High rate oxide deposition onto web from rotatable magnetrons

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### Structure of presentation

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- Transparent Conducting Oxides, TCO’s
- Planar vs Rotatable magnetron cathodes
- Reactive deposition and process control
- Reactive oxides from double rotatable magnetrons
- Conclusions
Industrial Uses of TCO's

- Transparent electrodes for flat panel displays
- Transparent electrodes for photovoltaic cells**
- Low emissivity glass*
- Window heating – defrosting
- Transparent TFT’s, LED’s and semiconductor lasers

* $15/m² (total layer stack), 7.5B$ worldwide by 2012
** $6/m² (TCO only)

TCO glass demand predicted to be 500M m² by 2012 >>10B$
• ITO dominates FPD’s and touch screen due to the <100nm thickness required. ITO wins due to good properties and corrosion resistance

• FTO Flourinated tin oxide (SnO$_2$:F) is widely used in the architectural glass industry – Asahi-U high haze film shown

• AZO (aluminium doped zinc oxide, ZnO:Al) used in low scatter format for low-E glazing and high scatter chemically etched for solar cells

Cardinal Solar Technologies
A Cardinal Glass Industries Company
Lessons from the mature ITO Flat Panel Display market

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- All commercial production now in Asia

- Why:
  - Asia provides high quality and assured supply
  - Supply assurance from Asian manufacturers is too high a barrier to entry for new EU or US producer
  - A customer will not risk long term supply by switching to a new entrant as the supply contract will be lost and difficult to re-establish
  - High quality ITO needs great attention to detail and processes with strict procedure adherence – a key advantage of Asian manufacturers
  - Technically the process is simple but suffers from target ‘nodules’ and arcing – so all processes and products revolve around management of those problems
  - The added costs of human interaction of the problems gives the Asian manufacturers a cost advantage
TCO usage in thin film solar cells

Common across all thin film cells

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Commercial production modes for TCO’s

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CVD
- APCVD - on-line by atmospheric chemical vapour deposition. FTO layers with high endurance.
- LPCVD - off-line commercial solutions exist - Oerlikon.
- Pre-coated TCO glass is CVD based as it has longer ‘shelf-life’

Sputtering:
- Offers great flexibility to adapt to different production modes
- Planar single cathode DC, DC pulsed – cooled or HOT
- Single rotatable cathode DC, DC pulsed
- Dual planar cathode – MF (AC)
- Dual rotatable cathode – MF (AC)
AZO, Aluminium doped zinc oxide is preferred for sputtered TCO for solar cells

- AZO lower cost than ITO – solar films thicker than display market
- A ceramic AZO offers a ready made composition to create the TCO
- AZO offers a solution that works – but little attention been paid to the potential cost saving elements
- Most effort expended so far to create the photo-active layers in the cell not the TCO
- AZO can be wet etched for light trapping in silicon based cells

- More efforts are needed to improve and reduce costs of AZO based TCO’s
Some problems of ceramic AZO suffer from plasma arcs – affects the films

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Expensive power modes required

*Sittinger et al*
Ceramic AZO layer properties – variation of properties with process parameters

Problematic but presents an opportunity to improve
Ceramic TCO – different properties compositions

Proc. parameters common to all TCO’s

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The ideal environment for Solar TCO based upon sputtering

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- High rates
- Low material costs
- Stable arc free operation
- Short burn-in times for new targets
- Tuneable layer properties for the different cells / secondary properties
<table>
<thead>
<tr>
<th>gencoa: perfect your process</th>
<th>Cost effective TCO sputtering sources?</th>
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<tbody>
<tr>
<td>Planar vs Rotatable geometries</td>
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</table>

- Planar magnetrons
- Rotatable magnetrons
- Double rotatable magnetrons – AC power
- Double rotatable magnetrons – DLIM magnetics
Confinement between a negatively biased target and ‘closed’ magnetic field produces a dense plasma. High densities of ions are generated within the confined plasma, and these ions are subsequently attracted to negative target, producing sputtering at high rates.
Planar magnetrons

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Planar magnetrons commonly the most cost effective solution for non-reactive target use limited to 40-50% in practice for metals.
Rotatable targets can give 2-4 times longer uptime than planar.
• Very expensive ceramic targets - reducing
• Micro-arcing – leads to variable & non-optimum product quality
• Long target burn in before stable film properties can be > 24hrs
• Plasma damage of growing film - increasing resistivity
• Limitation of composition and crystal structure – good and bad

* SCI – Sputtering Components Inc
The above is the conventional magnetic arrangement for rotatables

- Lack of anode in DC power means plasma damage
- Magnetic design drives plasma to the growing TCO layer - DC & AC
- Magnetic / anode design increases target voltage
- Electron movement increases the chance of an arc
- High impedance plasma – higher energy costs
AC power mode and electron movement

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- AC provides excellent arc suppression – perfect for TCO’s and other oxides
- But increases the plasma at the substrate – definitely not perfect!

** US patent for this type of process owned by Von Ardenne, FRG
Lower impedance ‘linked’ magnetics

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Plasma to substrate interaction by asymmetric magnetics and tilting

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New Gencoa patent
Electron trajectories between the 2 cathodes determine the spread of plasma.

Angle and magnetic design can be modelled.
Plasma control by Double Low Impedance Magnetics - DLIM

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Adjustment of angle relative to substrate position
Anode solutions for non AC magnetrons

Prevents plasma damage and substrate heating
Different magnetic and anode designs for rotatable magnetrons based upon needs

<table>
<thead>
<tr>
<th>Design</th>
<th>Description</th>
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<tbody>
<tr>
<td>SSS</td>
<td>Standard Strength Single</td>
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<tr>
<td>HSS</td>
<td>High Strength Single for thicker targets or lower discharge voltages</td>
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<td>SS-TCO</td>
<td>Single cathode magnetics with active anode for reduced resistivity TCO layers for DC and DC pulsed operation</td>
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<td>DLIM</td>
<td>Double cathode Low Impedance magnetics for high rate reactive deposition of oxides with low substrate plasma interference (patent pending)</td>
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<td>DLIM-TCO-DC</td>
<td>Double cathode low TCO resistivity magnetics for DC powered double magnetrons with an additional active anode (patent pending)</td>
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<tr>
<td>DLIM-TCO-MF</td>
<td>Double cathode low TCO resistivity magnetics for medium frequency (MF) powered double magnetrons (patent pending)</td>
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One solution does not fit all production requirements!
• Large area reactive sputtering 30 years old in other fields
• Mature processing products available
• Highly unstable process so appropriate process control the critical factor
• Genco has implemented reactive TCO’s and AR layers over many different production plants with up-to 3m glass sizes
Rotatables best for reactive layers

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No reaction product on the surface – cleans itself
Reactive gas controllers are ‘standard’ in architectural glass coating

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P.E.M sensor head design very important for reliable operation
P.E.M uses the optical spectrum to analyse the plasma and a narrow band-pass filter measures the species of interest.
Multiple sensors control and trim gas over large areas

1.5% uniformity already commonplace on 1-3m glass

- For AZO P.E.M is the preferred sensor
- Lambda can work also – slower response than PEM
Sensors and gas bar design delivers gas quickly and uniformly

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P.E.M provides ~ 10msec process feedback response
GencoA can perform the reactive gas calculations for gas flows and MFC sizes based upon your system requirements.
All components need to be integrated correctly to ensure optimum operation.
Speedflo different sensor responses to a gas ramp - hysteresis

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Example of controlled reactive dual rotatable ITO deposition runs

InSn + O₂ Speedflo control during production tests

85% Transmission
13Ω Sheet resistance
Reactive dual rotatable AZO deposition process window

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Process control using plasma monitoring

ZnAl + O₂ reactive control dual rotatable

MFC feedback, sccm

O₂ PEM and target V Sensors (%)

Time, s

Gas Feedback (SCCM)
O₂ PEM value %
O₂ PEM setpoint %
Target V %
InSn+O₂ using Speedflo control for reactive production of ITO

Sheet resistance (ohms)

O₂ Set-point (%)

Transmission (%)
P.E.M based reactive sputtering controllers already work in large scale Low-E glass.

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P.E.M control response to load-lock activity

**SiOx AC dual 3 Master (A, B & C) and 1 slave (1G) control**

- **Sensor B setpoint = 50%**
- **Target voltage variation**
- **Slave O₂ flow 1G = 2 x (2B)**
- **Master O₂ flow (2B)**

**Axes:**
- **X-axis:** Time, s
- **Y-axis:** Sensor signal (left), Actuator signal (%)

**Legend:**
- **Sensor B (%)**
- **Sensor target V (%)**
- **Actuator 2B (%)**
- **Actuator 1G (%)**
Rate enhancement for reactive sputtering controllers

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P.E.M set-point verses dynamic deposition rate

Si and SiOx rates at 23 kW (dual rotatable)

Coating rate (nm . m/min) vs. Setpoint (O2 emission 777nm)
Rate or layer properties determine the controller set-point

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**NbOx-SiOx layer gain in thickness after climate tests**

- + 0.8 nm after climate test
- + 1.4 nm after climate test

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<tr>
<th>Sample reference</th>
<th>NbOx (SiOx at 45%)</th>
<th>NbOx (SiOx at 60%)</th>
<th>SiOx at 45%PEM</th>
<th>SiOx at 60%PEM</th>
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Controlled reactive sputtering is $3$ the rate in production than ceramic AZO

Price will be $< 50\%$ current ceramic based costs

* Szyszka et al
Conclusions

• Rotatable magnetrons are now becoming more established in the deposition of oxide layers.
• The added heat from these sources can be controlled via magnetic confinement of the electron movement.
• Reactive sputtering with feedback control is a high rate and more controlled alternative to ceramic sputtering and open loop reactive depositions.
• Usual rate increase is $x \times 3$ with a feedback controlled process.
• The components needed have been perfected in other industrial sectors, hence mature products are available to improve oxide based web coating.