The Potential Benefits of a Chemical "Kick Start" for the Autocatalytic Electroless Copper Plating Process

Dipl.-Ing. Edith Günther
Atotech Germany GmbH

1. Introduction

Electroless copper plating is widely used for the fabrication of printed circuit boards and other electronic devices. The manufacture of printed circuit boards is an established technology, encompassing low cost, high yield whilst maintaining a high quality deposit. Conventional electroless copper plating solutions contain a copper salt for the delivery of the copper ions, one or several complexing agents for the copper ions, a copper ion reducing agent (usually formaldehyde), a pH adjusting agent as well as stabilizers and other additives.

In the process of electroless copper deposition, it is necessary to activate the surface of a non-conductive dielectric with palladium. The catalytic palladium deposit is used to overcome the kinetic barrier of electroless copper deposition [1]. The electroless copper plating process is initiated on the randomly distributed catalyst seeds on the substrate. This mechanism facilitates communication between electrical components and related conductors.

The use of reducing agents in the electroless copper baths is necessary for achieving an autocatalytic plating process. Various common reducing agents lead to environmental and healths hazards or are very expensive. In addition, high reducing agent concentrations can cause undesirable side reactions in the copper solution.

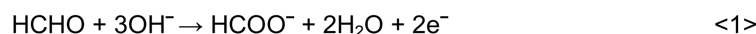
The aim of this study is to reduce the disadvantageous and injurious qualities of the autocatalytic reducing agents without affecting the quality of the copper deposits. This can be achieved with a low reducing agent concentration in the copper solution. To compensate for the resulting lack of reducing agent, and thus the lack of essential electrons for the copper deposition, additives are introduced. These additives support the startup process on palladium activated base material during the copper deposition.

This investigation demonstrates that additives can provide a significant benefit in terms of cost, health and environmental impact when compared to the traditional electroless copper process. In that way, a higher concentration of the mostly injurious and cost-intensive reducing agent can be avoided.

2. Reaction mechanism

Surfaces of epoxy resin substrates are easily metalized by the electroless copper plating technique. Electroless copper deposition reactions at Pd-catalyst-adsorbed surfaces consist of two partial reactions. At the anodic surface, the reducing agent is oxidized and at the cathodic surface, copper ions are reduced to a metallic state.

Oxidation of the autocatalytic reducing agent (exp.: formaldehyde):



$$HCHO + 3OH^- \rightarrow HCOO^- + 2H_2O + 2e^-$$ <1>

Reduction of cupric ions:

$$Cu^{2+} + 2e^- \rightarrow Cu$$ <2>

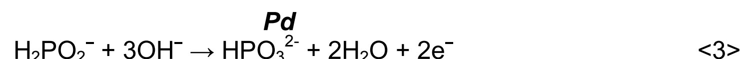
Both reactions occur simultaneously at the surface of the Pd catalyst. The emission of electrons is necessary for the copper reduction. Through the oxidation of the reducing agent, electrons are delivered and used for the autocatalytic copper plating process. In order to lower the disadvantageous qualities of the reducing agent, you have to reduce the reducing agent concentration in the copper solution to a minimum. Slight concentrations of reducing agent cause only few electrons. The insufficient amount of electrons leads to an inhomogeneous and scant copper deposition. Therefore, in order to produce high-quality copper coatings with low reducing agent concentration, additional electrons must be provided.

3. Electrolyte additives

The supply of electrons for the electroless copper deposition can be increased by the application of electrolyte additives, which are able to discharge additional electrons. At the beginning of the chemical copper plating process, a sufficient supply of electrons is important for creating a defect free and

uniform copper deposition despite the low concentration of the autocatalytic reducing agent. A locally inhibited deposition initialization will lead to a non homogenous deposit and thus is difficult to reverse. For a perfect and defect free startup process of the electroless copper deposition on palladium-adsorbed surfaces, additives can be used which react with palladium. From the literature [4] the following additives were investigated: sodium hypophosphite, glycolic acid and sodium formate.
Additional electrons are delivered by exploitation of the catalytic qualities of palladium. The electrons develop during the oxidation reaction of the electrolyte additives on the palladium seeds:

Additive oxidation (additive 1: hypophosphite):



$$H_2PO_2^- + 3OH^- \xrightarrow{Pd} HPO_3^{2-} + 2H_2O + 2e^- \qquad \text{<3>}$$

By use of such additives an accelerated copper deposition can be recorded. The deposition rate increases with raised additive concentration and high amount of adsorbed palladium on the surface (*Fig. 1*). This can be explained by the increased emission of additional electrons which can be used for the copper reduction. The palladium, with its catalytic qualities, acts as charge exchanger. It carries the electrons delivered from the additive oxidation process to the cupric ions to reduce them to metallic copper. The amplified supply of electrons leads to an enhanced copper reduction.
The maximum of deposition speed in copper solutions with an additive occurs in the initial phase of the electroless copper deposition. This peak is clearly greater than the deposition speed maximum in electrolytes without an additive (*Fig. 1*).

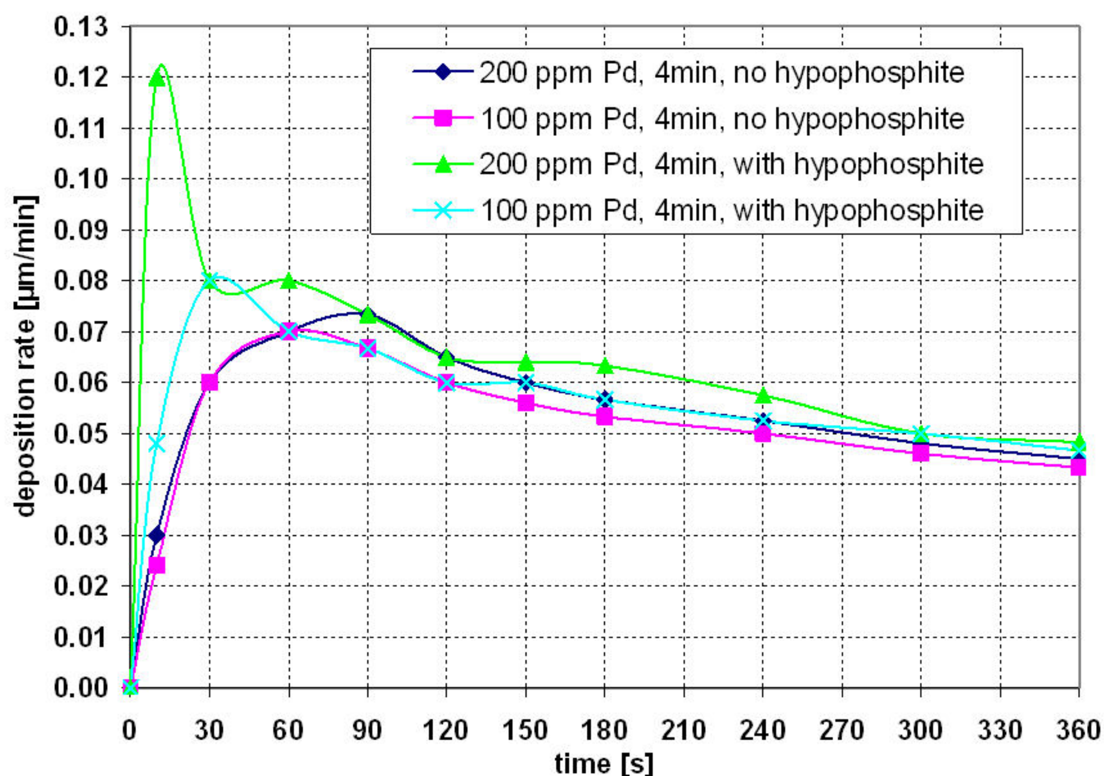


Fig. 1: Comparison of the deposition rate in copper solutions with and without an additive (additive 1: sodium hypophosphite)

Decreasing the palladium adsorption on the surface causes a shift of the deposition rate maximum to smaller values and higher deposition times (*Fig. 1, comparison between green and light blue curve*).
The use of sodium hypophosphite in the copper bath stimulates a maximum deposition rate within 30 seconds. Although the maximum deposition rate is also achieved without the additive, the lag time is over 1 minute and is less dramatic or significant. The maximum in the curve shape originates from the change in copper deposition which first takes place at the catalytic active palladium seeds and then continues on the chemically deposited copper (*Fig. 1, violet and deep-blue curve*). The oxidation of the autocatalytic reducing agent (e. g. formaldehyde) is larger on the palladium than on the chemically

deposited copper. Palladium is a better catalyst for the copper reduction than the copper itself. Thus the deposition rate decreases when all surfaces of the palladium are covered with deposited copper metal.
The curve shapes of the electroless copper solution with and without the sodium hypophosphite enhancement become nearly identical after a plating time of 90 seconds. After that time, hypophosphite has no more influence on the electroless copper plating process. In general, one can assume that a maximum deposition rate is achieved when a maximum activation and exposure of the palladium is present.
The additives could be referred to as startup agents because they only react in the initial phase of the electroless copper deposition. At the beginning of the chemical plating process palladium seeds are active and affect the additive oxidation. The raised supply of electrons can subsequently induce an accelerated deposition.
Beside sodium hypophosphite the copper deposition is also improved by using glycolic acid or sodium formate as “kick-starting” agents. The copper deposition speed and the homogeneity of the copper coverage improve.

4. Conclusions

In the initial phase of the electroless copper deposition, the palladium seeds adsorbed by the activation process of the non conductive substrate serve as an anode for the oxidation of the reducing agent. The electrons that are supplied by the oxidation reaction go through the palladium and cause the copper reduction.
In electroless copper solutions, the reducing agent is necessary to maintain the autocatalytic copper plating process. If the concentration of reducing agent is reduced in order to minimize injurious qualities and side reactions, the amount of delivered electrons by the oxidation of the reducing agent is not sufficient to generate a compact copper layer. Therefore, a high degree of copper coverage of the layer can not be achieved, especially at the beginning of the plating process. This leads to an inhomogeneous copper deposition.
By the additional use of a chemical substance (electrolyte additive) which can be easily oxidized at a palladium surface, more electrons can be created. The amount of electrons consists of the electrons that are formed by the autocatalytic copper reducing as well as by the electrolyte additive. By that, the electrons coming from two sources permit, in sufficient amount, the deposition of a homogeneous and compact copper layer. Suitable additives are sodium hypophosphite, glycolic acid and sodium formate. They can be oxidized at catalytic active palladium and provide additional electrons for the electroless copper deposition. However, the additives are no reducing agents for the autocatalytic copper plating process. The autocatalytic reducing agent has to be in the copper solution and cannot be substituted completely. The additives react exclusively with the palladium. Therefore, they can be considered as a sort of startup agent for the copper plating process on palladium activated base material. Palladium is not directly involved in the reduction-oxidation reactions, but works by its catalytic qualities intermediate as an electron carrier.
Without palladium additional generated electrons are not available. In that case, the autocatalytic copper deposition goes on steadily only by the reducing agent in the electrolyte (e.g. formaldehyde). The use of additives, to provide a chemical kick start, may provide the following benefits as there are indications that less traditional reduction chemistry is necessary to support a successful electroless plating mechanism:

- Lower health risks and costs
- A better quality of copper deposition.

By enhancing the plating reactivity in the initial phase, plating with lower concentrations of the reducing agent is realized.

5. References

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[4] Chowdhury, S.; Bauer, M.; Electroless Plating Baths for High Aspect Features; patent US 7220296 B1; 2007