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Feldstein et al.

[11] **3,753,816**

[45] **Aug. 21, 1973**

[54] **METHOD OF REPAIRING OR DEPOSITING A PATTERN OF METAL PLATED AREAS ON AN INSULATING SUBSTRATE**

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[52] **U.S. Cl.** **156/11,** 156/3, 29/401, 96/36.2

[51] **Int. Cl.** **C23f 1/02,** C23f 17/00

[58] **Field of Search** 156/3, 11, 24; 29/401; 96/36.2

[56] **References Cited**

UNITED STATES PATENTS

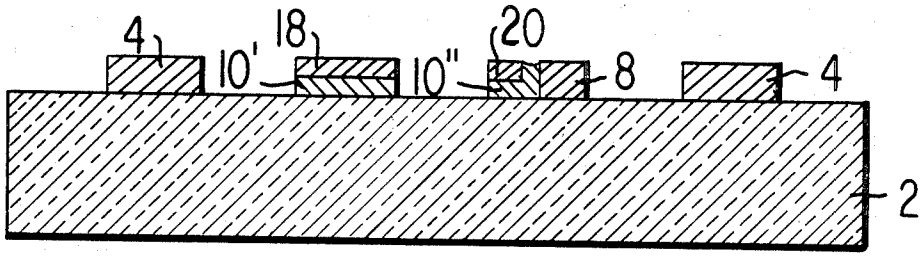
3,607,679	9/1971	Melroy et al.	204/15
3,642,476	2/1972	Mesley	96/24

Primary Examiner—Jacob H. Steinberg
Attorney—Glenn H. Bruestle

[57] **ABSTRACT**

The method comprises depositing a thin layer of a first metal having a relatively high degree of solubility in a particular etchant over both plated areas (if a previously deposited pattern is being repaired) and unplated areas on a substrate, this first metal being catalytic to electroless deposition of a second metal to be subsequently deposited, electrolessly depositing on the first metal either an overall pattern of areas of a second metal which has a relatively low degree of solubility in the etchant or a pattern limited to parts of a previously deposited pattern that were missing or incompletely formed, and then treating the plated areas with the etchant, where desired, so that the first metal is removed where it is not covered by the second metal but the second metal is substantially unaffected.

4 Claims, 11 Drawing Figures



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SHEET 1 OF 2

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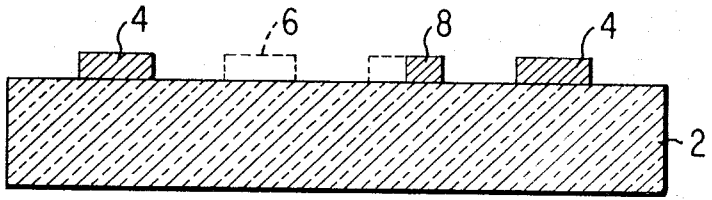


Fig. 1

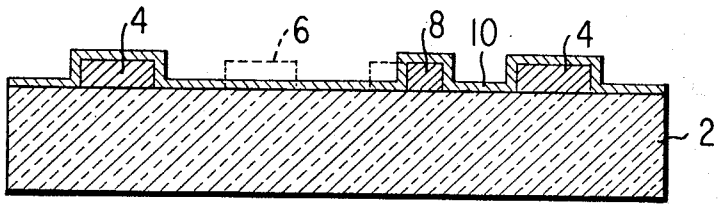


Fig. 2

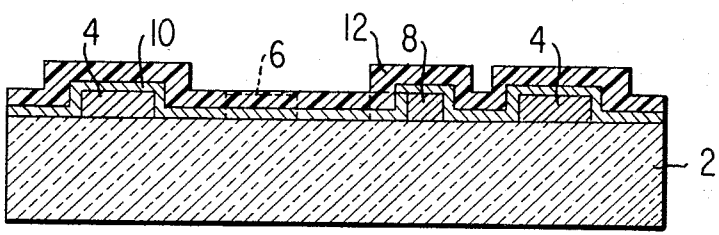


Fig. 3

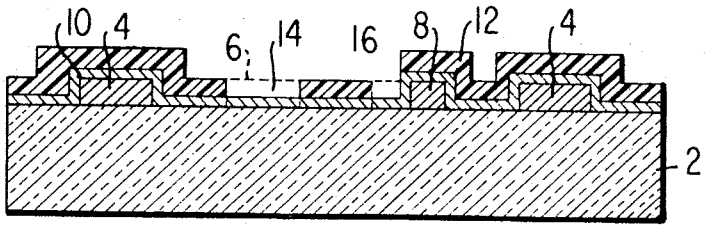


Fig. 4

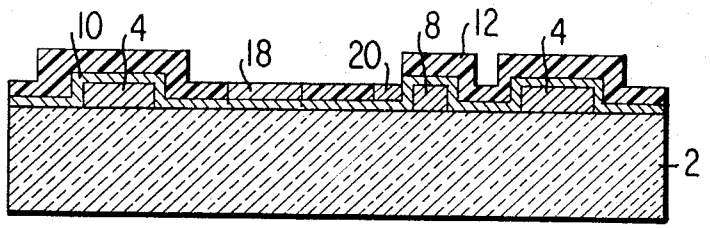


Fig. 5

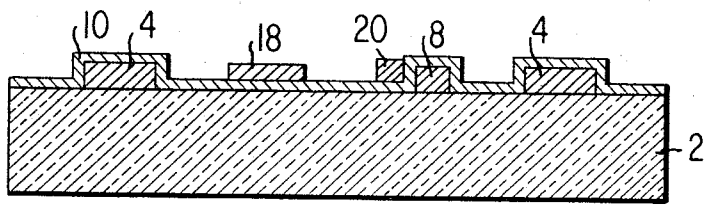


Fig. 6

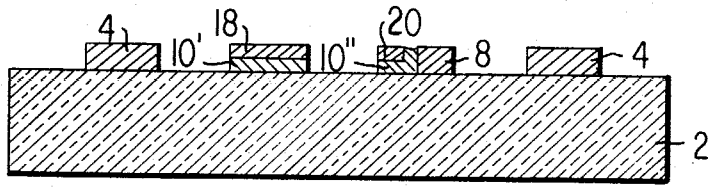


Fig. 7

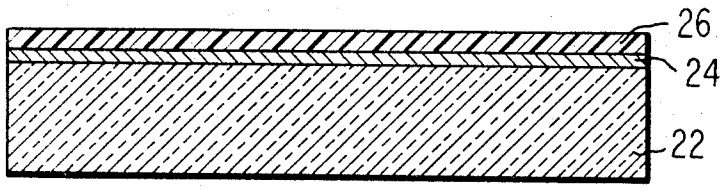


Fig. 8

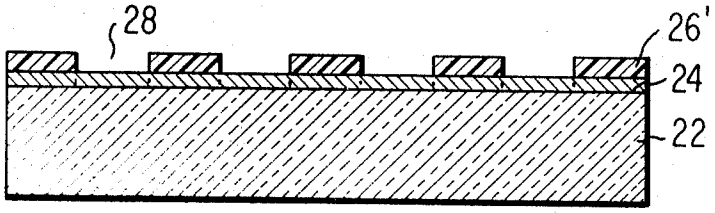


Fig. 9

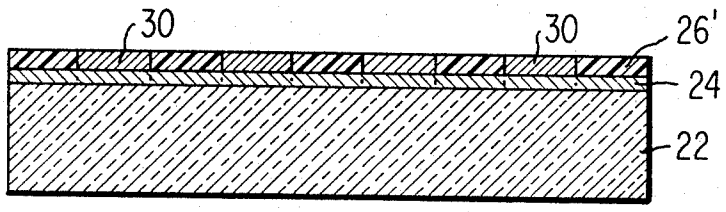


Fig. 10

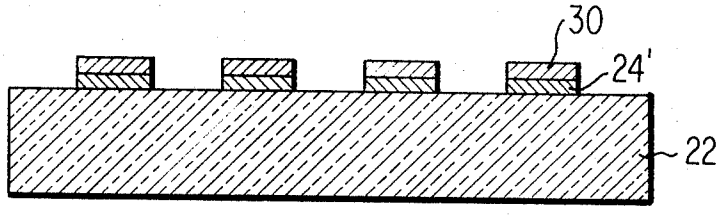


Fig. 11

METHOD OF REPAIRING OR DEPOSITING A PATTERN OF METAL PLATED AREAS ON AN INSULATING SUBSTRATE

BACKGROUND

There are numerous industrial applications which require forming a pattern of metal plated areas on an insulating substrate. One such application is printed circuits. Another application is making metal photomasks. Photomasks may be used in many different manufacturing operations such as the fabrication of the shadow mask used in a color TV picture tube.

Most electronics industry applications require that photomasks be capable of high resolution, be 100 percent complete with no parts missing, and have good wearing qualities. In the past, most photomasks in the electronics industry have been made from photographic emulsions. But, for some applications in the industry, especially those involving contact printing, it was found that this type of photomask did not have sufficient abrasion resistance. This was the case, for example, with photomasks used in manufacturing TV picture tube shadow masks.

It was also known that masks can be made from evaporated or sputtered chromium and that these have a harder surface than photographic emulsions. But evaporated or sputtered chromium masks were not found suitable for making picture tube shadow masks. Large size picture tubes have correspondingly large size shadow masks and evaporation and sputtering equipment for making this size metal mask is expensive. Furthermore, because of the large area, evaporated coatings tend to be nonuniform in thickness. It was also found that if chromium masks were made thick enough to compensate for nonuniformity, the chromium became much less resistant to abrasion.

It was found that improved photomasks could be made by electroless deposition of nickel alloy on glass substrates. It was found that this type of mask could be made with satisfactory resolution, good uniformity, with good adherence to substrate and good abrasion resistance. In fact, it was found that thicker layers of nickel had higher abrasion resistance than thinner layers. However, in making photomasks with hundreds of thousands of metal dots by electroless deposition of nickel, it was found that it was almost impossible to make a mask which did not have at least a few missing dots and/or some dots incompletely formed. The missing dots and the malformed dots could not be tolerated because, wherever a metal dot was missing or malformed on the mask, a corresponding imperfection appeared on the cathode ray tube viewing screen, and even small imperfections are visible to the viewer. There was need for a simple, reliable way to repair the metal photomasks in order for the masks to be successfully used in manufacturing.

Also, in making the original dot pattern, it was found that there was still room for a method which would provide better resolution along with good adherence and strain-free coating when the metal layer was relatively thick. Also there was need for a method which would produce screens with fewer missing dots. In methods which require etching of a relatively thick metal coating, the photoresist often has pinholes through which etching fluid penetrates and removes metal from areas where it is supposed to remain.

Past methods of making metal photomasks by electroless deposition of nickel have been based on depositing an overall layer of nickel having the final thickness desired, on a glass substrate and by a conventional photoresist exposing and developing process, followed by etching away unwanted metal, arriving at the final pattern desired. Since the coating of metal must be thick enough to be opaque to light, i.e., at least about 1,500 A, some lateral etching occurs in addition to the vertical etching desired. Although the amount of lateral etching can be tolerated in making photomasks for shadow mask manufacture, better resolution is desirable. This appears to be possible only by using an additive process of metal deposition rather than a subtractive one. However, past attempts to devise an additive process comprising first sensitizing and activating the substrate for autocatalytic electroless deposition of metal, then coating with a conventional photoresist, exposing and developing the photoresist to provide a pattern of openings where metal is to be deposited and then electrolessly depositing metal in these openings, have been unsuccessful. Lack of success is due to the fact that the photoresist and the processing to which it is normally subjected in development poison the palladium activator film (or any other monolayer activator film) deposited on the substrate thus preventing metal from being deposited autocatalytically. This is particularly critical when fine line resolution is involved.

The present invention is an additive process which solves the problem of catalyst poisoning previously encountered.

SUMMARY OF THE INVENTION

The invention can be used either as a method of repairing a pattern of previously deposited metal plated areas on an insulating substrate in which some missing metal is to be replaced, or it can be used as a method of depositing an entire pattern of metal plated areas on an insulating substrate. In either case, the basic steps of the method are the same. They comprise depositing, for example, by electroless deposition, a relatively thin layer of a first metal having a relatively high degree of solubility in a particular etchant over both plated areas (if any) and unplated areas on the substrate, the first metal being catalytic to electroless deposition of a second metal to be subsequently deposited, applying a layer of photoresist on top of the first metal layer and exposing and developing the photoresist to remove portions thereof only where additional metal is to be deposited. The method also includes electrolessly depositing on those metal portions not covered with resist a relatively thick layer of a second metal which has a relatively low degree of solubility in the particular etchant, removing all remaining portions of the photoresist, and treating the pattern with the etchant so that the first metal is removed where it is not covered by the second metal, and the second metal is not removed.

THE DRAWINGS

FIGS. 1–7 are cross-section views illustrating successive stages in repair of a metal photomask in accordance with the method of the present invention, and

FIGS. 8–11 are similar cross-section views illustrating the successive steps in making a metal photomask in accordance with the method of the invention.

First, the method will be explained as applied to repairing a metal photomask which may have been made

by either the present method or some other method. The mask (FIG. 1) may comprise a glass substrate 2 which is 2 ft. by 3 ft. in area, on one surface of which is a pattern of more than 300,000 nickel dots 4 nearly all of which are assumed to be perfect. The dots in this type of mask usually range in diameter from 9 to 14 mils. The term "dot" is meant to include shapes other than round, for example, elongated and the term "diameter" would refer to the smallest dimension of the dot.

The photomask has one or more completely missing dots 6 (indicated in dotted outline) and may also have one or more dots 8 incompletely formed. In the drawing the missing portion of the dot 8 is indicated in dotted outline.

In order to make the mask commercially usable, the missing dots must be deposited and the incomplete dots must be restored to full dimensions. This must, of course, be done with great accuracy and without disturbing the perfect portion of the pattern.

The pattern of metal dots 4 originally laid down is made of a metal composition which is relatively resistant to the action of a particular etchant. In this example, the dots are composed of a nickel-phosphorous alloy deposited by an electroless process.

The complete process (not a part of the present invention) includes sensitizing and activating the surface to be plated prior to depositing the metal. Sensitization is carried out by dipping the cleaned glass plate in a solution of $SnCl_2.2H_2O$, HCl and water. The sensitizing solution may be made by first making a concentrate consisting of 214 gms. $SnCl_2.2H_2O$ and 290 cc. Conc. (37%) HCl. The actual sensitizing solution comprises 50 cc. of the concentrate diluted to one liter with water. Immersion of the glass plate in the sensitizing solution for one or two minutes is sufficient. After the sensitization step, the plate is rinsed thoroughly with warm water.

The sensitized surface is next activated with a solution of palladium chloride. The activating solution consists of 1 gram per liter of palladium chloride and 1 cc. per liter of concentrated hydrochloric acid. The remainder of the solution is water. The plate is again rinsed with water after treatment with the activating solution for a brief period.

The activated surface is now plated with nickel by an electroless process. A stock plating bath is made up by dissolving 154 grams of $NiCO_3$ and 252 grams of sulfamic acid in sufficient water to make a liter of solution. This is a concentrate from which portions can be taken to make a working bath. The preferred working bath is made by taking 200 cc. of the concentrate and 25 grams of $NaH_2PO_2.H_2O$ and diluting to one liter with water. Thus, the preferred working bath consists essentially of about 31 grams $NiCO_3$, about 51 grams sulfamic acid and 25 grams $NaH_2PO_2.H_2O$ per liter. The bath is maintained at a pH of 4 to 5 and a temperature of about 50° to 70° C., preferably 60° C.

The sensitized and activated plate is immersed in this solution to provide a nickel-phosphorus plating about 1,500 A to 4,000 A in thickness. At 70° C., the plating will contain about 11% by weight phosphorus which is co-deposited with the nickel.

After the above deposition is completed, the plate is removed from the bath and thoroughly rinsed and then dried in warm air.

To improve the adhesion of the metal layer to the substrate so that it can be easily further processed, the dried plate is mildly baked at a temperature of about 100° – 250° C. At a temperature of 250° C., baking time is preferably about 1 hour. If the baking is carried out at an appreciably higher temperature than 250° C., later etching away of unwanted metal is very difficult. If a lower temperature is used, baking time is longer and may be as long as several hours or more at 100° C.

Next, an overall coating of photoresist is applied to the nickel surface. This may be a positive type photoresist such as Shipley AZ–1350 or AZ–111. Alternatively, other negative or positive resists may be used along with the necessary artwork. The photoresist is developed in a conventional manner to provide a pattern of photoresist dots. The uncovered nickel-phosphorus surface is then etched in 30 to 50 percent (by volume) concentrated nitric acid until the nickel-phosphorus is removed from all areas not covered by the photoresist. The remaining photoresist is then removed with a solvent such as isopropyl alcohol or acetone, which exposes the pattern of nickel-phosphorus dots on the glass substrate. The nickel-phosphorus surface is hardened by baking in air at about 380° C. for about one-half hour.

In the above example, the entire thickness of nickel is deposited in a single plating step. The nickel may also be deposited in two steps or more, if desired. In this case, if a two-step plating process is used, all of the preliminary operation steps are carried out as described above up to the immersion in the electroless plating bath. Then an electroless plating step is carried out for about 5 minutes at pH4 and 60° C., for example, so that about one-third the ultimate thickness of nickel desired is deposited.

The plate is then removed from the bath and rinsed with water after which it is dried and baked in air at about 250° C. for 1 hour.

Then the preplating steps are repeated, preferably including cleaning, sensitization and activation, after which the plate is again immersed in the same nickel plating bath. This time the plating is permitted to continue for about 10 to 15 minutes. After the second nickel-phosphorus deposition step, the plate is again removed from the bath, rinsed, and baked at about 250° C. for 1 hour.

As in the previous example, the nickel-phosphorus surface is coated with a positive photoresist, rinsed, the resist is developed, and the plate is etched with concentrated (30 – 50 percent by volume) nitric acid. After etching is completed and the photoresist is removed, the plate receives a final baking at about 380° C. for 1 hour.

The nickel-phosphorus alloy dots formed as above described are relatively resistant to the etching action of dilute hydrochloric acid.

The repair process is carried out as will now be described. The repair can either be done by treating the entire surface or the treating can be confined to a limited area. First, a thin layer of a nickel composition 10 (FIG. 2) which is relatively soluble in dilute hydrochloric acid, is deposited over the entire top surface (or the selected part) of the substrate 2 and over the nickel dots 4 and 8 of the metal pattern. This layer of nickel may have a thickness of about 100 A – 500 A, for example. An example of a nickel composition which is relatively soluble in dilute hydrochloric acid is a nickel-

boron alloy which is deposited electrolessly or nickel-phosphorus alloy with low phosphorus content.

Before depositing the nickel-boron alloy layer **10** the substrate surface is again sensitized and activated as described above. To deposit the metal layer the sensitized and activated substrate is dipped in a bath made up of:

$Na_4P_2O_7.10H_2O$	50 g./L
$NiSO_4.6H_2O$	25 g./L
NH_4OH (approx. 58% Conc.)	20 cc./L
$(CH_3)_2NH\ BH_3$	1.5 g./L

This bath operates at room temperature. When a nickel-boron layer about 100 – 500 A thick is deposited, the plate is removed from the bath and thoroughly rinsed, then dried. Plating takes about 30 – 45 seconds.

Applicants have found that the nickel-boron layer **10** should be less than about 500 A thick and preferably from about 100 – 500 A thick. If the layer is too thick its adherance is very poor and it peels away from the substrate. On the other hand it must be at least thick enough so that it is not impaired when it is subsequently covered with a photoresist and parts of the photoresist are removed by solvent action. The nickel-boron layer is so thin as to be highly electrically resistive. Therefore it is not possible to successfully electroplate an additional thickness of metal directly upon it.

Next a layer of photoresist **12** (FIG. **3**) is deposited over at least a part of the top surface which includes the parts to be repaired. Then (FIG. **4**) the photoresist layer **12** is exposed and developed to form openings **14** where dots are completely missing and other openings **16** where dots are partially missing. One way to carry out the above steps is to draw a circle around the area to be repaired with a water-repellent marking crayon. This area is then coated with a photoresist of type opposite that used when the dot pattern was originally deposited. That is, if a negative photoresist was used the first time, a positive resist is used the second time. The original master may be used to expose this second layer of photoresist. Openings are formed in the photoresist where metal is to be deposited. If the area being treated also includes some good dots (because of the difficulty of excluding them) openings will also be formed over them.

The next step in the process (FIG. **5**) is to build up nickel deposits in the openings **14** and **16** in the photoresist layer **12** where metal dots or parts of dots are missing. As previously indicated, if some good dots have also been inadvertently included in the repair area, metal will also be deposited on them. This metal deposition may be done by immersing in or dispensing into the assembly a bath comprising:

Ni^{++}(from concentrated nickel sulfamate)	2.0 g./L
The sulfamate concentration is twice the molar concentration of the nickel.	
$NaH_2PO_2.H_2O$	20 g./L
pH	about 5.0
Temperature	50°–90° C.

Plating usually starts within one minute. Usually there is no need to sensitize or activate the surface within the openings **14** and **16** since the previously deposited nickel-boron layer is autocatalytic to the deposition of nickel. If some activation is required it can be produced by briefly treating the surface with a 10 percent aqueous hydrochloric acid solution. Plating is continued until the combined thickness of the thin, underlying nickel layer **10** and of the newly deposited nickel-phosphorus layer is sufficient to be opaque to visible light. Thickness should be at least about 1,500 A. The newly deposited layer of nickel-phosphorus has a composition similar to that of the originally deposited dots and is similarly resistant to the etching action of a 15 percent hydrochloric acid solution. At this point a complete and substantially perfect dot pattern has been formed.

To complete the mask-repairing process (FIG. **6**), the remainder of the layer of photoresist **12** is removed with a suitable solvent. Then, (FIG. **7**) that part of nickel-boron layer **10** not shielded by newly deposited nickel-phosphorus, is removed by treating the entire surface with 15 percent aqueous hydrochloric acid solution just long enough to etch away the unshielded parts. This acid treatment has little or no effect on the nickel-phosphorus layers. This leaves the original dots **4** and new dots composed of part **10'** of nickel-boron layer **10** and an upper layer **18** of nickel-phosphorus. It also leaves repaired dots composed of originally deposited layer **8**, a part **10''** of nickel-boron layer **10** and a partial upper layer **20** of newly deposited nickel-phosphorus on top of the layer **10''**.

Using the method of the present invention as above described, it is possible to salvage most photomask plates with missing metal dots or incomplete dots and thus greatly reduce the cost of manufacture of this article.

The method of this invention can also be used to advantage in depositing the original pattern of dots in a metal photomask. Referring now to FIG. **8**, a glass substrate **22** which is to have a pattern of dots deposited on a surface thereof, has deposited on this surface a thin coating **24** of a metal having relatively low resistance to attack by an etchant such as 15 percent hydrochloric acid. As in the previous example, this can be about 100 – 500 A of nickel-boron deposited as previously described. A layer of photoresist **26** is deposited on top of nickel-boron layer **24**.

A pattern of openings **28** (FIG. **9**) corresponding to the desired pattern of metal dots is then formed by exposing and developing the photoresist layer. The remainder **26'** of the original photoresist layer **26** forms a lattice work matrix for the openings **28**.

Next (FIG. **10**) the openings **28** are filled in by electrolessly depositing a nickel-phosphorus layer from a sulfamate bath as in the previous example. This forms metal dots **30** on top of the nickel-boron layer **24**.

As shown in FIG. **11**, the remainder **26'** of the photoresist layer is dissolved. Then that part of the nickel boron layer **24** not shielded by nickel-phosphorus dots **30** is removed by etching the entire surface with **15** percent hydrochloric acid leaving a dot pattern in which each dot is composed of a thin bottom layer **24'** of nickel-boron and a top layer **30** of nickel-phosphorus.

One of the advantages of this method is that, first of all, the dots are mostly formed by building up metal rather than by etching. Only the lower very thin layer of metal **24** is removed by treating with an etchant. When etching is used to define dots or other elements in a relatively thick layer of metal, the dots tend to have sloping sides since etching occurs laterally as well as vertically.

Another advantage is that the thin bottom layer can be selected for good adherence properties and little regard for hardness. Only the top layer need be selected

for abrasion resistance. Also the method almost entirely eliminates the effect of pinholes usually present in layers of developed photoresist due to presence of unavoidable dirt particles.

The method can also be used to deposit metal patterns on insulating substrates other than glass. When plastics such as Mylar are used, the plating conditions are the same as given in the above examples. In using photoresists for masking purposes, however, it must be remembered to keep baking temperatures below that which would damage the plastic.

Combinations other than the nickel-boron first layer and nickel-phosphorus second layer, described above, can be used in the method of the invention. For example, the thin, low-etch resistant first layer may be a low-phosphorus content nickel-phosphorus alloy and the high-etch-resistant top layer may be made of a high-phosphorus content nickel-phosphorus alloy. The low-phosphorus layer may be made by electrolessly depositing nickel from a bath comprising:

$Na_4P_2O_7.10H_2O$	50 g./L
$NiSO_4.6H_2O$	25 g./L
NH_4OH (approx. 58% Conc.)	20 cc./L
$NaH_2PO_2.H_2O$	25 g./L

This bath operates at room temperature and provides a nickel-phosphorus alloy deposit having less than 5 percent phosphorus. The layer is rapidly etched by dilute hydrochloric acid solutions.

The high-phosphorus coated layer is deposited as described in the previous example.

Another example is a combination of a first layer made of a low-phosphorus content cobalt-boron alloy and a second layer made of a high-phosphorus content cobalt-phosphorus alloy. The low-phosphorus content layer can be electrolessly deposited using the following composition:

$Na_4P_2O_7.10H_2O$	70 g./L
$CoSO_4.7H_2O$	50 g./L
NH_4OH (approx. 58% Conc.)	7.5 cc./L
$CH_3NH\ BH_3$	1.5 g./L

The bath operates at room temperature.

The high-phosphorous content cobalt-phosphorus layer may be deposited from a composition like that immediately above except that 25 g./L of $NaH_2PO_2.H_2O$ is substituted for the methyl amine borane and the bath is operated at 65° C.

Another combination is a first layer composed of a low-phosphorus (less than 5 percent) nickel-phosphorus alloy and a second layer composed of a high-phosphorus (at least about 8 percent phosphorus) cobalt-phosphorus alloy.

Another example is to use a first layer of evaporated or sputtered nickel or cobalt. Such layers are relatively pure metal and are relatively soluble in dilute hydrochloric acid. High phosphorus content nickel or cobalt alloys can be used for the second layer as in the previous examples.

When a "relatively thin layer of a first metal" is referred to herein, it is meant to exclude the palladium activator layer which is actually so very thin as to be discontinuous. The palladium is present substantially as a monolayer not having a measurable thickness.

Etchants other than dilute hydrochloric acid can be used to remove the thin layer of first metal. It has been found, for example, that 3 percent (by volume) nitric acid can also be used with all of the metal combinations mentioned.

Although, in explaining that aspect of the present method which relates to the repair of metal patterns, as applied to metal dots which are either missing or incomplete, it sometimes happens that a defective dot (or other pattern unit) is larger than it should be. When such is the case, this type of defective unit should be removed completely and an entirely new unit formed.

We claim:

1. A method of repairing a repetitive pattern of metal plated areas on an insulating substrate in which some missing metal contiguous to said pattern is to be replaced, comprising:

depositing a relatively thin layer of a first metal having a relatively high degree of solubility in a particular etchant over both the plated areas and unplated areas on said substrate, said first metal being catalytic to electroless deposition of a second metal to be subsequently deposited,

applying a layer of photoresist on top of said first metal layer and exposing and developing said resist to remove portions thereof where additional metal is needed to repair missing portions of said pattern,

electrolessly depositing on said portions to be repaired a relatively thick layer of said second metal which has a relatively low degree of solubility in said particular etchant,

removing all remaining portions of said photoresist, and

treating said pattern with said etchant so that said first metal is removed where it is not covered by said second metal, and said second metal is not removed.

2. A method according to claim **1** in which said pattern consists of many thousands of dots each about 9–14 mils in diameter.

3. A method according to claim **1** in which said substrate is glass and said first and second metals are different nickel alloys.

4. A method according to claim **3** in which said etchant is dilute hydrochloric acid.

* * * * *