

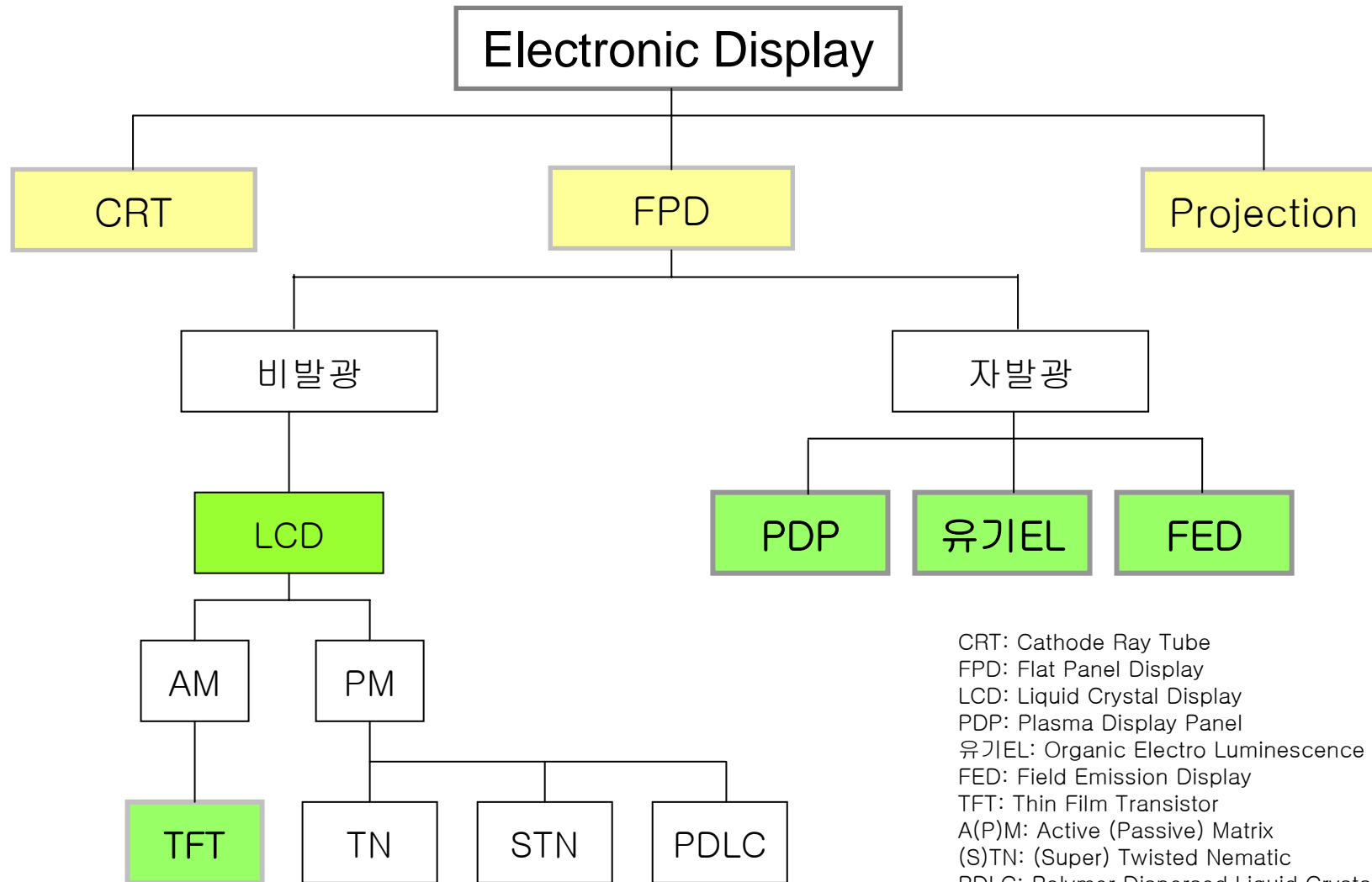
FPD 세정 공정

2006년 5월 3일

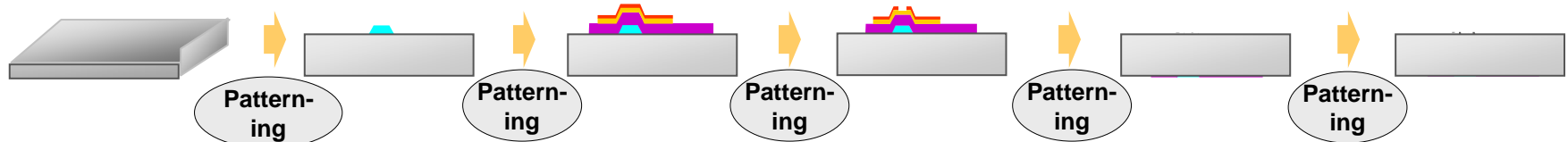
배재흠

수원대학교 화공생명공학과

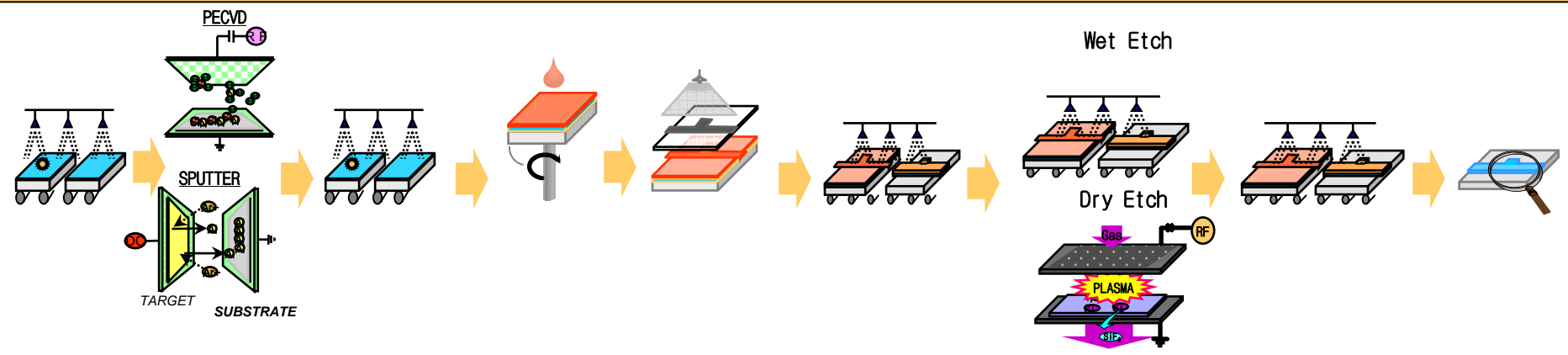
디스플레이 분류



FPD Process Overview

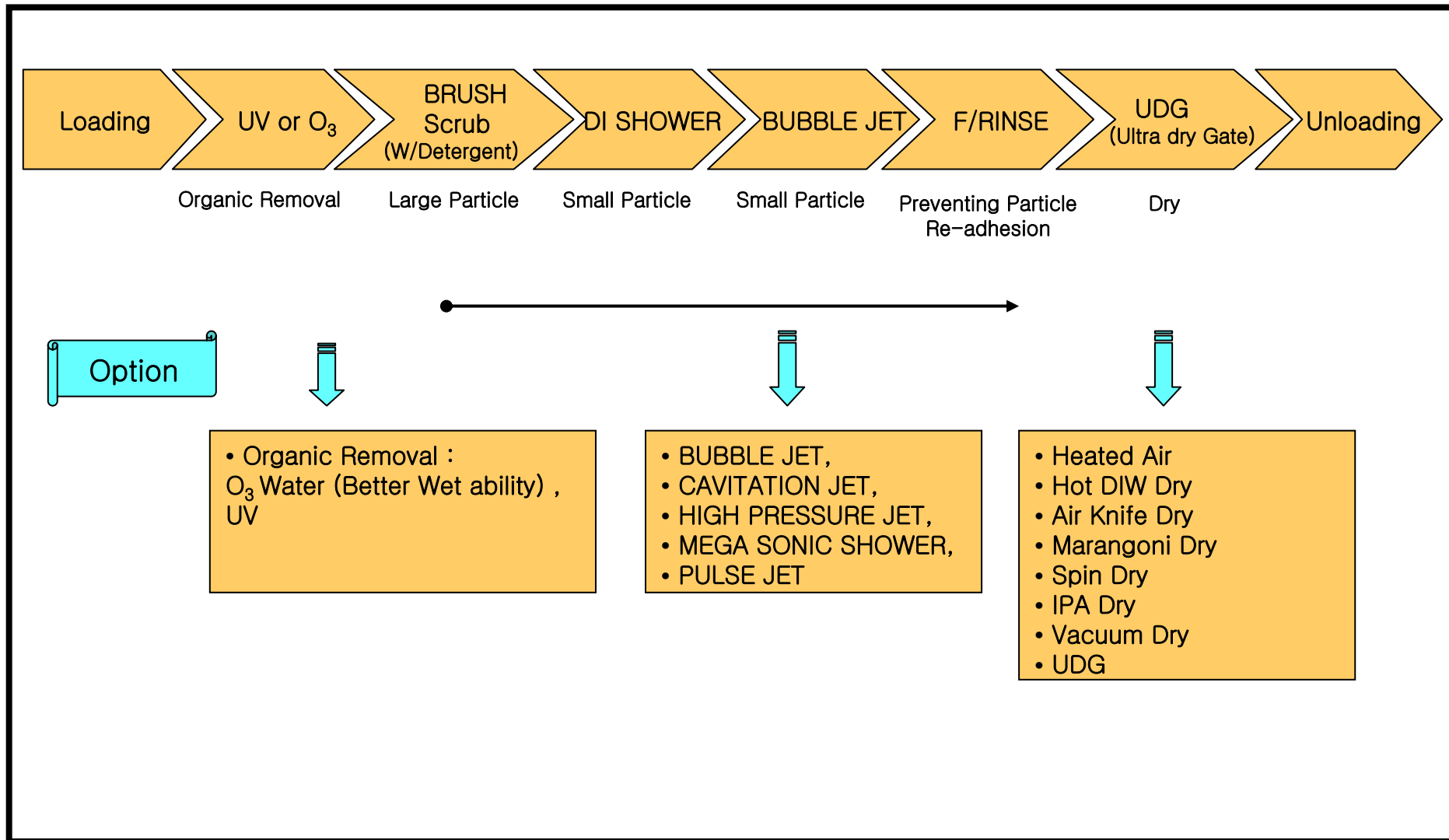


Deposition & Patterning Process in Detail



FPD Cleaning Process

Process Sequence

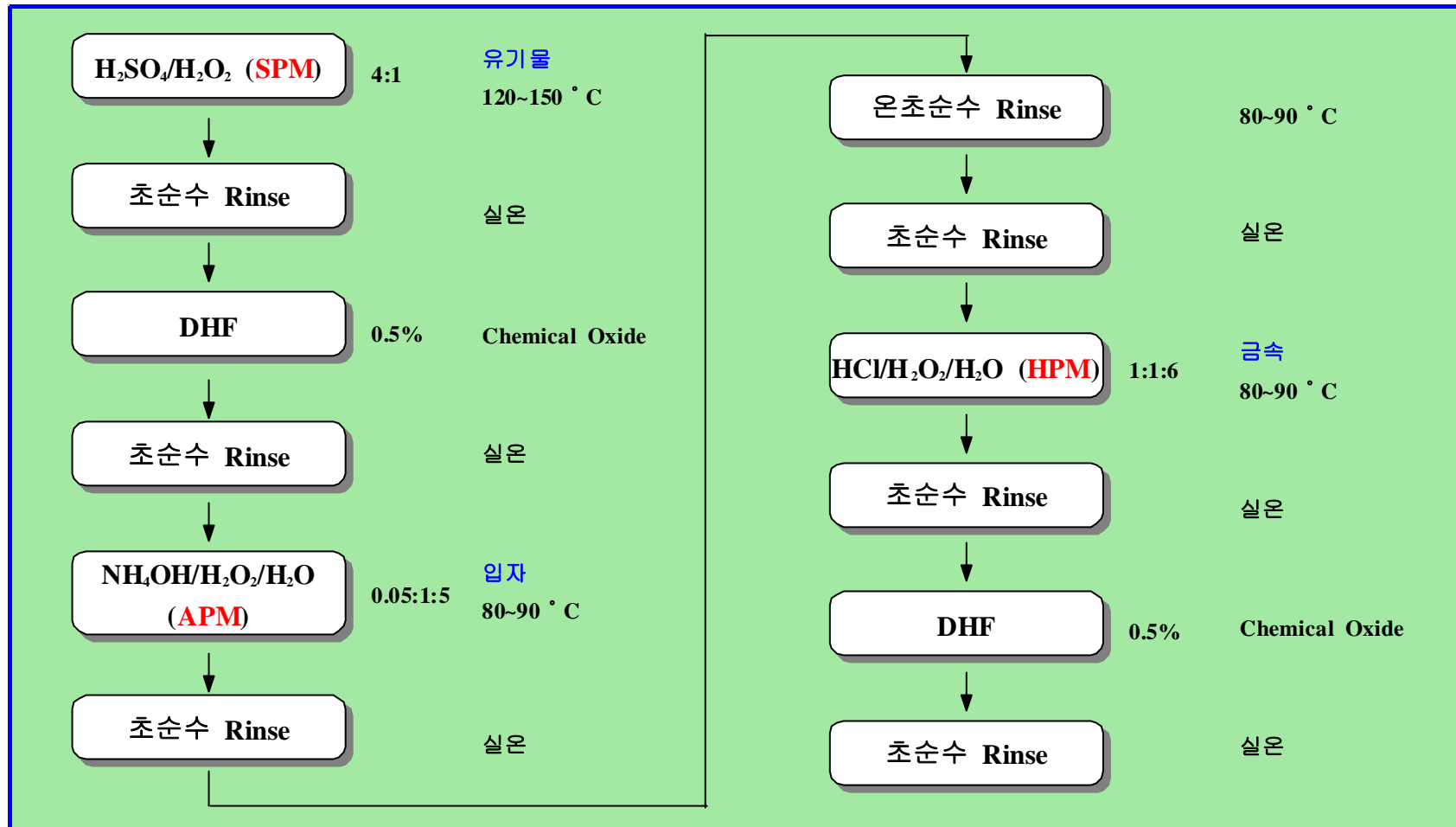


FPD Cleaning Technology Trend*

| Cleaning Method | Trend | | | Target | | | | |
|-------------------|--|--|---|-------------------------------------|--|-----|--|--|
| | '94~'96 | '97~'99 | '00 ~ | | | | | |
| Chemical Cleaning | <div style="border: 1px solid black; border-radius: 10px; padding: 5px; width: fit-content;"> Brush U/S M/S DI Shower </div> | <div style="border: 1px solid black; border-radius: 10px; padding: 5px; width: fit-content;"> Bubble Jet High Pressure Jet Cavitation Jet </div> | <div style="border: 1px solid black; border-radius: 10px; padding: 5px; width: fit-content;"> Pulse jet HPM/SJ VUV </div> | One Chamber / Multi Cleaning | <ul style="list-style-type: none"> ▪ Floor-Space-effective ▪ Environment-friendly ▪ Performance Enhancement ▪ Yield-up ▪ Scalability ▪ Running-cost-effective ▪ Investment-cost-effective | | | |
| | <div style="border: 1px solid black; border-radius: 10px; padding: 5px; width: fit-content;"> Function Water - O₃ Water : Oxidative - H₂ water : Reductive - Elctrolyzed Water </div> | | | | | | | |
| Dry Cleaning | <div style="border: 1px solid black; border-radius: 10px; padding: 5px; width: fit-content; display: inline-block;"> UV Cleaner : Excimer, DUV </div> | | <div style="border: 1px solid black; border-radius: 10px; padding: 5px; width: fit-content;"> LASER, Plasma </div> | | | | | |
| | <div style="border: 1px solid black; border-radius: 10px; padding: 5px; width: fit-content; margin: 5px auto;"> CO₂ Cleaning </div> | | | | | | | |
| | <div style="border: 1px solid black; border-radius: 10px; padding: 5px; width: fit-content; margin: 5px auto;"> Ice Particle Cleaning </div> | | | | | | | |
| Dry system | Hot Air | Hot DI | Spin Dry | IPA Dry | Air knife | UDG | | |

* 박영순, 태화일렉트론

Example of Semiconductor Cleaning Process



Conventional Wet Cleaning Process

| 과목 | Cleaning Methods | Cleaning 목적 및 Mechanism | Comments |
|----------|---|---|---|
| 화학 세정 | APM, SC-1 (NH ₄ OH/H ₂ O ₂ /H ₂ O) 75~90 °C | <ul style="list-style-type: none"> ➤ Light Organics, I/II 족 Metals, Particle 제거 ➤ $2\text{H}_2\text{O}_2 + \text{C} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ ➤ $\text{M} + \text{H}_2\text{O}_2 \rightarrow \text{MO} + \text{H}_2\text{O}$, $\text{MO} + 4\text{NH}_4\text{OH} \rightarrow \text{M}(\text{NH}_4)^{4+}$ | Metal Re-Adsorption (Alkali 계 Metal) due to low Redox potential Si- wafer micro-roughness |
| | HPM, SC-2 (HCl/H ₂ O ₂ /H ₂ O) 75~85 °C | <ul style="list-style-type: none"> ➤ Metal(알칼리 이온, 중금속) 제거 ➤ Ion Exchange : $\text{Na}^+ + \text{HCl} \rightarrow \text{NaCl} + \text{H}^+$ ➤ Complex : $\text{M} + \text{H}_2\text{O}_2 \rightarrow \text{MO} + \text{H}_2\text{O}$ $\text{MO} + 2\text{HCl} \rightarrow \text{MCl}_2 + \text{H}_2\text{O}$ | Formation of thin hydrophilic chemical oxide film Difficult in maintenance of hardware due to high corrosiveness |
| | SPM (H ₂ SO ₄ /H ₂ O ₂ /H ₂ O) 90~130 °C | <ul style="list-style-type: none"> ➤ Heavy Organic, Metal 제거 ➤ $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_5(\text{CARO'S ACID}) + \text{H}_2\text{O}$ ➤ $\text{H}_2\text{SO}_5 + \text{Hydrocarbon} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{H}_2\text{SO}_4$ | Formation of thin hydrophilic chemical oxide film Generation of SO ₄ ²⁻ Residue on the substrate |
| | Dilute HF (HF/H ₂ O) | <ul style="list-style-type: none"> ➤ Natural Oxide Film, Metal 제거 ➤ $6\text{HF} + \text{SiO}_2 \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$ ➤ $3\text{HF} + \text{M} \rightarrow \text{MF}_3 + 3\text{H}^+$ | Removal of surface oxide and metal in the metal oxide film by dilute HF solution Removal of noble metal by H ₂ O ₂ |
| | BOE (HF/NH ₄ Cl/H ₂ O/ 계면활성제) | <ul style="list-style-type: none"> ➤ Oxide Film 제거 | Buffered oxide etchant HF/NH ₄ F=1:7 |

FPD와 Semiconductor의 세정 비교*

| Classification | Semiconductor Process | Flat Panel Display Process |
|----------------|---|---|
| 1. 세정의 대상 | Wafer. ~ 300 mm dia. | <i>300*400mm(1st G)</i> Glass, ~ 1870*2200 mm (7 th G) |
| 2. 세정제 | SC1, SC 2, SPM.. RCA cleaning.. <i>Acid & Base Mixture</i> | <i>1000(3G) ⇒ 12,000m³/day(6G)</i> Detergent, THAM**, 電解水 |
| 3. 세정 목적 | Organics, Metal, Particle, Oxide | Organics, Particle, Water Marks, <i>Metal, Oxide</i> |
| 4. 반송 단위 | 약 25 매/lot, Carrier | 1 매, 연속 반송 |
| 5. 세정 방식 | Dip, Bath | Shower, Spray |
| 6. 세정 시간 | about 10 min/each bath | Below 1 min /1 매, chamber <i>연속반송 1000 ~ 8000 mm/min</i> |
| 7. 기타 | | <i>얼룩 (Water Marks)</i> |

* 권정현, 삼성SDI ** tetra methyl ammonium hydroxide

Mechanism of Organic Removal

1. PRINCIPLE

Remove an electron from organic molecules to oxidize and decompose them to CO_2 , H_2O , and etc.

2. HOW TO REMOVE AN ELECTRON?

To remove an electron by high ORP solutions such as H_2SO_4 , HCl , HNO_3 , etc. have been used.

3. WHY OZONIZED WATER?

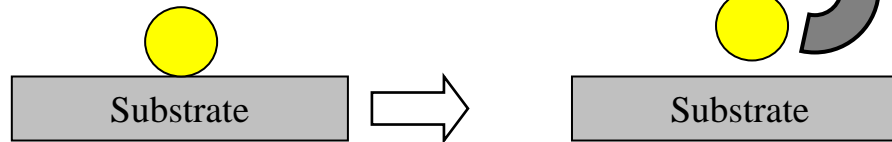
ORP of ozonized water (DIW with a few ppm of ozone) is higher than those of H_2SO_4 , HCl , HNO_3 .

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. 1ST Step....lift off



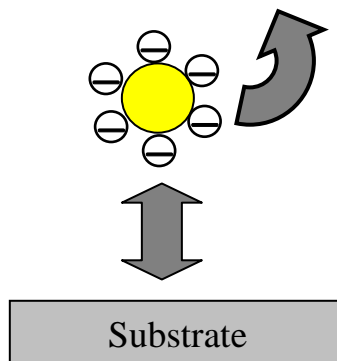
* Mechanical lift off

- Ultra sonic (MHz)
- Brush scrub

• Chemical lift off

- Substrate etching with alkaline and HF
- Use of H₂ Water : H radical generation
⇒ inactivation of soil or detachment of soil
- Particles are dissolved with HF or decomposed with O₃

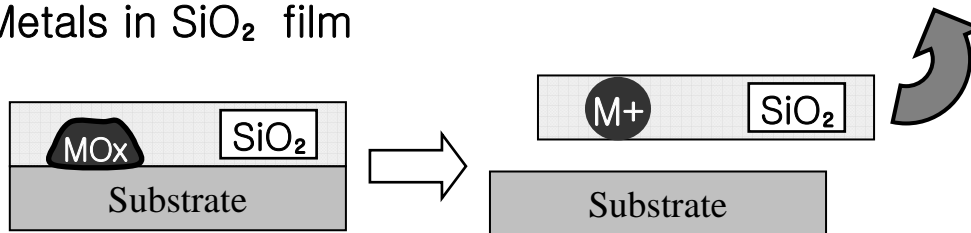
1. 2ND Step....Prevention of re-adhesion



- 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

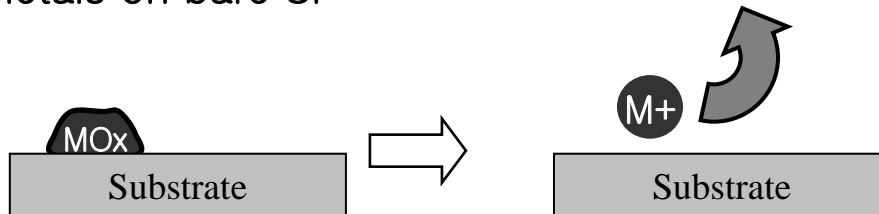
Mechanism of Metal Removal

1. Metals in SiO₂ film



* Metals are removed together with SiO₂ by etching with HF.

2. Metals on bare Si



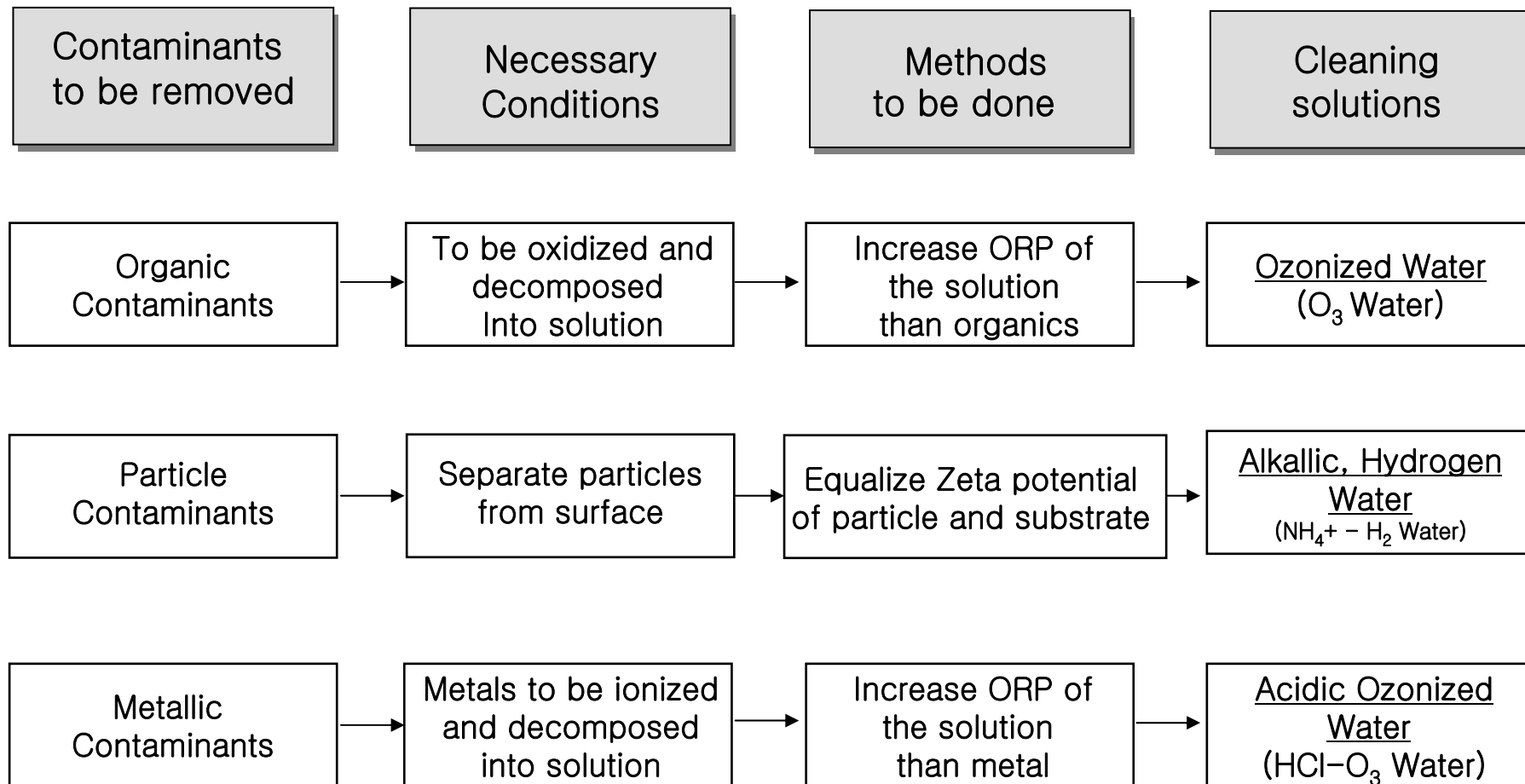
* Metals are ionized by acidic and oxidative solutions.

acidic and oxidative solutions.

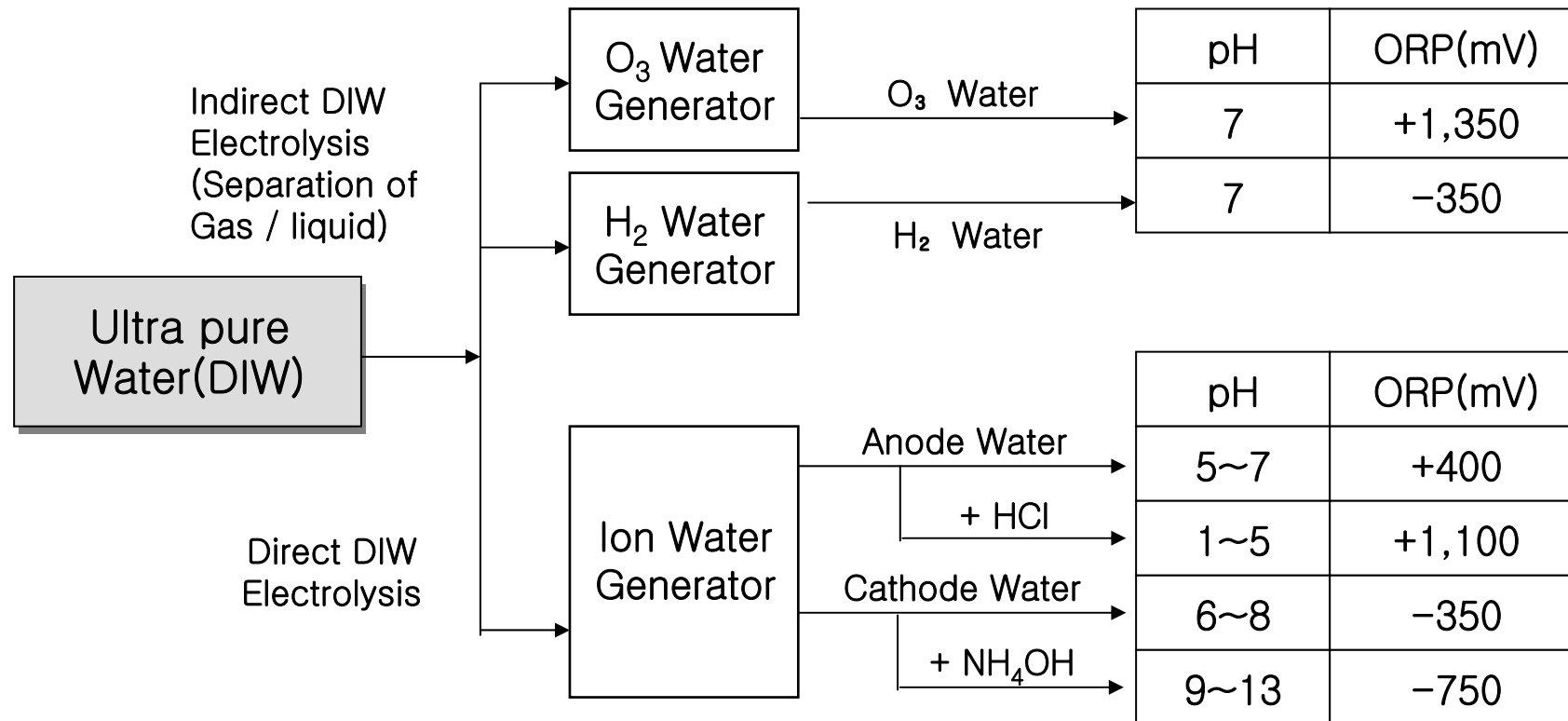
Conventional : Acid & oxidizer at Hot temp & High conc.

Activated UPW : Diluted acidic oxidative solutions(HF/O₃ or HCl/ O₃ solution)
 → ORP of Ozonized water is higher than those of H₂SO₄, HCl, HNO₃
 etc.

Cleaning Principles

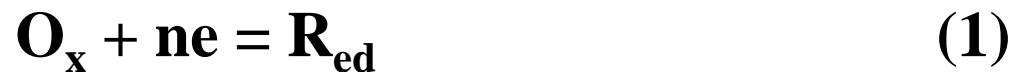


Functional Water



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)

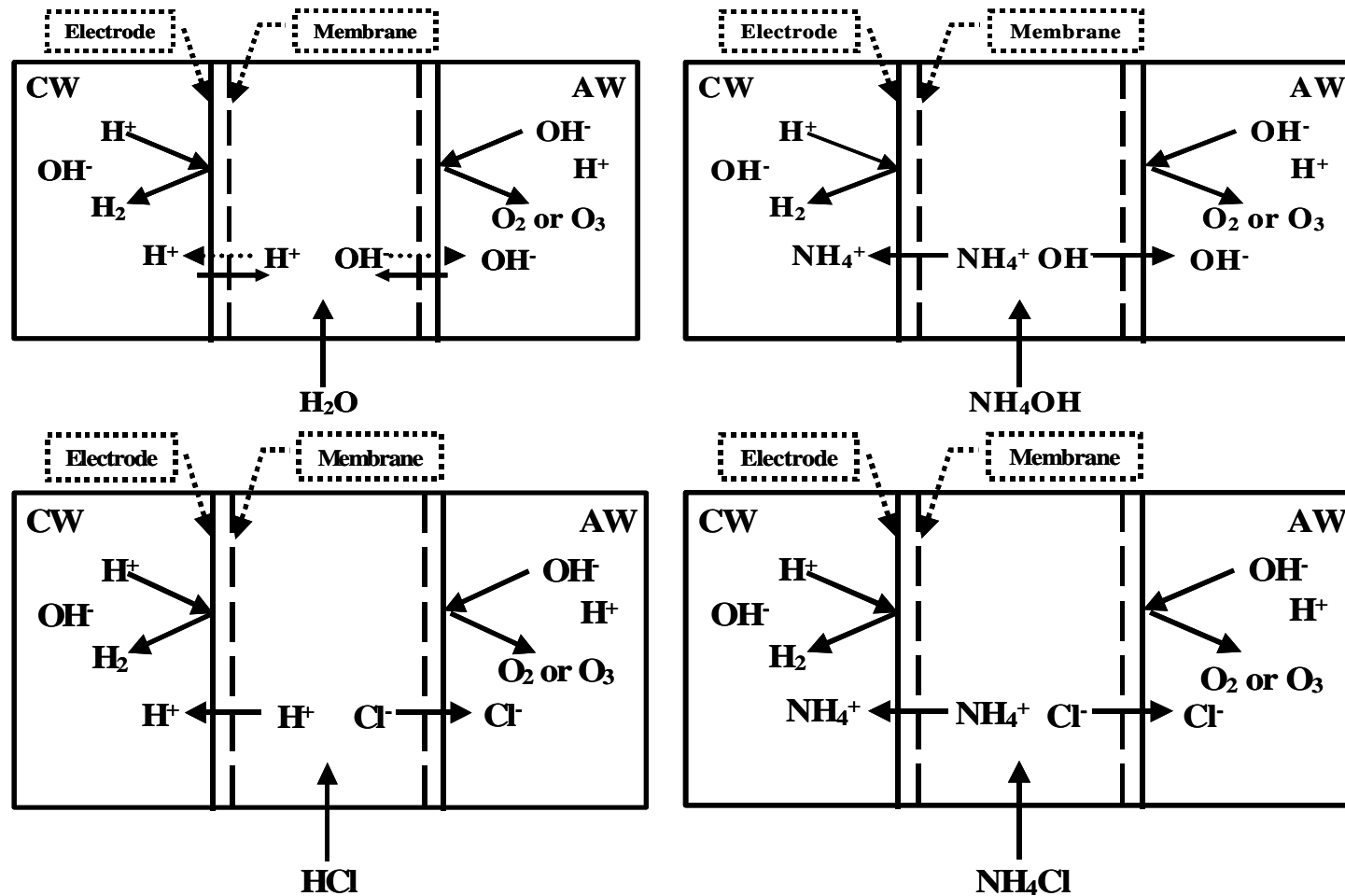


$$\mathbf{E = E_0 - RT/(nF) \log (C_{red}/C_{ox})} \quad (2)$$

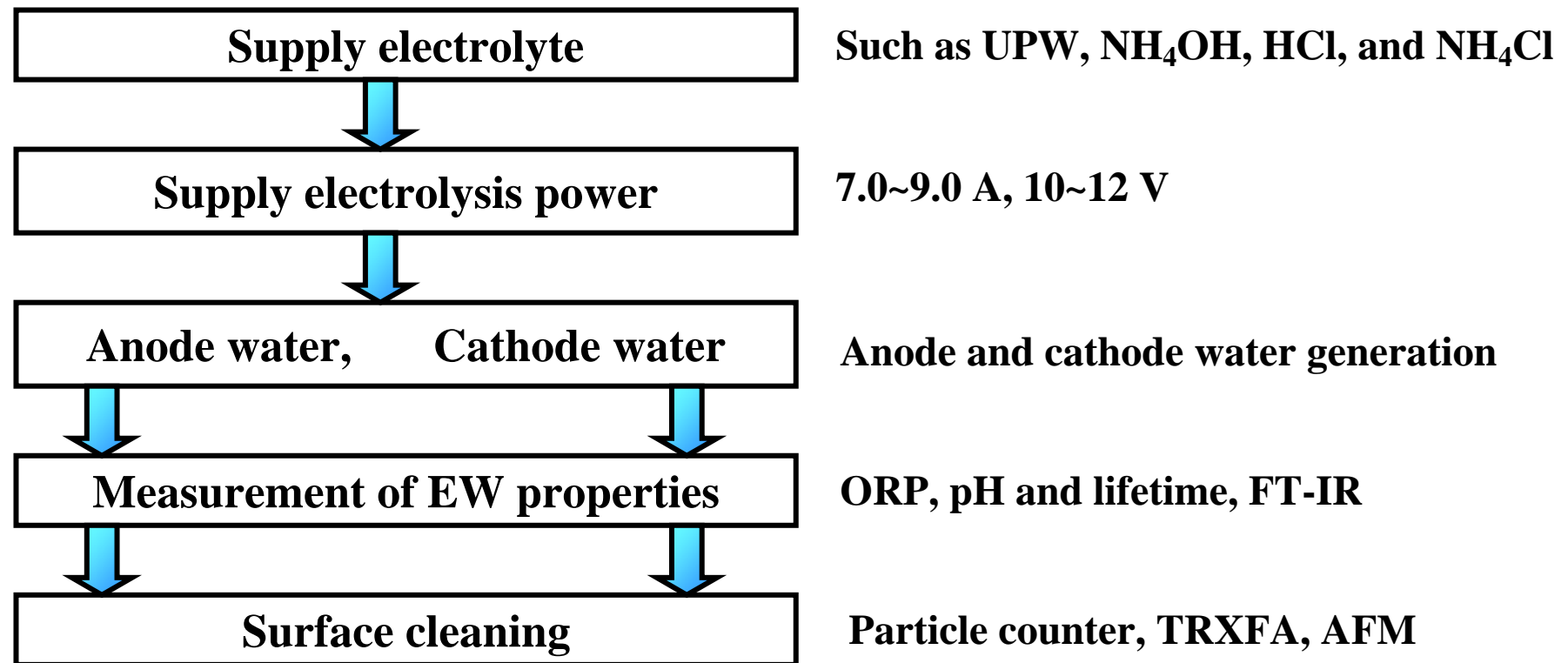
at $C_{red} > C_{ox}$, ORP is negative value (reductive water)

at $C_{red} < C_{ox}$, ORP is positive value (oxidative water)

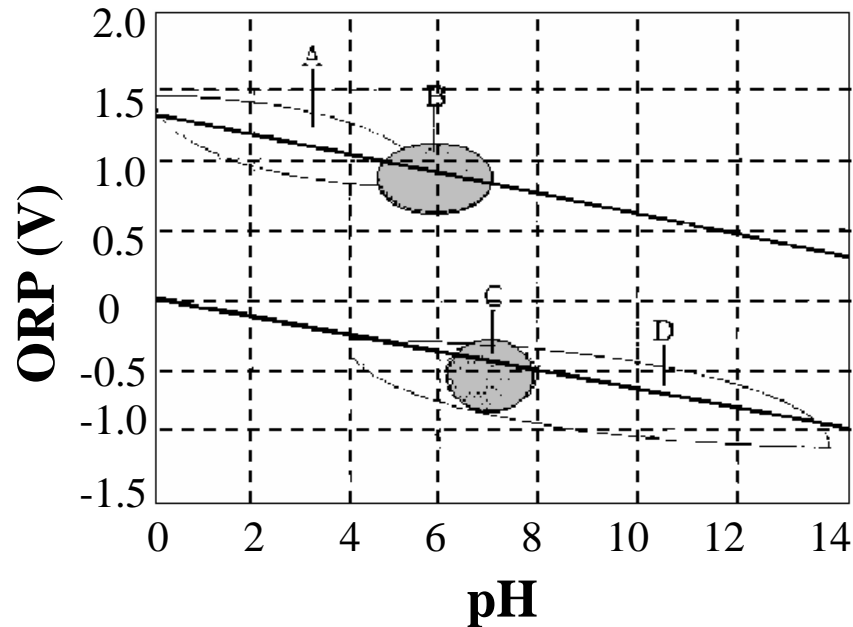
Principle of EW Generation



Procedure for Generating Electrolyzed Water



EW Properties



A : Anode water with electrolyte

B : Anode water by UPW

~ Effective for removal of metal ions

Oxidative water, High H⁺ Conc.

Similar to properties of O₃ water

C : Cathode water by UPW

D : Cathode water with electrolyte

~ Effective for removal of particles

Reductive water, High OH⁻ Conc.

Similar to properties of H₂ water

Normally used with NH₄OH

국내 전해이온수 공급업체

1. 마이크로뱅크 (<http://www.micro-bank.co.kr> ; 031-905-3420)
 - 산업자원부의 청정생산기술과제 수행(Hynix와 공동수행)
 - 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
 - 음용 이온수기 개발: (주)한국세라스톤에 알칼리성 이온수기 공급

2. 맥스산업(주) (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. (주)서양에이아이 (<http://www.seoyang.co.kr> ; 02-488-8444)

일본 전해이온수 공급업체

1. REIKEN, INC. (<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 약취제거, 유지비저렴(ROI = 1~1.5 year)

2. Nissin seiki Co., Ltd. (<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, 약취 제거 및 살균 효과

3. NITTO KOSHIN CO., Ltd.

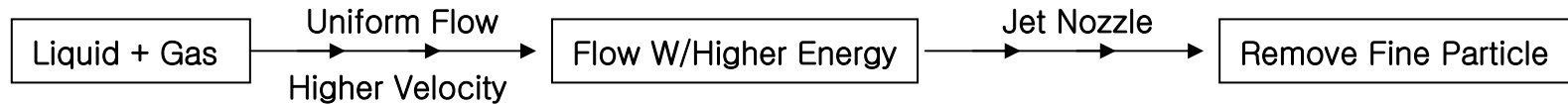
- 전해수 생성 unit
 - 본체에 수돗물을 직접 연결하여 연수와 알칼리성 전해수 생성(전해질 사용)
 - 연수기의 재생은 완전 자동
 - 응용 사례 :
 - i) 액정 유리의 최종 세정
 - ii) AI 가공유 세정에서 탄화수소계 세정제 대체

Applications of Functional Water

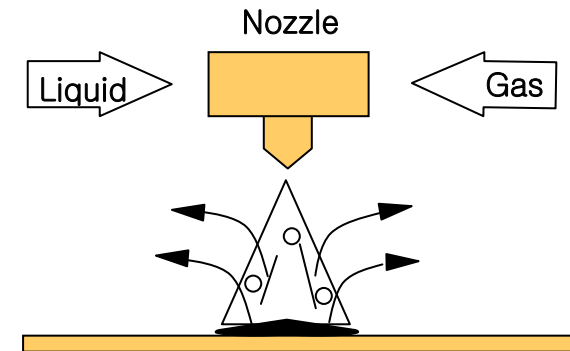
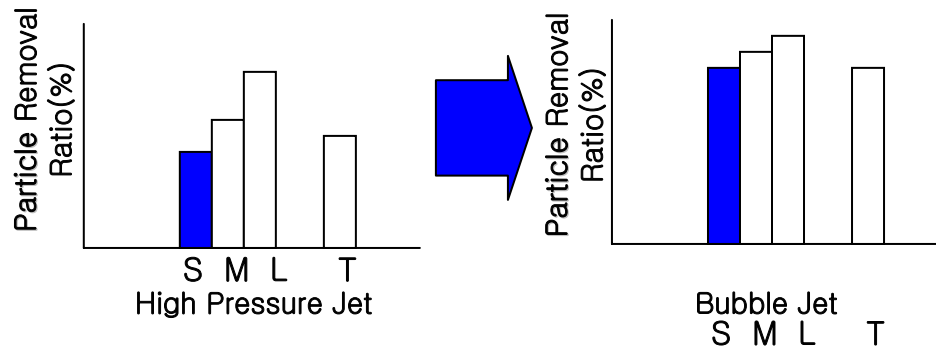
| Classification | FPD | Semicon | Wafer |
|--|--|--|---|
| O ₃ Water Organic Removal | 1. Pre-Cleaning 2. Pre-Deposition 3. Post-Deposition 4. P/R Strip | 1. Post-SPM Rinse 2. Pre/Post-CMP 3. Post-Ashing 4. P/R Strip | 1. Growth of Protective Oxide |
| H ₂ Water Particle Removal | 1. Clean bare glass 2. Rinse after etching | 1. Post-CMP | 1. Rinse after Chemical Bath |
| Electrolyzed Water | Removal of Metal & Particle | 1. Post-CMP | 1. Removal of Metal, Particle & Organics 2. SO ₄ ²⁻ removal after SPM cleaning |

Bubble Jet Technology*

1) Principle



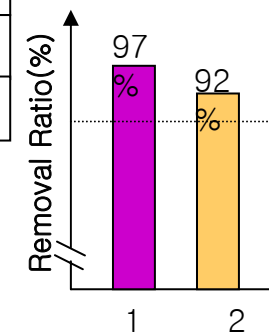
2) Performance



(Initial Particle : 1000-3000ea
 $S \doteq 1\sim 3\mu m$, $M \doteq 3\sim 5\mu m$, $L \doteq 5\mu m$, $T \doteq \geq 1\mu m$)

3) TEST : BM Pre-deposition

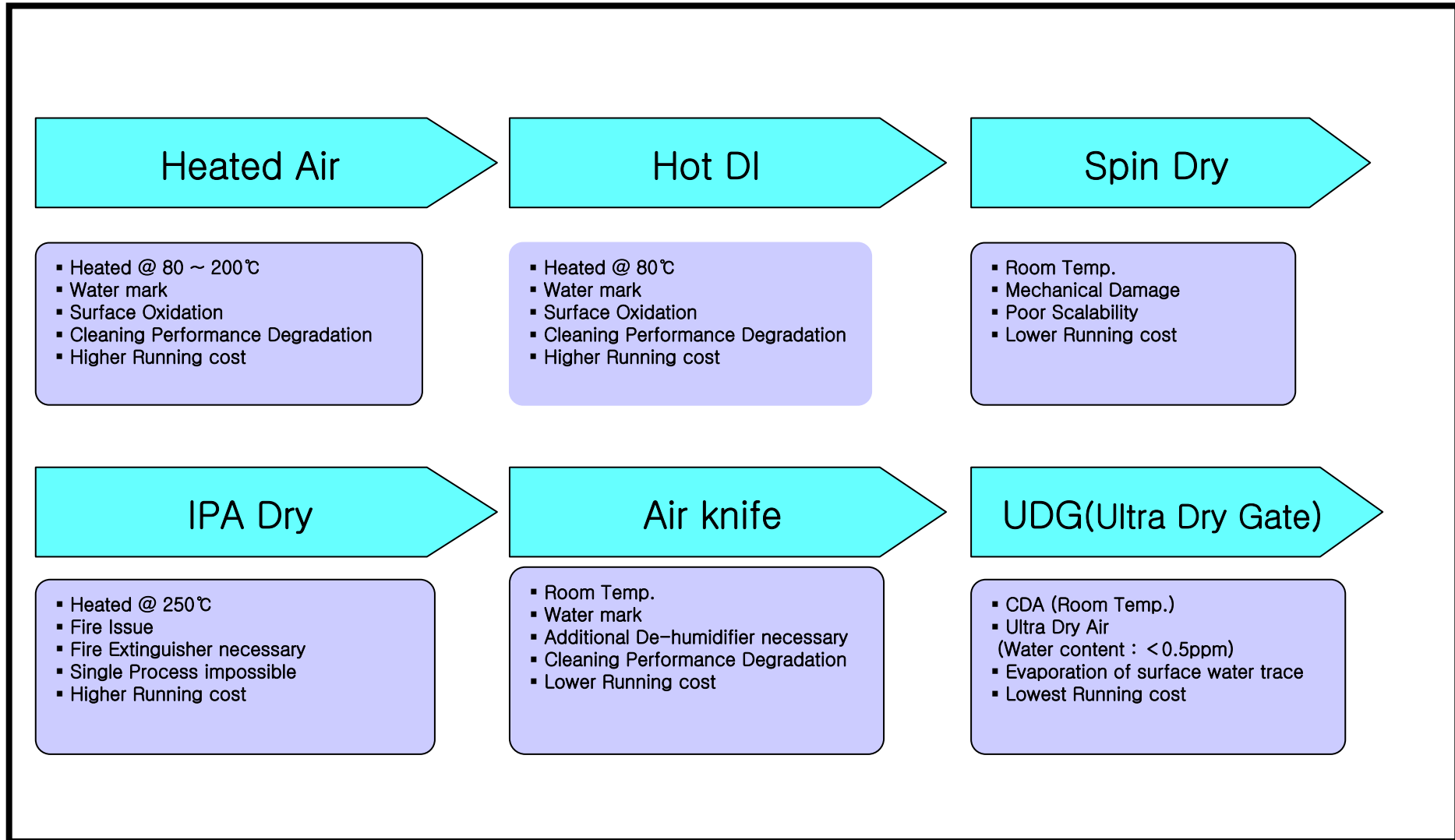
| NO | Item | O ₃ Water | Roll Brush | Bubble Jet | Shower(M/S) | Di Shower | Aqua knife | Air knife | Avg. Particle Residue |
|----|-------|----------------------|------------|------------|-------------|-----------|------------|-----------|-----------------------|
| 1 | W/BJ | ● | ● | ● | ● | ● | ● | ● | 66EA |
| 2 | W/OBJ | ● | ● | | ● | ● | ● | ● | 170.3EA |



- 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, 태화일렉트론

Dry Systems*



* 박영순, 태화일렉트론