

# CHARACTERIZATION OF FORMALDEHYDE-FREE ELECTRO-LESS COPPER PLATING FOR SEMI-ADDITIVE PROCESS

Masaharu Takeuchi, Tomoharu Nakayama, Hisamitsu Yamamoto  
C. Uyemura & Co., Ltd.  
1-5-1, Degchi, Hirakata  
Osaka, 573-0065 Japan  
Ph: 81-72-832-8171; Fax: 81-72-832-6559  
Email : [masaharu-takeuchi@uyemura.co.jp](mailto:masaharu-takeuchi@uyemura.co.jp)

## Abstract

Typically, industrial electroless copper plating solutions use formaldehyde as a reducing agent. However, since formaldehyde has a strong odor and is a carcinogenic substance, it has an adverse effect on the working environment and the human body. Therefore, an electro-less copper plating solution containing no formaldehyde is desired. We have researched and developed a formaldehyde-free electro-less copper plating solution and evaluated its properties for applications such as panel level package (PLP). Price is the main reason for selecting agents with reducing power to copper for use in the plating market. We promoted to develop the plating solution using sodium hypophosphite as a reducing agent, which is the next least expensive after formalin solution. The reducing agent used in this plating solution has low catalytic activity for copper. As a result, when the palladium catalyst on the resin is covered with copper plating, the plating deposition rate is reduced. In order to prevent the deposition reaction from stopping during plating, a metal salt with high catalytic activity for this reducing agent is plated. The method of adding to the liquid was carried out. As a result, the bath stability of the development bath is excellent because no Cannizzaro reaction or disproportionate reaction of the first copper ion occurs, unlike ordinary electro-less copper plating solutions. This is a major advantage in terms of running costs and requirements for ancillary the plating equipment. When the characteristics of the plating film by development bath were examined, the internal stress was found to be as low as 150 MPa on the tensile side. The adhesion to the ABF resin was high, ranging from 500 to 700 gf/cm. Also it exhibits excellent plating deposition inside blind via hole (BVH) which is equivalent to that of general electro-less copper plating solution, it can be applied to semi-additive process package boards where electro-less copper plating film is etched.

## Key words

Electro-less copper plating, Formaldehyde-free

## I. Introduction

Typically, industrial electro-less copper plating solutions use formaldehyde as a reducing agent. However, since formaldehyde has a strong odor and is a carcinogenic substance, it is said to have an adverse effect on the working environment and human body [1].

The available chemicals under consideration as reducing agents other than formaldehyde are glyoxylic acid [2], Dimethylamine borane [3] and sodium hypophosphite. Since glyoxylic acid is a derivative of formaldehyde, it can be plated under the same conditions as the formaldehyde bath. However, it is difficult to remove the product because it generates oxalic acid ions with low solubility by the

Cannizzaro reaction, and the treatment cost is high because glyoxylic acid is expensive and the bath stability is not so good. In addition, dimethylamine borane has a strong amine odor, which has a negative impact on workers, and its high reducing power results in low bath stability and an expensive chemical price. Among them, sodium hypophosphite, which is less expensive than formaldehyde, has high bath stability because it does not cause Cannizzaro reaction like formaldehyde and therefore does not cause disproportionation reaction by copper ion [4].

In this study, sodium hypophosphite was used as a reducing agent, and the film characteristics such as plating depositing property was evaluated.

## II. EVALUATION METHOD

The evaluation of formaldehyde-free electro-less copper plating solution includes deposition thickness, internal stress, adhesion strength and specificity. Resistance, surface morphology of the plating film, deposition in BVH, bath stability of the plating solution, and etching of the film have been studied.

### Plating process

Table 1 shows the electro-less copper plating process. This process corresponds to a typical printed circuit board.

**Table 1.** Electro-less Copper plating

Steps
Cleaner conditioner
Soft etching
Acid rinse
Pre-dip
Activator
Reducer
Accelerator
Electro-less Cu

※Except for after the accelerator, hot water or water rinsing process is performed between each process.

### Measurements of plating thickness

Commercially available FR-4 substrate (Hitachi Chemical MCL-E-67) with copper foil etched out, was plated in a development bath, and cross-sectional observation was made by SEM to measure the plating thickness.

### Internal stress

The 0.5 dm<sup>2</sup> specimen was plated for 1 hour and the internal stress was measured that spiral contract meter (Made by Yamamoto MS corp., LTD) used.

### Adhesion

After plating with the development bath on ABF resin (manufactured by Ajinomoto Fine Techno, GX-92 and GX-T31), 25μm of electro-plated copper was deposited. The plated film was peeled off from the resin by an autograph (Made by Shimadzu) in the 90-degree direction, and its adhesion was measured.

### Surface morphology of plating film and deposition in BVH

The surface morphology of the electro-less copper deposition onto the ABF resin (manufactured by Ajinomoto Fine Techno, GX-92R and GX-T31) from the development bath was observed by SEM. The plating deposition in BVH

(50μmφ, depth: 30μm) was observed in cross section by SEM.

### Resistivity

After depositing about 25 μm of electro-less copper plating on the stainless steel plate in a development bath, the plating film was pulled of the stainless steel plate. The resistivity of this plating film was measured by milliohm meter.

### Bath stability

The plating solution was placed in a 50 mL glass bottle and left in a constant temperature chamber at 40°C until the copper precipitated in the bottle, and the elapsed time was measured.

### Etch ability of plating film

After depositing 1μm of electro-less copper onto the FR-4 substrate, which had copper foil previously etched away, the copper plating film was dissolved in an SPS-sulfuric acid mixture for 2 minutes, and the amount of etching of the plated copper film was measured.

### Nano void observation

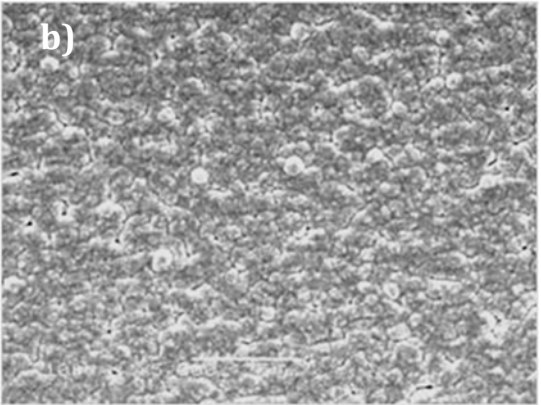
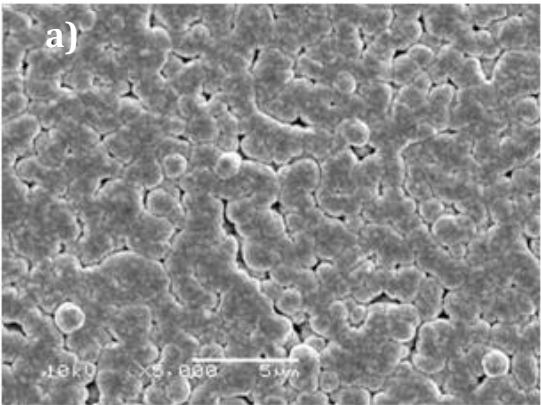
After plating electro-less copper with a development bath, acid copper sulfate electro-plating treatment was performed. And then, the interface of the copper foil and electro-less copper plating, and the interface of electro-less copper plating layer and copper electroplating layer were observed by TEM.

## III. RESULTS AND DISCUSSION

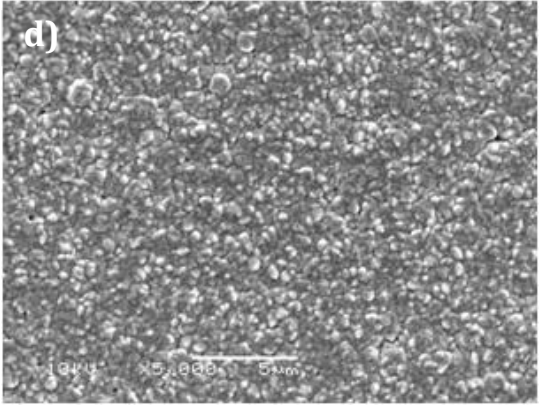
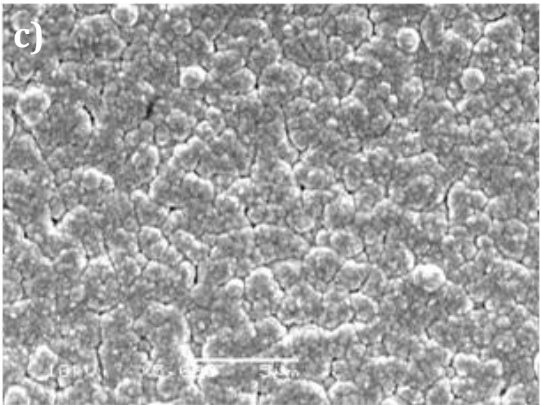
The results of the depositon film thickness, internal stress, and adhesion strength on ABF resin for the formaldehyde-containing bath as conventional bath and the developed bath are shown in Table 2. Except for the resistivity, the results were similar to the conventional bath. The results of SEM

**Table 2.** Plating characteristics

Reaction	Conventional	Development
Deposition rate* [μm/min] With FR-4 epoxy resin	0.06	0.09
Peel strength [gf/cm] with ABF GX-92	749	776
Peel strength [gf/cm] with ABF GX-T31	550	510
Internal stress [MPa] 1 μm thickness	100	150
Resistivity [μΩ·cm] 25 μm thickness	2.4	7.7



**Figure 1.** Surface observation by SEM with conventional bath  
a) GX-92R, b) GX-T31

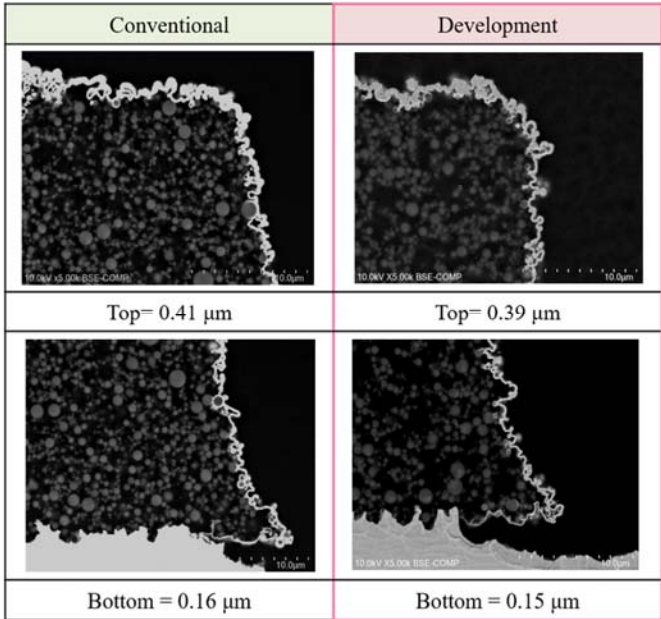
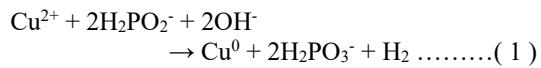


**Figure 2.** Surface observation by SEM with development bath  
c) GX-92R, d) GX-T31

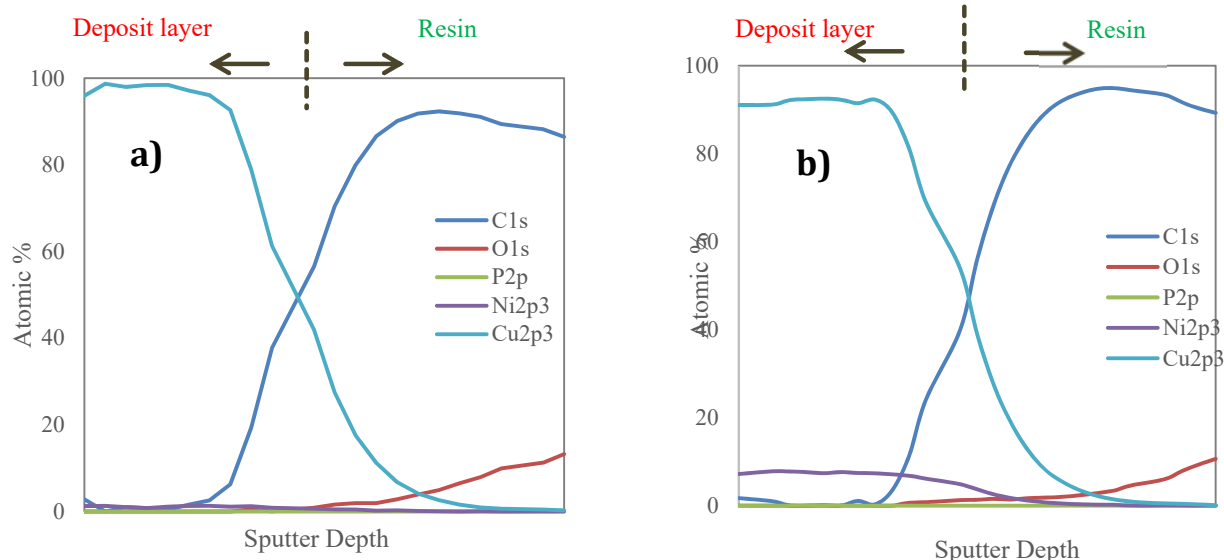
observation on the plating film surface are shown in Figure 1 and Figure 2. The plating surface of the developed bath was the same as the conventional bath.

The plating coverage in the BVH was confirmed by plating process in the developed bath. The results of cross-sectional observations by SEM are shown in Figure 7. The same degree of plating deposition was obtained as compared to the conventional bath. It is also evident that the plating is well deposited on the bottom of the BVH.

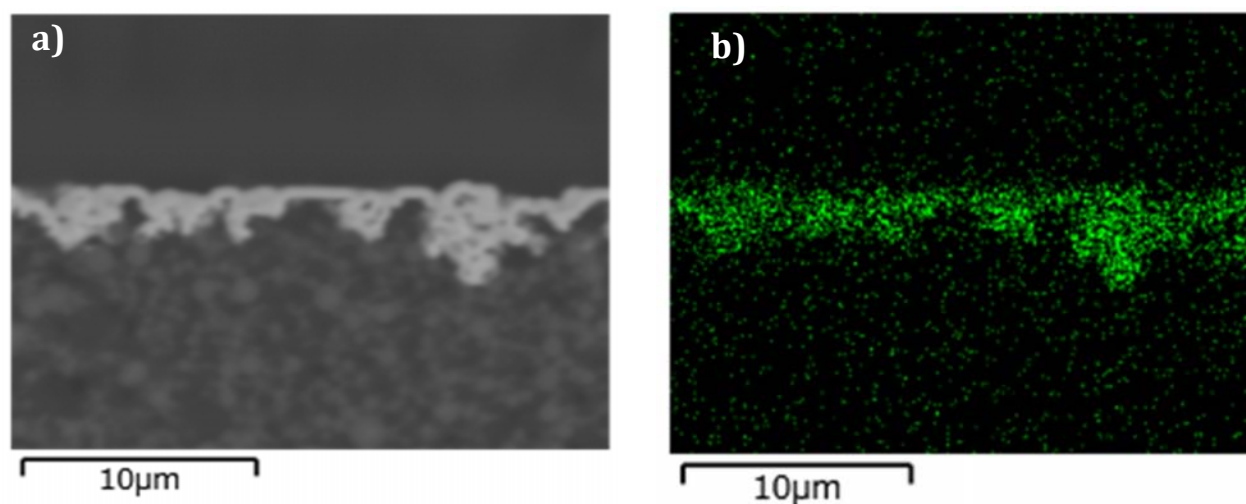
The resistivity was measured and was higher than the conventional bath. This is due to the fact that the development bath uses sodium hypophosphite as a reducing agent. The catalytic activity of the metals evaluated from the anodic starting potential of sodium hypophosphite is  $Au > Ni > Pd > Co > Pt > Cu > Ag$ , in that order. [4] Therefore, although the Pd adsorbed on the substrate material can be used as a catalyst in the main reaction in formula [4] to initiate a plating reaction, the deposition copper cannot be used as a catalyst to deposit a thicker layer of plating.



**Figure 3.** Cross-sectional observation after electro-less copper plating film in BVH of ABF resin



**Figure 4.** XPS measurement  
a) conventional, b) Development



**Figure 5.** Cross-sectional observation after electro-less copper plating film on ABF resin  
a) SEM observation, b) Nickel distribution of EDS

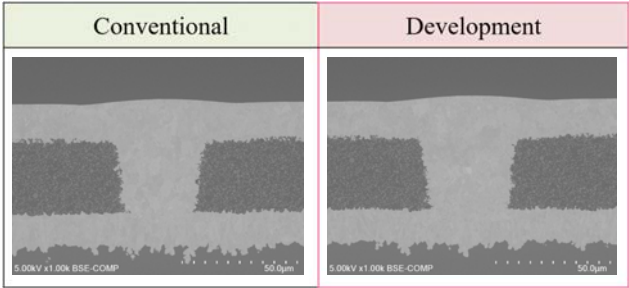
In order to obtain a thicker plating film, a metal with high catalytic activity, such as nickel, can be added to the bath and co-deposit in the plating film. As a result, the amount of nickel incorporated into the film increases and the resistivity is higher. XPS was used to check the nickel content in the plating film, and the nickel content was clearly observed in the developed bath as shown in Figures 4. Mapping by EDS was also performed to check the distribution of nickel content in the plating film. The results are shown in Figures 5. From Figure 5, it can be seen that nickel is contained in the entire plated film.

Because the higher resistivity may affect the filling characteristics of electro-copper plating, we have been plated

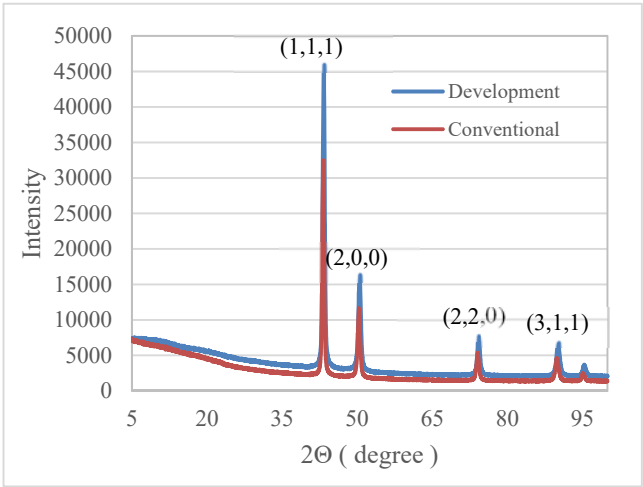
electro-copper after electro-less copper plating for using development bath. The results are shown in Figure 6. As a result, The BVH was well filled by copper electroplating.

In order to confirm the crystal orientation of the developed bath, XRD measurements were performed. The results are shown in Figure 7. In comparison with the conventional bath, the peaks are found in the same point and the peaks on the (1,1,1) surface are higher in both baths. This indicates that the developed bath has the same crystal orientation as the conventional bath containing formaldehyde.

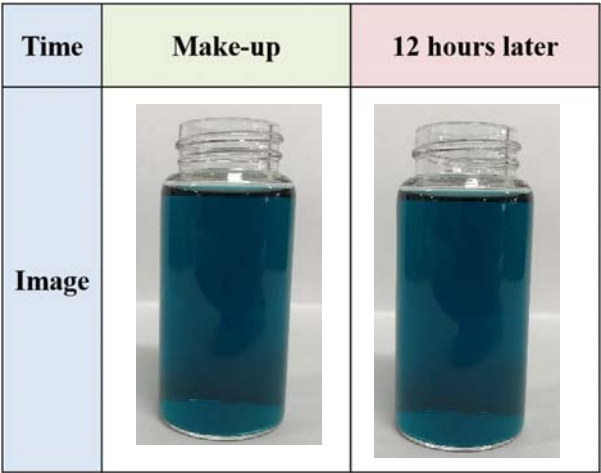




**Figure 6.** Cross-sectional observation after BVH filling type copper electroplating



**Figure 7.** Crystal orientation by XRD



**Figure 8.** Bath stability test with developed bath

The results of the bath stability tests of the developed bath are shown in Figure 8. No copper powder was found in the bath even after 12 hours of heating at 40°C, the working temperature. In the conventional bath, copper powder was

**Table 3.** Etching rate and crystal size of electro-less copper plating

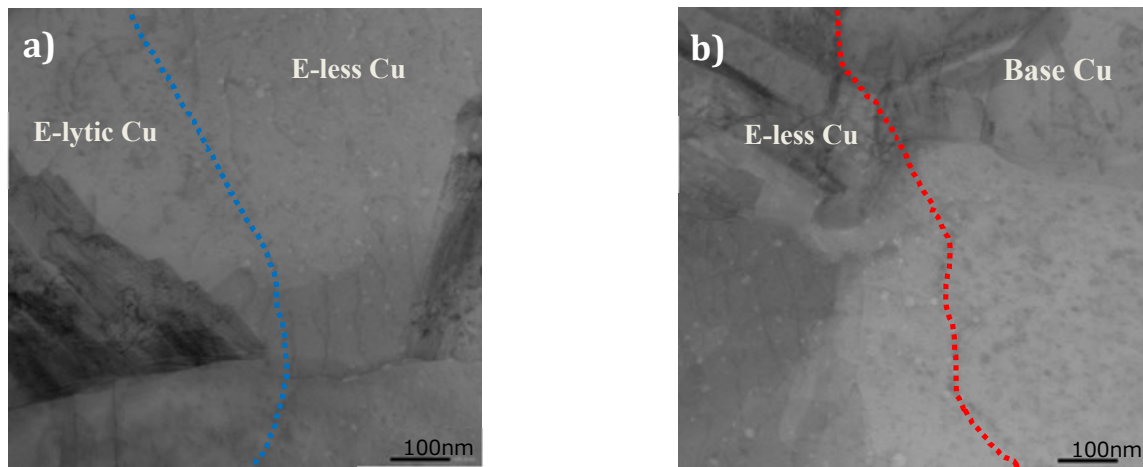
	Conventional	Development
Etching rate [μm]	0.44	0.65
Grain size average [μm]	0.41	0.31

Chemical	Conventional		Development	
	IPF Map*	Grain Map	IPF Map*	Grain Map
EBSD image				
Grain size average [μm]	0.41		0.31	

**Figure 9.** Crystal size measurement by EBSD

found after 8 hours. Conventional bath with formaldehyde cause Cannizzaro reaction and disproportionation of the first copper ion. Therefore, if the concentration of dissolved oxygen in the bath does not exceed a certain value, bath decomposition will occur. Since the developed bath uses sodium hypophosphite as a reducing agent, the Cannizzaro reaction and disproportionation reactions do not occur. Therefore the bath stability is considered to be high.

Next, the results of the evaluation of the etch ability of the plating film are shown in Table 3. The results showed that the etching rate was faster than that of the conventional bath. The crystal size of the plating deposition copper was confirmed by EBSD and it was found to be smaller in the development bath, as shown in Figure 9. It is inferred that the etching rate is faster due to the small crystal size and many interfaces. Therefore, the time for flash etching during



**Figure 10.** Nano void observation by TEM

a) Interface of Electro-less Copper and Copper electroplating, b) Interface of electro-less copper and inner copper layer

patterning is reduced, which is expected to reduce the side etching of the interconnects.

In recent years, the Nano void at the connection interface has received a lot of attention. Nano voids are small voids that appear at the interface between the inner copper layer or the electroplating film and the electro-less plating film. There are concerns that the presence of this will reduce the reliability of the copper and copper connection. No Nano voids were found in the conventional bath, but to check for Nano voids in the development bath, each interface was observed by TEM during the plating treatment on copper in the development bath and after the subsequent electro-copper plating treatment. The results are shown in Figures 10. No Nano void from the electro-less copper plating process was observed at the interface between the copper electroplating film and the electro-less copper film, or at the interface between the electro-less copper plating film and the base copper. This suggests that the development bath does not generate nanovoids, and therefore, it is expected that there is no decrease in the reliability of the copper-copper connection due to the nano void in the development bath, which is equivalent to that in the conventional bath.

#### IV. SUMMARY

In this research and development, we investigated an electro-less copper plating solution that does not use formaldehyde. Various comparisons with conventional bath were carried out, and the performance was almost equal to that of the conventional bath. Therefore, it can be applied to semi-additive process package boards as well as conventional bath. In addition, eliminating formaldehyde reduces the negative impact on the human body and the environment, so it is expected that we can introduce it to the market.

#### V. References

- [1] H. Kamei, T. Yamamoto, T. Yoshida, Y. Kuroiwa, M. Kawai, S. Kuroiwa, M. Koyama, Y. Kaneko : Eisei kagaku Vol 27, No.6, (1981)
- [2] T. Itahashi, H. Akasaka, T. Iida, E. Takai, N. Nishimura : Journal of Japan Institute of Electronics Packaging, Vol 5, No.3, (2002)
- [3] I. Ohno, O. Wakabayashi, S. Haruyama : Denki kagaku, Vol 53, No.3, (1985)
- [4] T. Fujinami ; Hyomen Gijyutsu, Vol 48, No.4, (1997)