

Description

This invention relates to electroplating.

Electroplating encompasses many scientific disciplines including electrochemistry, hydrodynamics and transport phenomena, organic and inorganic chemistry, materials science, and metallurgy, which, in turn, involves an appropriate selection of testing equipment and operating parameters. One of the most critical parameters of electroplating is the interfacial transport and its relation to current density. Once the choice for the bath composition has been narrowed down, the definition and the selection of current densities and transport conditions become critical factors which determine the bath performance and the plated product properties. To this end, several advanced techniques are being used in electrochemical research and development.

Rotating electrodes, such as rotating discs, disc-rings, ring-ring electrodes and rotating cylinders, create a defined hydrodynamic condition in the operating cell while the electrochemical measurements are being performed giving, in each experiment, information on a single current density. However, with few rare exceptions, the range of current densities in plating processes is typically wide. Ten to twenty percent variation from the nominal current density for more simple and up to 200 percent for more complex parts command a wide range of functional efficiency of the plating process. Under such conditions, information needed concerning the effect of a broad range of current densities requires numerous tests.

Hull cell, developed by R. O. Hull in 1939 as a quality control and developmental tool, permits in a single test to preview a range of current densities which provide a desired plating characteristic at a given total current. The Hull cell is described in R. O. Hull, "Proceedings of American Electroplaters Society", 27 (1939), pp 52-60 and in U.S. Patent No. 2,149,344 issued to R. O. Hull on March 7, 1939. Also see a book by Walter Nohse et al. entitled "The Investigation of Electroplating and Related Solutions with the Aid of the Hull Cell", Robert Draper Ltd., Teddington, England, 1966, especially pages 17-25.

The Hull cell is schematically represented in FIG. 31. The Hull cell, generally designated as 310, is a four-sided, flat bottomed container, 311, of certain capacity (typically in mls.) in which flat vertically positioned an anode, 312, and a cathode, 313, are arranged at an angle each to another. Typically, cathode is also at an angle to both of two side walls, 314 and 315, of the container. The test panel is only partially submersible in an electrolyte, 316. Several sizes of Hull cells are commercially available with solution capacities of 250, 267, 320,

534 and 1000 mls. The unique feature of the Hull cell, due to the arrangement of the anode to cathode geometry, is its ability to electrodeposit on the test panel a metal across a range of current densities depending on the total applied current. The current densities range from low current density at that end of cathode 313 which forms an acute angle with wall 314 to high current density at the end of the cathode forming an obtuse angle with wall 315. In FIG. 32 is represented a theoretical current density distribution in a typical standard Hull cell with applied total current of 2A.

The characteristic design feature of the Hull cell is the acute angle between anode 312 and cathode 313 combined with the effect of cell wall 314 making the acute angle to the cathode at the low current density end portion of cathode 313. The angle between the electrodes and the shielding of the cell wall 314 provide the current density distribution. At the low current end where wall 314 is at an acute angle to the cathode, the primary current density is infinitely small. Towards the center of the panel the current increases gradually reaching its maximum at the high current density end. A pattern of deposits obtained at this wide range of current densities is used as an indicator of the quality of the product that can be obtained if the plating is performed at any nominal current density within the given range. In a single test one can select a range of current densities which provide desired plating characteristics. However, the use of the Hull cell is limited, especially under high liquid velocity conditions, due to the lack of mass transfer control, uneven deposition rate at specified current densities and lack of high speed liquid mixing. In an experiment with varying hydrodynamics and mass transport along the panel, the obtained patterns could be a result of both current density and hydrodynamic conditions. Such a result would be irrelevant to the operating conditions and could not be used as a guide in bath performance evaluation.

A typical range of current densities and mixing conditions for a specific electroplating process is usually defined in the operating manual for that process. In order to keep the production quality at the specified level, operators perform a quality control tests at regular intervals employing the Hull cell. Based on such tests, corrective actions are applied to maintain the bath electrodeposition performance. Unfortunately, regardless of many common denominators, in most instances the pattern obtained is a result of vaguely defined variables such as the mixing speed, location of the stirring bar, preparation of the sample and others.

Irreproducible and limited solution agitation is usually provided in a Hull cell by a fixed rate reciprocating paddle, a magnetic stirrer or a forced

gas mixing near the cathode/solution interface. By using such an arrangement, it is difficult to obtain consistently reproducible results and to correlate these to a manufacturing operation where the solution agitation can vary significantly depending upon the application and the desired plating rate. For example, in barrel plating operations the solution is barely moving relative to the work piece while in jet plating applications the solution velocity can reach several meters per second. Over such a wide range of hydrodynamic conditions, the effects of chemical equilibria, additives, contaminants and other components of the plating solution on the quality of the product can vary considerably.

Particularly important is the interpretation of the effects of impurities on the pattern appearance such as peeling, dullness, or black deposit at low current density end of the panel. These symptoms will vary depending on the mixing conditions of the cell. However, the Hull cell apparatus is limited in providing information regarding a specific plating process which may be affected by variations in solution agitation.

Furthermore, in many instances, particularly in modern plating facilities, high speed plating baths with liquid velocity of several meters per second are being employed. For such conditions, information developed on the basis of the interpretation of a Hull cell panel obtained at typical Hull cell liquid velocities of 20-30 cm/sec. could be meaningless. Use of the Hull cell with higher mixing rates leads to spillage and usually gives little clue on the solution performance.

Another uncertainty is connected with inconsistencies in current density distribution. Hull cell panels are usually interpreted with the scale of current densities that are attributed to the position on the panel. The position of the liquid meniscus on one side and the vicinity of the cell bottom on the other side of the panel may influence the rate of deposition. As a result, the thickness distribution at each current density designation can vary considerably leading to erroneous interpretation. Such variations result from an uneven current distribution which is inherent to the Hull cell design and can significantly affect the reproducibility and the accuracy of panel interpretation leading to losses in production and disorientation in R & D efforts.

Unfortunately, there are no viable alternatives to the Hull cell, today. Therefore, it is desirable to have a device which combines, in a single unit, controlled cell hydrodynamics and resulting uniformity of mass transport at the panel interface with the capability of measuring wide range of current densities on a single experiment. Only in such experimental conditions, patterns obtained on the panel would reflect the expected performance of the process at specified mixing rate.

According to the present invention, there is provided a cell as defined in claim 1.

This invention is a Hydrodynamically Modulated Hull cell (hereinafter referred to as "HMH cell") which can be used for quality control and for developmental applications and which combines, in a single unit, the capability of providing for well-defined cell hydrodynamics and measuring wide range of current densities on a single experiment.

The HMH cell utilizes an elongated, cylindrically shaped measuring instrument in which a cathode and an anode are vertically spaced along a central longitudinal axis of the instrument, forming a single coaxially arranged unit with the anode being below the cathode. The instrument is capable of being rotated about its longitudinal axis. This permits one to vary in a controlled manner the solution agitation while effectively applying a panel size and current density range typical for a standard Hull cell. This apparatus can be used to establish the functionality of electroplating solutions in the liquid velocity range of the electrolyte from quasi stationary to up to several meters per second.

Brief Description of the Drawing

FIG. 1 is a schematic representation of a HMH cell;

FIG. 2 is a schematic representation of a HMH cell with a partially submerged test panel;

FIG. 3 is a schematic representation of an electric field distribution in the HMH cell of FIG. 2;

FIG. 4 is a schematic representation of a current density distribution along a test panel in HMH cell of FIG. 2;

FIG. 5 is a schematic representation of a HMH cell with a partially submerged test panel and one horizontal baffle;

FIG. 6 is a schematic representation of an electric field distribution in the HMH cell of FIG. 5;

FIG. 7 is a schematic representation of a current density distribution along a test panel in HMH cell of FIG. 5;

FIG. 8 is a schematic representation of a HMH cell with a partially submerged test panel and two horizontal baffles;

FIG. 9 is a schematic representation of an electric field distribution in the HMH cell of FIG. 8;

FIG. 10 is a schematic representation of a current density distribution along a test panel in HMH cell of FIG. 8;

FIG. 11 is a schematic representation of a HMH cell with a partially submerged test panel and three horizontal baffles;

FIG. 12 is a schematic representation of an electric field distribution in the HMH cell of FIG. 11;

FIG. 13 is a schematic representation of a current density distribution along a test panel in HMH cell of FIG. 11;

FIG. 14 is a schematic representation of a HMH cell with an insulating cone shield;

FIG. 15 is a schematic representation of an electric field distribution in the HMH cell of FIG. 14;

FIG. 16 is a schematic representation of a current density distribution along a test panel in HMH cell of FIG. 14;

FIG. 17 is a schematic representation of a HMH cell with a completely submerged test panel;

FIG. 18 is a schematic representation of an electric field distribution in the HMH cell of FIG. 17;

FIG. 19 is a schematic representation of a current density distribution along a test panel in HMH cell of FIG. 17;

FIG. 20 is a schematic perspective representation of a preferred embodiment of the HMH cell with three horizontal baffles;

FIG. 21 is a schematic representation of a preferred embodiment of the measuring instrument being used in the HMH cell;

FIGs. 22, 23 and 24 are a sequence of three charts presenting deposit thickness distribution on a test panel deposited in a HMH cell with three horizontal baffles at positions corresponding to 0.0043, 0.0216 and 0.0864 A/cm² (4,20 and 80 ASF), respectively, and a total applied current of 2A;

FIGs. 25, 26 and 27 are a comparison of burned deposit on a high current density portion of a test panel in a standard Hull cell (FIG. 25) with that on a test panel in a HMH cell at 10 and 100 cm/s liquid velocity (FIGs. 26 and 27, respectively) from an aqueous solution containing 25 g/l Pd at 40 °C and with a pH 7.5;

FIGs. 28, 29 and 30 are a schematic comparison of impurities effect on a low current density portion of a test panel in a standard Hull cell (FIG. 28) with that of a test panel in a HMH cell at 10 and 100 cm/s liquid velocity (FIGs. 29 and 30, respectively) from an aqueous solution containing nickel sulfamate at 45 °C, with pH=4.0 and with 100 ppm of copper as an impurity;

FIG. 31 is a schematic representation of the standard Hull cell;

FIG. 32 is a schematic representation of a current density distribution along a test panel in a standard Hull cell;

FIGs. 33, 34 and 35 are a sequence of three charts presenting deposit thickness distribution on a test panel deposited in a standard Hull cell at positions corresponding to 0.0043, 0.0216 and 0.0864 A/cm² (4,20 and 80 ASF), respectively, and a total applied current of 2A.

Detailed Description

The HMH cell is schematically presented in Figure 1. The cell, 10, includes a container, 11, for holding electrolyte, 12, and an elongated, cylindrically-shaped measuring instrument, 13, suspended vertically in the container. The instrument is capable of being rotated about its longitudinal central axis.

Instrument 13 includes an elongated cylinder, 15, of a suitable insulating material, a sleeve-like metal cathode, 16, arranged coaxially on the cylinder, and a metal anode, 17, positioned at a lower end of cylinder 15 coaxially with it and in a longitudinally spaced relation to the cathode. Two sliding electrode contacts ("slip rings"), 18 and 19, on the cylinder are provided above cathode 16 as current collectors for the cathode and the anode, respectively. Upper part of cylinder 15 is securable to an arm, 21, of a support arrangement (not shown). Arm 21 supports instrument 13 suspended within container 11 and includes a cover 22 and a suitable drive means, such as a belt drive or a motor (not shown). Cover 22 encloses container 11 and assists in positioning instrument 13 coaxially of container 11. Drive means is for providing rotation to instrument 13 about its longitudinal central axis at a desired rate. The rate of rotation may be selected to be within a range from 10 to 10,000 RPM.

Cathode 16 includes a flexible test panel, 212, (FIG. 21) removably affixable to cylinder 15. This may be accomplished in various ways, two of which are as follows. In one instance opposite vertical ends of a flexible test panel may be inserted into a vertical longitudinal slot (not shown) in the surface of cylinder 15 while conforming the panel to the circumference of the cylinder. Alternatively, horizontal ends of the test panel conformed to the circumference of the cylinder may be secured by means of suitable fasteners (not shown). Such fasteners may include rubber bands which are slid over end portions of the panel. Electrical contact to the test panel may be provided by at least one conductive contact embedded into the surface of the cylinder, such as an area, a ring or a sleeve. The contact area, ring or sleeve is electrically connected to slip ring 18, such as via a conductor, 213 (FIG.21), placed internally of the cylinder.

Anode 17 is positioned below cathode 16 and is spaced from it by means of a relatively short length of insulating cylinder 14. The spacing should not be less than that required to avoid undue bubbling at the space between the anode and the cathode. An excessive spacing is undesirable since it could adversely affect electric field distribution. A spacing of from 2 to 20 mm is useful, with 5-10

mm being preferred. Anode 17 is shown in FIG. 1 as being secured near the end of cylinder 15. Anode 17 may be secured to the cylinder in any suitable manner. This may involve a metallic fastener, such as a bolt exposed to the electrolyte or hidden within a removable insulating disc or an insulating disc provided with a threaded portion for mating with its counterpart in cylinder 15. The type of fastening anode 17 to the cylinder is not important so long as anode 17 is supplied with energy, for example, via slip ring 19. This may be accomplished by connecting anode 17 and slip ring 19 by a conductor (not shown) placed internally of cylinder 15. In FIG. 1, anode 17 is shown in the form of a thin disc, the radius of which is from 2 to 5 mm greater than the radius of cylinder 15. Other sizes and forms of anode 17 may be useful. For example, radial dimension of the disc may be equal or even smaller than that of cylinder 15. Also, the thickness of anode 17 may vary over a relatively large range. The important prerequisite is the symmetric geometry of anode 17 about the longitudinal axis of cylinder 15 in order to distribute the electric field uniformly about the anode.

Cylinder 15 may be provided with an internal rod or shaft placed along the longitudinal axis of the cylinder (e.g., see FIG. 21). The rod or shaft may be needed to reinforce the cylinder and to provide means for imparting rotation to the cylinder. A metal rod or shaft may act as a conductor for connecting anode 17 to slip ring 19.

Cylinder 15 is made of an insulating material which is not adversely affected by the plating reaction, is non-conducting and non-contaminating with respect to the solution and the resultant metal deposit. Suitable material for the cylinder may be selected from such insulating materials as epoxy, polyethylene, polypropylene, polyvinyl chloride, "Teflon", Registered Trade Mark fiberglass and other plastic materials possessing the above qualities. Container 11 and cover 22 are also of a material which is resistant to the effects of the electroplating solution and is non-conductive and non-contaminating with respect to the solution and the deposit. Suitable materials for the container and for the cover may be selected from such materials as glass, glazed ceramics, plastics, such as epoxy, polyethylene, polypropylene, polyvinyl chloride, "Teflon", fiberglass and other materials possessing the above qualities. The size of the container is at least such that the test panel is only partially immersed in a predetermined volume of an electroplating solution, e.g. about up to 80-90 percent of the panel height may be submerged in the solution. The panel is partially submerged so that a metal interface can be exposed to the solution and to the atmosphere above it for the purpose of a qualitative testing of the process. Typically, judge-

ments are made about the corrosive action of the solution on the basis of the effects of the vapors evolved from the bath. Also some contaminants can be identified only by their effect on the panel at the liquid/air interface only.

Dimensions of test panel 212 (FIG. 21) being used in the HMM cell typically approximate dimensions of test panels in a Hull cell. For example, in a 267 ml. Hull cell, the cathode size is 7.62cms (3") high by 10.32cms (4 1/16") long (of which only up to 6.35cms (2 1/2") is immersed). In a HMM cell with 20 mm diameter cylinder, the panel may be 11.43cms (4 1/2") high and 6.35 to 6.985cms (2 1/2 - 2 3/4") wide, of which only 10.16cms (4") may be immersed. Other sizes may be used as well.

In order to compare the primary current distribution resulting from the design of the HMM cell with that of the standard Hull cell of FIG. 31, a number of variants of the HMM cell shown in FIG. 1 were analyzed using a software program commercially available from L-Chem Inc., 13909 Larchmere Blvd., Shaker Heights, OH 44120, U.S.A. Also see, W. Michael Lynes and Uziel Landau, "A Novel Adaptation of the Finite Difference Method for Accurate Description of Non-Orthogonal Boundaries", The Electrochemical Society, Fall Meeting, Chicago, 1988, Abstract 332. The results of the analyses are presented for each specific variant in two graphs, one representing electric field distribution and the other the current density distribution. The resulting current density distribution for each variant was compared with one (FIG. 32) for the standard Hull cell. The low current density end in the HMM cell is that end of the test panel which is the farthest from the anode.

Comparison of the current density distribution presented in FIG. 4 for the variant with partially submerged panel, shown in FIG. 2, to the current density distribution (FIG. 32) in the standard Hull cell showed that the current density distribution of this embodiment effectively approximated the current density distribution results of the Hull cell. This embodiment was considered viable for use in place of the Hull cell; however, even closer approximation was desired.

Much closer approximation was obtained by the use of a partially submerged test panel with one or more horizontal baffles. These baffles represent minimal restriction to the flow of liquid while acting as a good shield to the electric field. The combination with one horizontal baffle (FIG. 5) shows that the actual current density distribution (FIG. 7) is very close to the one (FIG. 32) obtainable with the standard Hull cell. FIG. 8 shows that with two horizontal baffles, 26 and 27, the actual current density distribution (FIG. 10) is even closer to the one (FIG. 32) obtainable with the standard Hull Cell. FIG. 13 shows that with three horizontal

baffles, 26, 27 and 28, (FIG. 11) an excellent agreement with the Hull cell current density distribution (FIG. 32) was achieved. This combination was selected for our testing and further optimization.

A variant with an insulating cone-shield, 29, placed about instrument 13 as presented in FIG. 14 seemed to be a natural extension of the Hull cell design, namely, because the wall of the insulating cone is at an acute angle to the low density end of the cathode. However, with a cone-shield one obtains non-uniform hydrodynamics along the test panel. The cone-shield about the cylinder leads to a continuously varying geometry, thus, if a cone-shield is applied about the rotating cylinder, one can simultaneously obtain a whole range of hydrodynamic conditions over the test panel. The probable type of liquid flow is schematically presented in FIG. 14. Since the need for the uniform and controlled hydrodynamics in the HMH cell is the dominant factor, the cone shield with non-uniform hydrodynamics is not a suitable arrangement. In addition, the use of the cone shield demonstrated (FIG. 16) an inferior performance for developing the current density distribution pattern for Hull cell simulation.

An attempt to utilize the HMH cell with a test panel completely submerged in the electrolyte (FIG. 17) showed that the current distribution (FIG. 19) for submerged panel is clearly inferior to the one (FIG. 4) obtained with the partially submerged panel. The reason resides mostly in the "edge effect" which takes the primary current to infinity for a submerged electrode edge with a parallel or no insulator at all. In a partially submerged panel this edge effect is reduced by the solution surface which acts as an insulator perpendicular to the panel giving current density a finite value.

The embodiment with partially immersed panel and three horizontal baffles was rated the highest of these variants relative to the standard Hull cell and was chosen for further testing. This embodiment is shown in FIGS. 20 and 21. In these FIGS. the same numerals denote the same elements as those disclosed in FIGS. 1, 5, 8 and 11.

Cell 10 includes insulating container 11 holding electrolyte 12 in which is suspended measuring instrument 13. The measuring element comprises elongated insulating cylinder 15, a drive shaft, 24, arranged within and coaxially with the longitudinal central axis of the cylinder, and anode electrode 17 secured to shaft 24 at the bottom of the cylinder coaxially thereof. In this embodiment, anode 17 is in the form of a thin disk which extends a distance of from 2 to 5 mm beyond the circumference of the cylinder, diameter of which may vary over a wide range, including from 10 to 50 mm, preferably 20 mm, depending on the size of the cell and the volume of electrolyte therein. Other forms of anode

17 are useful as well, such as a disc or a ring having the same or smaller radial dimension as the cylinder. The important criteria is that both the anode and the cathode are arranged coaxially on the longitudinal axis of the cylinder in spaced relation each to another. Cathode 16 includes a sleeve, 211, of refractory metal embedded into cylinder 15 and is used for providing electrical contact to detachable test panel 212. The test panel is of a metal which does not react with the solution, such as copper or stainless steel. The sleeve is selected from the metals titanium, tantalum, niobium, aluminum which form a thin layer of oxide on their surface and thus, restrict plating of deposits on their surface. Other materials such as graphite or glassy carbon, stainless steel, or thin coating of the refractory metals on another metal substrate, are also useful. A slip ring, 18, mounted on the cylinder above the sleeve is electrically connected to and is used as a current carrier for the sleeve. Slip ring 18 is connectable to a negative (cathode) terminal of an energy source, 25, e.g. a rectifier.

Drive shaft 24 is preferably of a metal and provides the positive voltage to anode 17. Drive shaft 24 is connected to the positive (anode) side of energy source 25. Typically, the drive shaft is of a metal selected from stainless steel or brass. To avoid electrolyte attack on a lower portion, 214, of the drive shaft adjacent to the anode, the lower portion of the drive shaft may be made of the same metal as sleeve 211. Alternatively, the drive shaft may be of a rigid insulating material which is non-contaminating to the solution, with electrical connection provided to anode 17 via a conductor (not shown) inside of the shaft or of the cylinder. The connection may be to slip ring 19 (FIG. 1) on the cylinder 15 or on that portion of the insulating shaft which projects from the cylinder or via some other suitable means. Suitable material for the non-conducting shaft may be selected from such insulating materials as epoxy, polyethylene, polypropylene, polyvinyl chloride, "Teflon", fiberglass and other plastic materials.

In the preferred embodiment with partially immersed test panel (cathode) and three baffles, shown schematically in FIG. 20, cell 10 includes a baffle assembly including baffles 26, 27 and 28 arranged within container 11 horizontally about cylinder 13 at vertically spaced intervals each from another. For example, first baffle 26 is about 5 to 15 mm from the surface of electrolyte 14, second baffle 27 is 10 to 20 mm from the first baffle, and the third, lower baffle 28 is 10 to 30 mm from the second baffle. The baffles are made in the form of annular discs each having a central opening, 30, 31 and 32, respectively, so that each successive baffle is spaced from the wall of cylinder 11, a distance greater than each preceding baffle. Central open-

ing, 30, 31 or 32, of each succeeding baffle is progressively larger so that the body of each successive baffle is spaced progressively greater distance from the cylinder. For example, first baffle 26 is spaced 5 to 15, preferably 10 mm from cylinder 13, second baffle 27 is spaced 10 to 20, preferably 15 mm from the cylinder and third baffle is spaced 15 to 25, preferably 20 mm from the cylinder. A circular bottom anker 33 and at least two spacer connectors 34 complete the baffle assembly. Alternatively, the baffles may be suspended from the rim of the container. Still alternatively the baffle assembly may be in a form of a single spiral baffle beginning at one upper corner corresponding to the position of baffle 26 and spirally proceeding downwardly about the instrument 13 while an inwardly facing edge of the spiral baffle follows a progressively increasing spacing distance from instrument 13. The baffles are made of insulating material which is unaffected by the plating reaction and which does not contaminate the plating solution. Suitable material may be selected from such insulating materials as glass, glazed ceramic, plastics, such as polyethylene, polypropylene, polyvinylchloride, "Teflon", fiberglass and other plastic materials.

In a HMM cell holding 500 ml of plating solution, baffles 26, 27 and 28 are positioned, in a descending order, at 10, 20 and 30 mm from the top of the solution level in the container and are spaced radially 5, 10 and 15 mm from cylinder 11, respectively. Outer edge of each baffle is spaced from the walls of container 11 on the order from 1 to 10 mm sufficiently to permit at least some movement of the liquid between each baffle and the wall of container 11. For cells with a different volume, these dimensions could vary.

In FIGs. 22, 23 and 24 are shown measurements of the thickness distribution across panel 212 at three separate current density level positions corresponding to 0.0043, 0.02 and 0.086 A/cm² (4,20 and 80 ASF), respectively, at a total applied current of 2A. In contrast to thickness distribution measurements on the Hull cell panel for the same current density level positions (FIG. 32), these measurements indicate a very uniform distribution of thickness across these specific current density levels on the panel. The measurements of the current density distribution based on measurements of thickness distribution across a palladium panel plated from a proprietary plating process closely correspond to the calculated values of current density distribution shown in FIG. 13. The similarity to the actual Hull cell current density distribution (FIG. 32) is quite evident.

In FIGs. 25, 26 and 27 are shown deposition patterns obtained with the standard Hull cell (FIG. 25) and the HMM cell (FIGs. 26 and 27) from a

high speed palladium plating bath containing 25 grams per liter Pd, pH of 7.5, with plating conducted at 40°C. The panel plated at 10 cm/sec liquid velocity (FIG. 26) shows almost identical pattern as the one obtained with the standard Hull cell. The 100 cm/sec panel (FIG. 27) shows a decreased level of burning and dullness at the high current density end. This is to be expected if such features as burning and dullness on the panel are a result of the mass transport at the interface. Lack of dullness across the panel also means that the particular bath had no other contaminants which could be detrimental at increased velocity.

In FIGs. 28, 29 and 30 are shown deposition patterns obtained with the standard Hull cell (FIG. 28) and the HMM cell (FIGs. 29 and 30) from a nickel electroplating bath that had copper contamination. Nickel was deposited at 45°C from a plating bath containing nickel sulfamate, pH of 4.0 and 100 ppm of copper contamination. Approximately 100 ppm Cu is barely noticeable on the panel in standard Hull cell (FIG. 28) and on the 10 cm/sec HMM cell panel (FIG. 29). At 100 cm/sec 3/4" (1.9cm) of low current density side of the HMM cell panel plate had dull coppery finish (FIG. 30). Hence, the contamination was clearly evident and the range of current densities that could be applied for its removal would be easily determined.

These results indicate that HMM can give a current distribution analogous to the one obtained with standard Hull cell but with an improved control over the transport of matter across the interface. In addition HMM, as a tool, opens up new avenues for future exploration and quality control of electroplating solutions.

Claims

1. An electroplating test cell comprising a container (1) of non-conducting, non-contaminating material for holding an electrolyte (12), characterised by an elongated cylindrically-shaped measuring instrument (13) capable of rotation about its longitudinal axis within the container, the instrument comprising an elongated electrically conducting cathode section (16), an anode section (17), electrically separated by a spacer section (14) from the cathode, and contact means (18, 19) for providing current to the cathode and anode, said cathode and anode being vertically spaced along a longitudinal axis of the instrument, said anode being arranged below the cathode.
2. A test cell according to claim 1, or 10 characterised in that the measuring instrument is of insulating material suspendable within the container with its central axis substantially parallel



ing, 30, 31 or 32, of each succeeding baffle is progressively larger so that the body of each successive baffle is spaced progressively greater distance from the cylinder. For example, first baffle 26 is spaced 5 to 15, preferably 10 mm from cylinder 13, second baffle 27 is spaced 10 to 20, preferably 15 mm from the cylinder and third baffle is spaced 15 to 25, preferably 20 mm from the cylinder. A circular bottom anker 33 and at least two spacer connectors 34 complete the baffle assembly. Alternatively, the baffles may be suspended from the rim of the container. Still alternatively the baffle assembly may be in a form of a single spiral baffle beginning at one upper corner corresponding to the position of baffle 26 and spirally proceeding downwardly about the instrument 13 while an inwardly facing edge of the spiral baffle follows a progressively increasing spacing distance from instrument 13. The baffles are made of insulating material which is unaffected by the plating reaction and which does not contaminate the plating solution. Suitable material may be selected from such insulating materials as glass, glazed ceramic, plastics, such as polyethylene, polypropylene, polyvinylchloride, "Teflon", fiberglass and other plastic materials.

In a HMH cell holding 500 ml of plating solution, baffles 26, 27 and 28 are positioned, in a descending order, at 10, 20 and 30 mm from the top of the solution level in the container and are spaced radially 5, 10 and 15 mm from cylinder 11, respectively. Outer edge of each baffle is spaced from the walls of container 11 on the order from 1 to 10 mm sufficiently to permit at least some movement of the liquid between each baffle and the wall of container 11. For cells with a different volume, these dimensions could vary.

In FIGs. 22, 23 and 24 are shown measurements of the thickness distribution across panel 212 at three separate current density level positions corresponding to 0.0043, 0.02 and 0.086 A/cm² (4,20 and 80 ASF), respectively, at a total applied current of 2A. In contrast to thickness distribution measurements on the Hull cell panel for the same current density level positions (FIG. 32), these measurements indicate a very uniform distribution of thickness across these specific current density levels on the panel. The measurements of the current density distribution based on measurements of thickness distribution across a palladium panel plated from a proprietary plating process closely correspond to the calculated values of current density distribution shown in FIG. 13. The similarity to the actual Hull cell current density distribution (FIG. 32) is quite evident.

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high speed palladium plating bath containing 25 grams per liter Pd, pH of 7.5, with plating conducted at 40°C. The panel plated at 10 cm/sec liquid velocity (FIG. 26) shows almost identical pattern as the one obtained with the standard Hull cell. The 100 cm/sec panel (FIG. 27) shows a decreased level of burning and dullness at the high current density end. This is to be expected if such features as burning and dullness on the panel are a result of the mass transport at the interface. Lack of dullness across the panel also means that the particular bath had no other contaminants which could be detrimental at increased velocity.

In FIGs. 28, 29 and 30 are shown deposition patterns obtained with the standard Hull cell (FIG. 28) and the HMH cell (FIGs. 29 and 30) from a nickel electroplating bath that had copper contamination. Nickel was deposited at 45°C from a plating bath containing nickel sulfamate, pH of 4.0 and 100 ppm of copper contamination. Approximately 100 ppm Cu is barely noticeable on the panel in standard Hull cell (FIG. 28) and on the 10 cm/sec HMH cell panel (FIG. 29). At 100 cm/sec 3/4" (1.9cm) of low current density side of the HMH cell panel plate had dull coppery finish (FIG. 30). Hence, the contamination was clearly evident and the range of current densities that could be applied for its removal would be easily determined.

These results indicate that HMH can give a current distribution analogous to the one obtained with standard Hull cell but with an improved control over the transport of matter across the interface. In addition HMH, as a tool, opens up new avenues for future exploration and quality control of electroplating solutions.

Claims

1. An electroplating test cell comprising a container (1) of non-conducting, non-contaminating material for holding an electrolyte (12), characterised by an elongated cylindrically-shaped measuring instrument (13) capable of rotation about its longitudinal axis within the container, the instrument comprising an elongated electrically conducting cathode section (16), an anode section (17), electrically separated by a spacer section (14) from the cathode, and contact means (18, 19) for providing current to the cathode and anode, said cathode and anode being vertically spaced along a longitudinal axis of the instrument, said anode being arranged below the cathode.
2. A test cell according to claim 1, or 10 characterised in that the measuring instrument is of insulating material suspendable within the container with its central axis substantially parallel



to the axis of the container, in that the anode is in the form of a metallic disc secured to a lower portion of the cylinder, and in that the cathode section is in the form of a sleeve secured to the periphery of the cylinder.

3. The cell of claim 1 or 2, characterised in that the length of said cathode section is such that, when immersed in a predetermined volume of the electrolyte in the container, from 10 to 20 percent of the cathode section is exposed above the level of the electrolyte in the container.
4. The cell of claim 1, 2, 3, or 10, characterised in that said cathode section comprises a removable test panel.
5. The cell of claim 1, 2, 3, 4, or 10, characterised in that said cathode section comprises a metal, readily forming an oxide on its surface, said metal is selected from niobium, tantalum, titanium and aluminum.
6. The cell of any one preceding claim, or claim 10, characterised in that said instrument further comprises a cylindrical upper insulating section (15) about the cathode section, and said contact means for providing current comprises slip rings (18) (19) embedded into the upper insulating section and a conductor (213) for connecting one slip ring and the cathode.
7. The cell of any one preceding claim as appendant to claim 2, characterised in that said instrument comprises an insulating cylinder (15), including said upper and lower insulating sections, and a metal rod (214) passing through the insulating cylinder, the lower portion of the rod being in electrical contact with the anode, the rod acting as a conductor of current to the anode, and upper portion of the rod projecting from the cylinder and being usable for imparting rotation of the cylinder about its longitudinal axis.
8. The cell of any one preceding claim, or claim 10, characterised in that one or more spaced baffles are arranged about and coaxially with the said elongated cylindrical instrument with the inner edge of each baffle being spaced from the wall of the instrument, and in that when a plurality of baffles are used each successive baffle disc has a central opening which is greater than that of the preceding disc.
9. The cell of claim 8, characterised in that said at least one baffle is in the form of a flat band

spirally arranged about the instrument with inner edge of the baffle being progressively further positioned from the instrument.

10. An electroplating test cell comprising a measuring instrument (13), the measuring instrument comprising: an elongated cylinder (15) of insulating material, said cylinder being capable of rotation about its longitudinal central axis, a metallic cathode sleeve (16) secured to the periphery of the cylinder coaxially thereof, a metallic anode electrode (17) secured to a lower portion of the cylinder coaxially thereof, upper edge of the anode being spaced from the lower edge of the cathode, and means (18, 19) for providing current to the anode and the cathode, respectively.

Patentansprüche

1. Elektroplattierprüfzelle mit einem Gehäuse (1) aus nichtleitendem, keine Verunreinigung verursachendem Material zur Aufnahme eines Elektrolyten (12), gekennzeichnet durch ein langgestrecktes, zylindrisch geformtes Meßgerät (13), das um seine Längsachse innerhalb des Gehäuses drehbar ist und einen langgestreckten elektrisch leitenden Kathodenteil (16), einen von der Kathode durch einen Abstandshalterteil (14) elektrisch getrennten Anodenteil (17) sowie eine Kontakteinrichtung (18, 19) zur Lieferung von Strom an die Kathode und Anode umfaßt, wobei die Kathode und Anode entlang einer Längsachse des Gerätes senkrecht beabstandet sind und die Anode unterhalb der Kathode angeordnet ist.
2. Prüfzelle nach Anspruch 1 oder 10, dadurch gekennzeichnet, daß das Meßgerät aus Isoliermaterial besteht, das innerhalb des Gehäuses aufgehängt werden kann, wobei seine Mittelachse im wesentlichen parallel zur Achse des Gehäuses angeordnet ist, daß die Anode als an einem unteren Abschnitt des Zylinders befestigte metallische Scheibe ausgebildet ist, und daß der Kathodenteil als am Umfang des Zylinders befestigte Hülse ausgebildet ist.
3. Zelle nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Kathodenteil eine solche Länge aufweist, daß bei Eintauchen in ein vorgegebenes Volumen des Elektrolyten im Gehäuse 10 bis 20% des Kathodenteils über dem Elektrolytspiegel im Gehäuse freiliegen.
4. Zelle nach Anspruch 1, 2, 3 oder 10, dadurch gekennzeichnet, daß der Kathodenteil eine demontierbare Prüfplatte beinhaltet.



5. Zelle nach Anspruch 1, 2, 3, 4 oder 10, dadurch gekennzeichnet, daß der Kathodenteil ein Metall enthält, das auf seiner Oberfläche bereitwillig Oxyd bildet, wobei das Metall aus der Reihe Niob, Tantal, Titan und Aluminium ausgewählt ist.

6. Zelle nach einem der vorhergehenden Ansprüche oder Anspruch 10, dadurch gekennzeichnet, daß das Gerät weiter einen zylindrischen oberen isolierenden Teil (15) um den Kathodenteil beinhaltet und die Kontakteinrichtung zur Stromlieferung in den oberen isolierenden Teil eingebettete Schleifringe (18, 19) sowie einen Leiter (213) zur Verbindung eines Schleifrings und der Kathode beinhaltet.

7. Zelle nach einem der vorhergehenden Ansprüche soweit wie von Anspruch 2 abhängig, dadurch gekennzeichnet, daß das Gerät einen isolierenden Zylinder (15) einschließlich der besagten oberen und unteren isolierenden Teile sowie einen durch den isolierenden Zylinder hindurchgeführten Metallstab (214) enthält, wobei der untere Abschnitt des Stabs in elektrischen Kontakt mit der Anode steht, der Stab als Stromleiter zur Anode wirkt und der obere Abschnitt des Stabs aus dem Zylinder herausragt und dazu verwendet werden kann, den Zylinder um seine Längsachse in Drehung zu versetzen.

8. Zelle nach einem der vorhergehenden Ansprüche oder Anspruch 10, dadurch gekennzeichnet, daß eine oder mehrere beabstandete Leitwände um das besagte langgestreckte zylindrische Gerät coaxial mit demselben angeordnet sind, wobei der Innenrand jeder Leitwand von der Wand des Gerätes beabstandet ist, und daß bei Verwendung mehrerer Leitwände jede nachfolgende Leitwandscheibe eine mittige Öffnung aufweist, die größer ist als jene der vorhergehenden Scheibe.

9. Zelle nach Anspruch 8, dadurch gekennzeichnet, daß mindestens eine Leitwand als flaches, spiralförmig um das Gerät angeordnetes Band ausgebildet ist, wobei der Innenrand der Leitwand immer weiter vom Gerät entfernt angeordnet ist.

10. Elektroplattierprüfzelle mit einem Meßgerät (13), das einen langgestreckten Zylinder (15) aus isolierendem Material, der um seine mittige Längsachse drehbar ist, eine am Umfang des Zylinders coaxial mit demselben befestigte metallische Kathodenhülse (16), eine an einem unteren Abschnitt des Zylinders coaxial mit

demselben befestigte metallische Anodenelektrode (17), wobei der obere Rand der Anode vom unteren Rand der Kathode beabstandet ist, sowie eine Einrichtung (18, 19) zur Stromlieferung an die Anode bzw. die Kathode beinhaltet.

Revendications

1. Cellule de mesure d'électrodéposition comprenant un récipient (1) en matériau non conducteur, non contaminant, pour contenir un électrolyte (12), caractérisée par un instrument de mesure de forme cylindrique allongée (13), capable de tourner autour de son axe longitudinal à l'intérieur du récipient, l'instrument comprenant une section de cathode allongée (16), conductrice de l'électricité, une section d'anode (17), séparée électriquement de la cathode par une section d'espacement (14), et un dispositif de contact (18, 19) pour amener le courant à la cathode et à l'anode, ladite cathode et ladite anode étant espacées verticalement le long d'un axe longitudinal de l'instrument, ladite anode étant placée au-dessous de la cathode.

2. Cellule de mesure selon la revendication 1, ou 10, caractérisée en ce que l'instrument de mesure est en matériau isolant pouvant être suspendu à l'intérieur du récipient de manière que son axe central soit sensiblement parallèle à l'axe du récipient, en ce que l'anode a la forme d'un disque métallique fixé à la partie inférieure du cylindre, et en ce que la section de cathode a la forme d'un manchon fixé à la périphérie du cylindre.

3. Cellule selon la revendication 1 ou 2, caractérisée en ce que la longueur de ladite section de cathode est telle que, lorsqu'elle est immergée dans un volume prédéterminé de l'électrolyte dans le récipient, de 10 à 20% de la section de cathode sont exposés au-dessus du niveau de l'électrolyte dans le récipient.

4. Cellule selon la revendication 1, 2, 3, ou 10, caractérisée en ce que ladite section de cathode comprend un panneau de mesure amovible.

5. Cellule selon la revendication 1, 2, 3, 4, ou 10, caractérisée en ce que ladite section de cathode comprend un métal formant facilement un oxyde sur sa surface, ledit métal étant choisi parmi le niobium, le tantale, le titane et l'aluminium.



6. Cellule selon l'une quelconque des revendications précédentes, ou la revendication 10, caractérisée en ce que ledit instrument comprend, en outre, une section isolante supérieure cylindrique (15) autour de la section de cathode, et ledit dispositif de contact pour amener le courant comprend des bagues glissantes (18, 19) encastrées dans la section isolante supérieure et un conducteur (213) pour raccorder une bague glissante à la cathode. 5 10

7. Cellule selon l'une quelconque des revendications précédentes annexées à la revendication 2, caractérisée en ce que ledit instrument comprend un cylindre isolant (15), contenant lesdites sections isolantes supérieure et inférieure, et une tige métallique (214) traversant le cylindre isolant, la partie inférieure de la tige étant en contact électrique avec l'anode, la tige jouant le rôle de conducteur de courant pour l'anode, et la partie supérieure de la tige dépassant du cylindre et étant utilisable pour faire tourner le cylindre autour de son axe longitudinal. 15 20 25

8. Cellule selon l'une quelconque des revendications précédentes, ou la revendication 10, caractérisée en ce qu'un ou plusieurs déflecteurs espacés sont disposés autour dudit instrument cylindrique allongé, coaxialement avec ce dernier, le bord interne de chaque déflecteur étant écarté de la paroi de l'instrument, et en ce que, lorsqu'on utilise plusieurs déflecteurs, chaque disque déflecteur successif présente une ouverture centrale qui est plus grande que celle du disque qui précède. 30 35

9. Cellule selon la revendication 8, caractérisée en ce que ledit au moins un déflecteur a la forme d'un ruban plat enroulé en spirale autour de l'instrument, le bord interne du déflecteur s'éloignant progressivement de l'instrument. 40

10. Cellule de mesure d'électrodéposition comprenant un instrument de mesure (13), l'instrument de mesure comprenant: un cylindre allongé (15) en matériau isolant, ledit cylindre étant capable de tourner autour de son axe longitudinal central, un manchon de cathode métallique (16) fixé à la périphérie du cylindre, coaxialement avec ce dernier, une électrode anode métallique (17) fixée à une partie inférieure du cylindre, coaxialement avec ce dernier, le bord supérieur de l'anode étant écarté du bord inférieur de la cathode, et un dispositif (18, 19) pour mener le courant respectivement à l'anode et à la cathode. 45 50 55