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Prevention of blister formation in electrolessly deposited copper film on organic substrates

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Abstract−Electroless copper (Cu) plating is a key process to provide seed layers for the subsequent Cu electroplating in the printed wiring boards (PWBs). Due to the demand for lower power dissipation at higher temperatures and high signal frequencies, various kinds of organic materials have been newly introduced as substrates. However, they have come with defects such as delamination and/or blisters in the Cu layers on organic substrates, i.e., weak adhesion. Here we demonstrate the root cause and a prevention method of the blister formation. Various parameters affecting the blister formation have been investigated combined with the deposit thickness (internal stress), hydrogen gas evolution, and codeposited Ni content in the electroless Cu plating. It was not obvious that the compressive internal stress in deposits was directly related to the blister formation. Instead, the hydrogen gas evolution clearly turned out to be the key factor, and it was observed that Ni added plating solutions reduced the hydrogen gas evolution significantly and thus produced no blisters in the Cu deposits. The control of blisters would be more critical as the line and space become narrower in the production lines such as ball grid array (BGA) and high density interconnection (HDI).

Key words: Electroless Copper Plating, Blister, Adhesion, Printed Wiring Board (PWB)

INTRODUCTION

The nanocrystalline printed wiring board (PWB) build-up process is simply described by alternative stacks of organic insulation layers and conductive metals [1,2]. Semi-additive process (SAP) is widely used to form metallic conductive patterns which are electroplated on the electrolessly deposited copper (Cu) seed layers on top of insulating layers [3]. The problem of weak adhesion frequently occurs between resins and electroless Cu layers [4].

Recent advances are increasingly required to have finer and thinner PWB substrates for the highly integrated electronic devices. In addition, new organic materials are being used such as polyimide (PI), liquid crystal polyester (LCP) and bismareimide triazine (BT) resins, because of their superior performance as insulating layers at higher temperatures and high signal frequencies [5]. The most significant issues in these substrate materials are adhesion strength and interfacial stress between insulation resins and conductive metal layers. Warpage, delamination and blisters are well-known failure modes due to the poor control on stress and adhesion [6].

Here we investigate the root cause of blister formation in electroless Cu deposits on organic substrates, and suggest an efficient way to prevent blisters. Although the main causes of the blister formation are said to be compressive stress in deposits or hydrogen gas evolution and its incorporation into the deposits from several references [7,8], it has not been clearly elucidated which is the critical one. Thus, various experimental conditions of electroless Cu solution were tested to investigate their effects on the blister formation, while the apparent stress of Cu deposits and the hydrogen gas evolution volume were measured.

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EXPERIMENTAL SECTION

BT resin samples were prepared with a dimension of 5 cm×10 cm and thickness of 0.06 mm. Samples were pretreated prior to electroless Cu deposition by conditioning, pre-dip, Pd activation and reduction processes as typically used in the field. The electroless Cu solutions consist of Rochelle salts and formaldehyde as complexing and reducing agents, respectively. All the chemicals were supplied from manufacturer Z. Main compositions of tested baths are listed in Table 1. The additives, A, B, and C, are all types of stabilizers to make Cu^{2+} ion stable in the solution, mainly composed of 2,2′-dipyridyl compounds. The bath temperature was fixed at 35 °C with pump circulation and air agitation, simultaneously.

Both actual and artificially aged solutions were prepared to consider the effect of bath metal turn over (MTO). The actual aged solution was prepared by continuous plating with appropriate compositional maintenance until 3 MTO. The analyses of 3 MTO aged solutions with ion chromatography (IC, Dionex DX500) showed that the formate and sulfate were detected as HCOONa and Na_2SO_4 with concentrations of 26 g/L and 10 g/L, respectively, as shown in Fig. 1. Artificially aged two electroless Cu solutions were prepared

Table 1. Tested bath compositions

Components	Bath I	Bath II	Bath III	Bath IV
Cu (g/L)	3.25	2.44	2.44	2.44
Rochelle salt (g/L)	40	35	35	35
NaOH (g/L)	10	9	9	9
Formalin (ml/L)	22	15	15	15
Ni (g/L)	0.2	0.4	0.2	0.4
Additive	A	B	C	C

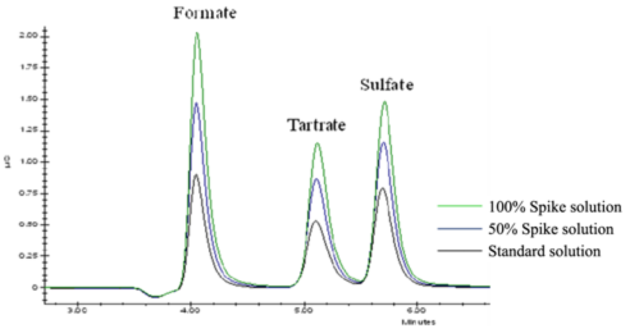

Fig. 1. Analysis results of 3 MTO aged solution, 50% spike solution and 100% spike solution with IC.

by addition of HCOONa and Na_2SO_4 with 26 g/L+10 g/L and 40 g/L+40 g/L, respectively, based on the IC analysis results. The 50% and 100% spike solutions indicate that formate, tartrate, and sulfate are added to the standard solution by 50% and 100% of the initial concentration of each species to identify the peaks more distinctly.

The formation of blisters was easily determined by Cu electroplating after electroless Cu deposition with bare eyes. Acidic sulfuric Cu electroplating bath composed of copper sulfate of 200 g/L, sulfuric acid of 30 g/L, and Cl^- of 40 ppm was used for the Cu electrodeposition under the current density of 2 amperes per square decimeter (ASD) for 40 minutes. Scanning electron microscopy (SEM, Hitachi S-3000N) and focused ion beam (FIB, FEI800XP) were used to observe the surface morphology and cross sectional microstructures. Adhesion strengths were evaluated by measuring the forces to peel the deposit of 1 cm width from the substrate using universal testing machine (UTM, Instron 4206).

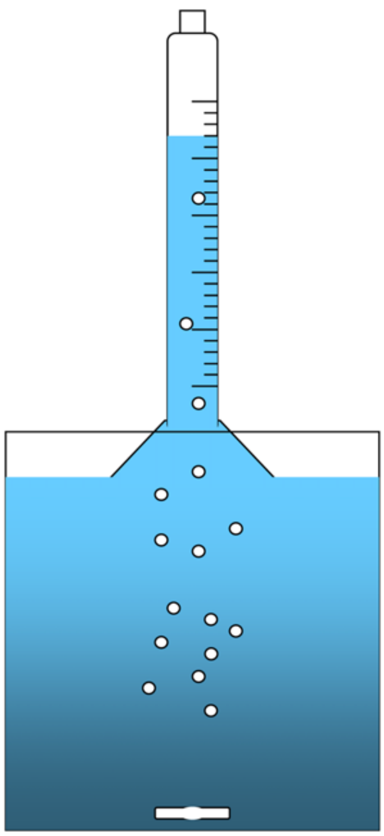

Fig. 2. Schematic diagram of the apparatus for sampling hydrogen gas.

Table 2. Blister formation depending on the bath aging, deposition time, and Ni content

Bath		Deposition time	
		5 min	30 min
Fresh	I	No	Yes
	II	No	No
	III	No	Yes
	IV	No	No
Aged	I	Yes	Yes
	II	No	No
	III	Yes	Yes
	IV	No	No

The deposited amount of Cu was measured by the weight difference before and after plating with electronic balance (OHAUS P250D). Codeposited Ni content was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, Jobin Yvon Optima 2) after the deposits were dissolved in 60% nitric acid solution.

The quantity and the rate of hydrogen evolution during electroless plating were measured by the apparatus shown in Fig. 2.

RESULTS AND DISCUSSION

Table 2 shows the results of blister formation depending on bath aging and deposition time. Blisters were not found in the samples deposited for 5 minutes in fresh bath I and bath III. However, deposited samples with longer dipping time (30 minutes) resulted in blister formation in the same baths. Blisters were also observed even at 5 minutes in aged baths. It is interesting that bath II showed no blister formation regardless of the deposition time and aging. From the above results, we can summarize that blisters are easily formed in aged baths and/or with longer deposition time, in other words, at thicker deposits, and they are not formed in the bath with higher content of Ni. To verify the effect of Ni content on the blister formation, Ni content in bath III (denoted bath IV in Table 1 and 2) was increased and it resulted in the same observation as in bath II.

1. Effect of Internal Stress

Interfacial separation of layers with different materials known as delamination (or blister) is caused by internal stress mainly due to the difference of materials' thermal expansion coefficients [9,10]. Intrinsic stress in the deposit is usually developed during metal deposition on a substrate, which can also cause blister formation. The stress of electro or electroless deposit can be either tensile or compressive as shown in Fig. 3 [11]. Excessive tensile stress may induce a crack defect on the deposit. On the other hand, unacceptably large internal compressive stress may induce delamination or blister formation. Fig. 4 shows the actual blister defect found on the surface of electroplated Cu after electroless Cu deposition.

Types and magnitudes of internal stress in deposits from various baths are investigated. Internal stress was measured using standard test strips (ST & DC copper test strips 1194) after 30 minutes de-

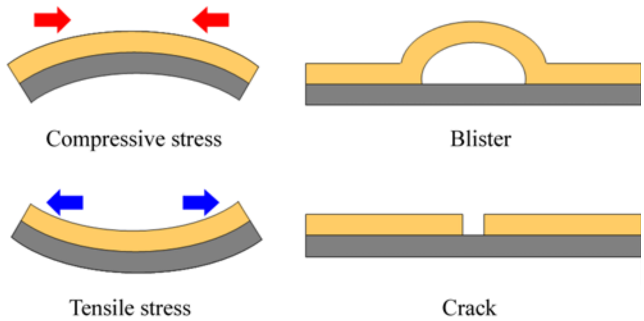

Fig. 3. Effect of stress types on failure modes.

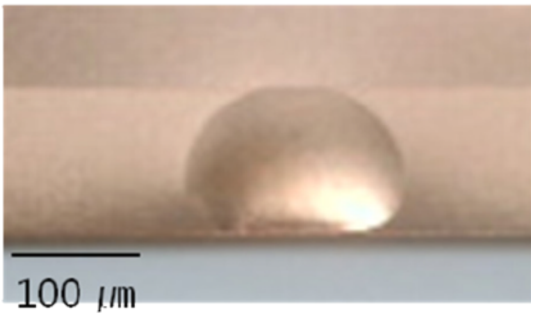

Fig. 4. Blister defect on Cu metalized PWB.

Table 3. Blister formation depending on the stress type of deposits from various bath conditions

Bath	Compressive stress	Blister
I fresh	−6.66**	Yes
I aged	6.42	Yes
I (26/10)*	6.09	No
I (40/40)	6.66	Yes
II fresh	−4.69**	No
II aged	−10.66**	No
II (26/10)	−6**	No
III fresh	−3.89**	Yes
III (26/10)	9.36	No
III (40/40)	10.4	Yes

*(A/B); A is the amount of sodium formate and B is the amount of sodium sulfate
**Negative sign means tensile stress

position on only one side with the opposite side being masked. It resulted in strip warpage in a specific direction, depending on the type and magnitude of internal stress in the deposit. From the results, blisters can be thought to be more easily formed in the deposits with compressive stress. However, blisters were also found in the deposits with tensile stress (Table 3). It is thus hard to say that the internal stress is the decisive factor on the blister formation in this system. To find the major cause of blister formation, bath I with blisters easily formed and bath II behaving oppositely were investigated in more detail.

2. Effect of Hydrogen Evolution

Hydrogen gas trapped in the deposit is also known to be a major cause of blister formation, which evolves inevitably during electroless Cu deposition. Main reaction mechanism of electroless Cu includes the oxidation of 2 mol formaldehyde in alkaline solution, resulting in the reduction of Cu^{2+} to metallic Cu by accepting the released electrons [12-15]. Then, 1 mol of hydrogen gas evolves at the reaction as shown below:

$$Cu^{2+}+2HCHO+4OH^{-}\rightarrow Cu^{0}+2HCOO^{-}+H_2+2H_2O \quad (1)$$

The surface and cross-sectional microstructures were examined for the deposits on BT substrate from bath I and bath II. The results are shown in Fig. 5. The deposit from bath I shows blisters on the surface as shown in Fig. 5(a). FIB image shows numerous large voids of around 300 nm length over the cross-sectioned area as shown in Fig. 5(c). However, the deposit from bath II shows no blisters (Fig. 5b), and less and much smaller voids are found in cross-sectioned image (Fig. 5(d)). Therefore, it is apparent that the blister formation in electroless Cu deposits on BT substrate is dependent strongly upon the bath type, which affects the degree of hydrogen evolution and following void defects in the deposits.

The quantity and the rate of hydrogen evolution were measured on the above two types of baths. Fig. 6(a) and Fig. 6(b) show the total volume of sampled hydrogen gas during electroless plating and the change of evolution rate with deposition time, respectively. Bath II shows the gradual increase of gas evolution rate with deposition time. On the other hand, bath I shows 4 to 5 times higher gas evolution rate than bath II especially in the early stage of reaction as shown in the peak in Fig. 6(b), which might lead to the significant difference of void defect density and hence blister formation.

3. Effect of Codeposited Ni

Based on the results thus far, it appears that the blister formation is probably prevented by reducing hydrogen gas evolution during deposition. It is known that pure metallic Ni has a strong effect to inhibit the hydrogen gas evolution in electroless Cu deposition [16].

Reaction (1) can be rewritten in terms of the oxidation of formaldehyde.

$$2HCHO+4OH^{-}\rightarrow 2HCOO^{-}+2H_2O+H_2+2e^{-} \quad (2)$$

This reaction also can be divided by three partial reactions [17-22].

Dehydrogenation:
$$RH\rightarrow R\bullet+H\bullet \quad (2\text{-}1)$$
Oxidation:
$$R\bullet+OH^{-}\rightarrow ROH+e^{-} \quad (2\text{-}2)$$
Recombination:
$$H\bullet+H\bullet\rightarrow H_2\uparrow \quad (2\text{-}3)$$

When Pd, Pt or Ni exist on the electrode surface, proton radicals are combined with OH^{-}, generating H_2O and one electron (Reaction 3) instead of hydrogen gas evolution (Reaction 2-3).

Oxidation:
$$H\bullet+OH^{-}\rightarrow H_2O+e^{-} \quad (3\text{-}1)$$
$$HCHO+3OH^{-}\rightarrow HCOO^{-}+2H_2O+2e^{-} \quad (3\text{-}2)$$

According to the reaction 3-2, 1 mol of formaldehyde is consumed for the deposition of 1 mol of metallic Cu without hydrogen evolution.

Therefore, the high content of codeposited Ni in Cu deposits could

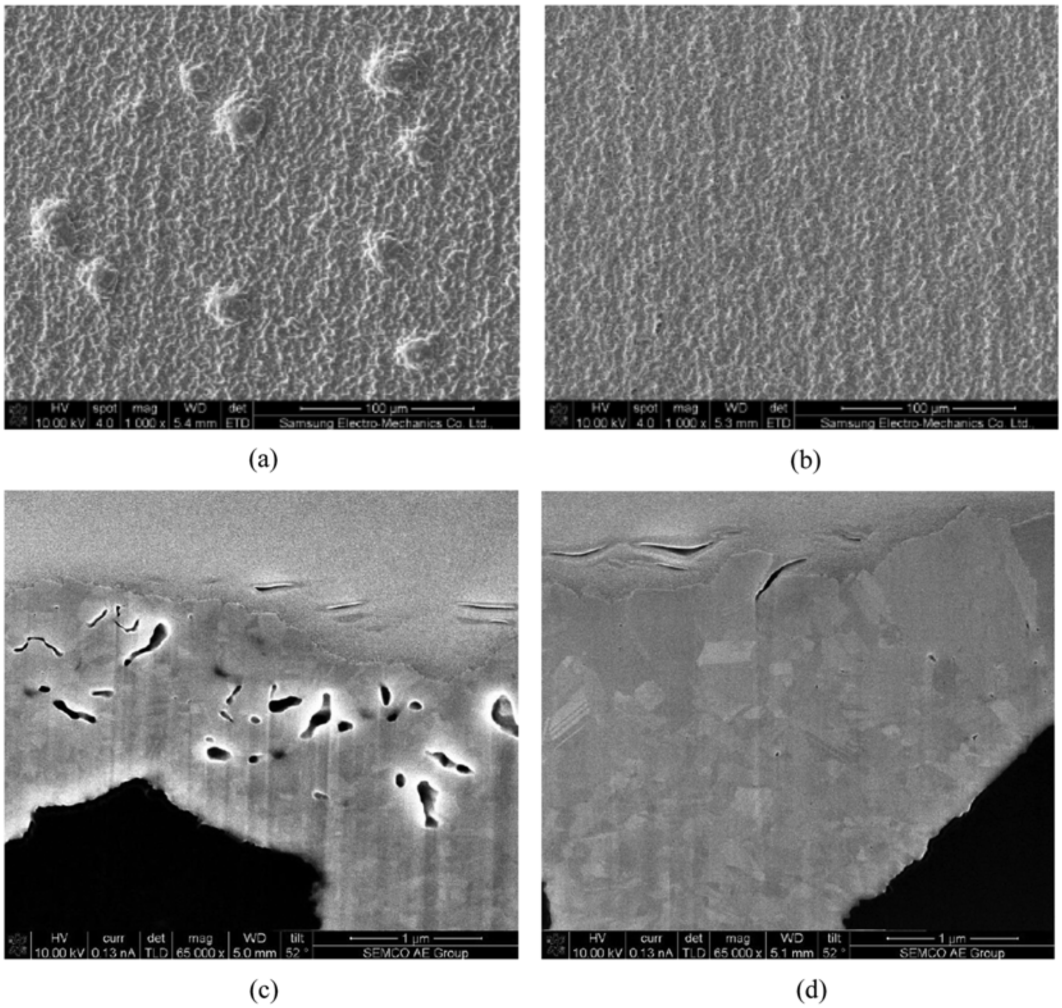

Fig. 5. Microstructures of electroless Cu deposits from; (a) bath I, SEM surface image (×1,000), (b) bath II, SEM surface image (×1,000), (c) bath I, FIB cross-sectioned image (×65,000), and (d) bath II, FIB cross-sectioned image (×65,000).

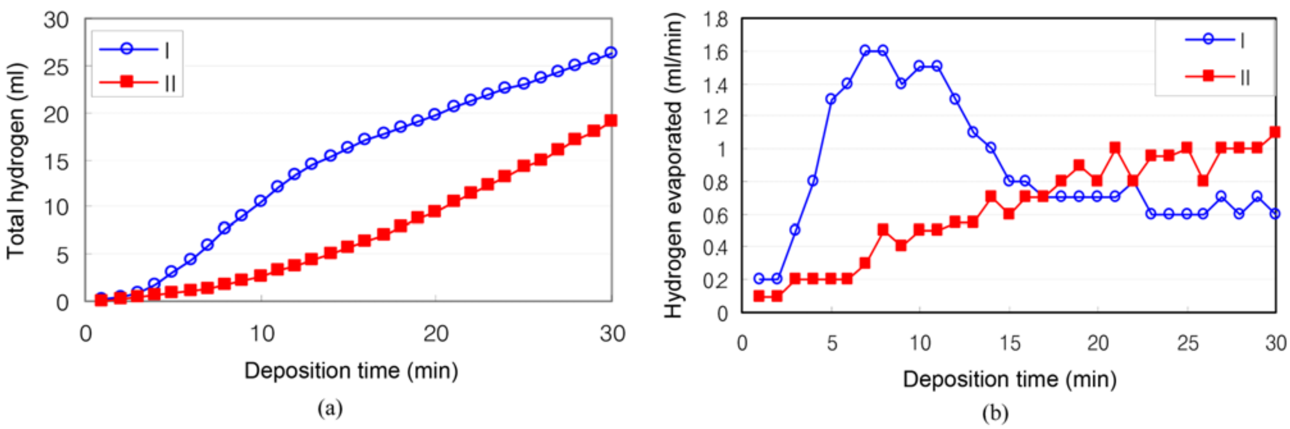

Fig. 6. Amount of hydrogen evolution (a), and hydrogen evolution rate (b) with respect to the deposition time and the type of electroless plating solution.

prevent the hydrogen gas evolution and hence blister formation. Codeposited Ni content in the deposits from two baths was investigated by ICP analysis. The results are listed in Table 4. The deposit obtained from bath II after 5 minutes dipping shows five-times higher codeposited Ni content than the one from bath I. Longer dipping for 30 minutes shows slightly reduced codeposited Ni content, which is consistent with the reduced hydrogen gas evolution rate at longer deposition time in bath I as shown in Fig. 5.

Table 4. Codeposited Ni content in the Cu deposits

	5 min	30 min
I (Ni at%)	0.25	0.23
II (Ni at%)	1.24	0.76

CONCLUSION

The factors affecting the blister formation in electroless Cu deposits were investigated using various plating solutions and a prevention method was suggested. The main cause of blister formation was believed to be the presence of hydrogen gas trapped in the deposits, which originated from the oxidation of reducing agent. The Ni codeposition of greater than 1 at% in electroless Cu deposits was confirmed to be effective to prevent the blister formation by significantly reducing hydrogen evolution. It is expected that this prevention method for the blister formation may reduce the lead time and process cost greatly by removing trimming process that cuts the blister area out in the panel.

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