Novel Cu electroplating using suspension of supercritical carbon dioxide in copper-sulfate-based electrolyte with Cu particles

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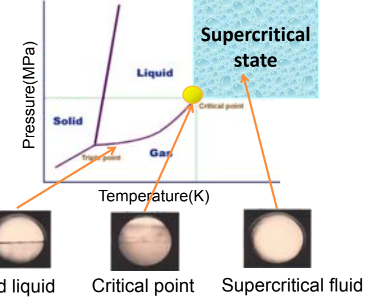
Introduction

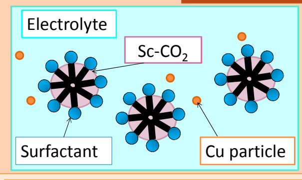
Supercritical carbon dioxide (Sc-CO_2)



Low viscosity & zero surface tension

Enhance transport of reactants to confined geometries

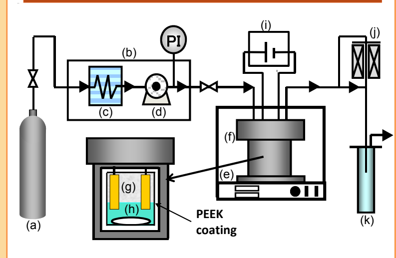
Sc-CO_2 suspension



- Sc-CO_2 is non-polar → Make the emulsion
- Desorption of H_2 from cathode → Void- and pinhole-free
- Cu particles in the emulsion → **Make the suspension**

Experimental Procedures

High pressure apparatus



(a)CO_2 gas tank, (b)CO_2 liquidization unit, (c)liquidization unit, (d)high pressure pump, (e)thermal bath, (f)reaction cell (SUS316L) with PEEK coating inside, (g)substrate, (h)cross stirrer, (i)power supply, (j)back pressure regulator, (k)trap

Materials

Substrate
- Cathode : Cu substrate or hole test element group (TEG) (TiN barrier layer and Cu seed layer spattered on Si substrate)
- Anode : Pt

Electrolyte
- $CuSO_4\cdot 5H_2O$ (0.85 mol/L)
- H_2SO_4 (0.55 mol/L)
- Additive : Top Lucina α-M, α-1, α-2, Cl^-
- Average size of Cu pariticles : 63 μm

Surfactant
- Polyoxyethylene lauryl ether ($C_{12}H_{25}(OCH_2CH_2)_{15}OH$) 1.0 vol% with respect to volume of electrolyte

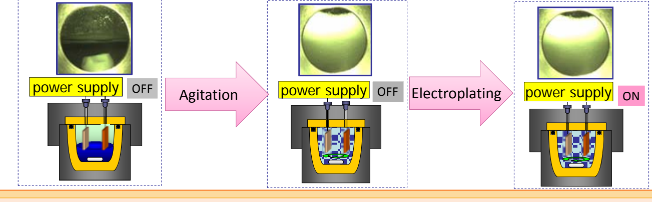
Condition

- Pressure: 15 MPa
- Temperature: 323 K
- Current density: 1.0 A/dm^2

Pretreatments

- Degreasing solution (Ace clean, Okuno) for 1 min
- 10 wt% H_2SO_4 for 10 sec

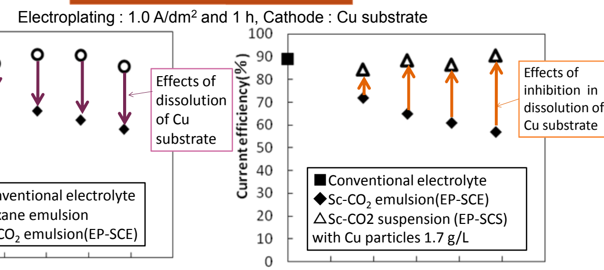
Electroplating using sc-CO_2 suspension (EP-SCS) method



Results and Discussion

Current efficiency

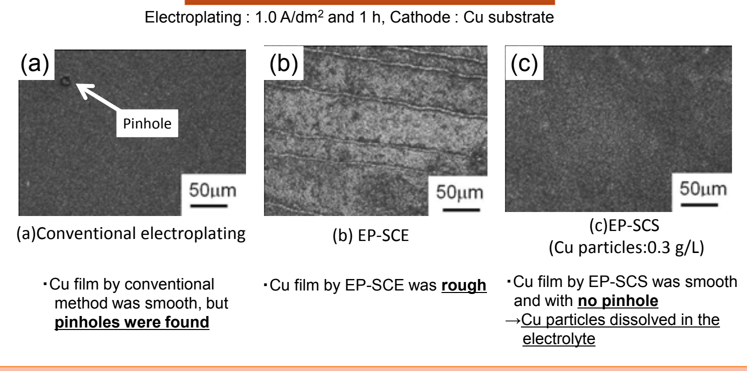
Electroplating : 1.0 A/dm^2 and 1 h, Cathode : Cu substrate



- Current efficiency of sc-CO_2 emulsion (EP-SCE) was lower than hexane emulsion → Cu substrate dissolved in sc-CO_2 emulsion
- Current efficiency of EP-SCS was higher than sc-CO_2 emulsion → Cu particles inhibited dissolution of Cu substrate

Morphology of Cu films

Electroplating : 1.0 A/dm^2 and 1 h, Cathode : Cu substrate



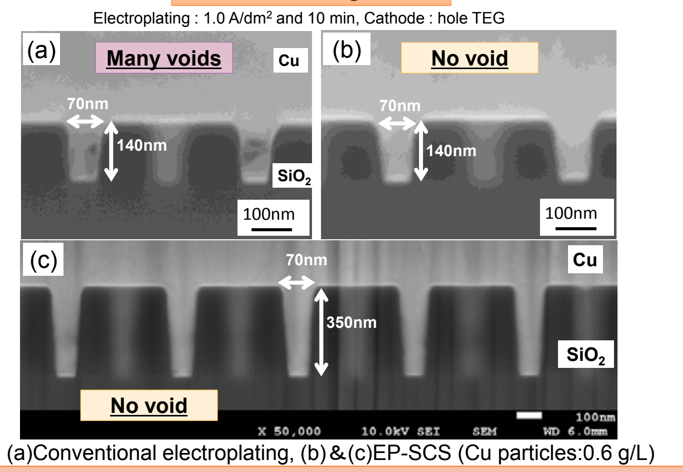
(a)Conventional electroplating (b) EP-SCE (c)EP-SCS (Cu particles:0.3 g/L)

- Cu film by conventional method was smooth, but **pinholes were found**
- Cu film by EP-SCE was **rough**
- Cu film by EP-SCS was smooth and with **no pinhole** → Cu particles dissolved in the electrolyte

Filling of Cu into nanoscale holes

SEM image

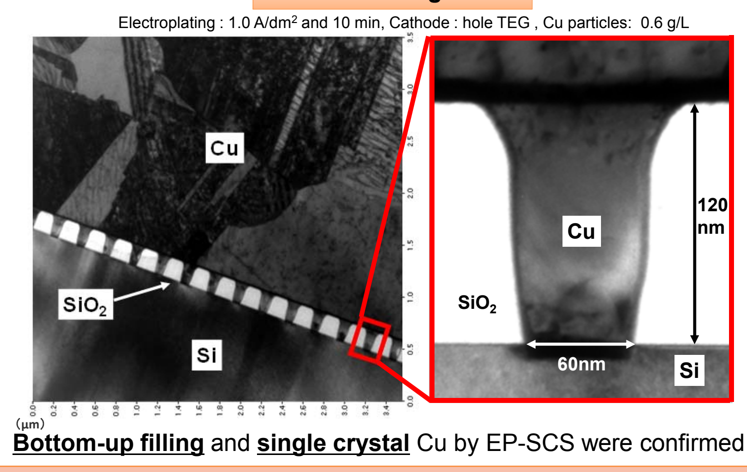
Electroplating : 1.0 A/dm^2 and 10 min, Cathode : hole TEG



(a)Conventional electroplating, (b)&(c)EP-SCS (Cu particles:0.6 g/L)

TEM image

Electroplating : 1.0 A/dm^2 and 10 min, Cathode : hole TEG , Cu particles: 0.6 g/L



Bottom-up filling and **single crystal** Cu by EP-SCS were confirmed

Conclusions

- We proposed a novel Cu electroplating method using sc-CO_2 suspension (EP-SCS) for filling of nanoscale holes.
- Current efficiency was increased by addition of Cu particles to inhibit dissolution of Cu substrate in EP-SCS.
- The Cu film by EP-SCS was smooth, because Cu particles dissolved in the electrolyte.
- Nanoscale holes with 70 nm in diameter and aspect ratios of 2 and 5 could be filled by electrodeposited Cu with no void.
- Bottom-up filled Cu was found to be single crystal in all holes with 60 nm in diameter and aspect ratio of 2.

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