Improvement of Solder Bonding Characteristics Using New Electroless Thin Ni/Au Plating Process

Tomohito KATO¹³, Hajime TERASHIMA³, Hideto WATANABE³, Mitsuhiro WATANABE², Hideo HONMA², Osamu TAKAI¹,²

¹. Graduate School of Engineering, Kanto Gakuin University, 1-50-1, Mutuurahigashi, Kanazawa-ku, Yokohama-shi, Kanagawa, 236-0004, Japan.
². Material Surface Engineering Research Center, Kanto Gakuin University, Yokohama Kanazawa High-Tech Center, 1-1-1, Fukuura, Kanazawa-Ku, Yokohama-shi, Kanagawa, 236-0004, Japan.

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Abstract: Fine pattern formation (Line Width/Line Space is less than 50µm) using electroless Ni/Au plating, extraneous Ni deposition on the resin area of fine pattern often observed due to the residual Pd catalyst on the patterns. Thinner Ni plating was applied to solve the problem. However, the tendency for local Ni corrosion by the immersion Au plating step increases, and solder connection reliability decreases compared to conventional Ni/Au process. Accordingly, the influence of Pd catalyst deposition conditions on electroless Ni/Au plated film properties was investigated. We propose the direct electroless Ni strike plating on the Cu patterns without the Pd catalyst. Generally, solder bonding strength with the electroless thin Ni/Au plating decreased with increase in Pd catalyst treatment time. On the contrary, solder bonding strength does not influence by the Ni strike plating time. Uniform Ni deposition and good solder bonding strength was accomplished by the application of the electroless Ni strike plating method.

Key words: Thin electroless Ni/Au plating process, Electroless Ni strike plating, Uniformity of Ni plating film, Intermetallic, Solder ball shear strength

Corresponding author: Tomohito KATO, Graduate School of Engineering Kanto Gakuin University, 1-50-1, Mutuurahigashi, Kanazawa-ku, Yokohama-shi, Kanagawa, 236-0004, Japan, Kojima Chemicals Co., LTD., 337-26, Kashiwabara, Sayama-shi, Saitama, 350-1335, Japan. E-mail: t.katou@kojima-c.co.jp.
1. Introduction

Packaging densities of printed circuit boards, on which electronic components are mounted, have a progressively higher level of functionality as electronic devices and are becoming increasingly sophisticated and wiring of finer lines at narrower pitches is also required [1]. Electroless Ni/Au plating is ordinarily applied on Cu wiring to bond electronic components with printed circuit boards, using solder and bonding wires. However, the Pd catalyst remaining on the resin between the Cu wiring are activated during electroless Ni plating, and hydrogen gas is generated by the oxidation reaction of the reducing agent over a Pd catalyst and Ni. Then, the hydrogen gas generated along with the electroless Ni plating film causes extraneous deposition of Ni [2, 3]. Reducing the film thickness of the electroless Ni plating film to 1 µm or less and then performing electrolessAu plating is essential to resolve this issue [4]. On the other hand, the solder bonding characteristics of electroless Ni/Au plating films have been reported to decrease when the film thickness of the electroless Ni plating is reduced in comparison with conventional electroless Ni/Au plating processes [5]. There are, however, only a few reports that covered mechanisms of deteriorating solder bonding characteristics. This implies that resolving this problem is essential in order to achieve a favorable solder bonding characteristic in the thin electroless film Ni/Au plating process performed on a high density Cu wiring.

The conditions of the electroless Ni plating that deposits on Cu is generally influenced by the activity of the Cu surface, as well as the conditions in which the hydrogen gas is generated while the electroless Ni plating is performed. Stabilizing the surface conditions of the substrate Cu wiring and the Pd catalyst treatment conditions and essential in order to avoid extraneous deposition during electroless Ni plating films [6, 7]. Chemical species such as Pd ions, inorganic ions, and organic ions exist in general purpose Pd catalyst solutions of hydrochloric acid type (hereinafter referred to as the "HCl type") and sulfuric acid type (hereinafter referred to as the "H_2SO_4 type") [8]. Deposition of Pd catalyst concentrates on the edges of the wirings, independent microelectrodes as well as ground electrodes due to linear diffusion and non-linear diffusion when Pd catalyst is deposited on Cu wirings [9]. Controlling Pd catalyst treatment conditions at the Cu wirings and achieving uniform deposition of Ni are essential, since excessive dissolution of Cu and excessive absorption of Pd catalyst occur at such plated parts [10].

The paper describes the influence of electroless Ni plating film on solder bonding characteristics in electroless Ni/Au plating processes. This was investigated first by this study, followed by the consideration of the mechanisms of deteriorating solder bonding strength during the formation of a thin Ni plating film. A
Improvement of Solder Bonding Characteristics Using New Electroless Thin Ni/Au Plating Process

2. Experimental Methods

2.1 Preparation method of electroless Ni / Au plated substrates for evaluations

Acidic degreasing, etching, and desmutting were performed on the evaluation substrates. Then the HCl type was used to as an initiation of electroless Ni plating on the Cu wiring. And followed by the electroless Ni plating, displacement type cyanide Au plating were deposited on the Ni plating films of 0.5, 1, 3, and 5µm thickness. In addition, an Au plating film of 0.05 µm thickness was deposited on the Cu wiring as electroless Ni/Au plating was performed on the Cu wiring.

On the other hand, electroless Ni and displacement type Au plating that are similar to those described above were performed. This was done after the Ni catalyst film was formed instead of the Pd catalyst on Cu, using the electroless Ni strike plating (hereinafter referred to as the "Ni strike process") of the composition described in Table 1. This was following the acidic degreasing, etching, and desmutting of the evaluation substrates when electroless Ni/Au plating films were formed on the Cu wiring during the new electroless Ni/Au plating processes. The thickness of the Ni plating film on these occasions was set to 0.5 µm, whereas the film thickness of the Au plating was set to 0.05 µm. Electroless Ni/Au plating (0.5 µm/0.05 µm) was performed using the HCl type and the H$_2$SO$_4$ type as described in Table 1. This was performed in order to form films of the referenced electroless Ni/Au plating for the purpose of consideration. The immersion time of evaluation substrates in respective catalyst solutions was set to 60 sec. and 180 sec., presuming excessive absorption of catalyst metal ions in fabricating the respective evaluation substrates.

<table>
<thead>
<tr>
<th>Electroless Ni strike plating solution</th>
<th>HCl type Pd catalyst solution</th>
<th>H$_2$SO$_4$ type Pd catalyst solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO$_4$ · 6H$_2$O  0.1 × 10$^{-3}$mol/dm$^3$</td>
<td>PdCl$_2$  0.5 × 10$^{-3}$mol/dm$^3$</td>
<td>PdSO$_4$  0.3 × 10$^{-3}$mol/dm$^3$</td>
</tr>
<tr>
<td>C$_2$H$_7$N · BH$_3$  0.07 mol/dm$^3$</td>
<td>HCl  0.4 mol/dm$^3$</td>
<td>H$_2$SO$_4$  0.05 mol/dm$^3$</td>
</tr>
<tr>
<td>H$_3$BO$_3$  0.16 mol/dm$^3$</td>
<td>Temperature  25 ℃</td>
<td>Temperature  25 ℃</td>
</tr>
<tr>
<td>Malic acid  0.015 mol/dm$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH  9.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature  25 ℃</td>
<td></td>
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</tr>
</tbody>
</table>
Improvement of Solder Bonding Characteristics Using New Electroless Thin Ni/Au Plating Process

2.2 Measurement method for the solder ball bonding strength

Evaluation substrates after electroless Ni/Au plating were heat treated at 175 °C for an hour. And then, rosin flux was applied on solder ball pads with a pad diameter of 0.6 mm and a pitch of 1.3 mm, to mount lead-free-type solder balls with 0.7 mm ball diameter. Solder balls were then mounted on the substrates using a reflow oven. A solder ball shear strength measurement instrument (RHESCA Co., LTD., PTR-1102) was used to take 20 point measurements on each substrate at a shear speed of 300 µm/sec. and calculated the average solder bonding strength. A field emission scanning electron microscope (FE-SEM; JEOL Ltd., JSM-7000F) and energy dispersive X-ray spectrometry (EDS; JEOL Ltd., JED-2300F) were used to observe the fracture surfaces after solder ball shear strength measurements.

2.3 Metal composition analysis on solder bonded segments

Evaluation substrates that had solder balls mounted were cut into pieces of 5 mm × 5 mm and then coated with cold embedding resin. The cross-section was then polished with a cross-section polisher (CP; JEOL Ltd., SM-09010) to expose the bonded interface between the plating and solder ball to perform analysis with the FE-SEM and EDS on the respective metal components at the solder bonded segments.

2.4 Observations on the conditions of electroless Ni/Au plating film depositions

The appearance of electroless Ni plating films were observed using an FE-SEM. The conditions of the local corrosions were analyzed using the CP, the cross-section of the evaluation substrate, which had been electroless Ni/Au plated, exposing the Ni/Au plated film cross-sections, and followed by observing the exposed surfaces with an FE-SEM.

2.5 Deposition reaction behavior of displacementtype Au plating on film of electroless Ni plating

The deposition reaction behavior of displacement type Au plating on film of electroless Ni plating was considered, by observing the changes using an electrochemical measurement instrument on the electric potential of the Cu plate, which was electroless Ni plated as it was immersed in an Au plating bath. A Cu plate was used as a working electrode. Pd catalyst treatment was performed on the Cu plate to form films of electroless Ni plating with a thicknesses of 0.5, 1, 3, and 5 µm. An Ag/AgCl electrode was used as a reference electrode, while a potentiosstat (HOKUTO DENKO CORPORATION; HAL30001) was used as the electrochemical measurement instrument to investigate the Au deposition reaction behavior on the Ni plating film of the respective film thicknesses.
2.6 Observation of the catalyst metal deposition conditions on Cuwiring

The amount of the catalyst deposited on the Cuwiring was investigated using an Auger electron spectroscope (AES; JEOL Ltd., JAMP-7810F).

2.7 Observation of the Cu dissolving behavior in catalyst treatment

The corrosion conditions of the Cuwiring surface after the respective catalyst treatments were observed using an FE-SEM. The corrosion conditions in the direction of the depth were considered by observing the boundary conditions between Cu and Ni using an FE-SEM. The specimens were prepared by cutting the evaluation substrate after electroless Ni plating into 5 mm × 5 mm pieces, which were then coated with cold embedding resin and the cross-section was polished using the CP.

The Cu dissolving behavior in the respective catalyst treatments was investigated by anode polarization measurements of Cu in the respective catalyst solutions using an electrochemical measurement instrument. The anode polarization measurement conditions are described below. A Cu plate, with the sealing implemented and evaluation area set to 10 mm × 10 mm, was used as a working electrode. An Ag/AgCl electrode was used as a reference electrode, while Pt wirings were used as a counter electrode. The respective catalyst solutions were used as electrolytic solutions, while a potentiostat was used as the anode polarization measurement instrument.

2.8 Evaluation on uniformity of electroless Ni plating films

Cu and Ni were prioritized in performing anodic dissolution, and the Cu dissolution rates were derived based on Cu and Ni ion concentration using a potentiostat in order to investigate the uniformity of electroless Ni plating film on Cu. Working electrodes used in this consideration were prepared by applying electroless Ni plating of 0.5 µm on Cuwirings (10 mm × 10 mm), using respective catalyst solutions. An Ag/AgCl electrode was used as the reference electrode. A 1 g/L KCN aqueous solution was used as the electrolytic solution. The Ni plated films under the respective conditions were immersed in the electrolytic solution at 25 °C and the controlled potential reverse electrolytic treatment was performed for 30 min with a potentiostat operating at 300 rpm. After controlled potential reverse electrolysis was performed, the concentrations of Ni and Cu ions that dissolved in electrolytic solution were measured using an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP; Hitachi High-Tech Science Corporation, PS3520). The uniformity of electroless Ni plating film was calculated by the following equation, using the ion concentration values for Ni and Cu that dissolved in the electrolytic solution.
Cudissolution rate (%) = \[\frac{\text{Cu concentration mg/dm}^3}{\text{Cu concentration mg/dm}^3 + \text{Ni concentration mg/dm}^3}\] \times 100

3. Results and Discussion

3.1. Influence of Ni plating film thickness on solder ball bonding characteristics

Thinning the film thickness of Ni plating is necessary in order to solve the potential threat of sorting between wirings. When the Ni plating film is thinned down, however, there is a tendency of the solder bonding characteristics to deteriorate. There has been little reported on details of the mechanism of this phenomenon. HCl type was first used to form a Ni plating film of 0.5, 1, 3, and 5µm thickness over Cu, after which, an Au plating film of 0.05 µm thickness was formed over Ni film. Shear strength and fracture conditions of the solder balls on the evaluation substrate, which had been heat treated at 175 °C for 1 h, were investigated.

The shear strength of the solder ball was indicated to be of same value in cases where the thickness of the Ni film of electroless Ni/Au plating film was between 1 µm and 5 µm, as shown in Figure 1. Furthermore, no significant variance was confirmed when the standard deviation (σ) of the solder ball shear strength values was derived and the strength variance was compared based on 3σ value. On the other hand, in cases where the thickness of the Ni plating films of electroless Ni/Au plating film was 0.5 µm, the minimum shear strength value for the solder ball declined by about 30% compared with cases where the Ni thickness was 5 µm. Furthermore, the variance of the solder ball shear strength values was confirmed to increase by 30% when compared based on the variance of the ball shear strength values (3σ). All fractures of solder balls were occurring between solders.

The solder ball fixing strength characteristics declined in the case where the Ni plating film thickness was 0.5 µm, as described above. Cross sections of ball bonding segments after solder mounting were observed and the conditions of shapes of intermetallic compounds were investigated in cases where the respective Ni plating film thicknesses were varied, in order to investigate the causes.

Intermetallic compounds, composed primarily of \((\text{Cu, Ni})_6\text{Sn}_5\), were formed on the solder side of the bonding boundary as shown in Figure 2. Furthermore, the thickness of intermetallic compounds increases as the thickness of the Ni plating film decreased. In addition, voids were observed between intermetallic compounds, \((\text{Cu, Ni})_6\text{Sn}_5\), and Ni + Ni₃P layers, and the number of voids increased as the thickness of the Ni decreased.
On the other hand, the solder reached the Cu film when the thickness of the Ni was 0.5 \( \mu \text{m} \), and \((\text{Cu, Ni})_6\text{Sn}_5\) was formed on the Cu film side of the solder bonding boundary layer. Since intermetallic compounds generally have mechanically brittle characteristics \[11\], the solder ball shear strength is decreased due to the formation of intermetallic compounds on the Cu film side. Thus, controlling the scattering of solder onto the Cu film layers from Ni during solder mounting and maintaining the Ni thickness was important.

![Graph showing shear strength vs. Ni film thickness](image)

**Fig. 1 Relationship between solder ball shear strength on each Ni film thickness**

![SEM images of cross section at the BGA jointed area](image)

**Fig. 2 SEM images of cross section at the BGA jointed area.**

### 3.2 Solder bonding strength deteriorating mechanism during the application of thin Ni plating film

The shear strength of the solder ball on the electroless Ni/Au plating film decreased, as the intermetallic compound \((\text{Cu, Ni})_6\text{Sn}_5\) was formed on the Cu film side of the solder bonding boundary layer, when the Ni film thickness was 0.5 \( \mu \text{m} \), as a result of the descriptions provided above. Electroless Ni plating films of 0.5, 1, 3 and 5\( \mu \text{m} \) thicknesses were therefore formed on Cu to observe the surface appearance conditions of the
Ni plating film. Furthermore, an Au plating film of 0.05µm thickness was formed on top of the respective Ni plating films and the views of film cross-section were observed using the FE-SEM. The results are shown in Figure 3.

The deposited Ni particles became finer as the Ni plating film thickness decreased, indicating a trend of increasing variance in grain boundaries and particle sizes, as well as irregularities in shape.

A CP was used to treat cross sections of the electroless Ni/Au plating films and the cross sections were observed using an FE-SEM. Local corrosion of the Ni increased as the thickness of the Ni plating film became thinner. The progression of corrosion was observed to occur in the direction of the depth as well as in the lateral direction.

Electroless Ni of respective film thicknesses were immersed in 1 mol/L NaCl aqueous solution and the rest potential was measured. This was because there were variances with the Ni deposition conditions as well as with the conditions of local corrosions of the Ni when the displacement type Au plating was performed, due to the changes in the thickness of the Ni plating film, as described above.

The rest potential of the Ni plating film was indicated to be about -310 mV for cases where the thicknesses of the electroless Ni plating films were 1 to 5 µm. On the other hand, the rest potential of the Ni plating film was indicated to be about -264 mV for the case where the thickness of the electroless Ni plating films was 0.5 µm. This confirmed that the Ni plating films of 0.5 µm was close to the value for the potential of the Cu film (-206 mV), which is the Cu substrate.

Electroless Ni plating films of the respective film thicknesses were immersed in a displacement type Au plating bath to measure the immersion potential as Au deposition reaction behavior. The results are shown in Figure 4. In cases where the thickness of the Ni plating film was 1 µm or greater more than, the immersion potential of the Ni film was indicated to be -400 mV, and it reached -350 mv after 100 sec. On the contrary, thickness of the Ni plating film was 0.5 µm, on the other hand, the immersion potential was confirmed to increase gradually even after the immersion time of 100 sec. and that the displacement type Au deposition reaction did not stable. This suggests that the Ni dissolution and displacement reaction of Au were still continuing [12].
The mechanism for the decreasing solder bonding strength during the formation of thin Ni plating film was estimated as described below, according to the results shown in Figure 2 to Figure 4.

(i) The coverage of the Ni plating was not consistent while the film of electroless Ni plating was being formed on the Cu wiring, with fine Ni particles and an increased grain boundary. This led to the Ni surface potential being indicated at a value that is close to that of the Cu surface potential.

(ii) Local corrosions of the Ni occurred at numerous locations while the displacement type Au plating was performed and the corrosion progressed in the direction of the depth.

(iii) Solder scattering reaction reached the Cu film via portions such as segments where local corrosions of the Ni were occurring or where the Ni coating did not exist, forming intermetallic compounds of (Cu, Ni)$_6$Sn$_5$ of strengths that were brittle within Cu films, when the reflow of solder balls was performed.
The bonding strength of the solder balls on the thin electroless Ni/Au plating films was estimated to have declined due to the factors described above. Furthermore, controlling the formation of the intermetallic compound (Cu, Ni)$_6$Sn$_5$ in the Cu film portion by improving uniformity of Ni plating films was confirmed to be essential in order to derive favorable solder bonding characteristics on the thin electroless Ni/Au plating films.

### 3.3 Influence of catalyst treatment process on corrosion behaviors of substrate Cu film

It has been studied that failure of solder bonding strength in due to the local corrosion of Ni during displacement type Au plating [13, 14]. This is primarily due to the excessive dissolution of grain boundaries of the substrate Cu and the application of Pd catalyst [6, 7]. Chemical species such as Pd ions, and inorganic and organic ions are existing in Pd catalyst solutions, these ions are preferentially adsorbed around the edge of Cu patterns due to non-linear diffusion especially high density Cu wiring. This implies that excessive dissolution of Cu and excessive absorption of catalyst occur these parts and decrease uniformity of electroless Ni deposition. Electroless Ni strike plating as a displacement of Pd catalyst has already reported [15] and Ni catalyst on Cu followed by for the improvement of the solder bonding characteristics by implementing the thin electroless Ni/Au plating process. Uniformity of electroless Ni plating film is essential in order to improve the solder bonding characteristics, as described in Section 3.2. The influence of catalyst treatment on uniformity of electroless Ni plating and corrosion behaviors were investigated. Pd displaced on Cu was about 20atm% after treatments of the HCl type and the H$_2$SO$_4$ type were performed for 60 sec., as shown in Table 2. Variance with the amount of Pd displaced on the Cu electrodes that depended on Cu electrode sizes was confirmed to occur more often, in cases where the HCl type were used, when compared with the H$_2$SO$_4$ type. On the other hand, the presence rate of Ni on Cu electrodes was confirmed to reach 80% atm or higher, when the Ni strike process was applied.

<table>
<thead>
<tr>
<th>Table. 2</th>
<th>Concentration of catalyst metal on Cu electrode</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(a)ϕ 5 mm</td>
</tr>
<tr>
<td>HCl type</td>
<td>Pd : 17.4 atm%</td>
</tr>
<tr>
<td>Pd catalyst</td>
<td></td>
</tr>
<tr>
<td>H$_2$SO$_4$ type</td>
<td>Pd : 10.2 atm%</td>
</tr>
<tr>
<td>Pd catalyst</td>
<td></td>
</tr>
<tr>
<td>Electroless strike Ni</td>
<td>Ni : 80.9 atm%</td>
</tr>
</tbody>
</table>
Next, respective catalyst solutions were used to make observations using an FE-SEM on the Cu wiring surface conditions after catalyst treatment and the conditions of the cross-section of electroless Ni plating films of 0.5µm thickness that were formed on Cu wiring. Numerous corrosion sites were observed on the surface of Cu after the catalyst was applied in cases where HCl type were used, as shown in Figure 5. The number of corrosion sites was less than that of the hydrochloric acid HCl type when the H₂SO₄ typewere used. Furthermore, there was a decreasing trend with irregularities on the surface of Cu, since the Cu surface was minutely dissolved. No corrosion of Cu was observed and only a few variations in irregularities on the surface of Cu were confirmed in cases where Ni strike process was used.

The deposition conditions on the electroless Ni plating films were observed next, since variation in the conditions of Cu wiring was seen after the catalyst treatment as described above. Minute voids were confirmed to have occurred at electrodes with a diameter of 5 mm in cases where respective Pd catalyst solutions were used. Furthermore, the void sizes were revealed to increase and the number of local corrosions increased when segments with minute electrode sizes (0.3 mm diameter) were observed. On the other hand, no local corrosion on Ni and Cu films was confirmed to occur when the Ni strike process was used.

Fig. 5 SEM images of Cu surface and cross sectional SEM images of Cu/Ni interface after each catalyst treatment
Since voids were confirmed to be formed between Cu and Ni films when Cu dissolved in the catalyst treatment as described above, the dissolution behavior of Cu in the respective catalyst solutions was investigated next using the anode polarization method.

A rapid increasing of anode current density due to Cu film dissolution was confirmed. This suggested that the Cu readily dissolved when Cu film was immersed in HCl type as well as H2SO4 type and the applied voltage was scanned in the positive direction (direction in which the electric potential is positive), as shown in Figure 6. On the other hand, anode current density was not increased even if the applied voltage was scanned in the positive direction in the Ni strike process. Therefore, it confirmed that Cu was extremely difficult to dissolve in comparison with the treatment of both Pd catalysts.

Pd catalyst solutions containing chloride ions or sulfate ions and readily dissolved Cu during the catalyst treatment. Furthermore, since Pd is displaced on Cu due to the local dissolution of Cu, numerous voids were formed on Cu films. However, no voids were formed on the Cu films since the corrosion of Cu films was suppressed applying the Ni strike process.

3.4 Influence of catalyst treatment on uniformity of Ni plating films

From above results, chemical species in the catalyst solutions accumulated on minute electrodes due to non-linear diffusion and excessive absorption of catalyst, voids were confirmed to have occurred due to the corrosion of substrate Cu film. Deposition uniformity of electroless Ni plating was influenced by the conditions of substrate film as well as the conditions of catalyst applications [5, 6]. The absorption of
chemical species in the catalyst influences on fine electrodes during catalyst treatment, therefore the catalyst treatment time was extended to period longer than the standard to evaluate the influence of excessive absorption of catalyst and chemical species on fine electrodes in order to investigate the influence of excessive displacement characteristics of both electroless Ni plating and electroless Ni/Au plating films. To evaluate the above idea, controlled potential reverse electrolysis was used to investigate the coating conditions of the electroless Ni plating films.

The Cu dissolution rate on the electroless Ni deposits using HCl type was indicated to be 3.5%, since Cu films of the substrate are readily dissolve, due to the reverse electrolysis as shown in Figure 7. The Cu dissolution rate also tended to increase as the catalyst treatment time increased. This is due to the many nodules and faults on the Ni deposits, being formed as a result of progressive localized plating deposition reactions that occurred when electroless Ni plating was conducted following the formation of localized Pd catalysts and voids were formed on Cu films during the application of Pd catalyst. On the other hand, the Cu dissolution rate was 30% lower than that of the Pd catalyst treatment in cases of Ni strike process, and Cu dissolution not increased even the catalyst treatment time was extended. Subsequent electroless Ni plating reaction progressed on the entire surface of Cu films due to the Ni catalyst that deposit on the entire surface of the Cu film, therefore, Ni plating films with little defects and high uniformity were achieved. As a result, the Cu dissolution is lower than that of the Pd catalyst treatment.

![Figure 7](image_url)
3.5 Influence of catalyst treatment on solder ball bonding strength

Above these results, high uniformity was achieved using the Ni strike process, even when the catalyst treatment was introduced over a long period of time. The uniformity of the electroless Ni plating film was influenced to the solder ball shear strength on described Sections 3.1 and 3.2. The shear strength of the solder ball on electroless Ni/Au plating films, for which both catalyst treatment processes were used.

As shown in Figure 8, When the HCl type was used to as an initiation catalyst for electroless Ni/Au plating films, the solder ball shear strengths were indicated to be a value of the same level for the respective catalyst treatment time of 60 sec. and 180 sec. The minimum solder ball shear strength indicated a decreasing trend as the catalyst treatment time was extended when the Pd catalyst solution was used to form electroless Ni plating films of 0.5 µm thickness and then the displacement type Au plating was performed. The reduction of minimum solder ball shear strength by about 30% in comparison with the electroless Ni/Au plating films with Ni film thickness of 5 µm was confirmed, particularly when the HCl type was used. Furthermore, standard deviation of the value for the solder ball shear strength was derived and the strength variance was compared based on 3σ value. This revealed that compared to the process involving a Ni film thickness of 5 µm, the variance was confirmed to increase. The variance increased particularly in cases where HCl type were used, where the variance approximately doubled.

When the Ni strike process was used for the catalyst treatment process, the solder ball shear strength using catalyst treatment time of 180 sec. indicated the same value as the solder ball shear strength for a catalyst treatment time of 60 sec. This confirms that the solder bonding strength was consistent even when an excessive amount of the catalyst metal was applied. The average solder ball shear strength and minimum solder ball shear strength for cases where the Ni strike process was used were both favorable values, even when compared to the solder ball shear strength for films of electroless Ni/Au plating with a Ni plating film thickness of 5 µm. Furthermore, the solder failure mode was a failure between solders and no variance that depended on the catalyst treatment was seen when the elemental analysis of the electrode surface was performed by the EDS after measurements of the solder ball shear strengths were taken.

The behavior of the solder bonding strength is confirmed to vary when the catalyst treatment time is extended to longer durations depending on the catalyst solution used to trigger electroless Ni plating reaction, as described above. Many reports have been made in the recent years on the involvement of the metal structures of solder bonding segments on solder bonding strengths [16, 17]. Metal structures of Ni/Au plating films, derived from the respective catalyst treatment processes, were investigated using the EDS for that reason.
When Pd was used as catalyst metal, intermetallic compounds were observed not only on the solder side of the bonding boundary but also on the Cu film side for both the HCl type and the H₂SO₄ type, showing irregular film thicknesses and shapes, as shown in Figure 9. The inconsistency of the film thickness increased due to the catalyst treatments over an extended period of time and voids were formed on the Cu film side of the solder bonding surface.

Intermetallic compounds, consisting primarily of (Cu, Ni)₆Sn₅, were formed on the solder side of the solder bonding boundary when Ni was used as a catalyst metal, while the formation of intermetallic compounds were being suppressed on the Cu film side. Furthermore, the formation of intermetallic compounds was suppressed on the Cu film side even when the catalyst metal was applied over an extended period of time and no variance in state of formed intermetallic compounds that depended on the catalyst treatment duration was observed. Superior solder bonding strength is surmised to have been derived as electroless Ni plating films with high uniformity were formed on Cu film when the Ni strike process was used and the Ni film inhibited the formation of intermetallic compounds on the Cu film side of the solder bonding surface.

![Fig. 8 Relationship between solder ball shear strength on each catalyst treatment condition.](image-url)
The mechanism of film formation for thin electroless Ni/Au plating films through respective catalyst treatment were surmised based on the results described above. Displacement type deposition of Pd progressed on the Cu wires first when the Pd catalyst treatment was applied, as shown in Figure 10. In such instances voids occurred between Cu and Ni when electroless Ni plating was performed as the chemical species in the catalyst solutions concentrated on the protruding segments of the Cu surface due to the influence from the non-linear diffusion reaction. This led to an inconsistent concentration and coagulation of Pd catalysts as well as Cu film dissolution and non-uniformity of Pd catalysts. Ni plating reaction progressed rapidly due to the Pd catalyst with a high level of activity during the initial reaction of electroless Ni plating and electroless Ni plating films with a large number of nodules and particle boundaries being formed, due to Pd has a hydrogen storage property [18]. During subsequent displacement type Au plating, the local corrosion of Ni reaction progressed in the direction of the depth, and inconsistent intermetallic compounds were formed on the solder and Cu boundary surfaces as a result, which is surmised to have caused a decline in the solder bonding strength.

On the other hand, when the Ni strike process was applied, the Ni strike film was formed over the entire surface of Cu wirings while inhibiting Cu dissolution, due to the electroless Ni strike plating solutions were of reduction types. A uniform electroless Ni plating reaction progressed since Ni has lower hydrogen storage property than Pd [18] and smooth Ni films with little particle boundaries were formed. Minute and accurate Au plating films could be derived with displacement type Au plating as a result, due to there was little local corrosion of the Ni on the substrate. It became evident that Ni plating film characteristics did not vary
according to the amount of catalyst adsorption on Ni strike process, it was possible to form Ni/Au plating films with little film defects that provided superior solder bonding characteristics.

![Diagram](image)

**Fig. 10** Mechanism schematic of electroless Ni/Au film formation in each catalyst process.

### 4. Conclusion

The factors relating to the decline in the solder ball shear strength of electroless Ni/Au plating films due to the formation of thin Ni plating films were considered. The Ni strike process was applied to the thin electroless Ni/Au plating process to consider respective film characteristics with Pd catalyst treatments performed by the usual procedures by comparison. The following knowledge was gained as a result.

1. The uniformity of Ni plating films that deposit decreased in cases where the Ni plating film thickness is 0.5 µm with Pd catalyst treatments performed by usual procedures. As a result, scattering of solder reached Cu films during solder mounting, which was confirmed to have triggered a decline in the solder ball shear strength of electroless Ni/Au plating films.

2. Measurements taken on the solder ball shear strength indicated that there was a tendency of the average solder ball shear strength to decline with a prolonged catalyst treatment time to extended durations in the usual Pd catalyst treatment processes and confirmed an increase in the variance of strengths.

3. The components of the solutions dissolved the substrate Cu and formed voids in the boundary between Cu and Ni during electroless Ni plating, due to the increased amount of catalyst treatment time.
required for the usual procedures of the Pd catalyst treatment. The uniformity of the electroless Ni plating film decreased as a result.

(4) The solder ball shear strength was higher in case of the Ni strike process when compared with Pd catalyst treatments of usual procedures and confirmed that the solder ball shear strength did not depend on the catalyst treatment time.

(5) Voids and corrosions were not formed on the Cu and Ni boundary even with catalyst treatments that lasted over long periods. This is because the components included in the electroless Ni strike plating solution did not easily corrode Cu and made it possible to form electroless Ni films with high film density. Furthermore, when the displacement type Au plating was implemented, it was confirmed that there was lesser local corrosion of the Ni when compared to the Pd catalyst treatment.

(6) The Ni strike process was confirmed as the pretreatment suitable for the electroless Ni/Au plating process for fine wiring, since the uniformity of the Ni strike process is stable and not susceptible to the influence from Ni/Au plating film that depend on catalyst treatment time.

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References


