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ENHANCED INTERFACE ADHESION OF PATTERN PLATED COPPER IN PRINTED WIRING BOARDS

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Abstract
Trend in electronic packaging towards reduction in the dimension of conductive tracks in printed wiring boards continues, adhesion at the interface between the laminated copper and the electroplated copper becoming critical issues. In order to improve the adhesion at copper-to-copper interface, several chemical micro-etchant solutions are known to alter surface topography prior to pattern electroplating in the manufacturing of Printed Wiring board. In this paper ammonium peroxodisulphate and sulphuric acid compositions as micro-etchant was studied. Copper circuit patterns generated on glass epoxy copper laminate samples are treated in freshly prepared micro-etchant solution as well as cooled and stirred micro-etchant solution. It was observed from the experiments that sample processed in freshly prepared peroxodisulfate etchant, had random peeling of plated copper track from base copper and measured adhesion strength is very low, which is less than 0.72kg/cm. Sample processed in cooled, stirred etchant had higher peel strength of the tracks and measures more than 1.64kg/cm. This is attributed to the low exotherm of cooled and stirred etchant results in enhanced hydrophilicity of the micro-etched surface. This leads to the favorable interlocking of the copper grains at the interface during electrodeposition process. Interlocking of the grains results in the extension of base copper lattice with electroplated copper called "Epitaxial Growth" which is responsible for enhanced adhesion.

Keywords:
Ammonium Peroxodisulphate, Micro-Etchant, Grain, Peel Strength

1. INTRODUCTION

Miniaturized Surface Mount Devices (SMDs) are becoming predominant choice of components to accommodate more functions as well as to reduce the real estate. Typically, these components occupy about 80% of the printed wiring board area in the consumer products such as mobile, handy-cam etc [1]. Incorporation of these devices calls for smaller land patterns and finer features on the printed wiring board (PWBs), which provide necessary mechanical and electrical interconnections. As the SMD land pads and associated circuits are becoming finer, adhesion at the interface becomes critical in PWBs due to the low contact area. Therefore, two critical requirements for better integrity of these copper patterns are; adequate adhesion to the dielectric laminate and good interface adhesion between laminated base copper and electroplated copper. These fine circuits are realized in pattern plating process during the fabrication of PWBs.

In pattern plating process, initially photo-imagable resist is coated on glass epoxy copper clad laminate followed by circuit image transfer using ultraviolet light source. Image transferred panel is then developed in developer solution, to create copper circuits on the panel. These circuits are copper electroplated to achieve required copper thickness.

There are several surface treatment methods such as mechanical and chemical cleaning are explored in the literature to alter the topography of base copper for better adhesion [2], [3]. In case of mechanical cleaning process such as pumice spray, impingement of fine pumice particles increases surface area by creating deep peak and valleys. However, these types of mechanically modified surfaces are not suitable for the realization of fine features owing to their highly textured surface. In addition, the risk of embedding pumices particles within the copper, which can contaminate the electroplating solution also. Another mechanical cleaning process is treatment using silicon carbide brush, which removes thin copper layer tangentially, resulting in increased surface area. But due to aggressive nature of brushing operation, possibility exists for dimensional distortion of thin core laminate [4].

Chemical surface treatment method called "micro-etching" is becoming popular to meet the demands for fine line circuits [5], [6]. This method yields a suitable copper surface topography without dimensional distortion seen with mechanical process on thin core laminates. In micro-etching, copper surface is etched or oxidized only to a limited extent so as to leave intact the original pattern of the copper being etched. This chemical micro-etchant acts along the grain boundary of the etchable surface results in "zig-zag" texture and thereby surface topography of specimen gets modified in few-microns level. Several micro-etchant based chemical compositions are being used in the manufacturing of PWBs.

Chromic acid etchant was used initially in the printed circuit board industries, however due to the adverse environmental effect and carcinogenic nature, it is no longer being used. Commonly used micro-etchant in the fabrication of PWBs are ferric chloride, oxidiser based etchants like as peroxide and peroxodisulfate [7]. Due to the highly corrosive atmosphere generated by ferric chloride etchant and staining problem to the operator, usage of this class of etchant is limited only to prototype application.

Oxidative micro-etchant contains the combination of oxidizer such as hydrogen peroxide, ammonium or sodium persulphate and proton donor such sulphuric acids are quite common [8]. Generally oxidative process creates etched surface depth up to max 0.5 microns. Hydrogen peroxide-sulphuric acid compositions are well known formulation used in copper micro-etching process and are very clean to operate. Due to the auto decomposition reaction of this formulation there is a difficulty in controlling the stability [9].

In this study we have used a combination of ammonium peroxodisulfate and sulphuric acid as micro-etchant prior to pattern electroplating of copper circuits. It was observed from the experiments that copper pattern processed in freshly prepared micro-etchant has very low copper- to- copper adhesion after plating. Highly stirred and cooled peroxodisulfate etchant shows enhanced copper-to-copper interfacial adhesion. It has been inferred that the high exothermic nature of the freshly prepared ammonium peroxodisulfate etchant, results in generation of gas bubbles, which gets physically adsorbed on the surface of the base copper circuit pattern. This adsorbed bubble stops the action of micro-etchant results in improper surface treatment and the plated copper deposited on such surface has very low adhesion. Surface treated with highly stirred, cooled micro-etchant is chemically low exotherm, leading to better surface treatment. A properly micro-etched surface promotes better interlocking of the grain at the interface during electroplating process resulting virtually in the extension of base copper lattice called epitaxial growth.

2. EXPERIMENTAL: MATERIALS AND METHODS

2.1 PRE-TREATMENT AND PHOTOLITHOGRAPHY PROCESS

In this study, single side PWB was fabricated using glass epoxy copper clad laminate (Source: Park Nelco, 4000-13EP, Tg 210°C, thickness 2.2±0.05mm, base copper thickness 35 microns) as per standard subtractive fabrication process. Initially glass epoxy copper clad laminate was degreased in ultrasonic tank containing 1,1,2 trichloroethylene for three minutes and dried. Dried laminate was then mechanically scrubbed in automatic conveyorised machine augmented with 320 grit silicon carbide brushes. It was then dried in air-circulated oven at 80°C for 10 minutes and cooled. Photolithography technique was used to transfer the circuit image. Dry film photoresist (Source: Dupont, Thickness 37µ) was coated on the epoxy substrate using hot roller lamination technique (Lamination temperature: 110°C, Lamination speed: 3inch/min). Using contact standard photolithography technique (λ = 365nm exposure time = 5sec, Energy 40millijoules/cm) image of copper test pattern coupon were transferred on glass epoxy laminate followed by development in 1% sodium carbonate solution maintained 32°C. Panel was then cut into three specimens and each containing one set of test coupons with each coupon having twelve numbers of 3 mm width copper patterns. One end of the copper patterns in two samples is masked with polyimide film (In this study we have used 3M make). Another sample was not masked with polyimide tape. The Fig.1 is the optical photograph of copper test pattern.

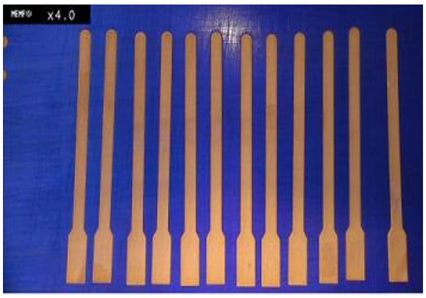


Fig.1. Optical photograph of copper test pattern

2.2 SURFACE PRE-TREATMENT METHODS

We have used two types of chemical micro-etchant solutions for the surface treatment. Chemical compositions and parameters of micro etching process as per Table.1.

Table.1. Chemical Compositions and Process Parameters

Etchant description	Chemical compositions	Operating parameters
Freshly prepared etchant	$(NH_4)_2 S_2O_8$:1.5M H_2SO_4:10% V/V	Temperature: 45°C Immersion time: 3 minutes with gentle shaking
Highly stirred and cooled etchant	$(NH_4)_2 S_2O_8$:1.5M H_2SO_4:10% V/V	Temperature: 25°C Immersion time: 3 minutes with gentle shaking

One of the specimens was dipped in freshly prepared micro-etchant solution for 3 minutes with gentle shaking. (Source: Merck Brand chemicals Emplura Grade). Temperature of the freshly prepared etchant was 45°C. Second specimen was immersed in highly stirred and cooled micro-etchant for 3 minutes with gentle shaking. All the micro etched samples were washed in water and finally dipped in 10%V/V sulphuric acid solution for two minutes and washed with water and dried. Surface of the micro-etched samples were recorded using Optical microscope (Leica, DFC290). Contact angle measurement was carried out using goniometer on micro-etched and un-treated surface to study the wettability prior to electroplating process. In brief, 10 micro litre of triple distilled water was dropped on each sample and was allowed to adhere on the surface for ten seconds. Digital image of the droplet was recorder after 10 second. Using contact angle J software measurement, interface angle between water droplet and copper surface was measured. Polyimide mask from each sample was then removed.

2.3 ELECTROPLATING OF MICRO-ETCHED SURFACE AND REALISATION OF COPPER TEST PATTERN.

All the micro-etched specimens are then subjected to copper electroplating followed by tin electroplating process. In this study direct current assisted electroplating method was used to deposit copper over the copper pattern up to 35 microns thickness (Source: MacDermid electroplating chemistry, bath compositions and process parameters as per technical data sheet). Tin electroplating (Source: Enthone Solderex TB Tin plating Chemistry, Bath compositions and process parameters as per technical data sheet) was used as etch resist coating.

Dry film photoresist from each specimen was removed using amine based stripper solution and washed thoroughly and dried. All specimens are etched in standard ammonia based etchant and finally protective tin coatings were stripped in nitrate stripper (Source: Artek surfin Chemistry).

In order to measure the interface adhesion strength of electroplated copper with the base copper and base copper to epoxy laminate quantitatively, mechanical peel strength test was conducted for all generated copper patterns on each specimen as per IPC-TM-650.2.6.8. (Institute for Interconnecting and Electronics Packaging Circuits) In peel strength test one end of the copper patterns was peeled manually about 10mm and was then clamped in the jaws of Chatillon TCD-200 tensile equipment and pulled at the constant rate of 0.5mm/minute. Pull out of plated copper from the base copper is the failure criteria for copper-to-copper interface adhesion.

In order to study the adhesion integrity at the interface between electroplated copper and the base copper, optical microscope [Leica] and SEM [Carl ZEISS EV050] pictures were recorded for each of the specimens

3. RESULTS AND DISCUSSIONS

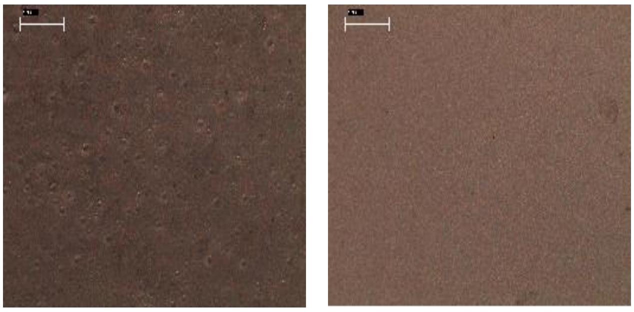
The Table.2 compares the mechanical peel strength at the interface between base copper to epoxy laminate and base copper to electroplated copper after micro etching using two types of micro-etchant.

It is observed that base copper to electroplated copper interface formed using stirred, cooled etchant had peel strength (1.64kg/cm) twice more than that of the interface formed with freshly prepared micro-etchant (0.72kg/cm). This indicates that surface treatments play a key role in improving the interface adhesion at base copper to electroplated copper.

Table.2. Comparison of the Interface Adhesion in kg/cm [Average Value of Ten Readings]

Interface description	Peel strength
Epoxy to base copper	1.64
Base copper to copper (freshly prepared etchant)	0.72
Base copper to copper (stirred and cooled etchant)	More than 1.64

The Fig.2 are the optical photographs of micro-etched copper surface using freshly prepared micro-etchant, stirred and cooled etchant. It clearly shows the presence of shiny dots over the entire surface obtained with freshly prepared micro-etchant. The surface etched using stirred and cooled etchant has uniform pink color without any shiny dots and has matte finish.



(a) (b)

Fig.2. Optical photographs of micro- etched copper surface using (a) freshly prepared micro-etchant (b) stirred and cooled micro-etchant

Epoxy dielectric to copper interface is formed by laminating electroplated copper foil on semi-cured glass epoxy resin under temperature and pressure. This electroplated copper foil has irregular tooth like profile due to columnar nature of the copper deposited. This is confirmed by Fig.3, TEM (Transition Electron Microscope) analysis shows the surface topography of copper foil used for the construction of glass epoxy copper clad laminate has tooth like profile.

When such surface topography of the foil is laminated, adhesion strength of the interface is mainly contributed by encapsulation of epoxy resins around the highly profiled tooth like structures. As per IPC specifications acceptable minimum peel strength of 3mm width laminated copper is 0.78kg/cm. Average obtained value in our experiment is 1.64kg/cm, which is well agreed with specified value.

It is well known that, metal-to-metal bond strength is generally greater than metal to dielectric bond due to the change in the mechanism of adhesion at this interface. Since it is difficult to quantify exactly the cohesive force between the electroplated copper and laminated base copper, therefore adhesion strength between the base copper and dielectric epoxy laminate interface was considered as standard reference during peel strength test in our study.

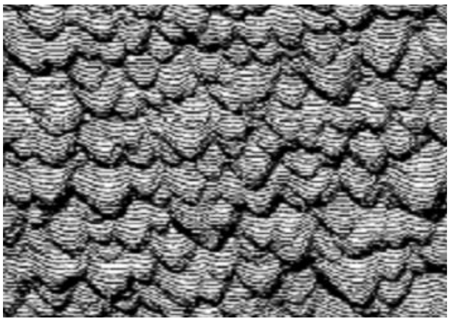


Fig.3. TEM of electroplated copper foil shows tooth like profile structure

From the Table.2, it is evident that, interface generated by freshly prepared micro-etchant had peel strength value of 0.72kg/cm, which is grossly inadequate. Interface created using stirred and cooled micro-etchant, had peel strength more than 1.64Kg/cm. Low peel strength by freshly prepared etchant is attributed to insufficient surface treatment prior to electroplating process. Higher peel strength by stirred and cooled etchant is attributed to the optimum level of surface treatment.

During the micro-etching process, acidified ammonium peroxodisulphate selectively corrodes the copper surface and etches downward along the grain boundaries of the crystalline structure of the base copper foil resulting in a “zig-zag” path. Since the corrosion occurs more quickly along such grain boundaries, the result is a surface comprising of peaks and valleys that increases the contact surface area. Incorporation of add copper atom inside these topography during the electroplating process leads to interlocking of the copper grain, results in enhanced adhesion of electroplated copper [10] [11]. This phenomenon is possible only when micro-etched surfaces are free from foreign hydrophobic contaminants and possess good wettability.

Generally, “water break test” gives the qualitative information about the wettability of the micro-etched surface, in which continuous film of water indicates the better-etched surface [12].

In our study we have measured the contact angle (θ) to know the hydrophilicity of the micro-etched surface. Contact angle is quantitative measurement of wettability of solid (in this case copper surface) by a liquid (water). Low value of θ indicates that liquid spreads or wets surface, while high values indicate the poor wettability. If the angle is less than 90 degrees then the liquid is set to wet the solid. If it is greater than 90 it is said to be non-wettability [13] [15]. The digital image of the water drops on treated and untreated samples are shown in the Fig.4. It shows that, contact angle is more in case of freshly prepared micro-etchant and least in case of stirred and cooled etchant. Moreover, drop profile gradually becomes flattened. The Table.3 compares the wetting angle performed on three types of surface. This shows that, wettability of micro-etched surface is more in case of cooled and stirred etchant than freshly prepared micro-etchant and least for untreated surface. This shows that sample treated in unstirred, stirred and cooled etchant moved towards hydrophilic domain.

(a) (b) (c)

Fig.4. Profile of micro litre water droplet on (a) non-etched surface (b) surface treated in freshly prepared micro-etchant, (c) surface treated in highly stirred micro-etchant

Table.3. Comparisons of Wetting Angle

Sample description	Contact Angle in degree
Non treated surface	105.6
Freshly prepared etchant	87 to 94.8
Stirred etchant	79.7

In case of freshly prepared ammonium peroxodisulphate solution, due to the exothermic reaction by the addition of sulfuric acid, creates a lot of gas bubbles throughout the bulk of the micro-etchant solution. When copper pattern was micro etched in this type of solution in hot condition, thin layer of gas bubbles get physically adsorbed randomly on the surface of the copper track. An adsorbed gas bubble prevents the attack of copper by micro-etchant along the grain boundary, which leads to improper surface treatment.

The Fig.5 is the enlarged optical photograph of surface treated using freshly prepared solution. It shows that micro-etching action did not take place around the shiny dots, in which gas bubbles get adsorbed during micro-etching.

This improper treated surface acts as weak junction, at which mismatch in the grain interlocking between the base copper and the plated copper leads to low interface adhesion [15]. Hence peeling of electroplated copper takes place from the base copper. This in confirmed by following optical photographs (Fig.6).

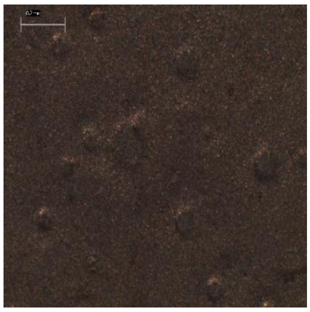


Fig.5. Optical photograph of micro-etched surface using freshly prepared peroxodisulfate solution shows improper surface treatment

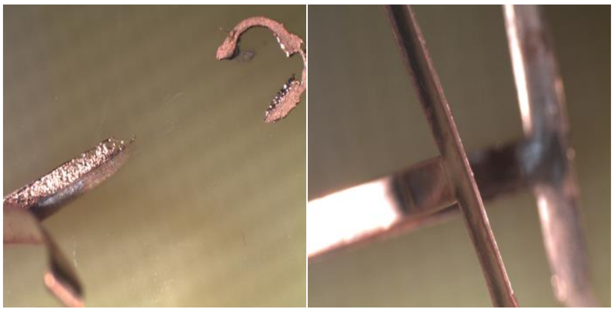


Fig.6. Optical photographs of peeled electroplated copper from base copper, in which freshly prepared ammonium persulphate acts as micro-etchant

It also inferences from the Fig.6 that only the electroplated copper gets peeled from adjoin base copper and base copper is well in intact with the epoxy dielectric and hence improper surface treatment leads to copper-to-copper interface adhesion (0.72kg/cm) failure. This type of interface will fail to provide adequate strength as mechanical and electrical interconnects for future miniaturized SMD devices. The Fig.7 are the SEM micrographs of interface generated in freshly prepared microetchant. It clearly shows the absence of grain interlocking at the copper-to-copper interface.

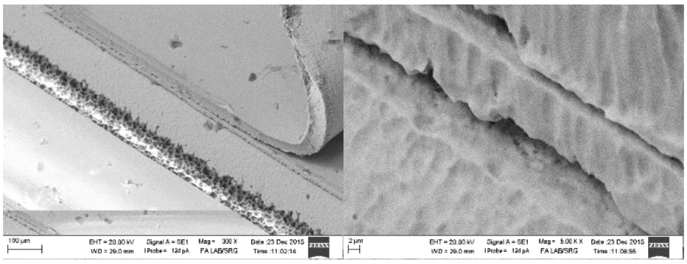


Fig.7. SEM Micrographs of interface generated using freshly prepared ammonium persulphate as micro-etchant shows the absence of grain interlocking at the interface

The Fig.8 shows the optical photographs of copper tracks generated on the copper base using stirred and cooled etchant. There is no plated copper peeled off from the base copper and failure occurred at the epoxy to copper interface adhesion. Also, peel strength obtained using stirred and cooled micro-etchant is several orders higher than that between epoxy-copper interfaces.

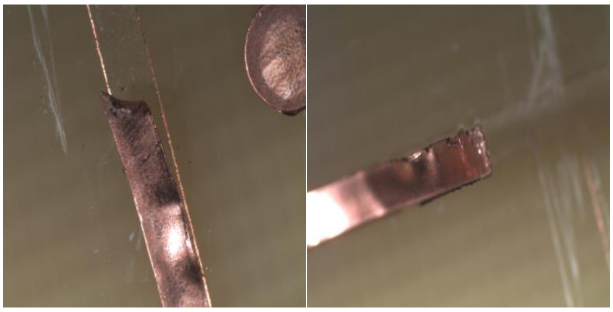


Fig.8. Optical photographs of peeled electroplated copper from base copper, in which interface at the laminated copper and dielectric separated rather than the copper-to-copper interface failure

Stirred and cooled microetchant has very low exothermic property. Due to low exotherm chemistry, this micro-etchant creates excellent matte finish surface topography by eliminating the physical adsorption of gas bubbles on the base copper. This promotes good interface adhesion during electroplating of copper. Hence enhanced peel strength generated by stirred microetchant and cooled etchant is attributed to excellent surface topography without incorporation of gas bubbles, which favors the interlocking of grain structure at the interface during pattern plating.

SEM micro-graphs in Fig.9 show that there is no separation between base copper and electroplated copper indicating interlocking of the grain at the interface during plating.

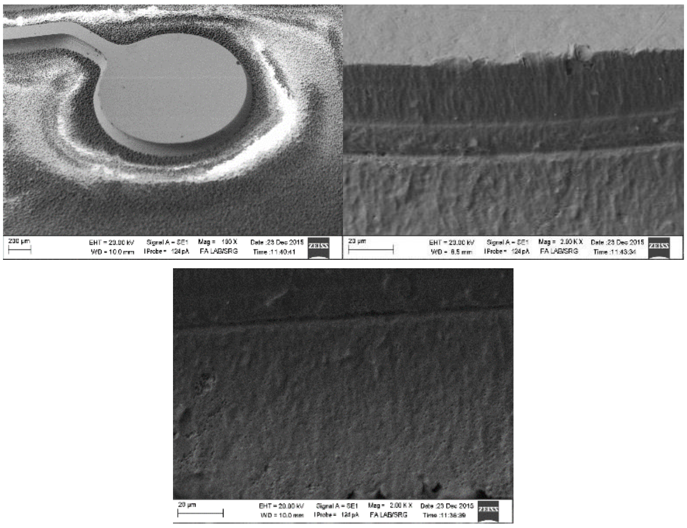


Fig.9. SEM photographs of conductive copper tracks show the good interlocking of grains at the interface

Virtually this type of interlocking of grains leads to geometrical extension of base copper crystallites finally converges to "epitaxial growth". This type of interface acts as reliable interconnects for future miniaturised SMD devices.

4. CONCLUSION

In this paper role of micro-etching solutions to improving the interface adhesion between laminated base copper and electroplated copper in pattern electroplating process is described. Micro-etched copper surface using combination of ammonium peroxodisulphate and sulphuric acid, in freshly prepared, stirred and cooled conditions are studied. Results show that micro-etched copper surface using freshly prepared ammonium peroxodisulphate in combination with sulphuric acid produce very low peel strength of electroplated copper. This interface failure is attributed to improper surface treatment of base copper due to high exotherm of freshly prepared micro-etchant, results in the physical adsorption of gas bubbles that prevents the grain boundary attack. However same micro-etchant after stirred and cooled enhance the copper-to-copper interface adhesion results in better peel strength of electroplated copper. Enhanced interface adhesion in case of stirred and cooled, etchants is due to very low exotherm. Low exotherm results in absence of physical adsorption of gas bubbles, which favors the etching action along the grain boundary of the base copper. During subsequent electroplating process interlocking of the add copper atoms at the interface results in the extension of base copper crystalline structure without any inclusion of foreign materials in this case gas bubbles. Hence well-stirred and cooled ammonium peroxodisulfate solution can be used as micro-etchant to ensure good adhesion at copper-copper interface during pattern plating of PCBs.

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