FPD 세정 공정

2006년 5월 3일
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Electronic Display

CRT
FPD
Projection

비발광
자발광

LCD

PDP
유기EL
FED

AM
PM

TFT
TN
STN
PDLC

CRT: Cathode Ray Tube
FPD: Flat Panel Display
LCD: Liquid Crystal Display
PDP: Plasma Display Panel
유기EL: Organic Electro Luminescence
FED: Field Emission Display
TFT: Thin Film Transistor
A(P)M: Active (Passive) Matrix
(S)TN: (Super) Twisted Nematic
PDLC: Polymer Dispersed Liquid Crystal
FPD Process Overview

Glass | GATE Electrode | Insulator & a-si | DATA Electrode | Passivation | Pixel Electrode

Deposition & Patterning Process in Detail

Cleaning | Deposition | Cleaning | PR Coating | Exposure | Develop | Etching | PR Strip | Inspection

Clean process & product lab
FPD Cleaning Process

Process Sequence

Loading - UV or O₃ - BRUSH Scrub (W/Detergent) - DI SHOWER - BUBBLE JET - F/RINSE - UDG (Ultra dry Gate) - Unloading

- Organic Removal
- Large Particle
- Small Particle
- Small Particle
- Preventing Particle Re-adhesion
- Dry

Option

- Organic Removal: O₃ Water (Better Wet ability), UV
- BUBBLE JET, CAVITATION JET, HIGH PRESSURE JET, MEGA SONIC SHOWER, PULSE JET
- Heated Air, Hot DIW Dry, Air Knife Dry, Marangoni Dry, Spin Dry, IPA Dry, Vacuum Dry, UDG

Clean process & product lab
## FPD Cleaning Technology Trend*

<table>
<thead>
<tr>
<th>Cleaning Method</th>
<th>Trend</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Cleaning</td>
<td></td>
<td>One Chamber / Multi Cleaning</td>
</tr>
<tr>
<td></td>
<td>'94~96</td>
<td>'97~99</td>
</tr>
<tr>
<td>Chemical Cleaning</td>
<td></td>
<td>Function Water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry Cleaning</td>
<td></td>
<td>UV Cleaner : Excimer, DUV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LASER, Plasma</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry system</td>
<td></td>
<td>Hot Air</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spin Dry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Air knife</td>
</tr>
</tbody>
</table>

- Floor-Space-effective
- Environment-friendly
- Performance Enhancement
- Yield-up
- Scalability
- Running-cost-effective
- Investment-cost-effective
Example of Semiconductor Cleaning Process

1. H₂SO₄/H₂O₂ (SPM) 4:1  유기물 120~150 °C
   - 초순수 Rinse
   - DHF 0.5%
   - 초순수 Rinse
   - NH₄OH/H₂O₂/H₂O (APM) 0.05:1:5  입자 80~90 °C
   - 초순수 Rinse

2. 온초순수 Rinse 80~90 °C
   - 초순수 Rinse
   - HCl/H₂O₂/H₂O (HPM) 1:1:6  금속 80~90 °C
   - 초순수 Rinse
   - DHF 0.5%
   - 초순수 Rinse

- 초순수 Rinse
- 초순수 Rinse
- 초순수 Rinse
- 초순수 Rinse
- 초순수 Rinse

## Conventional Wet Cleaning Process

<table>
<thead>
<tr>
<th>Section</th>
<th>Cleaning Methods</th>
<th>Cleaning 목적 및 Mechanism</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>화학 전</td>
<td>APM, SC-1 (NH₄OH/H₂O₂/H₂O) 75~90 ºC</td>
<td>➢ Light Organics, I/II 계 Metals, Particle 제거 ➢ 2H₂O₂ + C --&gt; CO₂ +2H₂O ➢ M + H₂O₂ --&gt; MO +H₂O, MO+4NH₄OH --&gt;M(NH₄)⁴⁺</td>
<td>Metal Re-Adsorption (Alkali 계 Metal) due to low Redox potential Si- wafer micro-roughness</td>
</tr>
<tr>
<td>화학 전</td>
<td>HPM, SC-2 (HCl/H₂O₂/H₂O) 75~85 ºC</td>
<td>➢ Metal(알칼리 이온, 중금속) 제거 ➢ Ion Exchange : Na⁺ +HCl --&gt; NaCl + H⁺ ➢ Complex : M + H₂O₂ --&gt; MO + H₂O MO +2HCl --&gt;MCl₂+H₂O</td>
<td>Formation of thin hydrophilic chemical oxide film Difficult in maintenance of hardware due to high corrosiveness</td>
</tr>
<tr>
<td>제 정</td>
<td>SPM (H₂SO₄/H₂O₂/H₂O) 90~130 ºC</td>
<td>➢ Heavy Organic, Metal 제거 ➢ H₂SO₄ +H₂O₂ --&gt; H₂SO₅(CARO'S ACID) + H₂O ➢ H₂SO₅ + Hydrocarbon --&gt; CO₂ + H₂O +H₂SO₄</td>
<td>Formation of thin hydrophilic chemical oxide film Generation of SO₄²⁻- Residue on the substrate</td>
</tr>
<tr>
<td>제 정</td>
<td>Dilute HF (HF/H₂O)</td>
<td>➢ Natural Oxide Film, Metal 제거 ➢ 6HF +SiO₂ --&gt; H₂SiF₆ + 2H₂O ➢ 3HF + M --&gt; MF₃ +3H⁺</td>
<td>Removal of surface oxide and metal in the metal oxide film by dilute HF solution Removal of noble metal by H₂O₂</td>
</tr>
<tr>
<td>제 정</td>
<td>BOE (HF/NH₄Cl/H₂O/계면활성제)</td>
<td>➢ Oxide Film 제거</td>
<td>Buffered oxide etchant HF/NH₄F=1:7</td>
</tr>
</tbody>
</table>
FPD와 Semiconductor의 세정 비교*

<table>
<thead>
<tr>
<th>Classification</th>
<th>Semiconductor Process</th>
<th>Flat Panel Display Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 세정의 대상</td>
<td>Wafer. ~ 300 mm dia.</td>
<td>300*400mm(1st G)</td>
</tr>
<tr>
<td>2. 세정제</td>
<td>SC1, SC 2, SPM.. RCA cleaning.. Acid &amp; Base Mixture</td>
<td>Glass, ~ 1870*2200 mm (7th G)</td>
</tr>
<tr>
<td>3. 세정 목적</td>
<td>Organics, Metal, Particle, Oxide</td>
<td>Organics, Particle, Water Marks, Metal, Oxide</td>
</tr>
<tr>
<td>4. 반송 단위</td>
<td>약 25 매/lot, Carrier</td>
<td>1 매, 연속 반송</td>
</tr>
<tr>
<td>5. 세정 방식</td>
<td>Dip, Bath</td>
<td>Shower, Spray</td>
</tr>
<tr>
<td>6. 세정 시간</td>
<td>about 10 min/each bath</td>
<td>Below 1 min / 1 매, chamber</td>
</tr>
<tr>
<td>7. 기타</td>
<td></td>
<td>연속반송 1000 ~ 8000 mm/min</td>
</tr>
</tbody>
</table>

* 권정현, 삼성SDI  ** tetra methyl ammonium hydroxide

Clean process & product lab
1. PRINCIPLE
   Remove an electron from organic molecules to oxidize and decompose them to CO$_2$, H$_2$O, and etc.

2. HOW TO REMOVE AN ELECTRON?
   To remove an electron by high ORP solutions such as H$_2$SO$_4$, HCl, HNO$_3$, etc. have been used.

3. WHY OZONIZED WATER?
   ORP of ozonized water (DIW with a few ppm of ozone) is higher than those of H$_2$SO$_4$, HCl, HNO$_3$.

4. O$_3$ and OH$^-$ (hydroxyl ion) in water generates OH$^*$ (hydroxyl radical) which promotes oxidation of organics.

5. Initiators such as high pH or UV radiation may be necessary for OH$^*$ reaction.
Mechanism of Particle Removal

1. 1\textsuperscript{ST} Step...lift off
   - *Mechanical lift off*
     - Ultra sonic (MHz)
     - Brush scrub
   - *Chemical lift off*
     - Substrate etching with alkaline and HF
     - Use of H\textsubscript{2} Water: H radical generation
     ⇒ inactivation of soil or detachment of soil
     - Particles are dissolved with HF or decomposed with O\textsubscript{3}

1. 2\textsuperscript{ND} Step...Prevention of re-adhesion
   - Change of surface potential charge of particle and substrate
     - Alkaline pH
     - Negative potential may help the enhancement of negative charge.
     ⇒ Same polarity of Zeta potential between particle and substrate
**Mechanism of Metal Removal**

1. Metals in SiO$_2$ film
   - MOx
   - SiO$_2$
   - M$	extsuperscript{+}$
   - SiO$_2$
   - Substrate
   - Substrate
   - *Metals are removed together with SiO$_2$ by etching with HF.*

2. Metals on bare Si
   - MOx
   - SiO$_2$
   - M$	extsuperscript{+}$
   - SiO$_2$
   - Substrate
   - Substrate
   - *Metals are ionized by acidic and oxidative solutions.*

*酸性和氧化性溶液.*
- Conventional: Acid & oxidizer at Hot temp & High conc.
- Activated UPW: Diluted acidic oxidative solutions (HF/O$_3$ or HCl/ O$_3$ solution)
  - ORP of Ozonized water is higher than those of H$_2$SO$_4$, HCl, HNO$_3$, etc.
Cleaning Principles

**Contaminants to be removed**

- **Organic Contaminants**
  - To be oxidized and decomposed into solution
  - Increase ORP of the solution than organics
  - Ozonized Water (O$_3$ Water)

- **Particle Contaminants**
  - Separate particles from surface
  - Equalize Zeta potential of particle and substrate
  - Alkallic, Hydrogen Water (NH$_4^+$ – H$_2$ Water)

- **Metallic Contaminants**
  - Metals to be ionized and decomposed into solution
  - Increase ORP of the solution than metal
  - Acidic Ozonized Water (HCl–O$_3$ Water)

**Necessary Conditions**

**Methods to be done**

**Cleaning solutions**

Functional Water

- **Ultra pure Water (DIW)**
  - Indirect DIW Electrolysis (Separation of Gas / liquid)
  - Direct DIW Electrolysis

**O₃ Water Generator**
- O₃ Water

**H₂ Water Generator**
- H₂ Water

**Ion Water Generator**
- Anode Water + HCl
- Cathode Water + NH₄OH

**Table:**

<table>
<thead>
<tr>
<th>pH</th>
<th>ORP (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>+1,350</td>
</tr>
<tr>
<td>7</td>
<td>-350</td>
</tr>
<tr>
<td>5~7</td>
<td>+400</td>
</tr>
<tr>
<td>1~5</td>
<td>+1,100</td>
</tr>
<tr>
<td>6~8</td>
<td>-350</td>
</tr>
<tr>
<td>9~13</td>
<td>-750</td>
</tr>
</tbody>
</table>
Electrolyzed water (EW)

☐ The controlled water in terms of pH and oxidation-reduction potential (ORP) by the electrolysis

☐ Easy to control pH/ORP in wide range with only current/voltage changes

☐ Oxidation-reduction potential (ORP, E)

\[ O_x + ne = R_{ed} \]  \hspace{1cm} (1)
\[ E = E_0 - \frac{RT}{nF} \log \left( \frac{C_{\text{red}}}{C_{\text{ox}}} \right) \]  \hspace{1cm} (2)

at \( C_{\text{red}} > C_{\text{ox}} \), ORP is negative value (reductive water)

at \( C_{\text{red}} < C_{\text{ox}} \), ORP is positive value (oxidative water)
Principle of EW Generation

- CW → H⁺
- OH⁻ → H₂
- H⁺ ↔ H⁺
- OH⁻ ↔ OH⁻
- H₂O
- AW

- CW → H⁺
- OH⁻ → H₂
- H⁺ ↔ H⁺
- OH⁻ ↔ OH⁻
- H₂O
- AW

- CW → H⁺
- OH⁻ → H₂
- H⁺ ↔ H⁺
- OH⁻ ↔ OH⁻
- H₂O
- AW

- CW → H⁺
- OH⁻ → H₂
- H⁺ ↔ H⁺
- OH⁻ ↔ OH⁻
- H₂O
- AW
Procedure for Generating Electrolyzed Water

Supply electrolyte

Supply electrolysis power

Anode water, Cathode water

Measurement of EW properties

Surface cleaning

Such as UPW, NH₄OH, HCl, and NH₄Cl

7.0~9.0 A, 10~12 V

Anode and cathode water generation

ORP, pH and lifetime, FT-IR

Particle counter, TRXFA, AFM
EW Properties

A: Anode water with electrolyte
   ~ Effective for removal of metal ions
   Oxidative water, High H⁺ Conc.
   Similar to properties of O₃ water

B: Anode water by UPW
   ~ Effective for removal of metal ions

C: Cathode water by UPW
   ~ Effective for removal of particles
   Reductive water, High OH⁻ Conc.
   Similar to properties of H₂ water
   Normally used with NH₄OH

D: Cathode water with electrolyte
국내 전해이온수 공급업체

1. 마이크로뱅크 (http://www.micro-bank.co.kr ; 031-905-3420)
   • 산업자원부의 청정생산기술과제 수행(Hynix와 공통수행)
   • 반도체/LCD 세정용 3조식 전해장치 제조기술 개발 및 응용
     (금속오염물, 유기물, SiO₂ 미립자, SO₄²⁻ 이온제거)
   • Redox를 이용한 산업공정에서의 일반세정기술 개발 및 응용
     (하드디스크, PCB, 광학렌즈 등)
   • 전해 산성수에 의한 살균 소독 시스템 개발
   • 응용 이온수기 개발: (㈜)한국세라스톤에 알카리성 이온수기 공급

2. 맥스산업㈜ (02-716-6883~4)
   • 직류전원에 의하여 산성/알칼리성 전해수(pH 2.0~12.0, ORP±1000mV이상)
   • 응용: 반도체, LCD 및 PCB 기판 세정
   • 각종 배관라인의 세정 및 살균

3. ㈜서양에이아이 (http://www.seoyang.co.kr ; 02-488-8444)

Clean process & product lab
일본 전해이온수 공급업체

1. REIKEN, INC. ([http://www.reikeninc.co.jp](http://www.reikeninc.co.jp))
   - Dynakleen.D
     • 고주파(30~34 kHz) 전기분해
       : 부식 예방 및 스케일 제거, 화학 물질 미사용
     • 3조 시스템(+, −, earth)
       : 이물질이 전극에 미부착 - 전극 유지용이, 자체 세정 효과
     • 활성수: 살균 및 악취제거, 유지비저렴(ROI = 1~1.5 year)

2. Nissin seiki Co., Ltd. ([http://www.nissin-seiki.co.jp](http://www.nissin-seiki.co.jp))
   - 강알칼리 이온 세정수 생성시스템(NEWSEW-01-RO)
     • 강알칼리 이온수 생성(pH 12~12.5)
     • 순수 세정 장치가 있어 알칼리수와 순수를 별도로 생산가능
     • 전해질로 CaCO₃ 사용
     • 피세정물의 산화 및 부식 방지, 악취 제거 및 살균 효과

3. NITTO KOSHIN CO., Ltd.
   - 전해수 생성 unit
     • 본체에 수돗물을 직접 연결하여 연수와 알칼리성 전해수 생성(전해질 사용)
     • 연수기의 재생은 완전 자동
     • 응용 사례:
       i) 액정 유리의 최종 세정
       ii) AI 가공유 세정에서 탄화수소계 세정제 대체

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Clean process & product lab
## Applications of Functional Water

<table>
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<th>Classification</th>
<th>FPD</th>
<th>Semicon</th>
<th>Wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Removal</td>
<td>2. Pre-Deposition</td>
<td>2. Pre/Post-CMP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. Post-Deposition</td>
<td>3. Post-Ashing</td>
<td></td>
</tr>
<tr>
<td><strong>H$_2$ Water</strong></td>
<td>1. Clean bare glass</td>
<td>1. Post-CMP</td>
<td>1. Rinse after Chemical Bath</td>
</tr>
<tr>
<td>Particle Removal</td>
<td>2. Rinse after etching</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Electrolyzed Water</strong></td>
<td>Removal of Metal &amp; Particle</td>
<td>1. Post-CMP</td>
<td>1. Removal of Metal, Particle &amp; Organics</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2. SO$_4^{2-}$ removal after SPM cleaning</td>
</tr>
</tbody>
</table>
Bubble Jet Technology*

1) Principle

- **Principle**
  - Initial Particle: 1000-3000ea
  - $S \approx 1~3 \mu m$, $M \approx 3~5 \mu m$, $L \approx 5 \mu m$, $T \approx \geq 1 \mu m$

2) Performance

- **Particle Removal Ratio (%)**
  - High Pressure Jet
  - Bubble Jet

<table>
<thead>
<tr>
<th>NO</th>
<th>Item</th>
<th>O₃ Water</th>
<th>Roll Brush</th>
<th>Bubble Jet</th>
<th>Shower(M/S)</th>
<th>Di Shower</th>
<th>Aqua knife</th>
<th>Air knife</th>
<th>Avg. Particle Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>W / BJ</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>66EA</td>
</tr>
<tr>
<td>2</td>
<td>W/O BJ</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>170.3EA</td>
</tr>
</tbody>
</table>

Note:
1. Avg. Initial Particle: 2166EA
2. Sample Size(N): 3Pcs, Each
3. Particle Counter: $\geq 1 \mu m$ (Hitachi: GI-4700)
4. Glass Size: 590 * 670

* 박영순, 대화일렉트론

Clean process & product lab
Dry Systems*

- **Heated Air**
  - Heated @ 80 ~ 200°C
  - Water mark
  - Surface Oxidation
  - Cleaning Performance Degradation
  - Higher Running cost

- **Hot DI**
  - Heated @ 80°C
  - Water mark
  - Surface Oxidation
  - Cleaning Performance Degradation
  - Higher Running cost

- **Spin Dry**
  - Room Temp.
  - Mechanical Damage
  - Poor Scalability
  - Lower Running cost

- **IPA Dry**
  - Heated @ 250°C
  - Fire Issue
  - Fire Extinguisher necessary
  - Single Process impossible
  - Higher Running cost

- **Air knife**
  - Room Temp.
  - Water mark
  - Additional De-humidifier necessary
  - Cleaning Performance Degradation
  - Lower Running cost

- **UDG(Ultra Dry Gate)**
  - CDA (Room Temp.)
  - Ultra Dry Air
    - (Water content : < 0.5ppm)
    - Evaporation of surface water trace
    - Lowest Running cost

* 박영순, 태화일렉트론