Printed metal oxide materials and TFT devices

Jaakko Leppäniemi D.Sc. (Tech.) / VTT
Outline

Introduction:
- Printing methods
- Printed oxide materials
- Printing inks for metal oxides
- Annealing methods

Printed metal oxide devices with focus on metal oxide TFTs:
- Example 1: inkjet-printed S/D-contacts for oxide TFTs
- Example 2: flexographic printed oxide layers for TFTs
- Summary
Introduction
Printing methods

**Inkjet**
- Thermal inkjet
- Piezoelectric inkjet

**Roll-to-roll methods (R2R)**
- Gravure printing
  - Impression cylinder
  - Printed film
- Flexographic printing
  - Anilox cylinder
  - Printed film
- Flexography
  - High-throughput possible with R2R
  - Design of gravure rolls expensive
  - Flexography has limited resolution
  - Cup shape pattern
  - Pressure on sample

**Reverse offset**
- PDMS inking
- Off-step
- Set-step

+ Fast customization, low cost for R&D
+ No pressure exerted to substrate
- Droplet shape & film non-uniformity
- Limited throughput
+ High-throughput possible with R2R
+ High-resolution (< 1 µm possible)
+ Uniform film thickness
+ Vertical side walls
- Step coverage in multilayer films
- Limited throughput
# Printing methods: overview

<table>
<thead>
<tr>
<th>Method</th>
<th>Linewidth (µm)</th>
<th>Overlay (µm)</th>
<th>Layer d control</th>
<th>Optimal in TFTs for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravure</td>
<td>~50 (~2)*</td>
<td>&gt; 30</td>
<td>OK</td>
<td>SC/SD/GD</td>
</tr>
<tr>
<td>Flexography</td>
<td>~75</td>
<td>&gt; 30</td>
<td>OK</td>
<td>SC/GD</td>
</tr>
<tr>
<td>Screen</td>
<td>~50 (~10) +</td>
<td>&gt; 10</td>
<td>Poor</td>
<td>-</td>
</tr>
<tr>
<td>Reverse offset</td>
<td>&lt; 1</td>
<td>&lt; 10</td>
<td>Good</td>
<td>SC/SD/GD</td>
</tr>
<tr>
<td>Inkjet</td>
<td>~30</td>
<td>~10</td>
<td>OK</td>
<td>SC/SD</td>
</tr>
<tr>
<td>SIJ &amp; EHD</td>
<td>~1</td>
<td>~1</td>
<td>Good</td>
<td>SD</td>
</tr>
</tbody>
</table>


Printed oxide materials

- Conductors: ITO, ATO (Sb-doped SnOx), ACO (Al-doped CdOx) etc.

- Dielectrics: AlOx, ZrOx, HfOx, YOx, doped AlOx etc.

- Semiconductors: In$_2$O$_3$, ZnO, SnOx, IZO, ZTO, IGZO, ITZO, etc.
Printing inks for metal oxides

Nanoparticle route

Sol-gel/precursor route
Printing inks for metal oxides

- Colloidal dispersions of electrosterically encapsulated oxide nanoparticles
- Water or organic solvent
- Removal of encapsulant by mild heating or ionic destabilizer
- Results in porous films even with high temperature sintering for higher $\rho$

**Nanoparticle route**

- Thin layer of encapsulation
- Metal oxide core ($\text{In}_2\text{O}_3$, ZnO, IGZO etc.)
- $d \sim 10 - 100 \text{ nm}$

- Encapsulated particle
- Bare oxide particle
- Coalesced or necked particles
- Remnant porosity

- Low-\(T\) or ionic destabilizer
  - $\rho \sim \text{low}$

- High-\(T\) (> 500 °C) or laser
  - $\rho \sim \text{medium}$
Printing inks for metal oxides

- **Sol-gel/precursor route**
  - Dissolved metal salts or metal alkoxides in aqueous or organic solvent
  - Ligands coordinating metal cation centers
  - Requires thermal (or other) energy to i) form oxide through hydrolysis and condensation reaction, ii) removal of contaminants, and iii) film densification
  - Dense films possible (ρ ~ 80 % of bulk)
General trends during annealing?

What limits the maximum annealing temperature?

- Substrate CTE and glass transition limits annealing temperature
  - $T_{max1} \leq 150 \, ^\circ\text{C}$ for low-cost plastics (transparent)
  - $T_{max2} \leq 350 - 400 \, ^\circ\text{C}$ for speciality plastics (opaque)

Alternative, low-temperature annealing required to reach high performance on plastics!
Alternative annealing methods

- Combustion synthesis[1]

  Combustion
  \[ M^{n+} + \text{oxygen} + \text{fuel} \]
  \[ T_a \sim 200-250 \, ^\circ \text{C} \]
  \[ M_{O_y} \]

  Conventional
  \[ M^{n+} + X^- + \text{stabilizer} + \text{ROH or H}_2\text{O} \]
  \[ X^- = \text{Cl}^-, \text{CH}_3\text{COO}^-, \text{NO}_3^-, \text{and so on} \]
  Typically \( T_a > 400 \, ^\circ \text{C} \)

  \( t_{process} \sim 30 \, \text{min} \)

Alternative annealing methods

- Combustion synthesis
- UV-assisted annealing

Photodissociation of ink components and in situ radicals (e.g. HO*)

Evaporation of volatile ink components and condensation reaction products and M-O-M network rearrangement & film densification

$t_{\text{process}} \sim 5 - 180 \text{ min} \quad (t_{\text{drying}} \sim 15 \text{ min})$


Alternative annealing methods

- Combustion synthesis
- UV-assisted annealing
- Microwave-assisted annealing\[1\]

Microwave energy

\[ t_{\text{process}} \geq 3 \text{ min} \]

Thermal energy 140 °C

Ref. [1]

Prof. J. Moon, Yonsei, Korea


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Alternative annealing methods

- Combustion synthesis
- UV-assisted annealing
- Microwave-assisted annealing
- Pulsed light annealing\[1\]

Xenon flash light (Novacentrix)

Rapid heating & cooling

$T_{\text{surface}} \sim 1000 \degree \text{C}$

$T_{\text{bottom}} \sim 300 \degree \text{C}$

$t_{\text{process}} < 20 \text{ s}$  
($t_{\text{drying}} \sim 20 \text{ min}$)


Journal of materials chemistry. C, Materials for optical and electronic devices by Royal Society of Chemistry (Great Britain) Reproduced with permission of Royal Society of Chemistry in the format Presentation/Slides via Copyright Clearance Center.
Alternative annealing methods

- Combustion synthesis
- UV-assisted annealing
- Microwave-assisted annealing
- Pulsed light annealing
- Laser annealing\[^{[1]}\]

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Alternative annealing methods

- Overview on precursor-derived low-temperature annealed TFTs
- Binary oxides like ZnO, In$_2$O$_3$ reach lower annealing temperatures
- Recent reports on laser annealing and pulsed light annealing show promise as they enable rapid low-temperature annealing

Printed metal oxide devices: focus on TFTs
Oxide TFTs using printing methods

- Overview on printed and low-temperature annealed oxide TFTs
- In$_2$O$_3$ is most often used material
- Inkjet is most often used method
- Only a few reports on readily R2R-compatible methods (gravure, flexo etc.)

Current S-o-A of printed oxide TFTs

- Large device size (W = 450 µm / L = 250 µm)

- Rigid (Si wafer) substrate

- Relatively high processing temperature < 250 °C (2h)

+ All-oxide materials

+ Inkjet-printing of all layers

+ High-performance (\(\mu > 10 \text{ cm}^2/\text{V}\cdot\text{s}\))

Ref. [1]


Prof. V. Subramanian, UCLA, USA
Challenges with printed oxide TFTs

**Semiconductor:**
- Printing of thin (~ 10 nm) and continuous layers on flexible substrates
- Semiconductor annealing temperature vs. thermal tolerance of substrates
- Annealing time vs. web speed of printing lines
- Low-performance of p-type oxide for CMOS

**Gate dielectric:**
- Stabile capacitance at low frequency
- Pinhole free films: contamination from printing, purity of materials

**Contact electrodes:**
- Poor understanding of what constitutes a good S/D contact
- Optimum S/D contact materials vs. readily available metal inks
- TFT dimensions vs. printing resolution/registration accuracy

No Al, Ti, Mo etc. NP dispersions
Ag and Au form Schottky contact
Cu (CuO) requires photonic flash sintering
TCO’s require high annealing temperature

Our solutions

Flexographic printing continuous, thin oxide semiconductor layers on plastic

Inkjet-printed In$_2$O$_3$ layers on PEN substrate at 150 °C enabled by far UV-assisted annealing

High-gain nMOS-depletion load inverters utilizing inkjet-printing for channel thickness optimization


J. Leppäniemi et al ACS Appl. Mater. Interfaces 2017, 9, 10, 8774-8782

Our solutions

Inkjet-printed Ag S/D-semiconductor contact engineering using n-doped interface layers

Revere-offset-printed MoOₓ S/DContacts from metal-acetyleneacetonate ink

Dr. Yasuuki Kusaka
Dr. Nobuko Fukuda


L. Gillan et al J. Mater. Chem. C, 2018, 6, 3220
Example 1: inkjet-printed S/D contacts layers for TFTs
Inkjet-printed Ag S/D-contacts

- Evaporated Al works well with inkjet-printed In$_2$O$_3$ semiconductor: no printable inks for Al, Ti, Mo etc.
- Inkjet-printed nanoparticle Ag contacts result in poor performance and Schottky barrier


Inkjet-printed Ag S/D-contacts

- Interface layer with high $n$-doping could help to reduce contact resistance between Ag and In$_2$O$_3$ semiconductor
- Branched PEI has large tertiary amine groups that can give out electrons

![Diagram](image)

<table>
<thead>
<tr>
<th>TFT stack</th>
<th>Material &amp; method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Wafer</td>
</tr>
<tr>
<td>Gate</td>
<td>Si p++</td>
</tr>
<tr>
<td>Dielectric</td>
<td>100 nm of SiO$_2$</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>2 layers inkjet printing In$_2$O$_3$ + 300 °C annealing</td>
</tr>
<tr>
<td>Interface layer</td>
<td>Inkjet printing In$_2$O$_3$ with 0.1 wt% of PEI + 300 °C annealing</td>
</tr>
<tr>
<td>S/D electrodes</td>
<td>Inkjet-printed Ag nanoparticles</td>
</tr>
</tbody>
</table>


Inkjet-printed Ag S/D-contacts

- PEI-containing interface layer between inkjet-printed Ag and inkjet-printed In$_2$O$_3$ helps to reduce hysteresis and increase mobility

<table>
<thead>
<tr>
<th>Interlayer</th>
<th>S/D</th>
<th>$\mu_{\text{sat}}$ cm$^2$/Vs</th>
<th>$V_{\text{on}}$ (V)</th>
<th>$V_{\text{hyst}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>Ag</td>
<td>0.03 $\pm$ 0.01</td>
<td>$-0.5 \pm 1.8$</td>
<td>$5.7 \pm 0.7$</td>
</tr>
<tr>
<td>0.1% PEI-In2O3</td>
<td>Ag</td>
<td>3.0 $\pm$ 1.8</td>
<td>$-5.2 \pm 0.9$</td>
<td>$4.0 \pm 0.7$</td>
</tr>
</tbody>
</table>

With interface engineering, printed Ag can be used as potential S/D contact for printed oxide TFTs

## Inkjet-printed Ag contacts for oxide TFTs

- Mechanisms behind the improved performance?

<table>
<thead>
<tr>
<th>Interlayer</th>
<th>$R_{sh}$ (Ω/sq)</th>
<th>$R_c$ (Ω)</th>
<th>Ahdesion</th>
<th>Ag at% (3d XPS)</th>
<th>$\phi$ (eV)** [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>4.7 ± 0.4 M *</td>
<td>280 ± 29 k</td>
<td>0B, &gt;65% removed</td>
<td>~2.5 at%</td>
<td>4.6</td>
</tr>
<tr>
<td>0.1 % PEI-In2O3</td>
<td>0.5 ± 0.1 k</td>
<td>29 ± 8 k</td>
<td>1B, 35 - 65% removed</td>
<td>~1.5 at%</td>
<td>3.6</td>
</tr>
</tbody>
</table>

* Bare In$_2$O$_3$

Reduced contact resistance leads to improved performance


Example 2: flexographic-printed oxide layers for TFTs
Flexography-printed In\textsubscript{2}O\textsubscript{3} TFTs

- Flexographic printing of In\textsubscript{2}O\textsubscript{3} ink on flexible substrate (Xenomax\textsuperscript{®} PI)
- Ink: In(NO\textsubscript{3})\textsubscript{3} 2.5H\textsubscript{2}O dissolved in 2-methoxyethanol (0.2 M) without additives

<table>
<thead>
<tr>
<th>TFT stack</th>
<th>Material &amp; method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>38 µm Xenomax\textsuperscript{®} polyimide</td>
</tr>
<tr>
<td>Gate</td>
<td>Evaporated Al or Au</td>
</tr>
<tr>
<td>Dielectric</td>
<td>75 / 100 nm of ALD-grown Al\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>1-3 layers flexographic printing + 300 °C annealing</td>
</tr>
<tr>
<td>S/D electrodes</td>
<td>Evaporated Al with W/L ~12.5</td>
</tr>
</tbody>
</table>

[1] “Flexography-Printed In\textsubscript{2}O\textsubscript{3} Semiconductor Layers for High-Mobility Thin-Film Transistors on Flexible Plastic Substrate”, J. Leppäniemi et al Advanced Materials (2015)
Flexography-printed $\text{In}_2\text{O}_3$ TFTs

- Varied anilox transfer volume: minimized transfer volume helps to form uniform films

Excess ink in start of the print

Smooth, uniform layer

Excess ink throughout the print

Flexography-printed In$_2$O$_3$ TFTs

- Oxygen plasma treatment for full wetting regime improves printed layer morphology

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Al$_2$O$_3$ surface

In$_2$O$_3$ ink

$\theta_c \approx 17^\circ$

1 min O$_2$ plasma

$\theta_c \approx 5^\circ$

2 min O$_2$ plasma

$\theta_c < 2^\circ$

Flexography-printed In$_2$O$_3$ TFTs

- Metal gate selection (Al vs. Au) results in different roughness for the Al$_2$O$_3$-In$_2$O$_3$ interface which will affect device performance.

Flexography-printed In$_2$O$_3$ TFTs

- Varied layer amount for thickness control: multilayer printing without intermediate drying results in uniform films

<table>
<thead>
<tr>
<th># layer</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7 ± 3</td>
</tr>
<tr>
<td>2</td>
<td>15 ± 2</td>
</tr>
<tr>
<td>3</td>
<td>25 ± 6</td>
</tr>
</tbody>
</table>

(b) & (c) Without intermediate drying
(d) With intermediate drying

Flexography-printed In$_2$O$_3$ TFTs

- Effect of layer amount on TFT electrical performance

Increasing thickness with layer amount:
- Mobility increases
- Increasing variation in thickness leads to increasing variation in mobility

Optimize 2 layer device

Increasing thickness with layer amount:
- Turn-on voltage shifts more negative
- Indicates excess charge carriers

Flexography-printed In$_2$O$_3$ TFTs

- Optimized process with 2x In$_2$O$_3$, 2 min O$_2$ plasma, Au-gate (smooth interface) and reduced dielectric thickness (75 nm)

---

<table>
<thead>
<tr>
<th># layer</th>
<th>G</th>
<th>d (nm)</th>
<th>$R_a$ (nm)</th>
<th>$\mu_{sat}$ cm$^2$/V·s</th>
<th>$V_{on}$ (V)</th>
<th>SS (V/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al</td>
<td>7 ± 3</td>
<td>1.2</td>
<td>&lt; 0.4</td>
<td>0.7 ± 0.9</td>
<td>1.2 ± 0.6</td>
</tr>
<tr>
<td>2</td>
<td>Al</td>
<td>15 ± 2</td>
<td>1.1</td>
<td>2 ± 1</td>
<td>−0.2 ± 0.4</td>
<td>0.8 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>Al</td>
<td>25 ± 6</td>
<td>1.0</td>
<td>5 ± 3</td>
<td>−1.0 ± 0.5</td>
<td>0.8 ± 0.4</td>
</tr>
<tr>
<td>2</td>
<td>Au</td>
<td>14 ± 4</td>
<td>0.5</td>
<td>8 ± 4</td>
<td>−0.6 ± 0.5</td>
<td>0.4 ± 0.1</td>
</tr>
</tbody>
</table>

Flexography-printed In$_2$O$_3$ TFTs

- Reasons for high variation in device performance?

![Graph showing percentage of devices vs. saturation mobility](image1)

Nanocrystalline semiconductor

- Nanocrystalline SC mobility heavily dependent on $d$.
- Thickness variation due to flexo printing.
- Large variation in mobility.

$d = 14 \pm 4$ nm

Summary

- Metal oxide precursor layers can be deposited using printing and converted to metal oxide materials using various low-temperature annealing methods.

- State-of-the-art focus on printed MO TFTs developing TFT material stack and fabrication process.

- Novel printing methods that can deliver linewidths that are electronics-industry relevant (~1 μm) are needed.

- More work is needed to combine all-printed oxide materials, high-resolution printing and low-temperature processing to reach circuit-level demonstrations.
Thank you!

Ari Alastalo, Liam Gillan, Kim Eiroma, Himadri Majumdar, Terho Kololuoma, Olli-Heikki Huttunen