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International Journal of Current Research
Vol. 5, Issue, 08, pp.2222-2224, August, 2013

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

COMPARATIVE STUDIES OF CU AND AU ELECTROLESS PLATING A REVIEW

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ARTICLE INFO

Article History:
Received 19th May, 2013
Received in revised form
10th June, 2013
Accepted 22nd July, 2013
Published online 23rd August, 2013

Key words:
Elecrtroless plating,
Electroless Gold plating (EGP),
Copper, Resistance, Properties, Reaction,
Deposition, Reductant, Substrate.

ABSTRACT

Metal displacement reaction is a common method, well known and practiced world wide in decorative and electron ic IndustriesElectroless plating has gained importance to satisfy the demands of the niche and gamet technologies. The chemical deposition of a metal from an aqueous bath solution of a salt, onto any other metal surface immersed in it, involves an electrochemical mechanism (oxidation and reduction reactions). The oxidation of a substance is characterized by the loss of electrons, while reduction is distinguished by a gain of electrons. Electroless nickel plating is the most commonly used plating method.Copper and gold are equally competent and are also used in el ectroless plating. Their physical and chemical properties, surface morphology, thickness characterization, applications and efficiency are significantly studied.

INTRODUCTION

Electroplating is a conventional and traditional method of plating, essential electrical connections designed to plate every surface must be removed after plating, thickness variation along the surface of substrate due to uneven coating was a major problem, to overcome these disadvantages, a chemical deposition process without electrical connections was first developed by Brenner and Riddell in 1940's this controlled, stable, electroless deposition contributed a lot to plating industries to achieve smooth surfaces which was an issue century ago[1]. It also provides an even coating on complex geometries[2] which was a task accomplished by electroless plating. This method involves the selective reduction of metal ions only at the surface of a catalytic substrate immersed into an aqueous solution of metal ions, with continued deposition on the substrate through the catalytic action of the deposit itself. The deposit catalyzes the reduction reaction; hence this method is also called as autocatalytic [3]. Eugene (2011) surveyed and suggested a typical electroless plating solution consisting of metal ions, a reducing agent or reductant, a complexant to minimize homogenous reaction between the metal ions and the reducing agent and most importantly pH adjusted buffer that showed electroless deposition.

The following reaction is seen in all electroless deposition

Reductant ==> Oxidation product + ze^-

M^{z+} + ze^- ==> Metal on substrate

Reductant + M^{z+} ==> Oxidation product + Metal on substrate
Nickel electroless plating is extensively used in plating industries. Electroless Cu and EGP are equally competent and are widely used in industries. Recent developments using this technique have produced pore free films with a considerable thickness.

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Electroless Copper Plating

Copper metal occurs in group I B of the periodic table possesses physical and chemical properties like malleability, ductility, non magnetic, non sparking and also a good conductor of heat and electricity [4, 5]. Table 1. Shows the ideal physical properties of copper for industrial application. It also exhibits low specific and excellent electro migration resistance. Hence, used in electroless plating which is a method of plating a metal film by the reaction of a reductant and an oxidant in solution to provide the deposition of the metal on the surface of an activated substrate.

Table 1. Properties of Cu [lenntech/elements]

Atomic number	29
Atomic mass	63.546 $g.mol^{-1}$
Density	8.9 $g.cm^{-3}$ at 20°C
The Melting point	1083 °C
Boiling point	2595 °C

According to Ki Yong Song *et al.*, Cu electroless plating method does not require an additional primary layer to be coated on the substrate, the entire substrate is uniformly and evenly coated. A simple process with low manufacturing cost and high productivity. His team's contribution to the plating industry is enormorous, an invention of electroless copper plating solution to provide a plating film having excellent adhesivity, low electrical resistance and highly stable film. Though the pH range of the electroless copper plating solution depends on the kind of reductant. A high pH is used, to increase plating speed, the normal pH range of copper plating solution is about 11.5 to 13.0, and specific range is 12.3 to 12.8. The Cu film coating speed on the substrate drops when its pH is below

11.5, resulting in blisters after copper plating, thereby causing insufficient adhesivity for the copper plating film. In contrast, the stability of the plating solution decreases when its pH about 13.0.This being disadvantageous, modifications were appreciated by skilled researches. The factors responsible for blister formation and delamination on smooth substrates are film stress and hydrogen evolution from the electroless Cu plating solution. To avoid blister formations, effect of thermal substrate contraction that influences the film adhesion upon termination of plating was considered, to Improve electroless copper plating technology find applications to coat smaller structures and achieve smoother substrates, where the copper film adhesion was a difficult task to achieve according toTanu Sharma *et al.(*2013). Table 2 Shows component composition for an electroless copper plating bath generally used in industries.

Table 2. Copper plating bath composition (ECE4803)

Component	Concentration (g/l)
Formaldehyde	10
Ethylene diamine tetraacetic acid (EDTA)	20
Formaldehyde	10
Sodium potassium tartrate	10
Sodium hydroxide	15

According to Nixon *et al.* (2013), Acid Copper method is a well known Cu plating process, unique and easy to operate, it minimizes thermal expansion and flexing problems because of its high ductility, finds its application on steel, bronze, brass and other metal alloys. The copper deposit is extremely bright, at low density areas, hence often required, to simplify and minimize searching problems and resistant to burning at high density. Though Cu has these properties, precious metal Gold has also been appreciated for its durability, unique appearance and properties like good conductor, totally resistant to corrosion, wear and tear also makes it ideal for decorative application. A reliable film coating metal with improved adhesivity and specific resistance for electrical and electronics industry to achieve plating goals.

Electroless Gold Plating

Gold metal also occurs in group IB of the periodic table known as noble metal possesses properties like malleability, ductility and a good conductor of heat and electricity. It is usually alloyed with other metals to increase its strength since it is a soft metal[6], Table 3 shows the specific properties of gold.

Table 3. Properties of Au [lenntech/elements]

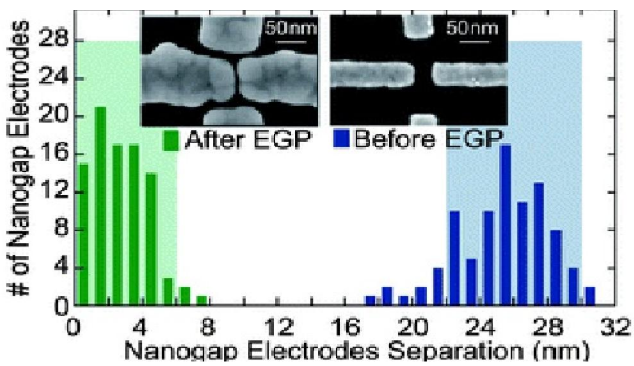
Atomic number	79
Atomic mass	196.9655 $g.mol^{-1}$
Density	19.3$g.cm^{-3}$ at 20°C
The Melting point	1062 °C
Boiling point	2000 °C

As it shows amazing electro migration resistance, electroless gold plating is an efficient method of plating and is widely used in many decorative and electronic industries, it is a process of plating gold onto a substrate surface from a solution, purely as the result of the reaction of chemicals in the bath. The electroless plating bath includes reducing agent chemicals to provide electrons for the reaction and other chemical chelating agents and stabilizers to control the reaction and ensure a controlled manufacturing process. According to Yukata Okinaka (1969), electroless gold plating process is highly stable and yields about 90% Au deposition on the substrate, the gold plating bath may be of Au cyanide alkali metal or free cyanide to increase the bath stability and prevent the liberation of metallic Au in the presence of the reducing agent. The advantage of this process, is comparatively high and thicker gold deposit on the substrate. Invention of electroless gold plating solution with varying component cyanide composition by Nishiyama *et al.* (1987), showed excellent stability and improved plating speed 5 to 10 times higher than the existing one. One such specific composition is shown in Table 4. Along with air agitation pH higher than 12.0. With these effective background invention of electroless gold plating solutions, many researchers have encouraged further modifications, improved techniques, to achieve excellent plating standards and advance in process to maximize its application in all decorative, electronic, electrical and mechanical industries.

Table 4. Composition of Au plating bath [Nishiyama, 1987]

Component	Concentration (g/l)
Potassium gold cyanide(as a gold)	1-5
Hexamethylenetetramine	0.1-10
Ethylenediaminetetraacetic acid	1-20
kali hydroxide	5-100
Dimethylamine borane	1-20

According to an invention patented in 1995, developed, a desired EPG solution consisting of cyanoaurate, alkaline cyanide, reducing agent, alkaline hydroxide, crystal condition controlling agent and stabilizer to minimize plating span, maximize the stability of the solution and also significantly improved the properties of gold film deposit, such as bonding and adhesion to a substrate and extremely satisfied continuous operating process. According to a patented invention of non-cyanide electroless gold plating bath solution and process for EGP (2008), a cyanide free solution comprising of disulphide as complexing agent provides excellent gold stabilization with pH value 7 or lower. With different component composition and improved aerating conditions of plating bath solution have optimized its use in advanced technology. Jiangxin Song *et al.* (2012), reported, the need of an optimized electroless gold plating bath to achieve selective gold deposition and improved adhesion. The research developed, demonstrated good electrical conductance by the advanced use of electroless gold and modified laser femto seconds for the fabrication of gold microelectrode. Zambeli *et al.* (2012), advanced the use of electroless gold plating solution to prepare CdZnTe detectors by scanning pipette technique. These detectors showed optimized current voltage characteristics and excellent spectroscopic response. Victor *et al.* (2012), demonstrated the use of EGP along with electron beam lithography yield 90% of robust nanogap electrodes for nano devices with a separation of 3.0 +or - 1.7nm. This yield is achieved by controlling one of its parameter, the heat treatment of reproducible EGP. The nano transistors based on the nanogap electrodes exhibit reproducible Coulomb that are ideal and stable. Graph I shows the achieved result of maximum yield of robust nanogap electrodes with heat treated EPG.



Graph I-Maximum yield of nanogap electrodes with EPG [Victor *et al.*, 2012]

Recent research studies showed the use of electroless nano gold deposition; Kobayashi and Ishii (2013) demonstrated gold nano particle deposition of size 34.6 +or-11.4nm on the surface of the glass substrate that proved to be an excellent sensor for measuring dielectric constant. Ito *et al.* (2013), Contributed to the printed electronic industry, a fabrication technique of EGP and platinum films as a source to drain electrodes in high performance solution and processed organic field effect transistors in a promising environment at ambient conditions for large production of the best field effect circuitry arrays. Component surface industry [7] declared, using EGP process, saves the manufacturer several process steps to design circuits and fabricate in their final desired configuration. Most importantly electroless gold plated deposits are uniform in thickness, around corners, on exposed surfaces of the substrate and even on the inside walls of small holes that are very deep.

DISCUSSION

Unique physical and EPG properties of gold have proved that it is cur rently indispensable for the electronics, electrical, decorative and ma ny other industry, in spite, of its high price, comparatively. Further, invention and relative progress is much appreciated to meet the standards of growing uncompromised innovative technology in the electroless plating industry.

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