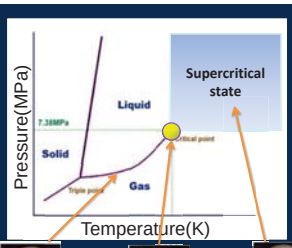
Mechanical Strength of Cu Electroplated in Supercritical CO_2 Emulsion Using Micro-Compression Test

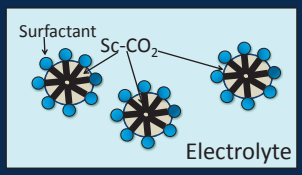
Hikaru Kinashi, Takashi Nagoshi, Tso-Fu Mark Chang , Tatsuo Sato, Masato Sone

Precision and Intelligence Laboratory, Tokyo Institute of Technology, Japan

Introduction



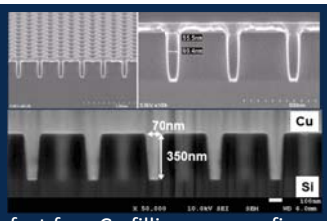
Electroplating with sc-CO_2 emulsion (EP-SCE)



Advantage of sc-CO_2 emulsion

- **Low viscosity (high diffusivity)**
- **Non-polar, such as compatibility of H_2**

We applied this sc-CO_2 emulsion to electrochemical reaction field



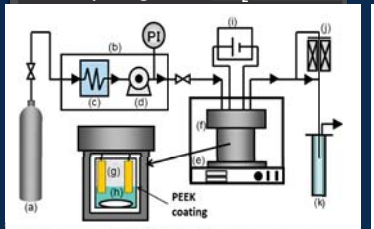
Defect free Cu filling was confirmed[1]

In this study,
we investigated mechanical property of Cu film obtained by this novel method

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

Experimental procedure

1. Electroplating with sc-CO_2 emulsion



(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
- Anode : Pt

Electrolyte
- $CuSO_4 \cdot 5H_2O$ (0.85mol/L)
- H_2SO_4 (0.55mol/L)
- Additive : Top Lucina α-M, α-1, α-2, Cl^-
- CO_2 40 vol.%

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

Condition

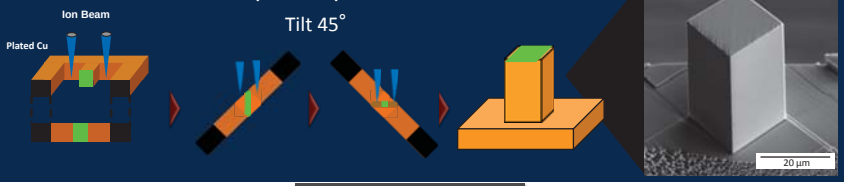
- Pressure: 15 MPa
- Temperature: 313 K
- Current density: 2.0 A/dm²

Pretreatment

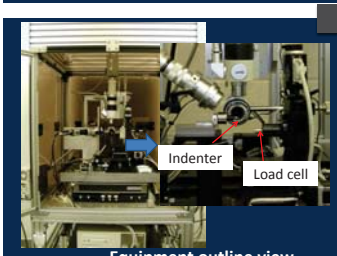
- Degreasing solution (NaOH 10 wt%) for 1min
- HCl 10 wt% for 10 sec

2. The processing method using FIB

How to make non-taper Cu pillar



3. Compression test



Equipment outline view

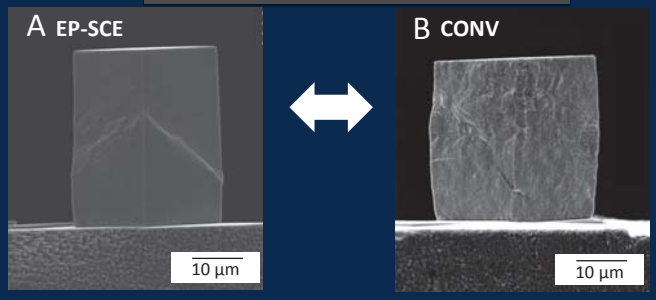
Sample size
20×20×40 (μm)

Machine spec

Load resolution	Displacement resolution	x-y minimum step	Control	Strain rate
10 [μN]	5 [nm]	0.1 [μm]	Displacement rate	0.0025 [/s]

Results and discussion

1. SEM image of Cu pillar after compression test



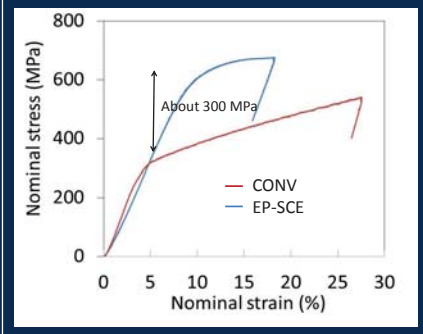
- Shear band was observed for EP-SCE

Reduced work hardening due to grain refinement ➡ Localized deformation

CONV: Conventional electroplating

2. Compression test result of Cu micro-pillar

- Stress-Strain curve of Cu micro-pillar



Cu micro-pillar of EP-SCE, showed higher nominal stress than that of CONV

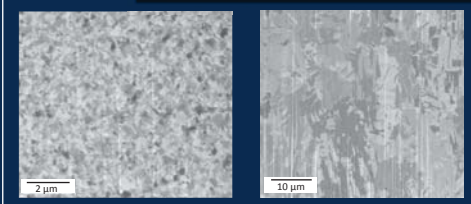
✚

Work hardening was hardly seen

The following can be considered as a material strengthening mechanism

- Grain refinement strengthening
- Solute strengthening

3. SIM image of Cu electroplated film and Hall-Petch relationship



A: EP-SCE — **Grain size: about 0.1 μm**

B: CONV — **Grain size: about 1 μm**

The grain size of film obtained EP-SCE became fine grain

Considering Hall-Petch relationship,

σ_y : Yield stress,
σ_f : Friction stress
k: material constant,
d: grain size

$$\sigma_y = \sigma_f + \frac{k}{\sqrt{d}}$$

k (MPa·$m^{0.5}$)=0.14 *

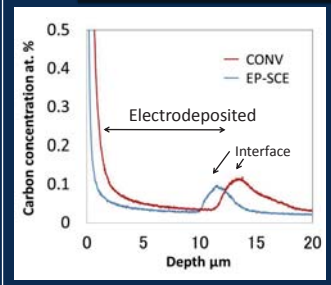
If average grain size decrease from 1 to 0.1 μm,

$\Delta\sigma_y \fallingdotseq 300$ MPa

Good agreement with experimental result

* Hansen. N. Scripta Materialia 51 (2004) 801–806.

4. Carbon concentration of electrodeposited Cu film by GDOES



Theoretical film thickness, about 12 μm

1. Before electroplating
   - The additives adsorbed to cathode surface
2. During electroplating
   - carbon was co-deposited with Cu
3. After electroplating
   - carbon diffusion from interface to substrate and film

No significant difference in carbon content between EP-SCE and CONV

Conclusion

- Compression tests of Cu micro-pillars obtained by EP-SCE and CONV were conducted, and EP-SCE case showed higher nominal stress.
- Grain size of film obtained EP-SCE was finer than the case of CONV and the increase in the strength by this plating method was explained by Hall-Petch relationship.
- No significant difference in carbon content between EP-SCE and CONV.

Acknowledgement

The authors acknowledge Japan Copper & Brass Association (JCBA) and Funding program of NEXT program, Cabinet Office (CAO), Japan.