

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 April 2004 (15.04.2004)

PCT

(10) International Publication Number
WO 2004/031454 A2

(51) International Patent Classification⁷: **C25D 17/00**

Robert [GB/GB]; QinetiQ Limited, Cody Technology Park, Ively Road, Farnborough, Hampshire GU14 0LX (GB).

(21) International Application Number:
PCT/GB2003/004080

(74) Agent: **RICHARDSON, Mark**; IP QinetiQ Formalities, Cody Technology Park, A4 Building, Room G016, Ively Road, Farnborough, Hampshire GU14 0LX (GB).

(22) International Filing Date:
25 September 2003 (25.09.2003)

(25) Filing Language: English

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(26) Publication Language: English

(30) Priority Data:
0222711.4 1 October 2002 (01.10.2002) GB

(71) Applicant (*for all designated States except US*): **QINETIQ LIMITED** [GB/GB]; Registered Office, 85 Buckingham Gate, London SW1E 6PD (GB).

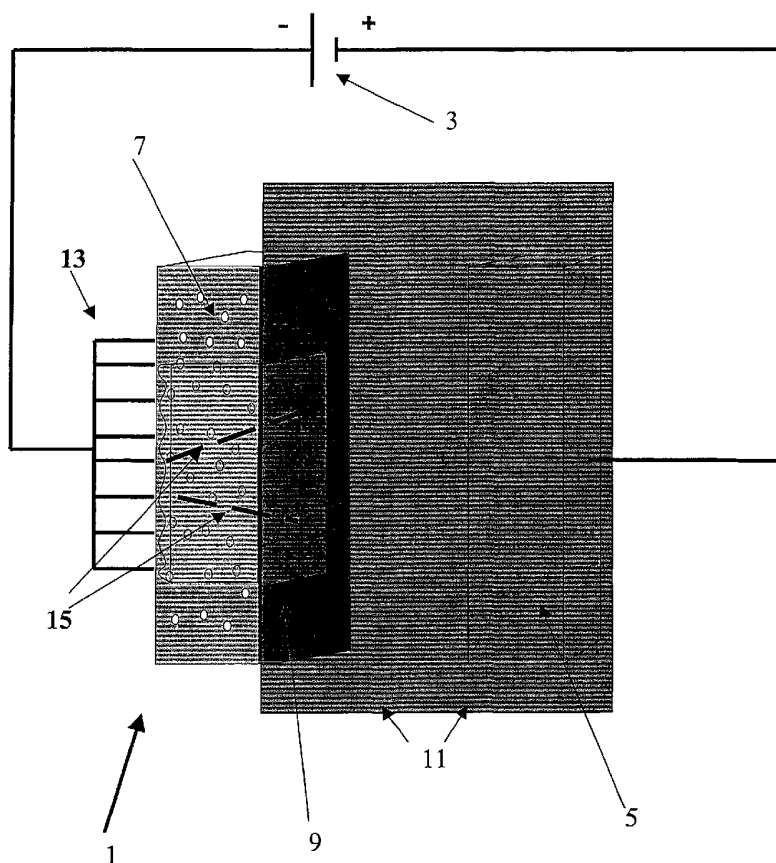
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **JOHNSON, Daniel**,

[Continued on next page]

(54) Title: NOVEL CATHODE DESIGN FOR USE IN ELECTRODEPOSITION CELL



(57) Abstract: Electrodeposition is an attractive deposition technique since it allows the deposition of metal to be controlled to a high level (material composition, crystallinity and quality can all be controlled) and is an efficient and low waste process. However, the deposition of metal patterns onto a non-conducting substrate requires that suitable conducting tracks are present on the substrate in order to complete the electrolytic cell. Such conducting tracks are difficult to design for complex or discontinuous features. The present invention provides an electrode configuration that overcomes or substantially mitigates these problems by providing a cathode design based on a porous substrate.

WO 2004/031454 A2



ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished
upon receipt of that report*

Declaration under Rule 4.17:

— *of inventorship (Rule 4.17(iv)) for US only*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Novel Cathode Design for use in Electrodeposition Cell

This invention relates to the field of electrodeposition and in particular relates to a novel design for a cathode for use in an electrodeposition reaction.

Electrodeposition (also called electroplating) is a process that produces a thin metallic coating, or other material, such as polymer or semiconductor on the surface of another metal (or any other conductor, e.g., Graphite). The metal substrate to be coated is made the cathode in an electrolytic cell where the cations of the electrolyte are the positive ions of the metal or material that is to be coated on the surface.

When a current is applied, the electrode reaction occurring on the cathode is the reduction of the coating material ions to coating material. For example, gold ions can be discharged from a gold solution to form a thin gold coating on a less expensive metal to produce "gold plated" jewellery. Similarly, chromium coating is often applied to steel surfaces to make them more "rust resistant." Electroplating is also used in the production of integrated circuits on computer chips and other modern electronic instrumentation. The anode can be either the metal to be deposited with the electrode reaction being electrodisolution, continuously supplying the metal ions to be deposited in the solution, or the anode can be nonreactive and the anodic reaction is oxygen evolution.

Insulating substrates can also be used for the electrodes but in this case the substrate surface (or a part or parts thereof) needs to be made conducting before the electroplating reaction can take place. For example, a conductive pattern could be formed (by, for example, an electroless deposition process) on the insulating substrate and then further metal could be deposited onto this metal pattern.

However, for this to work the pattern must include suitable conducting tracks to connect with the electrolytic cell in order to make it into a cathode. This has the obvious drawbacks of adding to the design complexity of the system and also wasting areas on the substrate because of the need to provide suitable electrical connections. Furthermore, it is difficult to design conducting tracks when there are complex or discontinuous features. A still further problem is that the thickness of the plating deposit depends on current path, which means that plating of a pattern is non-uniform and it requires multiple and complex electrical connections to minimise this.

Electrodeposition is, however, an attractive deposition technique since it allows the deposition process to be controlled to a high level (material thickness, composition, crystallinity and quality can all be controlled) and is an efficient and low waste process. Therefore, it is an object of the present invention provide an electrode configuration that overcomes or substantially mitigates the problems associated with existing electrodes based on an insulating substrate.

Therefore, accordingly this invention provides a cathode for use in an electroplating cell comprising a porous electrically non-conducting substrate having a first surface which is arranged, during operation of the plating cell, to be coated with deposited metal and a second surface which is arranged, in use, to be electrically connected to the plating cell wherein there are one or more electrically conductive pathways between the first and second surfaces of the substrate.

Metal deposits onto the cathode in an electroplating cell. The invention therefore provides a cathode which is porous and which has electrically conductive pathways running through the inside of this porous structure. Since the electrical connections are "housed" within the substrate itself there is no requirement for conducting tracks to be added to the surface of the cathode which is to be metal plated (the "plating area").

Furthermore, by appropriate control of the manner in which the cathode is constructed, as explained more fully below, the pathways within the substrate can be arranged to meet the "plating area" in such a way that deposition will only occur in a pre-determined pattern. In other words, the plating surface will only be conductive (due to the pathways leading into the substrate below) in certain areas.

The substrate may be in the form of a mesh-like structure which can be treated to provide conducting pathways or could alternatively be in the form of a porous paper-like material.

Conveniently, the electrical pathways can be formed by material generated by an electroless (or "autocatalytic") plating process.

Processes are known for the autocatalytic deposition of a large number of metals, particularly cobalt, nickel, gold, silver and copper from a suitable solution bath. Basically, the solutions contain a salt of the metal to be deposited and a suitable

reducing agent such as SnCl_2 , glucose, hypophosphite, hydrazine, amine boranes, borohydride, aldehydes and tartrates. When a metal substrate which is catalytic to the reaction is introduced into the solution bath it becomes covered with a layer of the coating metal which itself is catalytic so that the reaction can continue. In this manner the plating thickness can be allowed to increase until a desired thickness is attained.

Deposition will only occur if the conditions at the surface of the substrate are suitable for the autocatalytic process to be initiated and then sustained. In cases where the substrate is formed of a plastics or ceramic material for example, additional steps are required to create suitable surface properties. In the present case, the substrate is chosen specifically to be non-conducting and so additional preparation steps will be required as explained below.

Usually, in such cases the substrate is "sensitised" with a reducing agent, e.g. SnCl_2 . Also, the surface may be "activated" with a thin layer of an intermediate catalytic material, e.g. palladium (itself a candidate metal for autocatalytic deposition), in order to aid the deposition process. Such "deposition promoting materials" are generally referred to in the literature as "sensitisers" and "activators" respectively.

The non conducting substrate that forms the cathode can therefore be prepared by laying down deposition promoting material within the substrate. Immersion in an autocatalytic solution bath will then deposit metal onto (and into) the substrate thereby forming the conducting tracks. The configuration of the deposited electrical pathways will mirror the configuration of the deposition promoting material within the substrate.

The substrate is chosen to allow adequate passage of deposition promoting material between the surfaces of the substrate needed to prepare conducting pathways, but limit lateral spreading or "blooming" of the same, which leads to loss of definition in features making up the plated area. The substrate may therefore be a mesh, porous, microporous, semi-permeable membrane or other membrane-like material provided that a conductive medium can be formed from what permeates through it. Preferably the material should have some anisotropy which favours material deposited to flow in the z direction, being the direction in which precursors to, and the electrical circuit, is desired. Such anisotropy depends on how the substrate is made. Almost any material could be made with this, from ceramics to reticulated foam.

Since cellulose-based material will swell (so distort the pattern) during any wet stages (electroless and electrolytic, and if printed with water-based ink) plastics-based paper, mainly PET (polyethylene terephthalate or polyester) and PP polypropylene are more preferably used.

Conveniently the electrical pathways can be constructed using the process as disclosed and claimed in applicant's co-pending international patent applications Nos. GB02/02412 and GB02/02470. In this method some or all of a substrate material is printed with a deposition promoting material using a pattern transfer mechanism such as screen or inkjet printing. By this means the deposition promoting material can be laid down onto the surface of the substrate in a pre-determined pattern, for example to represent an electrical circuit or other desired pattern. When the printed surface is then brought into contact with an autocatalytic deposition solution a metal coating is deposited from the autocatalytic solution onto the printed areas of the substrate only i.e. to provide a substrate which has metal tracks or regions according to a desired pattern.

Conveniently the deposition promoting material can be in the form of an ink which is ink jetted onto the substrate. The substrate could be constructed from a synthetic polymeric material such as microporous inkjet media which will absorb the ink throughout its depth.

Once introduced into an autocatalytic solution bath metal pathways will form throughout the substrate under the area of the surface coated with the ink. Further, the substrate chosen can conveniently be resistant to lateral spread of deposited ink in order to ensure and maintain the resolution of the printed pattern.

The inclusion of a filler may serve to improve contact between a deposition promoting material and the autocatalytic solution bath. Suitable fillers include fine particulate forms of carbon such as carbon black or carbon powder and ceramic or other inorganic materials such as one or more selected from titanium dioxide, alumina (aluminium oxide), calcium carbonate, talc, mica, silica or silicates.

Preferably, the electroless metal is any of the metals in Group 1b or Group 8 of the Periodic Table, i.e. copper, silver, gold, iron, cobalt, nickel, ruthenium, rhodium,

palladium, osmium, iridium and platinum. Copper, cobalt or nickel are preferred but in the case of these metals it is advantageous to provide a layer of an activator such as palladium metal on the surface on which it is desired to deposit the electroless metal. This can, for example, be prior deposited by some method such as printing or coating with a suitable catalyst, like palladium or a precursor material like PdCl_2 , that is chemically reduced to palladium following exposure to a suitable reagent, for example SnCl_2 .

As an alternative to depositing the conducting pathways by means of an electroless deposition technique a conductive paste can be used. In this case the substrate is preferably a mesh material into which a paste (for example, a carbon containing conductive paste) is forced. The paste penetrates into the interstices of the mesh thereby forming the conductive paths. A screen printing technique can conveniently be used to determine the pattern of the deposited paste.

It may also be advantageous to render the remaining area of substrate impervious, by printing the residual areas with a sealing ink. Pattern transfer may achieve this more easily by printing from the same side an insulating ink coincidentally as the negative of the conductive pattern. Alternatively, the insulating ink may be a photoresist, printed continuously on the same side and cured using transmitted light in the transparent areas of the substrate but remaining uncured and removeable where conducting ink acts as a photomask to the light source.

Correspondingly there is provided a method of making a cathode for use in an electroplating cell comprising the steps:

- i) directing a deposition promoting material onto a porous non-conducting substrate so as to coat an area on a first surface of the substrate and extending through the substrate to a second surface and then;
- ii) applying an electroless plating solution to the said area so as to deposit metal thereon and form an electrical connection through the substrate thereby electrically connecting the two surfaces of the substrate.

A further method of making a cathode for use in an electroplating cell comprises directing a conductive paste into the interstices of an electrically non-conducting substrate in the form of a mesh thereby forming an electrical connection between two faces of said substrate.

Furthermore, the invention provides a method of depositing a metal onto a substrate via an electroplating process comprising the steps of:

- i) forming a cathode from a porous substrate according to either of the methods described above, and;
- ii) connecting one face of the cathode to an electroplating cell comprising a power source, anode and electrolyte, and;
- iii) activating the electroplating cell to thereby deposit metal from the electrolyte onto the second face of the cathode.

Where the porosity of the substrate causes the electroplating solution to percolate through it and undergo unwanted electroplating at the second surface, then additional insulating materials (for example pastes or other inks blends containing polymeric sealant) may be deposited into these areas alongside the deposition promoting material. This can be performed using printing or lithographic processes prior to, during or after the printing of the deposition promoting material in order to provide a barrier to unwanted percolation of the electroplating solution.

The cathode can conveniently be constructed on a continuous roll of substrate. The substrate can then be passed into and through an electroplating cell in order to deposit metal onto the roll.

The invention is now further described with reference to the accompanying drawings, in which:

Figure 1 shows a schematic of an electrodeposition cell with a cathode according to the present invention.

Figure 2 shows a cathode according to the present invention where the cathode is formed from a mesh.

Figure 3 shows a method of forming a cathode according to the present invention.

Figures 4 and 5 show two further electroplating cell set-ups with cathodes according to the present invention.

Turning to Figure 1 an electroplating cell 1 is shown comprising a power source 3, an anode 5 and a porous cathode 7. The anode 5 and front surface 9 of the cathode 7 are in contact with an electrolyte 11. The cathode 7 is electrically connected via contacts 13 to the power supply 3. The cathode 7 is porous and conducting paths 15 run from the contacts 13 to the front surface 9 of the cathode thereby providing the electrical circuit required for the cell 1 to operate. In use, metal is deposited from the electrolyte onto the front surface of the cathode.

Figure 2 shows a variant on the set up shown in Figure 1. In this case the cathode 21 comprises a mesh-like material 23 which has a number of holes 25 between its top and bottom face. A conductive area 27 which passes through holes 29 to connect the cathode with the electrical circuit 31 (power source and anode not shown) covers parts of the top face of the mesh 23. The conductive area 27 is in contact with the electrolyte 33. An inert material 35 which also plugs holes in the mesh covers areas of the mesh 23 which are to be left clear of metal deposit. In use, metal will plate onto the top 37 of the conductive area 27.

The set up shown in Figure 2 was used to electrodeposit metal onto a mesh structure which had been screen printed with a conductive paste. Carbon containing conductive paste was screen printed onto a non-conductive mesh structure having 100 micrometre holes in its structure. The paste was allowed to dry. Areas of the mesh which had not been coated with the paste were then sealed with an inert material. Both the inert material and the conductive paste filled the interstice of the mesh.

The dried conductive paste provided an electrical path from the front of the mesh to the reverse side. Electrical connections were made to the reverse side and the mesh was placed into an electrodeposition bath. Metal deposited from the bath only onto the areas of the mesh coated with the conductive paste.

An advantage of the above cathode design is that the plating current can be set to a higher value than in conventional plating systems owing to the smaller resistive drop by connecting through the thickness of the substrate rather than through lengthy surface paths.

The conductive area on the cathode can be formed by screen-printing (as in Figure 2 above with the mesh). Alternatively a conductive area can be formed by means of an electroless deposition technique as shown in Figure 3.

Figure 3 shows an activating ink 40 being printed from a printer 42 onto the surface of a porous substrate 44 (which is to become the cathode for an electrodeposition cell). The activating ink 40 is chosen such that following immersion into an autocatalytic deposition solution metal will deposit onto areas of the substrate 44 coated with the ink 40. The substrate itself is initially inert to both electroless deposition and electrodeposition.

Since the substrate 44 is porous the ink penetrates throughout the depth 46 of the substrate. The substrate is chosen so as to reduce the lateral spread of the ink into areas that are not to be coated with metal.

Following the printing step the substrate is immersed into an electroless solution which coats the ink with metal. Metal also deposits throughout the substrate depth thereby forming conductive pathways between the front and reverse faces of the substrate such that the metalised substrate can be connected to an electrodeposition cell to act as the cathode.

Figures 4 and 5 show two configurations in which a continuous porous cathode according to the invention is passed through an electrodeposition cell.

Figure 4 shows an electrodeposition cell 50 comprising a power source 52, a sacrificial anode 54, a continuous porous cathode 56 and an electrolyte 58. The electrical circuit is completed by means of a conducting strip 60 which is connected via a roller 62 to the power source 52. The direction of motion of the cathode 56 is shown by arrows 64 and the direction of the strip 60 is shown by arrows 66.

Since the cathode 56 has conducting paths running through it an electrodeposition cell is created and metal will deposit onto the top surface (indicated as 68 on the left of the diagram) of the cathode as it passes through the electrolyte bath. The cathode in this case comprises a porous substrate roll which has had a metallic pattern printed onto it by, for example, an electroless deposition technique. Since the substrate of the cathode is porous metallic pathways extend throughout its depth

thereby creating a conducting path between the conducting backing strip 60 and the electrolyte 58.

A similar configuration to that of Figure 4 is depicted in Figure 5. The cell in this example having a power source 70, anode 72, electrolyte 74 and porous cathode 76. In this case however it is the lower surface of the cathode that is coated with metal on passing through the electrodeposition cell. A conducting backing strip 78 again is used to complete the electrical circuit and is mounted on two rollers 80. The direction of the cathode 76 is given by the arrow 84 and the direction of the backing strip 78 by the arrow 82.

Other possible arrangements of the electrodes, electrolyte, conducting paths and associated structures will be readily apparent to the skilled person and should be regarded as coming within the scope of the present invention.

CLAIMS

1. A cathode for use in an electroplating cell comprising a porous electrically non-conducting substrate having a first surface which is arranged, during operation of the plating cell, to be coated with deposited metal and a second surface which is arranged, in use, to be electrically connected to the plating cell wherein there are one or more electrically conductive pathways between the first and second surfaces of the substrate.
2. A cathode as claimed in Claim 1 wherein the one or more conductive pathways are formed by material generated by an electroless plating process.
3. A cathode as claimed in Claim 2 wherein at least some of the electroless plating forming the one or more connecting conductive pathways is activated by a deposition promoting material.
4. A cathode as claimed in Claim 3 wherein the deposition promoting material is introduced into the substrate by a printing process.
5. A cathode as claimed in Claim 3 wherein the deposition promoting material is in ink form and the substrate comprises plastics based synthetic paper.
6. A cathode as claimed in Claim 1 wherein the substrate is a mesh-like structure.
7. A cathode as claimed in claim 6 wherein the one or more conductive pathways are formed from conductive paste.
8. A cathode as claimed in any preceding claim wherein the electrically conductive pathways form a pre-determined pattern on the first surface of the substrate.
9. An electroplating cell comprising an anode, a cathode, an electrolyte and a power source wherein the cathode is a cathode as claimed in any of claims 1 to 6.
10. A process for making a cathode for use in an electroplating cell comprising
 - i) directing a deposition promoting material onto a porous non-conducting substrate so as to coat an area on a first surface of the substrate and extending through the substrate to a second surface and then;

- ii) applying an electroless plating solution to the said area so as to deposit metal thereon and form an electrical connection through the substrate thereby electrically connecting the two surfaces of the substrate.
11. A process as claimed in claim 10 wherein the deposition promoting material is applied to the surface of the substrate in a pre-determined pattern.
12. A process as claimed in claims 10 or 11 wherein the substrate is prepared for subsequent metal deposition using a printing method.
13. A process as claimed in Claim 12 wherein the printing method is the method described in applicant's corresponding British patent application No. 01 134 08.9.
14. A process as claimed in any of Claims 10 to 13 wherein the deposition promoting material is in the form of an ink formulation.
15. A process as claimed in Claims 10 to 14 wherein the substrate is formed from a porous material made from plastics based synthetic paper, polymer or ceramic.
16. A process for making a cathode for use in an electroplating cell comprising directing a conductive paste into the interstices of an electrically non-conducting substrate in the form of a mesh thereby forming an electrical connection between two faces of said substrate.
17. A process as claimed in claim 16 wherein the paste is applied to the substrate in a pre-determined pattern.
18. A method of depositing a metal onto a substrate via an electroplating process comprising the steps of:
- i) forming a cathode from a porous substrate according to the method as claimed in any of claims 10 to 17
 - ii) connecting one face of the cathode to an electroplating cell comprising a power source, anode and electrolyte
 - iii) activating the electroplating cell to thereby deposit metal from the electrolyte onto the second face of the cathode.
19. A method as claimed in claim 18 wherein the cathode is formed from a continuous roll of substrate and is passed through the electrolyte of the electroplating cell.

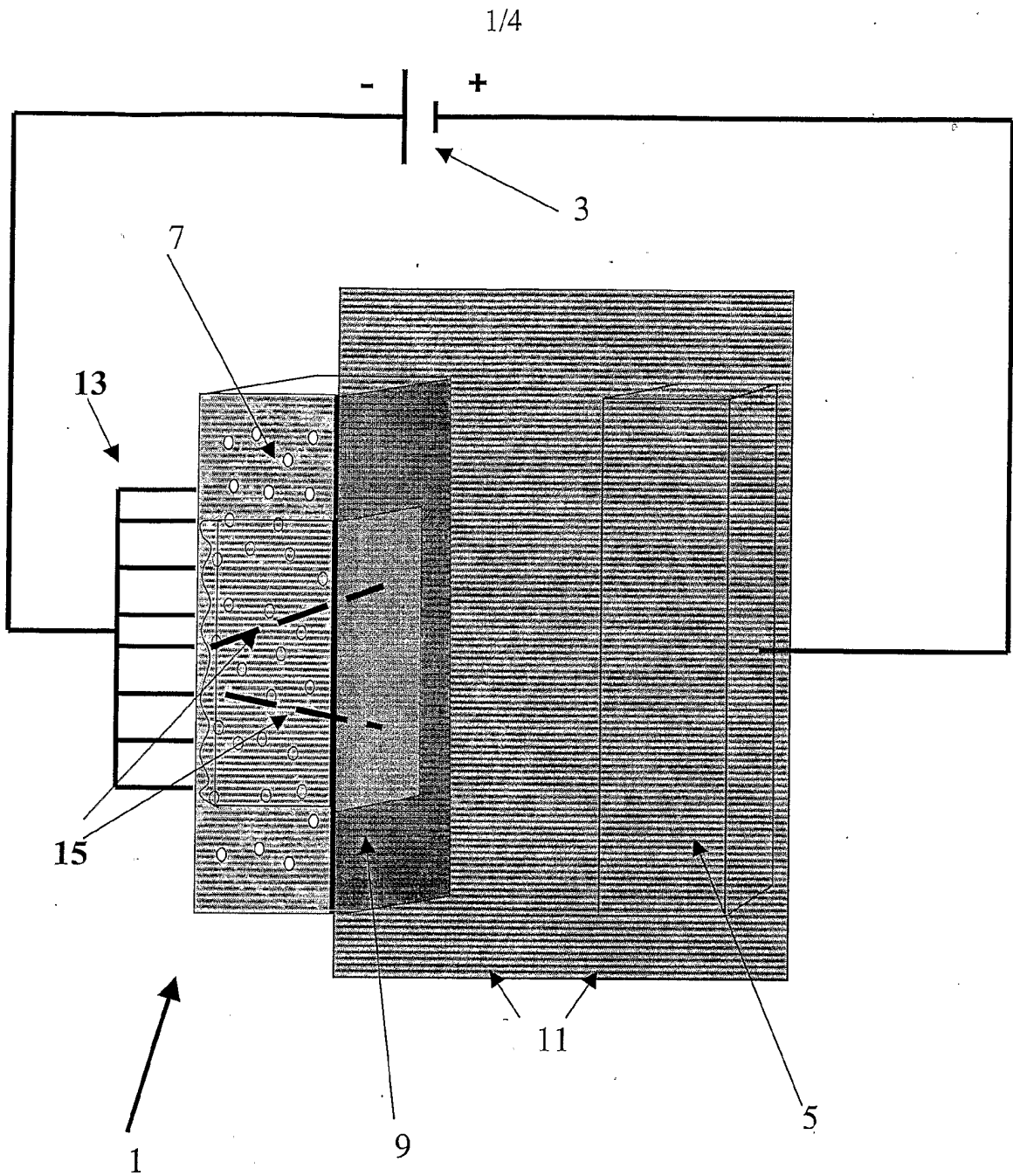


Figure 1

2/4

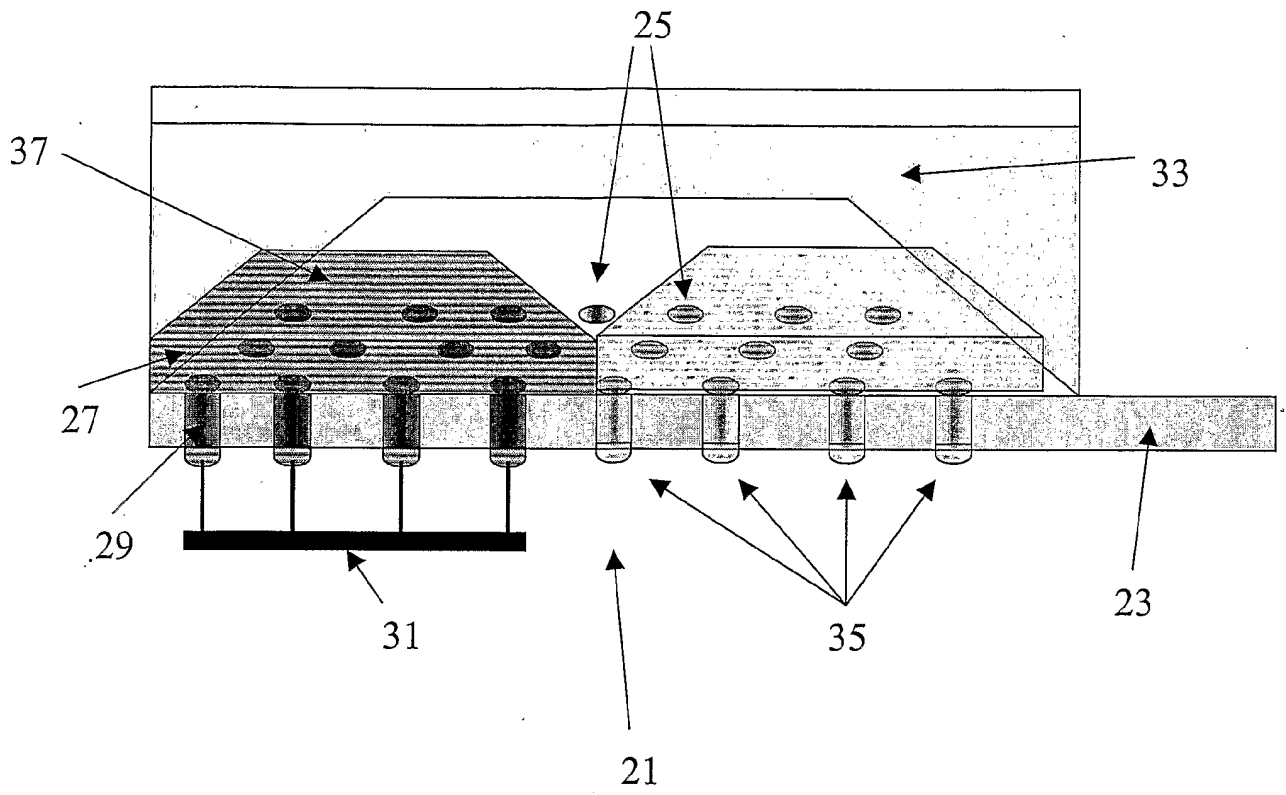


Figure 2

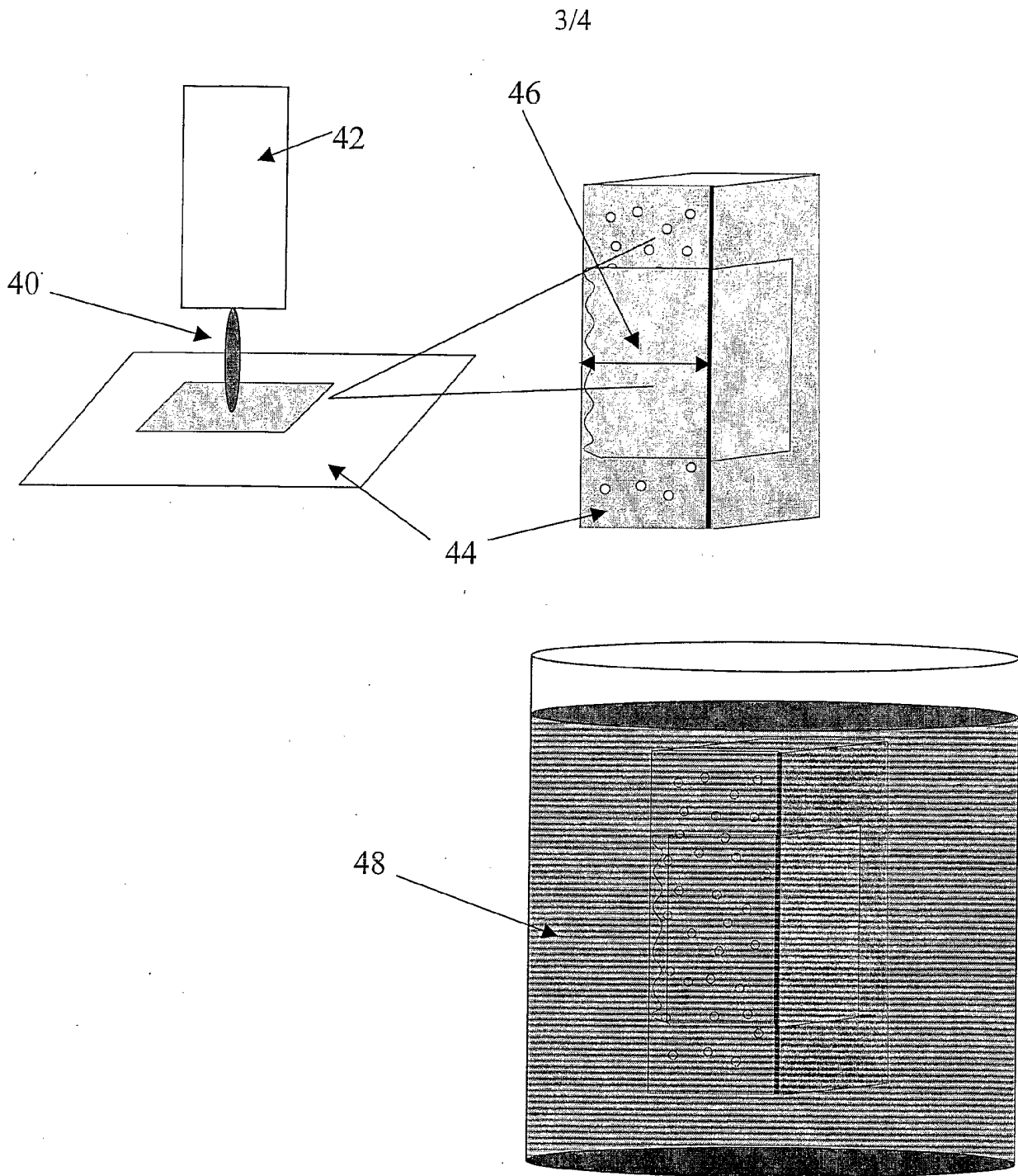


Figure 3

4/4

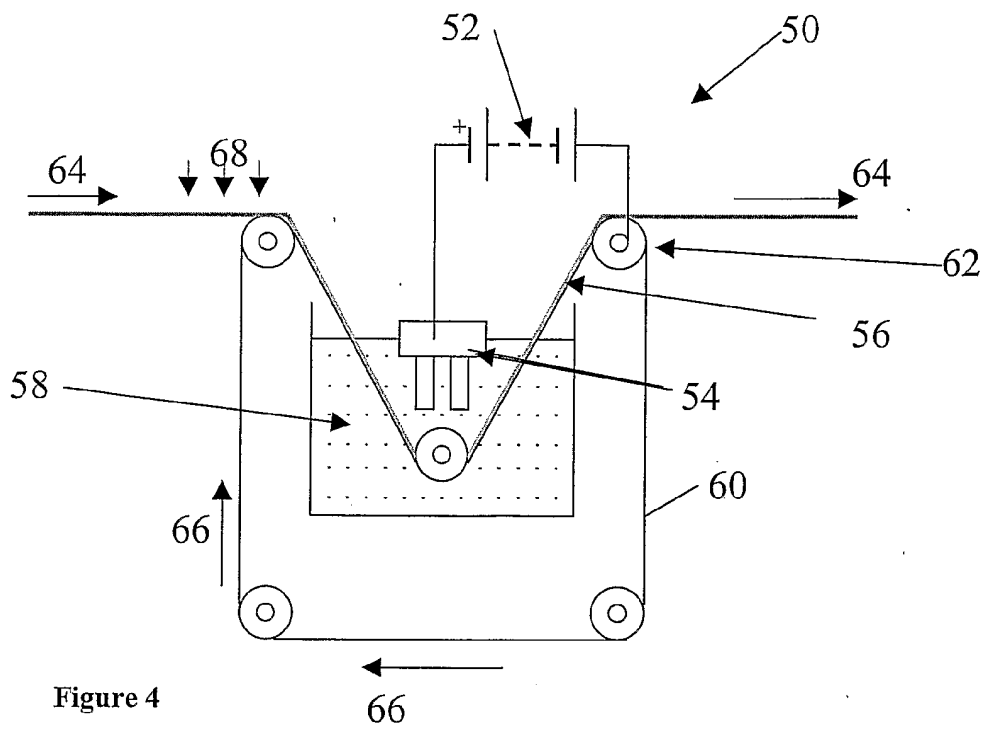


Figure 4

Figure 5

