Polymer-Ceramic Powder Composite Embedded Capacitor Materials for Organic Substrates Applications

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(KAIST)

Epoxy/$BaTiO_3$ ($SrTiO_3$) Composite Films for High Dielectric Constant and Low Tolerance Embedded Capacitors in Organic Substrates

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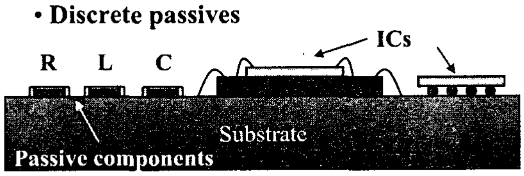
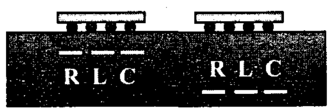
Embedded Passives

■ Embedded Passives

• **Discrete passives**



• **Embedded passives**



■ Advantages of Embedded Passives

• Smaller area • Shorter interconnection length • Less solder joints	⇨	• Miniaturization • Higher electrical performance • Better reliability

■ Embedded capacitors

- 40% of total passive components
- Important roles in electronic circuits – decoupling, bypass, etc.
- Thin film or thick film materials

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Overview of Commercial Capacitor Technology

Embedded passive materials

- **Paraelectrics**
- **Ferroelectrics**

Unfilled polymers

- Sanmina
  - ZBC 2000
- Oak Mitsui
  - FaradFlex™
- Gould
  - TCC

Ferroelectric-filled polymers

- Motorla-vantico
  - ProbelecTM 81 CFP
  - Mezzanine Cs
- 3M
  - C Ply
- DuPont
  - Interra HK10
  - Interra EP410

Thick/thin film

- Shipley
  - Insite™
- DuPont
  - Interra EP310
- Motorola
  - Gen3 Capacitor

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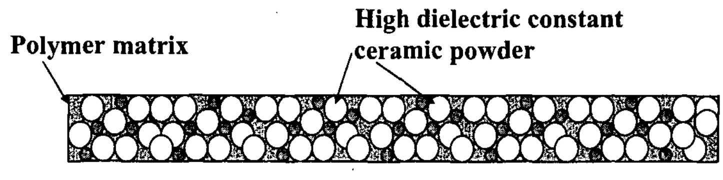
Why polymer/ceramic composite materials?

Polymer: **Good processability (T) and Low cost**

\+

Ceramic powder: **High dielectric constant**



- **Polymer: Epoxy (compatible with PCB), Polyimide, PVDF**
- **Ceramic powder: $BaTiO_3$, $SrTiO_3$, $Pb(Mg,Nb)O_3$-$PbTiO_3$, BST**

■ **Epoxy/$BaTiO_3$ & $SrTiO_3$ composites**

- **$BaTiO_3$ & $SrTiO_3$: well-known and commercially available high dielectric constant and low-Q ceramic powders**
- **Epoxy: compatible with PCB**

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Demands of new embedded capacitor materials

■ Requirements for embedded capacitor materials

- High dielectric constant
- Low tolerance (< ±5%) of capacitance
- Processability
- Low cost

$$\frac{C}{A} = \varepsilon_0 \varepsilon_r \frac{1}{d}$$

■ Desirable characteristics of embedded capacitor materials

- No materials waste
- Uniform thickness → low tolerance of capacitance
- B-stage film → long shelf life
- Transferable films or pastes → capacitors fabrication on selected areas

Advanced embedded capacitor materials is needed!!

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Epoxy/$BaTiO_3$ (& $SrTiO_3$) Composite Embedded Capacitor Films (ECFs)

Material Formulation for ECFs

Materials: $BaTiO_3$, $SrTiO_3$ powder, epoxy resin, curing agent, dispersant, solvent

❖ **Ceramic powder**

➢ $BaTiO_3$: high dielectric constant

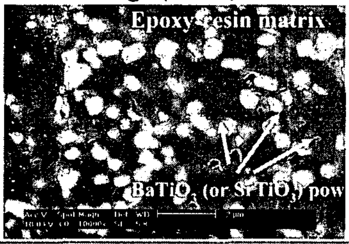
➢ $SrTiO_3$: low loss & stable frequency dependence

❖ **Specially formulated epoxy resin**

➢ Epoxy

➢ Good compatiblity with PCB & processability in B-stage (not cured at film stage)

❖ **X-section image (ECFs)**

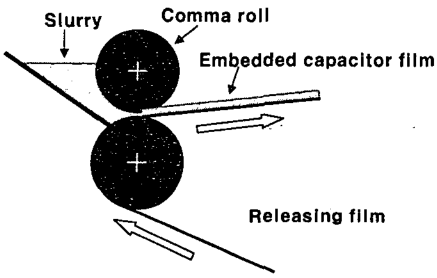


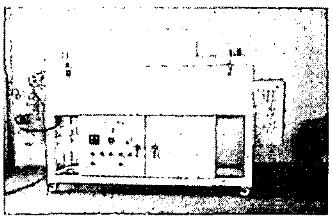
- **BT powder, dispersant, solvent mixing**
- **Ultrasonic & ball milling**
- **Polymer resin & curing agent mixing**
- **Ball milling**
- **Film coating on releasing film or metal foil**
- **Solvent drying**

ECF Film Formation Methods

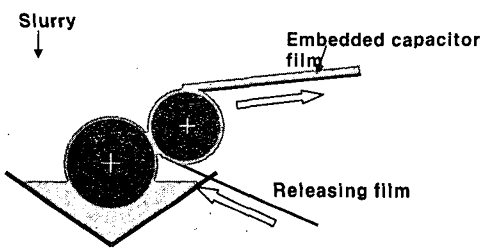
❖ **Two film coating methods**

- **Comma roll (Film thickness >10um)**

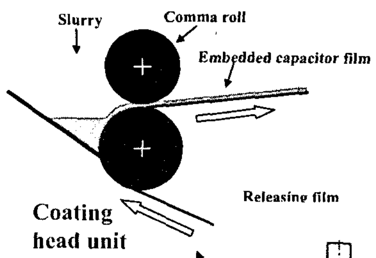




- **Gravure roll (Film thickness < 10um)**



Coating Processes Using a Roll Coating Method

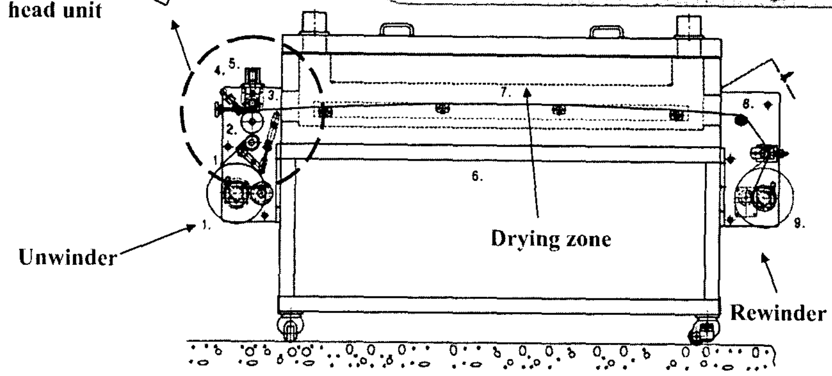


❖ **Film formation process**

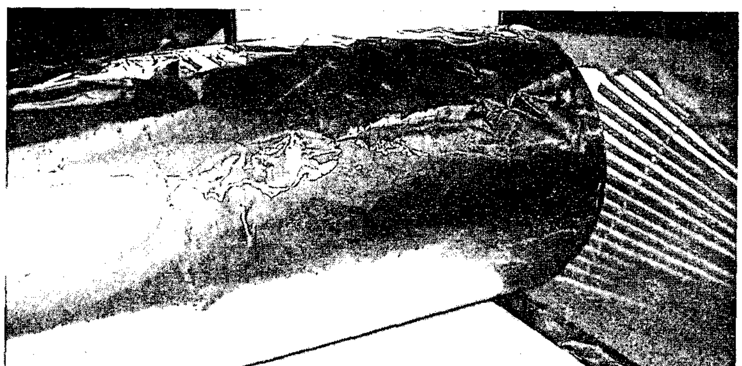
○ Roll coating on a releasing film or Cu foil

- ➢ Uniform thickness coating (>10μm)
- ➢ Large area & continuous coating
- ➢ No waste & low cost

(Relative with spin coating)



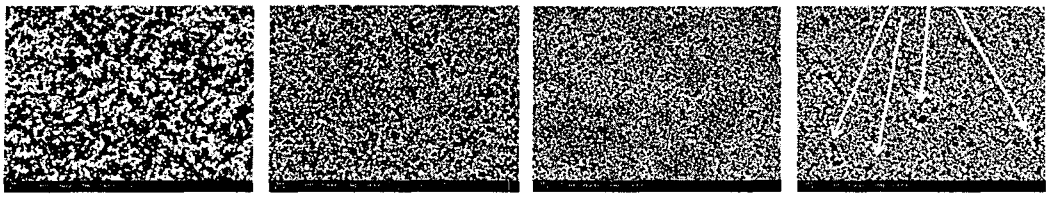
ECFs coated on a copper foil



ECF surface morphology (Comma roll coated)

- **Unimodal**

voids

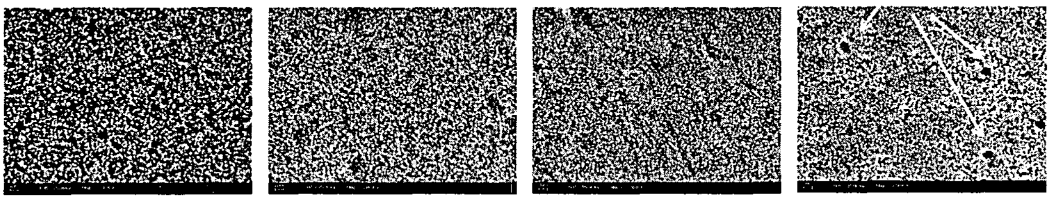


40 vol% **60 vol%** **73 vol%** **80 vol%**

density increase → **density decrease** →

- **Bimodal**

voids

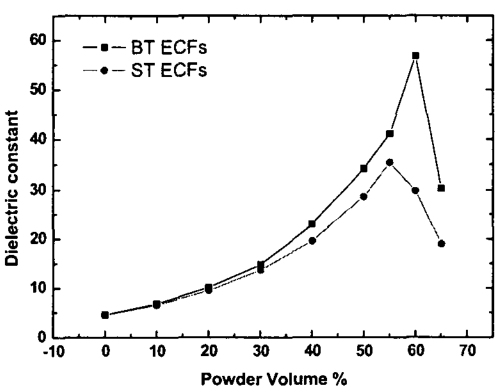


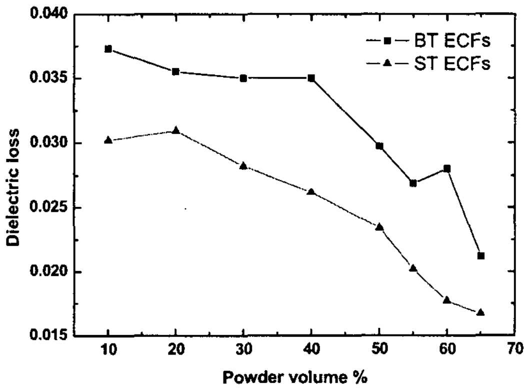
60 vol% **73 vol%** **80 vol%** **85 vol%**

Dielectric Constant & Dielectric Loss

◆ Measurement condition

- Level 1V, frequency 100kHz
- Equipment: HP4284A LCR meter



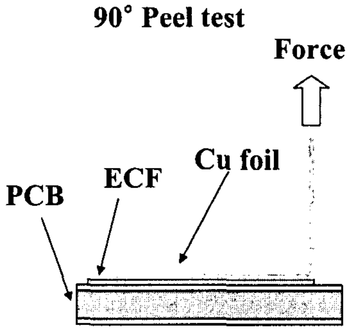


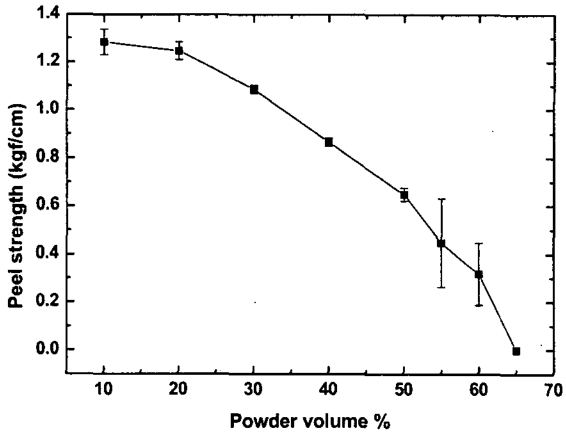
- **Dielectric constant increased with powder content.**
- **Epoxy/$SrTiO_3$ composite shows lower dielectric constant and lower loss than epoxy/$BaTiO_3$.**

ECF Adhesion Strength on Cu Foils

◆ Measurement condition

- Peel speed : 10mm/cm
- Equipment: tensile tester (Ck trade ©)



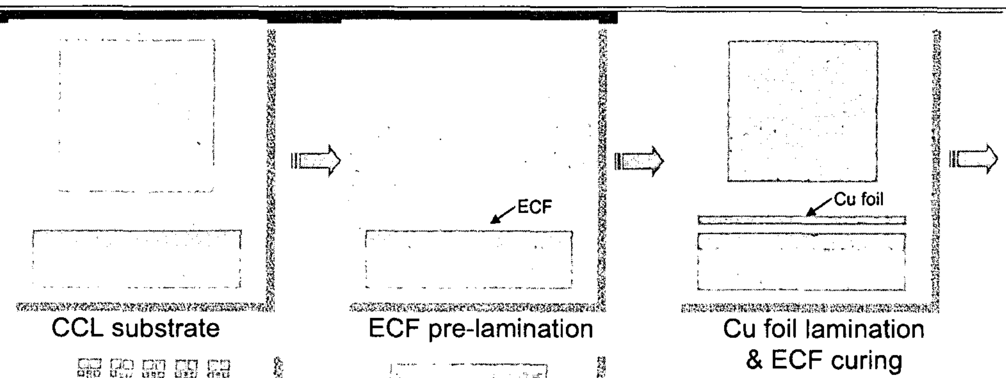


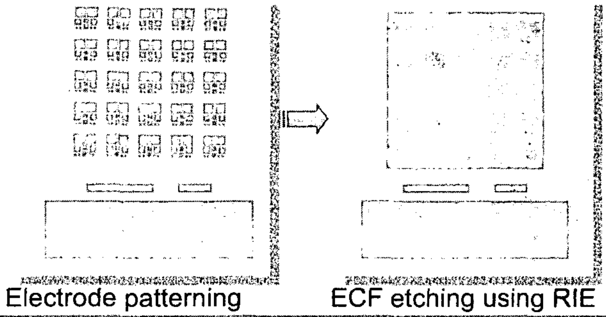
➢ Interface adhesion strength between ECF and Cu foil

➢ Smooth surface of Cu foil was used.

➢ Thickness: Cu foil-18μm, ECF- 10~20μm

Capacitors fabrication processes of ECFs coated on a PET film



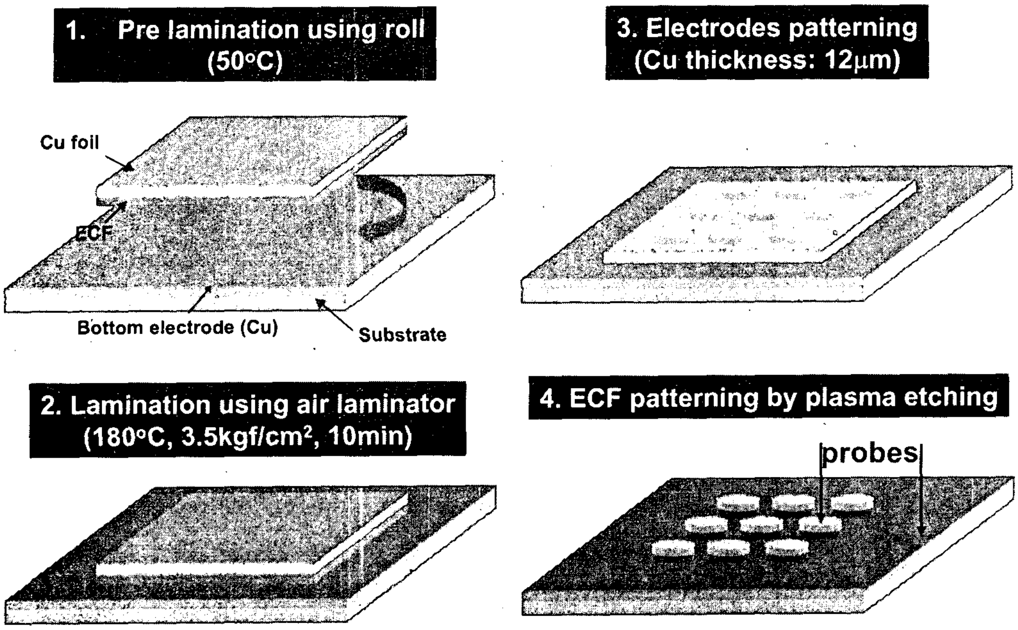


< Dielectric properties>

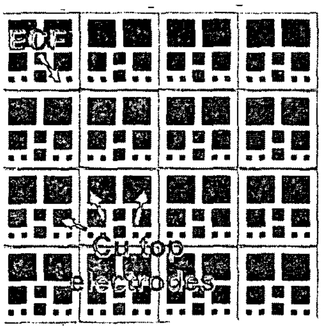
Avg. Cap.	337.4 pF
S.D.	8.85 pF
Tolerance(3σ)	7.87
Avg. loss	0.016

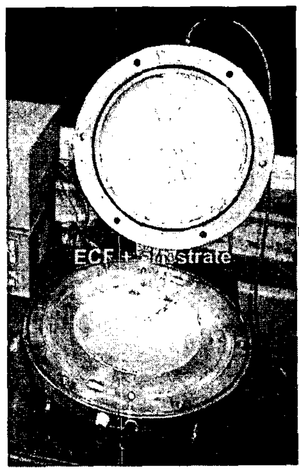
(4 mm square, 60개 기준)

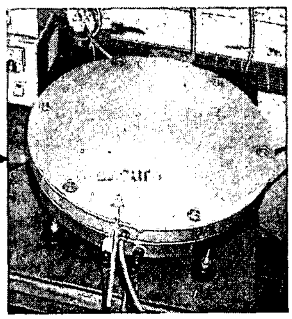
Capacitors fabrication processes of ECFs coated on a copper foil



❖ **Laminator**

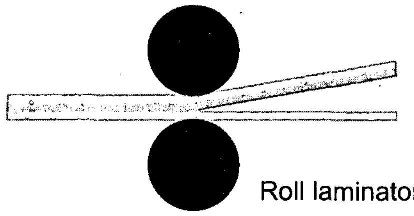






ECF Lamination Process & Properties

- ➢ Pre roll lamination & Air lamination
  - ✓ Pre roll lamination condition
    - • T = ~50°C
    - •Air lamination in vacuum
- ➢ ECFs properties in various size capacitor



Roll laminator

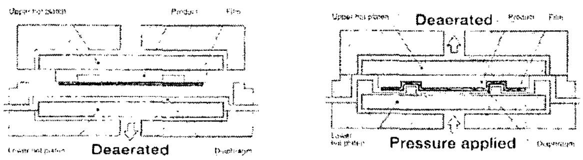
Capacitor size (mm)	4.5 x 4.5	3 x 3	2 x 2	1 x 1
Capacitance (pF)	528.4	238.4	107.9	29.0
Dielectric loss	0.0151	0.0154	0.0159	0.0175
Standard deviation of capacitance	11.32	5.41	2.77	1.05
Tolerance (3σ)	6.43	6.80	7.69	10.81

◆ Measurement condition
- Temp. = R.T.
- Frequency = 100kHz
- Sample size = ($12x12cm^2$) x 2
- # of sample : (4.5x4.5, 3x3, 2x2 64 dot), (1x1 128 dot)

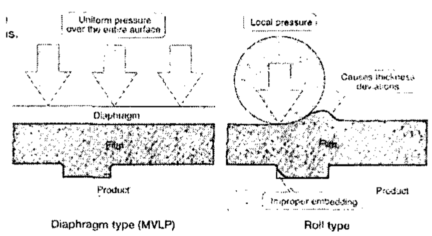
Tolerance much better than the ECF coated on a releasing film!

Vacuum Laminated ECF

- **Vacuum lamination method**



- **Comparison btw. Vacuum and roll lamination type**



- Vacuum lamination process
  - ✓ Pre-lamination in 80°C (at SEMCO, vacuum method)
  - ✓ Lamination in 180°C (at KAIST, conventional method)

Properties	Capacitance tolerance (3σ)
Conventional laminated (coated on releasing films)	±8.39% ($0.2025cm^2$) ±11.55% ($0.01cm^2$)
Conventional laminated (coated on Cu foil)	±7.76% ($0.2025cm^2$) ±10.03% ($0.01cm^2$)
Vacuum laminated (coated on releasing films)	±3.57% ($0.2025cm^2$) ±9.49% ($0.01cm^2$)
Vacuum laminated (coated on Cu foils)	±4.04% ($0.2025cm^2$) ±7.89% ($0.01cm^2$)

- **Capacitance tolerance**
  - ✓ **Vacuum laminated type < Roll laminated type**
  - ✓ **ECFs coated on Cu foils < coated on releasing films**

(# of samples : 92)

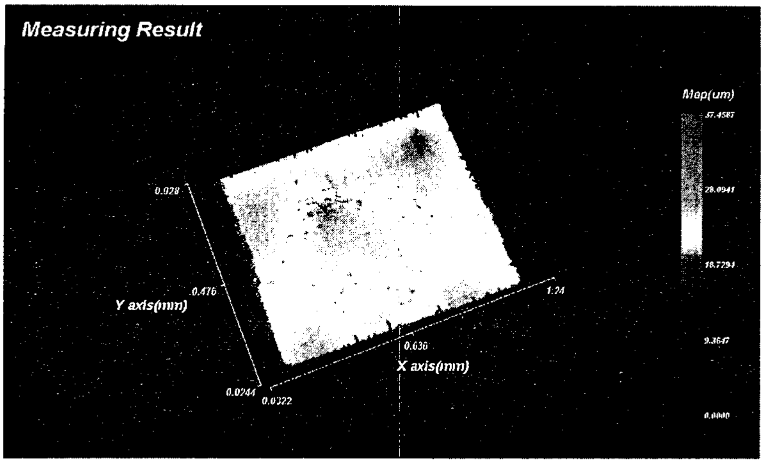
Metal electrode area tolerance -White-Light Scanning Interferometer

- **Measurement of electrode morphology**

✓ **Equipment : WSI (White-light Scanning Interferometer) in BUPE.**

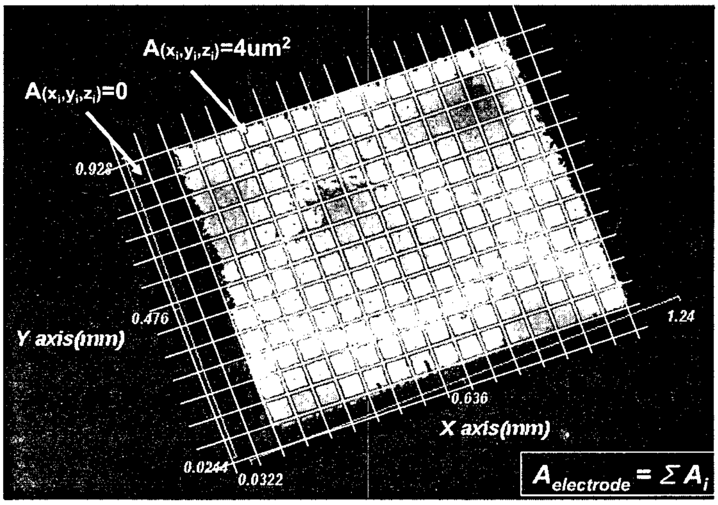
✓ **CCD scale : 640x480 pixel, x5, resolution : few nm in z-axis**

✓ **Test sample must be reflective.**

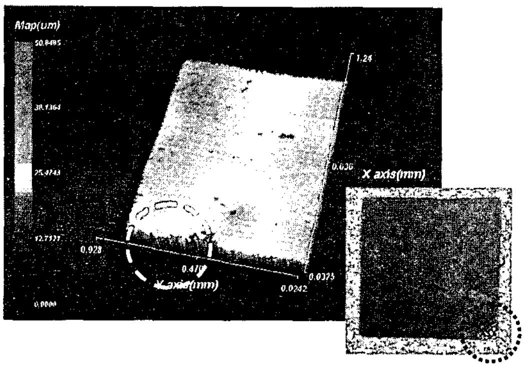


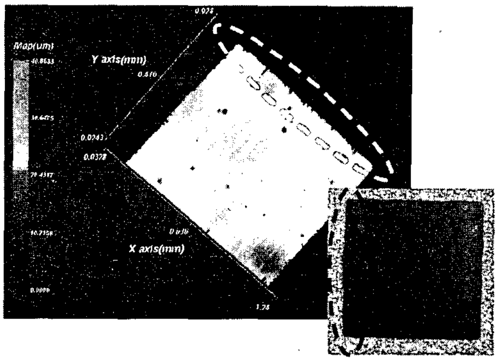
Calculation of Top Electrode Area

- **RIE treated Cu had very low reflective index.**
- **Test samples were coated by 0.5um Cu using sputtering.**
- **Measured sample : 1x1mm^2 Cu electrode, # of samples : 92**



Tolerance of Top Electrode Area





# of samples : 10 of 92

✓ <u>Area tolerance of Cu electrode T_{area} = ±2.98% ($A_{average}$: 1.0497mm^2)</u>

✓ ECFs thickness tolerance $T_{thickness}$ = ±1.74%

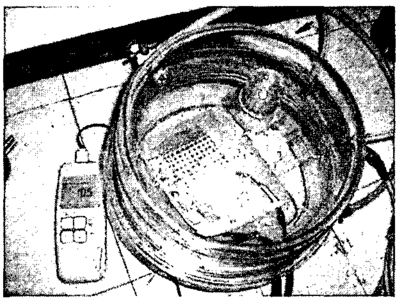
➔ **T_{total} = T_{area} x $T_{thickness}$ = 6.33% (Measured tolerance : 7.89%)**

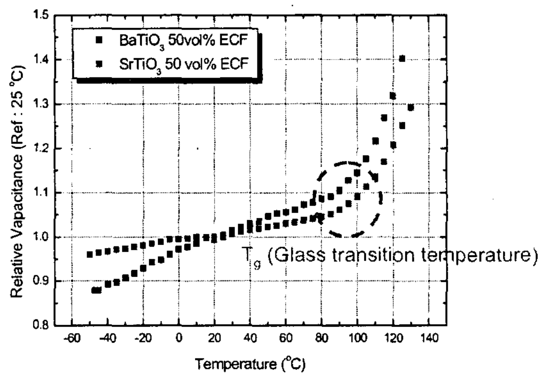
➢ Capacitance tolerance of ECFs was mainly determined by tolerance of electrode area, ECFs thickness, materials, and Cu surface roughness.

Temperature dependency of ECF capacitors

❖ Conventional ECFs

- Using thermo-electronic device, ECFs capacitor was heated and cooled.

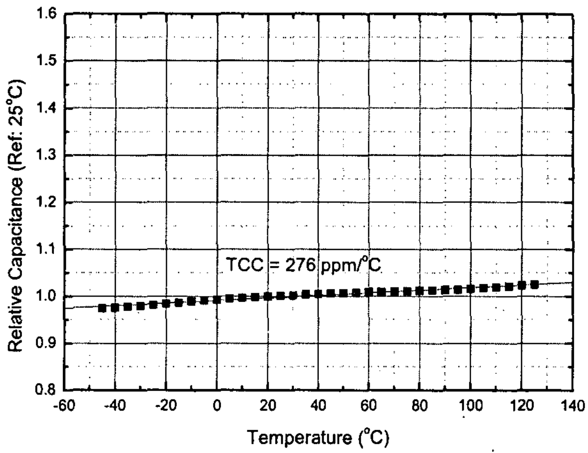




➢ **Requirements of cap. change for passive components (X7R, 'muRata co.') : 15% at -50°C ~ 125°C**

TCC of modified ECF capacitor

❖ Modified ECF capacitor
- Modified High Tg epoxy resin & $SrTiO_3$ powder were used
  - $SrTiO_3$ 50 vol% ECFs



Characterization of Materials for Gravure coating – TP & Solvents Contents

❖ Thermo-plastic resin contents

TP content (vol%)	40 (conventional)	45	50	60
Film forming capability	Only comma coating	Only comma coating	Only comma coating	Gravure available
Viscosity (Pas)	0.219	0.322	0.376	0.614

✓ **BT powder contents : 50vol%**
✓ **New Solvents – less volatile solvent**

❖ Solvent contents

Solvent content (cc)	12	14	16	18
Thickness (μm)	ECF not soluble	3.2	3.16	ECF not coated

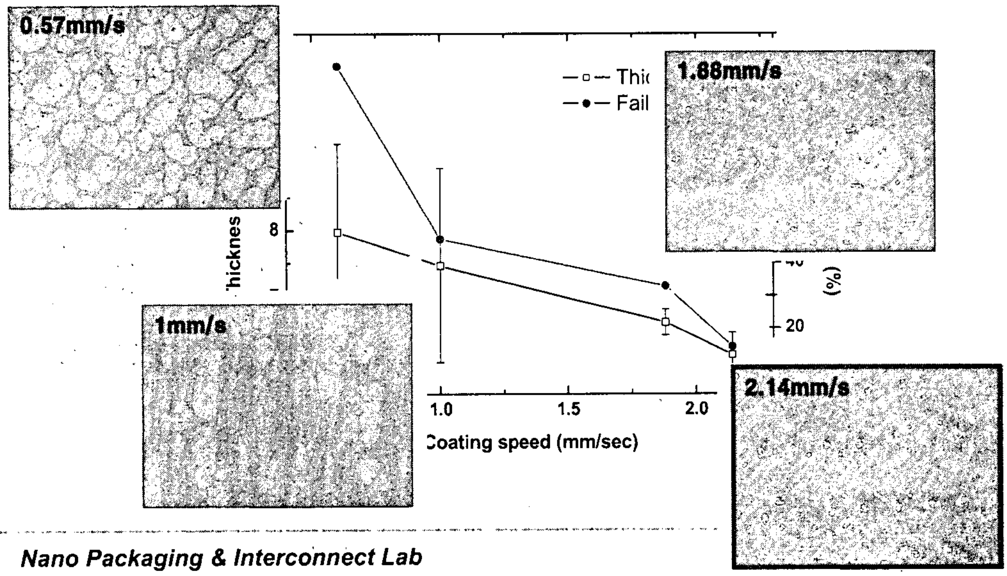
(Solution 10cc 기준)

✓ **BT powder contents : 50vol%**
✓ **Thermo-plastic resin: 60vol%**
✓ **Gravure coating**

Characterization of Materials – Coating Speed

❖ Gravure coating speed

➤ **Coating speed : 2.14mm/s**

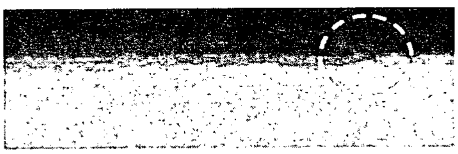


Characteristics of Comma & Gravure Coated ECFs (on a PET releasing film)

❖ Failure reason of the Gravure coated ECF film

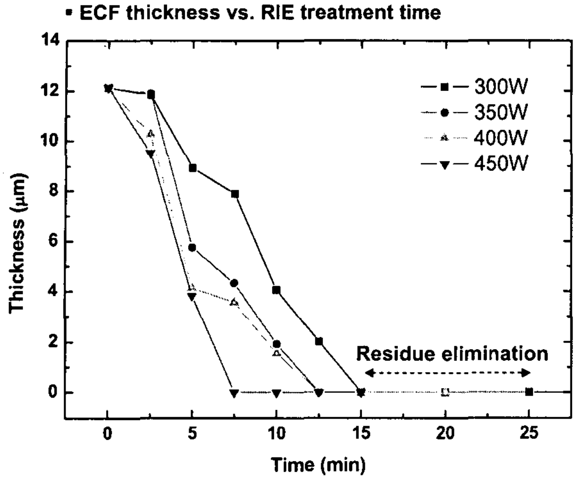
	Comma coated film	Gravure coated film (1 layer)	Gravure coated film (2 layer)
Dielectric loss	0.017	0.04	0.022
Thickness (μm)	12	3.16	6.09
Thickness tolerance (%)	1.74%	16.16%	4.38%
Capacitance (nF/cm²)	2.89	10.96	5.19 nF/cm²
Cap. Tolerance (%)	4.6	N/A	10.64
Failure	< 1%	61.5%	14.3%

- Cap. Area = 4mm dia. (92 EA)
- Sputtered Cu top electrode
- BTO powder 50 vol.%



✓Capacitor electrode short problem
→ Smoother surface PCB substrates needed.
→ Pinholes and voids during coating and drying – resin

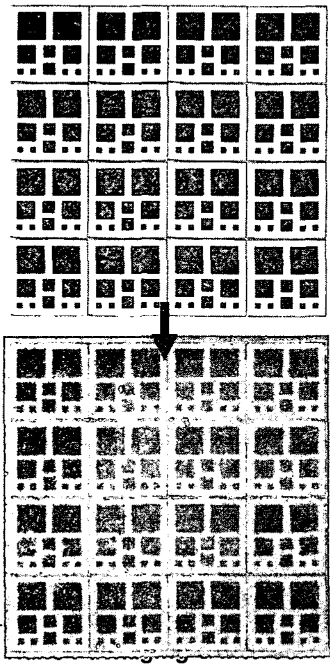
ECF Etching Process (RIE & Ultrasonic Cleaning)

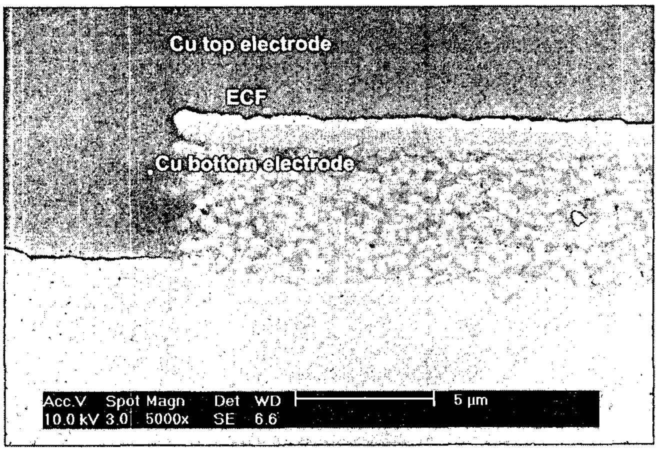


- Gas: O_2+CF_4
- Ultrasonic cleaning

RF power (W)	300	350	400	450
Time (min)	35	25	20	15

Patterned ECFs by Plasma Etching

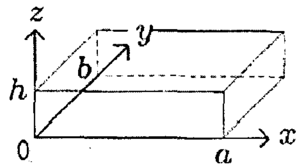




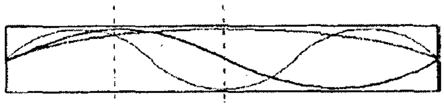
Cross-sectional image of a plasma etched embedded capacitor With 7 um ECF and 1um sputter-deposited Cu

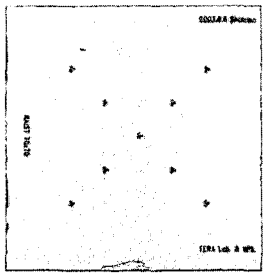
ε_r – *high frequency measurement*

◆ **Rectangular cavity resonator**



▪ **Distribution of electric field in cavity resonator**





❖ Resonance frequency

$$f_{mn} = \frac{c}{\sqrt{\varepsilon_r}} \sqrt{\left(\frac{m}{2a}\right)^2 + \left(\frac{n}{2b}\right)^2}$$

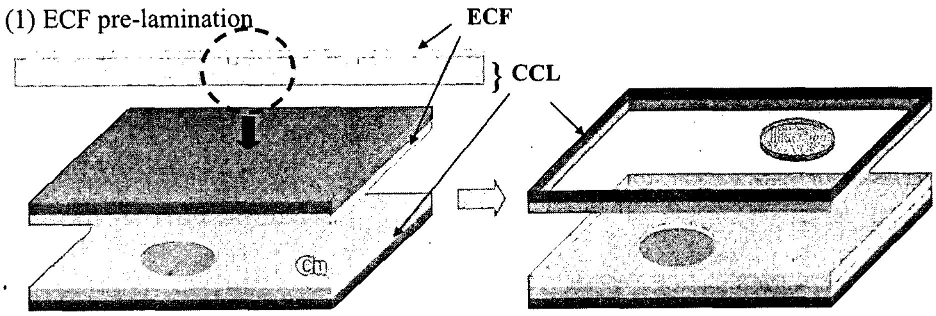
- m, n: cavity mode numbers
- c: speed of light
- ε_r: relative permittivity

❖ Test conditions

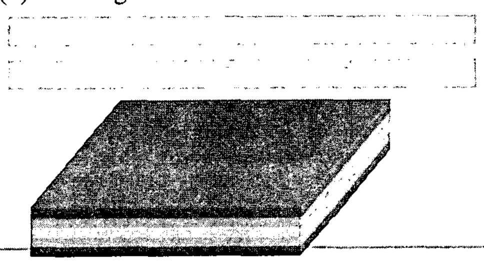
- Equipment : HP8510C
- Frequency range : 100MHz ~ 15GHz
- Frequency step size : 25MHz
- S11 parameter (reflection parameter)
- Sample size : 60mm×60mm

ECF Embedding in PCB & Electrodes Formation

(1) ECF pre-lamination



(2) Bonding & Lamination



◆ **ECFs had tacky and little viscosity in B-stage. → By only PCB etching process, electrode formation is available and there was no void between electrode and PCB.**

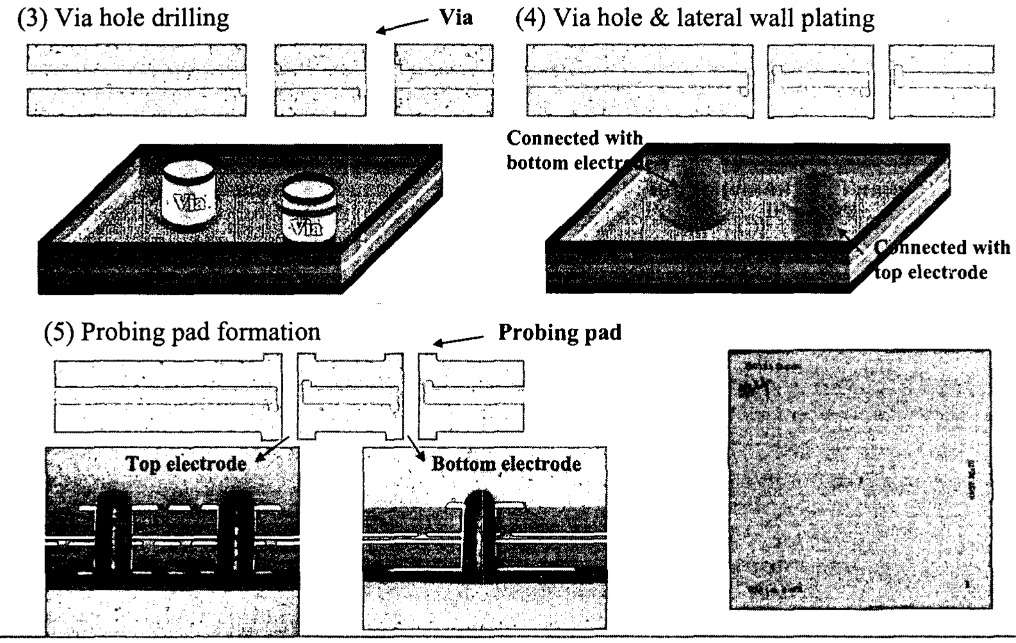
◆ **Pre-lamination condition**

80°C (B-stage), 3.54kgf/cm²

◆ **Lamination condition**

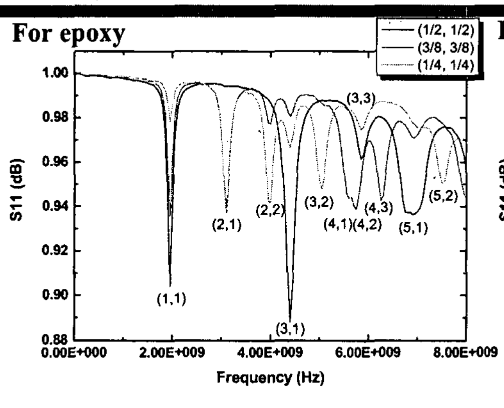
180°C, 3.54kgf/cm², 10min

ECF Embedding in PCB & Electrodes Formation

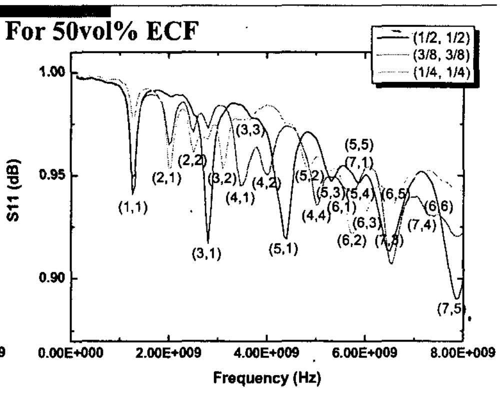


Result – Epoxy & Powder A 50vol% ECF

For epoxy



For 50vol% ECF



◆ **Mode numbers were identified for each resonance frequency**

◆**Rules**

✓ **(1/2, 1/2) point → 2× mode impossible**

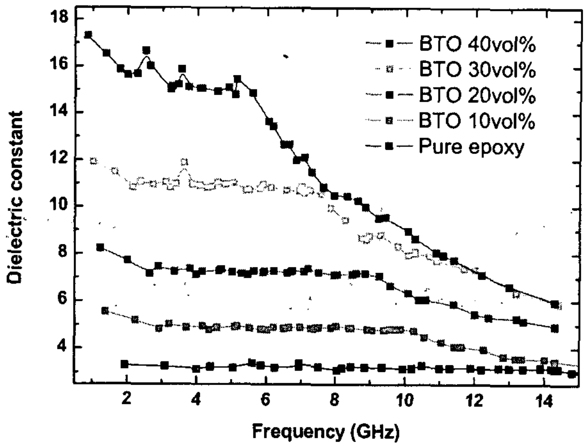
✓ **(1/4, 1/4) point → 4× mode impossible**

✓ **(3/8, 3/8) point → 8× mode impossibe**

◆ **As dielectric constant is bigger, the resonance frequencies were shown at lower frequency.**

$$f_{mn} = \frac{c}{\sqrt{\varepsilon_r}}\sqrt{\left(\frac{m}{2a}\right)^2 + \left(\frac{n}{2b}\right)^2}$$

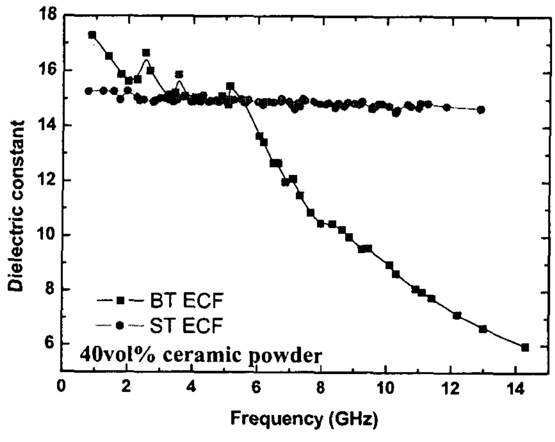
ε_r – *high frequency measurement*



- **As powder loading increases,**
  - **Dielectric relaxation reveals at lower frequency.**
  - **→ Effect $BaTiO_3$ particles is bigger than that of epoxy matrix.**

Frequency Dependency of Dielectric Constants

◆ Measurement condition
- Rectangular cavity resonator method
- Frequency range : 100MHz ~ 15GHz
- Equipment : HP8510C Network analyzer



➢ **BT ECF showed dielectric relaxation at ~ 5GHz, but ST ECF showed no relaxation.**

Epoxy/$BaTiO_3$ Composite Embedded Capacitor Pastes (ECPs)

Advantages & Disadvantages of ECPs

Advantages

Capacitors can be formed in **local area** via a screen printing method.

Simple process for embedded capacitors fabrication.

Higher powder volume loading. (compared with ECF coating process)

Disadvantages

Less tolerances (surface morphology and thickness)

Lower Repeatability (Sometimes unstable to hold their values over time and temperature)

Procedure of fabricating ECPs

Epoxy/TP resin + Dispersant + Coupling Agent

↓ Mixer : 3min

$BaTiO_3$ powder

↓ Mixer : 5min | 3-roll mill : 3 times

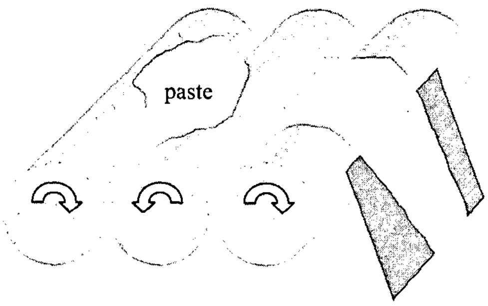
Curing Agent

↓ 3-roll mill : 1 times

Additives

↓ Mixer : 3min

ECP



3 roll mill mixing

Capacitor fabrication procedure

Screen printing

↓

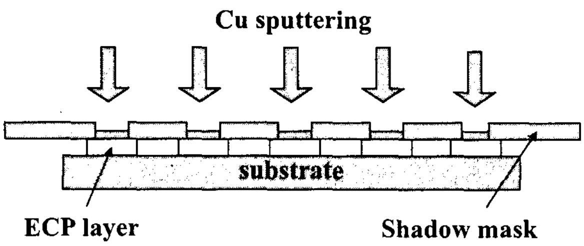
Drying ; 80°C, 20min (in vacuum)

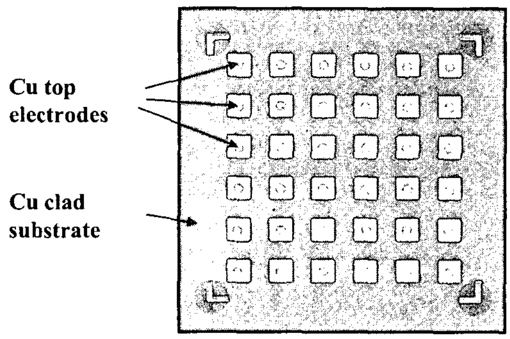
↓

Curing : 180°C, 1 hr

↓

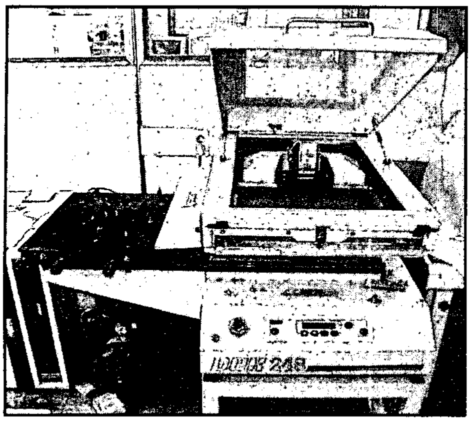
Top electrode deposition (Cu sputtering)





Sample Image

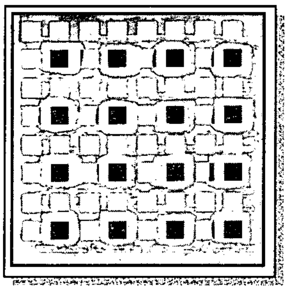
Optimization of screen printing parameters



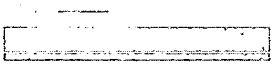
DEK 248 Screen Printer

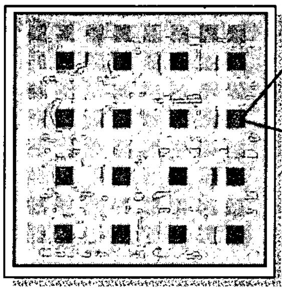
- Squeege hardness : 90 durometer
- Squeege angel : 45°
- Printing mask mesh : 325 mesh
- Mask emulsion thickness : 10 μm
- Snap-off distance : 1mm
- Printing speed : 30mm/s

Thickness enhanced & plasma etched ECP capacitor

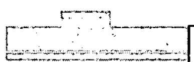


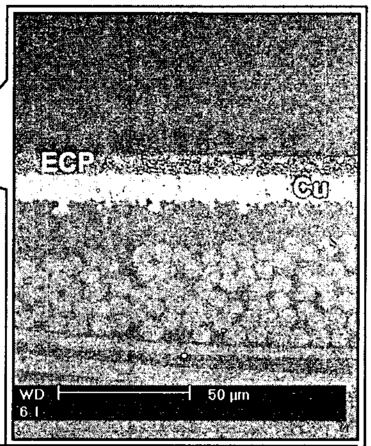
Top electrode patterned (lithography)





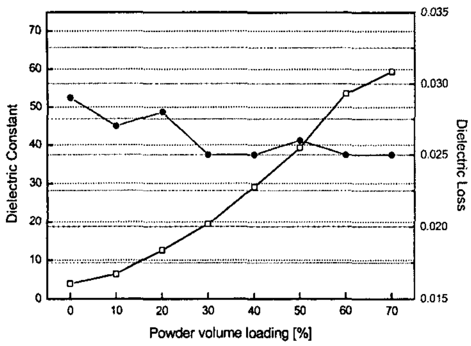
After RIE

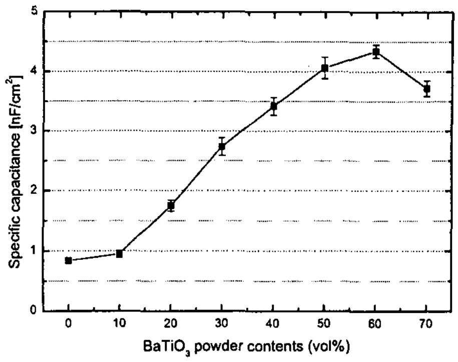




- Powder content : 50vol%
- Specific capacitance : 2.6 nF/cm²
- Dielectric Thickness : ~ 11μm
- Capacitance Tolerance (=3σ) : 22.6 %
- Average dielectric loss : 0.023

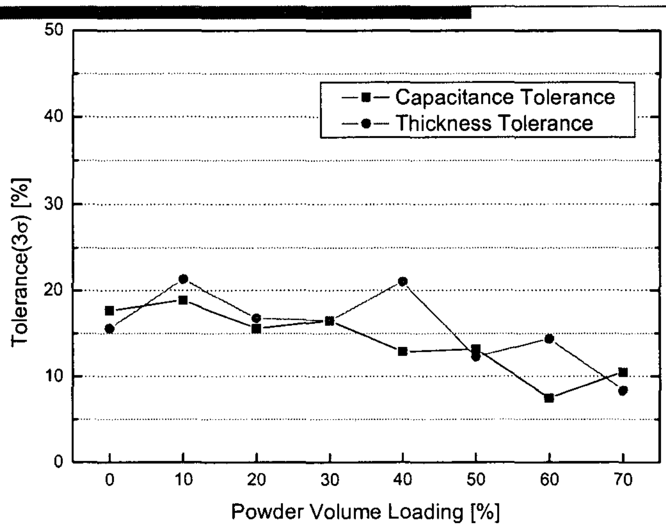
ε_r and specific capacitance at 100kHz





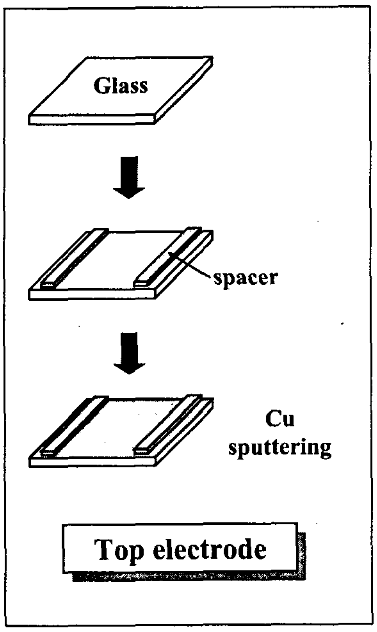
- Maximum dielectric constant was about 60 at 70vol%.
- But maximum specific capacitance, 4.34 was obtained at 60vol%.
- Tolerance has lower value at higher volume loading.

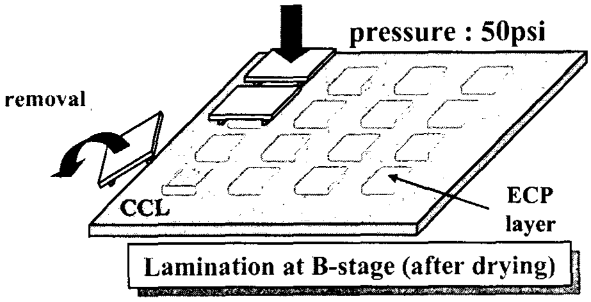
Tolerance

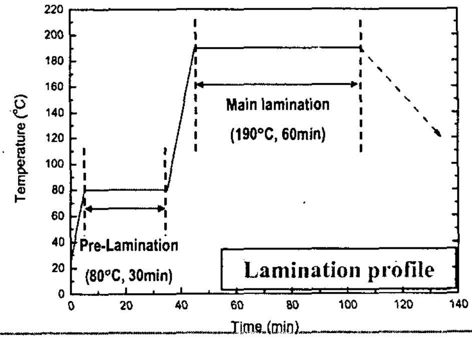


- Tolerance has lower value at higher volume loading.

Modified lamination method (patent pending)







Summary & Conclusions

◆ **PCB substrate compatible less than 10% low tolerance $BaTiO_3$ ECFs were successfully demonstrated on 14 X 14 cm PCB substrates.**

◆ **ECFs can be selectively etched using a plasma etching.**

◆ **Dielectric constants of epoxy/$BaTiO_3$ ECF in 0.1~10GHz range were measured using a cavity-mode resonator method.**

- **Dielectric relaxation of ECFs was caused by transferred from dipole polarization region to ion polarization region.**
- **As powder loading increased, relaxation frequency decreased.**

◆ **At high frequency range, $SrTiO_3$ ECFs show more stable dielectric behavior than BaTiO3 ECFs.**

◆ **Less than 10 micron thickness and low tolerance ECPs were successfully demonstrated using a screen printing and planarization technique.**