Impregnation of Metal Complex into Epoxy Insulation Materials Using Supercritical Carbon Dioxide and Its Application for Copper Plating

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Shinji Sumi - Guangzhou Meadville Electronics Co., Ltd., China

Abstract

Metal plating of epoxy polymer has been widely applied for industrial products for a long time, especially in the field of Printed Circuit Boards (PCB's). This technique is one of the most important technologies of electronics devices with high reliability and guaranteed quality. The authors are developing a new concept of PCB's for next decade generations to improved the techniques of which including more fine line circuitries, higher densities and narrower spaced conductor lines. An essential part of subject for this technology is to improve the weak copper adhesion peel strength on epoxy insulation materials. To obtain the good adhesion property of copper plating, it is now widely used the Pd Colloid Solution method. In order to further improve more excellent adhesion for next decade generation PCB's, we are investigating Super Critical Fluid (SCF) method. In this paper, an attempt has been made to impregnate some metal complexes into epoxy resin and then decomposed the complexes to produce free metal in the resin by reduction . Using the deposited metal is efficient electro-less Cu plating can be achieved. We will discuss the selection of the metal complexes and impregnation conditions on the complexes as well as peel strength of the plating.

Introduction

PCB's consumers market is rapidly shift to the high density and high reliability circuit technologies [1] [2]. Especially in Portable Handy (Cellular) Phone and Laptop Computer markets, they're very strongly requesting those latest technologies applications. Those technical demands background, there are challenging to satisfy with smallest size, lightly weight and high multiple functional equipments. Then PCB's apply to change into more fine lines and high density circuits boards. Those fine circuitry condition demands for next decade period PCB's Era will be strongly requesting to excellent copper conductor peel strength and reliability. On those markets requesting background to satisfy with the excellent PCB's quality level, we are investigating on Super Critical Fluid (SCF) method and an attempt has been done to impregnate some metal complexes into epoxy resin and decomposed them to produce free metal in the resin by the reduction of complex.

Currently PCB's main plating technology is the Pd Colloid Solutions process combining with electro-less plating and electric plating for connecting the both side circuits and inner layer circuitries. This plating technology has strong point for cost performance and very popular using, but weak point is not excellent copper peel strength on epoxy direct surface plating.

Using the SCF deposited metal an efficient electro-less Cu plating is achieved [3] [4] [5].
In this paper we are presenting the SCF application development to epoxy insulation which is the first approach to impregnate metal complex. After some pre-experiments a few Pd complexes were selected and suitable conditions for their impregnations into epoxy polymer plate were investigated, considering the peel strength of the Cu plated polymer plate.

Experimental

The impregnated material was an Epoxy C stage plate. This epoxy resin for testing was applied with Bis Phenol A-type resin (Liquid type property) which is widely used in the PCB's industries.

Figure 1 shows the Bis Phenol A-type chemical formulation.

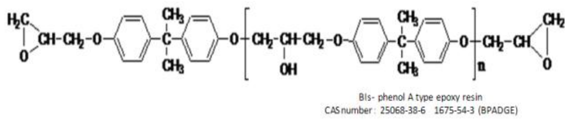


Figure 1 Bis Phenol A-type Epoxy resin (Liquid type)

As impregnation medium, Supercritical Carbon Dioxide [SC (CO_2)] was used. Temperature, pressure and treatment time were controlled for metal complex impregnation.

Table 1 shows the SC (CO_2) variable factors combination and conditions for epoxy impregnation test.

Table 1 Impregnation conditions

	Level1	level2	level3	Level4
Temperature (Deg.)	60	100	140	150
Pressure (Mpa)	10	15	20	25
Time(Min)	30	60	90	120
Leakage time(Min)	1	10	30	

Selected Pd complexes were Pd(II) hexafluoroacetylacetonate (Complex A) , Bis-acetylacetonate Pd(II) (Complex B) and Pd(II)acetate (Complex C).

Figure 2 shows appearance of the selected complexes before and after SC(CO_2) treatment and their chemical structures. The epoxy plates were treated under various SC(CO_2) conditions to impregnate with Pd complexes. Pd complex impregnated epoxy samples were further treated to decompose the complexes to produce free metal Pd. Then Pd impregnated epoxy plates were applied through electro-less and electric copper sulfate plating processes for metallization. Impregnated Pd complex samples and plated samples are checked by PST (Peel Strength Test), SEM (Scanning Electron Microscope), XPS (X-ray Photoelectron Spectroscopy), EDX (Energy Dispersive X-ray Fluorescence Spectrometer) and TEM (Transmission Electron Microscope) to obtain the Pd complex conditions in the epoxy material and to compare the currently plating peel strength.

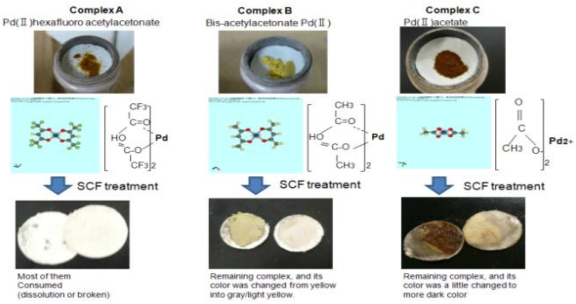


Figure 2 Three typical type of complexes conditions before and after SC (CO_2) treatments

Results and Discussion

We will discuss in this paper, if the SC (CO_2) is effective or not in existence for Pd complexes impregnation into epoxy materials and which kind of complexes is effective, for high amount of complex impregnation into epoxy material to obtain high performance Cu plating.

As the first step, we checked the effect of SC (CO_2) to epoxy materials and to the adsorption of complex on epoxy material.

Firstly, a blank treatment of epoxy material without both SC (CO_2) and complexes on epoxy material was checked.
Secondly, epoxy material was treated with SC (CO_2) and without complexes. Thirdly, the materials were treated with both SC (CO_2) and some complex.

Figure 3 shows one of the test results.
Excellent results were found with good copper metal plating performances using SC (CO_2). In the other two processes, poor the copper metal plating on the epoxy resin surfaces was given.

It is clear that SC (CO_2) is one of good technical approach for impregnating the complexes onto epoxy materials, and also SC (CO_2) makes better copper plating adhesion performances compared with blank treatments.

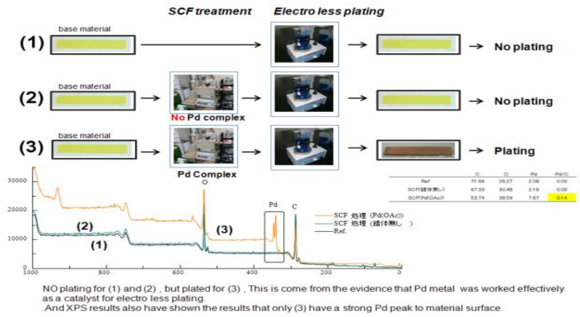


Figure 3 Verification check for impregnation test.

As the second step, the complex impregnation using SC(CO_2) was carried out for three kinds of complexes for longer time. We used complexes singly or mixed parameter. The Pd complex impregnated samples were put into the electro-less plating solution.

Figure 4 shows the appearances of electro-less copper plating after impregnation of one kind of complexes or some mixture complexes.

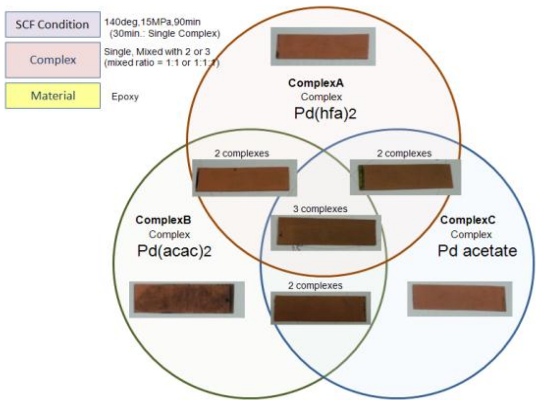


Figure 4 Electro-less plating visible conditions after three complexes combination impregnations

Cu plating was carried out easily. To increase the thickness of the Cu plating layer, the electric plating has been done by treating the electro-less plated plate into copper sulfate plating solution with 2 ASD for 30 minutes. The thickness of the Cu plating was controlled around 15μm.

Figure 5 shows the results of copper peel strength test after electric copper plating. In the case of single complex Pd (II) acetate (complex C), the highest peel strength of copper plate was obtained. In the case of mixed state with two or three mixed complexes, good peel strength was found by mixture of Pd (II) hexafluoroacetylacetonate and Pd (II) acetate (Complex A＋C).

It is very interesting that better copper peel strength was obtained in the case of mixed state with 2 complexes comparing in the case with single complex impregnation.

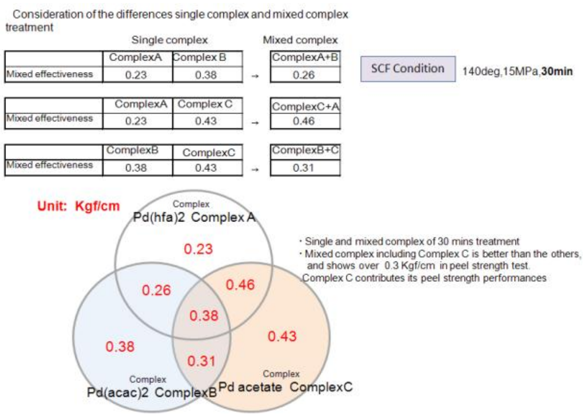
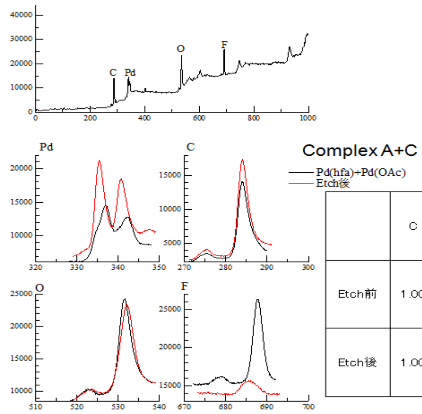


Figure 5 Copper plating average peel strength deviations for three complexes impregnations territory

Finally, we compared Cu plated sample using SC(CO_2) and the current plating method. As results, the better copper peel strength by Cu plating applying SC(CO_2) method was obtained comparing with the current plating method (Pd Colloid solution plating).

The stronger peel strength complex was illustrated mainly in the case of Pd (II)acetate (Complex C) or a mixture of Pd(II)hexafluoroacetylacetonate and Pd(II)acetate (Complex A+C). From XPS analysis, we found the metal state of Pd was not located on the polymer surface, but in a little deeper region of the polymer plate.

Figure 6 shows XPS analysis for mixed complexes (A+C) which applied impregnated condition and after Ar gas etching treatments removing skin surface contaminations. Pd intensity strength is a little bit increased as results. Then Pd complexes are located on near the skin surfaces on Epoxy materials.



	C	O	Pd	F
Etch前	1.00	0.64	0.11	0.49
Etch後	1.00	0.50	0.13	0.24

Figure 6 XPS analysis of mixed complex (A+C)

Figure 7 shows EDX mapping conditions result for mixed complex (A+C). Pd is also presented epoxy surface and very strongly and naturally existing on resin surfaces.

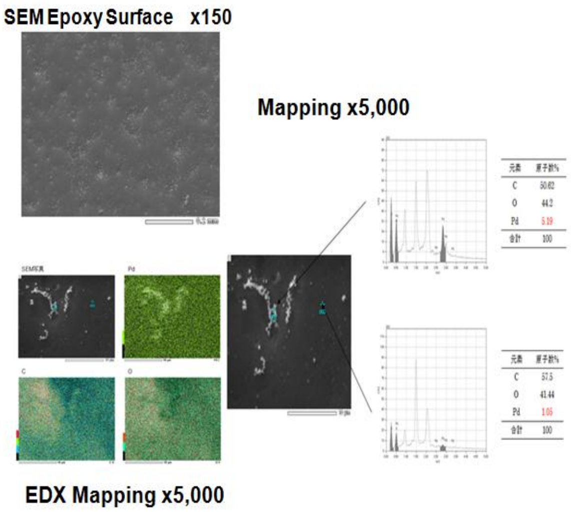


Figure 7 Pd EDX mapping condition of Complex (A+C)

Finally we observed TEM analysis for visible check.

Figure 8 shows TEM cross section analysis. The Epoxy surface Pd exists on both shiny surface and mat surface.

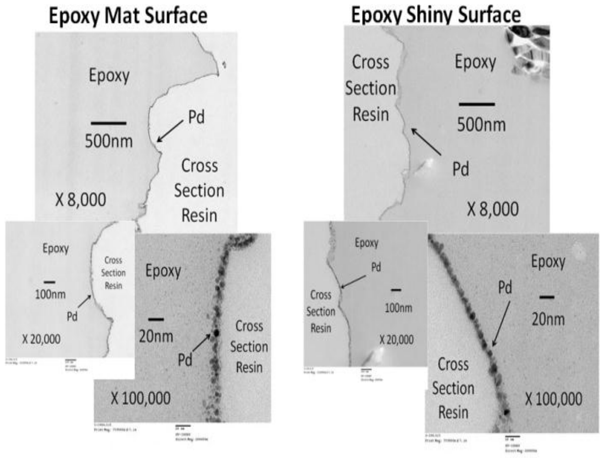


Figure 8 Pd Impregnation condition on Epoxy by TEM

Pd thickness is 20nm deep on the skin surfaces. This 20nm impregnation thickness was called ***Skin Impregnation***. We got the Pd complex impregnation area on Epoxy skin surfaces.

In **Figure 9**, copper plating peel strength was summarized for each Pd complex impregnation and current plating cases. This peel strength level is approximately 0.4~0.5kgf/cm. These values are about 2.0~2.5 times stronger, compared than current sulfate copper direct plating peel strength on bare epoxy surfaces plating.

	Max	Ave	Min
Complex A	0.51	0.23	0.06
Complex B	0.56	0.38	0.21
Complex C	0.70	0.43	0.24
Complex A+B	0.50	0.26	0.06
Complex B+C	0.48	0.31	0.12
Complex C+A	0.50	0.46	0.42
Complex A+B+C	0.38	0.38	0.38
Current technology	0.19	0.18	0.17

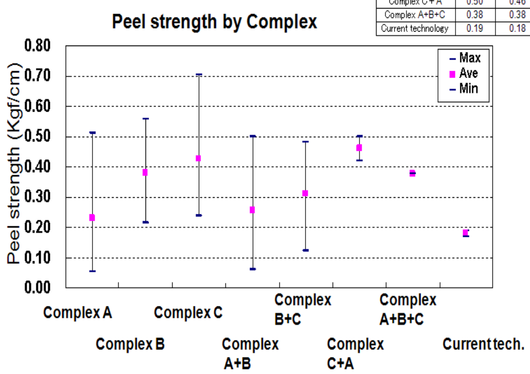


Figure 9 SC (CO_2) and current Cu plating peel strength.

Figure 10 shows all of the summarized results. Better Cu plating peel strength was achieved by using SC (CO_2) with both selected SCF conditions and selected metal complexes.

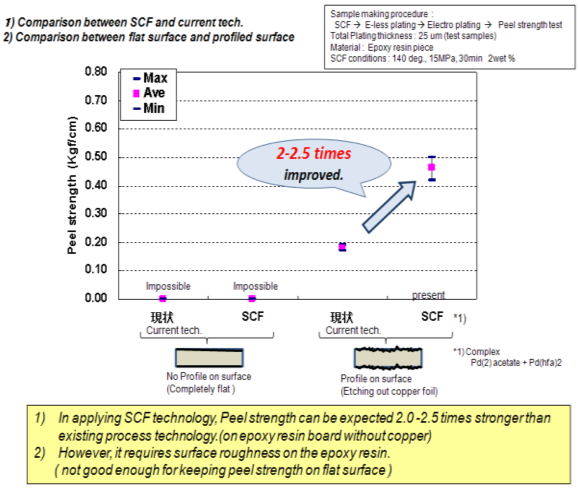


Figure 10 SC(CO_2) and current Cu plating peel strength and it surface conditions impact

But there are some un-expected results that are impacted Epoxy surface treatment conditions. It is clear that profile surface (mat) is good for adhesion result and non profile surface (shiny) is poor or not peel strength result by SC(CO_2) impregnations. Pd complex can be impregnated onto both surfaces by SC(CO_2). But the copper peel strength is affected from Epoxy surface materials roughness. Plated copper peel strength is affected from its anchor phenomenon. These anchor phenomena consisted by Epoxy surface roughness.

Conclusions

We found some of good metal complexes for impregnation into epoxy insulation plate using SC(CO_2) treatment.
The selected metal complexes are Pd(II)acetate (Complex C) for single complex usage, and for mixed use case, Pd(II) hexafluoroacetylacetonate and Pd(II)acetate (Complex A+C).

As the best case, we choose the mixed complexes combination. It is considered that the dissolution of the complexes in CO_2 and the affinity of the complexes are more important for enough impregnation into epoxy resin.
The best impregnation condition was 140℃, 15 MPa and 30 min. At lower temperature and lower pressure is not enough Cu plating. Under those conditions, not satisfied Cu plating was obtained.

The better peel strength of the Cu plating can be obtained using SC(CO_2) method, not conventional Pd Colloid Solution processes. Currently this SC(CO_2) process has some undefined technical items, such as not clearly fixed to the surface on epoxy surfaces.

Pre-surface treatment levels before applying the SC(CO_2) cannot be and the volume of the complexes amount into epoxy impregnation cannot measured

References

[1] H.Ohnuki and S.Sumi, "*JPCA 2008 Seminar*", the 2nd advance electronics pavilion seminar, P71~P88, June 11, 2008.

[2] H.Ohnuki and S.Sumi, "*HKPCA & IPC 2008*" International Technical Conference, Dec. 4, 2008.

[3] T.Hori and et al, "*Introduction for Super Critical Fluid"*, Maruzen Tokyo, p.176~ (Dec. 31, 2008).

[4] H.Ohnuki and et al, "*Impregnated the Compound complex Initiators into Epoxy Insulation Materials by SC(CO_2) methods and analysis for the Copper Plating Peel Strengths Evaluations*" June Annual meeting of The Society of Fiber Science and Technology, Tokyo, Vol.64,No.1 p.262 (June 11, 2009).

[5] Japan Patent, "*JP 2006-131769 A 2006.5.25*".

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Acknowledgements

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Impregnation of Metal Complex into Epoxy Insulation Materials

Using Supercritical Carbon Dioxide & Its Application for Copper Plating

Meadville Enterprises (HK) Limited

美維企業(香港)有限公司

a member of TTM Technologies, Inc.

Present by: Hidebumi Ohnuki

Co-present by: Shinji Sumi

2011-04-13~15

Many thanks to USA’s great *disaster relief* assistant.
Tohoku-Pacific Ocean Earthquake/Tsunami

Tsunami strike northern Japan coast area

Car on the roof after tsunami disaster

US president Mr. Obama
make condolences

Great assistant by US army, and navy

Japan
Quake / Tsunami / Nuclear crisis

Japan faces unprecedented crisis (11 Mar. 2011)

✓**Great earthquake (Magnitude 9.0)**
✓**Tsunami**
✓**Nuclear plant disaster**
--Scheduled blackout to save power
--Radioactive food, water

We never give up and launch reconstruction soon !!
I would like to express deepest appreciation to
US citizen , government, military.
Also about 134 countries and 39 international organizations.

We hope you to support
the continuous cordial assistants.

Impregnation of Metal Complex into Epoxy Insulation Materials

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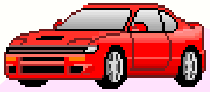
2011-04-13~15

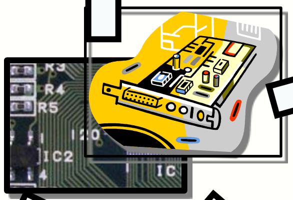
Application industry of PCB

Computer, Communication
Smart phone
Tablet PC
Cellar phone
W-less LAN,3G
GPS, Bluetooth,
Ubiquitous



Automobile device
Hybrid car, Electric car,
Navigation
Security system
Car audio,
System control

Advanced Engineering
Photovoltaic Power
Space engineering
Robot engineering



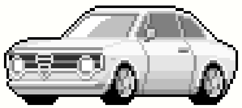
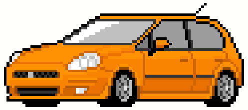
PCB

Audio Visual
3D-TV,Google TV
digital TV, Game
Digital camera

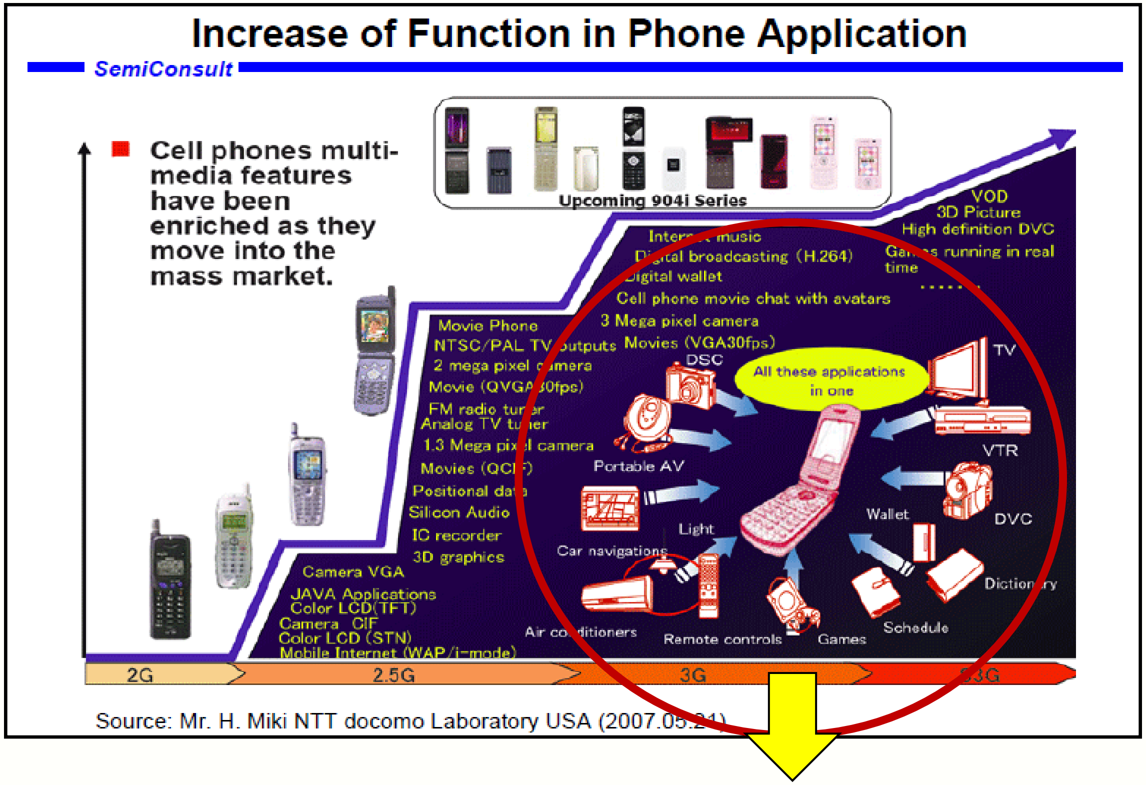
Medical engineering
Recognition, management
RFID,QR code
Biometrics
Voice / Face outline verification

Important role as a basis of various industries

PCB application example

	Past	Present	Future
Cellar Phone	 Analog	 High speed／Data transformation 3G	 Multi-function／Huge volume Data communication 3.5G,4G
Car	 Electronic ratio≒0%	 Electronic ratio≒40%	 Eco car Electronic ratio>80%

Background : Technology trend & Customer requirement



By NTT docomo Researcher.

In mobile phone development and evolution, following items are required.

✓Most advanced technologies with high density and downsizing level.

✓And not only in HDI but also in Rigid-Flex, module package.

✓High quality and reliability with mass pro. level.

✓Tough cost reduction against competitors

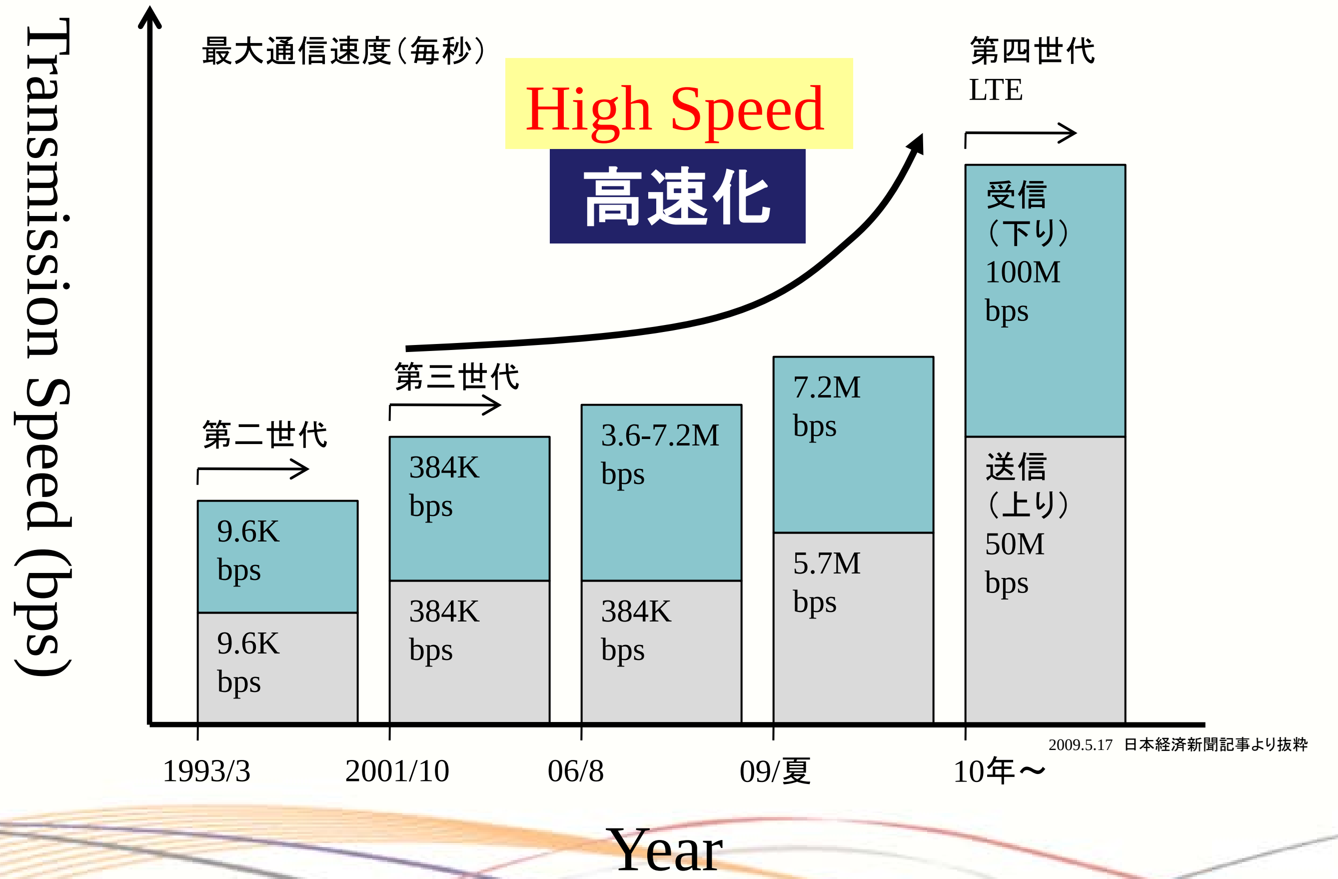
Research Mobile phone trend → Strong hint for R&D activities

Technology trend & Customer requirement

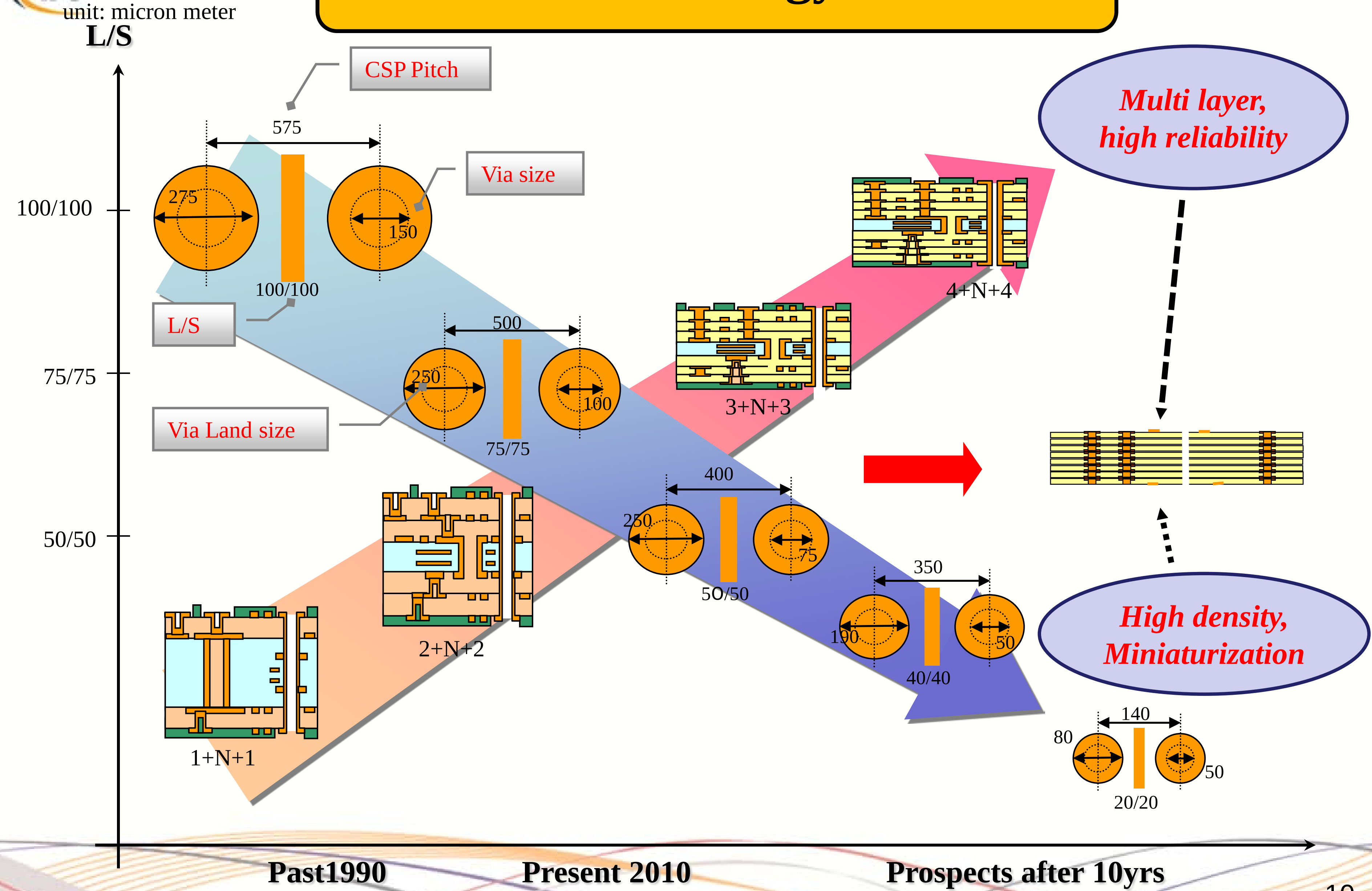
Required property	Key word
High Speed	Huge data transaction (Video streaming), Low transmission loss, embedded tech, Optical tech, high frequency
Downsizing	Portable, Lighter, Any layer HDI,
IC downsizing	High density design(Fine line, Small via, Fine pitch CSP,LDD) Chip size downsizing
High reliability	High reliability material & process, Simulation analysis, New concept assembly tech,
Inspection & repair	High accurate inspection (4 wire test, AOI,,), repairing tech (Op,Sh for fine design)
Registration	Stable dimension material, LDI, LDD, Scale factor data linkage system and auto analysis and feedback.
Cost reduction	Simplify process, Improve yield (systematic failure feed back system or machine development)
Green electronics	HF, Lead free, World level common target, Brand image

NTT docomo Mobile Phone Transmission Speed

NTT docomoの携帯電話の通信速度



PCB Technology trend



Why to use the SCF for PCB ?

Expect to get the

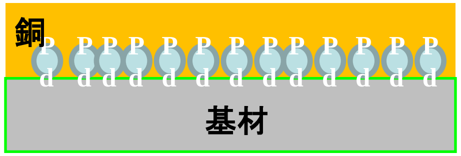
Good copper peel strength for fine line

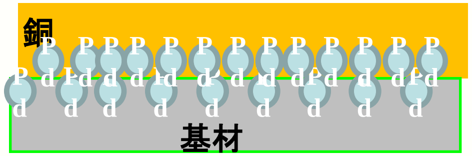
And

Perfect small VIA hole Cu plating

Expecting the Technical Items by SCF

Pd Colloid	SCF
現行：樹脂表面にPdに付着	SCF：樹脂にPd取り込み



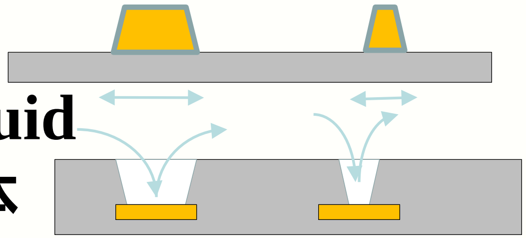


Technical Items
- Peel Strength
- Material Free

Pd錯体の注入による密着強度向上
材料に非制約

- Ultra Small VIA Filling
- Plating Controlled

Liquid
液体



SCF
超臨界
（液体・気体）

超臨界による微細ビアへの入り込み性改善を期待。液体レベルの限界を打破

1）SCF後のダイレクトめっき
2）薬品費用の削減

Cost
- Cost Performance

Environment
- Green Ecology
- No E-Less Waist Water Treatment

ドライ化、クリーン化への期待。
世界的な環境負荷軽減への積極的取り組み

SCF Study results

SCF: Super Critical fluid Technology

Test details

(1) Application SCF technology to Epoxy resin
(2) SCF treatment condition and Complex selection
(3) SEM observation on Epoxy surface after SCF
(4) Measurement of complex impregnation by XPS analysis
(5) Epoxy EDX Mapping check
(6) TEM Analysis for Epoxy Matte & Shiny Surface
(7) Verification peel strength performance

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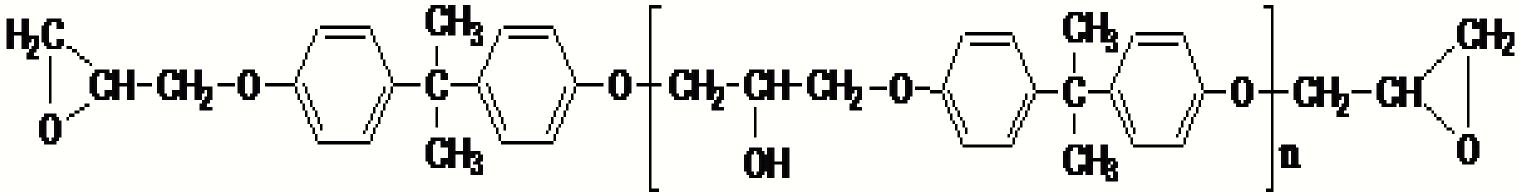
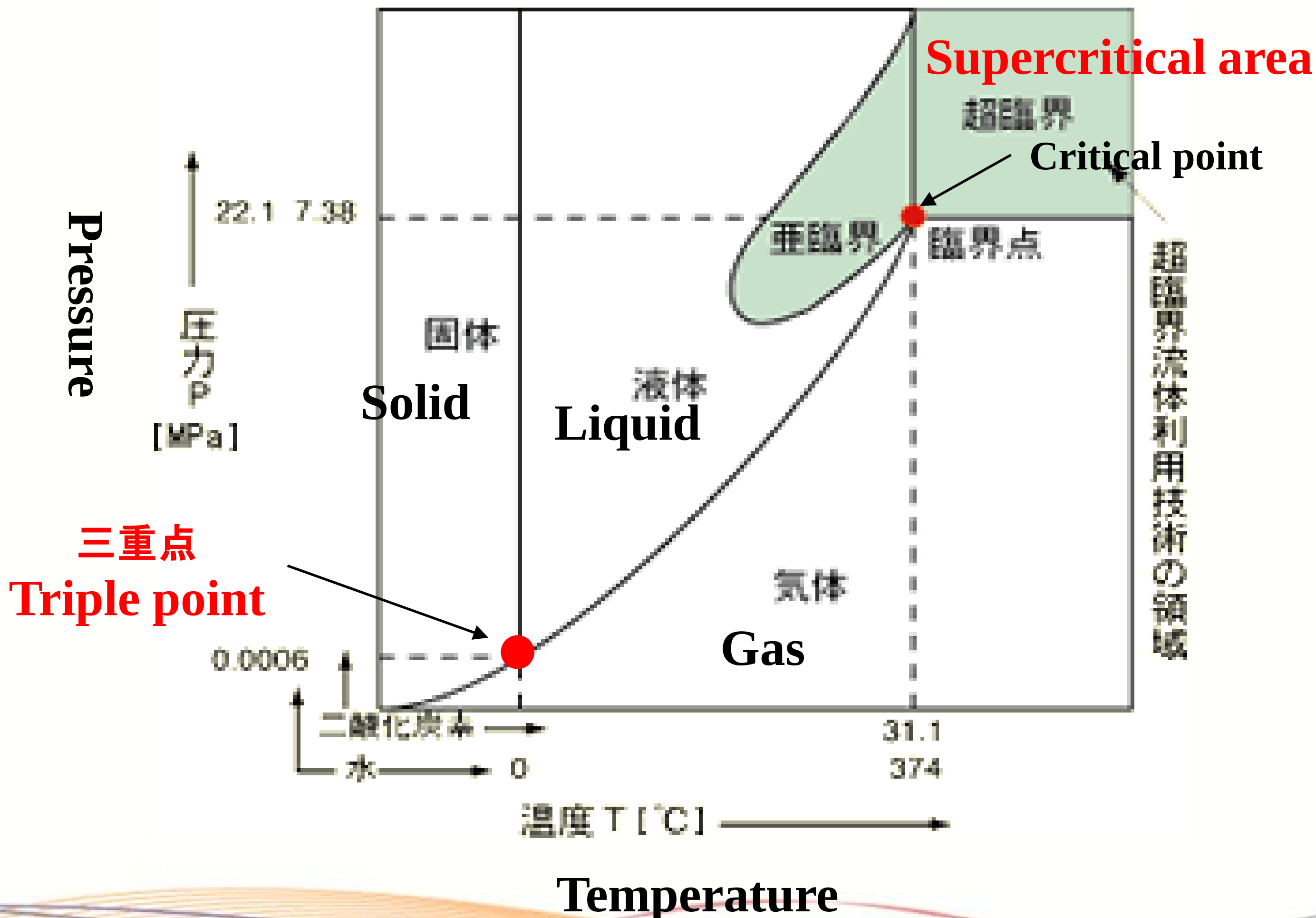
Epoxy Material molecular formula and structure

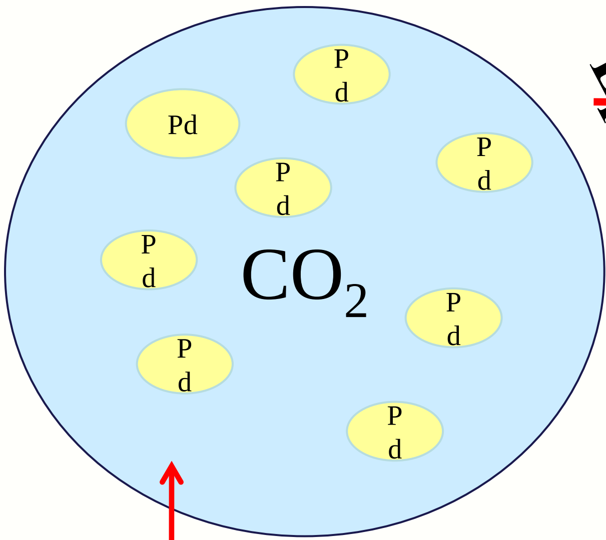


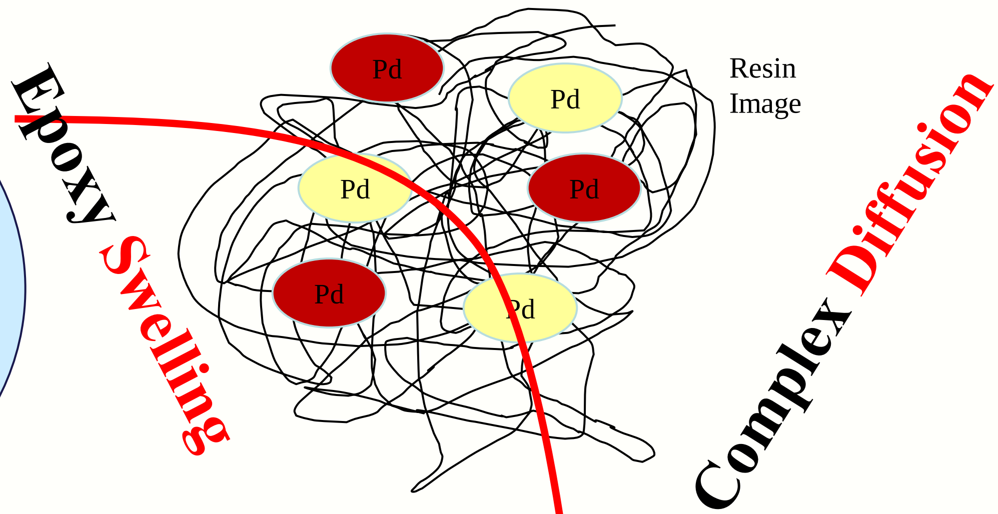
Bis- phenol A type epoxy resin
CAS number: 25068-38-6 1675-54-3 (BPADGE)

Supercritical Conditions



Mechanism by SCF technology



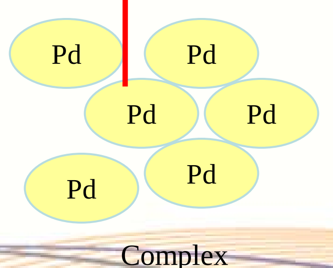


1st STEP

Dissolution of complex into CO2

2nd STEP

Penetration into Epoxy resin with complex Pd by CO_2



3rd STEP

Impregnation of complex to Epoxy resin

What is SCF technology ?

	SCF Super Critical Fluid	Chemical (Current method)
Process category	Dry process	Wet process
Reaction process	Supercritical 超臨界	Liquid 液体
	High pressure (15MPa)& High temperature(140deg.) In chamber	Temperature (<100deg.) In dipping tank
	Impregnation	Adhesion
Catalyst	Complex powder with metal 金属錯体粉末	Soluble liquid chemical 溶解液体薬品
Machine	Special Reacting machine	Chemical treatment tank

Test details

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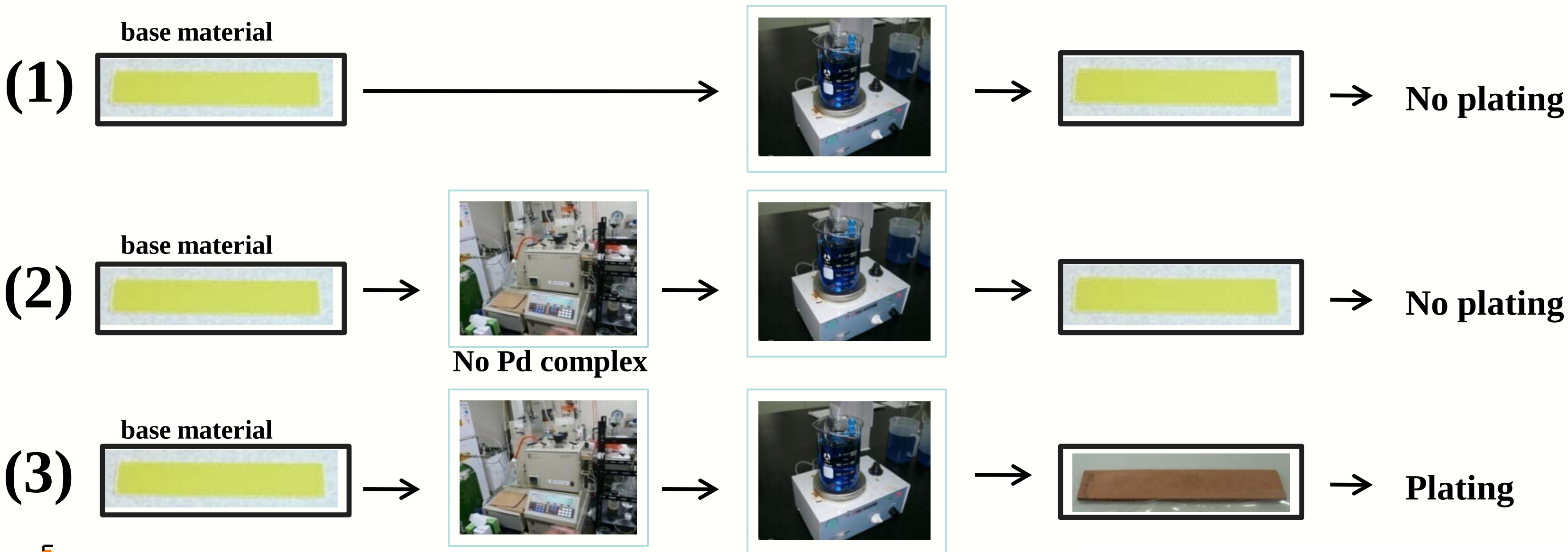
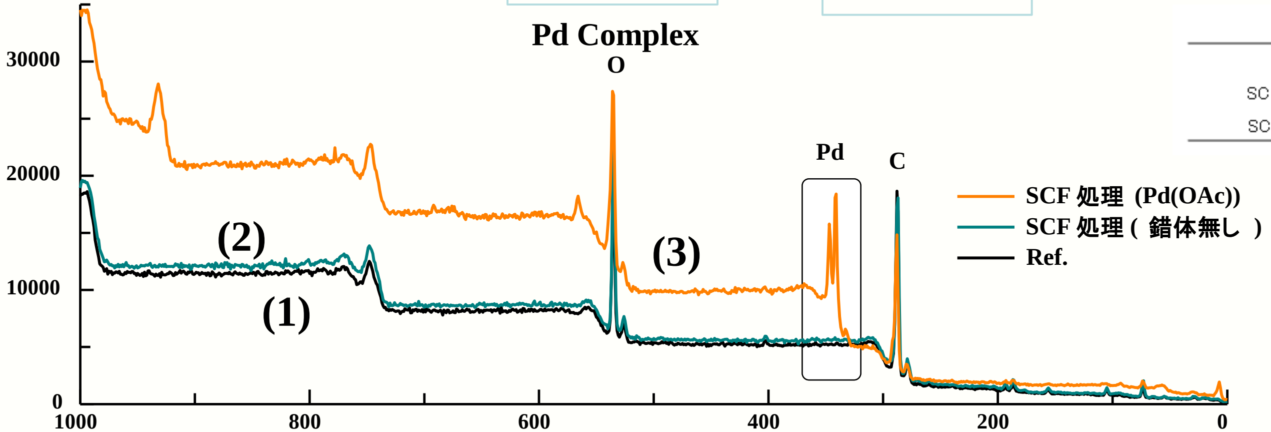
(6) TEM Analysis for Epoxy Matte & Shiny Surface

(7) Verification peel strength performance

Verification of impregnation by SCF

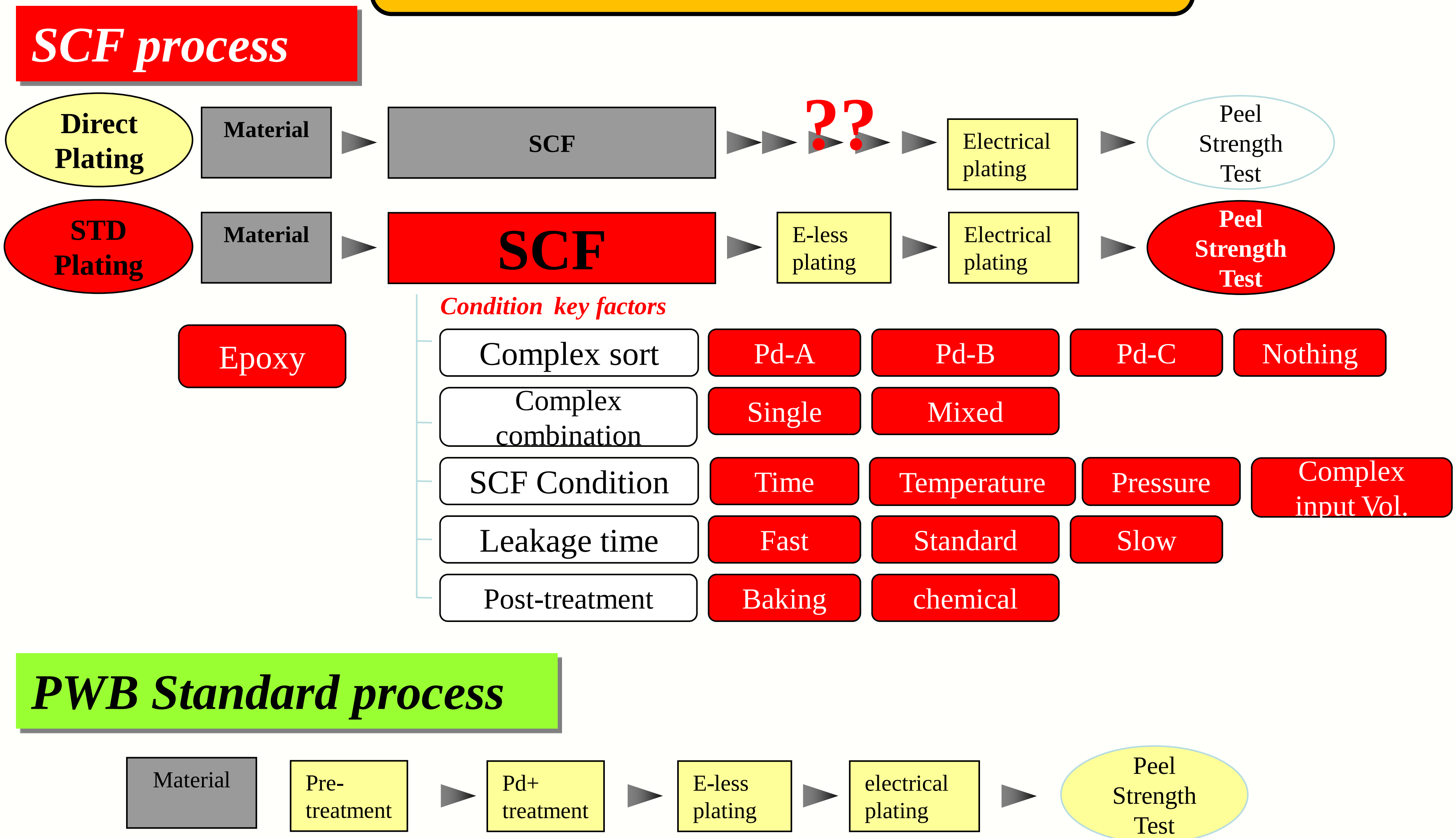


	C	O	Pd	Pd/C
Ref.	71.66	26.27	2.08	0.03
SCF(錯体無し)	67.33	30.48	2.19	0.03
SCF(Pd(OAc))	53.74	38.59	7.67	0.14



NO plating for (1) and (2) , but plated for (3) , This is come from the evidence that Pd metal was worked effectively as a catalyst for electro less plating.
.And XPS results also have shown the results that only (3) have a strong Pd peak to material surface.

SCF Evaluation process



SCF Treatment condition

	Condition1	Condition2	Condition3	Condition4
Temperature (Deg.)	60	100	140	150
Pressure (MPa)	10	15	20	25
Time(Min)	30	60	90	120
Leakage time(Min)	1	10	30	

Test instruments

1) Impregnation treatment by SCF machine

SCF machine : ISCO SFX2-10
Test Condition :
- Temperature : 140 deg.
- Pressure : 15MPa (to 25MPa)
- Treatment time : 30 min (to 90min)

2)Electroless plating

PTH Chemical : Atotech
Temp. 30-35 deg.
Time : 5 min
Agitation : ON (stirrer)

3)Electro plating

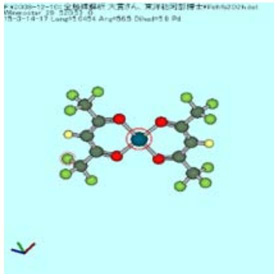
Plating Chemical : Atotech
Temp. 25 deg. (Room Temp.)
Time : 50 min (20um Target)
Bubbling : ON

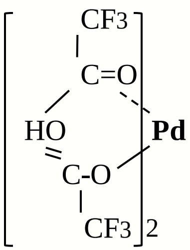
4) Measurement peel strength

Complex structure image and molecular formula

Complex A

Pd(II)hexafluoro acetylacetonate



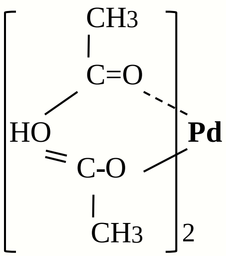


SCF treatment

Most of them
Consumed
(dissolution or broken)

Complex B

Bis-acetylacetonate Pd(II)

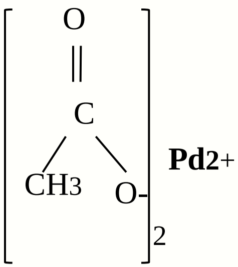


SCF treatment

Remaining complex, and its color was changed from yellow into gray/light yellow.

Complex C

Pd(II)acetate



SCF treatment

Remaining complex, and its color was a little changed to more dark color

Color change on material after SCF treatment & Electroless plating

Base material color

SCF treatment

	Complex A Complex Pd(hfa)2	**Complex B** Complex Pd(acac)2	**Complex C** Complex Pd acetate
SCF 140deg. 15MPa **30 min**			
SCF 140deg. 15MPa **60 min**			
SCF 140deg. 15MPa **90 min**			

Electroless Plating (PTH)

SCF 140deg. 15MPa **30 min + PTH**			
SCF 140deg. 15MPa **60 min + PTH**			
SCF 140deg. 15MPa **90 min +PTH**			

Test details

(1) Application SCF technology to Epoxy resin
(2) SCF treatment condition and Complex selection
(3) SEM observation on Epoxy surface after SCF
(4) Measurement of complex impregnation by XPS analysis
(5) Epoxy EDX Mapping check
(6) TEM Analysis for Epoxy Matte & Shiny Surface
(7) Verification peel strength performance

SEM observation on Epoxy surface after SCF

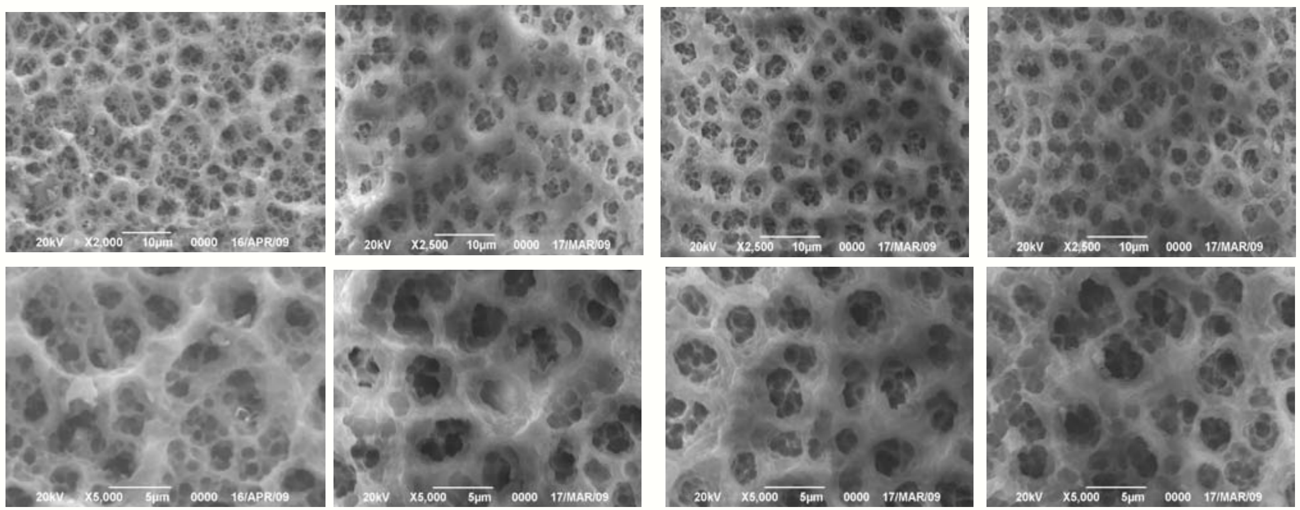
<SCF Conditions >
Material : Epoxy resin
(after copper etching)
Complex: Pd based complex
Temperature : 140 deg.
Time : 30-60 mins
Pressure: 15Mpa

ComplexA: Pd(Ⅱ)hexafluoro acetylacetonate
ComplexB: Bis-acetylacetonate Pd(Ⅱ)
ComplexC: Pd(Ⅱ)acetate

No pre-treatment | **Complex A** | **Complex B** | **Complex C**

x2500

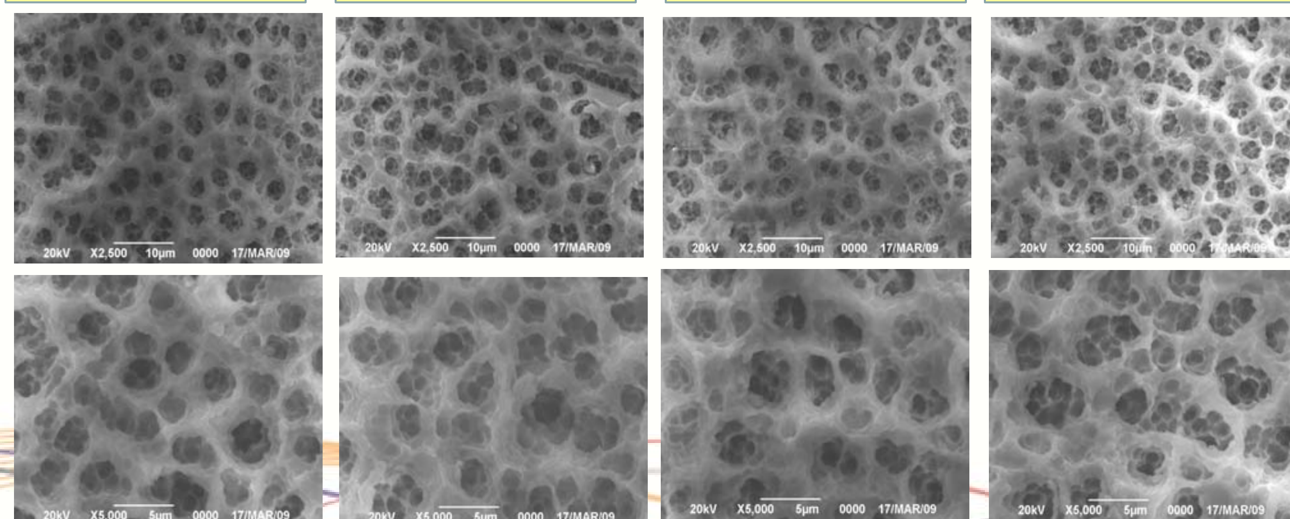
x5000



Complex A+B | **Complex B+C** | **Complex C+A** | **Complex A+B+C**

x2500

x5000



Test details

(1) Application SCF technology to Epoxy resin
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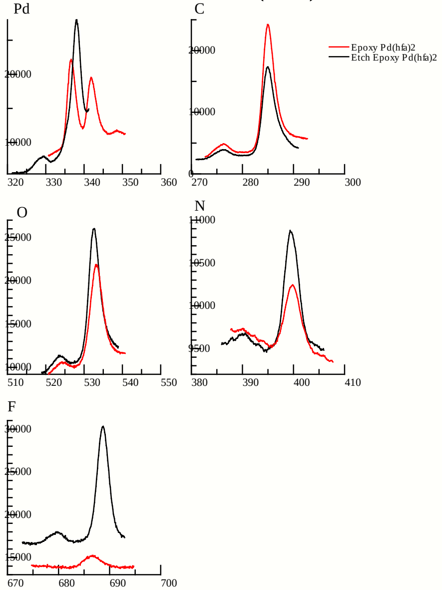
XPS Analysis results by SCF with Pd based complex (Complex A, B, C)

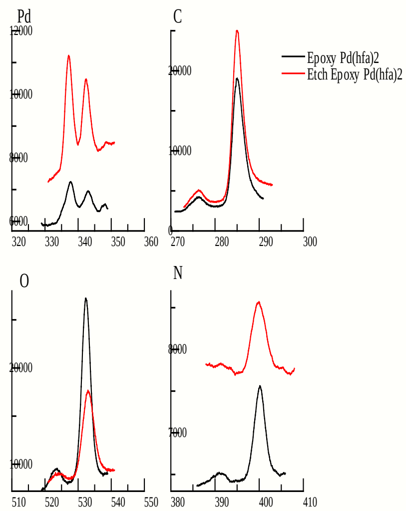
Complex A

Material : Epoxy resin
Complex : Complex A
Pd(hfa)2



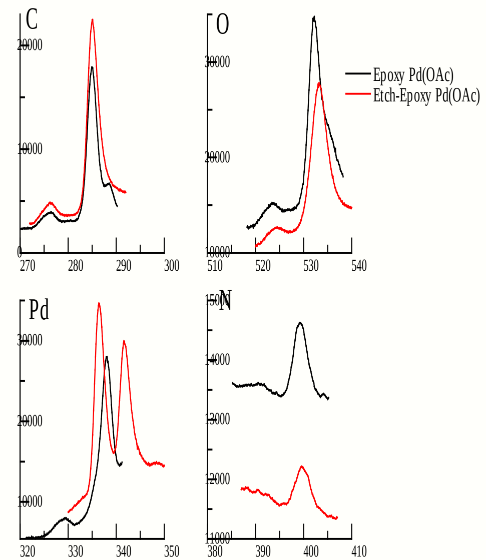
Complex B

Material : Epoxy resin
Complex : Complex B
Pd(acac)2



Complex C

Material : Epoxy resin
Complex : Complex C
Pd(Oac)



Complex A

Value : Peak ratio (No unit)

	Pd	C	N	F	O
Before Etching	0.09	1.00	0.36	0.46	0.56
After Etching	0.10	1.00	0.25	0.16	0.34

Complex B

Value : Peak ratio (No unit)

	Pd	C	N	O
Before Etching	0.04	1.00	0.23	0.53
After Etching	0.05	1.00	0.20	0.26

Complex C

Value : Peak ratio (No unit)

	C	O	Pd	N
Before Etching	1.00	0.72	0.17	0.48
After Etching	1.00	0.46	0.17	0.32

Peak ratio of Pd after SCF treatment with Pd based complexes

Value : Peak ratio (No unit)

Complex A

	Pd	C	N	F	O
Etch前	0.09	1.00	0.36	0.46	0.56
Etch後	0.10	1.00	0.25	0.16	0.34

Complex B

	Pd	C	N	O
Etch前	0.04	1.00	0.23	0.53
Etch後	0.05	1.00	0.20	0.26

Complex C

	C	O	Pd	N
Etch前	1.00	0.72	0.17	0.48
Etch後	1.00	0.46	0.17	0.32

Complex A+B

	C	O	Pd	F
Etch前	1.00	0.62	0.08	0.35
Etch後	1.00	0.48	0.11	0.25

ComplexB+C

	C	O	Pd
Etch前	1.00	0.76	0.18
Etch後	1.00	1.15	0.51

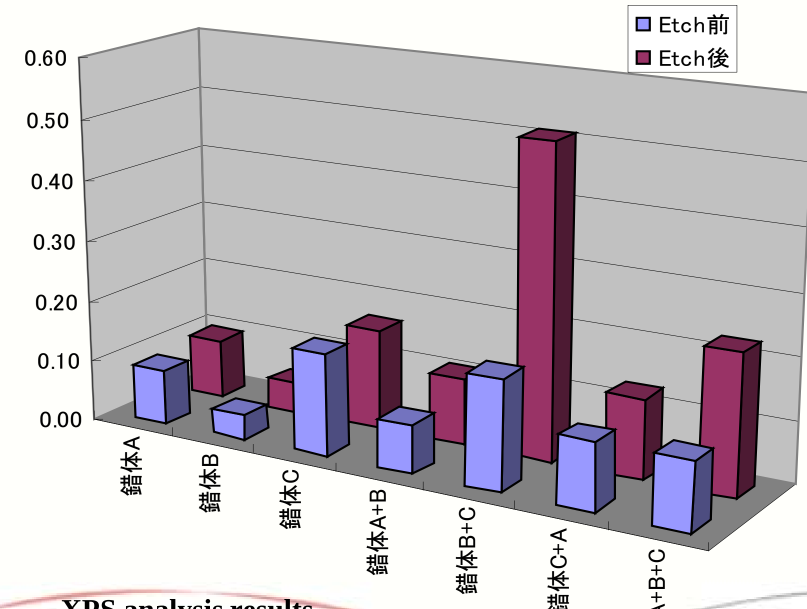
ComplexC+A

	C	O	Pd	F
Etch前	1.00	0.64	0.11	0.49
Etch後	1.00	0.50	0.13	0.24

ComplexA+B+C

	C	O	Pd	F
Etch前	1.00	0.59	0.11	0.32
Etch後	1.00	0.73	0.23	0.31

	Pd Concentration		
Complex	Before Etch	After Etch	Fluctuation（%）
ComplexA	0.09	0.10	9
ComplexB	0.04	0.05	18
ComplexC	0.17	0.17	-2
ComplexA+B	0.08	0.11	38
ComplexB+C	0.18	0.51	183
ComplexC+A	0.11	0.13	18
ComplexA+B+C	0.11	0.23	109
Average	0.11	0.18	66



XPS analysis results
（Before Etching : blue and after Etching : purple ）
（Pd concentration in case of assuming Carbon concentration 1.0 ）

Test details

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(5)Epoxy EDX Mapping check
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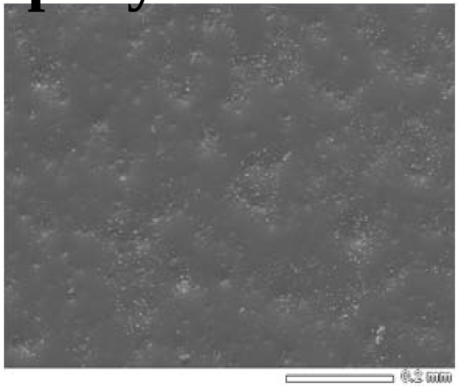
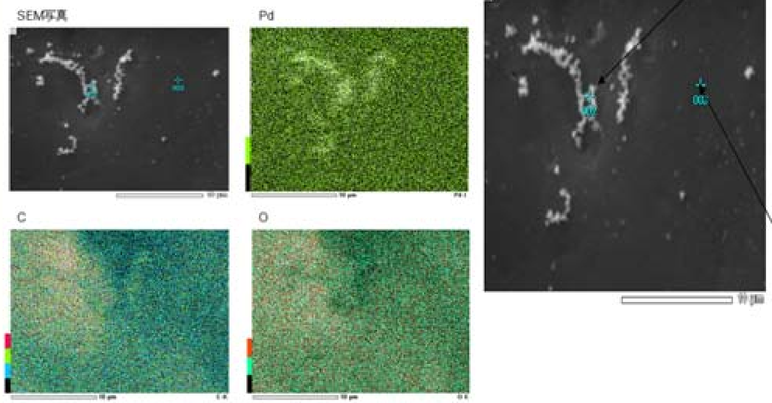
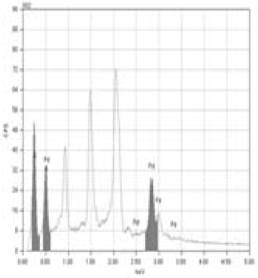
Epoxy EDX Mapping

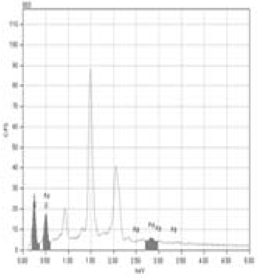
Epoxy Surface







元素	原子数%
C	50.62
O	44.2
Pd	5.19
合計	100



元素	原子数%
C	57.5
O	41.44
Pd	1.05
合計	100

EDX Mapping x5,000

Test details

(1) Application SCF technology to Epoxy resin
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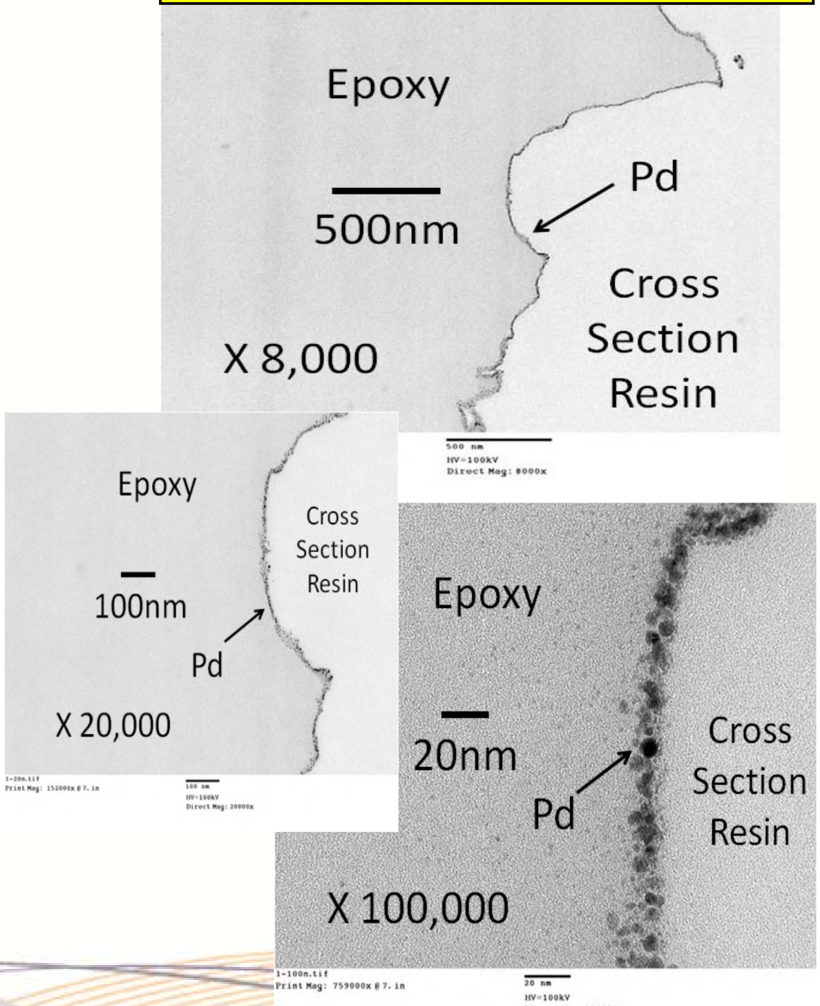
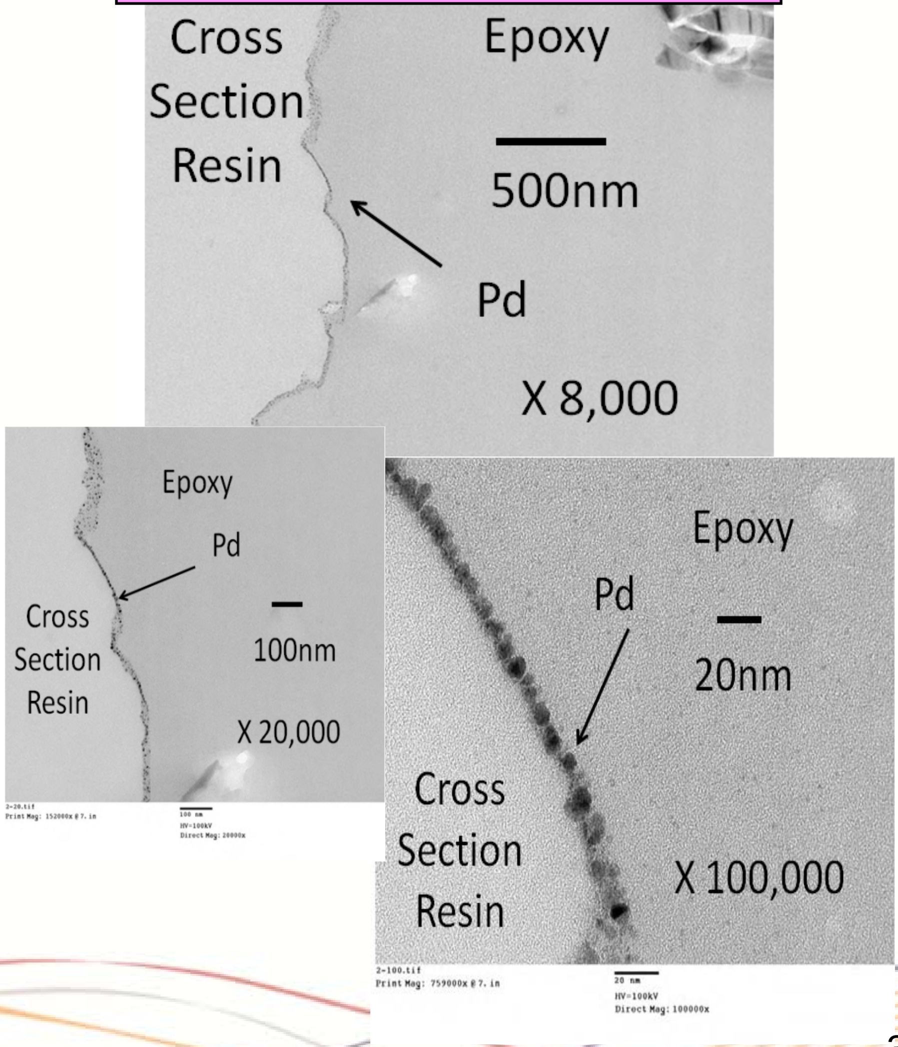
Skin Impregnations by TEM Analysis for Epoxy

Epoxy Matte Surface



Epoxy Shiny Surface



Test details

(1) Application SCF technology to Epoxy resin
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(3) SEM observation on Epoxy surface after SCF
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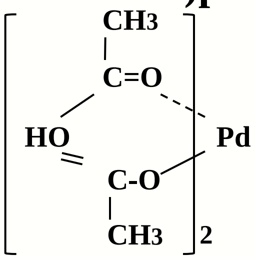
(7)Verification peel strength performance

Peel strength effective factor for Complex B

Complex B **Bis(acethylacetonate)palladium(II)**

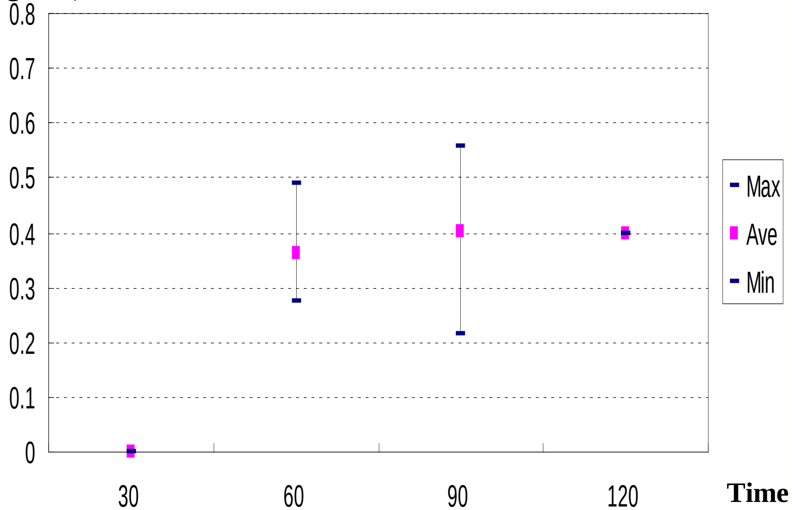




Temperature : 140 deg.
Time : test factor
Pressure: 15Mpa

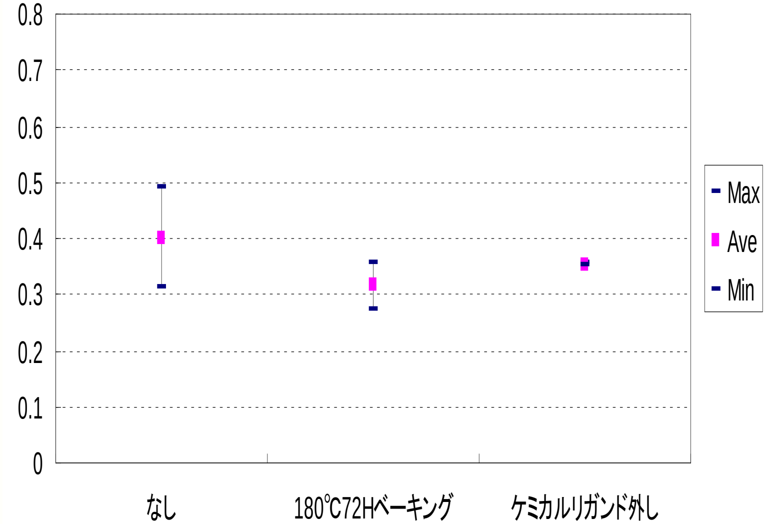
Peel strength (Kgf/cm)

Time



Peel strength (Kgf/cm)

Post-treatment



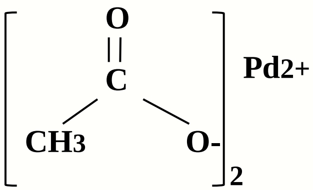
No plating in 30 mins treatment. It means it needs at least more than 60 mins treatment.
Peel strength test results is around 0.4 Kgf/cm.

It can't be seen effective peel strength improvement after Post treatment by heat baking or removing ligand treatment by chemical.

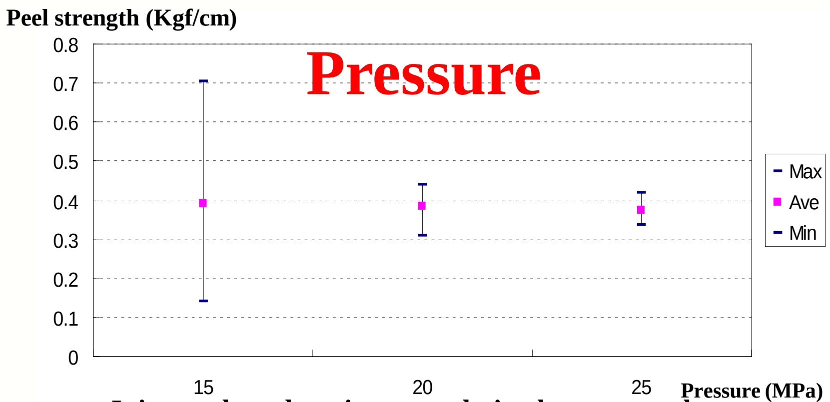
Peel strength effective factor for Complex C

Complex C

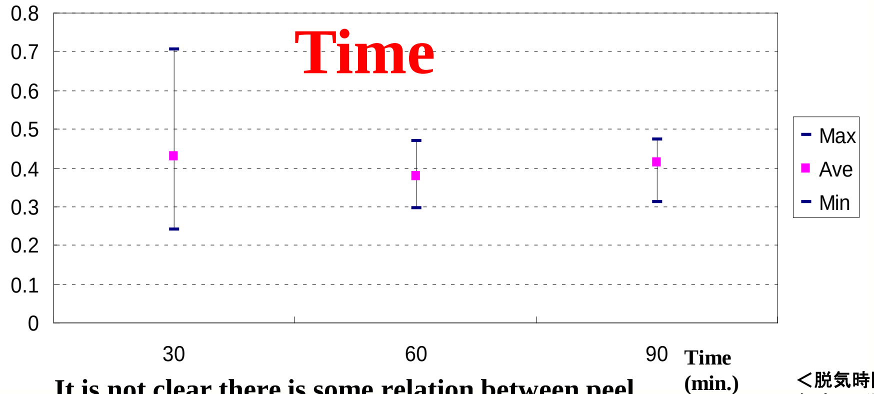
Palladium(II) acetate



Temperature : 140 deg.
Time : 30min
Pressure: test factor

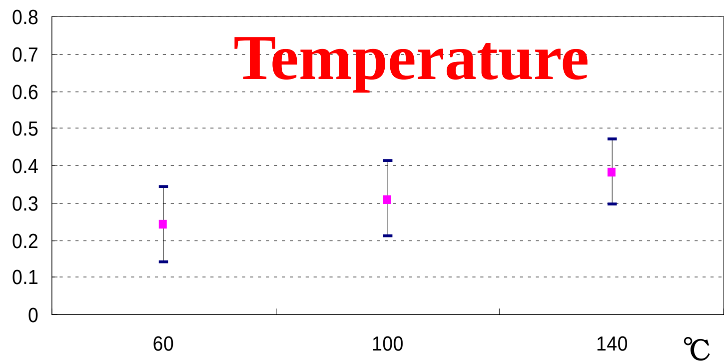


It is not clear there is some relation between peel strength and pressure. It is good enough at 15MPa.

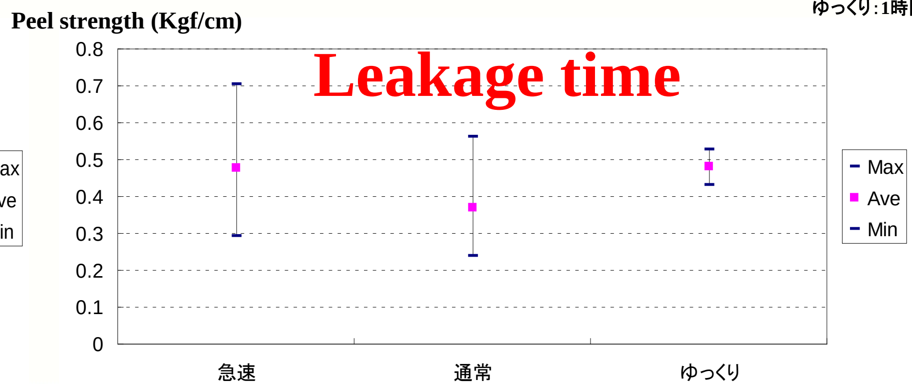


It is not clear there is some relation between peel strength and time. 30mins is good enough.

＜脱気時間＞
急速：30秒-60秒
通常：10分前後
ゆっくり：1時間以上



Peel strength is increasing in accordance with temperature.



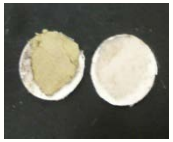
Rapid leakage is better than the others.

Complex properties from test results

Consideration the effectiveness to peel strength by complex type.

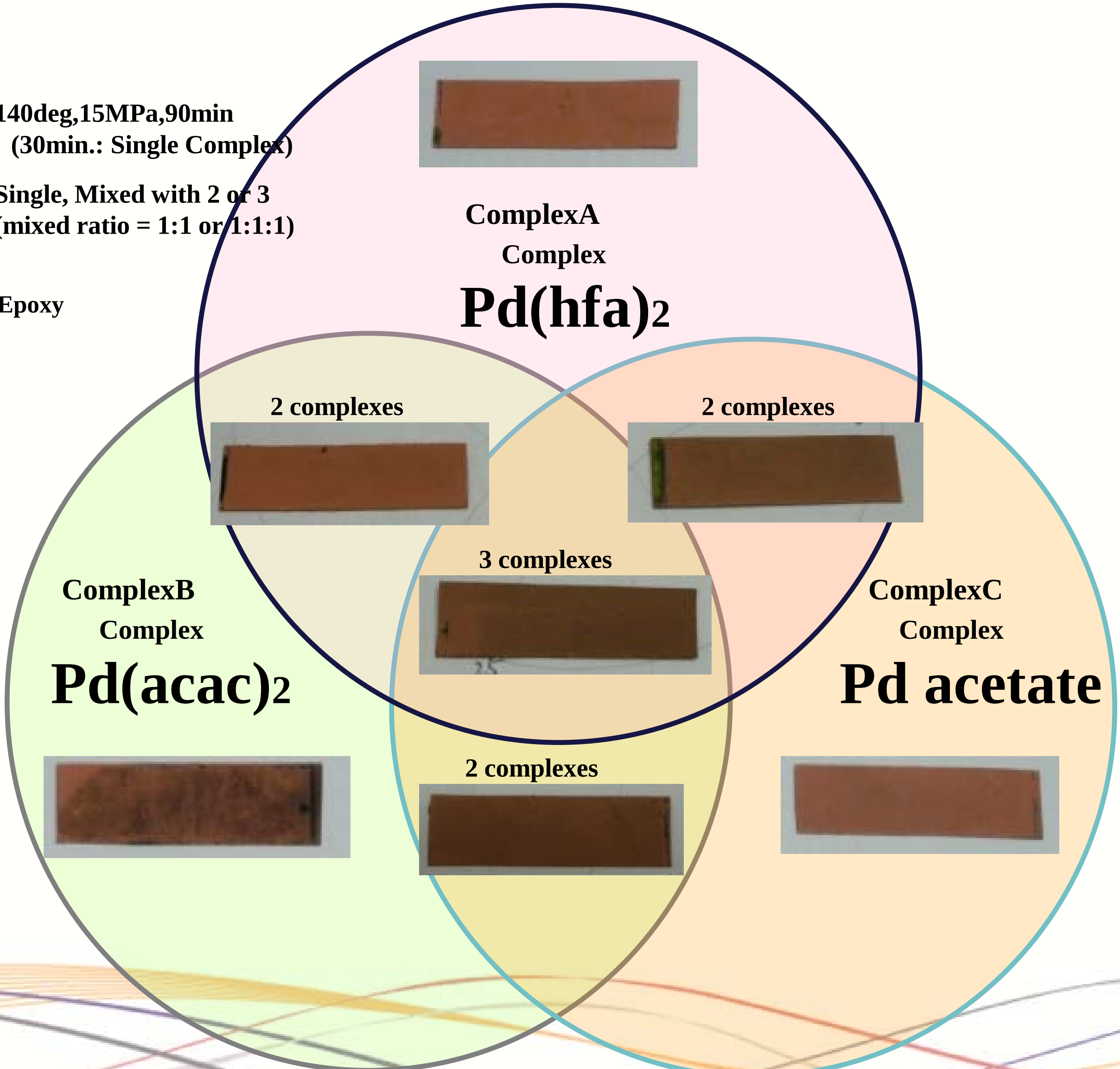
	Complex	Pressure	Temp.	Time	Leakgage
Pd系	 **Pd(Ⅱ)hexafluoro acetylacetonate** Dark Blown powder Complex A	○	—	×	—
	 **Bis-acetylacetonate Pd(Ⅱ)** Yellow powder Complex B	—	—	○	—
	 **Pd(Ⅱ)acetate** Red blown powder Complex C	×	○	×	△

○ : Effective
× : Not effective
△ : Unknown
— : Unconfirmed

	Complex	Complex feature	After SCF	Dissolution to CO2
Pd系	 **Pd(Ⅱ)hexafluoro acetylacetonate** Dark blown powder Complex A	Dependence on pressure. High pressure tends to be higher peel strength		High. Most of all were consumed after SCF
	 **Bis-acetylacetonate Pd(Ⅱ)** Yellow powder Complex B	Short time treatment is not good enough for plating. It requires at least 1 hour treatment for plating		Low. Most of them are still remaining after SCF. It changed coloring
	 **Pd(Ⅱ)acetate** Dark blown powder Complex C	As a whole, peel strength is higher level and performance is good. Better to be combine to another complex		Low. Hardly consumed after SCF.

Appearance after SCF & Electroless plating

SCF Condition	140deg,15MPa,90min (30min.: Single Complex)
Complex	Single, Mixed with 2 or 3 (mixed ratio = 1:1 or 1:1:1)
Material	Epoxy



Peel strength test result

Consideration of the differences single complex and mixed complex treatment

Single complex / Mixed complex

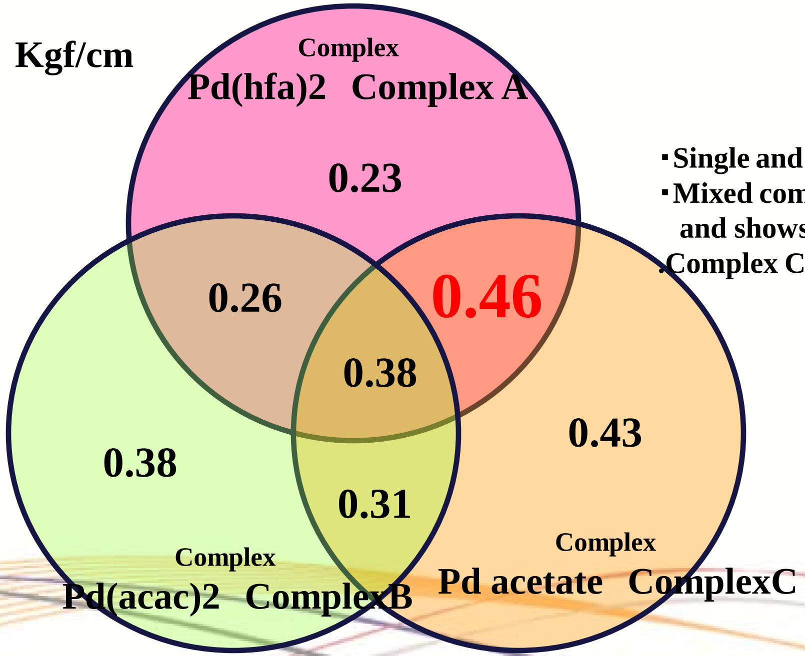
	ComplexA	Complex B		ComplexA+B
Mixed effectiveness	0.23	0.38	→	0.26

	ComplexA	Complex C		ComplexC+A
Mixed effectiveness	0.23	0.43	→	0.46

	ComplexB	ComplexC		ComplexB+C
Mixed effectiveness	0.38	0.43	→	0.31

SCF Condition 140deg,15MPa,30min

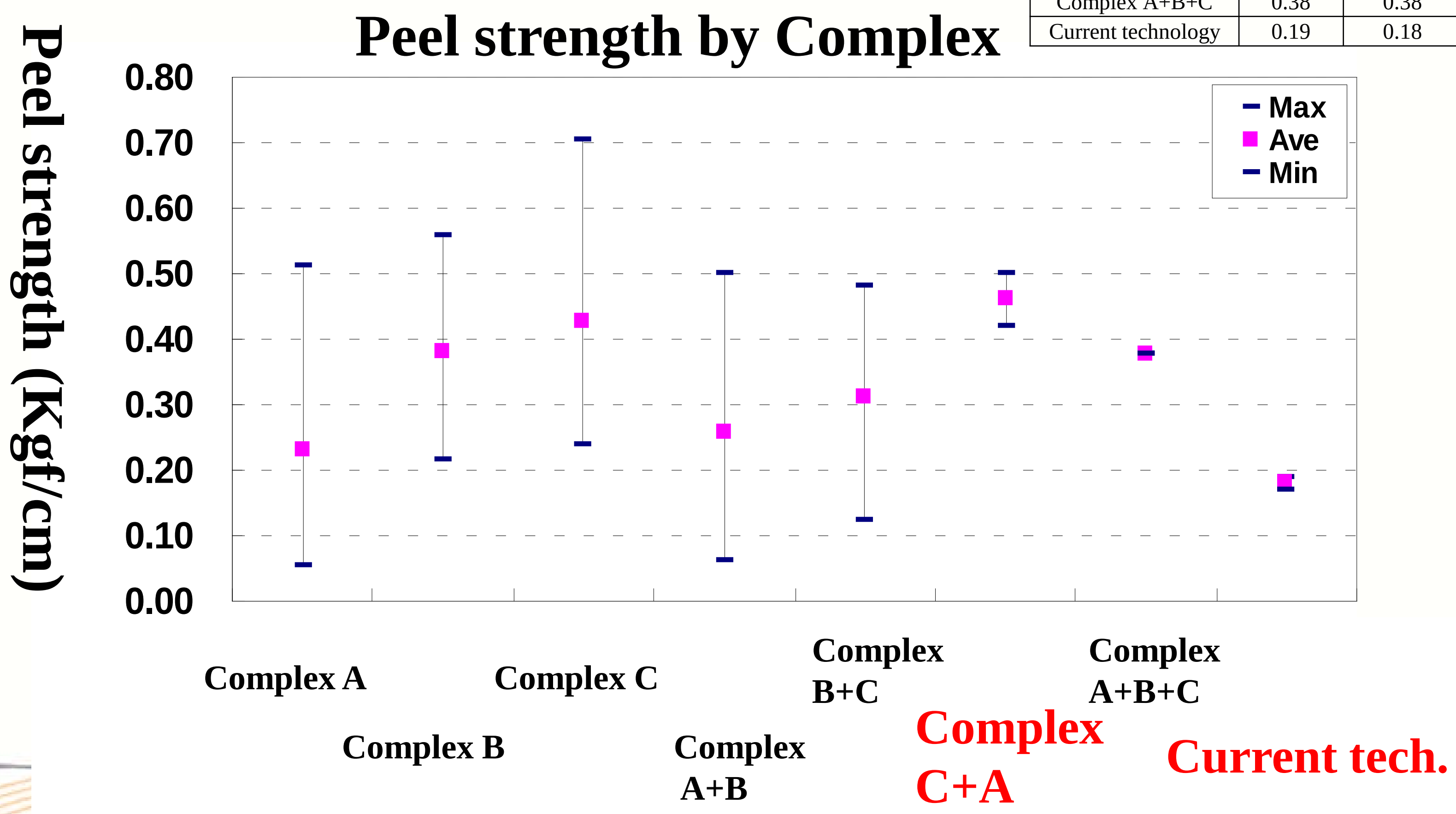
Unit: Kgf/cm



- Single and mixed complex of 30 mins treatment
- Mixed complex including Complex C is better than the others, and shows over 0.3 Kgf/cm in peel strength test.
- Complex C contributes its peel strength performances

Comparison of peel strength test result

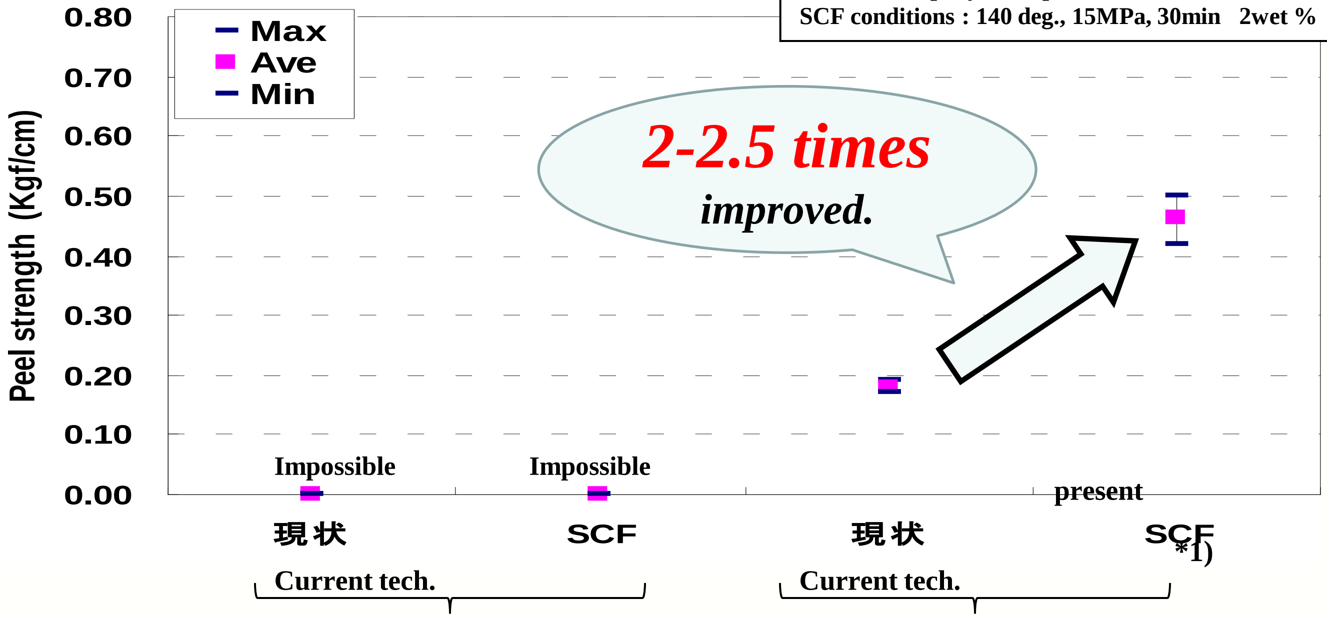
	Max	Ave	Min
Complex A	0.51	0.23	0.06
Complex B	0.56	0.38	0.21
Complex C	0.70	0.43	0.24
Complex A+B	0.50	0.26	0.06
Complex B+C	0.48	0.31	0.12
Complex C＋A	0.50	0.46	0.42
Complex A+B+C	0.38	0.38	0.38
Current technology	0.19	0.18	0.17



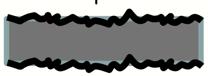
Peel strength to Epoxy resin by SCF

1) Comparison between SCF and current tech.
2) Comparison between flat surface and profiled surface

Sample making procedure :
SCF → E-less plating → Electro plating → Peel strength test
Total Plating thickness : 25 um (test samples)
Material : Epoxy resin piece
SCF conditions : 140 deg., 15MPa, 30min 2wet %




No Profile on surface
(Completely flat)


Profile on surface
(Etching out copper foil)

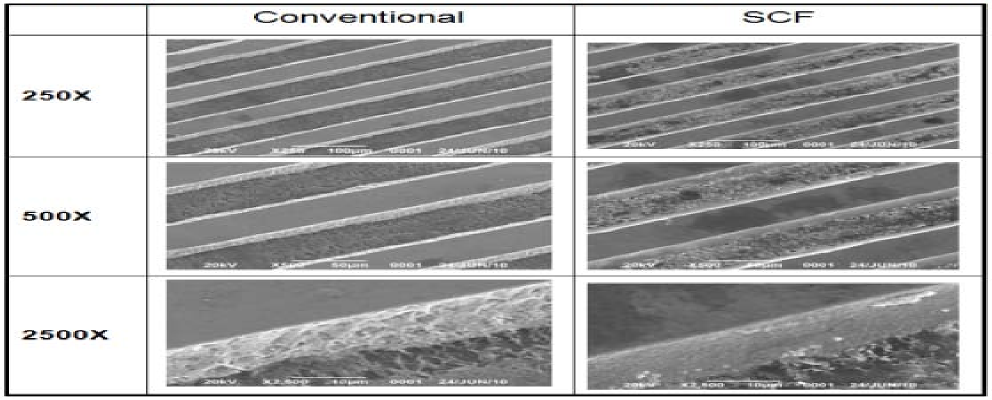
*1) Complex
Pd(2) acetate + Pd(hfa)2

1) *In applying SCF technology, Peel strength can be expected 2.0 -2.5 times stronger than existing process technology.(on epoxy resin board without copper)*
2) *However, it requires surface roughness on the epoxy resin.*
(not good enough for keeping peel strength on flat surface)

PCB Sample making status by SCF

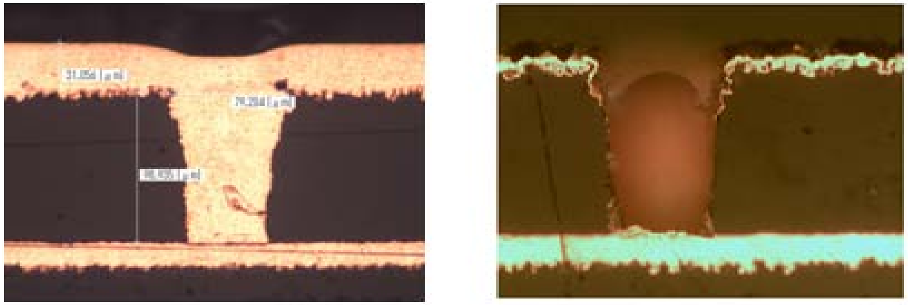
Circuit Conductors
L/S=50/50 µm

First time: L/S design= 50/50µm ⇒ Actual L/S= 50/50µm



VIA Plating Coverage
VIA Aspect ratio=2.0

SCF technology Current technology



Insulation thickness:100µm, Laser VIA diameter : 50µm, Aspect ratio : 2.0

Conclusions and Future Examine Items

As a effective results

1:It has recognized that SCF technology works effectively as a method of impregnation to epoxy resin.

2:Copper peel strength on Epoxy resin by complex impregnation of SCF can make it possible to improve 2.0 -2.5 times better than existing technology.

As a issue

3:Peel strength performances will be affected by surface condition (issue of surface treatment on material)

4:Relation between complex impregnation volume to epoxy resin and Pd ion contribution to plating (affection by removing Ligand) is not yet confirmed.

5:It would be important point that confirming to impregnate complex and ligand status condition in improving peel strength in future study.

The Nobel Prize in Chemistry 2010

"for palladium-catalyzed cross couplings in organic synthesis"

Richard F. Heck, Ei-ichi Negishi, Akira Suzuki

Akira Suzuki

Photo: Hokkaido University, Japan

Ei-ichi Negishi

Photo: Purdue University, USA

Richard F. Heck

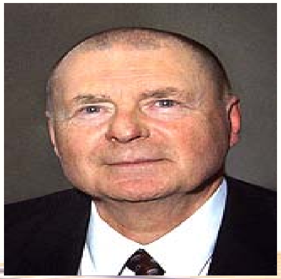
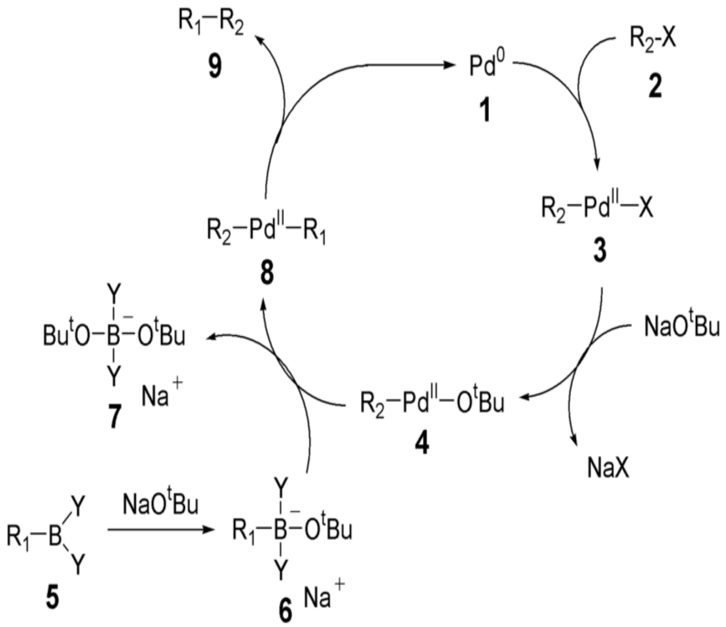


Photo: University of Delaware, USA

Suzuki/Miyaura Coupling Comprex Recycle

鈴木・宮浦カップリングの触媒サイクル



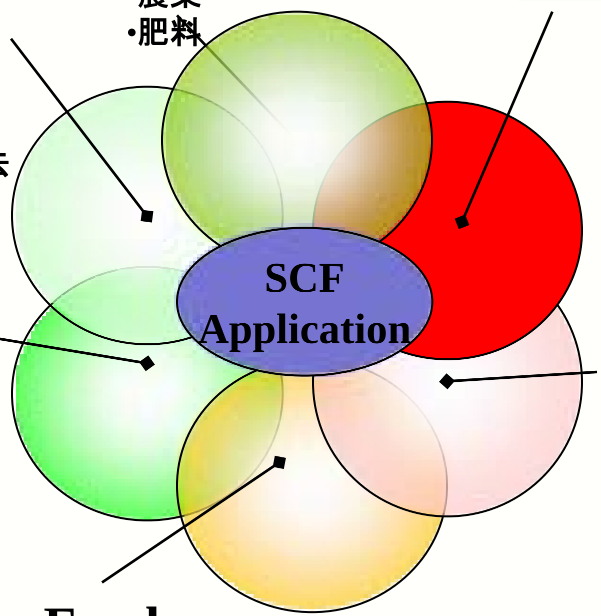
Negishi Coupling　根岸カップリング

$$R\text{-}ZnX + R'\text{-}Y \rightarrow R\text{-}R'$$

Application in various field

a) Application : antenna, condenser, battery, Environmental technology
応用技術:アンテナ、コンデンサー、電池技術、環境技術ほか

b) Application in various business field
各種ビジネス領域での応用



Agricultural
- 農薬
- 肥料

Electronics
- 超臨界めっき技術(プラスチック、めっき)
- ドライクリーニング(表面処理、衣類)
- 半導体分野
  ウエハ/レジスト剥離/ITパーツ洗浄
- 精密機械分野(油洗浄、溶剤除去)
- 電池

Medical
- 医薬品
- サプリメント
- 残留溶媒除去

Cosmetic
- 超臨界微粒子
- 精留

Environment
- 有害汚染物質の除去
- 超臨界洗浄
- 超臨界乾燥
- 超臨界腐食

Food
- 超臨界抽出(味成分、香り成分)
- 残留有害物質、農薬除去
- 滅菌処理
- サプリメント

PCB solution– Challenge for core technology

High Speed

PCB Solution

- ✓Low transmission loss Mat'l

PCB challenge

- ✓Optical tech
- ✓Embedded tech

High reliability

PCB Solution

- ✓Apply special Mat'l
- ✓High reliability soldering mat'l

PCB challenge

- ✓Introduce simulation system (accelerate R&D, accurate analysis & feed back)
- ✓New concept assembly proposal (Ex. Flip chip bonding, Au-Au, ACF,)

Downsizing

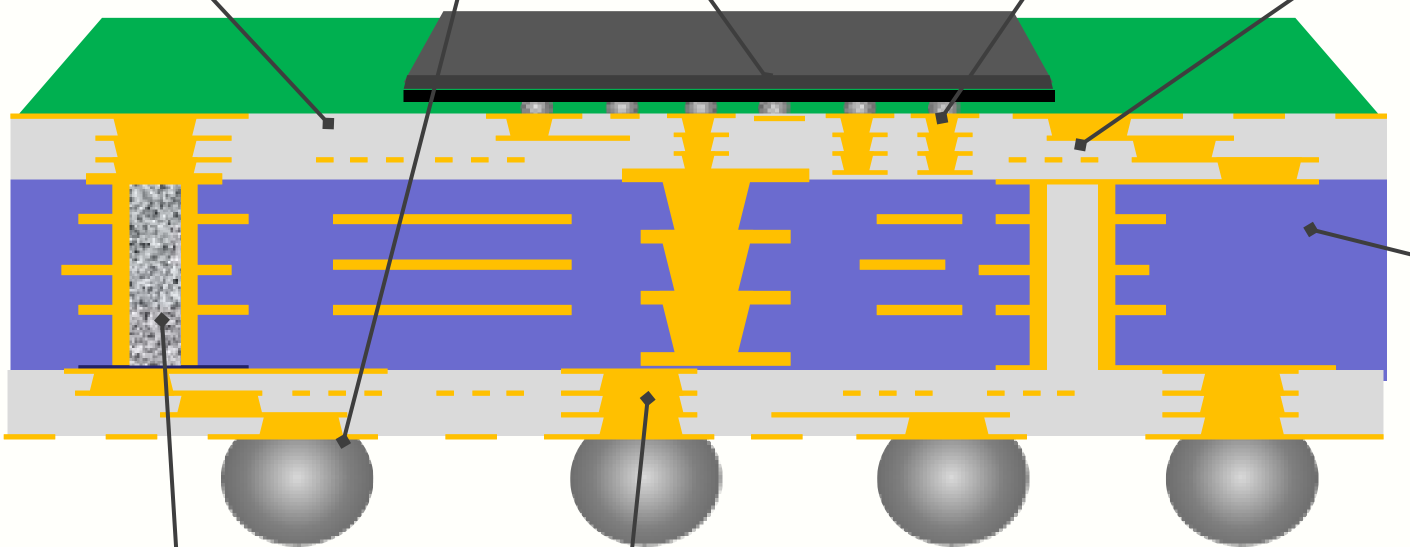
IC downsizing

PCB Solution

- ✓Any layer HDI
- ✓High A/R via (A/R>1.0)
- ✓Fine line (L//S>50um)

PCB challenge

- ✓Film based very thin & multi layer HDI
- ✓High A/R via (A/R <1.0)
- ✓Fine line (L//S <50um)



Inspection & repair

PCB challenge

- ✓ 4 wire testing
- ✓ high speed & accurate inspection, Low misjudgment
- ✓ high speed OP/SH repairing

Green electronics

PCB Solution

- ✓HF
- ✓Lead free

PCB challenge

- ✓Group original Mat'l development

Registration

PCB Solution

- ✓LDI introduction
- ✓Stable dimension Mat'l
- ✓High accuracy machine

PCB challenge

- ✓ Data linkage system between machines, Auto analysis and feed back to scale factor management
- ✓New concept process , material (like LDI,LDD,,,,)

Cost reduction

PCB Solution

- ✓ Apply low price Mat'l
- ✓Improve yield

PCB challenge

- ✓ Simplify process development (Cf. ALIVH, B2it,,,,)
- ✓Feed back system of failure mode analysis results (Ex. AOI results & patterning process) (Ex.. E-test results & via,pattern,plating)

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