

## Cost-Effective Alternatives to Palladium Activation – A Study on Autocatalytic Electroless Copper Deposition

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### Abstract

Electroless copper plating is the most important and critical step for through-hole metallization of printed circuit boards. Conventional electroless copper solutions contain formaldehyde as the standard reducing agent. Due to the toxic nature of formaldehyde, there is a need to change to a reducing agent that is more environmentally friendly and safer to use. Many reducing compounds have been proposed to replace formaldehyde. For example, glyoxylic acid has been described in the literature as an especially attractive alternative because of its relative safety. In preparation for electroless copper plating, substrates are typically catalyzed by the adsorption of palladium. However, a change in the reducing agent can also lead to a change in the activation process, primarily because there is no single metal that appears to be a good catalyst for the oxidation of all reducing agents that have been employed for electroless deposition. In the present study, electrochemical measurements were carried out in order to obtain information about the catalytic activity of copper, silver, nickel and palladium in the oxidation reaction of formaldehyde as well as glyoxylic acid. Metals with high catalytic activity for each reductant oxidation can be determined by using cyclic voltammetry. These metals are candidates for an improved activation process. Electrochemical measurements showed that palladium does not have the highest catalytic activity of all tested metals. Therefore, more cost-effective, alternative metals were examined as catalysts for electroless copper plating reactions. The paper presents the results of a PhD thesis, which included tests on cheaper alternatives to palladium for activation of autocatalytic electroless copper deposition. It also includes production scale studies and conclusions on possible replacement of formaldehyde as a reducing agent for electroless copper deposition.

Keywords: Electroless copper, formaldehyde-free, activation, palladium-free, cyclic voltammetry, catalytic activity

### 1 Introduction

Electroless copper plating on polymer substrates is one of the key processes in printed wiring board manufacturing. The standard electroless copper bath is a stable, autocatalytic process using formaldehyde as a reducing agent. Since formaldehyde is a volatile carcinogenic substance, electroless copper solutions using non-formaldehyde reducing agents such as glyoxylic acid have been investigated [1; 2].

If the reducing agent is to be modified, it may be of use to alter the activation process as well. Generally, a palladium catalyst is used for the pretreatment of the substrate in the electroless copper plating process based on formaldehyde. Nevertheless, palladium is not necessarily the best choice for other reducing agents.

For electroless copper plating, an important item is what combination of catalyst and reducing agent is effective in reduction reactions of  $\text{Cu}^{2+}$  to  $\text{Cu}^0$ .

The active catalyst should ideally be a precious metal in order to prevent passivation. The catalyst acts as an electron carrier for the transfer of electrons from the reducing agent to the copper ions. For a suitable activation system, a good electron transfer and the ability to adsorb the reactants are required. The adsorption is the step preceding the electron transfer.

The electron transfer from the reducing agent to the copper ions has to occur on the surface to be plated. Otherwise, copper deposition is not feasible. Various metals can act as catalysts/activators in the electroless copper process. The choice of the activator needs always to be related to the reducing agent used.

The catalytic activity of the metal has an influence on the reductant oxidation and thus on the electroless copper deposition. The adjustment of the activation process to the properties of the reducing agent is necessary for an optimal yield of the oxidation reaction at the catalytically activated substrate.

The aim of this study is the investigation of the catalytic activities of selected metals in reductant oxidation. Based on the results of experiments, the development and optimization of activation processes in electroless copper plating can be advanced.

Therefore, formaldehyde, as the standard reductant, and glyoxylic acid, as the alternative reductant, were selected for measurements.

## 2 Catalytic Aspects

The critical reaction in electroless deposition from the viewpoint of catalysis is the oxidation of the reducing agent at the catalyzed base material. During the activation process, active colloids are adsorbed on the substrate surface and act as catalysts. They function by providing an alternative reaction path having a lower energy of activation.

At the initial stage of the electroless copper process, the catalyst serves as the anodic site at which the reductant can be adsorbed and oxidized. The electrons released on oxidation travel through the metal and allow copper reduction. The catalytic particles act as electron transfer carriers from the reducing agent to the metal ions. Hence, the structure and composition of the catalyst can affect the deposition rate and reaction kinetics [3].

The role of a heterogeneous catalyst is to adsorb the reactant or intermediate and transform it to the species that can more readily undergo the desired chemical reaction. Thus, the oxidation of the reducing agent depends on the activation step in the electroless copper plating process. In electrocatalysis, the relation between reductant transformation and catalytic adsorption is described by "volcano-plots" (Figure 1).

The volcano-plot shown in Figure 1 compares the exchange current density  $j_0$  for the hydrogen evolution reaction as a function of the metal-hydrogen bond energy on different electrodes. The magnitude of the metal-hydrogen bond energy can influence the reaction rate. If the metal-hydrogen bond energy is very low, the extent of adsorption will be very small. The molecules adsorbed are weakly bound to the catalytically active surface and are not affected by it. As the bond energy increases, the adsorbed species can be modified and activated by its bond to the surface. But the surface coverage approaches saturation.

If the binding energy to the surface is too high, the adsorbed intermediate may adhere to the surface and effectively poison it. The rate of reaction can no longer increase with increasing energy of adsorption.

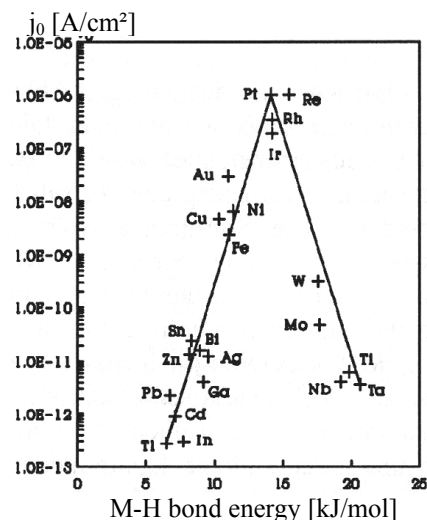


Fig. 1: Volcano-plot for the hydrogen evolution reaction [5]

The energy of adsorption must be high enough to attract the reactant to the surface, yet low enough so that the reaction product may be released into the solution. The best catalyst is one giving rise to an intermediate value of the energy of adsorption. At that point, high catalytic activity of the metal combined with high exchange current density is present. The volcano-plot indicates the metal with best catalytic activity with regard to the reactant reaction.

Electroless copper deposition requires the oxidation of the reducing agent at the catalyst so that the released electrons can be used for copper reduction.

## 3 Experimental

The activation process based on palladium as catalyst is the state of the art in electroless copper solutions with formaldehyde.

In order to evaluate the catalytic activity of various metals, the oxidation of reducing agents may be studied by electrochemical techniques. Thereby, it can be checked if palladium is ideally suited as a catalyst for formaldehyde oxidation and which metals may be the best catalysts for glyoxylic acid oxidation.

The metals copper (Cu), nickel (Ni), silver (Ag) and palladium (Pd) are appropriate as electrode materials.

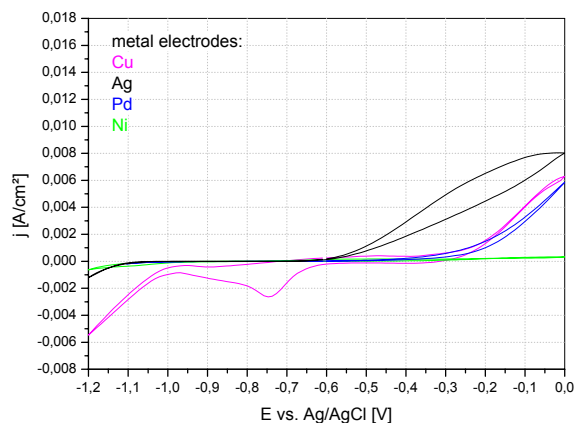
Each metal has its specific catalytic activity referring to the oxidation of the actual reducing agent in the copper bath.

The oxidation reactions of the reducing agents formaldehyde and glyoxylic acid were examined with cyclic voltammetry (CV). Cyclic voltammetry is a type of potentiodynamic electrochemical measurement. It is a diagnostic method to determine the mechanism and rate of chemical reaction that may follow an electron transfer step. As a result, current-potential-curves (cyclic voltammograms) of the reducing agent are recorded.

These experiments were performed in an electrochemical cell with a three-electrode configuration. The metals Cu, Ag, Ni and Pd served as the working electrodes. The counter electrode was Pt and the reference was Ag/AgCl. All experiments were carried out under a nitrogen atmosphere. The current-potential curves were measured at different temperatures (25 and 40 °C) and different scan rates (5 and 50 mV/s) with the *Autolab PG Stat 30* potentiostat (*Eco Chemie*). The concentration of the reducing agent solution was 0.3 mol/l and the pH of the solutions was set at 13.0 using sodium hydroxide.

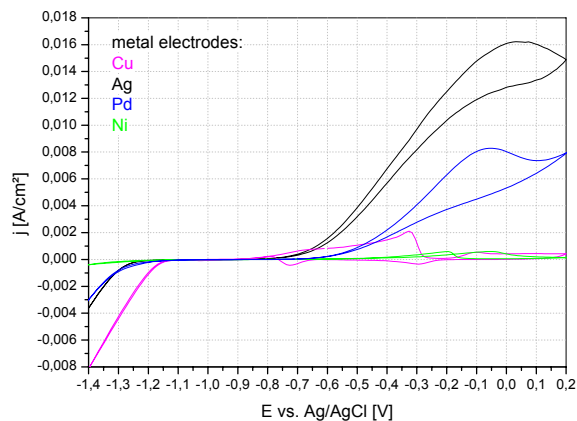
#### 4 Results and Discussion

Voltammetric curves were obtained in the formaldehyde and glyoxylic acid solution for an anodic reaction at various metals (Figure 2 and 3). The cyclic voltammograms indicate a difference in the extent of oxidation between the two reducing agents at each electrode.



**Fig. 2: Polarization curve of glyoxylic acid (0.3 mol/l; pH 13; RT) on different metals**

The oxidation maximum of the reducing agent can be related to the maximum current density. Regarding the oxidation of glyoxylic acid, the maximum current density of 0.008 A/cm<sup>2</sup> is reached at a silver electrode.



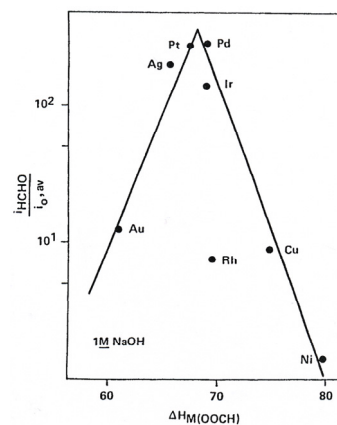
**Fig. 3: Polarization curve of formaldehyde (0.3 mol/l; pH 13; RT) on different metals**

For the formaldehyde oxidation, a maximum current density of 0.016 A/cm<sup>2</sup> is measured at a silver electrode, too. The current density of the formaldehyde oxidation is twice as high as that of the oxidation of glyoxylic acid under the same conditions.

Moreover, both reducing agents react with different reaction speeds at the various metals. It can be seen that the peak current density drops in the order of

Ag, Cu, Pd, Ni for glyoxylic acid and  
Ag, Pd, Cu, Ni for formaldehyde.

The electrocatalytic activity of various metals for formaldehyde oxidation has already been evaluated by a number of workers (Figure 4 and 5) [2].



**Fig. 4: Volcano-plot of HCHO oxidation currents in 1M NaOH vs. enthalpy of formation of metal formate [2]**

There is a correlation between the catalytic activities derived from the volcano-plot and those derived from the measured cyclic voltammograms.

In the volcano-plot in Figure 4, the normalized peak current for formaldehyde oxidation is compared to the enthalpy of formation of the metal formate.

Silver and palladium are the best catalysts because of their high exchange current density and high adsorption kinetics. Metals with such qualities can be found at the top of the volcano-plot. Copper and nickel are at the bottom of the plot and exhibit low current density and high enthalpy of adsorption. During formaldehyde oxidation formate is generated as a reaction product. It is strongly adsorbed at the copper or nickel surface and can not desorb. The catalytic surface is inhibited for further formaldehyde oxidation.

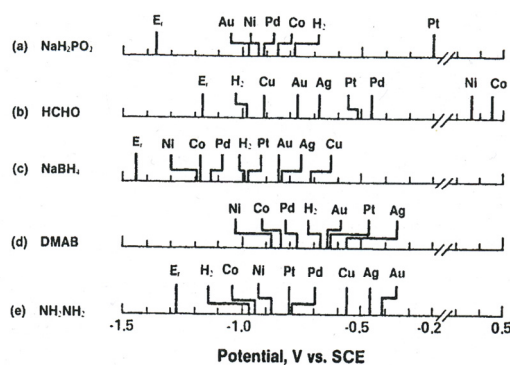
The analysis of the volcano-plot leads to the same order of metals for the formaldehyde oxidation as the cyclic voltammograms showed: silver, palladium, copper and nickel.

For choosing a suitable activator system for electroless copper deposition, very low current densities need to be regarded. The oxidation reaction of the reducing agent at the catalytic surface does not proceed at the maximum peak current, but near the mixed potential.

The mixed potential, which yields two curves of respective anodic and cathodic reactions, can be associated with low current densities such as  $j = 10^{-4}$  A/cm<sup>2</sup>.

Concerning low current densities, the order of catalytically active metals can change as compared to the order at the maximum peak current density. That is because the rate determining step of the reaction can change.

In the literature [2], the polarization behavior of a number of reductants was investigated on a variety of solid electrodes.



**Fig. 5: Catalytic activities of metals (as potentials measured at  $10^{-4}$  A/cm<sup>2</sup>) for oxidation of different reductants [2]**

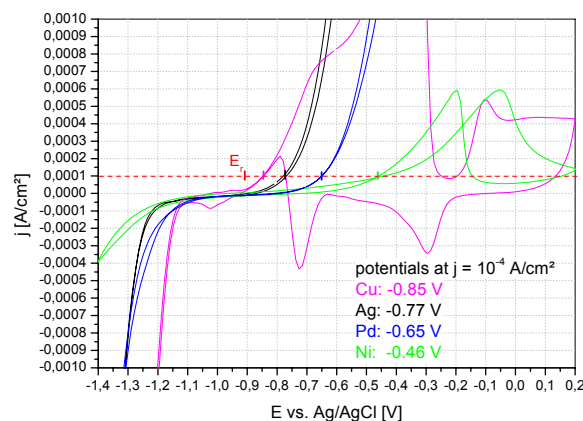
Figure 5 shows the potentials of metals exhibited by the reducing agent for a fixed current density of  $10^{-4}$  A/cm<sup>2</sup>. The potentials are compared with the standard redox potential  $E_r$  for each reductant.  $E_r$  has a very negative value that is even more negative than the mixed potential.

Catalytic activity increases on going from high to low potentials. So the metal has a high catalytic activity if its potential is close to  $E_r$ .

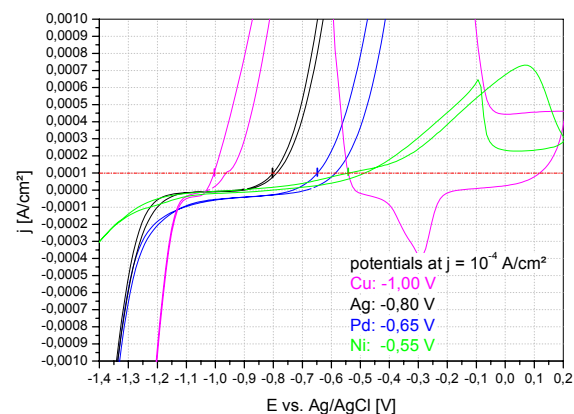
Potentials with negative values make the copper deposition thermodynamically favorable.

As one can determine from Figure 5, copper is most catalytically active for formaldehyde oxidation followed by silver, palladium and nickel at low current density. This metal order is different to the order from the volcano-plot plotted for high current densities. Electrochemically, copper would be an excellent activator due to its negative potential, which is closest to the  $E_r$  of formaldehyde.

In order to compare the published metal order (Figure 5) with the cyclic voltammograms presented here, the metal potentials have to be considered at the same current density of  $j = 10^{-4}$  A/cm<sup>2</sup> (Figure 6.1 and 6.2).



**Fig. 6.1: Polarization curve of formaldehyde ( $c = 0.3$  mol/l; pH 13; 25°C)**



**Fig. 6.2: Polarization curve of formaldehyde ( $c = 0.3$  mol/l; pH 13; 40°C)**

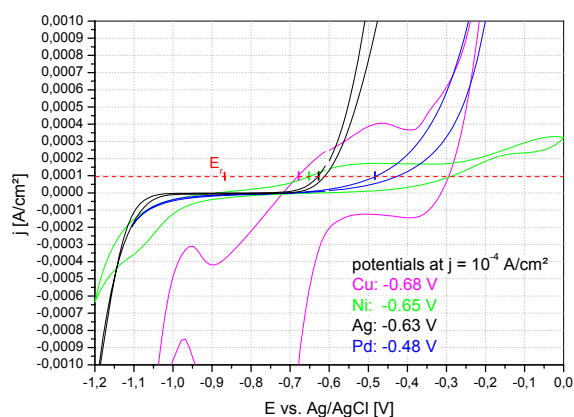
For low current density, the metal order in both voltammograms recorded at different temperatures (25 and 40°C) is the same as that observed in the literature for formaldehyde oxidation. Copper has the highest catalytic activity for the oxidation reaction, followed by silver, palladium and nickel. The potential of copper is closest to the redox potential of formaldehyde as already described in literature. That means copper is a potential catalyst for electroless copper plating. A change in the temperature of the reducing agent solution has no influence on the metal order.

There is just a drift of the potential value of each metal into the negative direction which means that the catalytic activity increases with temperature.

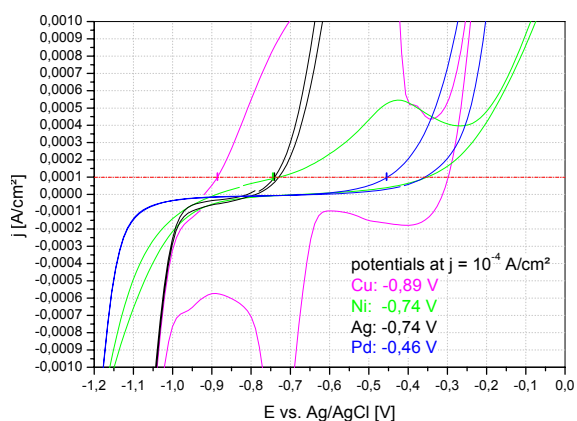
Surprisingly, palladium does not show the highest catalytic activity as would be expected of a good activator in formaldehyde-based electroless copper plating.

The same procedure of analyzing the cyclic voltammograms was done for the less widespread reducing agent glyoxylic acid.

The metal order of catalytic activities is nearly the same as that for formaldehyde at low current densities: copper, nickel, silver and palladium (Figure 7; Table 1).



**Fig. 7.1: Polarization curve of glyoxylic acid**  
( $c = 0.3 \text{ mol/l}$ ;  $\text{pH } 13$ ;  $\text{RT}$ )



**Fig. 7.2: Polarization curve of glyoxylic acid**  
( $c = 0.3 \text{ mol/l}$ ;  $\text{pH } 13$ ;  $40^\circ\text{C}$ )

At the current density of  $10^{-4} \text{ A/cm}^2$ , the potential value for glyoxylic acid oxidation at copper is the most negative one. This indicates that copper is the most active metal in the catalytic oxidation of glyoxylic acid.

As also seen in the formaldehyde voltammograms, there is no influence of the temperature on the metal order. Just the potentials are shifted to more negative values with increased temperature.

**Tab. 1: Order of catalytic activities for different current density ranges**

	Literature (theory)	Polarization curves (practice)	
	formaldehyde	formaldehyde	glyoxylic acid
$j_{\text{max}}$	Ag, Pd, Cu, Ni	Ag, Pd, Cu, Ni	Ag, Cu, Pd, Ni
$j_{\text{low}}$	Cu, Ag, Pd, Ni	Cu, Ag, Pd, Ni	Cu, Ni, Ag, Pd

As with formaldehyde-based electroless copper solutions, copper is also a potential catalyst for glyoxylic acid based solutions due to its high catalytic activity. Nickel and silver follow closely. From all tested metals, palladium has the lowest catalytic activity. But the potential value of  $-0.48 \text{ V}$  vs.  $\text{Ag/AgCl}$  where the oxidation of glyoxylic acid starts at the palladium electrode is still acceptable for a good activation. Practical experience demonstrates that the activity of palladium is high enough for electroless copper deposition using glyoxylic acid as a reducing agent.

## 5 Conclusions

Cyclic voltammetry is an appropriate method for analyzing the catalytic activity of metals concerning the oxidation reaction of different reducing agents. Information on formaldehyde oxidation from the literature can be easily reproduced by measuring polarization curves. Applying this analyzing procedure to unknown reducing agents e. g. glyoxylic acid, the catalytic activities of various metals for reducing agent oxidation can be investigated.

This study suggests that further improvement in electroless copper plating processes may be possible with an alternative activation procedure that yields higher catalytic activity. The catalytic activity of copper, silver or even nickel when glyoxylic acid is used as the reducing agent is higher than that of palladium. So these metals are electrochemically potential catalysts for electroless copper plating.

However, different aspects must be considered. An activator based on copper shows poor performance because of oxidation and instability problems. Commercial copper activation systems are not successful so far [6].

Although palladium is not the most catalytically active, it is so far the universal choice as a catalyst for initiating electroless copper deposition due to its resistance to dissolution and oxidation.

So, much more work needs to be done in order to establish a new activator system without using palladium.

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