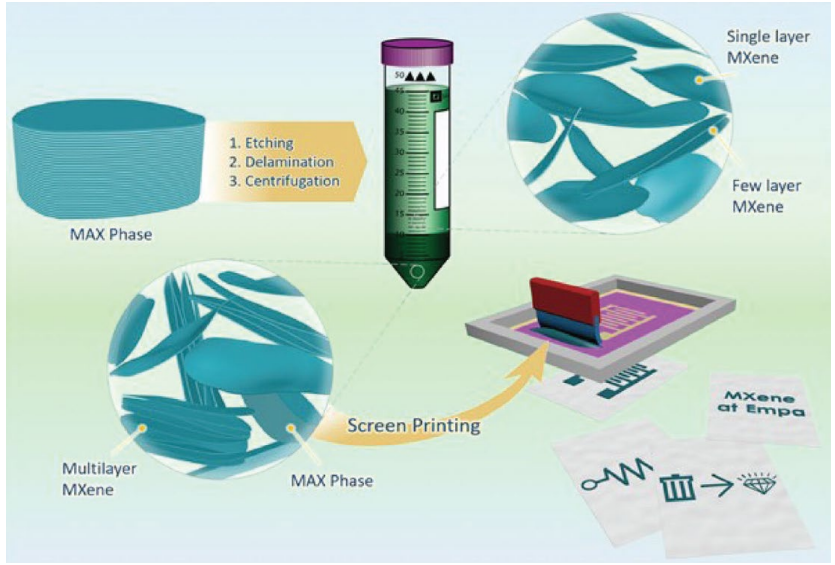
S. Abdolhosseinzadeh et al. Adv. Mater. 2103660 (2021)

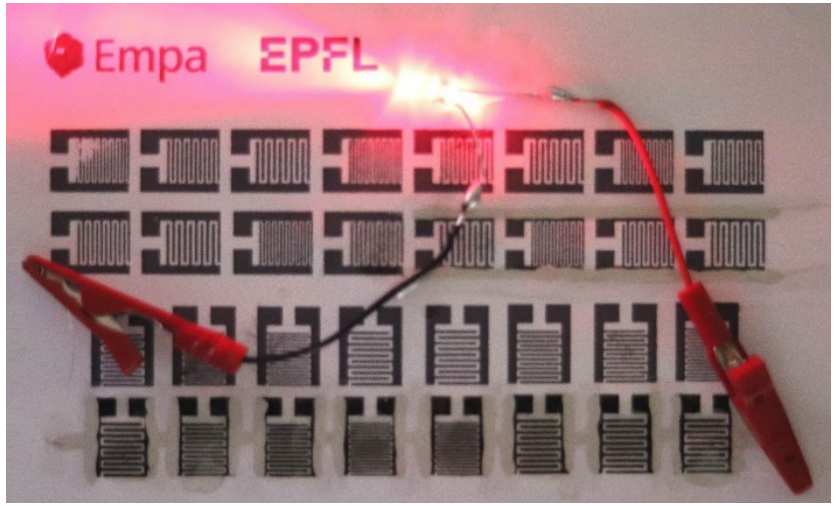
Dry-only Graphene conductive ink

S. Abdolhosseinzadeh et al. Adv. Mater. 2103660 (2021)

“Homogeneous Emulsion and Suspensions of 2-Dimensional Materials“
European Patent Application, EP3848420A1
International application number WO2021/140139A1

Printed devices from 2D material inks

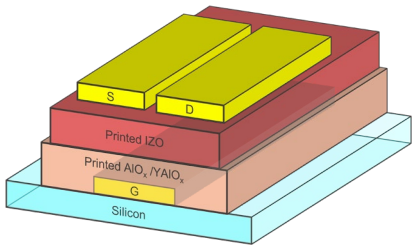


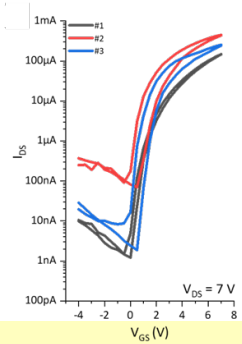


S. Abdolhosseinzadeh et al. *Adv. Mater*. 2000716 (2020)

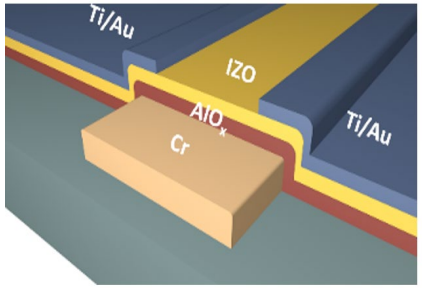
S. Abdolhosseinzadeh et al. Adv. Mater. 2103660 (2021)

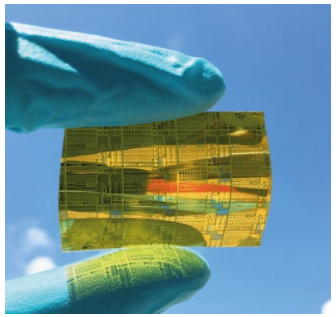
Examples of printed TFTs

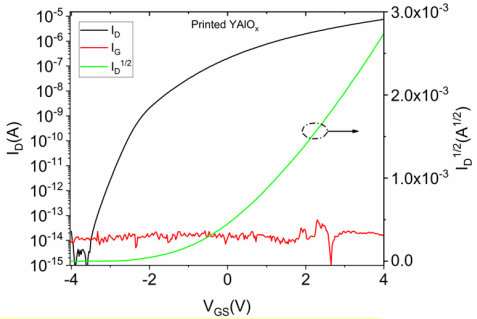




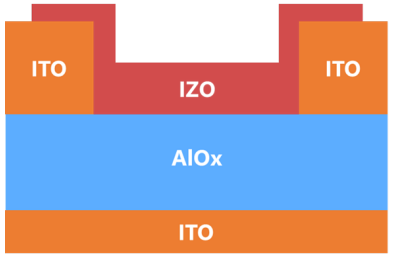
on Si wafer
Contacts: evaporated metals (Al & Cr)
Semiconductor: printed IZO;
Dielectric: printed YAlOx
$I_{ON/OFF} = 10^5$

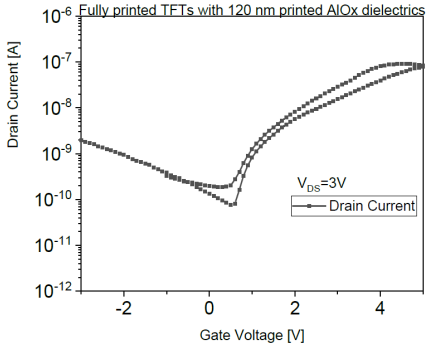


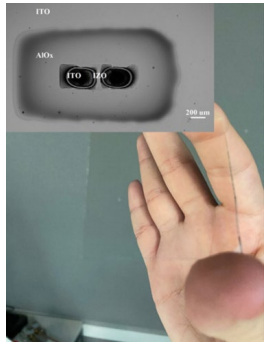




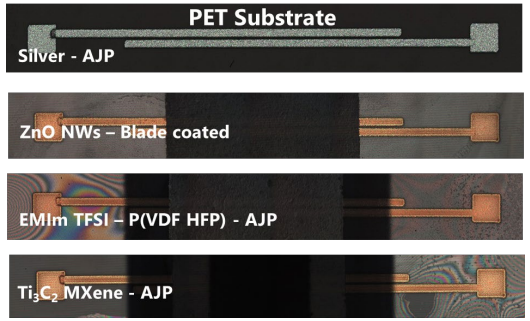
on PI foil
Contacts: evaporated metals (Cr, Ti, Au)
Semiconductor: sputtered IZO;
Dielectric: printed YAlOx
$I_{ON/OFF} = 10^9$

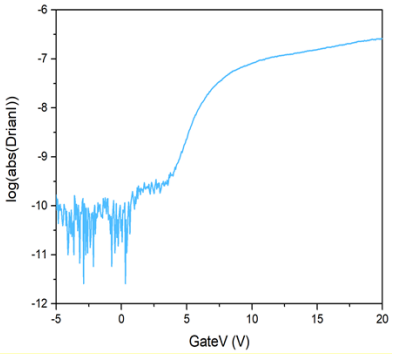






All-printed, all-oxide, fully transparent on glass
Contacts: printed ITO;
Semiconductor: printed IZO; Dielectric: printed YAlOx
$I_{ON/OFF} = 1 \times 10^3$





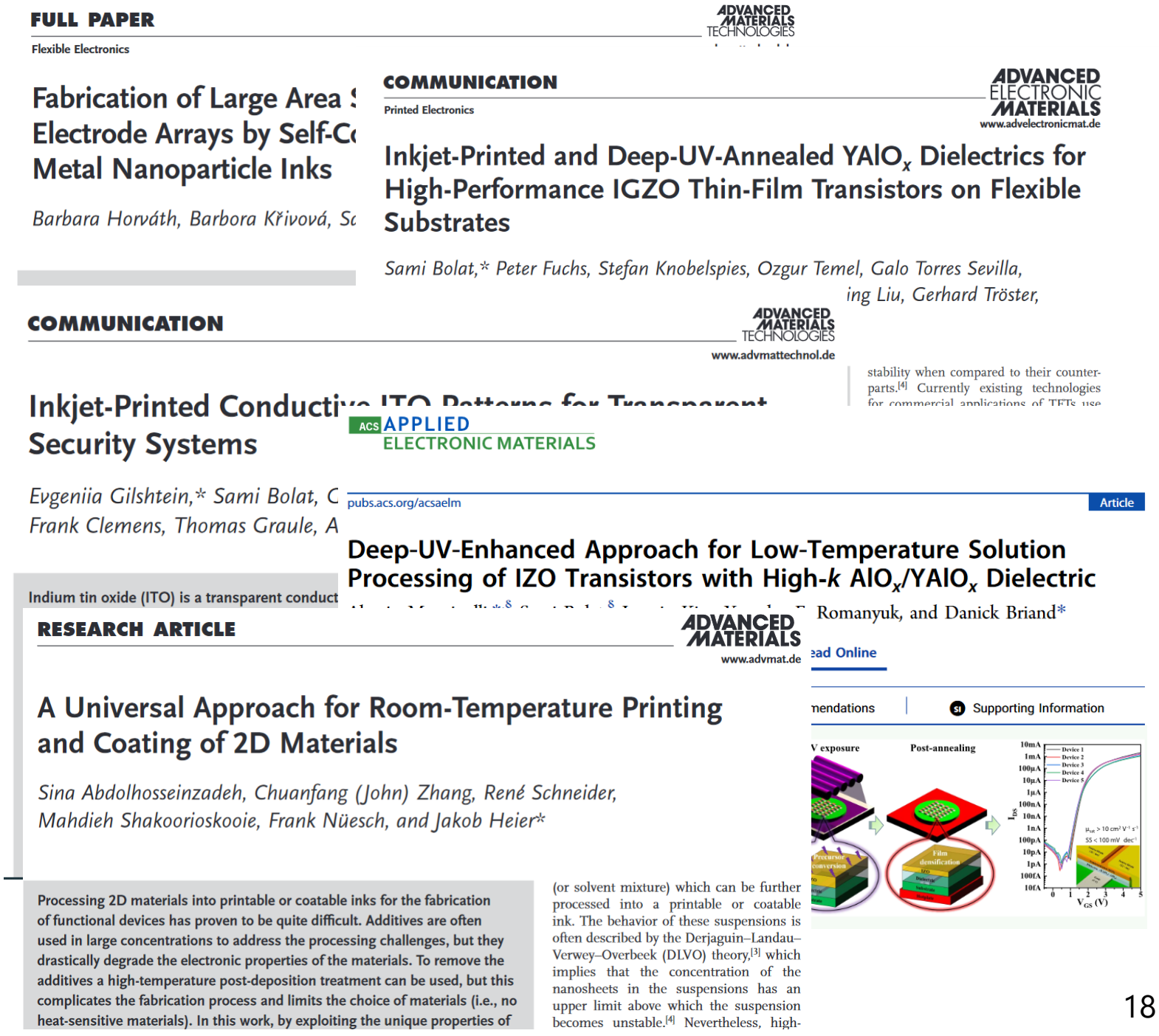
All-printed on PET
Contacts: printed Ag + printed MXene;
Semiconductor: ZnO NWs;
Dielectric: ionic liquid EMIM-TFSI + PVDF
$I_{ON/OFF} = 10^3$

Conclusions

- Printing of electronic oxide inks is possible: ink-jet, aerosol-jet – linewidth ~50 μm
- Photonic curing (UV lamp, FLA, excimer) enables electronic oxides at 150…200°C but not lower
- High-performance oxide TFTs realized on Si, glass, PI and PEI foils but not paper / PET
  (TFTs based on 2D materials, organics or electrolyte gates are feasible)
- Several results not foreseen in the intial plan:
  - flash sintering of refractive ceramics (ITO, Al_2O_3)
  - synaptic transistors with printed oxide dielectrics
  - self-confinement printing using pre-patterned polymers
  - additive-free dry-only vdW inks of 2D materials (graphene, MXenes)

Outputs

- 3 demonstrators
- 17 Publications
  (*x2 Adv Mater*
  x1 Adv Electron Mater
  x2 Adv Mater Techs
  x2 Sci Reps, and others)
- 2 patent applications
- enabled 3 new projects
- 3 PhD theses defended



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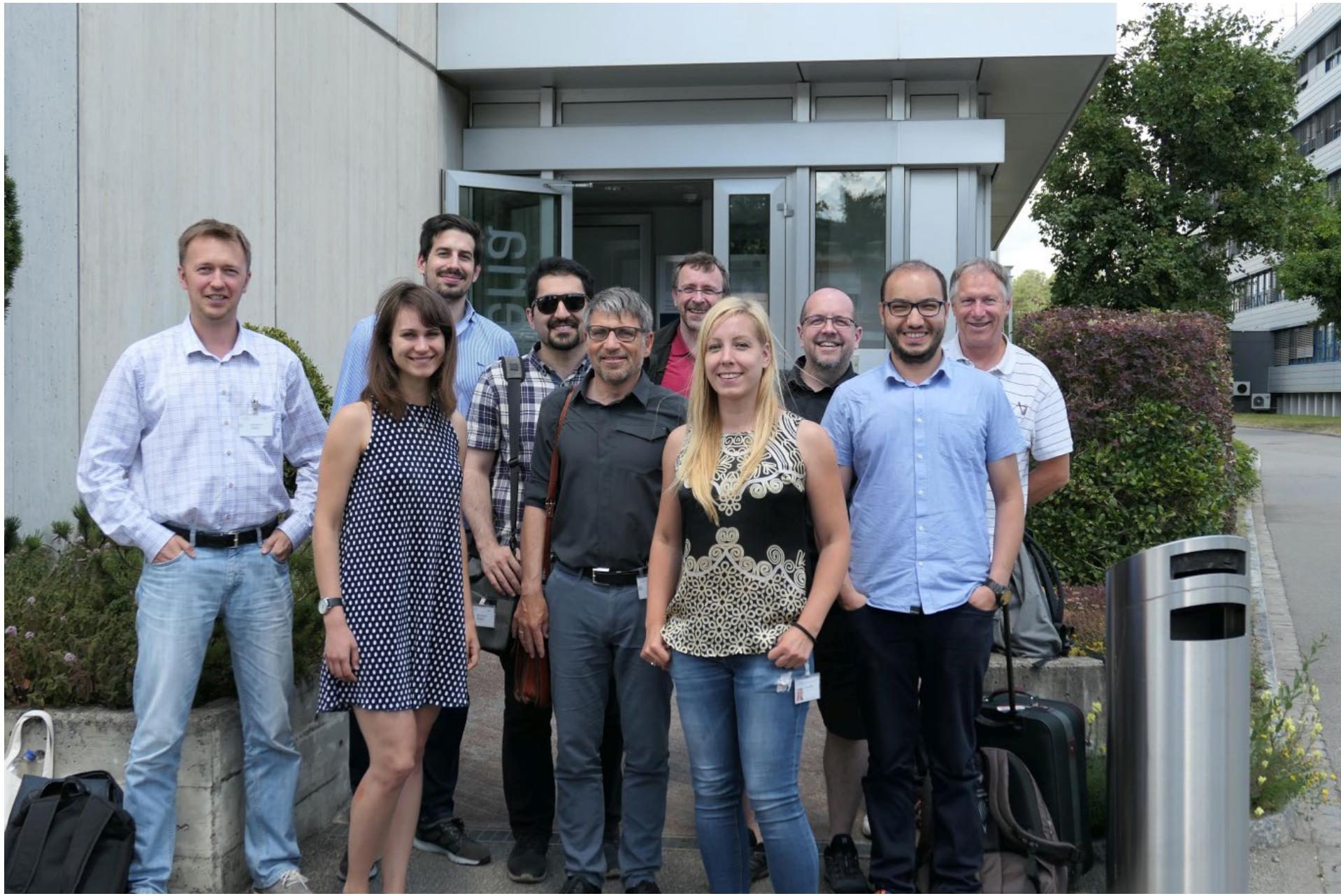
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