



Characterising nonuniform electrodeposition and electrodisolution using the novel wire beam electrode method

YONG-JUN TAN* and KIM YONG LIM

School of Materials Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore
(*author for correspondence, e-mail: asyjtan@ntu.edu.sg)

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Abstract

An electrochemically integrated multi-electrode system namely the wire beam electrode (WBE) has been applied as a new method of characterising nonuniform electrodeposition and electrodisolution, by measuring and identifying characteristic patterns in electrodeposition and electrodisolution current distribution maps. Various patterns of electrodeposition current distribution have been obtained from Watts nickel plating and bright acid copper plating baths with the effects of several affecting factors such as bath concentration, temperature, agitation and electrolyte flow. Typical patterns of electrodisolution current distribution have also been detected over a WBE surface under anodic dissolution. This work suggests that the WBE method can be used as a new tool for monitoring, characterising and optimising electrodeposition and electrodisolution processes in the laboratory, and can also be applied as an experimental method to verify the accuracy and completeness of mathematical models for electrodeposition and electrodisolution.

1. Introduction

Nonuniform distribution of electrodeposition and electrodisolution currents may significantly affect the applicability of electrodeposition techniques such as electroplating, electroforming and localised electrodeposition, and also of electrodisolution techniques such as electroetching, electropolishing and electromachining. For instance, in the electroplating industry nonuniform distribution of electrodeposition current is not desirable since it could result in an unevenly deposited electrode surface that cannot meet functional and dimensional requirements. Sometimes this may even result in burnt deposits or immersion plating when local plating currents are too high or too low [1]. On the contrary, in electrochemical machining and localised electrodeposition techniques nonuniform distribution of electrodeposition current is preferred since a highly focused electrodeposition current is required for creating a fine metallic structure of accurate dimensions.

Common practices of controlling the distribution of electrodeposition or electrodisolution current are largely performed on trial-and-error bases by adjusting bath parameters such as the geometry of the bath, the positions of anodes and cathode, the composition of electrolyte, and so on. These industrial practices rely upon personnel experience, and sometimes the assistance of the Hull cell test [2] and mathematical model-

ling. The Hull cell method is a conventional laboratory technique for qualitative characteristics and assessment of plating baths by determining the relationships between the distance of the cathode from the anode and the thickness of electroplated layer, for a given set of parameters. The Hull cell has a wedge-shaped plate with the cathode being purposely placed at an angle to the anode so that a nonuniform current distribution is normally attained. Mathematical modelling is usually based on the general theory of the potential field and involves the computation of the equipotential surfaces and the mapping of corresponding current paths by solving Laplace's equation. Although both the Hull cell and mathematical modelling methods could help favourable adjustments in the bath conditions such as bath geometry, they suffer from some drawbacks. For instance, the Hull cell test does not provide real time information regarding the distribution of electrodeposition currents and it is undoubtedly tedious. Mathematical modelling considers mainly the effects of bath geometry and electrolyte conductivity on current distribution, it might not delineate clearly the nonuniform distribution of electrodeposition currents in a practical bath, which is often under the influences of complex factors such as electrochemical polarisation and mass transport in the bath. In order to improve the Hull cell and mathematical modelling methods, some new developments have been made during recent years. For

instance, a modified Hull cell namely the Curvilinear Hull cell [3] and new mathematical equations [4] have been developed for determining both the primary and secondary current distributions in order to allow quantitative determination of the throwing power of a bath [3, 4]. New mathematical models have also been developed for calculating the local distribution of the secondary current along the cathode in a Hull cell [5] and for predicting cathodic shape change during electrodeposition [6–8]. However, to the knowledge of the authors, there is a lack of laboratory technique that is able to instantaneously measure electrodeposition or electrodisolution current distribution.

Aiming at overcoming this problem, an electrochemically integrated multi-electrode namely the wire beam electrode (WBE, Figure 1) [9–15] has been developed into a means of measuring electrodeposition current instantaneously from every location of an electrode surface and for mapping localised distribution of electrodeposition currents [14–15]. In such applications, the wire bundle surface in a WBE simulates a one-piece electrode under electrodeposition with each wire acting as an individual local electrochemical sensor to measure

electrochemical parameters from local areas. Since the surface area of each wire in the WBE is much smaller compared to the total electrode working area, each wire surface can be assumed to be electrochemically uniform even if the whole WBE surface is electrochemically nonuniform. This assumption allows electrochemical theories and methods of describing uniform electrodeposition and electrodisolution processes to apply to each wire in a WBE. Preliminary experiments have shown that a WBE surface can simulate a one-piece electrode surface under electrodeposition and can be employed to measure the distribution of electrodeposition currents for generating a current distribution map over the plated surface, at any point of time during the course of electroplating [14].

This present work is designed to investigate the relationships between characteristic patterns in nonuniform electrodeposition and electrodisolution current distributions and bath parameters such as bath concentration, temperature and electrolyte flow. The objectives are to further develop the WBE method into a new tool for monitoring, characterising and optimising electrodeposition and electrodisolution processes, and also for

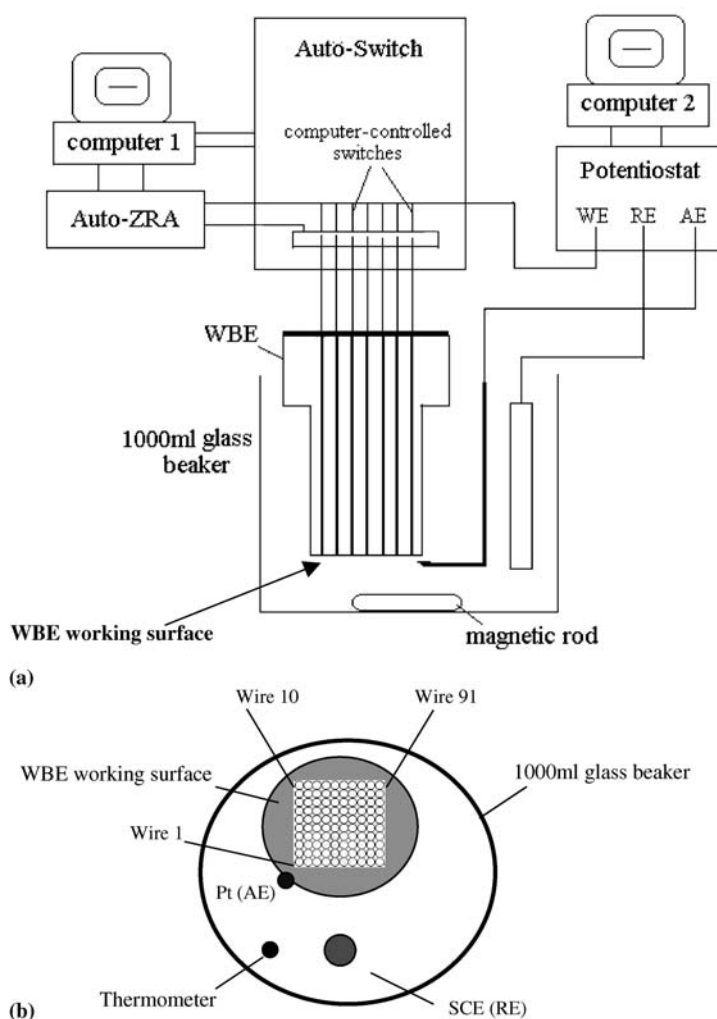


Fig. 1. Schematic diagrams showing experimental setup for electrodeposition and electrodisolution. (a) Setup for nickel plating; (b) plane view of apparatus layout for nickel plating.

verifying the accuracy and completeness of mathematical modelling of electrodeposition and electrodisolution.

2. Experimental

Figure 1 shows an experimental setup, which incorporates a three-electrode electrochemical cell with a WBE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and an auxiliary electrode. The WBE used in this work was made from 100 identical mild steel (UNS No. G10350) wires embedded in epoxy resin and insulated from each other with a very thin epoxy layer. Each wire had a diameter of 0.18 mm and the total area occupied by the wire beam was approximately 3.24 cm²; the total metallic area was approximately 2.55 cm². The working surface of the WBE was polished with 1000-grit silicon carbide paper and cleaned with ethanol. The auxiliary electrode, a fine platinum wire (for nickel plating) or a fine copper wire (for copper plating), was specially designed and positioned with only its tip exposed to the electroplating solution for the purpose of creating a nonuniform bath geometry that would help identifying 'primary' current distribution.

Electrodeposition experiments were carried out under potentiostatic control with the WBE as the cathode, while electrodisolution was carried out with the WBE as an anode. This was realised by connecting the WBE to the 'WE' terminal of an ACM Instruments GillAC device (AutoAC, ACM Instruments, UK) functioning as a potentiostat. The potentiostat was used to cathodically (or anodically) polarise the WBE surface below (or above) its rest potential when performing an electroplating experiment (or an electrodisolution experiment). The impressed electroplating current for each wire (e.g. I_k for wire k) was measured by connecting another GillAC device, which performed as a zero resistance ammeter, in sequence between the chosen wire terminal and all other terminals shorted together using a computer controlled automatic switch (custom made). This was repeated for all 100 wires so that an electrodeposition current distribution map could be generated. The data was then compiled with the Mathcad 2000 Professional software, from which a map representative of the current distribution across the WBE surface was generated. The measurements of anodic electrodisolution currents were carried out in a similar way.

2.1. Watts nickel electroplating

Nickel electroplating was carried out under potentiostatic control with the WBE immersed in 800 ml of Watts bath (329.79 g l⁻¹ NiSO₄ · 6H₂O; 45.04 g l⁻¹ NiCl₂ · 6H₂O and 37.94 g l⁻¹ H₃BO₃) [1] under static conditions at 47–52 °C. The inert anode, a platinum wire, was coated with a thick layer of epoxy so that only a tip of approximately 1.5 mm in length was left exposed

and conducting. This anode tip was placed approximately 4 mm from wire 1 of the WBE, as shown in Figure 1(b). The plating solution was warmed to approximately 52 °C before it was introduced into the Watts bath. After a settling time of 1 min, a cathodic polarisation voltage of -120 mV was applied to the WBE. The first current mapping was carried out after approximately 2 min of nickel plating. Subsequent current measurements were recorded after 30, 60 and 90 minutes' nickel plating. This nickel plating experiment formed the reference for a series of nickel electroplating experiments in which affecting parameters were individually investigated. In experiments studying the effects of bath stirring, prior to applying the cathodic polarisation voltage, magnetic stirring was applied to the bath and hence a flow pattern analogous to stirring a cup of coffee from the centre with a spoon was introduced to the plating solution.

2.2. Bright acid copper electroplating

The bright acid copper bath was prepared by mixing 217.5 g l⁻¹ of CuSO₄ · 5H₂O and 52.7 g l⁻¹ H₂SO₄. Copper electroplating was carried out under static conditions at approximately 25 °C with the WBE immersed in 800 ml of diluted bright acid copper bath, which was prepared by diluting the standard bath by 100 times. A copper wire with an exposed length of 1.5–2.0 mm was used as the anode and was placed approximately 5 mm from wire 1 of the WBE. After a settling time of 1 min, a cathodic polarisation voltage of -500 mV was applied to the WBE. This copper plating experiment formed the reference for a series of copper electroplating experiments in which affecting parameters were individually investigated.

2.3. Anodic electrodisolution experiment

After Watts nickel electroplating was completed, the applied polarisation was changed from cathodic to anodic (+40 mV) and thus the WBE surface was under anodic electrodisolution (in the same Watts nickel bath).

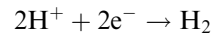
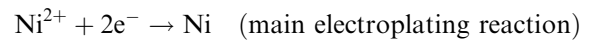
3. Results and discussion

The distribution of a deposit over an object is determined by the local current density at each point as well as by the cathode efficiency of the bath at that current density. The determination of characteristic patterns in local current distribution maps is important for characterising a nonuniform electrodeposition process. There are two major types of characteristic current distributions – primary and secondary current distributions. The primary current distribution is determined completely by the geometry of the plating cell. The secondary current distribution is the distortion of the

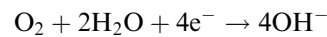
primary current distribution due to electrode polarisation, which is affected by factors including electrolyte concentration, conductivity of solution, temperature, agitation. If an electrochemical cell is very nonuniform, the primary current distribution is also markedly nonuniform. For a nonuniform electrochemical cell setup shown in Figure 1, if 'primary' current determines current distribution, the bath geometry would result in a current distribution pattern with the highest deposition current at wire 1 where the platinum inert anode is closely placed and the lowest at wire 91 that is located farthest.

In a Watts nickel plating bath, as shown in Figure 2, the characteristic pattern in electrodeposition current distribution maps is higher nickel electroplating currents distributing along the edges of a WBE with the magnitude decreasing in a contour-like manner towards the centre of the WBE surface. This characteristic feature is also the most common current distribution pattern reported previously for bright acid copper electroplating baths [14] and it is often referred to as the 'secondary' current distribution pattern. This pattern clearly indicates that the cell geometry was not the controlling factor in current distribution, since currents did not centre at wire 1 location where the anode wire was closely placed. This current distribution

pattern is in agreement with a well-known phenomenon that thick deposits tend to concentrate at edges and bumps of a workpiece. This phenomenon can be explained by chemical heterogeneity over the WBE surface – the edges and corners of a WBE would receive more reactants (metallic and hydrogen ions) from solution due to two- or three-dimensional ion diffusion to support three possible cathode reactions in the system:



(main side-reaction, hydrogen evolution)



(side-reaction, oxygen reduction)

After 5 h of electroplating under -40 mV of cathodic polarisation, the thicknesses of nickel deposits on the WBE surface were measured using a Nikon Epiphot 200 optical microscope. As shown in Figure 2(d), nonuniform cathodic current distribution resulted in an uneven distribution of deposit thicknesses with relatively thicker deposition at the corners and edges of the electrode. The thickness profile in Figure 2(d) correlates well with the current distribution map in Figure 2(c), i.e. thicker

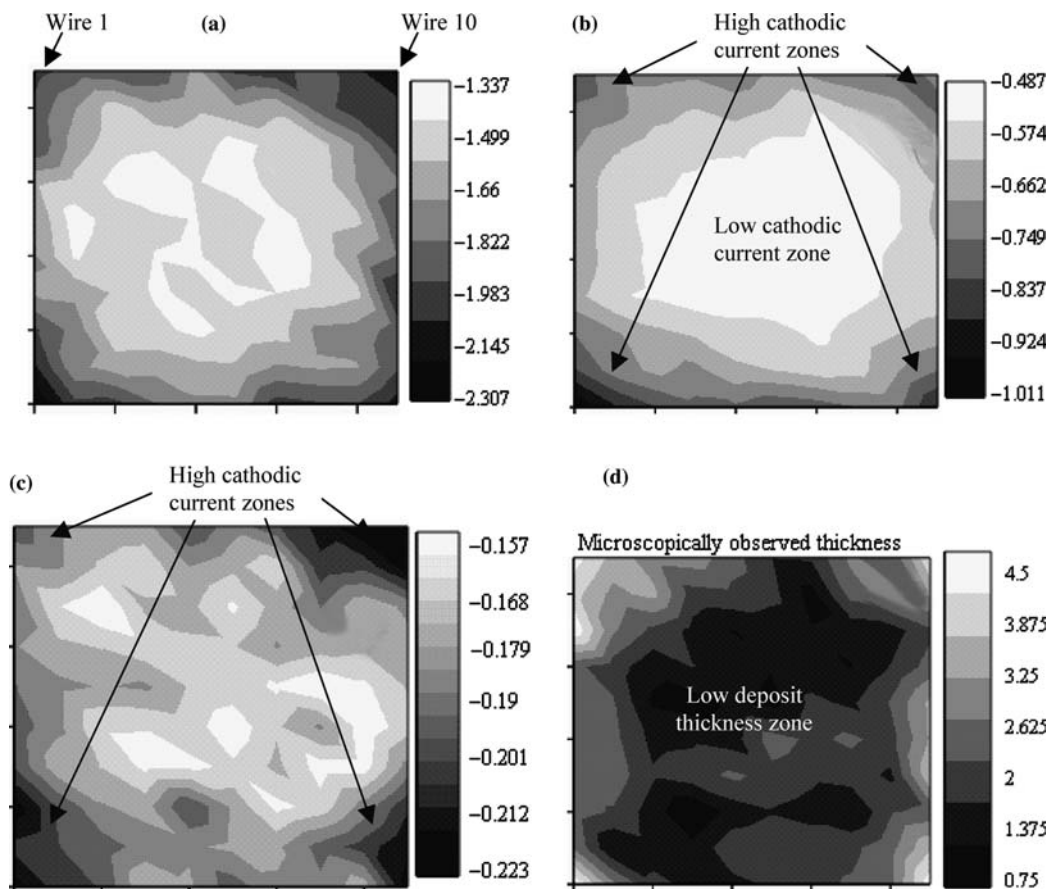


Fig. 2. Current distribution maps recorded from a Watts nickel bath after electroplating for 30 min. (a) -120 mV cathodic polarisation; (b) -80 mV cathodic polarisation and (c) -40 mV cathodic polarisation. (d) The thickness profile of nickel deposit on the WBE after five hours' plating with -40 mV of cathodic polarisation voltage (in μm , determined using a microscope). Current values are in mA cm^{-2} .

deposits were measured at locations where higher electroplating currents were registered.

The current distribution pattern was found to change with parameters, such as bath concentration, temperature, agitation and electrolyte flow. With the reduction in bath concentration, the current distribution pattern changed gradually from the 'secondary' current distribution type (shown in Figure 2) to a type shown in Figure 3. This new pattern, which is often referred to as the 'primary' current distribution pattern, has a characteristic of higher currents at locations in proximity to the anode and lower currents at regions away from the anode location, indicating an increase in dependence on bath geometry and platinum anode location. For instance, compared with Figure 2(a),

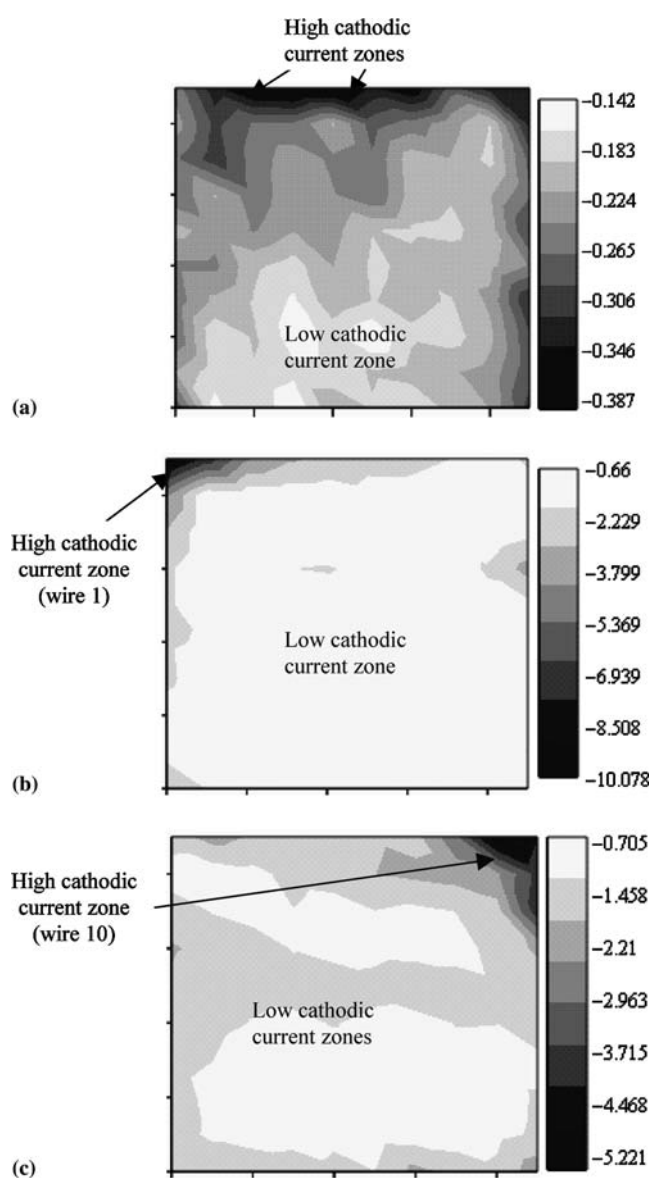


Fig. 3. Current distribution maps recorded from a 5% Watts nickel bath and a 1% bright acid copper baths. (a) 5% Watts nickel bath (-120 mV, after 120 min); (b) 1% bright acid copper baths (-500 mV, after 90 min); (c) 1% bright acid copper baths (-500 mV, after 60 min) with anode near wire '10'. Current values are in mA cm^{-2} .

Figure 3(a) clearly shows that the cell geometry was a key determining factor of current distribution, since currents were obviously concentrated at wire 1 location where the anode wire was closely placed. This current distribution pattern was found to depend heavily upon the concentration of solution, as shown in Figure 3(b) and (c); current distribution become more localised with the further reduction in bath concentration. Obviously the primary current distribution, which is determined completely by cell geometry and is independent of the properties of the electrolyte solution, played a controlling role in determining current distribution.

In many cases the effects from both primary and secondary currents coexist. The secondary current distribution is always more or less of an improvement in uniformity over the primary distribution, but in general, it cannot overcome the overriding influence of the primary current distribution [16]. The significance of secondary current can vary with experimental conditions and the duration of plating experiment. Obviously the nonuniform current distribution pattern shown in Figure 3 is mainly due to a less significant secondary current contribution. This is in agreement with industrial experience; a tendency for the actual current distribution to follow the 'primary' current distribution with decreasing bath concentration and electrolyte conductivity.

Figure 3(b) and (c) shows current distribution maps obtained from diluted bright acid copper bath (1% of the standard bright acid copper bath), where the current distribution was also of a 'primary' type with the majority of the plating current concentrated at either wire 1 or wire 10.

Adjusting fluid flow was found to change the pattern of current distribution. When nonuniform fluid movement was introduced to the Watts nickel plating bath with 200 and 600 rpm stirring, as shown in Figure 4, current distributions had the characteristic feature with higher currents along the wires 10–91 edge where the flow rates were higher. This phenomenon is ascribable to an enhanced rate of mass transfer. As shown in Figure 1(b), the wires 10–91 edge on the WBE is closest to the vessel wall hence there is more vigorous flow through this narrower channel portion.

The effect of flow on current distribution was further investigated by centring the WBE, which led to a change in flow pattern to spiral-type turbulence in the centre portion of the bath. Since the WBE was centred in the beaker, the centre region of the electrode surface was located in the eye of the spiral and experienced the least amount of agitation. Figure 4(c) shows that the centre portions of the electrode surface registered current values approximately three times lower than the edges. The results from this experiment have therefore confirmed that fluid flow significantly influences current distribution.

Bath temperature was found to be another factor that affected, not only the rate of deposition, but also the

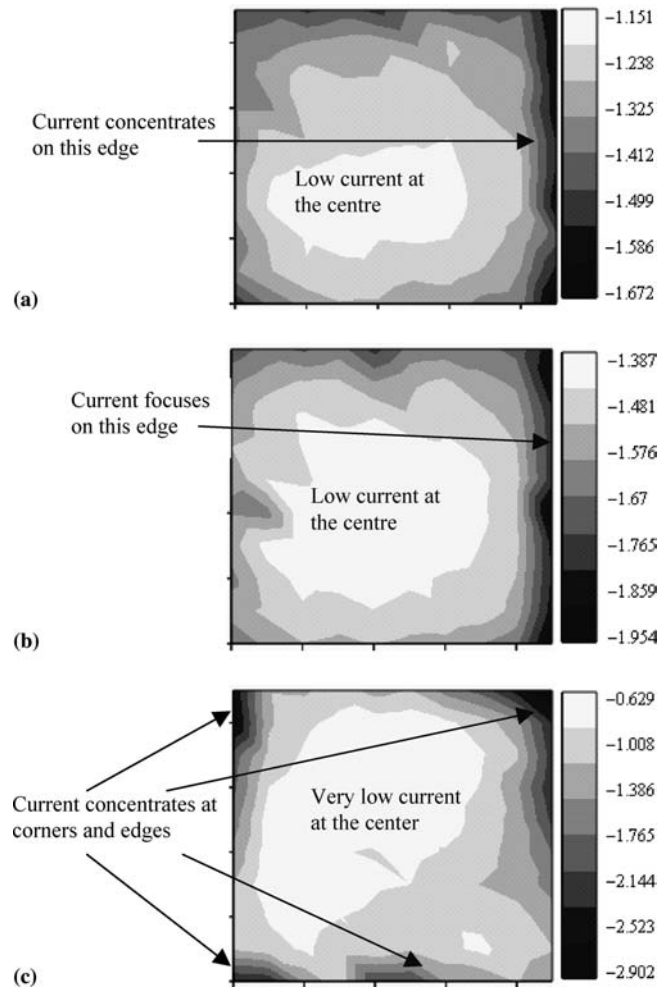


Fig. 4. Current distribution maps recorded from a Watts nickel bath after electroplating with -120 mV cathodic polarisation voltage for 90 min. (a) With 200 rpm stirring; (b) with 600 rpm stirring; (c) with 600 rpm stirring and the WBE centered. Current values are in mA cm^{-2} .

current distribution. For instance, when the temperature was reduced from the stipulated temperature range (48 – 53 °C) to ambient temperature (20 – 21 °C), the current distribution pattern showed low covering power. As shown in Figure 5, some of the electrode locations registered only negligible currents, indicating low covering power. When the WBE surface was visually inspected after rinsing with deionised water and dried after electroplating, such areas correlated well with wires whose surfaces suffered either partial or total absence of nickel. An increase in temperature was also found to significantly increase the rate of electrodeposition. The effects of temperature on the plating process are complex since higher temperature increases the rate of diffusion and increases ionic mobility, and therefore the conductivity of the bath. It also increases the rate of evaporation, rate of hydrolysis of bath constituents, and the rate of decomposition of additives. The opposing effects make it difficult or impossible to predict the best temperature of operation for any given bath, which therefore must be determined experimentally. This method could be used as a practical tool of instantaneous determination of the temperature dependence of a

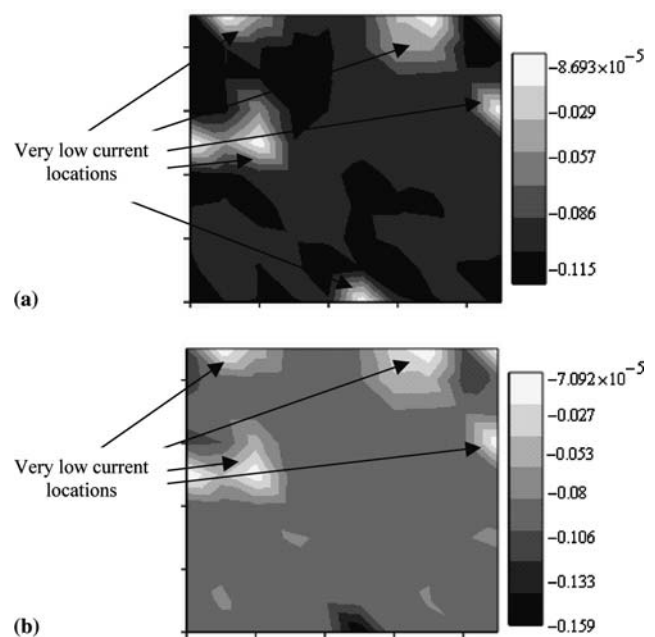


Fig. 5. Current distribution maps of plating at room temperature after (a) 30 min and (b) 60 min. Current values are in mA cm^{-2} .

bath. It can also be used as a means of evaluating the effectiveness of techniques that could improve covering power, such as the use of an undercoat, modifying bath composition, modifying the cathode surface and surface finish, applying an initial strike current or a special strike bath etc.

When depositing noble metals such as copper on active metals such as mild steel, a very common problem is immersion plating. Indeed, significant immersion plating, indicated by the positive current in Figure 6, was detected from acid copper plating bath. Although the general pattern from the bath was one of 'primary' type when the bath concentration was increased to 5% (i.e. -500 mV, 5%, 20–21 °C, static, 5 mm from wire '1'), it is evident that some wires had started registering positive current values from the 3rd measurement (i.e. after 60 min). At the end of 90 min, the number of wires with positive current values had increased as evident from Figure 6(b) and (c). During the experiments, the WBE was always polarised cathodically, and thus the measured current values should rightfully be a cathodic current with a negative value. The presence of positive currents signifies that anodic dissolution other than reduction was occurring over these wires with positive current values. This process is usually called immersion plating or displacement deposition – anodic dissolution

of the steel at sites adjacent (lowest internal iR drop) to those at which copper was plating. Such deposits are often spongy and nonadherent and thus it is not possible to plate copper satisfactory on steel surfaces from simple copper salt solutions. Indeed, visual inspections of the WBE surface after plating revealed that some wires had distinctive dark brown coloured deposits in contrast to the usual colour. The wires that registered positive currents corresponded well with the identified wires showing dark brown deposits. When the electrode surface was dried with a soft tissue upon completion of the experiments, nonadherent deposits were observed to collect on the tissue. This experiment demonstrates that the WBE method can be used to study immersion plating phenomenon.

In the above immersion plating experiment, despite having positive immersion plating currents recorded after 60 min, there had been no dislodgement of the deposits in the bath. However, deposit peeling-off was encountered in the copper bath when agitation was introduced to the bath by rotating the magnetic rod (-500 mV, 1%, 20–21 °C, 200 rpm, 5 mm from wire 1). Although the current distribution taken after 2 min (Figure 7(a)) is free from positive current, as shown in Figure 7(b), positive currents were initiated quickly and positive current areas increased remarkably with time.

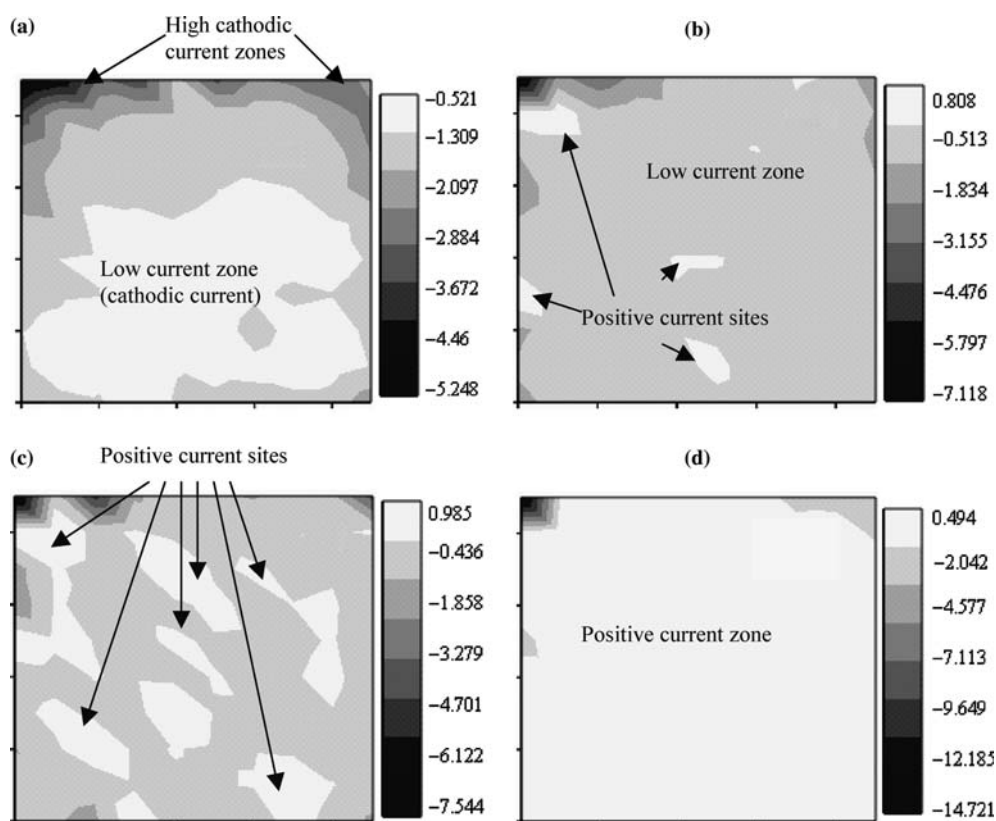


Fig. 6. (a)–(c) Current distribution maps of plating with 5% bright acid copper bath at 20–21 °C (-500 mV cathodic polarisation), and (d) at 33–37 °C. (a) After 30 min of plating; (b) after 60 min of plating; (c) after 90 min of plating; (d) 33–37 °C after 90 min of plating. Current values are in mA cm⁻².

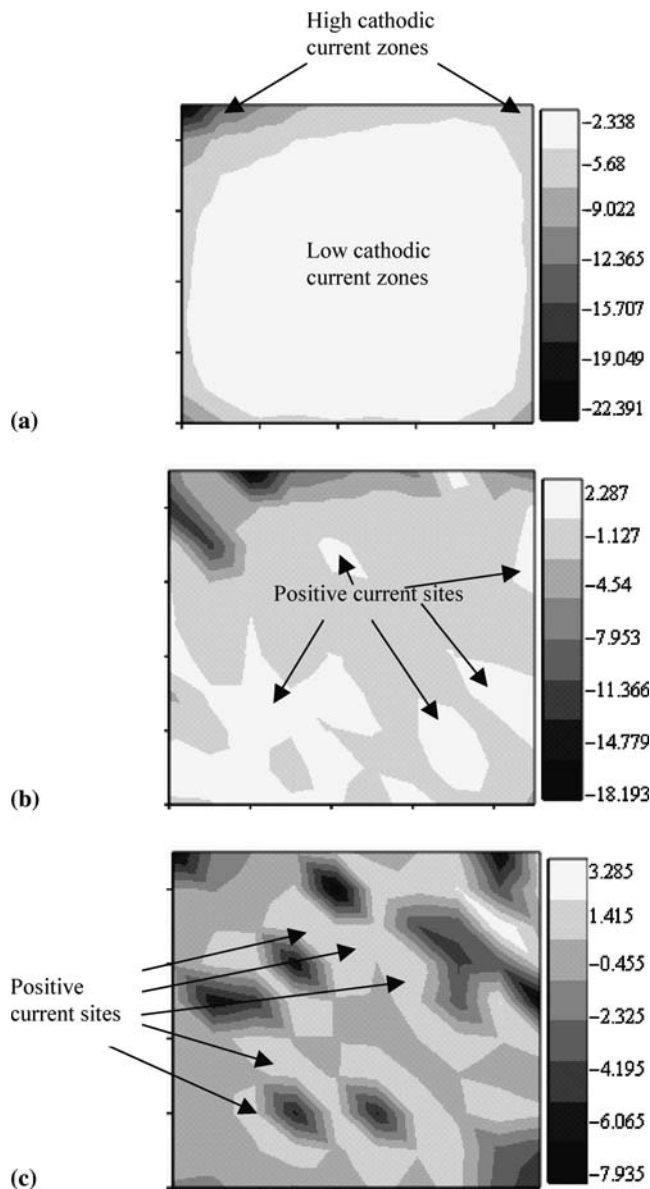


Fig. 7. Current distribution maps of plating with bright acid copper bath (-500 mV cathodic polarisation, 1% concentration, 20–21 °C, 200 rpm bath agitation, anode 5 mm from wire '1'). (a) After 2 min of plating; (b) after 30 min of plating; (c) after 60 min of plating. Current values are in mA cm⁻².

The positive immersion current values were much larger than those in Figure 6. Obviously the centrifugal force generated by the rotating magnetic rod in the bath led to dislodgement of nonadherent deposit from the WBE, resulting in significant increase in positive current areas with time. With the extension of the plating exercise, as shown in Figure 7(c), the current distribution map developed a characteristic feature that appeared to show local peeling-off of non-adherent deposit with large anodic current, adjacent to large cathodic current. At the end of 60 min, when the WBE was removed from the plating solution and visually inspected, the wires that suffered deposit dislodgement were found to match the positive current sites in

Figure 7(c). Indeed, in industry a cyanide copper bath is usually used for depositing a thin, adherent copper layer before the workpieces are transferred into a bright acid bath for high speed or bright deposit plating, where the final thickness is attained. Such practice leads to the significant reduction in free copper ion concentration through complexing with the cyanide ion and the effect of immersion deposition is avoided. Such practice is reported to overcome the non-adherent, powdery deposits produced from directly plating with acid baths [1]. This experiment suggests that the WBE method could be used to evaluate such process and could be a useful tool in the search for cyanide-free copper baths.

After nickel electroplating was completed, the polarisation was changed from cathodic to anodic and thus the WBE surface was under anodic dissolution (in the same bath). Figure 8 shows typical anodic current distribution maps recorded from the nickel-plated WBE. As shown in Figure 8, active electrodis-solution spots were clearly observable. The pattern of nonuniform electrodis-solution current distribution appeared to indicate etching of the WBE surface with active dissolution at spots that appeared to distribute randomly over the surface. The active dissolution area appeared to be growing over the electrodis-solution period.

4. Conclusions

The wire beam electrode (WBE) has been applied as a means of characterising nonuniform electrodeposition and electrodis-solution by measuring and identifying characteristic patterns in electrodeposition and electrodis-solution current distribution maps. Various characteristic current distribution patterns have been obtained from Watts nickel plating and bright acid copper plating baths with the effects of several affecting factors such as bath concentration, temperature, agitation and electrolyte flow. The most common pattern in the electrodeposition current distribution maps was 'secondary' current distribution. In low concentration baths, the typical electrodeposition current pattern was found to be 'primary' current distribution, a pattern that shows higher currents at locations in proximity to the anode and lower at regions further away. Characteristic electrodeposition current patterns showing the effects of nonuniform fluid movement, immersion-plating, peeling-off of noncoherent deposits on current distribution patterns have also been detected. Preliminary experiments have also revealed nonuniform electrodis-solution current distribution, a pattern of random distribution of active dissolution spots over a WBE surface that was under anodic polarisation. This work suggests that the WBE is a practical tool that can be utilised to monitor, characterise and optimise electrodeposition and electrodis-solution processes.

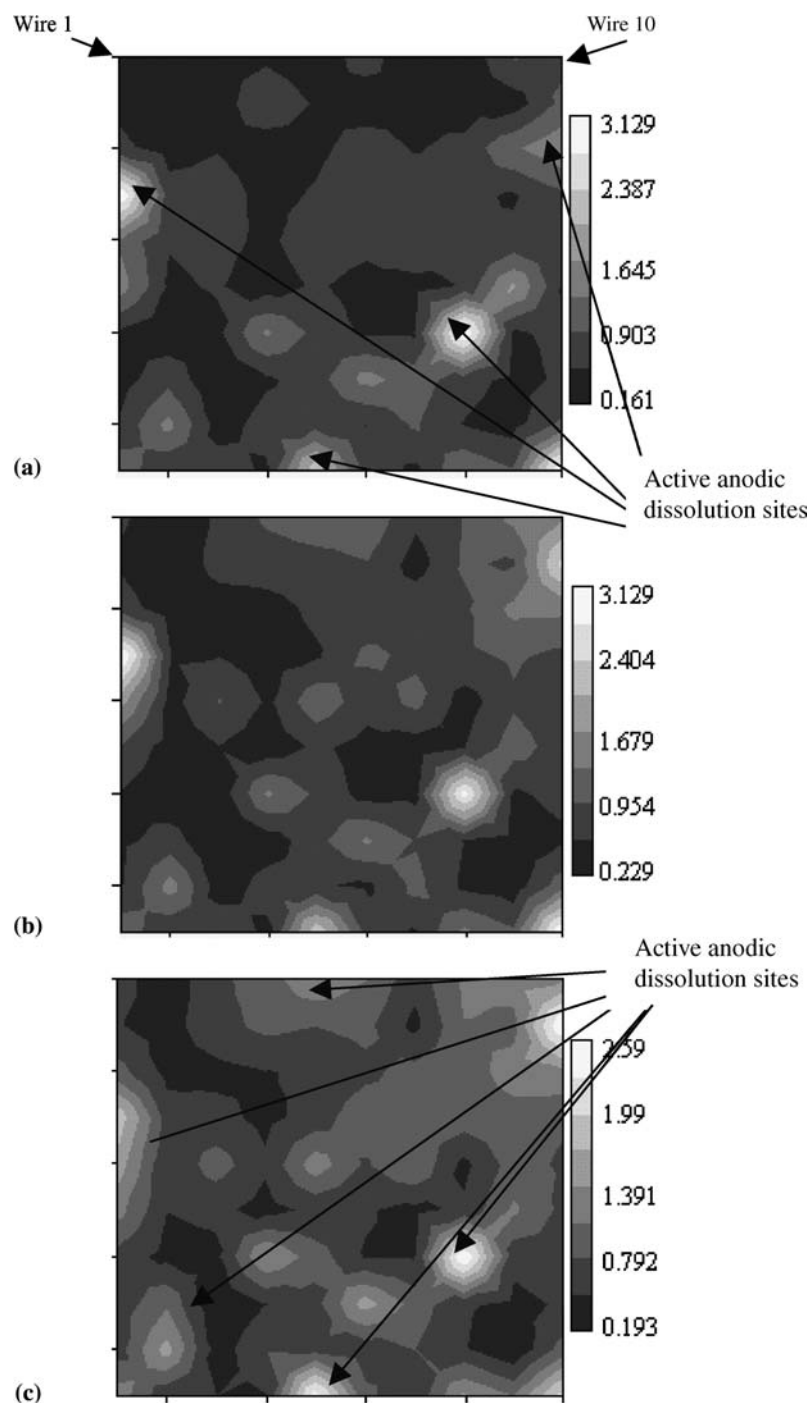


Fig. 8. Electrodisolution current distribution maps measured after a WBE was under anodic electrodisolution for various periods under anodic dissolution (+40 mV). (a) Measured between 2 and 19 min; (b) 33 and 50 min; (c) 61 and 78 min. Positive current indicates anodic reaction. Current values are in mA cm^{-2} .

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