

Cu Wiring by Electrodeposition in Supercritical CO₂ Emulsified Electrolyte Using Continuous Flow Reaction System

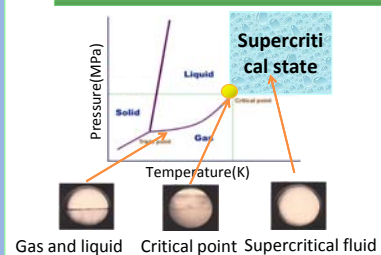


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Introduction

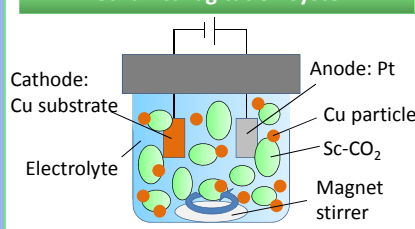
Supercritical carbon dioxide (sc-CO₂)



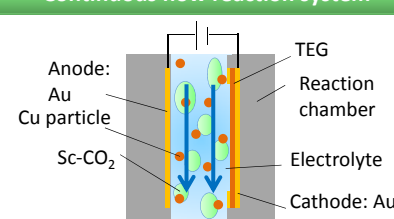
- Advantage**
- Low density
 - Viscosity
 - Surface tension

Improve transfer of materials into micro-structure

Mechanical agitation system



Continuous flow reaction system

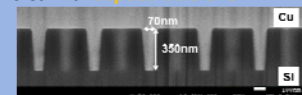


Problem

When applying EP-SCS in nano-scale wiring on large-area hole test element group (TEG).

- Not enough mixing to give homogenization of sc-CO₂ emulsion or suspension

- Not possible to fill 60 nm diameter holes with aspect-ratio of 5

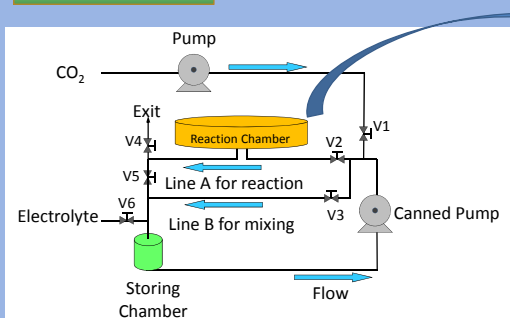


N.Shinoda et al., Microelectro.Eng. 97C, 126, (2012)

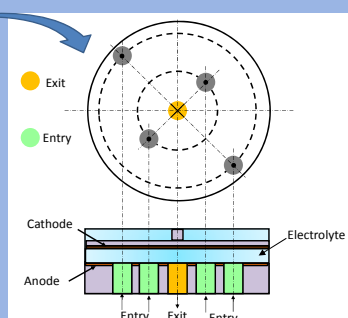
Objectives

- Develop a continuous flow reaction system with improved mixing efficiency for EP-SCS
- Examine the ability to fill Cu into round-type hole TEG by EP-SCS with this continuous flow reaction system

Experimental



Layout of a continuous flow supercritical reactor.
V: high pressure valve.



Layout of a reaction chamber.

Conditions

- Pressure: 15 MPa
- Temperature: 313K
- Current density: 1.41, 2.83, 4.24 A/dm²
- CO₂ volume fraction: 23 vol. %
- Homogenizing time: 10min
- Plating time: 10min

Materials

- Substrate**
- Cathode: 300 mm diameter hole TEG (nano-hole with 60 nm in diameter, 60 nm depth or 120 nm depth)
 - Anode: Au

Electrolyte

- CuSO₄·5H₂O (0.85 mol/L)
- H₂SO₄ (0.55 mol/L)

Pretreatment

- Degreasing solution (NaOH 10 wt. %) for 1min
- HCl 10 wt. % for 10sec

Additives

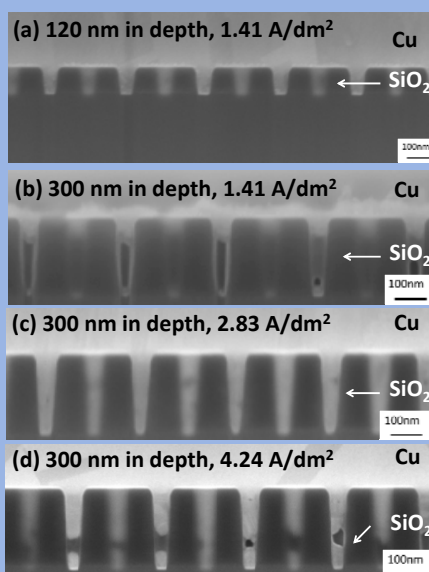
- Polyethylene glycol (100 mmol/L)
- Janus green B (29.4 mmol/L)
- bis(3-sulfopropyl)disulfide (21 mmol/L)
- Cl⁻ (NaCl) (1.7 mmol/L)
- Cu particles: 1.7g/L (for EP-SCS)
- Surfactant (for EP-SCE and EP-SCS) (C₁₂H₂₅(OCH₂CH₂)₁₅OH 1.0 vol. % with electrolyte)

Results and discussion

Photograph of plated Cu on hole TEG		
Applied current density	1.41 A/dm ²	2.83 A/dm ²
Plate area	50%	>95%
Thickness	thin	thick
Brightness	—	Bright

Photographic images of 300 mm diameter round-type hole TEG electroplated Cu by EP-SCS with continuous flow reaction system.

Current density value of 2.83 A/dm² is enough for Cu plating.



Cross sectional SEM images of electroplated Cu filled in ϕ 60 nm holes on 300 mm diameter substrate by EP-SCS.

Complete filling of all the holes with electrodeposited Cu was observed without voids

- At current density of 2.83 A/dm², complete Cu filling into 60 nm diameter holes was observed.

- At current density of 4.24 A/dm², the incomplete filling was obtained because of complete covering of Cu on substrate.

Conclusions

- In order to apply EP-SCS in nano-scale wiring of 300 mm diameter round substrate, a continuous flow reaction system was developed.
- 60 nm diameter holes with aspect ratio of 2 and 5 on 300 mm diameter round-type hole TEG were completely filled at current density of 2.83 A/dm².
- The round-type hole TEG was mostly coated by bright Cu and all of the holes were filled by Cu without any voids using EP-SCS.

Acknowledgement

This work was supported by Funding Program for Next Generation World-leading Researchers (NEXT Program), Cabinet Office (CAO), JAPAN and by New Energy Development Organization (NEDO), Japan.