Spatial Atomic Layer Deposition (SALD), a “new” tool for energy materials.

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1. Introduction

2. SALD

3. Application to PV
Background: Extensive experience in the preparation and characterization of novel materials via low T scalable methods & application in energy conversion & storage.

- Hybrid nanostructures
- Electrochemistry
- SALD/CVD
- Energy storage (Li)
- TCM
- Photovoltaics

New Ag-Cu oxides
1. Introduction

2. AP-SALD

3. Application to PV
Impact of processing in civilization: the case of Al
Impact of processing in civilization: the case of Al

Al not noble, found combined to Oxygen
Impact of processing in civilization: the case of Al

Molten $\text{Al}_2\text{O}_3 > 2000 \, ^\circ\text{C}$
Spatial Atomic Layer Deposition

Atomic Layer Deposition

Chemical Vapour Deposition

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Related to Chemical Vapor Deposition ➔ sequential, surface self-limited growth

**CVD vs ALD**

**Unique pros:** Thickness control + high quality at low T + edge coverage

Adapted from *Adv. Mat.* 2007 3425

*Chem. Rev.* 2010 111.
Related to Chemical Vapor Deposition ➔ sequential, surface self-limited growth

Nottingham Univ.

Diethyl zinc (ALD)

Zinc acetylacetonate (MOCVD)

A. Devy, Coordination Chemistry Reviews 257 (2013) 3332–3384

http://sites.google.com/site/workdmr/
Related to Chemical Vapor Deposition → sequential, surface self-limited growth

Unique pros: Thickness control + high quality at low T + edge coverage

Drawbacks: very slow + processing in vacuum

Increasing popularity (many reviews since ‘02)

Nanostructures for Energy & Env. Appl.

SOFC

SOLUTIONS???
Batch ALD / Reactor optimization / SALD
Key feature of SALD:

*Patented 1977, Suntola et al.*

Patent 1983, Suntola et al.

Vacuum, inspired in sputtering & MBE

AP, inspired in CVD

Temporal ALD

Spatial ALD

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First Publications on AP-SALD

APPLIED PHYSICS LETTERS 92, 192101 (2008)

Stable ZnO thin film transistors by fast open air atomic layer deposition

David H. Levy, a) Diane Freeman, Shelby F. Nelson, Peter J. Cowdrey-Corvan, and Lyn M. Irving
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2102, USA
(Received 2 April 2008; accepted 17 April 2008; published online 12 May 2008)

We report stable, high performance zinc oxide thin film transistors grown by an atmospheric pressure atomic layer deposition system. With all deposition and processing steps kept at or below 200 °C, the alumina gate dielectric shows low leakage (below 10⁻⁸ A/cm²) and high breakdown fields. Zinc oxide thin film transistors in a bottom gate geometry yield on/off ratios above 10⁸, near zero turn-on voltage, little or no hysteresis, and mobility greater than 10 cm²/V s. With alumina passivation, shifts in threshold voltage under gate bias stress compare favorably to those reported in the literature. © 2008 American Institute of Physics. [DOI: 10.1063/1.2924768]

Reproducing growth of p-type ZnO:N using a modified atomic layer deposition process combined with dark annealing

L. Dunlop, a) A. Kursumovic, and J. L. MacManus-Driscoll
Department of Materials Science, University of Cambridge, Pembroke St., Cambridge CB2 3QZ, United Kingdom
(Received 8 July 2008; accepted 16 September 2008; published online 31 October 2008)

Nitrogen doped ZnO (ZnO:N) films were deposited by atmospheric atomic layer deposition (ALD) between 100 and 300 °C. Postannealing was required to remove compensating defects. After a low temperature dark annealing, originally n-type films became p-type. Films deposited at low temperatures (<150 °C) have low hole mobilities (µ) of 0.2–0.4 cm²V⁻¹s⁻¹ and moderate hole concentrations (n_p) of around 1×10¹⁵ cm⁻³. Higher temperature deposited films (>200 °C) have higher µ values (6 cm²V⁻¹s⁻¹) but n_p values <1×10¹³ cm⁻³. This crossover in transport properties can be explained by the opposing effects of deposition temperature on nitrogen doping level and distribution, and film crystallinity. © 2008 American Institute of Physics. [DOI: 10.1063/1.3000604]
SALD versatile, can be implemented in many ways
SALD in the world (14 Labs and 6 commercial)
Kodak’s close proximity system

(a) Schematic diagram of the gas flow system.

(b) Frontal view showing water in and out channels.

(c) Substrate channel with multicomponent oxide formation.
TEMPORAL ALD

Atmospheric & Spatial ALD

AP-SALD

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High Quality films @ low temperature

Coating of ZnO nanorod arrays with Al$_2$O$_3$ @150 °C:

20 cycles @ 2 mm/s: ~12 minutes

40 cycles @ 2 mm/s: ~25 minutes

60 cycles @ 25 mm/s: !!! ~3.5 minutes

Average alumina thickness = 25 nm
Nanorods have tapered top facets

Average ZnO nanorod diameter = 60 to 80 nm
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http://sites.google.com/site/workdmr/
3. Application to PV

AP-SALD for new generation PV

AP-SALD for TCMs
Applications in new generation photovoltaics

Spatial atmospheric atomic layer deposition: a new laboratory and industrial tool for low-cost photovoltaics

David Murfiez-Rojas*abc and Judith MacManus-Driscoll

Recently, a new approach to atomic layer deposition (ALD) has been developed that doesn’t require vacuum and is much faster than conventional ALD. This is achieved by separating the precursors in space rather than in time. This approach is most commonly called Spatial ALD (SALD). In our lab we have been using/developing a novel atmospheric SALD system to fabricate active components for new generation solar cells, showing the potential of this novel technique for the fabrication of high quality materials that can be integrated into devices. In this minireview we will introduce the basics of SALD and illustrate its great potential by highlighting recent results in the field of photovoltaics.
Bulk Heterojunction Solar Cells: organic semicon.

Roll-to-roll PV pilot production at the Technical University of Denmark. Photo: Markus Hösel/Technical University of Denmark

**TiO$_2$ Blocking Layers in Bulk Heterojunction Solar Cells**

- Efficient dissociation
- Thick layers (more absorption)
- Recombination at electrodes

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**TiO$_2$ Blocking Layers in Bulk Heterojunction Solar Cells**

- AALD (100, 350 °C) vs. Spray pyrolysis (450 °C)
- Efficient dissociation
- Thick layers (more absorption)
- Recombination at electrodes

**Blocking/selective layers:**
Thin and transparent
Low temp. (comp. Plastic)
Roll-to-Roll

[http://sites.google.com/site/workdmr/](http://sites.google.com/site/workdmr/)

*From AP-SALD to devices*
TiO$_2$ Blocking Layers in Bulk Heterojunction Solar Cells

- AALD: 100 times faster, low T, comp. Plastic.
- High quality of films allows ultra thin BL

From AP-SALD to devices

D. Muñoz-Rojas et al, Progress in Photovoltaics 2013  accelerated publication
Cu$_2$O for Cu$_2$O/ZnO SCs (cupraselect + H$_2$O)

Range of stability of Cu$_2$O:

Films grown at 150 & 200 °C:
thickness = f(#cycles)

Transport properties study limited to: 150 to 250 °C

150 °C: 0.045 nm/cycle
200 °C: 0.021 nm/cycle
Conformal deposition on ZnO nanorods
Deposition in different substrates:

- **Al foil**
- **plastic**
- **glass**

- **RMS = 1.4 nm**
Phase pure Cu$_2$O

HRTEM

*HRTEM images showing Cu$_2$O phase with d-spacing of 2.46 Å for (111) plane.*

SEM

*SEM images at different deposition temperatures (125°C, 150°C, 175°C, 200°C, 225°C).*

**UV-VIS**

*Graph showing UV-VIS transmission spectra for different deposition temperatures (150°C, 175°C, 200°C, 225°C).*

- Only Cu$_2$O found in HRTEM
- Same Eg for different deposition temperatures
- Particle size = f(deposition temperature)
Highly conductive Cu$_2$O (AIP Advances 2012)

From AP-SALD to devices
Highly conductive Cu$_2$O

Cu$_2$O deposited with SALD: improvement of electrodeposited ZnO/Cu$_2$O cells

![Figure from T. Gershon et al., SEM&SC, 2012](http://sites.google.com/site/workdmr/)

Carrier concentration: ED ~ 10$^{13}$ vs. SALD ~ 10$^{16}$ cm$^{-3}$; mobility: SALD 10 times higher

Back Surface Field cell

- Highest reported $J_{sc}$ for a low temp. Atmospherically grown ZnO/Cu$_2$O cell

Fundamental studies on PV physics through doping


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3. Application to PV

AP-SALD for new generation PV

AP-SALD for TCMs
Significant need for transparent electrodes

Different roles and requirements for different applications

**Solar cells**

**Lighting: LED**

**Touch screen:**

**Transparent heater**
- Good electrical conductivity
- Optical transparency in the visible range
- Low cost, (relative) abundance of the raw material
- Flexible (if possible)

(Flexible electronic market of about 40-50 billiards of $ in 2020)

Optimisation between electrical & optical properties → compromise
Transpar. Cond. Oxides (TCO):

- Indium Tin Oxydes (ITO)
- Fluor doped Tin Oxides (FTO)
- Aluminium doped Zinc Oxides (AZO)

Advantages:
- Well known and used
- Very good physical properties

Drawbacks:
- Brittle
- Can be scarce/expensive (In)

Emerging TCMs:

- Graphene
- CNT
- Metallic NWs or grids

Advantages:
- Seem to be promising
- New scientific area: exciting & place for imagination/innovation!

Drawbacks:
- Not yet well known
- Stabilization ?
- Could be expensive for some ...

Ellmer, Nat. Photonics, 6 (2012) 808
Klein, J. Am. Cer. Soc. 96 (2013) 331

Hecht, Adv. Mater. 23 (2011) 1482
Langley et al., Nanotech. 24 (2013) 452001
• TCO for HET cell

Drawbacks:
- ITO contains Indium: expensive, rare
- ITO standard deposition method: magnetron sputtering which causes damage on a-Si layers

Solution:
Replacing ITO by In-free TCOs

Requirement of low-temperature, low-damage deposition method, high throughput, low cost: SALD

SALD for TCM @ LMGP:

- TCO for HET cell

Viet Nguyen

D. Bellet; D. Muñoz (INES)

From AP-SALD to devices

200 nm of AZO film on glass

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SALD for TCM @ LMGP:

- TCO for HET cell

**Viet Nguyen**

**D. Bellet; D. Muñoz (INES)**

100 nm of ZnO on Si wafer

80 nm of ZnO on textured S wafer
SALD for TCM @ LMGP:

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Ag nanowire synthesized by polyol process

Z.L. Wang, *Nanowires and nanoobjects material properties and devices, Vol. 1, Kluver academic publishers*

PVP : Polyvinylpyrrolidone

AgNW dimensions:

- **D**: 30 → 150 nm (100 nm)
- **L**: 5 → 50 μm (30 μm)
$$n_c = \frac{5.64}{L_{NW}^2}$$

Stick percolation

No percolation

Percolative regime

Bulk regime

$\text{Network density}$

$\text{Areal mass density}$

$\text{Transition much less known and understood}$

$\text{From AP-SALD to devices}$

Pike & Seager, PRB 10 (1974) 1421
Li & Zhang, PRE 80 (2009) 40104
De et al., ACS Nano 4 (2012) 7064
De et al., ACS Nano 3 (2009) 1767

http://sites.google.com/site/workdmr/
Mechanisms involved:

- desorption
- Sintering
- instabilities

Langley et al., Nanoscale 6 (2014) 13535
SALD for TCM @ LMGP:

Pente = $9,9 \times 10^{-7} \text{ s}^{-1}$

Pente = $3,74 \times 10^{-7} \text{ s}^{-1}$

Pente = $31,5 \times 10^{-7} \text{ s}^{-1}$
SALD for TCM @ LMGP:

- Coating of Ag NWs

Viet Nguyen  Sara Aghazadehchors
**SALD for TCM @ LMGP:**

![SEM image of AgNWs](image)

- **Bare AgNWs**
- **30 cycles ZnO**
- **40 cycles ZnO**
- **50 cycles ZnO**
- **60 cycles ZnO**

**Graph:**
- **Resistance (Ohm)**
- **Voltage (V)**

**Reactive precursors for SALD:** DEZ and H$_2$O

**From AP-SALD to devices**

**Viet Nguyen**

[http://sites.google.com/site/workdmr/](http://sites.google.com/site/workdmr/)

**Voltage breakdown**
AALD: “Novel”, variation of conventional ALD:
- Precursors separated in space rather than time
  - Same advantages than conventional ALD, but
  - Faster, Compatible with roll-to-roll processing, cheap & easy to scale
  - Fundamental studies: doping & and effect on PV

- High quality oxide films deposited → Passive and active components of solar cells and other devices (TFT, LED, …)
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Thanks for your attention!!!