Novel UV cross-linkable polymer dielectric for printable electronics

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Novel UV cross-linkable polymer dielectric for printable electronics

Marius G. Ivan, Yanguang Zhang, Neil Graddage, and Ye Tao

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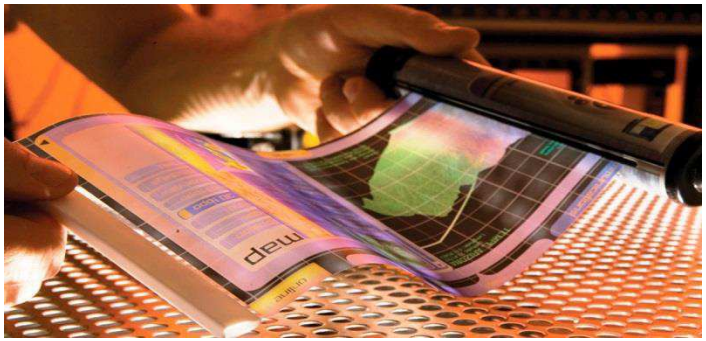
Outline

- Development and testing of a home-made UV curable dielectric
- Fabrication of capacitors
- Fabrication of transistors
- Conclusions

Electronics

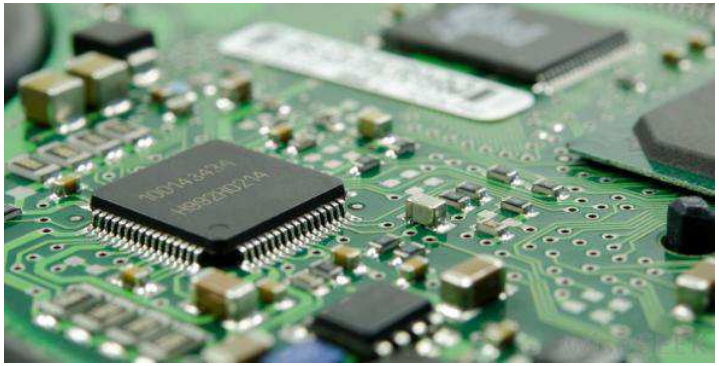
https://en.wikipedia.org/wiki/Flexible_electronics

Flexible Hybrid Electronics



https://news.cnrs.fr/articles/demain-lelectronique-flexible

Flexible Electronics



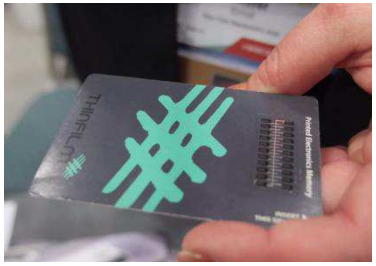
https://loonylabs.org/2014/10/14/carbon-electronics/

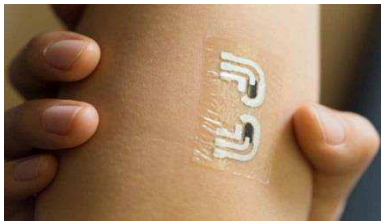
Si-based Electronics

Flexible Electronics - Applications

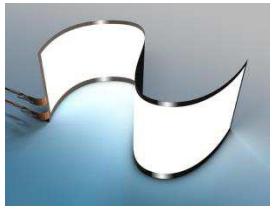
- Wearables
- Information displays
- Telecommunications
- Internet of Things
- Lighting

- Health care
  - Sensors
  - Drug delivery
- Automotive
- Energy scavenging





Forget about the killer application!
There are many applications!



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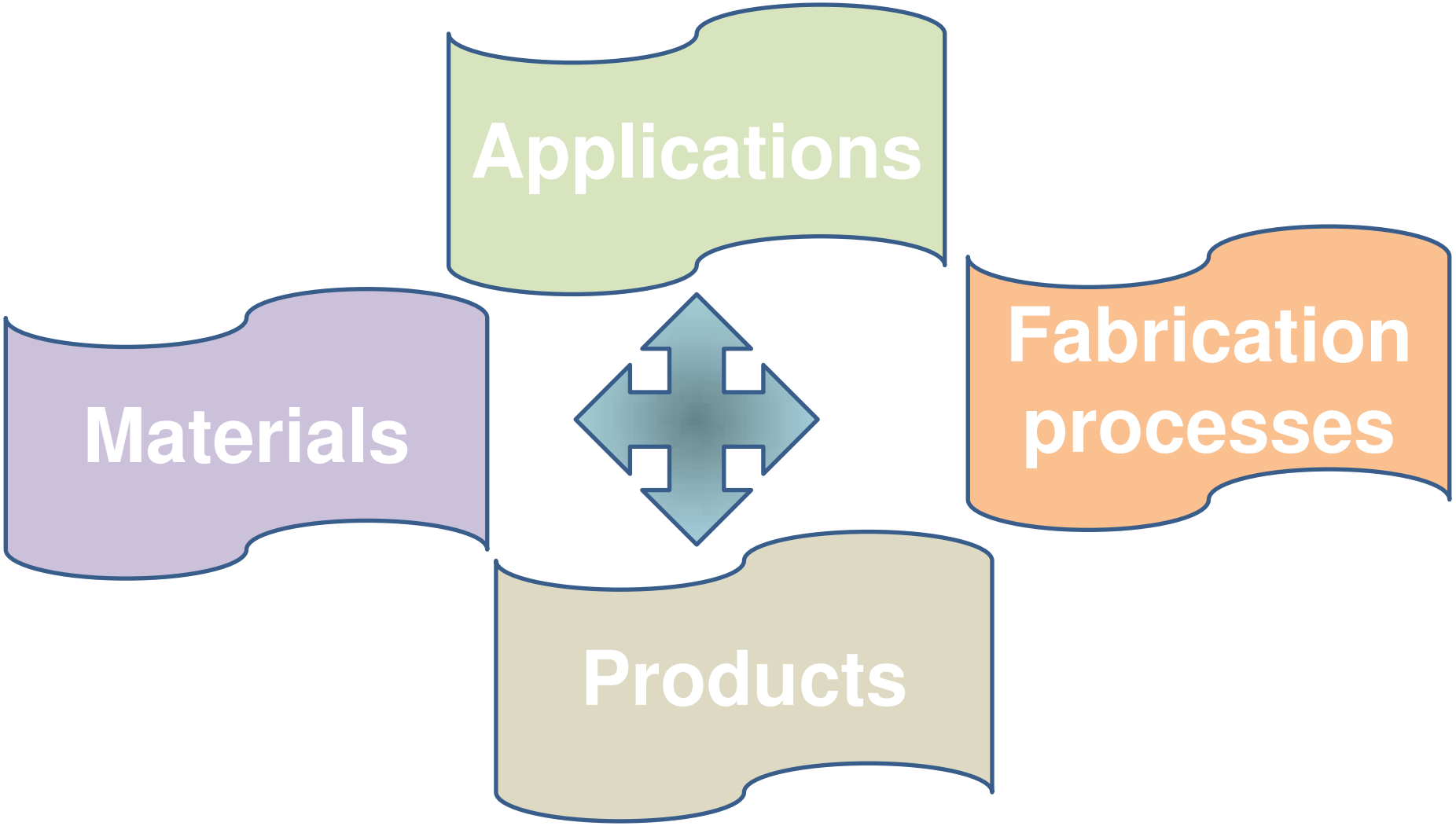
Flexible Electronics – Recipe for success?



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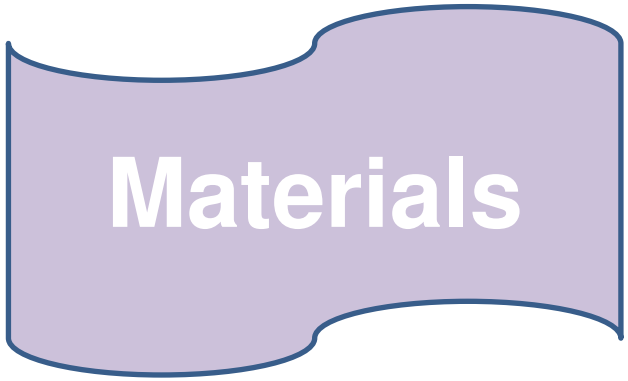
Printed Electronics - Materials

- **Conductive inks**
  - Metal NPs
  - Polymer (i.e. PEDOT-PSS)
- **Semiconducting inks**
  - Inorganic, polymers, small molecules
- **Dielectrics**
  - polymers
- **Substrates**
  - Plastic films, glass, metal, paper
- **Barrier films**



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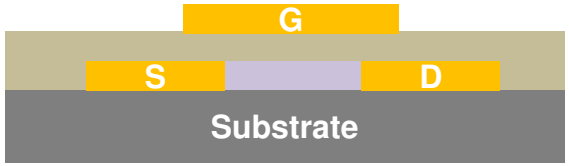
Dielectrics for Printable Electronics

- The ideal dielectric for PE would be



  - Solution processable
  - Deposited under ambient conditions (air, room temperature) by a printing technique
  - Insoluble in metal inks (water, alcohols based inks)
  - Pinhole free, form uniform films

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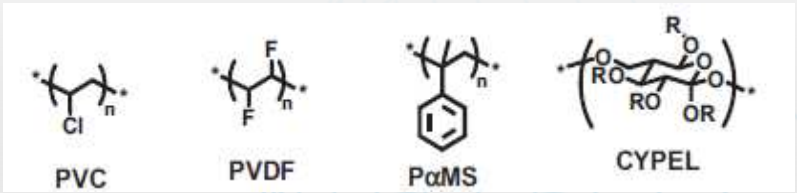
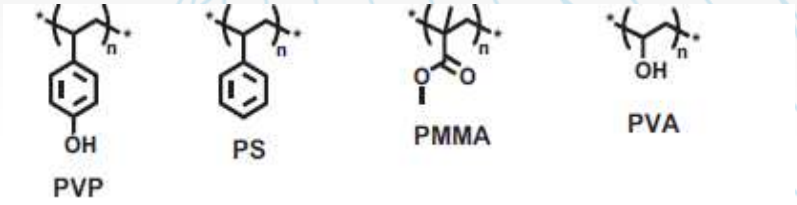
Dielectric constants of organic materials

- Most polymers are spin coated from solution, and are not cross-linked, which causes dissolution when top electrodes are deposited from solution

Ref.	Dielectric	Method [a]	d [nm]	C_i [nF cm^{-2}]	k
36	CYPEL	Cast		6	18.5
	PVA			10	7.8
39	PI	Print		20	
44	PVP-CP	SC	260	~12	3.6
	PVP-CL		380	~2	4.0
46	GR	SC	>1000	0.43–4.97	
49	CYPEL	SC	1200	8.85	12
	PVP		900	5.59	5
	PVA		500	17.8	10
50	Polynorb.	SI-ROMP	~1200	~3	
52	PVP-CL nanoTiO_2	Cast	600–700		3.5–5.4
53	BCB	SC	50	235	
57	CPVP-C_n	SC	~15	~300	~6
	CPS-C_n		~15	~225	~3

Adv. Mater. **2005**, *17*, 1705–1725





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Cross-linked dielectrics for Printable Electronics

- Thermally cross-linked
  - X-linked PVP through esterification reactions, heated **at 60 – 100 ºC for 2.0 h**, k ~ 4.0 – 4.5 (i)
  - X-linked cyanoethyl pullulan (CEP) with trimethylolpropane triglycidyl ether (TTE) after **3.0 h thermal treatment at 100 ºC**, k ~ 15 (ii)
  - Catalysts required

Energy (high t) and time-intensive (h)

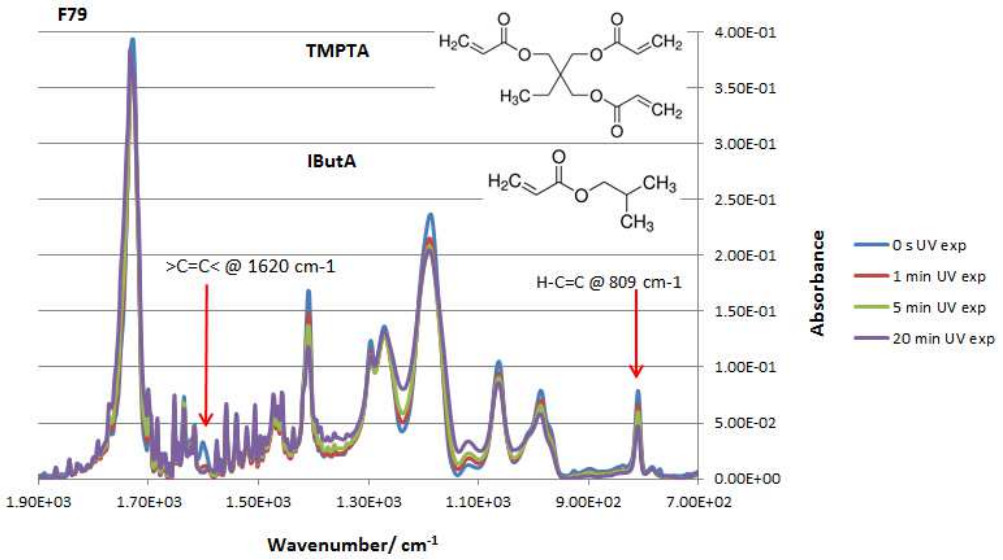
- UV crosslinked dielectrics
  - Cationic polymerization (formation of positively charged species)
  - Free radical polymerization (oxygen quenching of free radicals)

Ambient temperature, FAST (s)

i. Chem.Mater., vol. 21, pp. 2292-2299, 2009; ii. *J. Mater. Chem.,* vol. 1, p. 3955, 2013.;

UV curable dielectric

- UV curable formulations spin coated on top of Si wafer, followed by UV exposure under open air at room temperature; FTIR spectra

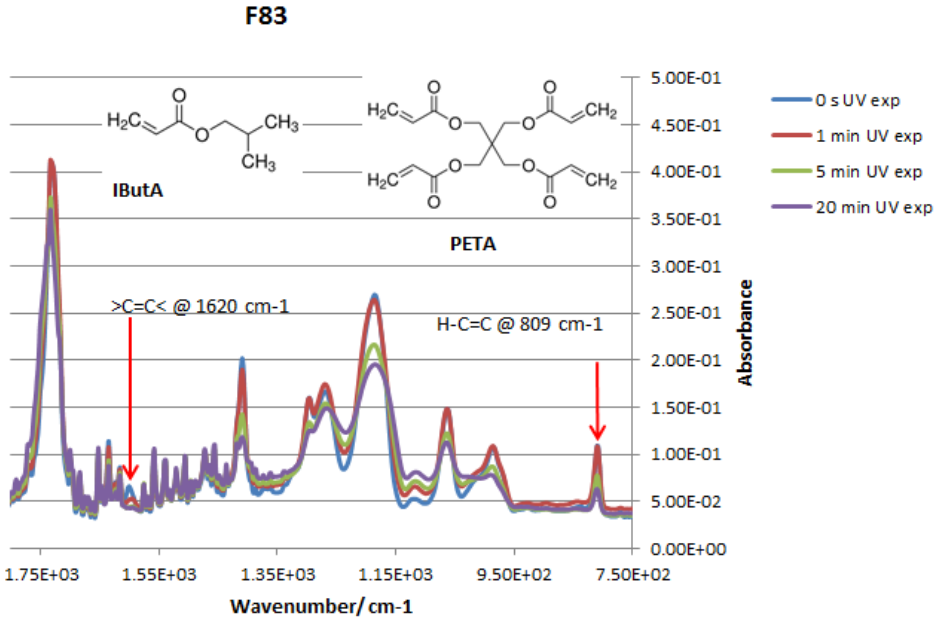


Frequency (Hz)	Capacitance nF/ cm^2	Dielectric constant (k)
100	6.62	5.09
1000	6.18	4.75
1 x 10^4	5.75	4.42
1 x 10^5	5.42	4.16
1 x 10^6	5.36	4.12

F79 spin coated on top of ITO coated glass, Al top electrode vacuum deposited, 680 nm thick

UV curable dielectric

- UV curable formulations spin coated on top of Si wafer, followed by UV exposure under open air at room temperature



Frequency (Hz)	Capacitance nF/ cm^2	Dielectric constant (k)
100	4.22	4.05
1000	4.15	4.00
1 x 10^4	4.06	3.90
1 x 10^5	3.98	3.82
1 x 10^6	3.95	3.80

F83 spin coated on top of ITO coated glass, Al top electrode vacuum deposited, 850 nm thick

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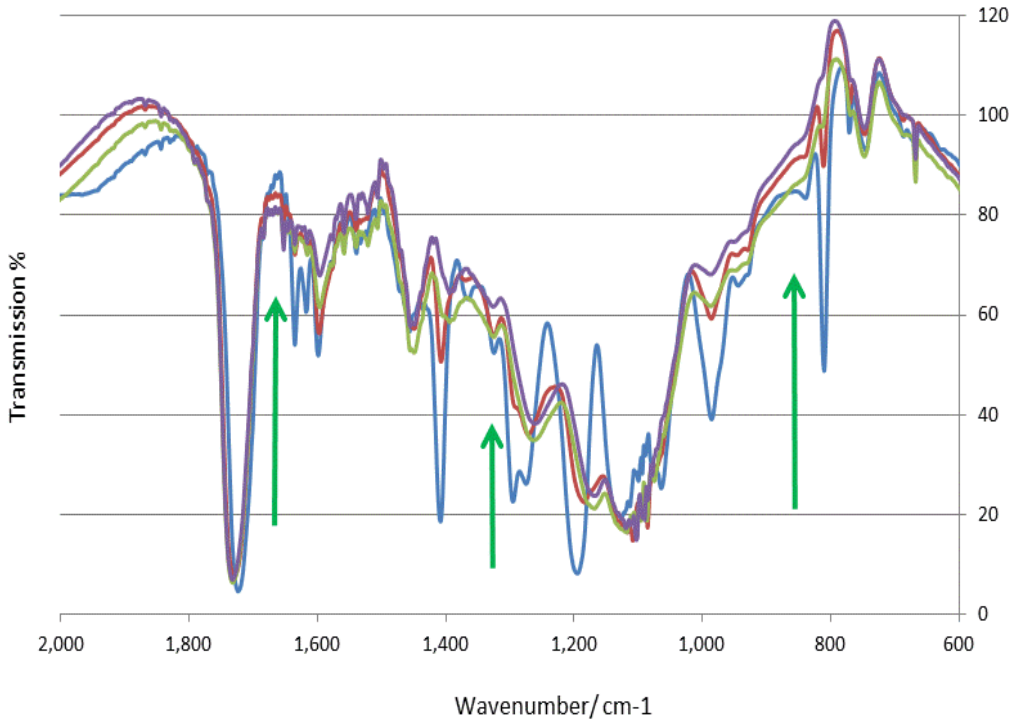
UV curable dielectric

- An UV curable, cross-linkable dielectric has been developed and tested in capacitors



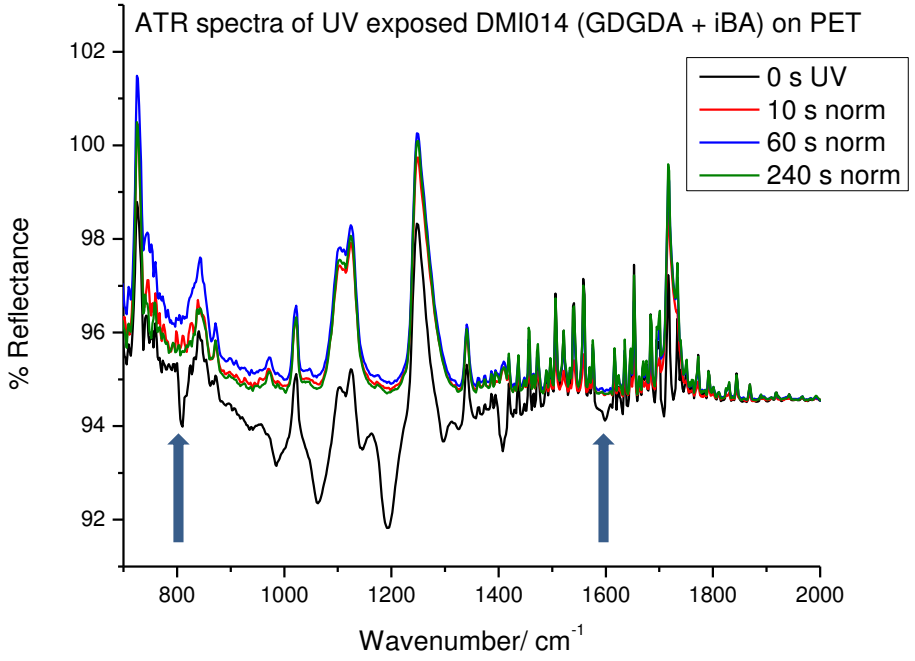
>C=C< stretch 1620 cm^{-1}

H-C=C< @ 809 cm^{-1}

FTIR spectra of UV cured acrylate films exposed @ 365 nm for increasing time periods: 0 s, 1, 10, and 20 minutes respectively.

UV curable dielectric - FTIR -ATR spectroscopy

- Curing speed of the home-made dielectric tested on PET foils with – FTIR – ATR following exposure with Dymax flood exposure tool under open air
- UV curable formulation was spin coated on top of PET substrates at 4000 rpm for 60 s; ~ 350 nm
- Exposure to UV for 0, 10, 30, 60, 90, 120, 240, and 600 s
- FTIR background – bare PET foil



–C=C- stretch at 1620 cm^{-1}
H-C= bend adjacent to the >C=C< in the acrylate moiety H-C=C< at 809 cm^{-1}

Even short exposures, ~ 10 s, appear to induce crosslinking in the acrylate dielectric.

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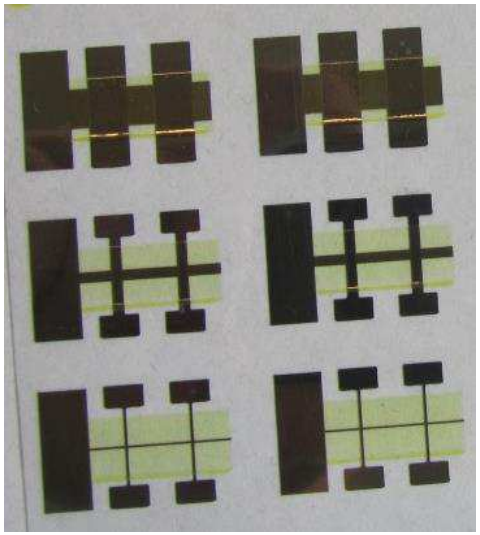
All flexo-printed capacitors

Dielectric constant as a function of frequency for acrylate dielectrics containing **3%** photoinitiator, and exposed to UV radiation for 10 and 20 minutes respectively.

Frequency	Dielectric constant 20 min UV	Dielectric constant 10 min UV
100 Hz	5.61	5.7
1 KHz	5.5	5.64
10 KHz	5.35	5.4
100 KHz	5.12	5.24
1.0 MHz	4.8	4.25



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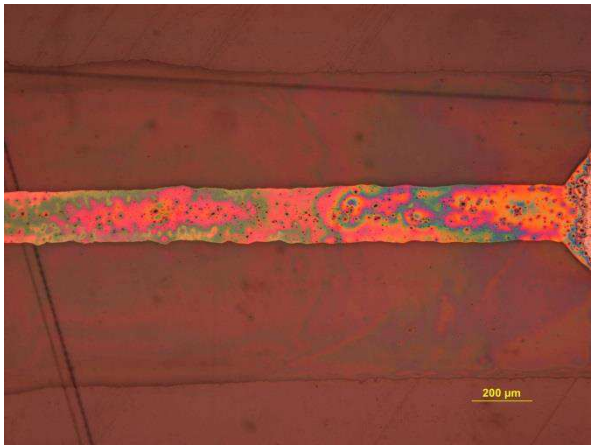
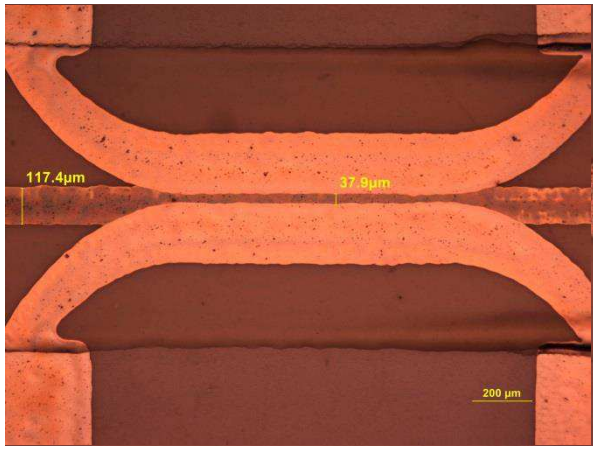
All Flexo-Printed TFTs

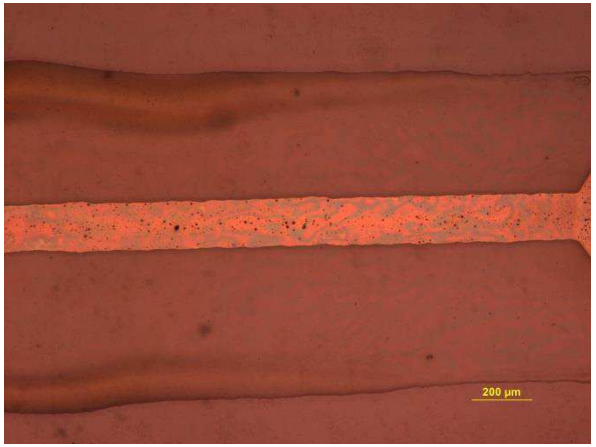
- Each printed layer was exposed to UV for 60 s



1 layer (500 nm),



2 layers (2nd layer printed after 2 min bake @ 100 °C and 1 min air plasma treatment),



2 layers (2nd layer printed after 3 min bake @ 100 oC) (1.2 um)

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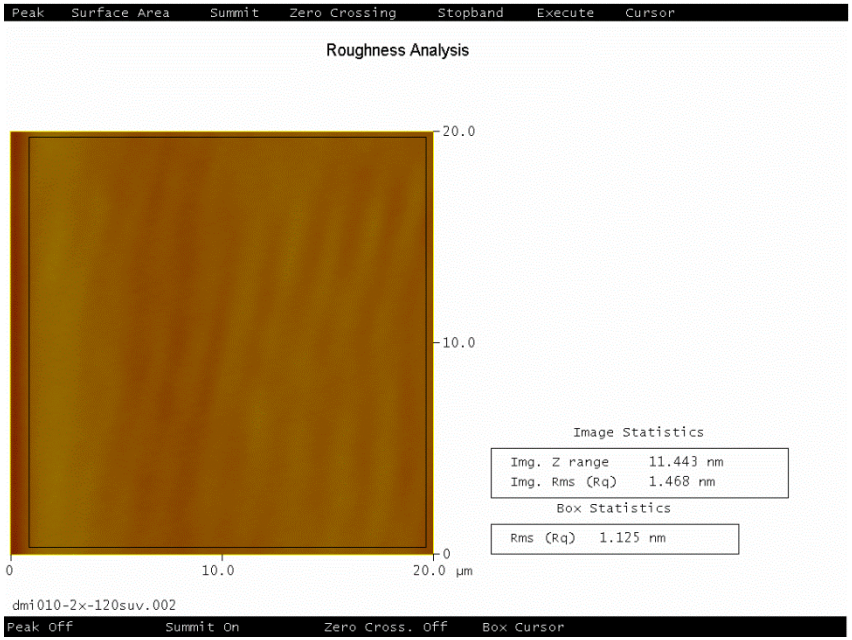
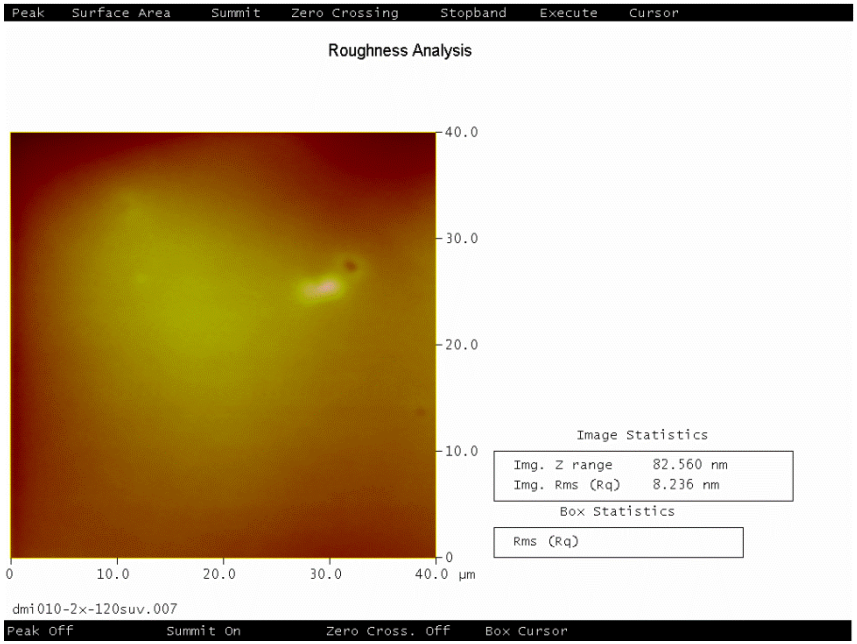
AFM

- AFM of UV cured dielectric, 2 layers, 120 s total UV exposure time





AFM shows pin-hole free film surface

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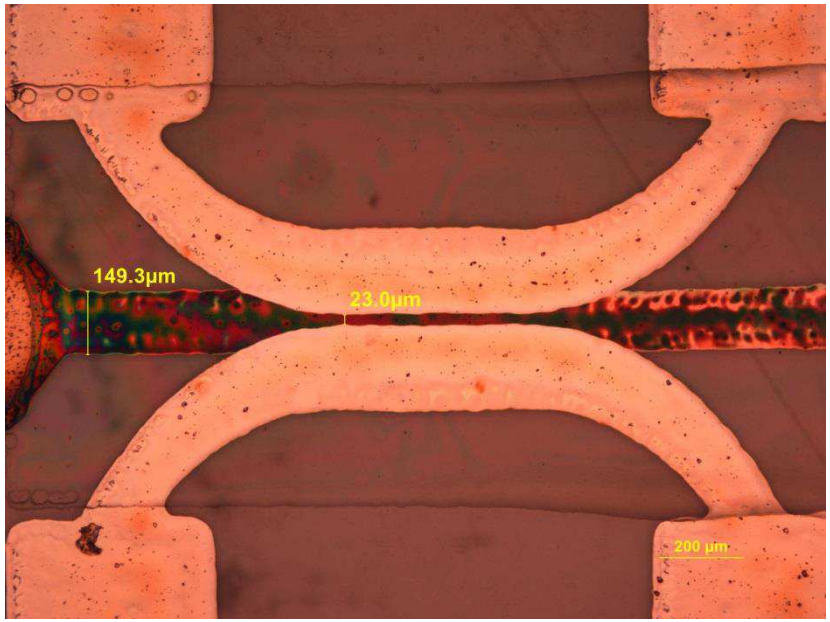
All-flexo printed TFTs with UV cured dielectric

- UV curable dielectric formulation, **1 layer**, 500 nm thickness
- Lisicon SP300 OSC from Merck,



W = 0.5 mm

W = 1.0 mm

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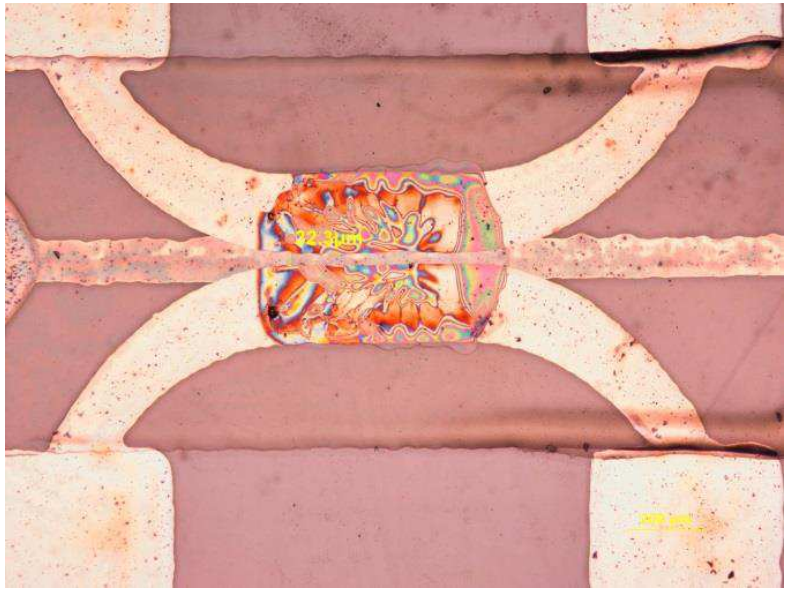
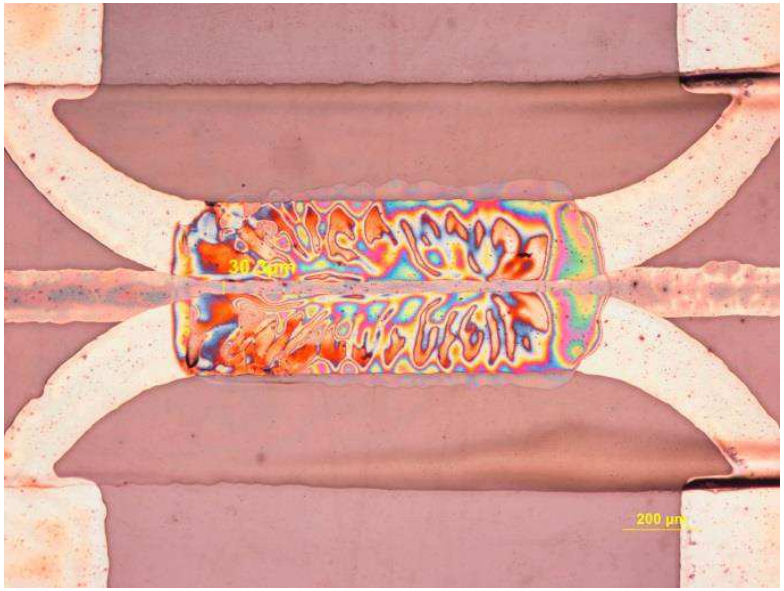
All flexo-printed TFTs with UV curable dielectric

- S-D electrodes adhere well to UV cured dielectric; **2 layers**
- Merck's OSC Lisicon SP300 does not wet well the dielectric, however it covers the Ag printed electrodes



W = 0.5 mm



W = 1.0 mm

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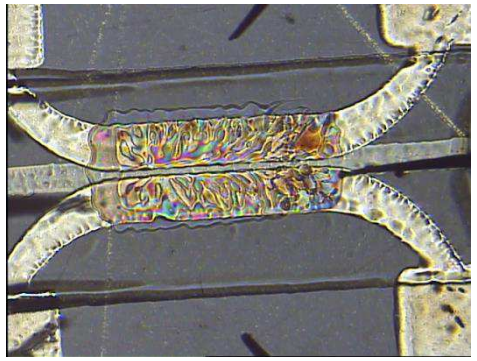
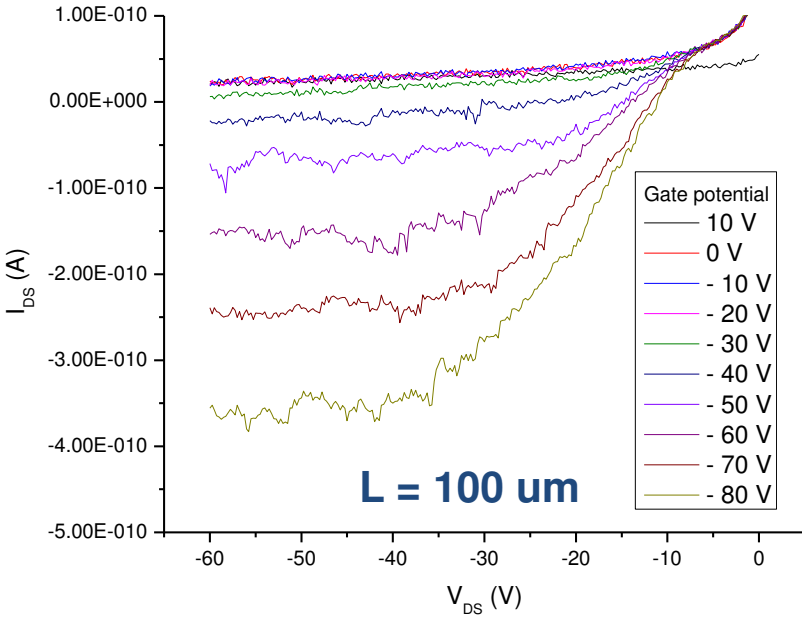
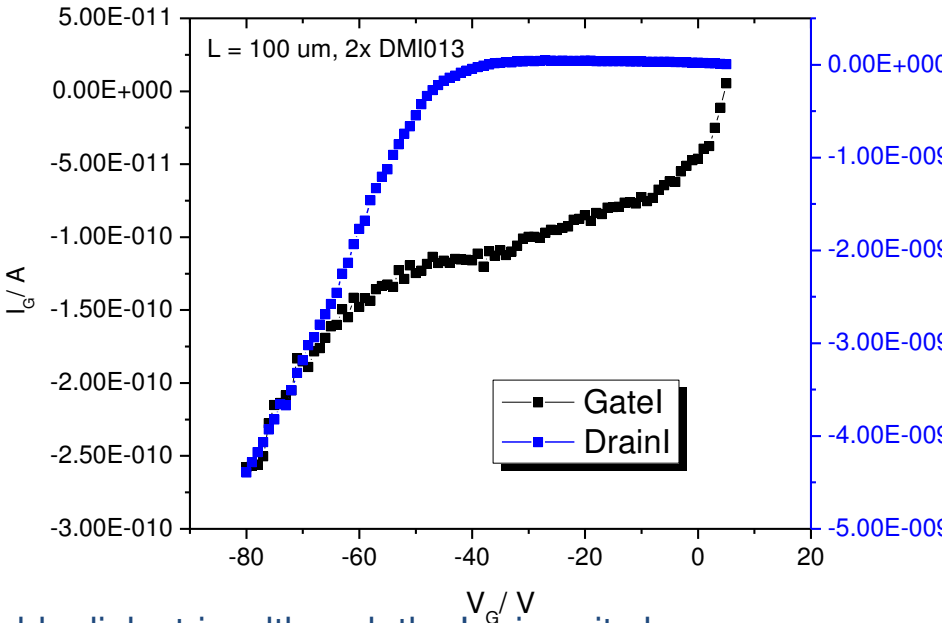
All-flexo printed TFTs with UV cured dielectric

- UV curable dielectric formulation, **2 layers**, 1.0 – 1.2 um thickness,
- Lisicon SP300 OSC from Merck
- S/D and G electrodes flexo printed







Functional TFTs are obtained with the UV curable dielectric, although the I_{DS} is quite low.

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All-flexo printed TFTs with UV cured dielectric

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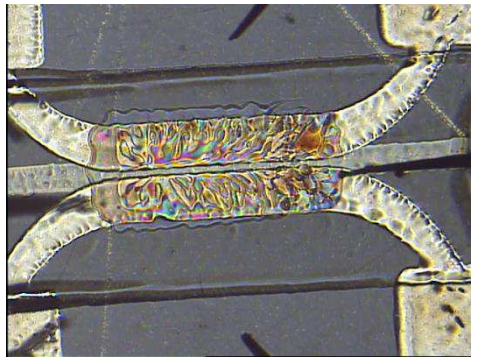

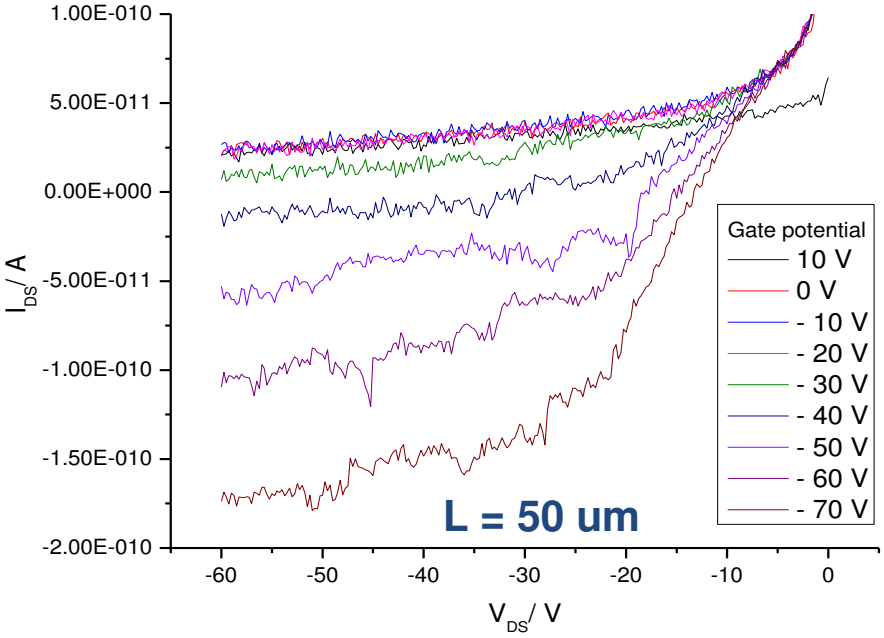

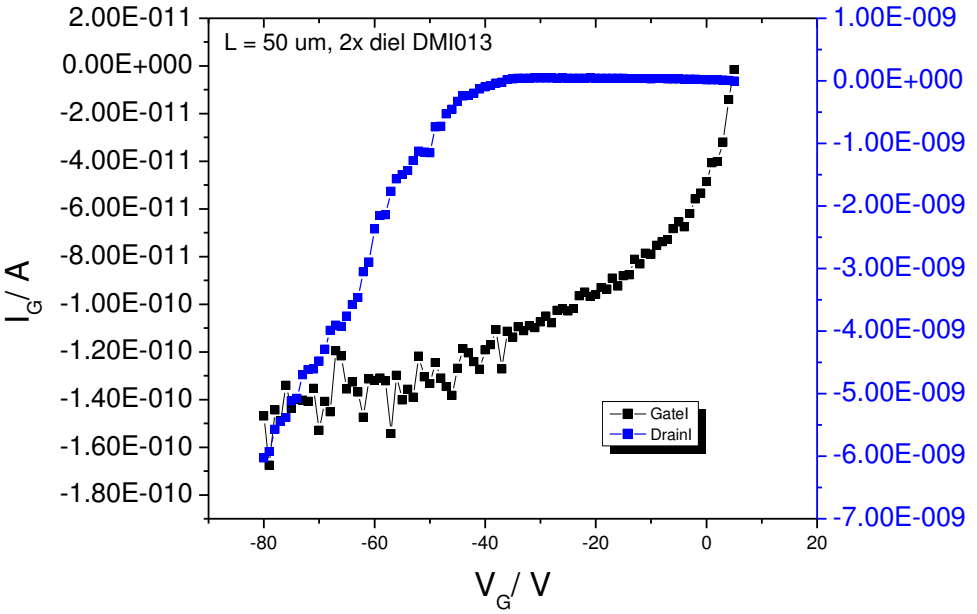

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Conclusions

- UV curable dielectric may be cured in s
- Dielectric constant ~ 4.8 – 5.1
- Insoluble in common organic solvents and water
- Functional capacitors all flexo-printed
- Functional TFTs with UV curable dielectric were printed by flexography

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Thank you

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