Study on chemical activity of electroless copper plating

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Abstract

Electroless copper plating of insulating substrates typically requires the pre-deposition of Pd/Sn catalyst layer onto the surface to initiate the chemical reactions; Accordingly, it's high-profile process to achieve efficient Pd/Sn cluster adhesion and good copper plating performance. This paper showed copper thickness and dimple hole depth of the electroless plating were affected by chemicals following different activation times. The composition, microstructure, size and roughness evolution were characterized using Transmission Electron Microscope (TEM). The structural studies revealed that copper particle size depends not only on the size and coverage of the Pd/Sn cluster, but also on the degree of activation of the chemicals. In order to make deposition copper more compact and uniform to decrease dimple hole depth, dummy boards are generally used to enhance the potion activity before electroless copper plating. This paper will provide chemical activity and plating efficiency relationship to avoid poor activity impact plating quality and process event.

Key words

Electroless copper plating, Pd/Sn cluster, chemical activity, plating efficiency.

I. Introduction

Electroless copper plating is widely used for the metallization of insulating substrates and especially in the manufacture of Printed Circuit Boards (PCBs) [1]. The technique is popular as it enables the deposition of high quality coatings simply by immersing the substrate in a series of chemical baths that activate the substrate surface and then deposit copper [2]. The main constituents of the electroless plating bath are a chemical reducing agent and copper ions: the reducing agent provides electrons to reduce the copper ions to metal on the surface (a redox reaction). However, this redox reaction can only take place on certain catalytically active surfaces: examples of these include metals such as copper that enables the electroless reaction to continue to build a coating of the required thickness. Insulating substrates are not active and therefore pre-treatment steps are required that often culminate in the deposition of a layer of catalytically active material [3-5].

Electroless deposition of Copper from Cu^{2+}/HCHO solutions onto non-conductive substrates, such as printed circuit boards, is considerable technical importance [6-7]. E'less copper plating reaction as in equation (1-5), and formaldehyde as reducing agent, and 'Y' as chelating agent in equation (1). The surface of the plating layer can oxidize formaldehyde and reduce copper ions, while generating hydrogen gas in equation (2). In base solutions, formaldehyde has a side reaction to produce methanol in equation (3). Formaldehyde also has a side reaction with copper ions to produce Copper(I) oxide in equation (4). Copper(I) oxide will produce a side reaction to produce copper ions in the plating solution, which is the so-called plate-out in equation (5). It requires catalytically active surfaces to initiate the Cu nucleation process. Pd/Sn Nano-colloids in acid suspension based catalysts are widely used to promote copper nucleation and growth of the electroless thin film initially at catalytic sites [8-11].

$$\mathrm{Cu(II)Y + HCHO + 3OH^- \longrightarrow Cu^0 + HCOO^- + Y^{2-} + 2H_2O} \quad \text{---} \tag{1}$$

$$\mathrm{Cu(II)Y + 2HCHO + 4OH^- \longrightarrow Cu^0 + 2HCOO^- + Y^{2-} + 2H_2O + 2H_2} \quad \text{---} \tag{2}$$

$$\mathrm{HCHO + OH^- \longrightarrow CH_3OH + HCOO^-} \quad \text{--------------------} \tag{3}$$

$$\mathrm{2Cu(II)Y + HCHO + 5OH^- \longrightarrow Cu_2O + HCOO^- + 2Y^{2-} + 3H_2O} \quad \text{---} \tag{4}$$

$$\mathrm{Cu_2O + H_2O + Y^{2-} \longrightarrow Cu^0 + Cu(II)Y + 2OH^-} \quad \text{-------------} \tag{5}$$

Pd-Sn catalysts possess high-profile catalyst performance for electroless metal deposition. They have attracted interest in converting non-conductive surfaces into conductive ones [12]. One of fundamental question is the structure and surface composition of the colloids, indeed, the Pd-Sn Colloids possess a large number of different crystalline phases: PdSn, $PdSn_2$, $PdSn_3$, $PdSn_4$, Pd_2Sn, Pd_3Sn and Pd_3Sn_2. However, surface tension of Tin about 3 times less than palladium lead to the surface energy of the crystalline phases differently. This status might effect Pd/Sn cluster adhesion onto the surface of substrates. And the other question is decomposition behavior of a Pd-Sn catalyst solution [13-14]. In addition, HCl gas is volatilized during spontaneous decomposition of Pd-Sn catalysts, which suggests that the stability of Pd-Sn catalysts is related to stannous ion complexation, depending on the chloride ion concentration [15-18].

Colloidal solutions of Pd-Sn nanoparticles as industrial Pd catalysts for electroless copper plating. However, the catalyst has problems such as particle decomposition and degradation under catalytic activity, which are related to the stability of the colloidal solution. Turning now to the factors like particle size, distribution, and anchorage of Pd clusters, of course, strongly affect quality and deposition rate of electroless Cu plating. The present investigation was undertaken to verify the decomposition behavior of a Pd-Sn catalyst solution and enhance the potion activity before electroless copper plating to make deposition copper more compact and uniform to decrease dimple hole depth [19-22].

II. Experimental

1. Pd/Sn catalyst solution preparation

The reagent used in this experiment was Pd-Sn catalyst AT-105-3 (a solution with a metal Pd component concentration of 3.37/Kg, synthesized according to the company's method), and PED-104-L was added. Dissolve PED-104-L in ion-exchange water, then add AT-105-3 and mix until uniform to prepare a catalyst solution with a concentration of 120 mg/Kg [23].

2. Transmission Electron Microscope (TEM)

The Pd-Sn particles were adsorbed on the M-Cu mesh for 10 min at room temperature, a piece of filter paper was placed against the M-Cu mesh. In addition, the M-Cu mesh was perfectly dried with a compressed inert gas. After that, adherent soluble salt on the surface of the sample were rinsed, in turn, with ethanol and deionized water to avoid charging phenomena of the image during observation

III. Results and discussion

Figure 1 shows the TEM images of the Pd-Sn catalyst solution samples. It can be seen from Figure 1(a) that the primary particle size of the Pd-Sn catalyst is 1~2nm. Looking at the secondary particles at higher magnification. From Figure 2(b) TEM observation, it can observe the image of the lattices arranged in random orientations (dotted circle), which shows that the primary particles are almost two-dimensionally aggregated to form secondary particles [24].

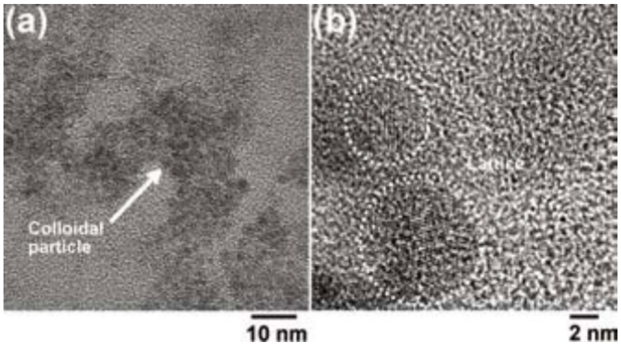

Fig 1. TEM images of the Pd-Sn catalyst solution samples

In general, the decomposition behavior of Pd-Sn catalysts is considered to be related to dissolved oxygen. Fujinami et al. accelerated the decomposition by passing oxygen through the catalyst solution and concluded from the analysis of $SnCl_2$ that the catalyst decomposed when the Sn^{2+} concentration changed to higher [25-26]. The decomposition of widely used Pd-Sn catalysts only focuses on the reduction

Table 1. Dispersion stability of Pd-Sn catalyst solutions with low Pd metal concentration. The solutions were prepared in the dispersion medium having various concentrations of chloride ions.

Solution composition	PED-104-L (g)	4.65	9.18	13.48	17.65	22.86
	AT-105-3 (g)	1.00	1.00	1.00	1.00	1.00
	Water (g)	95.35	90.82	86.52	82.35	77.14
Total		100.00	100.00	100.00	100.00	100.00
Pd metal concentration (mg/kg)		0.34	0.34	0.34	0.34	0.34
Solution Characteristics	Cl^- concentration	0.78	1.43	2.05	2.66	3.37
	Ion strength	1.15	2.21	3.21	4.19	6.48
	Solution pH	1.51	1.09	0.84	0.66	0.32
	Dispersion stability	instantaneous gelation	<2-3 days	<2-3 weeks	<2 weeks	<4 weeks

behavior of Sn^{2+} concentration, and hardly considers the influence of chloride ion (Cl^-). Choen et al. reviewed the chemical properties of tin chloride solutions when studying the chemical state of Sn ions during sensitization. In the Pd-Sn catalyst solution, Sn^{2+} and Sn^{4+} exist as chloride complexes of $(SnCl_3)^-$ and $(SnCl_6)^{2-}$. When Sn^{2+} and Sn^{4+} appear, the Cl^- coordinated with Sn increases, and the free Cl^- concentration should be reduced. Therefore, the balance between H^+, Cl^- and HCl gases shifts in the direction of suppressing gas production. However, it was also found that the natural decomposition of the Pd-Sn catalyst was accompanied by the volatilization of HCl gas. This indicates that we need to consider the chemical state of Sn ions in terms of Cl^- concentration and tin chloride complexes. Next we discuss the effect of Cl^- on the aggregation behavior of Pd-Sn catalysts. It was found that the dispensability of Pd-Sn catalysts varied with the concentration of Cl^- (Table 1). Besides that, the precipitate obtained by the spontaneous decomposition of the Pd-Sn catalyst reflected the characteristics of the secondary particles formed by the adsorption on the substrate surface [27].

The decomposition of the Pd-Sn catalyst stock solution accompanied by the volatilization of HCl gas indicates that the concentration of a large amount of Cl^- in the solution is related to the stability of the primary particles of the Pd-Sn catalyst. When synthesizing the stock solution of Pd-Sn catalyst, it was stabilized by co-existing HCl and $(SnCl_2)$. As a result, the total Cl^- concentration was about 7 M. When used as an electroless plating catalyst, it is stable by dispersing in a solution with sodium chloride as the main component, close to saturation concentration, and is a high ionic strength solution. The effect of ionic strength on the dispersion stability of colloids is one of the basic parameters of colloid chemistry. In the case of Pd-Sn catalyst solutions, the ionic strength of CI^- also affects the dispersion stability. That is, the Cl^- concentration becomes important. Furthermore, Müller et al. pointed out that the poly-nuclear form of the $(SnCl_n)_{(2-n)}$ complex does not form in chloride solutions of 0.01~2.9 M. Table 2 shows the formation reactions and formation constants of tin chloride complexes at an ionic strength of 4M, and shows the ratio of tin chloride complexes to CI^- concentrations. In the low pH region where the Pd-Sn catalyst is stable, the hydrolysis of Sn^{2+} is negligible, and it is sufficient to consider only the complexes shown in Table 2. The Cl^- concentration range in the Pd-Sn catalyst solution is indicated by a slash. It can be known from Fig 2 that Sn^{2+} and $(SnCl)^+$ do not exist in the Pd-Sn catalyst solution, mainly $(SnCl_3)^-$ and $(SnCl_4)^{2-}$, and a small amount of $(SnCl_2)$. The results showed that the catalyst dispersion became stable when the Cl^- concentration became higher. From Fig. 2, it can be seen that all $(SnCl_n)_{(2-n)}$ complexes co-exist at the gelling Cl^- concentration, and the proportions of $(SnCl_2)$ and $(SnCl_3)^-$ are similar (about 40%) [28].

Complex reaction	Formation constant pK
$Sn^{2+} + Cl^- \longrightarrow (SnCl)^+$	1.45
$Sn^{2+} + 2Cl^- \longrightarrow (SnCl_2)$	2.35
$Sn^{2+} + 3Cl^- \longrightarrow (SnCl_3)^-$	2.46
$Sn^{2+} + 4Cl^- \longrightarrow (SnCl_4)^{2-}$	2.27

Table 2. Formation reaction and formation constants of stannous chloride complexes at 25°C. Data were cited from the literature [27].

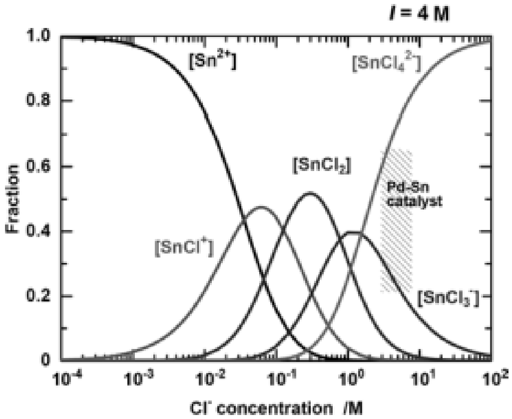

Fig 2. Distribution of stannous-chloride complexes as a function of Cl- concentration. The diagonal-lines square shown in the figure indicates a Cl- concentration range in Pd-Sn catalyst solution.

The formation of the $(SnCl_n)_{(2-n)}$ complex involves 5s orbital with an electron pair and three empty 5p orbitals. Therefore, all complexes have a lone pair of electrons on the Sn atom, and these complexes have a triangular pyramid structure with the Sn atom at the top and the Cl^- atom at the bottom. The electronic structure of Sn^{2+} becomes [Kr] $4d_{10}$ $5s_2$, because the two electrons in the 5p orbital present in Sn are reduced, and the 5p orbital becomes empty, except for $(SnCl_4)^{2-}$. Having a structure in which four Cl^- atoms occupy the base and the Sn atom is at the center, if the lone pair electron acts as a protecting agent for the Pd-Sn catalyst, it must exhibit the same protecting effect regardless of the coordination number of the Cl^-. As shown in Table 1, the experimental fact is that the dilute solution of Pd-Sn catalyst gels immediately when the Cl^- concentration is 0.78M. In addition, the abundance of $(SnCl_2)$ decreases with increasing Cl^- concentration. "The chloride Sn complexes adsorbed and oriented on the primary particle surface of the Pd-Sn catalyst as a protective layer should be oriented close to each other. The 5p orbitals of $(SnCl)^+$ and $(SnCl_2)$ are empty, while $(SnCl_3)$- All 5p orbitals are coordinated. For example, the crystalline hydrate of $(SnCl_2)$ has a water molecule coordinated to the empty p orbital of the Sn atom, and this coordinated water molecule further coordinates with a second water molecule, known to form $(SnCl_2)_2 \cdot H_2O$, and the hydrogen bonds between the coordinated second water molecules lead to a regular layered structure (crystal) of -O-Sn-Cl_2 units. It is well known that Sn and Pt group chlorides are formed by Cl^- aggregated. This hydrogen bond or Cl^- bridge suggests that the tightly oriented protective agent ($SnCl_2$) can become multinuclear. In other words, ($SnCl_2$) exists as a single complex in aqueous solution, but when it is adsorbed and oriented on Pd When on the primary particle of the Sn catalyst, the ($SnCl_2$) complex molecules approach each other and form multinuclear on the particle surface. As a result, Pd assumes a multinuclear ($SnCl_2$) complex structure and loses its protective function. Pd-Sn catalyst. The fact that gelation occurs instantaneously at a Cl^- concentration of 0.78 M suggests that multi-nucleation of chloride complexes with empty 5p orbitals fills a cross-linker and that all 5p orbitals are aligned, unlike (Tri chloride tin). From the above experiments " It was found that the stability of the Pd-Sn catalyst depends on the Cl^- concentration, and the proportion of the chloride complexes present is important. As shown in the shaded area in Fig. 2 [29-30].

IV. Conclusion

This study aims to elucidate the aggregation behavior of Pd-Sn catalysts, focusing on chloride ions. TEM observations showed that the primary particle size of the Pd-Sn catalyst was 2nm, and secondary particles with a length of 30nm were formed. When the HCl gas volatilized, the primary particles of the catalyst decomposed. On the other hand, the aggregation behavior of the Pd-Sn catalyst is considered to be related to the Sn^{2+} concentration, but the chloride complexes found to affect the aggregation behavior. The Pd-Sn catalyst is easy to aggregate in the region where the tin chloride complex of the empty 5p orbital exists. decomposes and becomes stable with increasing Cl^- concentration.

According to what was mentioned before, we control [Sn] concentration and ramp up [Cl^-] concentration to improve plating performance, dimple and un-plating situation, and get positive result to widely applied on application like Fig.3.

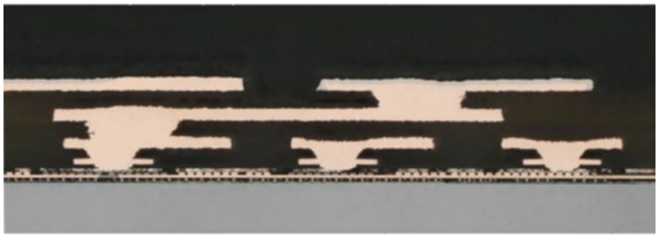

Fig 3. X-section of applied on application

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