JOURNAL OF MATERIALS SCIENCE **38** (2003) 3285–3291

Copper deposition by Dynamic Chemical Plating

G. STREMSDOERFER, F. GHANEM
Ecole Centrale of Lyon, Engineering and Surface Fonctionnalisation Laboratory, 36 Avenue Guy de Collongue, P.O. Box 163, 69131 Ecully Cedex, France
E-mail: ifos-lpci@cc.ec-lyon.fr

Y. SAIKALI
Lebanese University, Faculty of Sciences II, El-Fanar, Lebanon

A. FARES-KARAM
Ecole Centrale of Lyon, Engineering and Surface Fonctionnalisation Laboratory, 36 Avenue Guy de Collongue, P.O. Box 163, 69131 Ecully Cedex, France

The present paper describes a new direct chemical plating method of copper, called Dynamic Chemical Plating. This low cost technology is based on spraying separate aqueous solutions containing copper metallic ions and Borohydride reducing agent. It is able to plate chemical copper at 30 μm/h at room temperature and may be used as an industrial process for metallizing polymers and non-conductors in general.

The copper plating dynamic parameters were studied as well as the substrate characteristics in order to be metallized. The wettability of the plastics surfaces and the use of a coupling agent plate, as an under-coat metallic layer, are major important parameters to start plating and increase the adhesion of metallic copper layer to the substrate. Effects of pre-treatment conditions such as corona discharge, the plating kinetics and electrical properties of the copper film are also investigated. © *2003 Kluwer Academic Publishers*

1. Introduction

Autocatalytic or electroless copper plating is widely used to metallize non-conductor surfaces and it is a key technology for manufacturing printed circuits boards. It is also used for connectors applications and as well as to pre-plate a conductive thin film on plastics for subsequent electrochemical plating. One of its most successful applications also is Electromagnetic Interference Shielding (EMI/RFI). This "wet" plating technique is a unique approach to obtain perfectly homogeneous and uniform metal deposits on a catalytic surface and it can be applied to any complex or intricate shape substrate. In spite of all these advantages, electroless plating is still suffering from several practical problems such as:

- the bath control and limited solution life
- the toxicity (i.e.: carcinogen formaldehyde compound) and ecological disadvantages (wastes treatment, use of chromic etching, . . .)
- the difficulty to plate large dimensions parts
- the plating rate which is limited to 5 μm/h for most of commercial available baths.

Added to these problems, another very important industrial inconvenience concerns the high number of processing steps, particularly the activation step. So several processes have been developed as possible substitutes. They are usually referred to as "direct plating" since the non-conductive substrate can be copper electroplated directly after a specific activation step without the need for a conductive electroless copper film.

These processes can in general be categorised into three groups. The first alternative is based on colloidal carbon or on a conductive polymer film to replace the electroless copper film [1, 2]. The second group uses Bridging Ligands based on a mixed Pd/Sn catalyst coupled with a sulphide solution dip [3, 4]. The third group uses coupling agents such as silanes which fix Pd(II) or Cu(II) [5, 6] as ultra thin, not to say atomic, conductive layer.

Although these alternative processes decrease the number of the global plating process steps, they still have the problems pinpointed above. Moreover, they are very expensive. For example, the palladium, used to obtain a catalytic surface in view to copper or nickel deposition, has a price that increased from 100$ per oz in 1997 up to 850$ per oz in 2000 [7]. The great demand of this material and the rare sources of supply explain the financial market of palladium is so tense and unstable.

Stremsdoerfer *et al.*, have developed and presented a new "direct plating" process which avoid the disadvantages listed above and in particularly the Pd/Sn step activation [8, 9]. In few seconds, it is possible to plate non-conductor surface with a Ni, Cu or Co films without a Pd catalytic activation step. For example, on polymers, a 0.3 μm NiB metallic underlayer, which is enough to start electroplating deposition, is

plated in 90 s at room temperature. This process named JetMetal^{TM}, is also called "Dynamic Chemical Plating" DCP. A detailed explanation and discussion of the dynamic aspect of the process in comparison to different conventional wet techniques called "Static Chemical Plating" are given elsewhere [10, 11]. The novelty of this Dynamic Chemical Plating is based on a sequentially highly controlled supply of the material (metallic ions Ni^{2+}, Cu^{2+}, Co^{2+}, Ag^{+}) and the energy source (reducing agent) to the substrate. In other words it can be described as a metal plating process using intermittent spraying of two or several solutions simultaneously. Using compressed air and a double nozzle spraying gun, the reducing and oxidising agents are sprayed at the same time but separately onto a non-conductor surface. Thus, a very thin liquid film is formed. This film is adsorbed on the surface and contains the active species. This film is also thermodynamically unstable which means that the oxidation-reduction reaction will occur spontaneously. But under some experimental conditions, this spontaneous reaction can be controlled to avoid coarse precipitation. These conditions are the following:

- The sprayed liquid film, which is adsorbed on the substrate, must be thin enough. So the redox reaction occurs on the surface.
- The ratio of the sprayed oxidising and reducing solutions must be adequate to give an optimal stoechiometric electrochemical reaction on the surface. This corresponds to the ratio of electrons exchanged between the oxidising and the reducing agents for a fixed sprayed volume of solutions.
- The polymer substrate must have a uniform wettability and a relatively high surface energy ($\gamma s >$ 40 mJ/m^2). Consequently, a metallic substrate is easier to plate than a plastic material.

When these conditions are fulfilled, the redox reaction will be induced on the surface instead of a spontaneous precipitation of the metallic ions in the adsorbed liquid film. Then a compact, dense and adherent nickel or copper film is formed on the substrate. Once the reaction is over in the liquid layer, the thin liquid film is refilled with active species by spraying again the solutions. The time separating two successive refills is called "relaxation time" and during this time the spraying is off. In order to ensure the thickness growth of the metallic film, the spraying is carried out intermittently using successive liquid sprays. The procedure can then be described as a sequence of several spray/non-spray steps or in other words a sequence of several spraying/relaxation steps added. With one of the double nozzle spraying gun, it is possible to cover a surface of 3.8 dm^2.

NiB dynamic plating was thoroughly investigated and presented in the past papers listed above. This manuscript shows experimental investigation and detailed study of copper dynamic plating. It presents the experimental optimisation of plating conditions as well as its kinetic evaluation. The deposits morphological and electrical characteristics are also presented.

2. Experimental

The treatment of the substrates prior to metal plating consisted in degreasing with an appropriate organic solvent depending on the nature of the used plastic. 3 mm thick plastic substrates were cut into square shaped samples (100 mm × 100 mm). Commercial grades of non reinforced Poly(ethylene terephthalate) (PET), Acrylonitrile-Butadiene-Styrene (ABS) and Poly(vinyl chloride) (PVC) polymers were tested. In order to increase the surface energy and obtain a good wettability, a 20 KV Corona discharge (DMG Instruments—France) was used. The sample-electrode distance was fixed at 4 mm and treatments were made at ambient atmosphere. The contact angle were measured using a "DIGIDROP" contact angle meter coupled to a microcomputer for image analysis (GBX Scientific Instruments-France). A commercially available concentric double-nozzle spray gun (DeViliss-AGPV2K) was modified and used to spray the aqueous solutions for plating. The spraying apparatus was automated and controlled using a "home-made" software. An oil-free air compressor was used as a spraying system during experiments. It supplies compressed air to two different tanks that contain, respectively, the reducing agent solution and the metal salt solution. The air pressure in the different compartments is independently adjustable using two different manometers. Both tanks are linked to the automated spraying gun. In this study, samples are vertically fixed perpendicularly to the spray. The distance between samples and the double-nozzle spraying gun is maintained at 40 cm. This is illustrated in Fig. 1.

The thickness of the deposit was determined gravimetrically by weighing the substrate before and after plating, and also using a Maxtek PM 500 quartz micro-balance to validate measurements. Local thickness measurements was controlled using an X-ray Fluorescence apparatus from CMI "Coating Measurement Instrument". Surface morphology of the substrates and copper deposited films were examined by Scanning Electron Microscopy (SEM) using a "Philips XL20" SEM micrograph coupled to an "EDAX" X-ray probe for qualitative and semi-quantitative elemental analysis. We used an Inductively Coupled Plasma (ICP-AES) to determine the exact elemental composition of deposits. The surface roughness was evaluated with a Perthen-Mahr type profilometer using a point which curvature radius is 0.1 μm. The Attenuated Transmission Reflectance (ATR-IR) spectroscopy technique was used to determine the chemical modifications produced on the polymer surfaces after different carried out treatments. Chemicals used Potassium Borohydride, Copper and Nickel Sulphate, Quadrol Chelated Titanium (coupling agent) were Sigma Aldrich standard grades without any further purification.

3. Results and discussion

3.1. Elaboration of a metallic primary thin film (metallic undercoat)

The preliminary simultaneous spraying of KBH_4 reducing solution and copper salt solution, using the assembly presented above, on a metallic substrate lead to

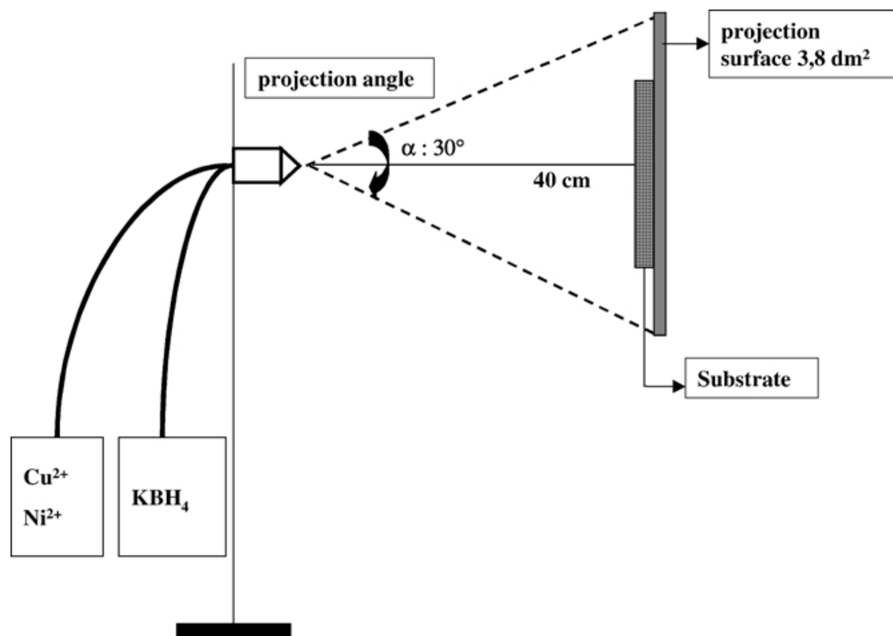

Figure 1 Schematic representation of Dynamic Chemical Plating (DCP) apparatus.

the creation of an adherent and homogeneous film. The spraying time used in this case is 100 ms and the time separating two consecutive sprays (relaxation time) is 200 ms [8]. The copper plating oxydo-reduction reaction starts immediately on the metallic surface. The same experimentation carried out on several types of polymers substrates show a completely different behaviour. The reaction start seems to depend on each substrate surface characteristics. In fact, as polymers show much weaker surface energy than metallic surfaces, this parameter seems to be crucial for a proper plating reaction.

This ascertains that for DCP an adequate high surface energy should be reached before plating a 0.5 μm metallic thin layer to serve as a primary conductive film for the next growth of electrochemical copper.

To investigate the influence of the polymer surface energy and its wettability, the process dynamic parameters have to be fixed first. The spraying and the relaxation times were kept constant at the same values mentioned above. These values were already used before to plate nickel-boron primary metallic films which thickness varied from 0.2 to 0.3 μm and obtained in 90 s of spraying at room temperature as described in details in references [10, 12].

Fig. 2 show the dynamic copper plating rate as a function of active species concentration in the sprayed solution. To determine copper sulphate optimal concentration, the reducing agent content was first kept randomly constant at 4 g/l. The sprayed volume of both reducing and oxidising solutions was the same during all measurements. It corresponds to 300 spraying. Taking into account that the spraying time is 100 ms and the relaxation time is 200 ms, the global plating time in this case is 90 s and it was used to evaluate the plating rate. We can notice that the optimal plating rate is obtained for a copper salt concentration of 30 g/l. Then, this value was fixed to determine Borohydride optimal concentration. The corresponding

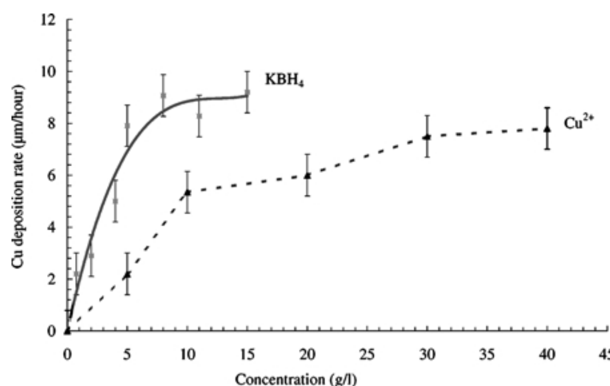

Figure 2 DCP Copper plating rate according to the reactive chemical species concentration.

curve shows that at 7 g/l of reducing agent content, the plating rate reaches its highest value. Beyond, those concentrations, both curves tend to an asymptotic evolution.

The Triethanolamine is used as a chelating agent [13, 14] at an optimal concentration of 10 g/l and the pH was fixed at 12 using Potassium Hydroxide (KOH) in order to obtain bright oxide free copper without precipitating copper hydroxides [15].

In both cases, e.g., nickel and copper plating, Titanium based coupling agents were mixed with the solution containing the metallic salt at very low content (<100 ppm). These coupling agents role is to enhance the deposition reaction start, to allow a better adhesion and to ensure an entanglement of the metallic coating on the surface of the polymer [16].

As we mentioned before, the oxidation-reduction reaction starts on the polymer surface under adequate surface energy conditions. So it is necessary to lower the wetting angle of the plastic surface to decrease the hydrophobic character of the surface and allows to the sprayed solutions to spread on the substrate surface and then to create a very thin film made of a mix of the

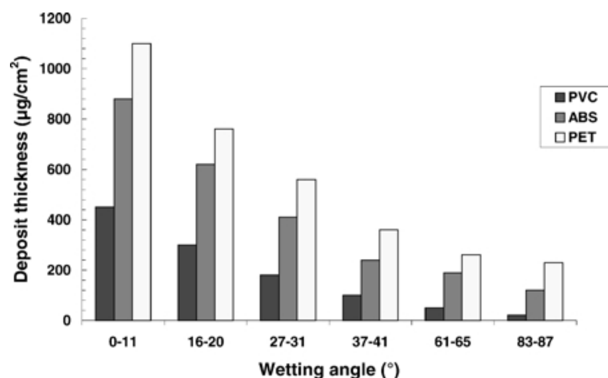

Figure 3 DCP copper film thickness as a function of surface wettability (water wetting angle) on different polymer surfaces.

solutions, the metal salt and the reducer solutions. A corona discharge treatment is used due to its wide industrial use.

By varying Corona treatment from 1 s to 60 s per cm, it is possible to change the ultrapure water wetting angle of the polymer surface from 80° to less than 10°. Fig. 3 shows, for the same volume of sprayed solutions, the mass of deposited copper according to the above mentioned wetting angle on three types of plastic substrates.

Whatever the type of polymer is, we note that for a wetting angle smaller than 10°, the weight of plated copper is 6 to 22 times higher than for the as-received degreased substrates. The analysis by infra-red spectroscopy (ATR-IR Spectroscopy) of the polymer surface before and after Corona treatment doesn't show significant modifications of the surface chemistry. This is in accordance with Romero-Sanchez *et al.* findings [17] on corona discharge for polymer surface treatment. Other authors has also established that corona treatment is more a harsh discharge technique that leads to morphological modification with few polymer chain scission and electrical charges accumulation rather than intensive chemical grafting of chemical moieties [18]. We may conclude that wettability variation is the only parameter responsible of the drastic increase of the copper plating reaction enhancement and output.

To quantify the ageing effect on the Corona Treatment as this is could be an important industrial parameter, while polymer substrates are stored to be metallized later, we measured the evolution on the wetting angle of the polymer surface with time at ambient air and room temperature. On Fig. 4, it can be noted that after

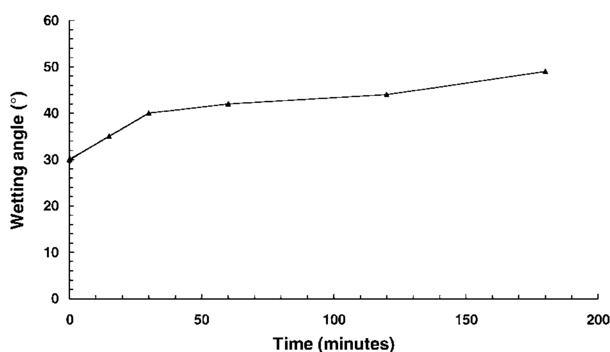

Figure 4 Effect of ageing time on water wetting angle of ABS plastic.

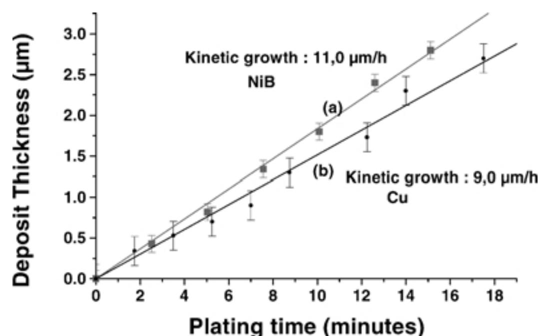

Figure 5 Growth curve of DCP Nickel (a) and Copper (b) metallic films when coupling agent is added with the metallic ions oxidising solution.

Corona treatment on ABS polymer, allowing to obtain an initial 30° wetting angle, wettability is dramatically altered after 30 min of ageing. The wetting angle of water increases greatly to reach and stabilise at 50° after 3 h. This means that dynamic chemical plating should be carried out during the 30 min after corona treatment. Impurities adsorption and the fast decrease of electrical charge load after corona effect on the material are probably the causes of the hydrophobicity increase of the surface [17]. The wetting angle of a substrate of ABS that are non-treated by Corona is about 77°.

For copper metallic coating, the simultaneous spray of the reducing agent, of the copper salt and the coupling agent on the substrate surface, leads to an homogeneous deposit when the substrate wettability angle is smaller than 30°. After thirty spraying sequences, the metallic film is uniform and continuous on the whole substrate. It is useful to remind that a sequence is defined as a spray followed by a relaxation time. Fig. 5 shows the growth of a copper metallic film and of a nickel-boron film, for comparison purposes, on corona treated ABS substrate. Kinetic growth at room temperature is linear and respectively of 11.8 μm/h for NiB and 9 μm/h for copper. It is important to note that these metallic films were plated on the plastic surface directly after degreasing without any acid etching or mechanical roughening operation and without using an expensive step of activation by immersion in a PdSn colloidal solution such as in conventional electroless plating processes.

ICP & EDS elemental analysis, of copper samples which thickness vary from 0.5 μm to 5 μm, indicates that the ratio of copper and boron, stay constant all over the metallic film growth. The metallic films contain 98% of copper, 0.17% of boron, and the remaining concerns the coupling agent element, mainly titanium. On Fig. 6 curve (a) shows the electrical resistance variation of a copper metallic primary according to the spraying sequences, in other words the film thickness. The electrical resistance, between 5 cm distant 2 points, on the surface regularly decreases and reaches 0.26 Ω for a metallic film thickness of 2.8 μm.

Curve (b) shows the same electrical resistance variation but for a nickel-boron metallic coating according to the film thickness. Although at a NiB film thickness of 2 μm, the electrical resistance tend to an asymptote around 2.55 Ω. These are quite high electrical resistance values, compared to conventional electroless NiB or

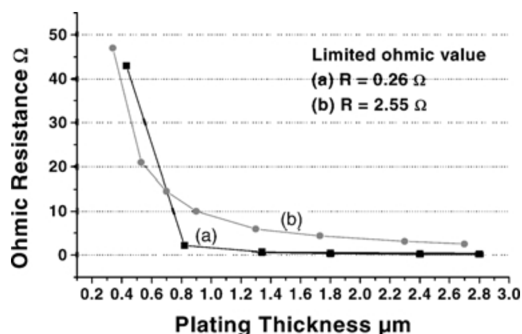

Figure 6 Electrical resistance variation of a DCP copper (a) and nickel (b) metallic films according to the layer thickness in the presence of coupling agent in the metallic ions solutions.

copper plated films, and are probably due to the intrinsic electrical properties of plated NiB or Cu as cross-section micrographs of such coatings did not show any significant porosity [10, 11]. In fact the presence of titanium, as a residue of the coupling agent, may form an intrinsic fine oxides layers which is probably responsible of these results.

3.2. Improvement of copper DCP metallic films

The deposition of a copper or nickel metallic films as described above does not allow to obtain films with high electrical conductivity. Electrical resistance reaches in both cases a relatively high limit value. Or, the interest of the first metallic copper or NiB film is to obtain a good conductive adherent layer on polymers thanks to the use of a coupling agent. In the next experiments we plated only 0.3 μm of Copper films as a primary adherent base metallic film and then we sprayed copper solutions with the same composition as before except for the coupling agent which was suppressed. Fig. 7 shows the growth of the copper films elaborated on a copper primary layer (a) and on a nickel primary one (b).

The suppression of the coupling agent allows to increase significantly the growth kinetic of copper films and to reach within a short time of plating, low values of electrical resistance.

In the first case (a), the copper growth kinetic is linear and the plating rate reaches 28 μm/h. In the second case (b), the film growth kinetic can subdivided into 3 steps. In step I, DCP copper plating has a rate of 12 μm/h. This step characteristic of the copper deposition start and the influence of catalytic properties of the nickel primary film, which contains the coupling agent, is dominating. In step II, NiB film is covered with the first copper layers and the catalytic influence of this pure copper is now preponderant and the kinetic of copper deposition reaches 17 μm/h during a temporary short time. In step III the kinetic growth reaches its nominal value of 28 μm/h and we may notice that this plating speed is proper to the pure copper that does not contain any coupling agent residues. Neither the substrate, nor the base primary film present any more influence on the growth kinetic. It is important to mention that all these experiments and measurements were done at room temperature. Consequently, DCP copper plating rate may be considered very high compared to the performance of conventional electroless copper baths that function at the same temperature.

Elemental analysis of the DCP pure copper films with different thickness indicate a copper content of 99.94% and 0.06% of boron. No other residues were found which confirms our previous hypothesis that residues of titanium based coupling agent alters copper films electrical properties while it enhances significantly its adhesion to the substrate. The global plating output can be defined as the weight of plated copper compared to the weight of sprayed copper. So it is the mass rate of: $MCu_{deposit}/MCu^{2+}_{spray}$ and this output rate is 60%. This can be eventually improved by using a more efficient dual nozzle spraying gun in the future. Fig. 8 shows the electrical resistance variation of DCP pure copper films measured between 2 points of a 5 cm distance. These films are plated on a 0.3 μm copper underlayer (curve a), a 0.3 μm NiB underlayer (curve b) and a 2 μm NiB underlayer (curve c). As a reminder, the underlayer is a coupling agent containing metallic film. We note that on one hand the limit value of

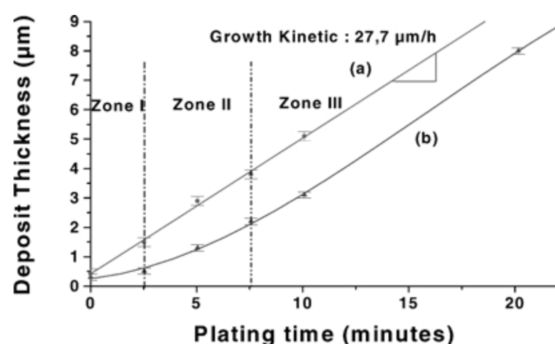

Figure 7 Growth curve of a pure DCP copper film on (a) 0.3 μm copper underlayer and (b) 0.3 μm NiB underlayer. Both underlayers contain titanium based coupling agent.

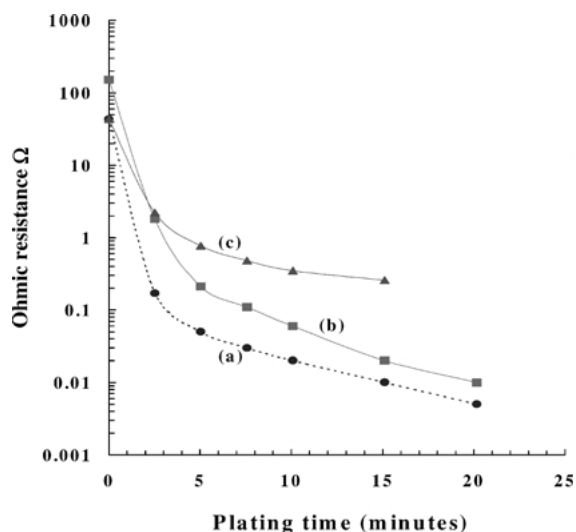

Figure 8 Electrical resistance variation of a DCP pure copper film according to the layer thickness on (a) a thin copper underlayer (b) thin NiB underlayer (c) thick NiB underlayer.

the resistance is less than 0.01 Ω and it is reached for a pure copper thickness of 5 μm. On the other hand, the plating time to reach a specific electrical conductivity is much shorter for a pure copper film plated on copper primary film than for the same pure copper but plated on a nickel primary film. We notice also that NiB underlayer should be kept as thin as possible when it is used, because it influences significantly the upper layer electrical conductivity (curve c). This is an important factor for an industrial process capacity where a certain conductivity is needed to ensure an electrochemical thickening after or for simple EMI shielding applications.

3.3. Characterisation of the film homogeneity

As noted in the experimental section, the spraying gun and the samples are in a fixed position. As illustrated in Fig. 1, The gun-sample distance is 40 cm and the spraying solid angle (cone shape spraying) is about 30°. In other words, the spraying gun can plate a circular zone which diameter is approximately 24 cm. XRF measurements show that the metallic film has an homogeneous thickness in the whole circular area if the deposit final thickness is under 1 μm. For thicker coatings we notice a different behaviour. Fig. 9a illustrate schematically a 3 μm plated circular zone. We have investigated the thickness profile all over this circular area using XRF also. Measurements made from the left to the right side at the middle of the plated area indicates a regular gaussian thickness distribution as shown in Fig. 9b. We can notice that the central area of the plated circular zone (between two dashed lines) has a thicker deposit than the left and right edges. At the extremity of these edges (data not shown on the curve), the metallic film becomes very thin (<0.5 μm). Fig. 9c shows thickness measurements made from the top side to the bottom side in the middle of the plated area. We can notice that deposit thickness of the top edge is very low compared to the central area (between two dashed lines) or to the bottom edge. Moreover, the bottom area show thicker deposit until the bottom end of the substrate. So, we may conclude that when the spraying gun is operating in a fixed mode, the plated circular zone can divided into 3 sub-areas A, B & C. In sub area A & B, the metallic film is relatively homogeneous but thicker in A than in B. In sub area C the metallic film is quite thick and homogeneous. In fact, when spraying, the reactive liquid solutions flow gravimetrically to the bottom side. As the oxidation-reduction reaction of Borohydride with Copper complexed ions is much slower than for Nickel ions [19], the reaction in liquid solution flowing or dropping from the top side occurs at the centre and the bottom of the circular zone. This explains the varied thickness of the DCP copper coating. It is important to note that this was not observed in DCP NiB metallic films even for 10 μm thick coatings [20] and it is attributed to the extremely fast redox reaction between Borohydride and Nickel ions. Consequently, for industrial DCP copper plating the spraying gun should not be fixed when operating but it should rather scan

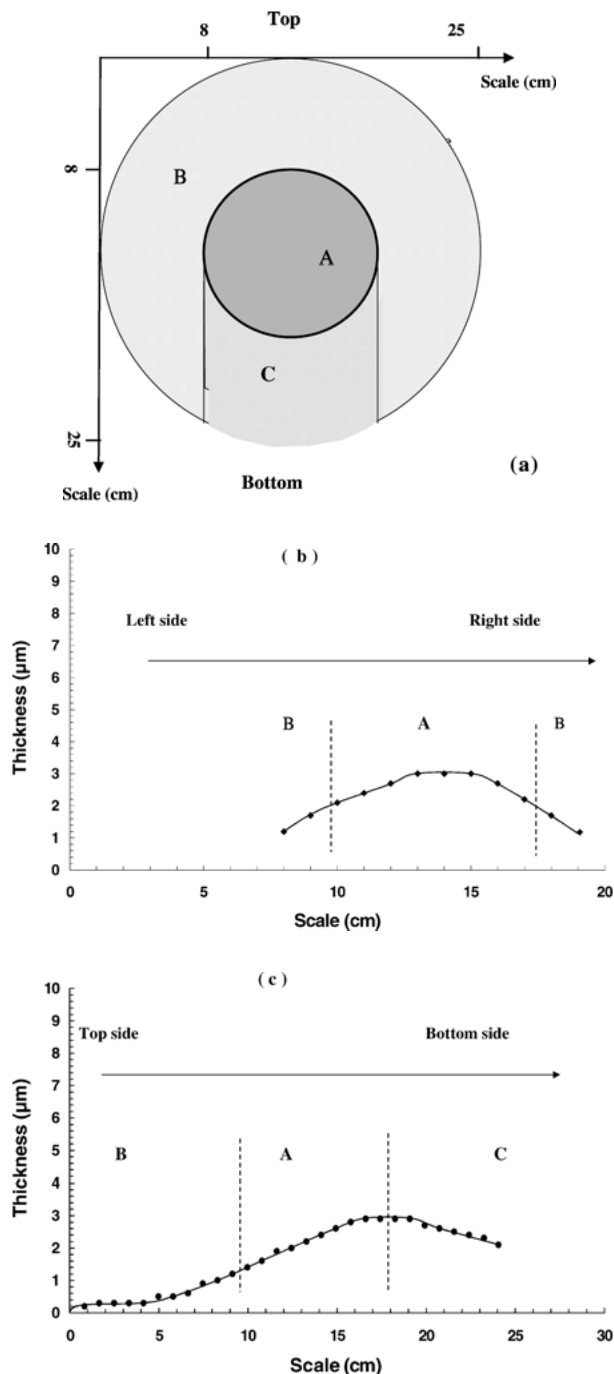

Figure 9 (a) Schematic representation of a copper plated circular zone using DCP spraying gun. (b) XRF thickness profile from the left side to right side and (c) from the top side to bottom side, of this circular shaped copper film.

the surface to be plated, similarly to organic painting processes.

Qualitative test of adhesion obtained by cross-hatching tests (ASTM D 3359) on the plated surface followed by a peeling operation using an adhesive tape (Scotch^{TM} 3M 250) indicates that metallic films are strongly adherent to the ABS substrates up to 10 μm. Below this thickness, surface etching and roughening becomes necessary. A more detailed study of the adhesion mechanisms should be made to better understand the reaction at the interface of the plastic substrate. SEM observation (Fig. 10) shows a granular microstructure and homogeneous morphology with average grain diameter of 8 nm.

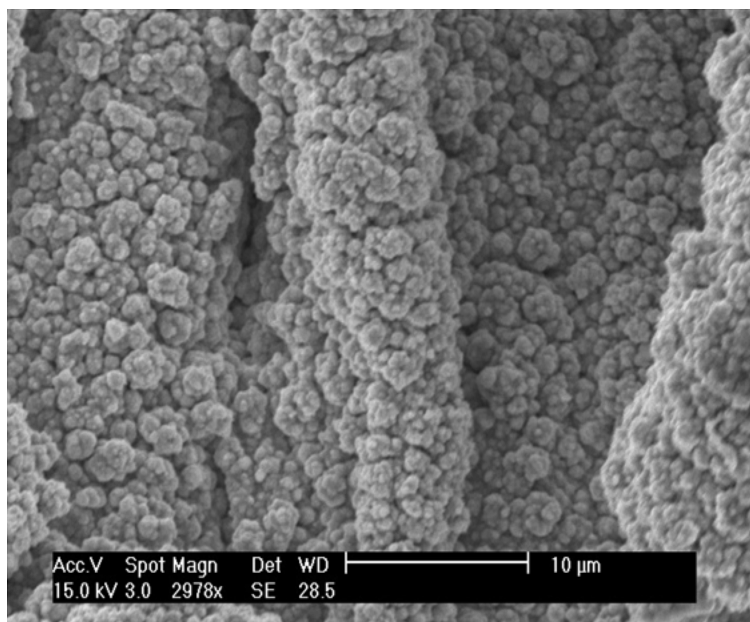

Figure 10 SEM photo of a pure DCP copper deposit plated on a copper underlayer. ABS polymer is the base substrate.

4. Conclusion

In order to reduce the number of electroless copper plating steps (catalysis step usually carried out in $SnCl_2/PdCl_2$ mixed colloidal solutions) and to overcome environmental problems, the copper metallization of polymers was performed using a direct Dynamic Chemical Plating process. The growth of copper plating film onto an under coat of NiB and Cu have been studied and it demonstrate that a decrease of water contact angles (good wettability and high surface energy) is a crucial parameter to start DCP. The new treatment process has its advantages in terms of electrical properties and desirable shielding effectiveness. Moreover copper plating speed reaches 30 μm/h at room temperature which is much faster than conventional electroless processes.

This process is suited for circuit boards manufacturing and electronic equipment that need electromagnetic shielding. As DCP uses spraying guns, it should operate by scanning the substrate to be plated while metallizing especially if this substrate has a complex geometrical shape. Adhesion properties of plated films are excellent and highly adherent films (thickness <10 μm) on non etched ABS were obtained.

References

1. F. A. LOWENHEIM, in "Modern Electroplating" (Wiley-Interscience, New York, 1976), Chap. 31.
2. K. H. DIETZ, *Plating Surface Finishing* **82**(7) (1995) 60.
3. C. H. YANG, Y. Y. WANG, C. C. WAN and C. J. CHEN, *J. Electrochem. Soc.* **143**(11) (1996) 3521.
4. C. H. YANG, C. J. CHEN, Y. Y. WANG and C. C. WAN, US Patent no. 08;643,232 (1996).
5. S. L. BRANDOW, W. J. DRESSICK, C. R. MARRIAN, G. M. CHOW and J. M. CALVERT, *J. Electrochem. Soc.* **142**(7) (1995) 2233.
6. W. J. DRESSICK, C. DULCEY, J. GEORGER, G. CALABRESE and J. M. CALVERT, *ibid.* **141**(1) (1994) 210.
7. Platinum 2000 Interim Review, edited by Johnson Matthey (2000) p. 15.
8. G. STREMSDOERFER and A. FARES KARAM, French patent, 97-06834 (1997), WO 9854378.
9. A. FARES KARAM and G. STREMSDOERFER, *Plating and Surface Finishing* **85**(1) (1998) 88.
10. *Idem.*, in "Metallized Plastics 5&6: Fundamental and Apllied Aspects" edited by K. L. Mittal (1998) p. 137.
11. *Idem.*, in Proceedings of the American Electroplaters and Surface Finishers Society Annual Meeting, Cincinnati, June 1999, edited by AESF, p. 1.
12. *Idem.*, *Metall* **53**(12) (1999) 682.
13. K. KONDO, J. ISHIKAWA, O. TAKENAKA, T. MATSUBARA and M. IRIE, *J. Electrochem. Soc.* **137**(6) (1990) 1859.
14. *Idem.*, *ibid.* **138**(12) (1991) 3629.
15. WOLFGANG RIEDEL, in "Electroless Nickel Plating" (ASM International, Ohio, 1991) Chap. 2.
16. A. J. KINLOCH, in "Adhesion and Adhesives" (Chapman & Hall Editions, London, 1987) Chap. 5.
17. M. D. ROMERO-SANCHEZ, M. M. PASTOR-BLAS, J. M. MARTIN-MARTINEZ, P. A. ZHDAN and J. F. WATTS, *J. Mater. Sci.* **36** (2001) 5789.
18. J. M. STROBEL, M. STROBEL, C. S. LYONS, C. DUNATOV and S. J. PERRON, *J. Adh. Sci. Technol.* **5** (1991) 119.
19. Y. OKINAKA and T. OSAKA, in "Advances in Electrochemical Science and Engineering," Vol. 3, edited by H. Gerisher and C. W. Tobias (VCH Publishers Inc., Weinheim & New York, 1994) p. 55.
20. A. FARES KARAM and G. STREMSDOERFER, *Mater. and Corr.* **52** (2001) 257.

Received 29 July 2002
and accepted 5 March 2003