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Selective Electroless Precipitation Of Copper On Non - Conductive Surfaces Using The Semiconductor Zinc Oxide.

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Abstract :

Zinc oxide layer being thermally precipitated on glass and ceramic strips (2x2.5 cm) before the electroless precipitation of copper utilizing the conventional Printed Circuit Boards(PCB) technologies in conjunction with the required modifications to optimize the quality of these layers .

The roughness of ZnO films was Ra 0.02 µm and its thickness about 0.7 µm. The films being characterized by X- ray diffraction . The bivalent Pd(I I) used as activator was reduced to Pd (0) on surface of ZnO layer by UV light in 1.5 – 2 minutes intervals .

Copper lines precipitated in the subsequent steps have an adhesion power of 2and 5 kg.mm^{-2} on glass and ceramic respectively . The specific conductance of the electrolessly deposited copper was found to be(5.3x 10^{6})ohm^{-1}.cm^{-1}, and the resistivity was (1.8 x10 $^{-6}$)ohm.cm . From the results of this study the method could be utilized in PCB fabrication

1.Introduction :

The conductivity of non- conductive materials like glass and ceramic were about 10^{-16}-10^{-8} ohm^{-1} cm^{-1}[1] . Their surface conductivity might be modified to fall in the range of 10^{3} -10^{8} ohm^{-1} cm^{-1} characteristic of conductive materials [2]. The modification was brought about by applying a thin film/s.

The application was carried out by immersing the non-conductive substrate in an aqueous solution containing the required metal ion followed by the reduction of the surface ions[3,4] .The technical importance were pronounced particularly in the fields of PCB [5] , very large scale integrated circuits (VLSE)[6] and protection of the surfaces from corrosion like precipitation of gold on copper[7] for microwave connections .

The conventional methods of PCB fabrication requires at the beginning an etching of the surface[8] which was a major setback when high frequency currents pass through it , or when the electronic components are heavily implemented . Both lead to excessive heat generation throughout working .

To overcome the problems encountered with the subtractive etching step which causes the roughness of the surface , an additive method

based on precipitation of intermediate layer (namely the n- type semiconductor zinc oxide of hexagonal wurtzite structure) between the substrate (glass or ceramic) and the final copper layer[9] . In addition to its capability of conducting heat to the substrate which may equipped with a heat sink , its also acts a good media for the adsorption of the bivalent palladium ions which triggers the electroless copper plating process .

Commercially, since 1955 , copper was reduced on the non – conductive surfaces in the plated through holes (PTH) ,from basic copper tartarate baths by formaldehyde . Fujishima [5] used ceramic as a base for PCBfabrication after precipitation of zinc oxide . The width of the precipitated copper line was 17 µm and required 2 kg mm^{-1} to peel out the coating from the substrate .Holden[10] adapted the same approach , the roughness of zinc oxide was(Ra 0.02 µm) and the width of the copper line was 20 µm which also required 2 $kgmm^{-1}$ to peel out . In 1998 , Fujishima used non- etched ceramic surface to host the zinc oxide layer[11] and the electrolessly plated copper line required 2.5 $kgmm^{-1}$ to peel out . Zinc oxide was precipitated at a temperature of 663 k on glass substrate at oxygen pressure of 0.03-0.1mbar [12] . It was found that the oxygen pressure has a pronounced effect on the photo and electro properties of the formed films.

The aim of this work is to precipitate copper on zinc oxide which acts as an intermediate layer between the non – conductive surfaces of glass and ceramic using new technique to enhance the adhesion process , in conjunction with electroless plating of copper using the conventional methods for PCB fabrication except for new formulation of palladium activator and other solution used throughout as indicated . The work was also extended to study the structural properties of the formed zinc oxide as well as the peeling strength of the eventually deposited copper lines .

2.Experimental :

A:.Chemicals :

Chemicals supplied from BDH : Zinc acetate 98.8% , palladium chloride 99%, Hydrochloric acid 37%, Roschell salt 98% , sodium carbonate 99%,

Chemicals supplied from Fluka : Copper sulfate 99.9%, sodium hydroxide 98% , Potassium cyanide 99%, Dichloroethylene 98% .

Chemicals supplied from Thiokol : Vinyl cinnamate monomer spread over photosoluble polymer .

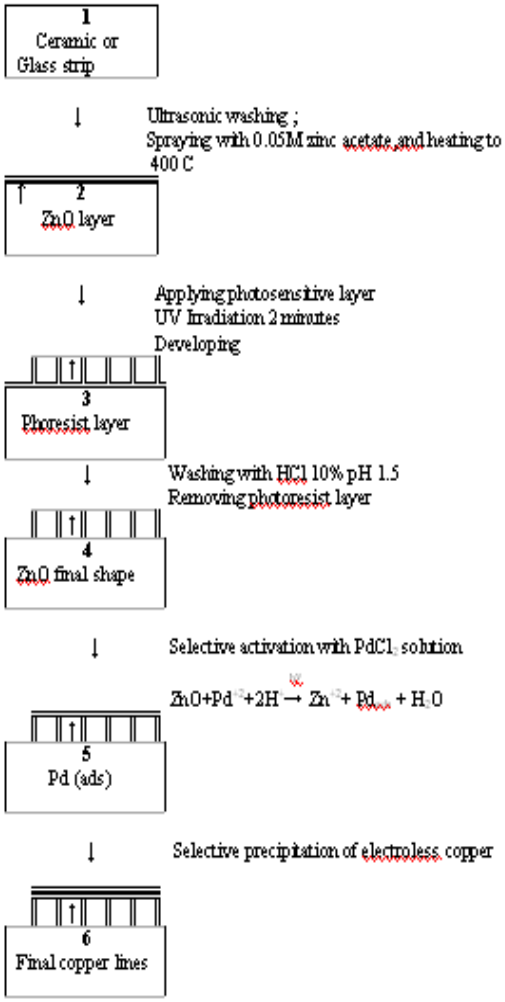
The details of solutions preparation as well as the detailed description of the procedures are fully illustrated in reference 15.

B : Apparatus and Equipments :

Spray chamber consist of :{ Glass nebulizer(Baird and tatlock),
Open tube furnace with temperature controller 200- 1100 C(Lindberg) }. Ultrasonic bath (Brasonic 220) . photosensitive layer applicator (Thiokol Idyano chem. Corporation). Ultraviolet source 450 watt (Colight m 218) . Balance (Mettler Ak-16). X-ray diffract meter (Phillips PW 18402 of Geo survey ,Baghdad) . Ultraviolet / Visible spectrophotometer (Hitachi 2000). Adhesion force measurements (Instron1122, of physics dept college of science , Baghdad Univ). Surface roughness measurements (Talysarf 6 system, of Mechanical Company Ministry of industry). Power supply (Tandwin) . pH meter(CG 825). Optical microscope equipped with a

camera model x 52 -11. Atomic absorption spectrophotometer flame (Shimadzu). Micrometer (Mituoyo) .Glass and ceramic strips 2x2.5 cm(R&S supplier for electronic parts).

C.: procedures *:* The following sketch outline the working steps for the preparation of printed circuits on glass and ceramic strips :



The thickness of the ZnO films were controlled by spraying conditions and calculated by the weight difference between the weights of the substrate before and after deposition(Δm) :

$$t = \Delta m / \rho A \qquad \text{…….1}$$

t : Thickness of the film

ρ; The density of the film

A: area of the film

The roughness of the surface were measured quantitatively by measuring the deviation from the continuous surface (Ra) :

$$Ra = 1/L_o \int^{\infty} |y(x)| dx \qquad \text{……..2}$$

L_o: Surface length

y : Height from base line

x : Length of deviation from the surface

After the deposition of ZnO films , the strips were laminated in a pre adjusted pattern by the aid of a photo plotter which also determine the width of the subsequent copper line from the next steps . They were laminated with a commercially available vinyl cinnamate monomer by the aid of a laminar applicator . The lines were developed by applying UV light were the monomer polymerizes to polyvinyl cinammate . Adsorbed palladium from the activator step were measured after being acid extracted from the processed strips followed by atomic absorption spectrometry measurmens . The thickness of copper lines were controlled by the time of electroless immersion and measured by a digital micrometer . the adhesion of electrolessly deposited copper was measured by Instron 1122 , while the strips are placed inside the cell of the instrument , then on pre solded wire attached to the copper line increased weights being loaded , their weights being recorded digitally until the line is peeled out .The resistance(R) of the

plated copper were measured directly from I/V curves for each sample.

$\rho = R \cdot A / L$ ……..3

The inverse of ρ gives electrical conductivity :

$\sigma = 1/\rho$ ……4

R: Resistance (ohm) , ρ : resistivity (ohm.cm),A: area ($cm^{2)}$, L: length of line(cm), σ: specific conductance ($ohm^{-1}.cm^{-1}$).

3.Results and discussion :

The roughness of the strips were measured before the deposition of zinc oxide , it was found (Ra = 0.01μm) , while reached 0.02 μm after the deposition of ethanolic solution of zinc acetate . Zinc oxide prepared from the aqueous $Zn(NO_3)_2$ solution gave Ra 0.03 μm (figure 1) . The superiority of ethanolic zinc acetate solution might be due to the reduced surface tension and to the finesse of ethanolic mist formed through sprayingfigure 1 . The films of ZnO were characterized by X-ray diffraction (figure 2) which is in a good agreement with the ASTM of ZnO , in addition both ZnO films and eventually formed copper lines were examined under a microscope of a magnification power of 50 which revealed that the films are free from pinholes, ruptures and well packed over the strips surface (figure 3) .

Table 1 shows the optimization of the parameters affecting the thickness of zinc oxide layer , the optimum recommended thickness was 0.7 [13] μm , less than 0.5 will be adversely affected by the action of the subsequent treatments with other solutions , while thickness of ZnO larger than 0.7 μm will cause short circuits of the copper line from the next step .

Table 1 : Optimization of zinc oxide thickness

Distance(cm	angle(Degree)	no. of sprayings	flow rate ml/min	thickness μm
40	90	10	8	-
40	90	15	7	-
40	90	20	6	-
35	90	25	5	0.1-0.2
35	90	30	5	0.2-0.3
35	75-85	35	5	0.2-0.4
30	75-85	40	5	0.5-0.6
28	75-85	40	5	0.5-0.8

Figure 4 shows the annealing of the ZnO layer at 500 C , which have a desirable effects in minimizing the lattice defects and the relief of stresses . Selective copper lines precipitation is governed by the elapsed time required to reduce Pd(11) to Pd (0) used as activator . The optimum time was found to be 1.5 – 2 minutes , figure 5 shows the thickness of copper lines as a function of immersion time .

In order to judge whether the fabricated copper lines are suitable for practical applications or not , they should have an adhesion power not less than 2 kg.mm-2(10) . Copper lines peeled out at ≈3 kg.mm-2 and 5 kg.mm-2 from glass and ceramic substrates respectively . Table 2 compare the results of this work with similar previous results of other workers (10,11).

Table 2 : comparison the results of this work with results of other workers

	ZnO on ceramic	ZnO on glass	ZnO on glass	ZnO on Epoxy	ZnO on Epoxy/Acrylate
	This work	This work	Previous work	Ref.[10]	Ref.[11]
Roughness (μm)	0.02	0.02	0.02	0.6-1	0.04-0.2
Adhesion power Kg.mm^{-2}	5	3	2	2.6	0.5

Figure 6 shows the effect of copper line thickness on the adhesion power . Its evident that copper lines is more adherent to ceramic than for glass substrate , the reason is not yet well known but it could be related to inter and intra atomic interactions and the inherited differences between the alumina and the silicate structures . Figure7 plotted between the current and the voltage for copper lines of fixed width but with different thickness , while figure8 shows those I/V plots for 5 µm thickness but different width . Although both figures have the same trend but they are differ in values . The specific conductance was found to equal $5.3x10^{6}ohm^{-1}.cm^{-1}$ at 25 C , and the specific resistivity was $1.8x10^{-6}ohm.cm$

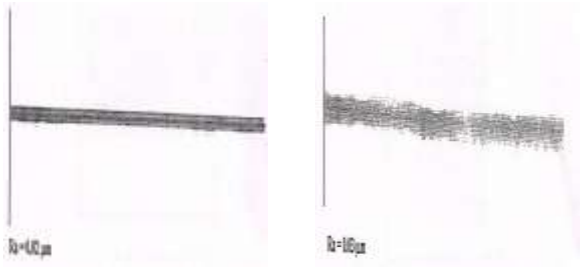
Figures9,10 shows the variation of resistance with the variation of cross section area of the line . The thickness were kept constant in the former , but the width is kept constant in the latter . Finally figure 11correlate the experimental and the theoretical[14] resistance values .

4. Conclusions *:*

The ethanolic solution of zinc acetate with the annealing temperature 500 C were found to be suitable to deposit zinc oxide layer , which has little imperfections . Zinc oxide films acts as an intermediate layer between the isolator (glass or ceramic) and the conductor (copper) has a good adhesion power . Exposure of Pd(11) to UV radiation is of great effect on the copper lines .

The whole process could well be adapted in PCB fabrication

Figure 1 : Comparison between the ZnO layers prepared by different methods A : Zinc acetate , B : zinc nitrate



A B

Figure 2: X-ray diffraction of deposited zinc oxide layer

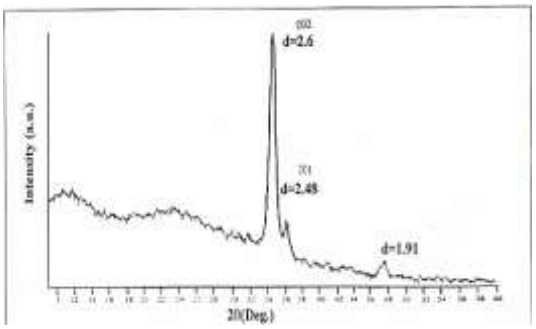
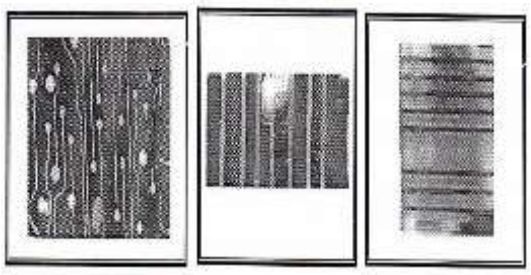
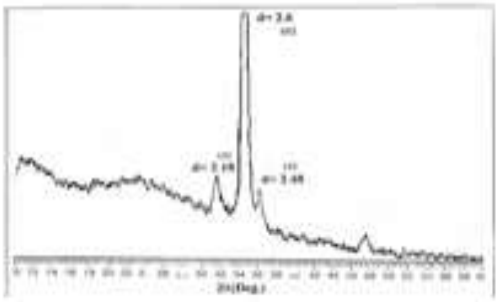


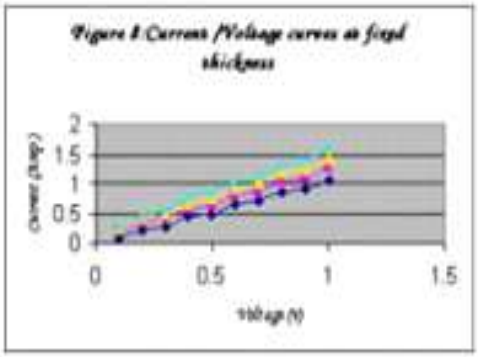
Figure 3: copper line of different widths printed on glass strips A: Printed circuit, B: 200 µm width copper, C :50 µm

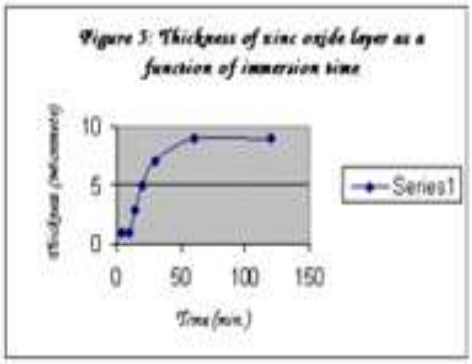


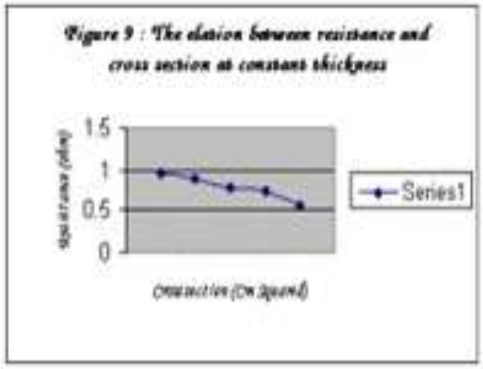
A B C

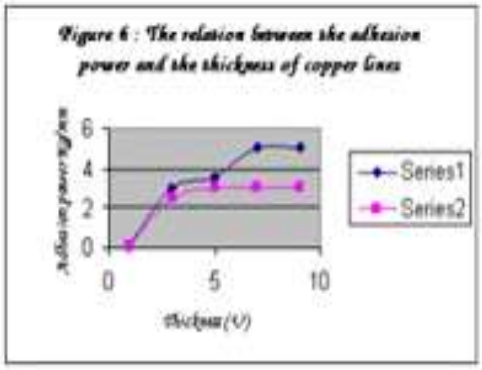
Figure 4: X- ray diffraction of deposited zinc oxide layer

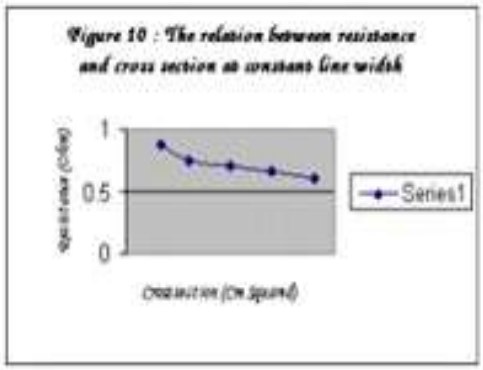


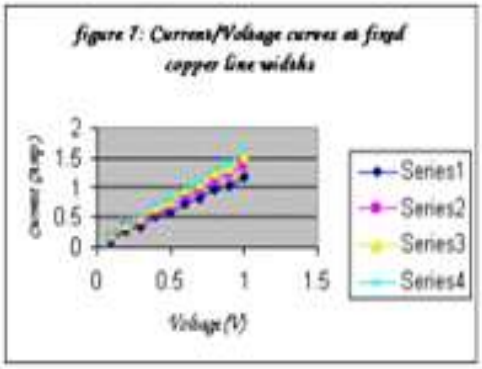


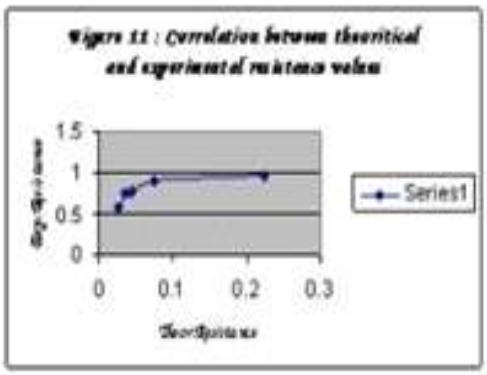












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الترسيب الانتقائي للنحاس على السطوح غير الموصلة باستخدام شبه الموصل اوكسيد الزنك

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الخلاصـــــــة

تم ترسيب طبقة خفيفة من اوكسيد الزنك حراريا على شرائح من الزجاج والسيراميك ، والتي ابعاد كل منهما ٢ * ٢,٥ سم قبل ترسيب طبقة النحاس التي تتم عادة باسلوب الترسيب اللاكهربائي ، وبالاستفادة من التقنيات المستخدمة بشكل صناعي في صناعة الدوائر الالكترونية المطبوعة مع التحويرات اللازمة لتحسين نوعية الطبقات المرسبة

كانت خشونة طبقة اوكسيد الزنك ٠.٠٢ مايكرومتر وسمكها٠,٧ مايكرومتر ، وقد تم تشخيص طبقة اوكسيد الزنك بوساطة حيود الاشعة السينية. ان البلاديوم الثنائي المستخدم كمنشط او باديء للترسيب الكهربائي قد اختزل الى البلاديوم على سطح طبقة اوكسيد الزنك بوساطة الاشعة فوق البنفسجية خلال دقيقة الى دقيقة ونصف .

وجد ان لطبقة النحاس المترسبة في الخطوات اللاحقة قوة التصاق بلغت (٢ و ٥) كغم . ملم$^{-٢}$ على التوالي . بلغت التوصيلية النوعية للنحاس المرسب لاكهربائيا (٥,٣ * ١٠^{٦}) اوم $^{-١}$. سم$^{-١}$ والمقاومة النوعية(١,٨ * ١٠$^{-٦}$) اوم.سم

يتضح من النتائج امكانية توظيف هذه الطريقة في صناعة الدوائر المطبوعة .