Kanto Gakuin University

Materials & Surface Engineering Research Center

Technology Report

- Potential Applications
- Plating on Glass/Silicon
- Direct Patterning
- Non-toxic Gold (RSG) Plating System

2013年2月15日

Chris Cordonier

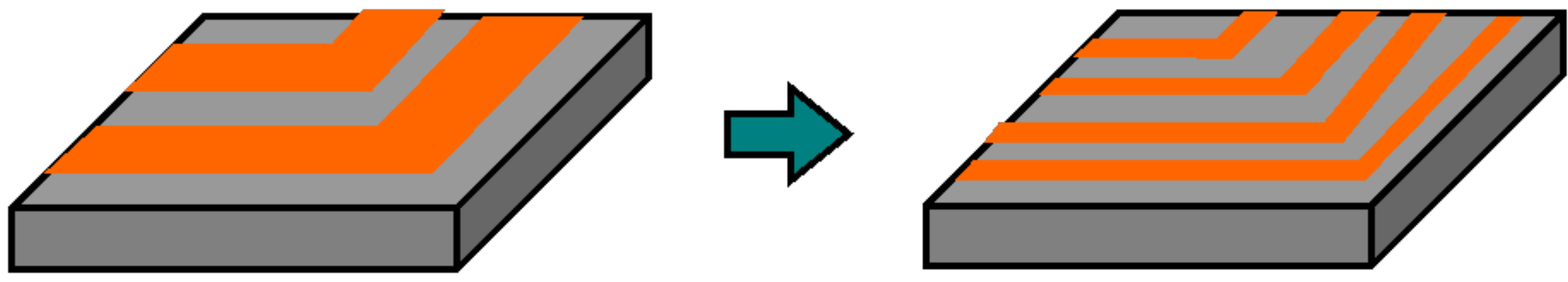
Potential Applications

for

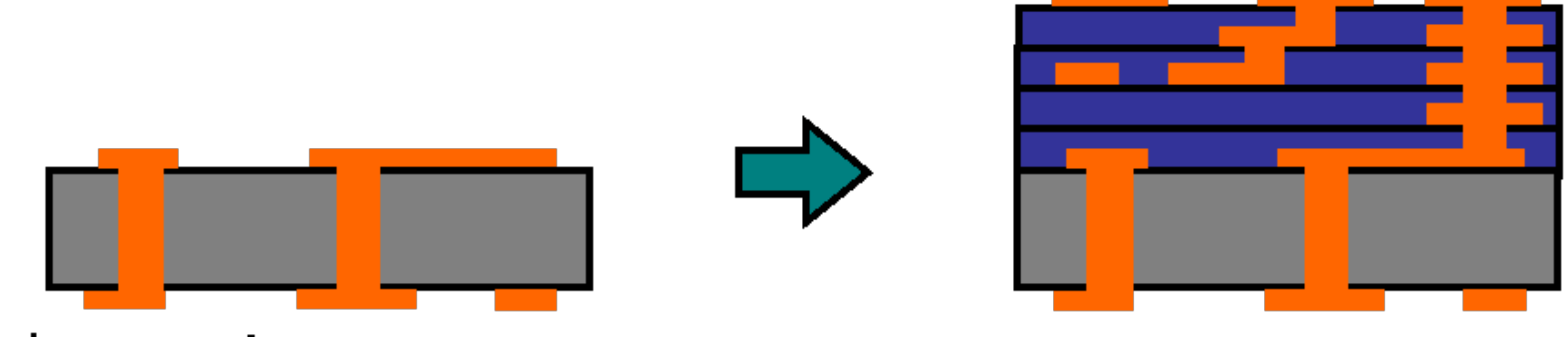
plating on glass & fine patterning (< 5 um)

Future Generation Circuitry

- **Smaller:** Finer pitch, smaller features, more precise shapes



- **More stacking:** More layer substrate & stacked devices (3D LSI)

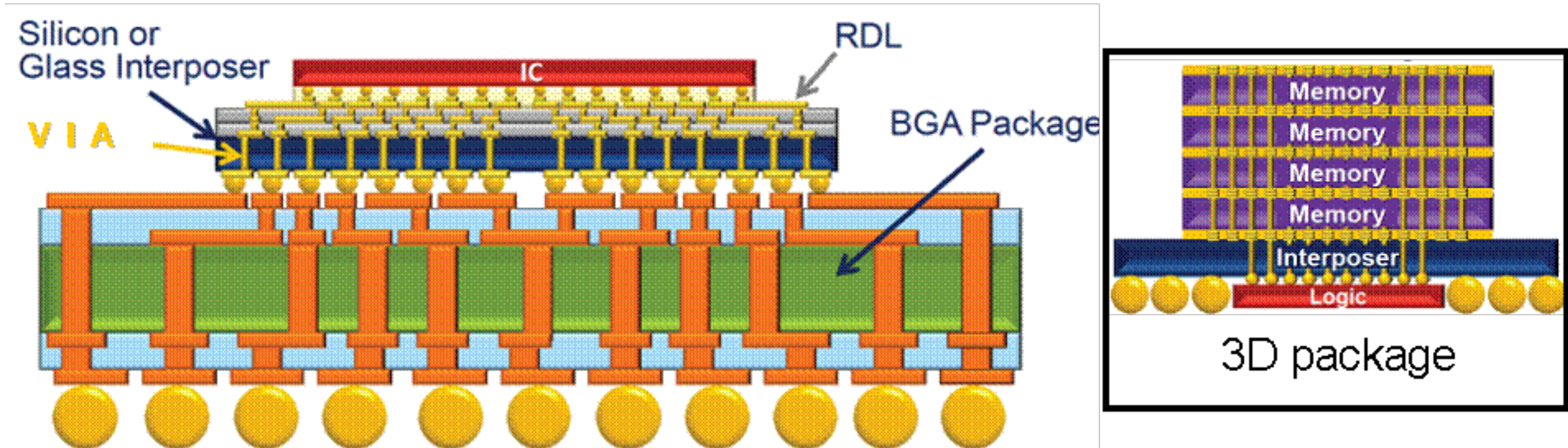


- **Lower cost**
- **Green:** Environmentally benign chemistry, process, materials, minimal waste

Glass Interposer

Direct pattern seed layer plating for interposer/RDL:

- Solution deposition of copper or gold seed layer to glass substrate with via holes. *Surface & inside via holes*



Silicon → GLASS interposer:

- low latency, strong insulation
- low cost, easy handling
- large area / roll to roll processing

Figure source: Prof. Tummala, GT-PRC, GIT 2011

Optical Electronics

- ⊿ Displays (fine circuitry)
- ⊿ Touch panels (electrodes)
- ⊿ Optical transmission
- ⊿ Photovoltaics
- ⊿ LED & Organic electroluminescent illumination (electrodes)

electrical conductor + transparent ⇒ transparent electrode

Windows 7

Smart phone / Tablet
display＋touch panel

Conventional: sputtered tin doped indium oxide (ITO) or fine metal wires (>5 um)

Transparent Electrodes

transparent electrodes for capacitive type touch panels

tin doped indium oxide	fine metal mesh wiring
(+) transparency, stability	(+) conductivity, inexpensive
(−) expensive, environmental impact	(−) not transparent → fine pattern

ITO

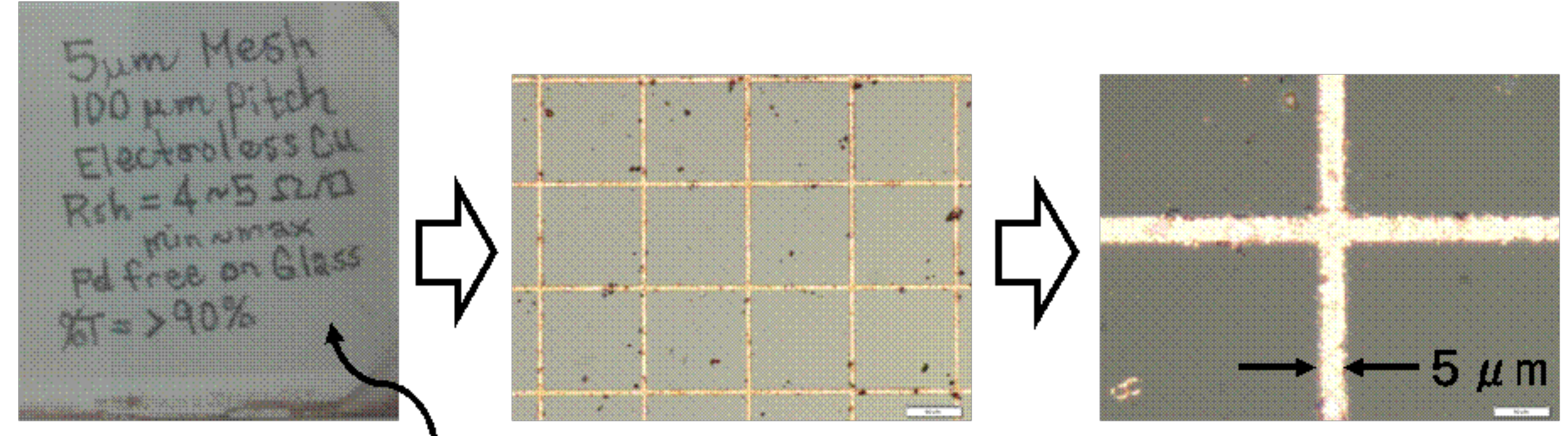
electroless Cu on patterned Cu catalyst mesh
2 μm wire / 10 μm pitch

2 μm

Current technology is ~10 μm, & 5 μm rumors but not invisible
⇒ Use < 5 μm lines.

Mesh Pattern / Transparent Electrode

Patterned copper on copper catalyst



Fine mesh as a transparent electrode

"More conductive than ITO with the same transparency"

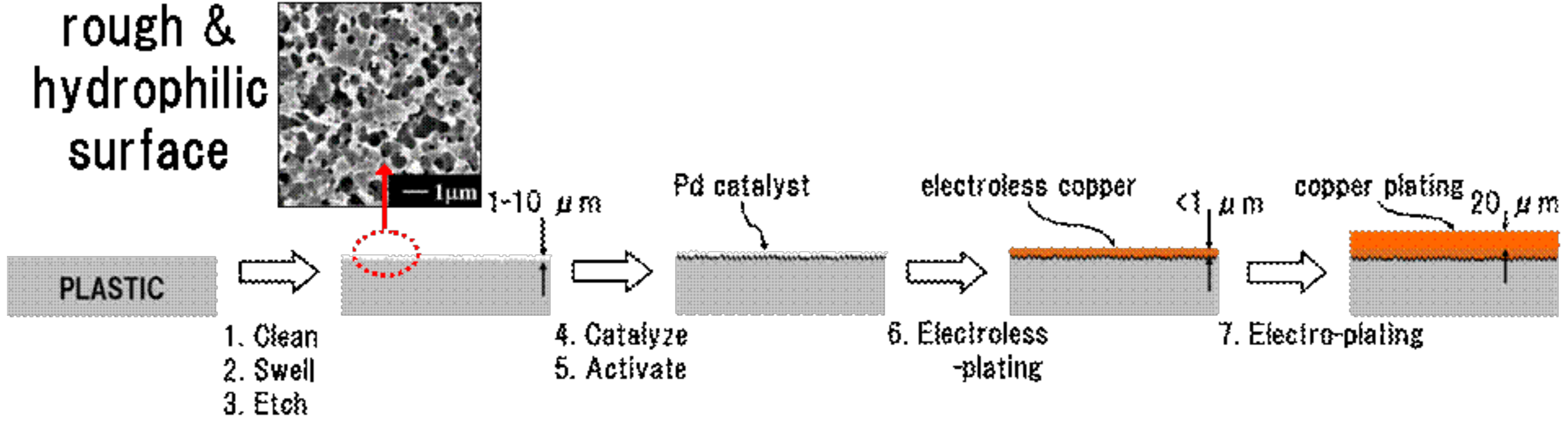
Sheet resistance, R_{sh} = 0.5-5 Ω/□, Transparency, %T = > 90%

Proposal: Dual side patterning × Fine mesh pattern electrode

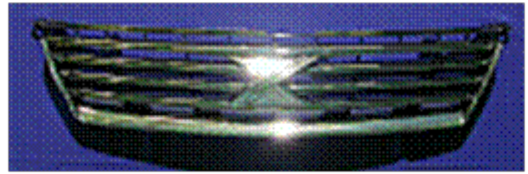
Touch panel functionality ⇧ cost ⇩ in an indium free × wet process

Plating on Glass

Conventional Plating on Plastics

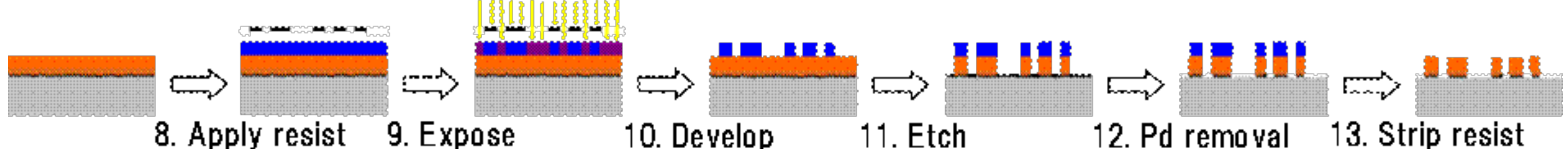


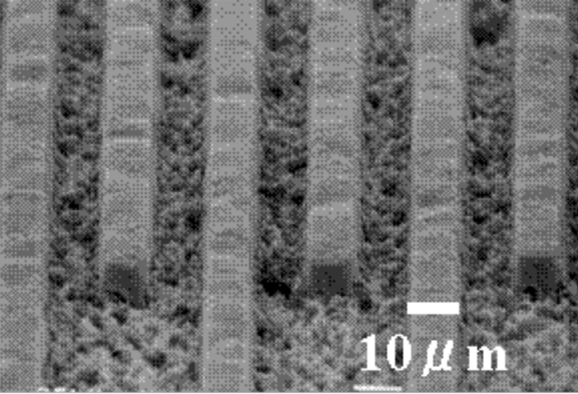
Decorative

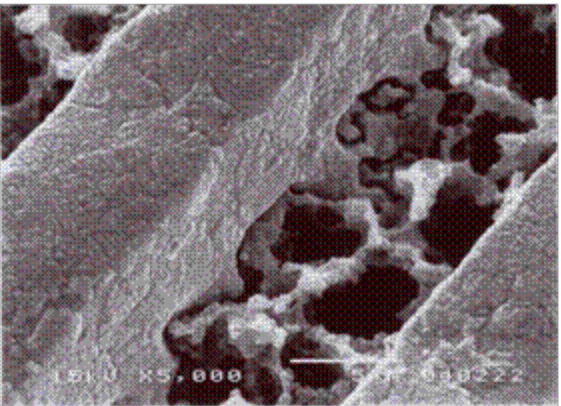


Electronic

Conventional Patterning







Problems

- Too many steps
- Rough surface:
  - -limited resolution
  - -high impedance @ high frequency
  - -Migration risk
- Bridging (short circuit)
- Chemicals with environmental impact & toxic effects

Objectives

⊿ Smooth substrate-plating interfaces (for increased pattern resolution & low loss high frequency transmission)

⊿ Precision & fine wire/structure formation

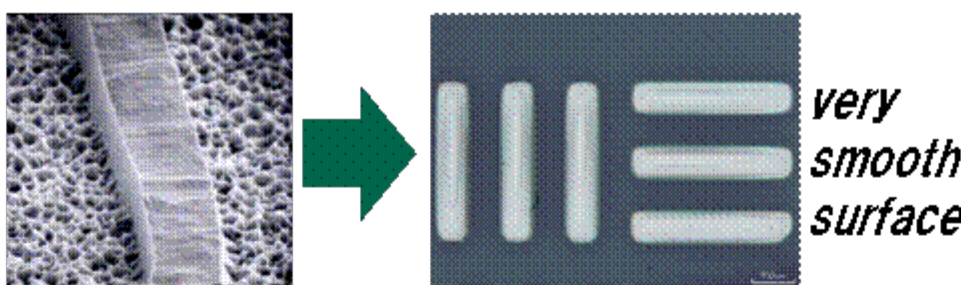
⊿ Lower cost

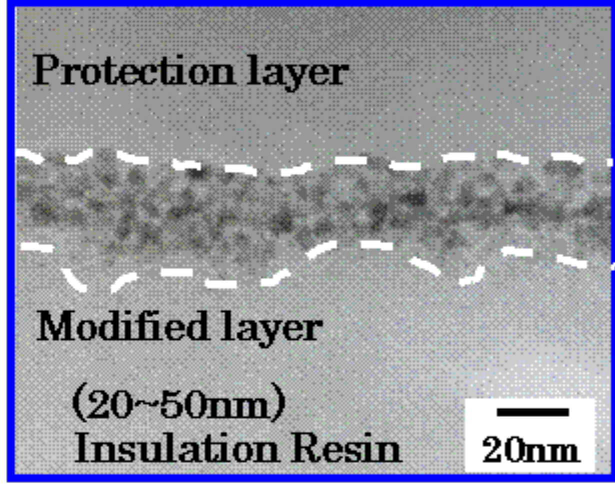
⊿ Increased environmental neutrality

⊿ Techniques to allow new or more refined functions to improve quality of existence.

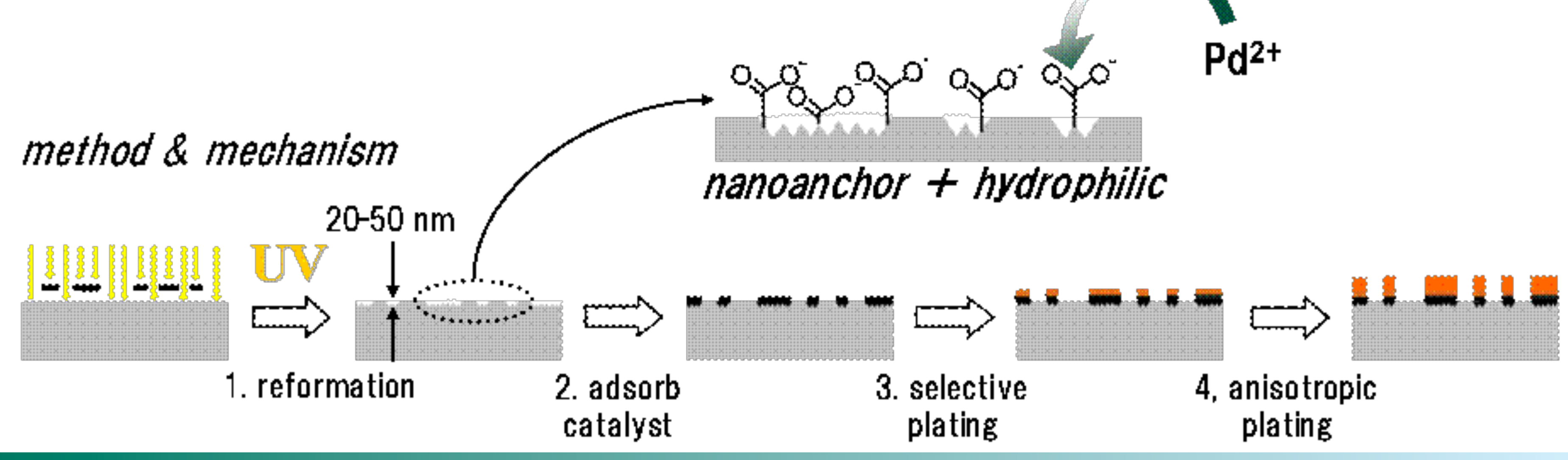
Ex: Shoulder Phone ⇒ i Phone

UV Surface Refomation





3 birds with one stone!
adhesion + patterning while maintaining a smooth interface

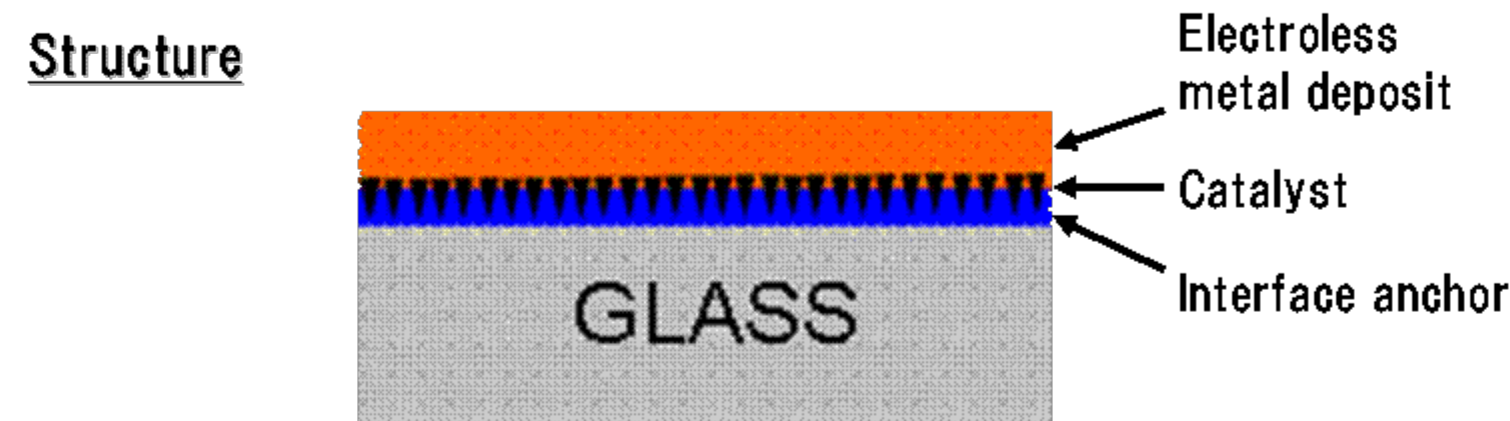


Same Model for Glass

Anchor Layer Formation

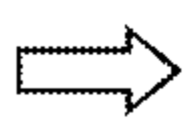
Glass surface reformation is difficult ⇒ Deposit a catalytic anchor layer

- Nano-anchor formation
- Polar material for hydrophilic surface/high metal bonding
- High adhesion fused/infused interface

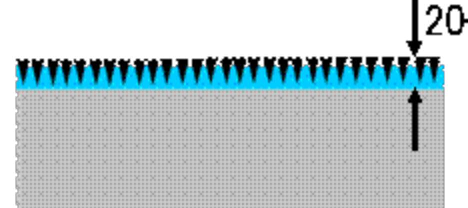


Plating on Glass

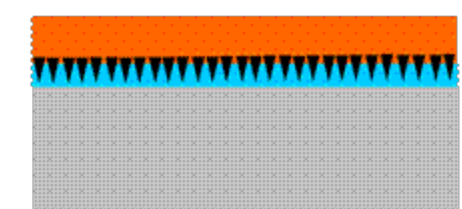
Catalytic nano-anchor precursor coating (solution deposition)



Nano-anchor layer (Ra = 1 nm) of 30-50% porosity containing electroless plating catalyst



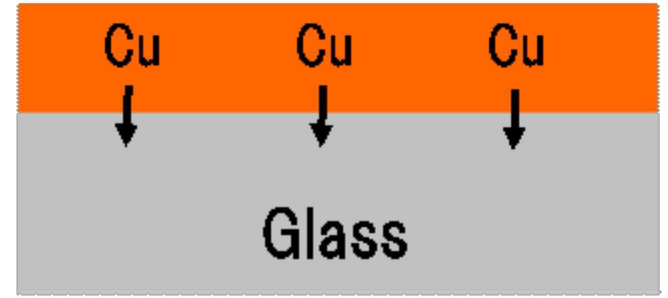
Electroless/electro plating

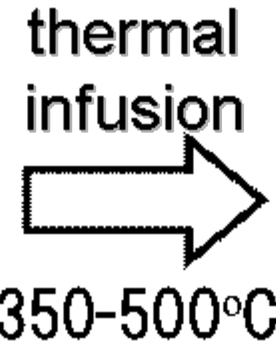


Electroless/electro plating

- Anchor layer penetration & filling
- Blister formation resistance
- Low stress deposit
- Cross cut test passed for thin films/seed layers
- Adhesion often fails for films thicker than 1 μm (electro Cu).
- Catalysts: Pd, Cu, Au
  (Cu for Pd free Cu plating & Au for all gold process)
- Electroless plating: Cu (formalin), Ni (PO_3^{3+}), alloys, Ag, Au, ENIG
- Electroplating: low stress bright copper sulfate, gold

Copper Stained Glass





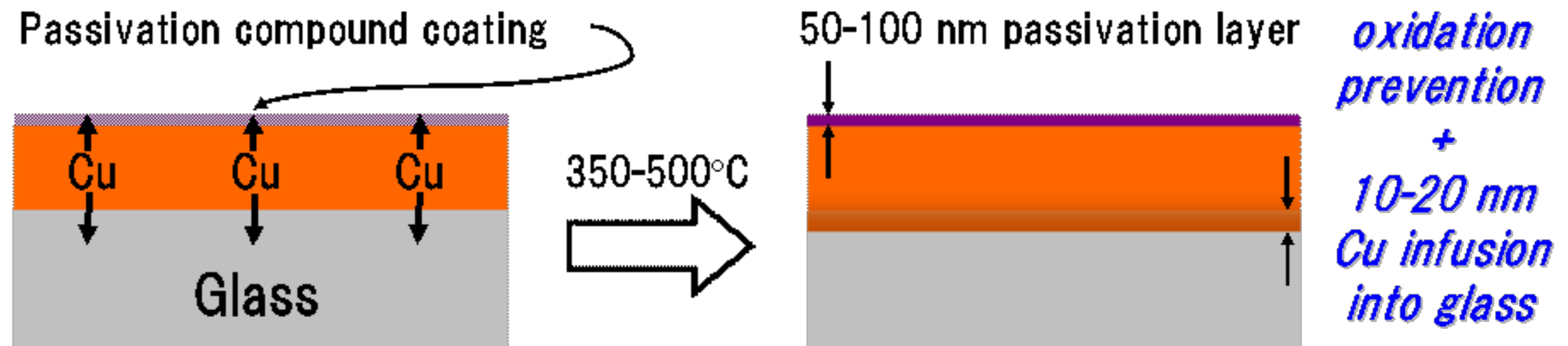
<u>Infusion of copper into glass</u>

- Formation for a Cu infusion layer
- Significant increase in adhesion is possible

BUT

- At high temperature severe Cu oxidation occurs
- At over 400°C, complete oxidation to CuO
- At high temperature Ni oxidation/discoloration occurs

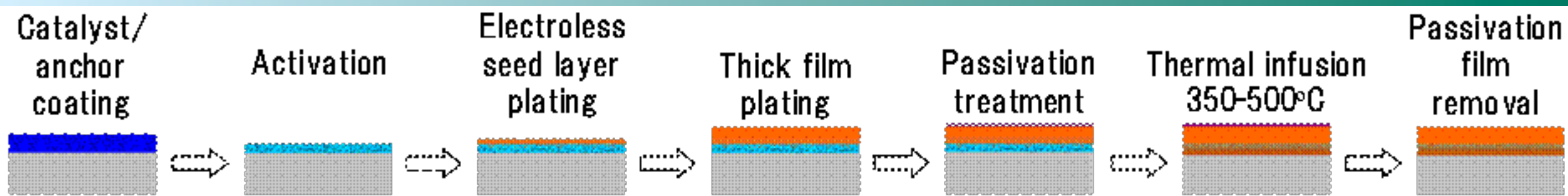
Copper/Nickel Passivation



Infusion of copper into glass

- Formation for a Cu infusion layer
- Conducting surface remains smooth
- Significant increase in adhesion (0→0.3 kN/m for Cu/Tempax)
- Oxidation does not progress beyond the passivation layer
- No discoloration of Cu or Ni at high temperature
- Easy removal of passivation film after thermal infusion

Overall Process



Example: Copper plating

Substrate: 5x5 cm Tempax glass

Catalyst: AHK1T-259 palladium catalyst (spin coat solution)

Curing: 200-500℃

Activation: Submersion in hypophosphite solution (50℃・2 min.)

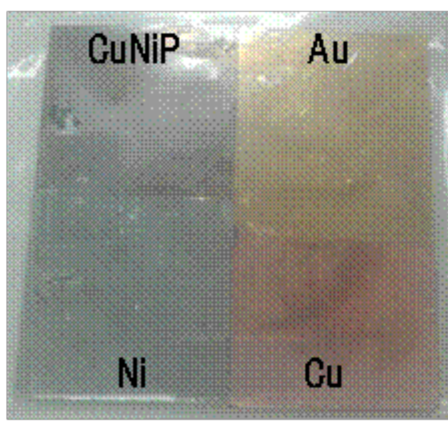
Electroless plating: 80 nm Copper

Electroplating: 17 um Copper (acid copper @ 2.5 ASD)

Passivation: CSA spin coat

Thermal infusion: 350-500℃

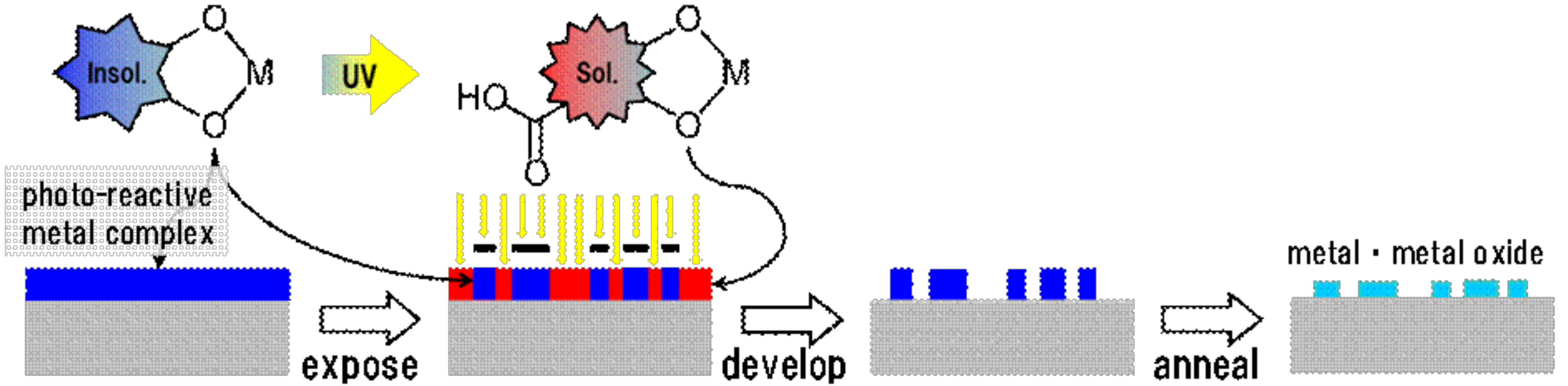
Passivation film removal: Submersion in NaOH solution (50℃・2 min.)



Direct Patterning

<5μm features

Photo-reactive Metal Complex



Some of the materials we have photo-patterned so far…

Complex M	→	metal・oxide	Complex M	→	metal・oxide	Complex M	→	metal・oxide
Mg	500°C	MgO	Ga	500°C	Ga_2O_3	Ce	500°C	Ce_2O_3
Al	500°C	Al_2O_3	Ge	500°C	GeO_2	Pr	500°C	Pr_2O_3
Si	500°C	SiO_2	Nb	500°C	Nb_2O_5	Sm	500°C	Sm_2O_3
Ti	500°C	TiO_2	Ta	500°C	Ta_2O_5	Eu	500°C	Eu_2O_3
Hf	500°C	HfO_2	Pd	200°C	Pd	Gd	500°C	Gd_2O_3
Fe	500°C	Fe_2O_3	Pd	500°C	PdO	Tb	500°C	Tb_2O_3
Co	300°C	Co	In	500°C	In_2O_3	Dy	500°C	Dy_2O_3
Co	500°C	CoO	In	flash lamp	In	Ho	500°C	Ho_2O_3
Ni	500°C	NiO	Sn	500°C	SnO_2	Er	500°C	Er_2O_3
Cu	500°C	CuO	La	500°C	La_2O_3	Lu	500°C	Lu_2O_3

Two-tone Patterning

for capacitive type touch panel sensors

300 nm
M1
HO
M2
365 nm

M1 = Nb
M2 = InSn

M1 = Ti
M2 = Ti

M1 = Nb
M2 = Nb

Absorbance
Wavelength (nm)
λ1
λ2
錯体1
錯体2

REF: *Nanomaterials* **2012**, *2*, 312−328.

Photo-patterning + Plating System

- Same apparatus as used for patterning photo resist / photolithography
- Same light source & amount of exposure
- Same aqueous developer
- No etching
- No resist stripping
- Fully additive circuit formation
- All solution processing
- High resolution (so far 400 nm features)

13 steps → 5-6 steps!!

Insol. — M — UV → HO — Sol. — M

1. Coat 2. Expose 3. Develop 4. Activate (fuse/reduce) 5. Plate

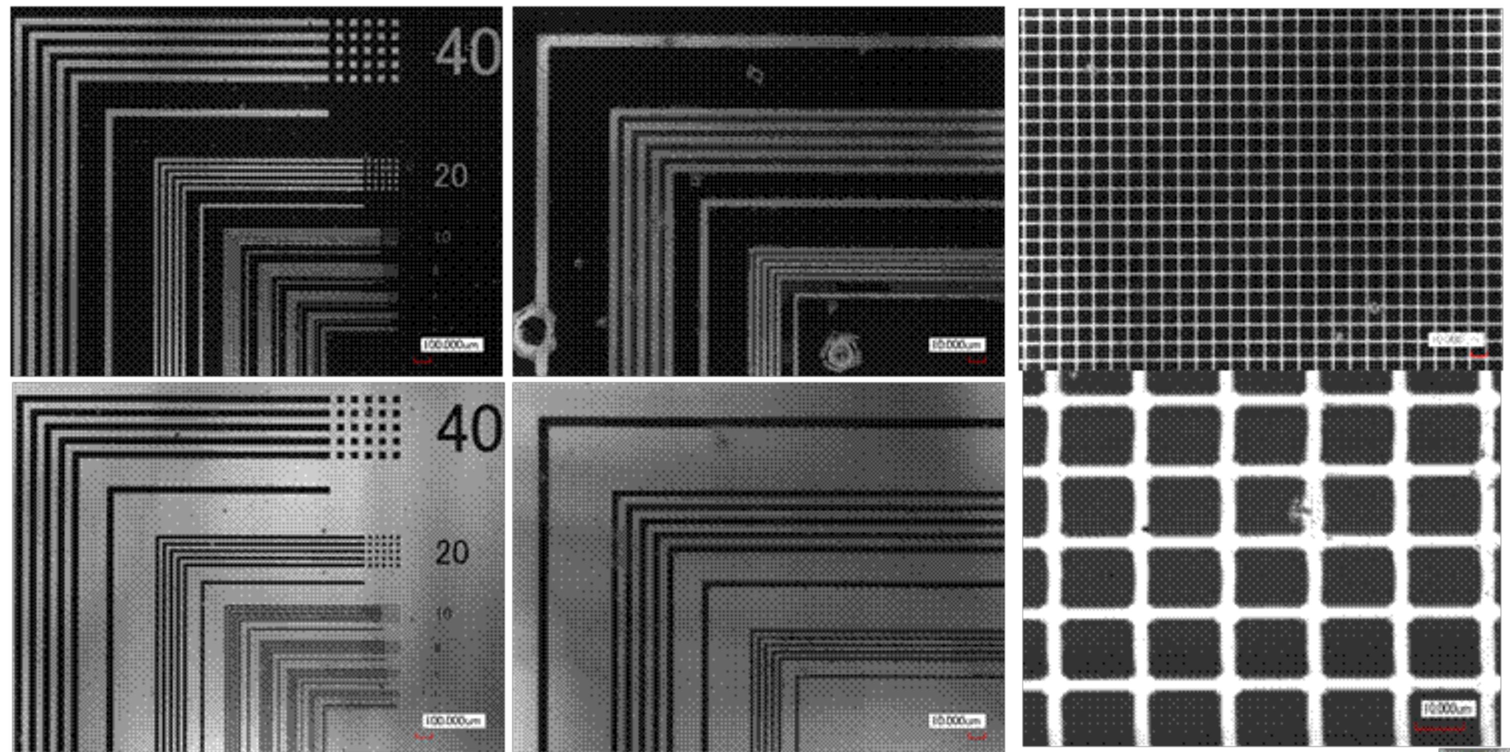
Same process for photolithography

Plating: Cu, Ni, Ag, Au, etc...

Palladium Patterning

L-line/trench & bump/hole: L/S = 2~100 μm on glass

Pd Mesh L/S = 1.5/10 μm

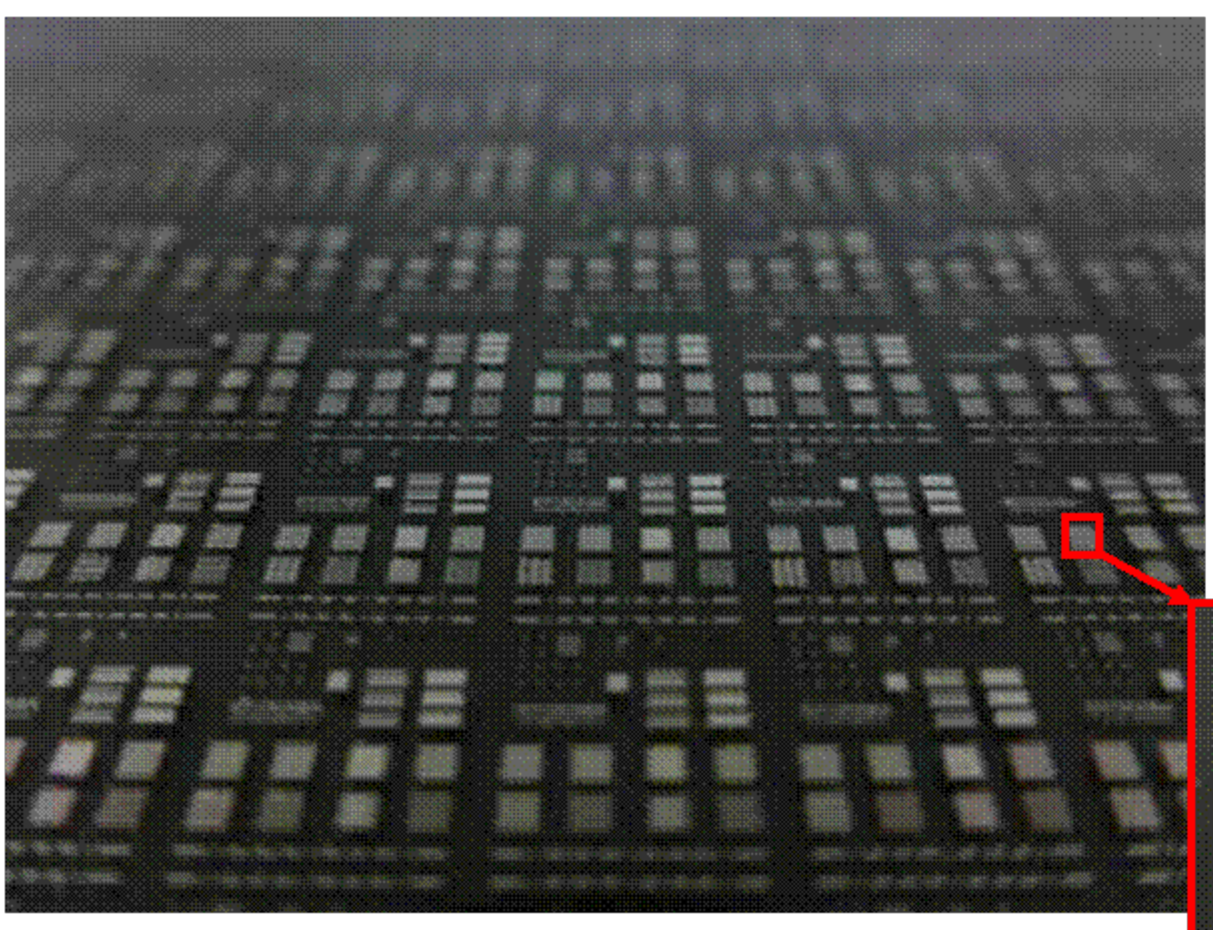


NVOC-Pd → Pd^0 (Positive tone)

☆ *glass, silicon, PC, PEN* ☆

REF: *Langmuir* **2012**, *28*, 13542−13548.

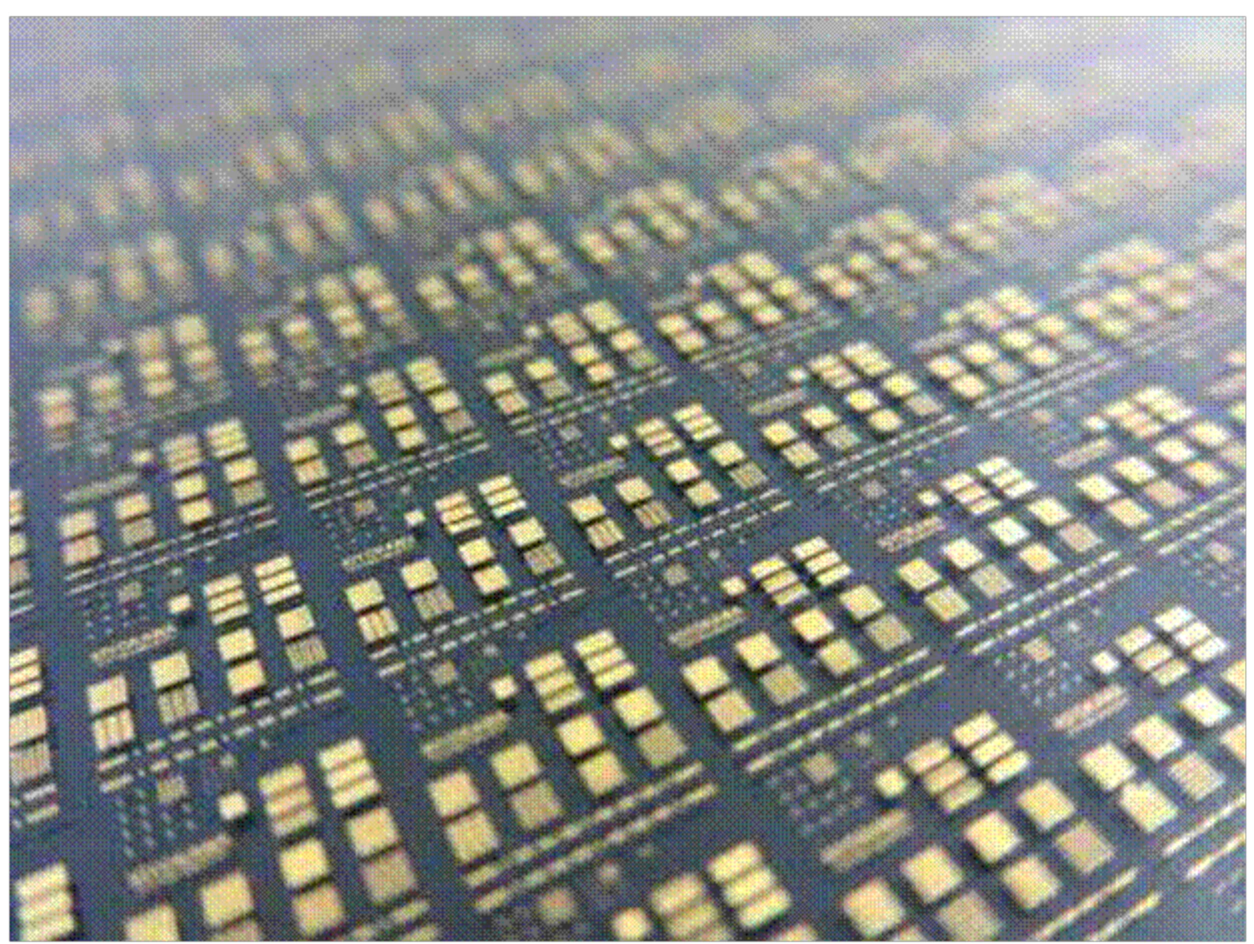
Direct Pattern Ni Plating



Selective nickel plating on TETC73-246A pattern

On display @ Semicon Japan 2012
Dec. 5-7th at Makuhari Messe
by Kiyokawa Plating Industry Co. Ltd.

Direct Pattern ENIG Plating



Selective electroless nickel / immersion gold plating on TETC73-246A pattern

On display @ Semicon Japan 2012
Dec. 5-7th at Makuhari Messe
by Kiyokawa Plating Industry Co. Ltd.

Cu Catalyst Patterning

trench / hole

2 μm

line / bump

2 μm

4 μm

6 μm

4 μm

2 μm

Copper plating on photopatterned copper catalyst on Tempax

Cu Catalyst Patterning

Photopatterned Copper Catalyst (BTC73-250) on 8" wafer

10um/30um

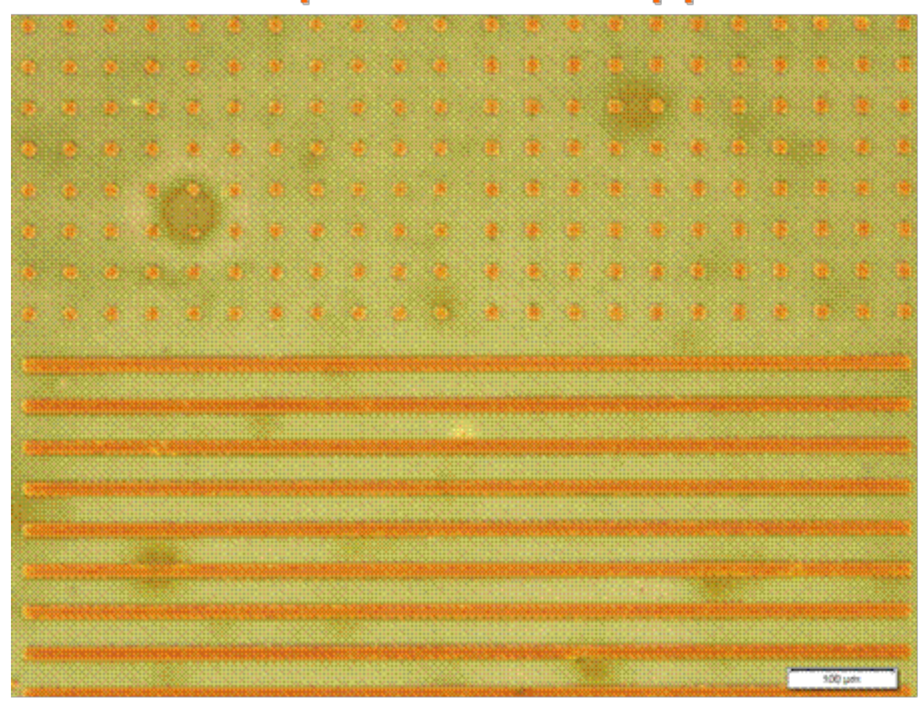
10um/30um

Line / Bump

Trench / Hole

Cu Plating on Cu Catalyst

Selective Electroless Copper (PB-506) on Photopatterned Copper Catalyst (BTC73-250) on 8" Wafer

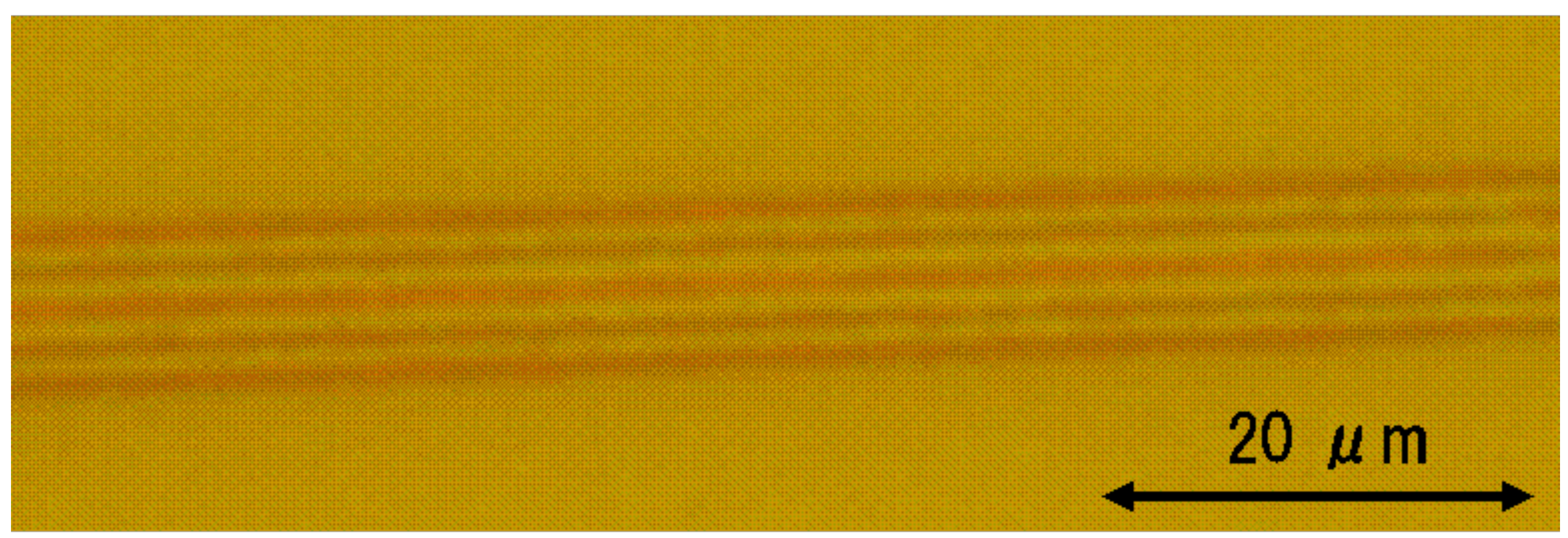


Line / Bump

Trench / Hole

Cu Catalyst Patterning

Selective Electroless Copper on Photopatterned Copper Catalyst

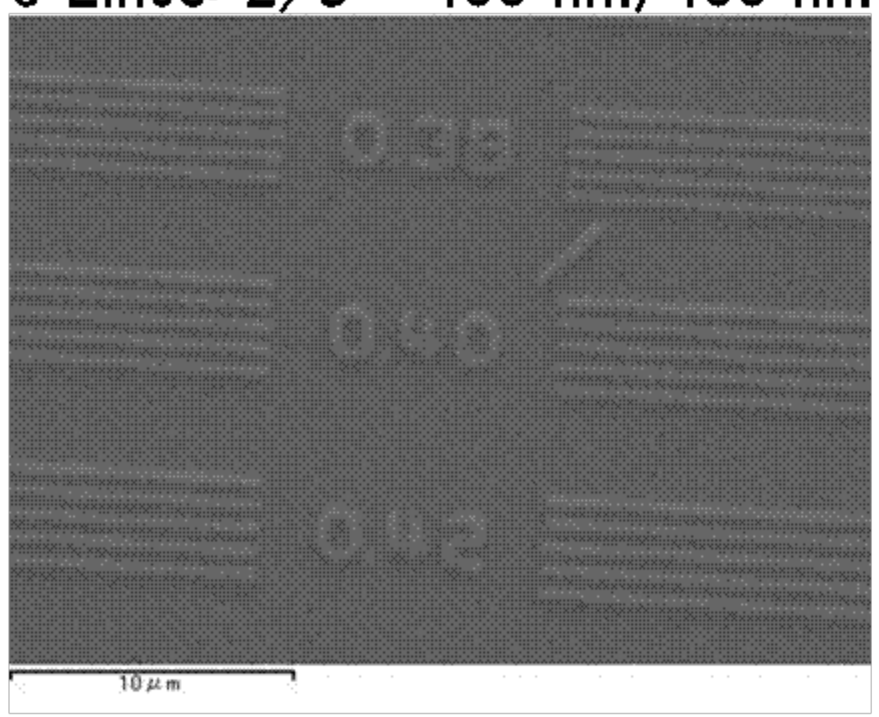


5 Lines: L/S = 1 μm/1 μm

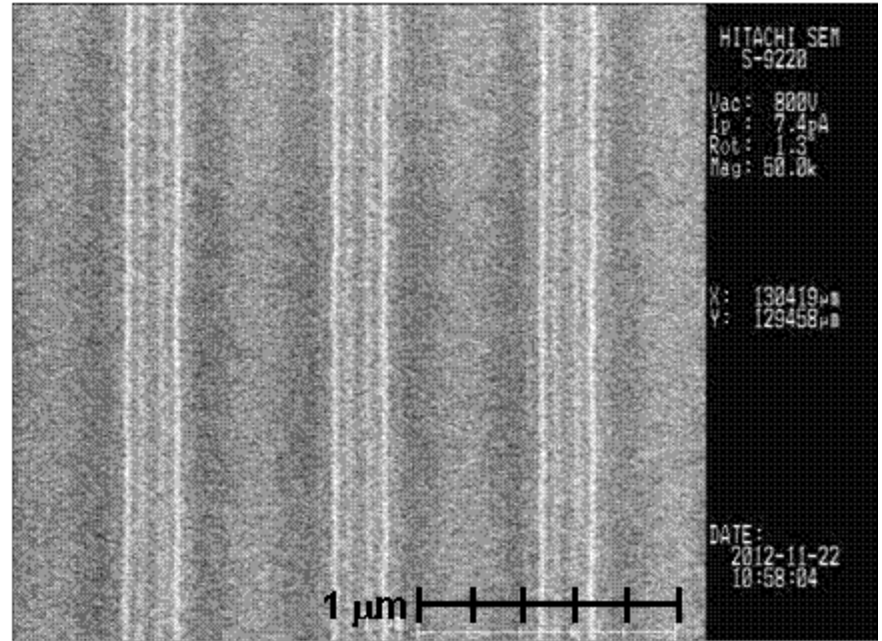
Cu Catalyst Nano-Patterning

Photopatterned Copper Catalyst (TETC73-246A)

5 Lines: *L*/*S* = 400 nm/400 nm



400 nm Line Patterns



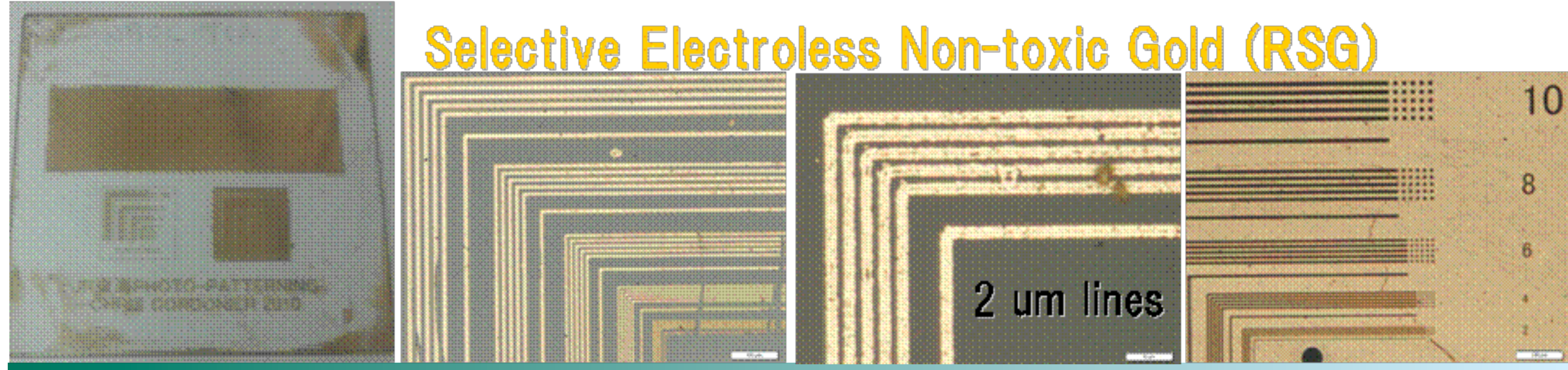
Patterned by
Tokyo Ohka Kogyo

Bio-compatible All-Au Plating

Posi: Line/Bump

Photopatterned Gold Catalyst on Glass or Silicon

Nega: Trench/Hole



Cyanide Free Gold Plating: RSG

Weakly acidic, non-toxic gold plating bath

for medical & bio device fabrication

Characteristics of RSG

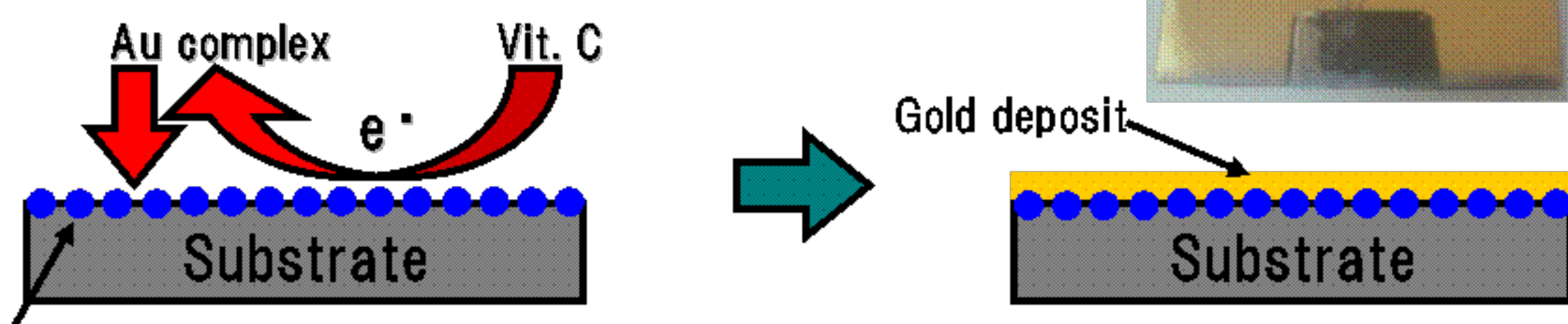
- Can be designed to function without use of toxic, hazardous, or environmentally harmful substances. No use of cyanide.
- Complexants and additives can be selected from amino acids, vitamins, minerals, antibiotics and other pharmaceutical intermediates.
- Reduced by vitamin C.
- Compatible with direct pattern plating methods described here, UV surface modification of resin method described by Koto Electric, with electrolytic reduction, or as immersion gold.
- Can be used over a wide pH range (4–14).
- Still in developmental stage, so deposit characteristics are not yet fully understood.
- Autocatalytic reaction initiation by gold or palladium catalyst.
- Simple gold(I) complex synthesis via sodium tetrachloroaurate(III). Easy isolation in a pure form free of chloride if necessary.
- More stable than gold sulfite baths, & no relation to “lemon gold” baths.

“THE GOLD PLATING SOLUTION YOU CAN DRINK”

Chemical Plating

Plating bath composition/parameters

- Gold(I) complex
- Electrolyte: Potassium Citrate
- Reducing agent: Vitamin C
- Additives: Accelerator (dietary supplement/amino acid), brightener (antibiotic), leveler (food additive), surfactant (food/cleanser additive)
- pH: 4-14
- Temperature: 70-85°C
- Deposition rate: Depends on additives and requirements



Summary

◿ High definition photo-pattern catalyst ⇒ Direct pattern plating

◿ Submicron metal structures (resolution limited by optical equipment) With diffraction patterns; nano level

◿ Dual side & 3D patterning ⇒ Simplified 2-side processes
⇒ Stacked multi-layer structures

◿ Electroless palladium-free copper & bio-compatible all-gold

◿ Plating on smooth surface / smooth interfaces

◿ Fine metal mesh as a transparent conductor (ITO alternative)