Functional Water Cleaning Technology
For LSI & LCD Manufacturing Processes

HAGER+ELSÄSSER
1. Cleaning Effects of Functional Water

2. Application for LSI Manufacturing Process

3. Application for LCD Manufacturing Process

4. Functional Water Production System San-Kan-Oh Series

5. Patents: Technology Advantage
What is Functional Water?

Functional Water is **Ultrapure Water** that

- Has its ORP by dissolved gases such as \( \text{H}_2 \) and \( \text{O}_3 \).
- Often has its pH controlled by low concentrations of \( \text{NH}_4\text{OH} \).
- Is a more effective cleaning method for various electronic components than using normal UPW.

Reduction Water = \( \text{H}_2 \) Gas-Dissolved Catholyte Water

Oxidation Water = \( \text{O}_3 \) Gas-Dissolved Anolyte Water
Advantages of using Functional Water

- Highly Efficient component cleaning reduces rejects
- Drastic reduction in chemical consumption
- Reduced UPW consumption and water supply costs
- Associated reduction in wastewater treatment costs
- Significantly reduced overall environmental impact
Characteristics of Functional Water

A: Oxidizing/Acid: (Metallic impurity removal)
B: Oxidizing/Neutral: (Organic impurity removal)
B*: Slightly Oxidizing: (Adsorbed chemical rinsing)
C: Reducing/Alkali: (Particle removal)
D: Reducing/Neutral: (Particle removal)
## Cleaning effects of Functional Water

<table>
<thead>
<tr>
<th></th>
<th>Particle removal/Adhesion prevention</th>
<th>Oxidation prevention (Wafer, Metal)</th>
<th>Removal Of Organics</th>
<th>Oxidation</th>
<th>Improvement Effect of MS</th>
<th>Pattern protection</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂ Water</strong></td>
<td>◎</td>
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<td>◎</td>
<td>◎</td>
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<tr>
<td><strong>O₃ Water</strong></td>
<td></td>
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<tr>
<td><strong>Degassed Water</strong></td>
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<td>◎</td>
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<tr>
<td><strong>Degassed/Re-gassed Water</strong></td>
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<td>◎ ◎</td>
<td>◎</td>
</tr>
</tbody>
</table>
Essentials of cleaning with Functional Water

**Contaminant**
- Particles
- Metals
- Organics

**Functionality**
- Lift-off and prevention of re-adhesion
- Alkaline • Reducing water
- Oxidizing - Ionization
- Acidic • Oxidizing Water
- Oxidative decomposition
- Oxidizing Water

**How to Remove**
- Megasonic + H₂ Water/Alkali
- O₃ Water + Acid
- O₃ Water
Mechanism of Particle Removal

1. 1st step....lift off

- Mechanical lift-off
- Chemical lift-off

2. 2nd step....prevention of re-adhesion

- Substrate etching with Alkali
- Particle dissolution with HF
- Enhancement of surface charge both on particle and substrate
  - Alkaline pH
  - Reductive potential may help the enhancement of negative charge.

Graph showing zeta potential (mV) vs pH
Mechanism of Organic & Metallic Removal

**Organic**

- Oxidation/ Decomposition by Oxidizing Agent
- Organic impurity
- Decomposition
- Oxidation
- $\text{CO}_2, \text{H}_2\text{O}$
- Oxidizing agent
- $\text{hv}$

**Metallic**

- Ionization by Oxidizing Agent
- $\text{M}^{n+}$
- Oxidizing agent
- $\text{e}^-$
- Oxidation
Equipment for Advanced water test with Megasonic Irradiation (Spin Processor)

Megasonic Irradiation (1.5MHz, 48W)

Cleaning Solution
Hydrogen Water and so on

Back Surface Rinse
UPW

by K. Mitsumori, N. Haga, Y. Kasama, T. Imaoka, N. Takahashi and T. Ohmi,
"New cleaning method for large size glass substrate and reducing chemicals and UPW consumption"
proceedings of 33th symposium on ULSI Ultra Clean Technology, pp162-167, May 28(1999), Tokyo
Cleaning Time with Hydrogen Water

Sample : Glass substrate with Cr film
Cleaning method : spin (300 rpm) 
ultra sound (MHz) irradiated by nozzle
H2 Gas conc. : 1.5mg/l
contamination : Al2O3 particles

Functional water improves the efficiency of Spin Processor ultrasonic cleaning, The results are as follows:
Cleaning effect: H2 Water ( pH10 ) > H2 Water ( Neutral ) > UPW
Hydrogen Concentration & Particle Removal

Sample: Glass substrate with Cr film
Cleaning method: spin (300 rpm), ultra sound (MHz) irradiated by nozzle
Time: 10 sec
Contamination: Al₂O₃ particles
Particle Removal Efficiency using $H_2$ - UPW

Dissolved Gas in UPW

- H2 2.0ppm/pH10.2
- H2 2.0ppm
- H2 1.3ppm
- N2 20ppm/pH10.2
- O2 14ppm
- N2 20ppm
- Degassed UPW

Particle Removal Rate (%)

Sample: Glass substrate with Cr film
Cleaning method: spin (300 rpm)
ultra sound (MHz): irradiated by nozzle
cleaning time: 10 sec (Degassed UPW:60sec)
initial contamination: $Al_2O_3$ particles
Comparison of H$_2$ DI & SC-1 (0.06µm)

Polishing Parameters
- Polisher: Strasbaugh
- Pad: Polypas
- Sturry: NP020

Cleaning Parameters
- 1st Batch Cleaning
  - Cleaner: PP-Bucket
  - NH$_3$: H$_2$O$_2$: DI = 1:10:500
  - 60°C 5 min
  - DI flow 15 min
- 2nd Single Peace Cleaning
  - Cleaner: SC200W/DBC
  - Megasonic: 1.6MHz 30W
  - NH$_3$: H$_2$O$_2$: DI = 2:1:200
  - or Cathode water
  - 25°C 120 s
  - Spin dry: 1600rpm 20s
Comparison of Haze damage - H$_2$ DI vs SC-1

### Haze (ppm)

<table>
<thead>
<tr>
<th>Wafer#</th>
<th>H2 DI</th>
<th>SC1</th>
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<tbody>
<tr>
<td>1</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

### Polishing Parameters
- Polisher: Stressbaugh
- Pad: PolyPak
- Slurry: NP8020

### Cleaning Parameters
- 1st Batch Cleaning
  - Cleaner: PF-Bucket
  - NH$_3$H$_2$O$_2$:DI=1:10:500
  - 60°C 5 min
  - Diflow 15min
- 2nd Single Peace Cleaning
  - Cleaner: SC200W/DBC
  - Megasonic: 1.6MHz 30W
  - NH$_3$H$_2$O$_2$:DI=2:1:200 or Cathode water
  - 25°C 120 s
  - Spin dry: 1500rpm 20s
CMP Post cleaning with H₂ Water
(Alumina particles following Cu-CMP process)

Particle counts (pcs/wafer 8’’):

- After CMP: >20000
- UPW w/o MS: 5500
- UPW + MS: 680
- H₂-UPW w/o MS: 2600
- H₂-UPW + MS: <200
Approach to Cleaning for Low-k/Cu process

- Removal of grinding particles and Cu contamination
- Particle removal with alkali $\rightarrow$ damage to Cu, Low-K
- Metal removal with HF $\rightarrow$ damage to Cu, Low-k

$\rightarrow$ Application of H$_2$ Water cleaning method
Prevention of Cu Wiring Corrosion with H₂ Water (Cu-CMP process)

Cu does not corrode in H₂ water.
Application of Functional Water to Low-k/Cu Process

Cu-CMP
↓
Particle Removal
H₂-water + Brush/MS
↓
Metal Removal
Chelating agent (0.3-3.4%)

(H.Aoki et al., NEC, 1998)
Energy Saving

**Single process**

<table>
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<tr>
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<th>UPW Usage</th>
<th>Chemical Usage</th>
<th>Energy Consumption (*)</th>
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<td>Conventional Cleaning</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Functional Water Cleaning</td>
<td>50</td>
<td>10</td>
<td>50</td>
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</tbody>
</table>

**Total Pure Water usage for Processes**

( Functional Water used is 50% of Total Process )

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<th></th>
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<th>Chemical Usage</th>
<th>Energy Consumption (*)</th>
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<tr>
<td>Conventional Cleaning</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Functional Water Cleaning</td>
<td>75</td>
<td>55</td>
<td>75</td>
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</table>

**Energy Saving achieved 50% for Single Process. and 25% saving of Total UPW usage.**

( *) Energy saving evaluated from UPW usage. Additional savings are also made in chemical consumption, air emission etc.
1. Cleaning Effects of Functional Water
2. Application For LSI Manufacturing Process
3. Application For LCD Manufacturing Process
4. Functional Water Production System San-Kan-Oh Series
5. Patents : Technology Advantage
Application of Functional water for LCD Process (Cleaning Recipe)

<table>
<thead>
<tr>
<th>Conventional Method</th>
<th>Proposed Process</th>
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<tr>
<td>Surfactant Cleaning (Brush)</td>
<td>O$_3$ Water (5ppm) Spray Cleaning</td>
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<tr>
<td>↓</td>
<td>↓</td>
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<tr>
<td>UPW Water Cleaning</td>
<td>NH$_4$OH (pH9-10) plus H$_2$ Water Cleaning (Brush)</td>
</tr>
<tr>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>UPW Cleaning (Brush)</td>
<td>H$_2$ Water Cleaning (Ultrasonic)</td>
</tr>
<tr>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>UPW Cleaning (Ultrasonic)</td>
<td>Dry</td>
</tr>
<tr>
<td>↓</td>
<td></td>
</tr>
<tr>
<td>UPW Cleaning (Bubble jet)</td>
<td></td>
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<tr>
<td>↓</td>
<td></td>
</tr>
<tr>
<td>Pure Water Rinse</td>
<td></td>
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<tr>
<td>↓</td>
<td></td>
</tr>
<tr>
<td>Dry</td>
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Approach for COST REDUCTION
Utilization of Functional Water → Surfactant saving → UPW saving for Rinsing → Improve Cleaning effect → Shortens Process Time & Improves Productivity
Application example of Functional water for LCD Process Part 1

ARRAY Process
- Glass Cleaning
- Pre-Cleaning for Deposit
- Deposit
- Pre-Cleaning for Resist coating
- Lithography
- Cleaning after Development
- Etching
- Cleaning after Etching
- Stripping
- Cleaning after Resist Stripping

COLOUR FILTER Process
- C F Production
- Cleaning after C F Pattern
- San-Kan -Oh H & Z

CELL Process
- Alignment layer coating
- Rubbing
- Rubbing Post Cleaning
- Gluing
- LC Injection
- LCD Panel

San-Kan -Oh H & Z
- O3 Water
- H2 Water
- O3 Water
- H2 Water
Application example of Functional water for LCD Process Part 2

**ARRAY Process**

- Glass Cleaning
- Pre-Cleaning for Deposit
  - Deposit
- Pre-Cleaning for Resist coating
  - Lithography
  - Cleaning after Development
  - Etching
  - Cleaning after Etching
  - Stripping
  - Cleaning after Resist Stripping

**COLOuR FILTER Process**

- C F Production
  - Cleaning after C F Pattern

**CELL Process**

- Alignment layer coating
  - Rubbing
  - Gluing
  - LC Injection
  - Rubbing Post Cleaning

**H₂ Water**

San-Kan-Oh H & Z 40m³/h
Green Area: Mo is in a corrosive environment, even in Pure Water.

Blue Area: Mo is in stable environment in H₂ Water.
Approach to issues associated with Larger Glass substrates Part 1

Getting difficult to remove particles with substrate growth in size...

Essential Removal points on the substrate

<table>
<thead>
<tr>
<th>Target</th>
<th>Conventional method</th>
<th>Proposed method</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Surfactant</td>
<td></td>
</tr>
<tr>
<td>Re-adhesion prevention</td>
<td>Slope Cleaning</td>
<td>Utilized Zeta potential and Bubble effect of H₂ Gas-dissolved water</td>
</tr>
</tbody>
</table>
Approach to issues associated with Larger Glass substrates Part 2

Higher consumption of UPW and Waste water with growth in substrate size...

Application of Functional Water treatment

H₂ Water improves the cleaning efficiency and product efficiency.

→ Contribution to Water Saving
### Water & Developer consumption vs LCD substrate size

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<tbody>
<tr>
<td>GEN.</td>
<td>Gen3</td>
<td>Gen4</td>
<td>Gen5</td>
<td>Gen6</td>
<td>Gen7</td>
<td>Gen8</td>
</tr>
<tr>
<td>SIZE (mm*mm)</td>
<td>550*650</td>
<td>730*920</td>
<td>1000*1200</td>
<td>1350*1650</td>
<td>1700*2000</td>
<td>2200*2600</td>
</tr>
<tr>
<td>AREA (m³)</td>
<td>0.358</td>
<td>0.672</td>
<td>1.200</td>
<td>2.220</td>
<td>3.400</td>
<td>5.720</td>
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<tr>
<td></td>
<td>12&quot;×6</td>
<td>15&quot;×6</td>
<td>24&quot;×6</td>
<td>32&quot;×6</td>
<td>42&quot;×6</td>
<td>50&quot;×6</td>
</tr>
<tr>
<td>UPW Consumption</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m³/h</td>
<td>300</td>
<td>600</td>
<td>1070</td>
<td>1980</td>
<td>3040</td>
<td>5040</td>
</tr>
<tr>
<td>m³/day</td>
<td>7200</td>
<td>14400</td>
<td>25680</td>
<td>47520</td>
<td>72960</td>
<td>120960</td>
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<tr>
<td>water demand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>m³/day (at 70%recycle)</td>
<td>2160</td>
<td>4320</td>
<td>7700</td>
<td>14300</td>
<td>21900</td>
<td>36288</td>
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</table>

**DEVELOPER Consumption (2.38%)**

<table>
<thead>
<tr>
<th>L/Series</th>
<th>2.5</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>26</th>
<th>42</th>
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</thead>
<tbody>
<tr>
<td>m³/d</td>
<td>12.5</td>
<td>25.0</td>
<td>50.0</td>
<td>98.2</td>
<td>130.9</td>
<td>208.0</td>
</tr>
</tbody>
</table>

(30k/month, 5 times)
Pure Water savings

PW Consumption
60000 m³/day

Application of Functional water treatment

PW Consumption
48000 m³/day

(60,000 - 48,000)m³/day*30days/month*@$2/m³ = $720,000/month (Profit)
Waste water saving

Wastewater
UPW 60,000m³/day*35%

IW and WW
Consumption
20% Saving

Application of Functional water treatment

Waste water
UPW 48,000m³/day*35%

60,000 m³/day*35% - 48,000m³/day*35%*30days/month*@$1.5/m³ = $189,000/month (Profit)
1. Cleaning Effect of Functional Water

2. Application For LSI Manufacturing Process

3. Application For LCD Manufacturing Process

4. Functional Water Production System
   San-Kan-Oh Series

5. Patent: Technology Advantage of ORGANO
San-Kan-Oh series

Type H  Hydrogen Water
Type Z  Ozone Water
Type D  Degassed Water
Type G  Degassed/Re-gassed Water
## Cleaning effect of San-Kan-Oh systems

<table>
<thead>
<tr>
<th>Type</th>
<th>Particle removal/Adhesion prevention</th>
<th>Oxidation prevention (Wafer, Metal)</th>
<th>Organic removal</th>
<th>Oxidation</th>
<th>Effect improvement of MS</th>
<th>Pattern protection</th>
</tr>
</thead>
<tbody>
<tr>
<td>H ( H₂ Water )</td>
<td>☺</td>
<td>☺</td>
<td></td>
<td></td>
<td>☺</td>
<td>❋</td>
</tr>
<tr>
<td>Z ( O₃ Water )</td>
<td></td>
<td></td>
<td>☺</td>
<td>☺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D (Degassed Water )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>❋</td>
</tr>
<tr>
<td>G (Degassed / Re-gassed Water )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>☺</td>
<td>☺</td>
</tr>
</tbody>
</table>
Functional Water System

Degas / Re-gas System

You can select:
Various gases.
Wide range of gas concentrations.
Wide range of flow rate of gasified UPW

Our Functional Water Systems will improve the performance of your Wet Cleaning Equipment

Hydrogen Water System

USP 6086057, 6509305

Ozone Water System

You can select various of gases!
Wide range of $\text{H}_2$ Gas Conc. and pH control

0.1 – 2.0 mg/l of $\text{H}_2$ Gas- dissolved water can be provided. Built-in Alkali Chemical supply equipment can control pH.

Built-in Degas equipment & Gas Pressure Control

High level of $\text{H}_2$ Water until saturation solubility level.

Addition of Alkali Chemicals

Effective Particle Removal without damage to the substrate.
Energy saving technology

No excess (un-dissolved) H₂ Gas!

The unique Structure of the system ensures that no excess gas is generated. Power consumption is minimized.

Generated Gas pressure control at fixed Pressure
Gas is replenished only at the same Rate as it is consumed by the system

The structure of San-Kan-Oh H System is Organo’s original product. (Patent: 特開平11-244677)
# Lineup of Hydrogen Water System

<table>
<thead>
<tr>
<th></th>
<th>H2 Water</th>
<th>Chemical injection</th>
<th>Degas (Option)</th>
<th>Meters (Option)</th>
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<tbody>
<tr>
<td>Built-in type 5LPM</td>
<td>○</td>
<td>External</td>
<td>External</td>
<td>External</td>
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<tr>
<td>Built-in type 15LPM</td>
<td>○</td>
<td>External</td>
<td>External</td>
<td>External</td>
</tr>
<tr>
<td>Stand-alone type 15LPM</td>
<td>○</td>
<td>○</td>
<td>Built-in Available</td>
<td>Built-in Available</td>
</tr>
<tr>
<td>Stand-alone type 40LPM</td>
<td>○</td>
<td>○</td>
<td>Built-in Available</td>
<td>Built-in Available</td>
</tr>
<tr>
<td>Custom-made</td>
<td>○</td>
<td>Built-in Available</td>
<td>Built-in Available</td>
<td>Built-in Available</td>
</tr>
</tbody>
</table>
Select from various combinations to suit your requirements!
System Advantages

❖ High Safety and Security

Generated Gas is dissolved in the system instantly.
So NO H₂ Gas is discharged from the system.
Shipped with H₂ Gas sensor inside as standard equipment.

❖ System extendability

Equipped with Control signal for the control from package operation.
~ Co-operation with Washing Machine and monitoring from Central monitor room.
Built-in Degas Unit inside the system.
~ Making a choice in response to customer’s PW grade and cleaning recipe.

❖ Ease of Operation and Maintenance

Simple On/Off operation via push-button.
Maintenance required only once a year.
San Kan Oh systems summary

★ “San-Kan-Oh” Series
   - Type H
   - Type Z
   - Type D
   - Type G

★ Applications
   - Si Wafer, Photo-Mask, LCD Glass, HD, Cu-CMP, Glass etc...

★ Various capacities
   - Large size: 100m³/h (Central supply)
   - Small size: 5l/min (Built-in type)

★ Many repeat orders

Over 350 systems supplied (January 2008)
1. Cleaning Effect of Functional Water

2. Application For LSI Manufacturing Process

3. Application For LCD Manufacturing Process

4. Functional water Production System
   San-Kan-Oh Series

5. Patent : Technology Advantage of ORGANO
Technology Advantage of San Kan Oh

Strategic and basic Patent

★特許3296405号、3296407号、3409849号
Main claim: H₂ Water is used to clean Electronic parts
Sub claim: Ultra Pure Water dissolves Gas after Degas treatment
Cleaning using H₂ Water in addition to Alkali chemicals.
Issued: Japan(02/3/12), Korea, USA and Taiwan
Examination request: China

★特開平11-71600
Main claim: Gas dissolved in Pure Water above atmosphere pressure

★特開平11-244677
Main claim: Gas-dissolved water production system which makes
the pressure of the gas-dissolved part control at the same level
## Patent list

<table>
<thead>
<tr>
<th>Japan</th>
<th>USA</th>
<th>Korea</th>
<th>Taiwan</th>
<th>China</th>
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<td>特開平9-255998</td>
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