

INVESTIGATION OF ELECTROLESS DEPOSITION
FOR THIN FILMS IN INTEGRATED CIRCUITS

by *580*

BEN-HUANG LIN

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Approved by:

M. P. Lucas

Major Professor

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CHAPTER 1

INTRODUCTION

The major methods for thin-film deposition are electroplating, chemical plating, thermal growth, anodization, vapour phase deposition, vacuum evaporation, sputtering and stencil screening. Several of these methods are used on a commercial scale, and many other techniques having important future applicability are still under investigation.

Most types of film required can be produced by the vapour phase, evaporation and sputtering methods. However, these methods use more expensive equipment and should be avoided if only a limited amount of funds are available. The choice of method depends on compatibility, the quality of component required and cost. Uniformity of film thickness, composition, electrical characteristics and good adhesion to the substrate are the major requirements for good thin films.

In electroplating, a metal ion in a suitable solution is reduced to the corresponding metal at a suitable cathode and deposited as a metallic coating by the use of an electric current. The rate of deposition is chiefly dependent on the current density. On the contrary chemical plating does not use an external current source to reduce metal ions but employs several other ways of reducing metal ions. The principal reactions of chemical plating are as follows:

1.1 Displacement

Campbell³ said, "If one metal is immersed in a solution containing another metal it is possible to obtain dissolution of the one and the deposition of the other in its place. The deposition is essentially electrolytic in action and generally results in an uneven deposit." e.g.



1.2. Non-Catalytic Deposition

Formaldehyde (HCHO) is a very strong reducing agent in alkaline solutions. Add HCHO to silver nitrate (AgNO_3) and ammonia (NH_4OH) solutions. The substrate surface in the bath gets a metallic silver deposit by reducing this solution with HCHO. This process differs from electroless deposition because plating thickness cannot be built up. Silver is not a catalyst for this reducing agent. Only a limited number of metals deposit in this way.



1.3. Electroless Deposition

Brenner² has written, "the development of the electroless plating process came about as the unexpected result of an electroplating experiment. The process is a unique method of chemical plating which differs from the displacement processes and the familiar silver reduction process in that thick coatings can be built up. In this respect it resembles electroplating and for that reason, has been given the name electroless plating. The process is a controlled autocatalytic reduction of nickel or cobalt ion by hypophosphite ion on certain catalytic surfaces and results in the production of a sound coherent coating of metal. Since nickel and cobalt catalyze the process, deposition of metal continues on nickel or cobalt deposits after they have once been laid down. The process has three distinct advantages over electrodeposition: 1. Coating deposit with uniform thickness in recesses as well as on exposed parts of objects. 2. No build-up of coating occurs on points or edges. 3. No electrical equipment is required."

Saubestre⁶ noted that, "some of the resulting significant advantages of electroless plating over other forms of chemical plating are: 1. May be applied to any substrate, including non-conductors such as glass, ceramics, etc. 2. May be built up to any desired thickness; may even be used for electroforming. 3. The plating solution, in many cases, may be continually maintained, much in the manner of an electroplating solution."

CHAPTER 11

REVIEW OF LITERATURE

2.1. History of Electroless Deposition

In 1819 hypophosphorous acid, H_3PO_2 , and the hypophosphite ion, H_2PO_2^- , were discovered. In 1845 Wurtz¹ observed the reduction of a nickel solution to nickel by the reducing power of the hypophosphite ion. The similar reduction of cobalt ion to cobalt was studied at that period. All these reductions were by a spontaneous chemical reaction yielding a black powder. They were catalyzed by the metals themselves and by palladium.

In 1916 the first U. S. patent was issued to Roux¹ for the deposition of nickel coating by the hypophosphite ion. His bath decomposed spontaneously to yield a plating on all objects immersed in it, including the tank walls.

In 1944 Brenner and Riddell made a major breakthrough in this field by discovering electroless deposition from the unexpected result of an electroplating experiment.² Without the bath spontaneously decomposing, electroless deposition occurs only on properly catalyzed surfaces and is capable of depositing adherent, coherent coatings.

The difference between electroless deposition and the deposition of nickel as accomplished by Roux is that the latter was a spontaneous decomposition, whereas the former was a catalytic process, so controlled that deposition occurred only on

catalytic surfaces immersed in the bath.¹

In 1946 the electroless process was announced. The plating industry itself was slow to commercialize the process.

2.2. The Advantages of Electroless Deposition

1. Uniformly thick deposits build up smoothly without producing nodular growths on edges and corners.

On a properly catalyzed surface, the driving potential for chemical reduction is constant at all points on the surface. Therefore, the very high degree of uniformity in thickness of deposit is obtained. Good agitation can insure uniform nickel ion distribution so as to obtain uniform plating thickness.

2. Metal and non-metal substrates can be plated.

3. The plating operation and equipment is simple and relatively inexpensive.

4. Parts can be processed at low cost.

2.3. Characteristics of Deposits of Electroless Nickel Plating

Electroless nickel plating baths deposit a nickel-phosphorus alloy, containing 5-10% phosphorus. Brightness increases with the increase of phosphorus content. Semibright means containing about 5% phosphorus. Full bright means containing over 10% phosphorus. The higher the pH, the lower the phosphorus content. The lower the hypophosphite/nickel ratio, the lower the phosphorus content of the deposit. Periodic variations in the phosphorus content during plating forms a lamellated columnar

deposit. After heat treatment, a crystalline, very fine grain structure consisting of 35% Ni_3P and 65% Ni is obtained. Deposits containing over 8% phosphorus are nonmagnetic and those with less phosphorus are less magnetic than pure nickel.⁶

The electrical resistance of nickel-phosphorus alloy is higher than that of pure nickel. It drops to a minimum when the alloy is heat treated at about 600°C .¹ The electrical characteristics of the metallic contact is greatly affected by surface treatment before plating and heat treatment after plating. On n-type silicon, electroless nickel contacts in the as-plated condition are mildly rectifying, but heating up to 350°C makes the contact more rectifying, and heating up to 650°C decreases contact resistance. An ohmic contact in the range of 0.05-1.0 ohm-cm is obtained by heating a nickel plated n-type silicon up to 650°C and then gradually diminishing heat. However, on p-type silicon, the contact resistance is low, but increases greatly with heating. Therefore, heating a nickel plated p-type silicon up to 600°C and then gradually diminishing heat, a rectifying contact is obtained. The diffusion of phosphorus, an n-type doping agent, across the contact interface causes these changes.⁶

Strong reagents which attack pure nickel will also attack the nickel-phosphorus alloy, such as nitric, monochloroacetic, concentrated chromic, sulfuric, hydrochloric acids, and sodium hypochlorite.¹

2.4. Alkaline Baths

There are two types of bath. Alkaline baths are operated in the pH range from 8 to 10. The regular addition of ammonia to the bath is required because of the rapid loss of ammonia at the high temperature of operation.

The rate of deposition is proportional to the hypophosphite concentration but almost independent of nickel concentration. Presence of ammonium salts greatly increases the rate of deposition. The poisoning effects of trace elements in the bath may retard plating rate. Alkaline baths are cheaper to operate than acid baths and require less critical control.

The alkaline electroless nickel deposition is the most suitable for plating on silicon.⁶

2.5. Acid Baths

Acid baths are operated in the pH range from 4 to 6. The plating rate is almost independent of the concentration of the nickel ion and the hypophosphite ion, but is affected by pH and the concentration of salts of organic acids. The plating rate can be increased by having a certain ratio of nickel to hypophosphite. Increasing pH causes higher plating rate, while the solubility of nickel phosphite decreases causing spontaneous decomposition.

2.6. Spontaneous Decomposition

The phenomenon of random bath decomposition first begins

with a mild and uniform evolution of hydrogen bubbles throughout the bath instead of only on the surface of the substrate. Then the gassing becomes more vigorous until the bath begins to foam over, accompanied by the appearance of a black precipitate.² If general gassing appears throughout the bath, one adds hydrochloric acid to the bath to stop deposition.

Spontaneous decomposition of the bath can be initiated by many causes, such as using direct immersion heaters, adding hypophosphite and alkali too rapidly, too much hypophosphite, plating on tank walls or heating coils, incomplete removal of activator, improper bath loading, and high phosphite content.¹

2.7. Bath Control

Chemical analytical control of bath composition is so slow that it is not practical. Bath control bases on observation and experience. For maximum efficiency and for optimum plating quality, bath can be control by pH and the concentration of hypophosphite, nickel, and phosphite. Using indicator paper or a standard pH meter determine the pH value of a bath. As plating proceeds, the phosphite content increase steadily. A limited solubility of the phosphite ion may cause the phosphite ion to precipitate out yielding rough deposits and nuclei for random bath decomposition.¹

CHAPTER 111

EXPERIMENTAL METHOD

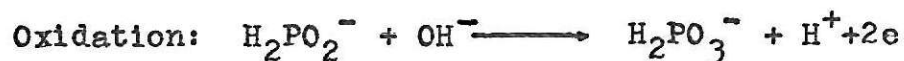
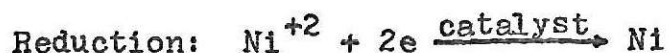
3.1. The Principles of Electroless Deposition for Ceramic Substrates

The term electroless deposition is used to describe a method of catalytic deposition of alloys by chemical reduction in aqueous solution. In an electroless plating solution, the hypophosphite ion acts as the reducing agent for the metal ions to the corresponding metal.

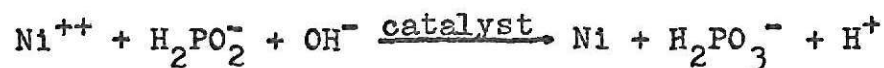
Most chemical plating methods are displacement processes. However, electroless deposition differs from the displacement processes, and does not depend upon the presence of a couple between galvanically dissimilar metals.

3.1.1. Reduction-Oxidation Reaction (Redox Reaction)

Electroless deposition involves reduction of metal salts to the metals by the simultaneous oxidation of the reducing agent, the hypophosphite ion. While the reduction reaction gains electrons, the oxidation reaction loses electrons. The equations of the principal reactants and products are as follow:



Adding the two separate reactions, one obtains



In words, while the hypophosphite ions are simultaneously oxidized to orthophosphite ions, nickel ions are catalytically reduced to metallic nickel by hypophosphite ions in aqueous solution.

In order to give metal reduction taking place under feasible conditions, it requires a suitable standard potential of the reduction-oxidation reaction. If the standard potential of the reduction-oxidation reaction is too high, the electroless plating solution will decompose spontaneously.

3.1.2. The Role of Catalyst

A catalyst will initiate the electroless deposition and limit the plating reaction to desired surfaces only. It will accelerate the rate of the reduction-oxidation reaction. After etching, sensitizing and activating, the palladium film on the surface of the ceramic substrate is a dehydrogenation catalyst and functions as a catalytic center after being first reduced to the corresponding metal. The metals to be deposited on the ceramic substrate are nickel, cobalt, and chromium. They will serve as their own catalysts. This "autocatalytic" reaction makes thick electroless deposits possible.

There are several interpretations of the mechanism of these reactions.

Bremner² suggests that the following equations represent the electron transfer at the catalytic metal surface M in an alkaline solution.



The overall equation is

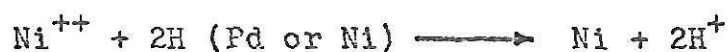
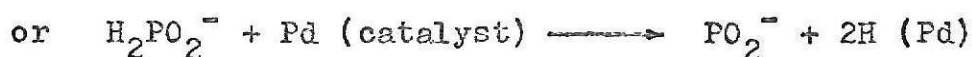
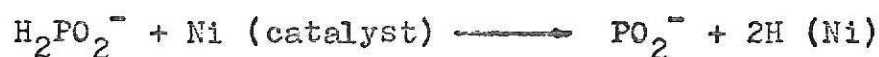


In words, the catalytic metal surface M is an electron source for the initial reaction. The monovalent nickel ion, Ni^+ , is formed by taking up an electron from the catalytic metal surface M. Between nickel and hydroxyl ions at the catalytic surface M, there is a one-electron transfer. The monovalent nickel ion then takes on another electron from metal by disproportionation.

However, Brenner² does not agree with Bremner's explanation. He views the mechanism of electroless deposition as a two-step process. The first step is that the catalytic decomposition of the hypophosphite ion results in the discharge of hydrogen. The second step is that the transfer of energy from the discharge of the hydrogen ion causes the activation of the nickel ion. Therefore, the activated nickel ion is able to react with the hypophosphite ion. The hydrogen effects activation and does not reduce the nickel ion to nickel.

Gutzeit¹ considers that the abstracted hydrogen adsorbed on or loosely bonded to the catalytic surface causes the reduc-

tion of nickel ion by hypophosphite ion in the electroless plating solution. This abstracted hydrogen is either in the atomic or in any "activated" form. In the broadest sense this stage could be considered a "hydride".



The hypophosphite ion, H_2PO_2^- , is dehydrogenated catalytically to the metaphosphite ion, PO_2^- . The metaphosphite ion reacts immediately with water to form the hydrogen ion H^+ , and the orthophosphite ion, HPO_3^{--} . Hypophosphorous acid H_3PO_2 , a monobasic acid, yields the hypophosphite ion, H_2PO_2^- . Orthophosphite acid, a dibasic acid, provides the orthophosphite ion, HPO_3^{--} . The reduction of the nickel ion to metallic nickel by the adsorbed active hydrogen forms the hydrogen ion. The adsorbed active hydrogen is a very strong reducing agent, and serves to reduce nickel ions to nickel metal, cobalt ion to cobalt, chromium ion to chromium, hypophosphite to phosphorus, and water to hydrogen. Therefore, the final products are a nickel-cobalt-chromium-phosphorus alloy and a hydrogen gas. The efficiencies of the electroless plating solutions are less than 35%.

3.1.3. Role of the Various Constituents in Electroless Plating Solution

Salts of nickel, cobalt and chromium supply the required source of metallic nickel, cobalt and chromium. The hypophosphorous H_3PO_2 , a powerful reducing agent, is a dehydrogenation catalyst and the source of phosphorus in the deposit.

By substituting dioxane ($\text{C}_4\text{H}_8\text{O}_2$) for water in a electroless plating solution, Gutzeit proved that water is required. The rate of deposition decreases with increasing replacement of water by dioxane until a 35% volume of dioxane causes complete stop of reduction.

Ammonium sulphate and ammonia solutions are used as buffer agents to maintain the pH of a solution in the desired range and to keep it constant during continuous operation. Sometimes, the buffer agent also acts as a complexing agent to keep metal ions in solution. The plating rate is greatly increased by ammonium salts and excess ammonia. Therefore, the regular addition to ammonia to the bath is the principal element of solution control.

Sodium citrate is used as a complexing agent to prevent metal hydroxides from precipitating out of the plating solution and to control the rate of deposition and the appearance of the deposit. This means that the complexing agent keeps metal ions in solution. Salts of organic acids are always used as the complexing agent. At a given pH, the effectiveness of a reducing agent depends on the state of the metal ion. An increase of the

concentration of the metal ion increases the effectiveness of a reducing agent.

In certain cases the complexing agent acts as a buffer agent to prevent rapid decrease in pH.

Additives may be included to serve as the exaltant, stabilizer, and wetting agent. The exaltant increases the rate of deposition by activating the hypophosphite ion. The stabilizer prevents solution random decomposition by masking active nuclei which might form in the plating solution. The wetting agent promotes wetting of parts to be plated.

3.1.4. Deposition Rate

The plating rates obtained are usually in the region of 8 Å/sec. The rate of electroless deposition is affected by temperature, hypophosphite concentration, initial pH, and the organic complexing agent.

Temperature

The plating rate about doubles for each 10°C rise of temperature in the temperature range from 70°C to 100°C. However, high temperature increases the tendency towards spontaneous decomposition. In general, an electroless plating solution is operated at 87°C or more. It is very important to keep the temperature variation within $\pm 1^\circ\text{C}$. The variation of temperature will change the phosphorus content. If the temperature varies too much during electroless deposition, a lamellar deposit will form which may subsequently come off in layers.

Hypophosphite Concentration

The plating rate increases proportionally with an increase in hypophosphite concentration. However, the plating rate is almost independent of nickel concentration. Stabilizing agents are needed to prevent spontaneous decomposition at high hypophosphite concentration. Krieg¹ said, "Moderate gassing indicates that more hypophosphite should be added. Violent gassing indicates excess hypophosphite and should be avoided."

pH

The rate of electroless deposition and of gaseous hydrogen evolution is a function of pH. Plating rate increases with increasing pH. Increasing pH causes decreasing solubility of nickel phosphite which may cause spontaneous decomposition. The buffer agent works best at pH values below 5. Saubestre⁶ noted that, "the greater the rate of deposition at any given pH, the greater the effect of pH on that rate. Thus, a bath operating at a rate of 1.2 mil/hr. at pH=5.0 will plate at a rate of 0.5 mil/hr. at a pH of 4." Decreasing pH values cause an increase in the phosphorus content of the deposit. The evaporation of ammonia and the formation of hydrogen ions due to poor buffering characteristics of the organic acids used in the bath cause the pH values to drop rapidly. One of the difficulties encountered with electroless deposition is that the rate of deposition is initially high in a fresh bath but rapidly drops off during the continued operation of the bath.

Organic Complexing Agent

The choice of an organic complexing agent is one of the most important factors affecting plating rate. Sodium citrate provides a high rate of electroless deposition by acting as a complexing agent to prevent precipitation of basis metal salts and by acting as a buffer agent to prevent the rapid drop in pH. In the control of the deposition rate concentration of the salt of the organic acid is important. Saubestre⁶ said, "the plating rate increases sharply with increase in concentration of complexing agent, up to certain concentration, and then generally decreases equally sharply with further increase in concentration, until the initial plating rate is obtained. It is noted that brightness of deposit is generally at a maximum when the deposition rate goes through a maximum."

3.2. Principles of Preplating Treatments for Ceramic Substrates

Purpose of Etching Solution

The chemical bonds between ceramic substrates and electroless deposits are fairly weak. Therefore, good bonding depends partly on chemical etching. Good electroless deposition occurs from an aqueous solution but without chemical etching the surfaces of the ceramic substrates show water-break. This means that the surfaces of the ceramic substrates are hydrophobic and do not completely wet with water. In order to obtain hydrophilic surfaces that show no water-break, a suitable etching step is adopted. In the absence of such a treatment, the bonding to subsequent electroless deposits will be very poor. The type of etchant employed will be determined by the substrate. It was noted that the success on plating ceramics depends on the

choice of a suitable etchant.

Etching is a room temperature treatment. The time required for the immersion may range from 1-30 min. depending on the nature of the ceramic surface and the time required for the surface to become hydrophilic.

Purpose of Sensitizing Solution (Stannous Chloride Solution)

After obtaining clean hydrophilic surfaces by chemical etching the next step is to sensitize these surfaces prior to deposition of a catalytic film. The sensitizer must be a material that is readily oxidized since it is this oxidation which serves to deposit the catalytic film. Stannous chloride (SnCl_2) has the property of being readily absorbed upon ceramic substrates and also a strong reducing agent. Therefore, stannous chloride will serve as a sensitizer with a supporting medium hydrochloric acid, (HCl). In addition, the sensitizing solution is itself a fair cleaning solution too.

Saubestre⁶ said, "the composition and concentration of the stannous chloride solution do not appear to be especially critical. It is extremely important, however, that the work be rinsed thoroughly after sensitizing, lest the excess sensitizer on the surface cause reduction of the catalyst in non-adherent form on the surface of the work, leading to poorly adherent deposits subsequently. Intricately shaped parts may require agitation of the solution for best results. It is necessary to maintain the tin in the stannous state (Sn^{+2}), since the purpose of the sensitizing step is to absorb a readily oxidized material, and stannic ion (Sn^{+4}) cannot be oxidized. Normally, this is not a great problem but, if the sensitizer solution is to be used over a long period of time, it is desirable to immerse a stick of tin in the bath."

Sensitizing is also carried out at room temperature with

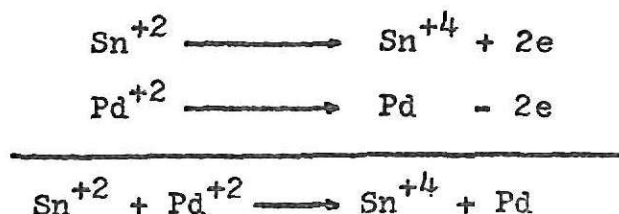
the immersed time ranging from 15 sec. to 3 min.

If the procedure is to go directly from the etching step into the activator, and skip the sensitizer step, it will narrow the permissible pH. Saubestre⁶ said, "this is not good practice, because it entails the work entering the electroless plating solution without a catalytic metal on the surface. Rather, a salt of the catalytic metal is present which, while capable of being reduced to the metallic state, may nonetheless diffuse away from the work, and become a catalytic center for decomposition of the electroless plating solution."

Purpose of Activating Solution (Palladium Chloride Solution)

If the activator step is omitted from the sequence between the sensitizing step and the plating step, it will lead to spotty coverage, or erratic adhesion. Therefore, it is advisable to use an activator solution after the sensitizer.

The activating solution will produce a thin film of palladium (Pd) upon ceramic substrates, thereby rendering the surface active for the reduction of nickel, cobalt and chromium from the electroless plating bath. After the sensitizing treatment, the SnCl_2 is readily oxidized. Thus when ceramic substrate is immersed into a PdCl_2 solution, palladium metal is promptly plated out on the surface.



The films formed by exposing of ceramic substrates in the PdCl_2 solutions are invisible. The presence of an activating film is ascertained by its ability to initiate nickel-cobalt-

chromium-phosphorus alloy deposition from the electroless plating solution. This film acts as a catalytic surface for localizing further plating. The effectiveness of the treatment is determined by the estimated percentage of the area which is found to have been coated with nickel alloy.

Again this is a room temperature treatment. However, if the palladium chloride solution is heated, the electroless plating is more rapid and more complete coverage is obtained.

It is essential that the work be rinsed thoroughly after activating. If the ceramic substrates are placed in the electroless plating solution without rinsing, most of the area is soon found to be coated with nickel alloy. Apparently, the reducing environment of the electroless plating solution causes reduction of the palladium chloride solution adhering to the ceramic substrates. This method rarely produces complete coverage of nickel alloy and excess palladium chloride solution entering the electroless plating solution results in its premature decomposition.

3.3. Four Kinds of Solutions for Electroless Deposition

Etching Solution (500 c.c.)

1. Add 278.62 c.c. of distilled water slowly to 121.38 c.c. of 0.58 ammonia solution (NH_4OH).
2. Add 100 c.c. of 48% W/W hydrofluoric acid (HF) slowly to above solution.
3. Store in clean, tightly capped polyethylene bottle.

4. Ceramics may be also treated as follows:

CrO_3	6.5 oz/gal.
H_2SO_4	10% (Vol.)
HF (48%)	10% (Vol.)

5. CAUTION

Bear in mind that these etchants are handtailored. The onset of hydrofluoric acid (HF) to skin is so slow and its duration is so long that it can cause severe burns. It is too late to do anything about the presence of HF on the skin to go unnoticed for a period of time. HF poses not only a potential hazard to the skin of the human being but also attacks many different equipment. In practice, HF should be used only in a special polyvinyl chloride (PVC) hood, with adequate protection for the hands and eyes.

Sensitizing Solution (500 c.c.)

1. Put 0.5 g stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 500 c.c. distilled water and heat it until dissolved.

2. Add 5 c.c. of concentrated hydrochloric acid (HCl) to above solution.

Activating Solution (500 c.c.)

A. Make 1% 100 c.c. palladium chloride solution (PdCl_2).

1. Dissolve 1 g palladium (Pd) in 13 c.c. concentrated nitric acid (HNO_3 , 70%) and 39 c.c. concentrated hydrochloric acid (HCl).

2. Heat above solution and evaporate off excess acid until the author gets palladium chloride powder.

3. Dilute above palladium chloride powder with distilled water to 100 c.c. Then, the author gets 1% 100 c.c. palladium chloride solution.

4. Keep above solution in glass container with tight rubber stopper (to prevent evaporation) for further use.

B. Make 500 c.c. 0.01% palladium chloride solution.

5. Take 5 c.c. 1% palladium chloride solution and make up to 500 c.c. with distilled water.

Electroless Plating Solution (500 c.c.)

1. Weigh following chemicals accurately.

Nickel sulphate (hydrated)

$\text{NiSO}_4 + \text{aq.}$ 7.1875g

Cobaltous sulphate (hydrated)

$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ 5.312g

Chromic chloride (hydrated)

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 1.25g

Ammonium sulphate

$(\text{NH}_4)_2\text{SO}_4$ 21.25g

Sodium Citrate

$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ 45.00g

2. Make above mixture up to 500 c.c. with distilled water when required for use and heat it until dissolved completely.

It is no good if solution stored for more than a day or two.

3. Add 4 c.c. of hypophosphorous acid (H_3PO_2 , THE REDUCING AGENT) to above solution.

4. Adjust above solution to $\text{pH}=9.0\pm0.2$ units by adding sufficient ammonia solution and measure by pH meter. (The author needs roughly 58% 20 c.c. ammonia solution).

- a. With power off, meter pointer must balance at red line.
- b. Depress ZERO KEY (Rotate clockwise to lock) apply power.
- c. Plug in electrodes and immerse in standard buffer solution.
- d. Set temperature compensation switch at manual position.
- e. Set TEMPERATURE KNOB at temperature of buffer.
- f. Release ZERO KEY. Set STANDARDIZATION KNOB so meter reads pH of buffer.
- g. Rinse electrodes and immerse in solution to be measured.
- h. Set TEMPERATURE KNOB at temperature of solution and read pH.

3.4. Order of Making Solutions

- a. Make 1% 100 c.c. palladium chloride solution according to 3.3.1.A.

b. Do first two steps of the procedure of making electroless plating solution according to 3.3.4. Do not go into third step until electroless plating solution is needed.

c. Make etching solution according to 3.3.1.

d. Make sensitizing solution according to 3.3.2.

e. Make 0.01% 500 c.c. palladium chloride solution according to 3.3.3.B.

f. Make electroless plating solution having $\text{pH}=9.0 \pm 0.2$ units according to 3.3.4.

3.5. Procedure of Electroless Deposition

1. Put two 1 x 1 inch ceramic substrates on one holder.
2. Wash both sides of the substrates with distilled water.
3. Etch substrate in the etchant for 1 minute.
4. Wash with distilled water until clean.
5. Keep under water till ready for use.
6. Take etched plates from distilled water and immerse in the stannous chloride solution for 15 seconds. Continuously agitating the plate during this process.

7. Remove from solution and wash thoroughly with distilled water.

8. Immerse in previously prepared palladium chloride solution (SnCl_2) for 10 seconds, agitating during this time.

9. Remove from solution and wash thoroughly with distilled water.

10. Plates now activated and ready for plating. Should be kept under water until needed.

11. Immerse the plating solution in a glass receptacle in a constant temperature bath (or frying pan with double thermal controlled) heated to give roughly 87°C or more in the plating bath. Allow appropriate time for solution to heat.

12. Immerse the activated plates in the plating solution. Coat for a predetermined time, 15 sec., 30 sec., 45 sec., and 60 sec., respectively. The greater uniformity is given when the plates are held horizontally in the coating solution. With the given solution the rates are usually in the region of $8 \text{ \AA}/\text{sec}$.

13. Remove plate from solution and dip in distilled water.

14. Wash with distilled water follow by distilled acetone and dry in air.

CHAPTER IV

RESULTS AND CONCLUSIONS

The method of plating ceramic substrates involves etching, sensitizing and activating, so as to produce a catalytic palladium film on the surface. On these relatively rough and catalytic ceramic surfaces the electroless deposition takes place from nuclei and grows satisfactory stable nickel alloy films. This process is the most economical, requiring the smallest outlay in capital equipment of any of the thin film processes.

The reasons for performing the experiment in the pH range mainly from 8 to 10 are as follows: 1. Cobalt behaves as a auto-catalyst only in an alkaline bath. 2. Alkaline bath with a higher value of pH reduces phosphorus content of the deposits. 3. Critical control of the alkaline solution is not absolutely essential.

A limited amount of data was obtained because of limited equipment and time available. The values of sheet resistances, obtained by dipping ceramic substrates in an electroless plating solution with a temperature variation from 80°C to 83°C for 30 seconds, were as follows: 54, 58, 84, 90, 108 and 124 ohms/square; thus giving average sheet resistance of 86.3 ohms/square.

By changing the dipping time to 60 seconds with the same plating solution, sheet resistances of 23.4, 26.4, 27, 28, 28, 30, 32, and 42 were obtained for different substrates, giving

average sheet resistance of 29.6 ohms/square.

The differences in the values of sheet resistances may be explained by the decreased hypophosphite concentration, varying pH values of the plating solution and temperature variation.

The sheet resistance increased only slightly even after heating the plated ceramic substrate up to 150°C.

Vacuum evaporation is by far the most widely used. However, Kirby⁵ said, "...vacuum techniques are always likely to compare unfavourably with an alternative system which has been developed. This involves electroless deposition of nickel alloys in a wet chemical process allowing resistive films of low temperature coefficient and high stability to be produced over a wide range of values." Electroless deposition provides the convenience of rapid or continuous plating without expensive apparatus. A range of sheet resistances from 1 ohm/square to 1000 ohms/square having film thicknesses less than 100 Å can be obtained. Kirby⁵ noted that "The ability to avoid the use of high polished glass with its attendant hazards, such as poor adhesion, liability to scratch, poor thermal conductivity and only moderate mechanical strength, are further advantages in favour of the electroless thin film process."

One feature of future work will be to make practical metal film resistors by electroless deposition and then use the stencil screen method of pattern production. With the stencil screen method impressions are made through the gaps in a stencil. The stencil is supported on a stainless steel screen mesh and viscous ink is forced through the screen mesh by a flat rubber squeegee. When the screen is placed in intimate contact with the ceramic substrate this method is then called in-contact masking. This

method produces modest accuracy at very low cost and has the basic requirements for film circuit pattern production for electroless deposited films.

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INVESTIGATION OF ELECTROLESS DEPOSITION
FOR THIN FILMS IN INTEGRATED CIRCUITS

by

BEN-HUANG LIN

Diploma, Taipei Institute of Technology, 1960

AN ABSTRACT OF A MASTER'S REPORT

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Department of Electrical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

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ABSTRACT

This investigation is an attempt to gather all the known useful information about electroless deposition for thin films in integrated circuits together under this report. This information should be of particular value to those who are not yet acquainted with this process and its advantages.

The equipment and the operation of electroless deposition is simple and relatively inexpensive. It is good for low capital outlay and teaching purpose. It also cuts down the price of the components. It has high commercial potential.

In the electroless deposition of thin metal films, a metal ion in solution is reduced to the free metal and deposited as a metallic coating without the use of an electric current. The author has deposited nickel-cobalt-chromium-phosphorus alloy on ceramic substrates. This involves reduction of a metal ion by the simultaneous oxidation of a chemical reducing agent using hypophosphite ions, H_2PO_2^- . Plating is initiated by the use of catalysts which limit the plating reaction to preferred surfaces only. The procedures for etching, sensitizing, activating, and plating the surfaces of the substrates are considered. The principle of each process is discussed.