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Comparison between Electroplating and Electroless on Plastic Surface

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Abstract

We report a method of converting non-conductive plastic surfaces into conductive by plating either copper electroless or copper electroplating -carbon black containing bending Agent onto Perspex plastics . Various approaches have been studied in order to comparing properties of the plated copper for two methods such as scanning electron microscopy (SEM),thickness, roughness, porosity, tensile Strength and elongation. The results show that the surface of electroplating was uniform, compact, and continuous and it had an obvious metallic sheen, while the surface of plated copper for electroless for it had many pores. Also observed that the coating was composed of small cells. These cells have been deposited together closely.

Thick copper layer was deposited a(38μm) electroplating while (5μm) for electroless plating tensile strength and elongation of copper electroplating became greater compared with copper electroless, whereas the roughness and Porosity became smaller.

The electroplating copper deposition process developed in this study may open up a new route of plating on plastics (POP) for printed circuit boards, electromagnetic interference shielding, and many other applications.

Keywords: Copper electroless, Electroplating methods, Non-conductive surface plating, Methods of copper deposition.

Introduction

Metallization of non-conductive surfaces is important in many industrial applications as it lowers cost, allows more flexibility in parts design, and reduces weight compared to its metal counterpart [1]. Plating on plastics (POP) therefore has been developed and widely involved in manufacturing printed circuit boards (PCBs) and automobile parts, and in the electromagnetic interference (EMI) shielding application [3]. Having excellent electrical conductivity and being relatively inexpensive, copper (Cu) has been widely studied for POP and a variety of plastics have been Cu plated including acrylonitrile-butadiene styrene (ABS), polypropene, and Teflon [1]. Currently, there are two technologies developed for Cu plating of plastics, via the electroless route or through a direct electroplating route. For the first route, a regular electroless plating procedure is needed to place a thin conductive Cu layer on the plastic surface. Such a Cu layer provides sufficiently high conductivity required for the subsequent electroplating to complete the materialization finishing.

However, the involvement of a regular electroless plating operation in POP is not desirable because of the disadvantages associated with electroless plating, including the complexity of the plating bath, a time consuming procedure, and the use of costly catalyst and environmentally unfriendly agents [4]. Alternatively, direct Cu electroplating on plastics was proposed as a substitute to the electroless route, which involves an essential step of seeding the plastics surface with an electronically conductive catalyst or activator, typically a Palladium (Pd) and/or Tin (Sn) colloid. On adsorption of the catalyst onto the plastics surface, the seeded surface is subjected to a regular electroplating procedure to complete the metallization [10]. Although many of the disadvantages associated with electroless plating have been circumvented by excluding this operation from the POP process, the requirement of costly catalyst for the direct electroplating is still undesirable. Besides, many operations such as etching, neutralization, activation, and acceleration are needed before the electroplating starts, making the direct electroplating route a multi-step and time-consuming process.Hence, elimination of the use of catalyst and development of simpler and more cost-efficient Cu plating bath with a view to further optimize the POP procedure are desired.

Recognizing these, we studied and developed an alternative to electroless deposition of conductive Cu on plastics by Carbon processes utilize a suspension of carbon black particles to deposit a conductive layer of carbon onto the substrate surface. The coated plastics were then scoured and subjected to a simple electroless procedure in a bath of 30 g/l copper sulfate (CuSO4) and 140 g/l complexing agent (EDTA). Good conductivity was obtained at a 10-min deposition time and leveled off after 20 min. For comparison, carbon black (C) particles were prepared and applied to Perspex as well, and subjected to the acid copper electroplating. It was found that incorporation of C particles into the paste shortened the time to reach the plateau conductivity and enhanced the adhesion of electrolessly deposited Cu layer to the substrate surface. The electroplating deposition process developed in this study may open up a route of POP for PCB, EMI shielding, and many other applications.

Experimental Work

Materials

The carbon black powder (particle size range 2–12 μm) supply from (LPKF Leaser & electronics AG company), acetic acid from (TETENAL – Photo Werk) Germany, for copper sulfate supplied from (Sojuz Chiem Export Company,Mosxww) sulphuric acid (98%) (Gainland Chemical company) and HCl (32%) (BDH company), perspex plastic board was supplied from (Basf,Germany Co.)

Sample Preparation

The dimensions of the substrate (perspex) was 5*5 cm.Substrate surface is at first roughened by mechanical roughening with abrasive paper. Then the surface is rinsed and etched with 4% sulfuric acid for 2 min followed by rinsing.

Preparation of Carbon Coating

Carbon powder, bonding agent, and acitic acid were mixed and magnetically stirred vigorously for 30 min. Carbon black were dispersed then applied on Perspex boards that were pre-cut into 5*5 cm2 squares, and Perspex was dipped into solution of Carbon black for 5 min and then dried in air at 60 ˚C to be ready for the subsequent experiments (electroless copper deposition). For comparison,

with acid copper electroplating were also prepared by following the same preparation procedure on Perspex boards.

Electroless Copper Plating

After carbon activation, electroless copper plating was performed. The bath composition and condition of this work is listed in Table 1. For the copper source, copper sulfate was used and for complexing agent, EDTA was used. The pH of the bath was fixed at the value of 12.8 which is reported by previous researchers to be a value where the deposition rate of copper is uniform. The selective deposition of electroless copper plating depends on the substrate and activation.The substrate was dipped into bath for15 min. Initial experiments were performed to compare the plating profiles for a variety of copper electroless and electroplating. Later tests were focused on plating thickness, roughness, porosity and tensile strength for surface.

Electroplating Process

The composition of the base electrolyte used in all plating tests is listed in Table 2. The plating additives used were: suppressor, accelerator, leveler and chloride [4]. Copper anodes were directly placed in a plating bath with a working volume of 5L. The substrate was dipped into bath for 15 min.

Table 1: Composition of electro less Cu bath

Chemical components	Conc.
Cupric sulphate (CuSO4) g/L	30
Formalin (HCHO) ml/L	10ml/L
Complexing agent (EDTA) g/L	140
Bath conditions	
pH adjuster NaOH (12.8)	NaOH (12.8)
Temperature ^{o}C	25

Table 2: Composition of electroplating Cu bath

Chemical components	**Conc.**
$CuSO_4 \cdot 5H_2O$, g/L	200
H_2SO_4, ml/l	50
Bath conditions	
Current density, A/dm^2	2
Temperature, ^{o}C	25

Measurement of Metal Deposition

Thickness of the surface and cross sectional morphologies were observed using optical microscope (OM)(Olympus BX-51) and scanning electron microscope (SEM) [5].

Measurement of Mechanical Properties

Tensile Strength and Elongation of plated copper were used in accordance with IPC TM-650, 2.4.18.1. Vertical and horizontal pulls were measured.

Macro-roughness was determined over a 315micron range and 5 locations were averaged to determine the substrate roughness and 7 trials were performed at each location.

Porosity measured by saturated method such tests are designed to attack the substrate revealing the corrosion occurring through the pores (TAYLORHOBSON Company).

Results and Discussion

Surface Morphology and Thickness of the plating

Typical SEM micrographs of copper electroplating at low and high magnifications

are presented in Figs.1 a and b, It can be observed that the surface of plated copper for electroplating , which was uniform, compact, and continuous and it had an obvious metallic sheen. Typical SEM micrographs of the opper elctroless at low and high magnifications are presented in Figs.1 c and d, respectively. It can be observed that the surface had many pores. Also observed that the coating was composed of small cells. These cells have been deposited together closely.

Fig. 2 shows the copper plating thickness as a function of time, for the electro and electroless plating. The plating rate for electroplating increased linearly with time, while the electroless plating is locally suppressed. An excellent thickness was achieved at time 35 min for thickness (38μm) electroplating while (5μm) for electroless plating. Increasing this time caused increasing of rate of decomposition for electroless plating. This possible reason was that the catalytic reactions were saturated when it was above 35min. while proved that plating thickness for electroplating depending on the current density of plating to achieve the required copper thickness on the plastic substrate.

Tensile Strength and Elongation

The results from the Tensile Strength and Elongation evaluation are given in Fig. 3 it can be observed the tensile strength value for copper electroplating more than value for copper electro less plating. This possible reason was that increasing copper thickness on the plastic substrate plating over -potential increases the nucleation rate and leads to formation of deposits with higher tensile Strength for electroplating. While electroless plating proved that the Cu atoms were deposited far from them this lead to formation weak tensile strength [10].

Roughness Test

The roughness value of copper electroplating and electroless were 0.65μm and 0.88 μm, respectively. The surface of copper electroplating was smooth comparing to the electroless the possible reason was that crystallographic planes and directions in crystal lattices of deposit more uniform than electroless deposition [11]

Porosity test

The porosity value of copper electroplating and electroless were 1.5 and 3.28, respectively the porosity of copper plating depends on the method of deposition. electroless plating are noticeably more porous than electroplating plated. The possible reason was its surface has its slowest growing crystal planes in the plane of the substrate electrodeposits of copper, developed continuous films at an average thickness of less than 38μm on plastic substrates, whereas, electroless copper 5 μm or less in thickness were not continuous and showed many holes or channels as shown in Fig. 4 [8].

Conclusions

1. Cu electroplating on Perspex surface activation by carbon black was successfully with improved Properties of Plated Copper Coatings and the structure of the deposits was examined compared with Cu electro less plating.
2. SEM analysis showed that the surface of Cu electroplating was uniform and continuous, while the pore structure of Cu electro less could be still seen clearly.
3. A preliminary study of mechanical properties showed that the mechanical properties of Cu electroplating and electro less exhibited as: The Tensile Strength and Elongation was 51MPa, Max force 2568 N and Elong at Max 5.54%, while the Cu electro less was 47.8MPa, Max. Force 2448 and Elong at Max 4.83%, the thickness was (38μm) electroplating while (5μm) for electro less plating. The value of the porosity and surface roughness about 1.5 and 3.28for electro less and 0.65μm for electroplating and 0.88μm for electro less. This good indicated the Cu electroplating was better than Cu electro less for Perspex surface.

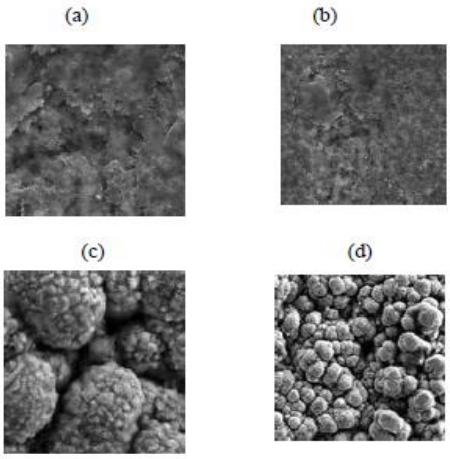


Fig.1: Surface morphology of Cu plating (a) SEM hotograph Cu electroplating (low magnifications) (b) SEM photograph Cu electroplating (high magnifications) (c) SEM photograph Cu electroless (low magnifications). (d) SEM photograph Cu electroless (high magnifications)

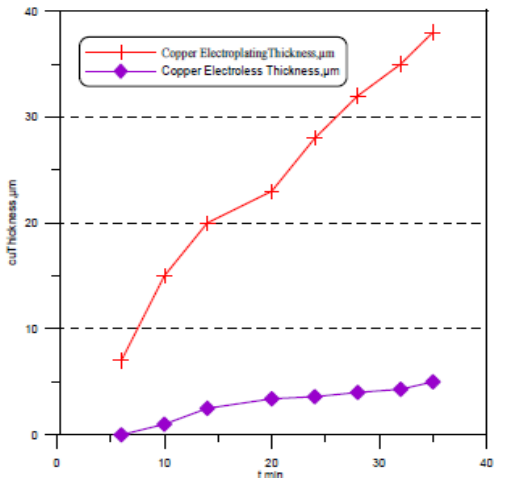
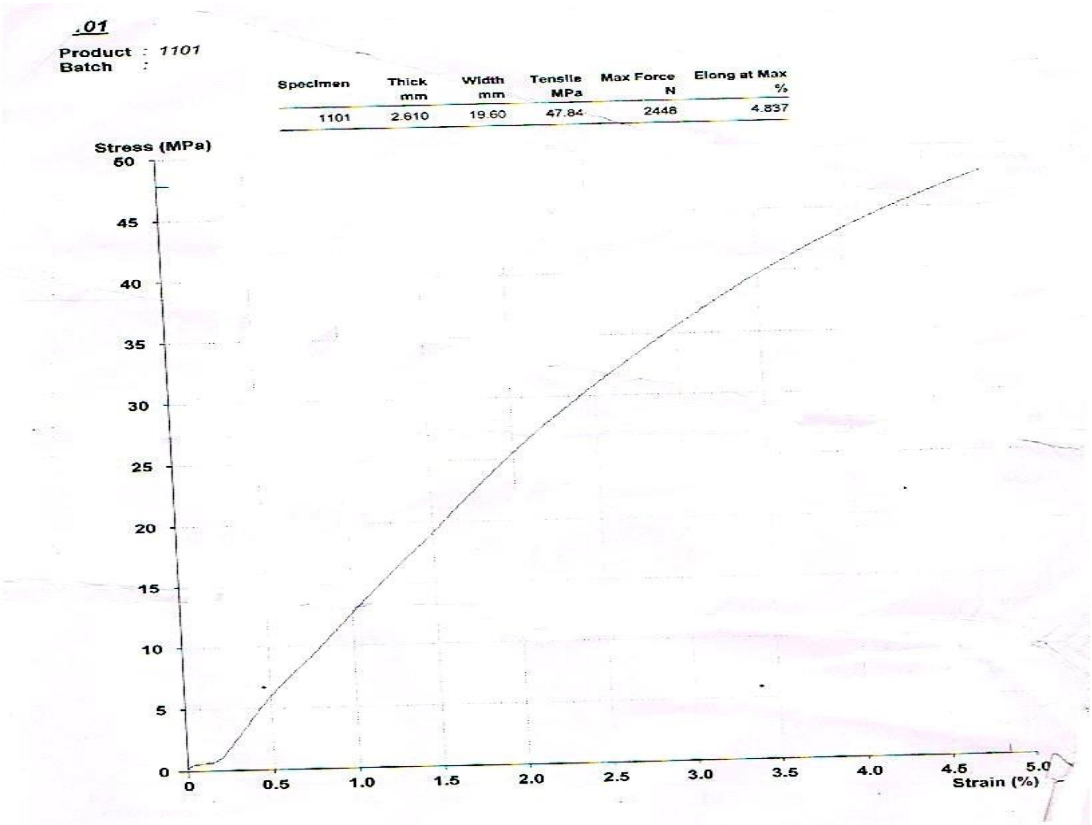
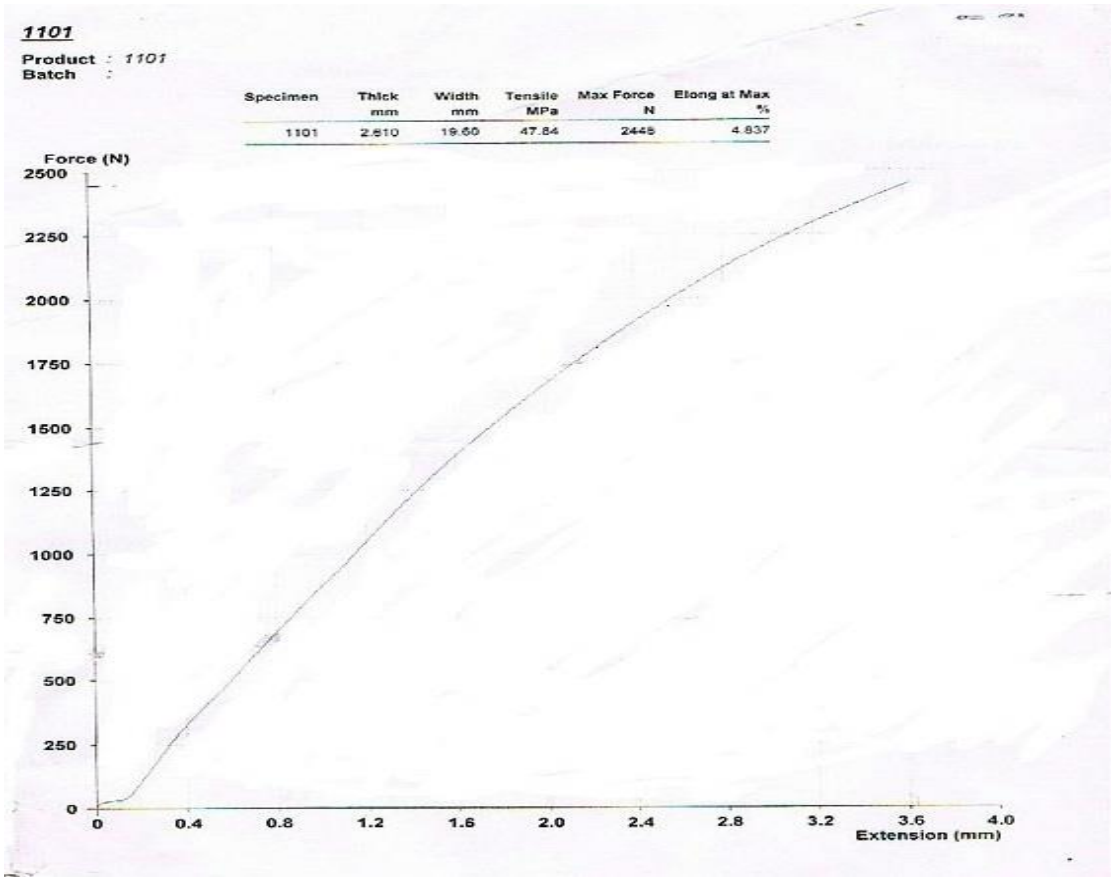


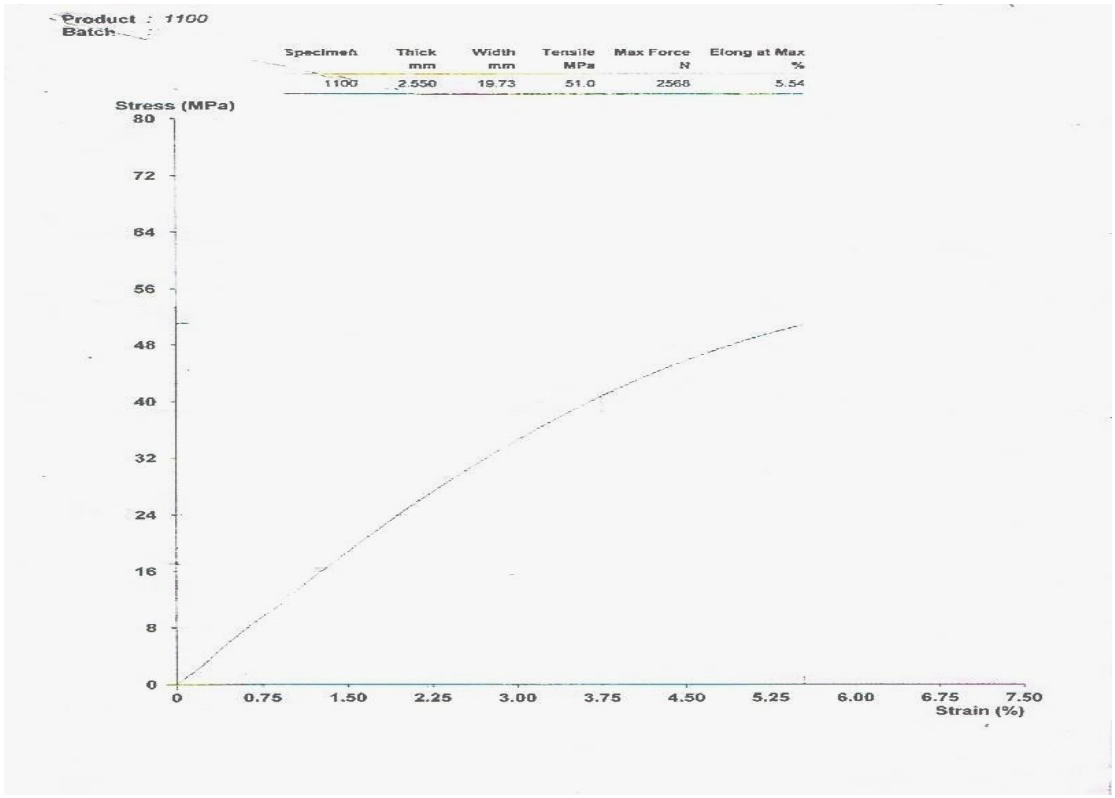
Fig. 2: Copper thickness as a function of plating time for electro and electroless plating, for surface 4cmx4cm



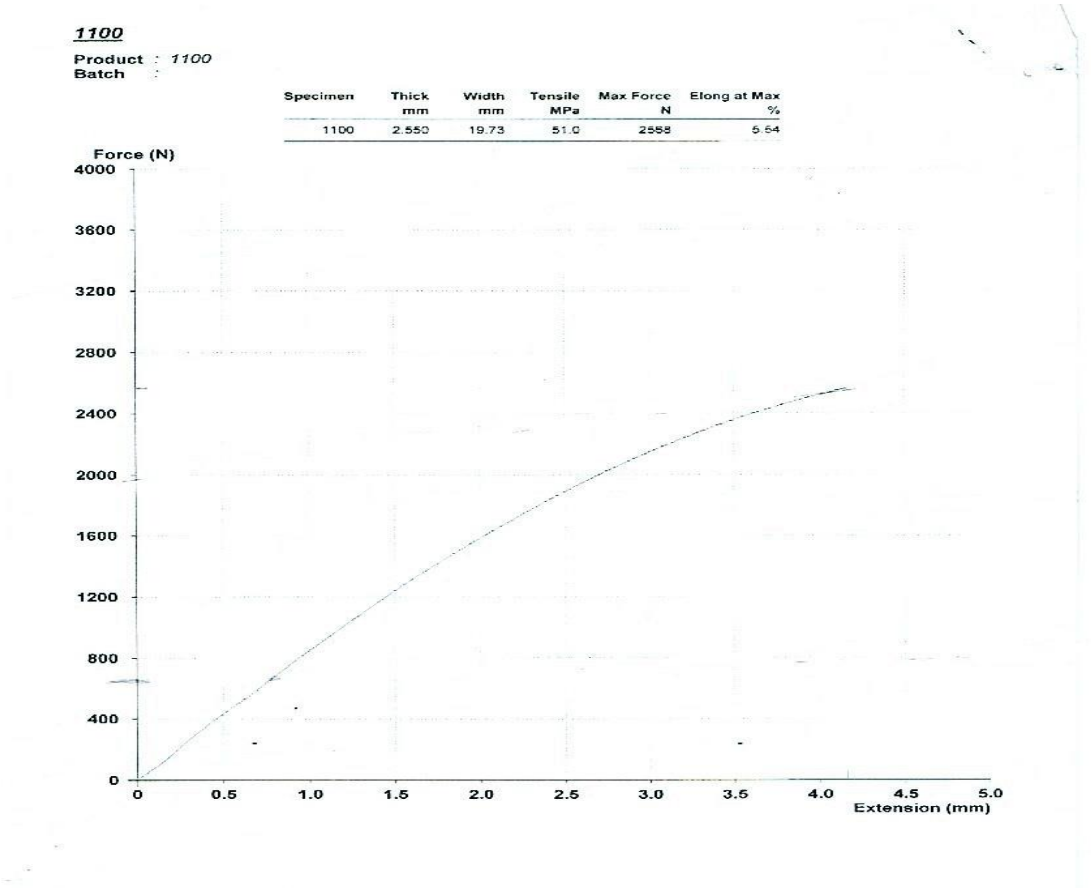
(a) Stress (MPa) versus Strain (%)for Cu electro less



(b) Force(N) versus Extension(mm)for Cu electro less



(c) Stress (MPa) versus Strain (%) for Cu electroplating



(d)) Force (N) versus Extension (mm) for Cu electroplating

Fig. 3: Tensile Strength of electroplating and electro less plated Cu on perspx substrate

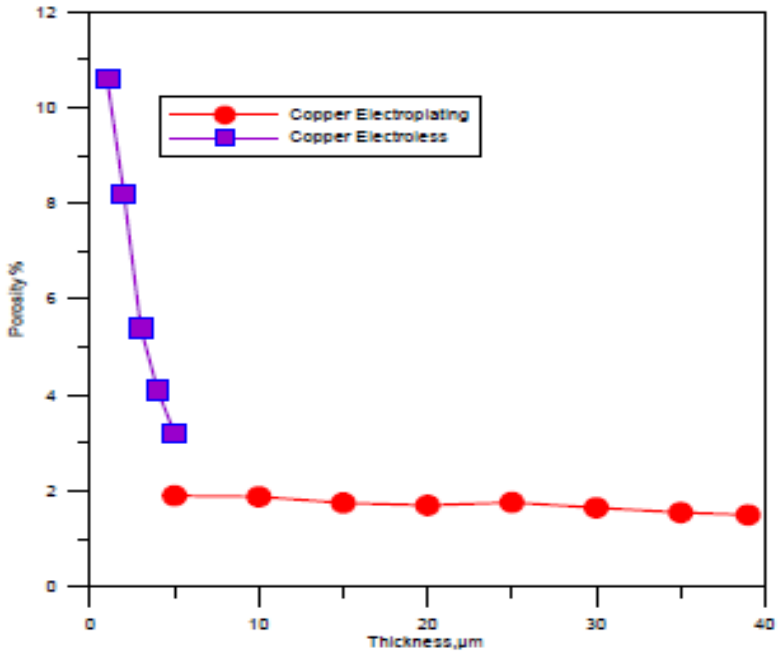


Fig. 4 Relationship between porosity and thickness of copper deposited by electroplating and electroless Substrate material was Perspex and saturated test was used to measure porosity

References

1- H. Yanagimoto, S. Dekia, K. Akamatsu, K. Gotoh,"Selective electroless copper deposition on aluminum nitride substrate with patterned copper seed layer," ThinSolid Films,Vol. 491 (2005) pp. 18~22

2- Wei-Ping Dow, Hsiang-Hao Chen, Ming-Yao Yen, Wei-Hsiang Chen, Kao-Hsuang Hsu, Po-Yao Chuang, HiroshiIshizuka, Nobuo Sakagawa and Ryoichi Kimizuka, Journal of the Electrochemical Society, 2008, 155, (12) pp. D750-D757.

3- Jia and Wang "Nickel-based activated Carbon," BioResources5 (4), 2010.

4- J. J. Kelly, C. Tian, and A. C. West, "Leveling and Microstructural Effects of Additives for Copper Electrodeposition," J. Electrochem. Soc., Vol. 146, No. 7 (1999) pp. 2540~2545

5- Charbonnier M, Romand M et al (2006) Copper metallization of polymers by a palladium-free electroless process. Surf Coat Technol 200(18–19):5478

6- Deckert CA (1995) Electroless copper plating - a review. 1. Plat Surf Finish 82(2):48

7- IEEE TRANSACTIONS ON APPLIED SUPERCONDUCTIVITY, VOL. 21, NO. 3, JUNE 2011

8- Surface & Coatings Technology 202 (2008) 5092–5102

9- Y. Zhang, T. Richardson, S. Chung, C. Wang, B. Kim andC. Rietmann, "Fast Copper Plating Process for

10- TSV Fill," Proc. of 2007 International Microsystems, Packaging, Assemblyand Circuits Technology Conference, Taipei,Taiwan, Oct. 2007, p.219-222.

11- Yang CH, Wang YY et al (1999) A kinetic study of direct copper plating via Pd catalyst and S ligand. J Electrochem Soc 146(12): 4473

12- Ono S, Naitoh K et al (1999) Initial propagation stage of direct copper plating on non-conducting substrates. Electrochimica Acta 44(21–22):3697