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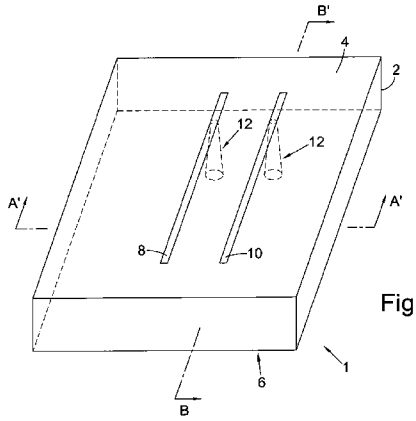


Fig. 1a

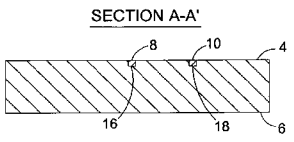


Fig. 1b

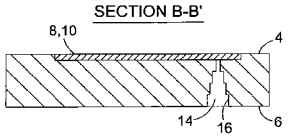


Fig. 1c

(57) Abstract: A microelectrode for electrochemical use is described. The microelectrode comprises: • (a) an electrically non-conductive diamond plate (2) having a first surface (4) containing at least two discrete recesses (16,18) and an opposed second surface (6); • (b) electrically conductive diamond material contained within said recesses and being substantially flush with the first surface of said diamond plate, the electrically conductive diamond material in each of said at least two discrete recesses providing respective working electrodes in use; and • (c) at least two electrically conductive connection members (12) that extend from the second surface of the electrically non-conductive diamond plate into the electrically non-conductive diamond plate, such that each of the connection members is electrically connected to respective ones of the working electrodes.

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DIAMOND MICROELECTRODE

Field

The invention relates generally to a diamond microelectrode for electrochemical use, the use of a microelectrode and a method of making a microelectrode.

Background

Diamond microelectrodes for electrochemical use are used for, for example, the monitoring of electrochemical reactions in which oxidation or reduction reactions occur at an electrode. Diamond microelectrodes for electrochemical use are distinct from electrodes in electronic devices and thermionic or field emission devices. In a diamond microelectrode for electrochemical use, the microelectrode enables electrons to be transferred either from the microelectrode to an ion (or other species) in solution or from the ion (or other species) in solution to the microelectrode, thereby changing the charge state of the ion (or other species). Electrodes in electronic devices simply allow the passage of the electrons from one solid electrical conductor to another. Electrodes in thermionic devices (such as cathode ray tubes) and field emission devices (such as cold cathodes) allow electrons to exit from a material surface into a vacuum.

Boron-doped diamond electrodes are known for use in electrochemistry. Boron-doped diamond electrodes have been developed for the destruction of waste by electrochemical means (e.g. US Patent Number 5,399,247), for chemical synthesis (e.g. Panizza et al, 'Electrochemical oxidation of phenol at boron-doped diamond electrode. Application to electro-organic synthesis and wastewater treatment', Ann. Chim., 92 (2002), 995-1006), and for chemical analysis (e.g. EP1651951).

D. J. Zhong et al, 'Fabrication and electrochemical characterization of boron-doped diamond interdigitated array disc electrode', Proc. IMechE. Part E: J. Process Mechanical Engineering, 221 (2007), 201-205, describes a device comprising an interdigitated array of boron-doped diamond electrodes that are deposited by

chemical vapour deposition (CVD) on an undoped diamond layer, itself deposited by CVD on a silicon wafer. Both the undoped and doped diamond layers are rough and there is a height difference between the surfaces of the doped and undoped layers.

A similar structure is disclosed in W. Zhang et al ('Electrochemical characteristics of an interdigitated microband electrode array of boron-doped diamond film', Collect. Czech. Chem. Commun., 74 (2009), 393-407).

In US 2008/0314744, an interdigitated microelectrode is disclosed in which the electrodes are initially screen printed as metal pastes and then their dimensions are controlled by a photolithography and etching process. In the same document the use of 'plated-through-holes' to connect the interdigitated electrodes to the back surface of the electrode array is described.

In WO2008/059428, an interdigitated electrode array comprising a diamond substrate with conductive electrodes that are optionally conductive diamond is proposed for use as a solid state radiation detector.

Summary

Viewed from a first aspect there is provided a microelectrode for electrochemical use comprising:

(a) an electrically non-conductive diamond plate having a first surface containing at least two discrete recesses and an opposed second surface;

(b) electrically conductive diamond material contained within said recesses and being substantially flush with the first surface of said diamond plate, the electrically conductive diamond material in each of said at least two discrete recesses providing respective working electrodes in use; and

(c) at least two electrically conductive connection members that extend from the second surface of the electrically non-conductive diamond plate into the electrically non-conductive diamond plate, such that each of the connection

members is electrically connected to respective ones of the working electrodes.

The arrangement of the working electrodes and the electrically conductive connection members allows the working electrodes to be addressed from the opposed second surface of the microelectrode. The microelectrode may be used in an environment that is chemically aggressive without risk that the electrical connections to the microelectrode will be attacked by the environment.

By "substantially flush" it is meant that the root-mean-square roughness R_q measured across any interface between a working electrode in the first surface and the first surface of the electrically non-conducting diamond plate is 50 nm or less.

The definition of R_q is well known in the art and may be found in 'Tribology: Friction and Wear of Engineering Materials' by I. M. Hutchings (published by Edward Arnold (London), 1992, pages 8-9). For completeness the R_q is defined as:

$$R_q = \sqrt{\frac{1}{L}\int_0^L y^2(x)dx}$$

where *y* is the deviation of the surface height from the mean height at a distance *x* from the origin, and *L* is the overall length of the profile under examination. Methods of determining values of R_q are well known in the art and include the use of probe profilometers, non-contact (e.g. optical) profilometers and other surface probe instruments such as atomic force microscopes.

Viewed from a second aspect, there is provided a method of using a microelectrode for electrochemical use for characterising or monitoring an electrochemical reaction or process comprising:

(a) providing a microelectrode comprising:

(i) an electrically non-conductive diamond plate having a first surface containing at least two discrete recesses and an opposed second surface;

(ii) electrically conductive diamond material contained within said recesses and being substantially flush with the first surface of said diamond plate, the electrically conductive diamond material in each of

said at least two discrete recesses providing respective working electrodes in use; and

(iii) at least two electrically conductive connection members that extend from the second surface of the electrically non-conductive diamond plate into the electrically non-conductive diamond plate, such that each of the connection members is electrically connected to respective ones of the working electrodes;

(b) connecting the working electrodes of the microelectrode via the connection members within an electrical circuit;

(c) immersing the microelectrode in an electrolyte such that at least part of each working electrode is exposed to the electrolyte;

(d) imposing a potential difference between the working electrodes; and

(e) measuring or monitoring the current flow between the working electrodes.

Viewed from a third aspect, there is provided a method of making a microelectrode for electrochemical use comprising the steps of:

(a) providing an electrically non-conductive diamond plate with substantially parallel first and second surfaces;

(b) forming at least two discrete recesses in the first surface;

(c) depositing electrically conductive diamond material in said recesses, the electrically conductive diamond material in said recesses forming working electrodes; and

(d) forming for each working electrode an electrical connection between the second surface of the electrically conductive diamond plate and the working electrode.

Detailed Description

The electrically non-conductive diamond plate may be rectangular when viewed in plan. Other shapes viewed in plan are possible including square, circular, oval, parallelogram-shapes, rhombus-shaped, kite-shaped, trapezoidal or any other regular or irregular shape.

The lateral dimensions electrically non-conductive diamond plate may be any suitable size. Typically lateral dimensions will range from of order 1 mm to several tens of mm depending upon the intended dimensions and separation of the working electrodes. The thickness of the electrically non-conductive diamond plate may be any suitable thickness, typically between 0.1 mm and 10 mm.

The electrically non-conductive diamond plate may comprise single-crystal diamond or polycrystalline diamond. The electrically non-conductive diamond plate may comprise natural or synthetic diamond. In embodiments where the electrically non-conductive diamond plate comprises synthetic diamond, the synthetic diamond may be produced by a chemical vapour deposition (CVD) process (often referred to as "CVD diamond" or "CVD diamond material") or a high-pressure/high-temperature (HPHT) process (often referred to as "HPHT diamond" or "HPHT diamond material"). In an embodiment of the invention, the electrically non-conductive diamond plate may comprise polycrystalline synthetic diamond produced by a CVD process (referred to hereinafter as "polycrystalline CVD diamond" or "polycrystalline CVD diamond material").

In an embodiment of the invention, the electrical resistivity of the electrically non-conductive diamond plate is 10^6 ohm.cm or greater. Alternatively the electrical resistivity may be 10^8 ohm.cm or greater, alternatively 10^{10} ohm.cm or greater, alternatively 10^{11} ohm.cm or greater. An advantage of using a substrate material with a high electrical resistivity is that the leakage current is reduced between the working electrodes enabling very small separations between electrodes, for example of the order of 1 μm to 100 μm.

The electrically conductive diamond material contained within the recesses may be electrically conductive CVD diamond material.

The electrically conductive diamond material contained within the recesses may be electrically conductive polycrystalline CVD diamond material.

The electrically conductive diamond material contained within the recesses may be made electrically conductive by any suitable means, for example by doping the diamond with, for example, boron, phosphorus, sulphur, lithium, or any other suitable element. In one embodiment the electrical conductivity of the electrically conductive diamond material is provided by doping with boron, the material referred to herein as "boron-doped diamond material". The preferred method of doping the diamond material is to add the dopant during the synthesis process.

Generally, in embodiments where the electrically non-conductive diamond plate is single crystalline in nature, then the electrically conductive diamond material contained in the recesses will also be predominantly single crystalline in nature. Similarly, generally in embodiments where the electrically non-conductive diamond plate is polycrystalline in nature, the electrically conductive diamond material contained in the recesses will also be polycrystalline in nature. These combinations are typical because of the relative ease of deposition of single or polycrystalline diamond material on, respectively, single or polycrystalline diamond plate. Other combinations may be possible and are not excluded.

In certain embodiments, the electrically non-conductive diamond plate contains additional recesses that contain electrically conductive diamond material to provide one or more counter electrode(s) and/or reference electrode(s) in addition to the two or more working electrodes already described. In these embodiments the electrically conductive diamond material making up any of the working electrodes, any counter electrodes, or any reference electrodes may be boron-doped CVD diamond.

The concentration of boron in the electrically conductive diamond material may optionally be 10^{18} atoms/cm^3 or greater, alternatively 10^{19} atoms/cm^3 or greater, alternatively 10^{20} atoms/cm^3 or greater, alternatively 10^{21} atoms/cm^3 or greater. The concentration of boron atoms in the electrically conductive diamond material may be 10^{22} atoms/cm^3 or lower, alternatively 10^{21} atoms/cm^3 or lower, alternatively 10^{20} atoms/cm^3 or lower. The concentration of boron in the electrically

conductive diamond material may be between 10^{18} atoms/cm^3 and 10^{21} atoms/cm^3, alternatively may be between 10^{19} atoms/cm^3 and 10^{21} atoms/cm^3.

The electrical resistivity of the electrically conductive diamond material that provides any of the working electrodes, any counter electrodes, or any reference electrodes may be about 10^4 ohm.cm or lower, alternatively 10 ohm.cm or lower, alternatively 5 x 10^{-1} ohm.cm or lower, alternatively 2 x 10^{-1} ohm.cm or lower, alternatively 1 x 10^{-1} ohm.cm or lower, alternatively 1 x 10^{-2} ohm.cm or lower, alternatively 10^{-3} ohm.cm or lower. Alternatively, the electrical resistivity of the electrically conductive diamond material that provides any of the working electrodes, any counter electrodes, or any reference electrodes may be in the range between 5 x 10^{-1} ohm.cm and 2 x 10^{-2} ohm.cm. An advantage of minimising the electrical resistivity of the material comprising the layer of electrically conductive diamond material is that as the electrical resistivity decreases the potential drop between any two points on a working electrode also decreases, so giving the microelectrode spatially more uniform performance. Whilst for some embodiments the electrical resistivities of the electrically conductive diamond material that provides the respective working electrodes are substantially the same, this need not necessarily be the case.

The working electrodes are those electrodes between which, during use of the microelectrode, an electrochemical reaction or process is monitored, or an electrochemical property of an electrolyte is determined. At any time during use at least one working electrode is an anode and at least one working electrode is a cathode. “In use” in this context means when there is a non-zero potential difference between the working electrodes.

One of the principle uses of microelectrodes is for performing cyclic voltammetry. In cyclic voltammetry, the voltage applied to one working electrode relative to the voltage applied to the other working electrode is swept from zero to a positive value, back through zero to a negative value before returning to zero. Consequently each working electrode is an anode for part of the cycle and a cathode for part of the cycle.

When a first working electrode is biased relative to a second working electrode such that anions (negatively charged ions) are attracted to the first working electrode, the first working electrode is an anode. When a first working electrode is biased relative to a second working electrode such that cations (positively charged ions) are attracted to the first working electrode, the first working electrode is a cathode.

The recesses in the first surface of the electrically non-conductive diamond plate may be any suitable shape.

For example any recess may be an elongate recess, for example a channel-shaped elongate recess. By "elongate" it is meant that the length of the recess is typically 2 or more, alternatively 5 or more, alternatively 10 or more, alternatively 20 or more times the greater than the mean width of the recess. Where a recess is an elongate recess, the length of the recess may typically be 0.5 mm or greater, alternatively 1 mm or greater, alternatively 3 mm or greater, alternatively 5 mm or greater, alternatively 8 mm or greater, alternatively 10 mm or greater.

The layout of the recesses in the first surface typically corresponds to a pre-selected desired ultimate electrode pattern. Electrode patterns include branched electrodes, such as interdigitated electrodes and unbranched electrodes. Where the electrode pattern includes unbranched electrodes, the electrodes may be straight or curved or a combination of straight sections and curved sections.

Where the recesses are generally channel-shaped, such channel shaped recesses may for example be generally "U"-shaped or "V"-shaped or "V"-shaped with a flat bottom in cross-section (profile). The recesses, when containing electrically conductive diamond material provide working electrodes. Recess configurations other than channel-shaped ones that could provide a desired pre-selected working electrode configuration could be deduced by the person skilled in the art.

The depth of the recesses in the electrically non-conductive diamond plate may be 300 μm or less, alternatively 100 μm or less, alternatively 30 μm or less, alternatively 10 μm or less, alternatively 3 μm or less, alternatively 1 μm or less, alternatively 300 nm or less, alternatively 100 nm or less, alternatively 30 nm or less.

The depth of the recesses in the electrically non-conductive diamond plate may be 10 nm or more, alternatively 30 nm or more, alternatively 100 nm or more, alternatively 300 nm or more, alternatively 1 μm or more, alternatively 3 μm or more, alternatively 10 μm or more, alternatively 30 μm or more, alternatively 100 μm or more.

The depth of the recesses in the electrically non-conductive diamond plate may be between 1 μm and 300 μm, alternatively between 1 μm and 100 μm, alternatively between 100 nm and 3 μm, alternatively between 1 μm and 100 μm, alternatively between 1μm and 30 μm, alternatively between 1 μm and 10 μm, alternatively between 3 μm and 300 μm, alternatively between 3 μm and 100 μm, alternatively between 3 μm and 10 μm, alternatively between 10 μm and 300 μm, alternatively between 10 μm and 100 μm, alternatively between 10 μm and 30 μm.

One factor to consider in selection of the recess depth (and also its profile) is the method involved in manufacturing the microelectrode, and in particular in making, and filling the recesses, and if necessary planarising any over-filled recesses so that the electrically conductive diamond material is substantially flush with the diamond plate surface. Deeper recesses disadvantageously take longer to make and fill than shallower recesses, but the margin for error in planarising any over-filled recesses is advantageously larger for deeper recesses than for shallower recesses.

By “over-filled” it is meant that the thickness of electrically conductive diamond material that is deposited in the recess is greater than the depth of the recess. A recess having such a thickness of material is said to be “over-filled”.

The width of the recess where the sides of the recess meet the first surface of the electrically non-conductive diamond plate may be about 1 μm or greater, alternatively about 3 μm or greater, alternatively about 10 μm or greater, alternatively about 30 μm or greater, alternatively about 100 μm or greater. The width of the recess where the side of the recess meets the surface of the electrically non-conductive diamond plate may be 2000 μm or less, alternatively 1000 μm or less, alternatively 300 μm or less, alternatively 100 μm or less, alternatively 30 μm or less, alternatively 10 μm or less, alternatively 3 μm or less.

The width of a recess may or may not be greater than its depth. In an embodiment the ratio of the width of the recess where the sides of the recess meet the surface of the diamond plate, *w*, to the depth of the recess, *d*, i.e. *w/d* is 1 or greater, alternatively 2 or greater, alternatively 5 or greater, alternatively 10 or greater. Considering the method used to make the microelectrode, it is advantageous for the recesses to have a width that is substantially greater than the depth in embodiments in which the recesses are filled with electrically conductive diamond material using a CVD process and the width of the recesses is greater than about 100 μm.

In an embodiment, the recesses have a width where the sides of the recess meet the surface of the diamond plate of 10-20 μm and a depth of 10-20 μm, such that the width is equal to or greater than the depth.

The cross sectional profiles of the recesses in which the working electrodes are formed may be any shape and may vary with position and may be the same or different for different working electrodes. In an embodiment, the cross-sectional profile of one or more of the recesses is of substantially constant depth and is the same for all working electrodes. This situation has an advantage that it is easier to fill the recess uniformly. Another advantage is that avoids the need to over-fill shallower parts of a recess to ensure that deeper parts of the recess are completely filled.

In some embodiments, when considering a cross-section through a recess, for example through a channel-shaped recess, the maximum width of a recess (at any point measured in its depth) is 150% or less of the width of the recess where it meets the surface of the electrically non-conductive diamond plate. Alternatively, the maximum width of a recess is 120% or less of the width of the recess where it meets the surface of the electrically non-conductive diamond plate. Alternatively, the maximum width of a recess is 110% or less of the width of the recess where it meets the surface of the electrically non-conductive diamond plate. Alternatively, the maximum width of a recess is the same as the width of the recess where it meets the surface of the electrically non-conductive diamond plate.

In some embodiment, the cross sectional profile of a recess may have substantially straight sides. The angle that the straight sides of the recess make with the first surface of the diamond plate may be in the range 90°±10°, alternatively 90°±5°, alternatively 90°±3°, alternatively 90°±2°, alternatively 90°±1°. In this case, the base of the recess may also be substantially straight and similarly at an angle of 90°±10°, alternatively 90°±5°, alternatively 90°±3°, alternatively 90°±2°, alternatively 90°±1°from the straight sides. An advantage of the angle that the sides the recess make with the surface of the diamond plate being close to 90° is that the width of the recesses, and hence separation between the working electrodes is constant with depth. This is advantageous in terms of the method of manufacture of the microelectrode, because it means that if the electrode is planarised after the conductive diamond material is deposited in the recesses then the variation in the width of the electrode at the surface after different extents of planarisation is reduced which provides tolerance in the planarisation process to achieve a particular electrode separation.

In some embodiments, the width of the recess is narrower at its base than where the sides of the recess meet the first surface of the electrically non-conductive diamond plate. For some embodiments the difference in the width may be in the range 0.1% to 25%. For example, the width of the recess at the base may be less than 100% and 99.9% or more of the width of the recess where the sides of the recess meet the first surface of the electrically non-conductive diamond plate,

alternatively less than 100% and 99% or more of the width of the recess where the sides of the recess meet the first surface of the electrically non-conductive diamond plate, alternatively less than 100% and 98% or more of the width of the recess where the sides of the recess meet the surface of the electrically non-conductive diamond plate, alternatively less than 100% and 97% or more of the width of the recess where the sides of the recess meet the first surface of the electrically non-conductive diamond plate, alternatively less than 100% and 95% or more of the width of the recess where the sides of the recess meet the first surface of the electrically non-conductive diamond plate, alternatively less than 100% and 90% or more of the width of the recess where the sides of the recess meet the first surface of the electrically non-conductive diamond plate, alternatively less than 100% and 85% or more of the width of the recess where the sides of the recess meet the first surface of the electrically non-conductive diamond plate, alternatively less than 100% and 80% or more of the width of the recess where the sides of the recess meet the first surface of the electrically non-conductive diamond plate, alternatively less than 100% and 75% or more of the width of the recess where the sides of the recess meet the first surface of the electrically non-conductive diamond plate. In some instances, particularly where adjacent recesses are close to each other (e.g. closer than about 10 μm), it an advantage for the width of the recess to be narrower at its base than where the side surfaces of the recess meet the first surface of the electrically non-conductive diamond plate. This is because the material adjacent to the edge of the recess at the first surface of the electrically non-conductive diamond plate is better supported by the sloping side surfaces compared to a recess with side surfaces that are perpendicular, or close to perpendicular, to the first surface of the electrically non-conductive diamond plate causing the structure to be less weak, thereby allowing a microelectrode having a small separation between a working electrode and an adjacent working electrode to be fabricated more easily.

In some embodiments, one side of the recess may be at an angle of approximately 90° to the first surface of the electrically non-conductive diamond plate and one side of the recess may be at an angle of less than 90° to the first surface (measured within the recess) such that the width of the base of the recess is less

than the width of the recess where the sides of the recess meet the first surface. This embodiment represents a compromise between embodiments with two substantially vertical sides in which the material separating a working electrode from another working electrode may be structurally weak and embodiments with two sloping sides in which more precision is required in any planarisation process applied to remove any electrically conductive diamond material overfill, in order to achieve a particular separation between the working electrodes. This embodiment finds particular application for embodiments where the electrodes are closely spaced, for example where two working electrodes are parallel and unbranched.

The recesses may be substantially uniform in depth or vary in depth over their length. By "substantially uniform" the inventors intend that over 75% or more of the length of the recess, the depth of the recess deviates by 10% or less from the average depth of the recess. Such a measurement may be made using any suitable means; suitable means include contact and non-contact surface profilometers. An advantage of the recesses having substantially uniform depths is that the amount of electrically conductive diamond material that needs to be deposited to completely fill the recesses is substantially uniform over the whole recess.

The separation of the recesses will in general eventually constitute the separation between the working electrodes (the anode and the cathode). The desired separation of the working electrodes is in some applications dependent upon the reaction or property that the device is intended to monitor. In some embodiments, the microelectrode of the invention may comprise multiple sets of working electrodes having different separations, for example a pH monitor may have one pair of closely spaced working electrodes for monitoring the pH of low conductivity electrolytes and a second pair of widely spaced working electrodes for monitoring the pH of high conductivity electrolytes. The presence of multiple pairs of working electrodes having different separations enables the microelectrode to have a wider sensing range.

The separation of the working electrodes measured at the surface of the electrically non-conductive diamond plate may be 0.5 μm or greater, alternatively 1 μm or greater, alternatively 10 μm or greater, alternatively 20 μm or greater, alternatively 30 μm or greater, alternatively 50 μm or greater, alternatively 100 μm or greater, alternatively 300 μm or greater, alternatively 1 mm or greater, alternatively 3 mm or greater, alternatively 10 mm or greater, alternatively 20 mm or greater. The separation of the working electrodes measured at the surface of the electrically non-conductive diamond plate may be 50 mm or less, alternatively 30 mm or less, alternatively 20 mm or less, alternatively 10 mm or less, alternatively 3 mm or less, alternatively 1 mm or less, alternatively 300 μm or less, alternatively 100 μm or less, alternatively 30 μm or less, alternatively 10 μm or less, alternatively 3 μm or less, alternatively 1 μm or less. Typically the separation between the working electrodes is between about 0.5 μm and 300 μm. In an embodiment of the invention the separation between the working electrodes is between 3 μm and 300 μm. Alternatively invention the separation between the working electrodes is between 10 μm and 100 μm. Smaller separations result in a higher electric field between the working electrodes (for a given potential difference) and shorter times for species to reach one of the working electrodes, thereby enabling the behaviour of shorter lived species to be measured or monitored. However there are practical difficulties associated with making the separation between the working electrodes too small, for example, the regions separating the recesses may become fragile and it may be difficult to ensure that there are no short circuits between created during the deposition of the electrically conductive diamond material and its subsequent processing. The problem of fragility may be exacerbated by the recess having side surfaces that are perpendicular to the first surface of the electrically non-conductive diamond plate and may be ameliorated by the recess having side surfaces that are not perpendicular to the first surface of the electrically non-conductive diamond plate as previously described.

For some embodiments, the separation at the surface of the diamond plate between the recesses forming the working electrodes is substantially constant. By “substantially constant” the inventors mean that for 60% or more of the length of the electrode or the maximum deviation from the mean separation is 10% or less.

The electrically conductive diamond material is substantially flush with the first surface of the electrically non-conductive diamond plate, by which we mean that the root-mean-square roughness, R_q, of the surface measured across any interface between a working electrode in the first surface and the first surface of the electrically non-conductive diamond plate is 50 nm or less. For some embodiments, the root-square-mean roughness, R_q, is even less; for example for some embodiments, the root-mean-square roughness, R_q, of the surface measured across any interface between a working electrode in the first surface and the first surface of the electrically non-conductive diamond plate is 20 nm or less. Alternatively the root-mean-square roughness, R_q, of the surface measured across any interface between a working electrode and the electrically non-conductive diamond plate is 10 nm or less, alternatively 5 nm or less, alternatively 2 nm or less. Low values of R_q measured across the interface are advantageous as this minimises the disruption in flow of electrolyte across the surface between the working electrodes giving more accurate results.

An interface between a working electrode in the first surface and the first surface of the electrically non-conductive diamond plate can also be characterised in terms of the height difference between the surface of the electrically non-conductive diamond plate and the surface of the working electrode. In an embodiment the height difference measured across any interface between a working electrode in the first surface and the first surface of the electrically non-conductive diamond plate is 10 μm or less. Alternatively the height difference is 1 μm or less, alternatively 0.1 μm or less, 10 nm or less, alternatively 5 nm or less, alternatively 3 nm or less, alternatively 2 nm or less, alternatively 1 nm or less, alternatively 0.5 nm or less. The height difference may be measured using an instrument of the type used to measure other surface characteristics (e.g. R_q), such as a contact or non-contact profilometer.

In all embodiments for each working electrode, an electrically conductive connection member is provided that connects the working electrode to the second surface of the electrically non-conductive diamond plate.

In some embodiments, each electrically conductive connection member comprises a cavity in the electrically non-conductive diamond plate that extends between the second surface of the electrically non-conductive diamond plate and the working electrode.

In alternative embodiments, each electrically conductive connection member comprises a cavity in the electrically non-conductive diamond plate that extends from the second surface of the electrically non-conductive diamond plate to the first surface of the electrically non-conductive diamond plate. In embodiments where the connection member extends from the second surface to the first surface, the connection member has a first end substantially flush with the first surface.

The cavity in the electrically non-conductive diamond plate has a surface. The surface may be metallised, for example with one or more metal layers. An example of suitable combination of metal layers is a Ti base layer, a Pt barrier layer and an Au capping or bonding layer. The remainder of the cavity may be unfilled. The remainder of the cavity may be partially filled or completely filled, for example with an electrically conductive polymeric material, such as silver-loaded epoxy resin, or a solder material or a braze material. Where the cavity is partially or completely filled, the choice of filling material may depend on the environment, for example the temperature, to which the microelectrode will be exposed when in use. In some embodiments, the cavity may be partially filled with electrically conductive diamond material.

A means of connection to an external circuit may be provided as part of the connection member. For example a wire may be soldered or attached using silver-loaded epoxy resin into the cavity or a socket soldered into the cavity. Other methods of connection are not excluded.

In embodiments where the connection members have first ends substantially flush with the first surface of the electrically non-conductive diamond plate, the first ends

of the connection members may be at least partially covered with a layer electrically non-conducting material.

In some embodiments, the first ends of the connection members may be completely covered with a layer of electrically non-conductive material.

In embodiments where the first ends of the connection members are partially or completely covered with electrically non-conductive material, the thickness of electrically non-conductive material used to at least partially or completely cover the first ends of the connection members may be chosen according to the application. For some applications, they are advantageously thick enough to ensure that the layer is continuous and sufficiently robust, but not so thick as to disrupt the flow of fluid (e.g. an electrolyte) across the microelectrode when the microelectrode is in use. In an embodiment, the electrically non-conductive material that at least partially or completely covers the first ends of the connection members may have a thickness of 10 μm or less, alternatively 3 μm or less, alternatively, the thickness is 1 μm or less, alternatively 300 nm or less, alternatively 100 nm or less, alternatively 30 nm or less, alternatively 10 nm or less.

In an embodiment, the electrically non-conductive material that at least partially or completely covers the first ends of the connection members may have a thickness of 3 nm or more, alternatively 10 nm or more, alternatively 30 nm or more, alternatively 100 nm or more, alternatively 300 nm or more, alternatively 1 μm or more, alternatively 3 μm or more.

In embodiments where the first ends of the connection members are partially or completely covered with electrically non-conductive material, the electrically non-conductive material that at least partially or completely covers the first ends of the connection members may be any suitable material. In one embodiment the electrically non-conductive material that at least partially or completely covers the first ends of the connection members comprises electrically non-conductive diamond-like carbon (DLC). An advantage of using electrically non-conductive DLC for the covering material is in terms of the method of manufacture of the

microelectrode, in that it easily applied, for example, as a thin layer and in a defined location. Another advantage of using electrically non-conductive DLC is in terms of the use of the microelectrode is that electrically non-conductive DLC is chemically compatible with the diamond material of the diamond plate. A further advantage is that where the connection members comprise electrically conductive diamond material, electrically non-conductive DLC is chemically compatible with the diamond material of the connection members and also has a similar level chemical resistivity. Thus when the covering material is DLC, the nature of the covering material does not significantly restrict the nature of the chemical environments in which the microelectrode can be used. Also the use of DLC is advantageous as it adheres well to diamond, being chemically very similar and its thermal expansion coefficient is also very similar to that of diamond such that there is a low possibility of delamination of the DLC layer from the underlying material. An example of a method for applying a DLC layer that is suitable for use in the current invention is disclosed in WO2008/099220. The compatibilities of DLC to diamond material of the plate and in some embodiments the connection members are particularly applicable to CVD diamond material which is used in some embodiments as the conductive diamond material in the recesses making up the working electrodes, and in the cavities comprising the connection members.

When the microelectrode of the current invention is in use for characterising an electrochemical reaction, the microelectrode may be arranged such the first ends of the connection members are not exposed to the electrolyte.

The cavities in the diamond plate that are in communication with the working electrodes can have any suitable geometry. In a simple form a cavity consists of a hole of approximately cylindrical or truncated cone shape extending from the second surface of the electrically non-conductive diamond plate. Where the cross section of the cavity is approximately circular, the diameter may be between about 5 µm and 1 mm, alternatively between about 5 µm and 100 µm. Where the cavity has an approximately truncated cone shape, the taper of the cone may be typically between 0.1° and 20°. As an example, the cavity may be approximately cylindrical or truncated cone shaped for its entire extent or a combination of the cylindrical for

part of its extent or truncated cone for part of its extent. In a particular embodiment in which the cavity extends from the second surface to a working electrode, the cavity has a substantially circular cross-section parallel to the second surface of the electrically non-conductive diamond plate and a stepped profile perpendicular to the second surface.

Other geometry cavities are also envisaged, for example those of rectilinear profile or any other regular or irregular profile.

The cavities may be formed by any suitable process. In one embodiment, cavities are formed by a laser drilling process using laser operating at a wavelength of approximately 1 μm (for example Nd:YAG). This process is also known as "laser trepanning".

Methods of use of microelectrodes have been described hereinbefore in the summary of the invention. In certain embodiments of method of use the microelectrode may have any one or more of the features that have been described hereinbefore.

Methods of making a microelectrode have been described hereinbefore in the summary of the invention.

The recesses in the first surface of the electrically non-conductive diamond plate may be formed, for example, by a plasma etching process. Inductively-coupled plasma etching is suitable for performing the plasma etching. In one embodiment the inductively-coupled plasma etching process utilises a gas mixture comprising argon and a halogen-containing gas. In a particular embodiment the halogen-containing gas is chlorine; the use of such a process and gas mixture for the etching of diamond surfaces is disclosed in WO2008/090511.

As another example the recesses may be formed by a laser processing technique. An example of a laser processing technique that is capable of ablating diamond and is therefore suitable for forming the recesses of the invention is a deep ultra-

violet (UV) argon-fluorine (Ar-F) excimer laser, which produces deep UV radiation at a wavelength of 193 nm.

Electrically conductive diamond material may be deposited in the recesses by a chemical vapour deposition process. Suitable processes include microwave assisted plasma chemical vapour deposition and hot filament chemical vapour deposition. Other chemical vapour deposition processes are not excluded. The electrically conductive diamond material may be deposited from a process gas comprising hydrogen, methane (or other hydrocarbon) and diborane (or other gaseous boron containing gas).

In certain embodiments methods involve depositing electrically conductive material so that it not only lies in the recesses but also extends over at least part of the surface of the electrically non-conductive diamond plate around the recesses. The deposition step may also involve overfilling the recesses so that the electrically conductive material extends above the level of the electrically non-conductive diamond plate above the recess. In these cases the method may involve planarising the surface after electrically conductive diamond material has been deposited. Planarising may be performed so as to make the surface of the working electrode flush with the electrically non-conductive diamond plate on either side of the recesses. Planarisation may also generally expose the electrically non-conductive diamond plate on either side of the recess. Planarisation may in some embodiments be to the original first surface of the electrically non-conductive diamond plate. Planarisation may in other embodiments be further, and be to a depth below the original first surface of the electrically non-conductive diamond plate, i.e. into the thickness of the electrically non-conductive diamond plate.

The planarisation process may be performed by any suitable means. Suitable processes include conventional lapidary processes such as lapping with diamond grit and diamond polishing using a diamond-loaded resin-bonded wheel.

The electrically conductive diamond material is generally laid down to provide the working electrodes in a desired electrode pattern. The planarisation process may

remove sufficient depth of material to expose that electrode pattern, but not so much that the desired electrode pattern is partially or completely removed. Thus careful measurement of the depth of material initially present, the initial thickness of the electrically non-conductive diamond plate is desirable. It is advantageous for the first and second surfaces of the initial electrically non-conductive diamond plate to be substantially parallel in order to facilitate precise and accurate planarisation. The angular separation between the normals to the first surface and the second surface of the electrically non-conductive diamond plate may be 3° or less, alternatively 2° or less, alternatively 1° or less, alternatively 0.8° or less, alternatively 0.5° or less, alternatively 0.2° or less, alternatively 0.1° or less, alternatively 0.05° or less. As another example, the variation in thickness of the initial electrically non-conductive diamond plate may be 52 μm/mm or less, alternatively 35 μm/mm or less, alternatively 17 μm/mm or less, alternatively 14 μm/mm or less, alternatively 9 μm/mm or less, alternatively 3.5 μm/mm or less, alternatively 1.7 μm/mm or less, alternatively 0.9 μm/mm or less.

In embodiments of the method according to the invention, subsequent to the formation of the at least two recesses in the electrically non-conductive diamond plate, the electrically non-conductive diamond plate may be cleaned to remove any debris from the recess preparation process. An example of a suitable cleaning process is a mixture of hot concentrated sulphuric acid and potassium nitrate; other cleaning processes are possible and may be used.

In embodiments of the method according to the invention, subsequent to the formation of the cavities in the second surface of the electrically non-conductive diamond plate by laser drilling, any debris may be removed by a cleaning process, for example using a mixture of hot concentrated sulphuric acid and potassium nitrate; other cleaning processes are possible and may be used.

In certain embodiments of method the electrically conductive diamond material is deposited into one or more recesses using a CVD process. In certain embodiments the method involves at least partially filling the cavities in the second surface of the electrically non-conductive diamond plate with electrically conductive

material other than electrically conductive diamond material. In other embodiments of method according to the invention, the recesses, cavities in the electrically non-conductive diamond plate, electrically conductive diamond material and electrically non-conductive material and other features have the characteristics set out above with respect to the description of the microelectrode and its features.

Some embodiments of the method may include the step of depositing a layer of electrically non-conductive material so as to at least partially cover the cover the first ends of the connection members. The electrically non-conductive material may be electrically non-conductive diamond-like carbon. Where the electrically non-conductive material is electrically non-conductive diamond-like carbon the thickness of the layer is 10 nm or greater. Where the electrically non-conductive material is electrically non-conductive diamond-like carbon the thickness of the layer is 2 μm or less.

Description of the Drawings

For a better understanding of the present invention and to show how the same may be carried into effect, embodiments of the present invention will now be described by way of example only with reference to the accompanying drawings, in which:

Figure 1a is a perspective view which shows an embodiment of a microelectrode for electrochemical use according to the invention having two working electrodes;

Figure 1b is a cross section through the microelectrode of figure 1a along AA';

Figure 1c is a cross section through the microelectrode of figure 1a along BB';

Figure 2 is a view showing the microelectrode figure 1 connected to an external circuit and immersed in an electrolyte; and

Figure 3a-e is a sequence of cross sectional views showing in schematic outline the steps for the fabrication of the microelectrode of figure 1.

Detailed Description of Certain Embodiments

Embodiments of the invention are described with reference to the figures.

Figures 1a to c show an embodiment of microelectrode 1.

The microelectrode 1 for electrochemical use comprises a planar, rectangular, electrically non-conductive polycrystalline CVD diamond plate 2, having a first surface 4 and a second surface 6 that is substantially parallel to the first surface.

Two discrete recesses 16, 18 (fig 1b) are arranged in the first surface, 2, in the pattern of the working electrodes (also referred to herein as the "electrode pattern"). The recesses are approximately 15 µm deep, approximately 50 µm in width and are separated from each other by approximately 1 mm. The side surfaces of the recesses are at an angle of 90° to the first surface. The recesses contain electrically conductive diamond material and this material thereby forms two working electrodes 8 and 10.

The microelectrode 1 contains two connection members 12 within the diamond plate 2 that extend from the second surface 6 to a working electrode 8, 10. Each connection member comprises a cavity 14 in the second surface 6 and has a surface 16. In Fig 1c, cavity 14 having surface 16 consists of a series of concentric cylindrical sections and/or truncated conical sections of progressively smaller diameters extending from the second surface 6 to each working electrode 8, 10.

The microelectrode 1 of fig 1 may be used for monitoring electrochemical reactions. Such an embodiment is shown schematically in figure 2. In fig 2, microelectrode 1 is immersed in an electrolyte 42 and connected by means of electrical connections 44 to a suitable external circuit 48 that enables a potential difference to be imposed between the working electrodes 8, 10 (not shown in fig 2) and also the current that flows between the working electrodes to be monitored.

This enables, for example, electrochemical oxidation and reduction reactions to be monitored.

A method of making the microelectrode 1 of fig 1 is described making reference to fig 3. Any or all of the optional features described with reference to fig 3 may be used herein in any combination.

The first step of the method shown in fig 3a comprises providing an electrically non-conductive diamond plate 50 having a first surface 52 and an opposed second surface 54. The first surface 52 and second surface 54 are substantially parallel.

In step 56 at least two separate recesses 58, 60 are formed in the first surface 52. The recesses are approximately 15 μm deep, approximately 50 μm wide when measured at the first surface 52 and the side surfaces of the recess are at an angle of 90° to the first surface 52. The at least two separate recesses 58, 60 are formed such that they are in a preselected electrode pattern. The recessed plate is shown in fig 3b.

In step 68, electrically conductive diamond material 70 is deposited in recesses 58, 60. The electrically conductive diamond material 70 is deposited by a CVD technique over the whole of the first surface 52 of the diamond plate 50 such that the whole surface is covered with electrically conductive diamond material to approximately the same. In CVD processes, the material is built up as a layer, the thickness of which increases with the duration of the deposition process. The layer of material that is deposited substantially conforms to the profile of the surface upon which it is being deposited. The plate with electrically conductive diamond deposited on its surface is shown fig 3c.

In step 72 the upper surface (in the orientation shown in Fig 3d) is planarised by removing deposited diamond material 70 down to the depth of the first surface 52 of the electrically non-conductive diamond plate 50, or further, thereby providing discrete exposed electrodes 74, 76 surrounded by electrically non-conductive diamond material on the planarised surface 92. The planarised surface 92 may

correspond to the first surface 52 of the plate 50 or be lower (in the orientation shown) than that surface. Because the side surfaces of the recesses are at an angle of 90° to the first surface 52, the process can tolerate the planarised surface 92 being lower than the first surface 52 without the separation between the electrodes 77 changing.

The planarisation process of step 72 may be performed by any suitable means. Suitable processes include conventional lapidary processes such as lapping with diamond grit and diamond polishing using a diamond-loaded resin-bonded wheel. Non-abrasive processes, for example plasma processes or laser processes, may also be used for planarisation.

Connection members between second surface 54 and working electrodes 74, 76 are formed in step 80. For each connection member extending between the second surface 54 and the working electrodes 74, 76, a cavity 82 having surface 86 is formed. In the embodiment shown in Fig 3(e), the shape of the cavity is a series of coaxial truncated conical sections of progressively smaller diameters. The cavity may be formed by laser drilling ("trepanning"). Surfaces 86 of the cavities can be metallised with one or more metal layers. Such metal layers may be applied by sputtering and an example of a suitable combination of layers is a Ti base layer, a Pt barrier layer and an Au bonding layer. A wire (not shown) providing electrical connection to an external circuit may be affixed into the cavity using a silver-loaded epoxy resin (or by any other suitable means, such as soldering or brazing).

The electrical connection may be encapsulated such that when the microelectrode is in use, access by the electrolyte to any conductive material that forms part of the electrical connection is not possible.

While this invention has been particularly shown and described with particular reference to preferred embodiments, it will be understood by those skilled in the art that various changes in form and detail may be made without departing from the scope of the invention as defined by the appended claims.

Claims

1. A microelectrode for electrochemical use comprising:
   (a) an electrically non-conductive diamond plate having a first surface containing at least two discrete recesses and an opposed second surface;
   (b) electrically conductive diamond material contained within said recesses and being substantially flush with the first surface of said diamond plate, the electrically conductive diamond in each of said at least two discrete recesses each providing respective working electrodes in use; and
   (c) at least two electrically conductive connection members that extend from second surface of the electrically non-conductive diamond plate into the electrically conductive diamond plate, such that each of the connection members is electrically connected to respective ones of the working electrodes.

2. A microelectrode for electrochemical use according to claim 1 wherein electrically non-conductive diamond plate comprises synthetic polycrystalline diamond material synthesised using a chemical vapour deposition process.

3. A microelectrode for electrochemical use according to claim 1 or claim 2 wherein the electrically conductive diamond material is boron-doped diamond material.

4. A microelectrode for electrochemical use according to any preceding claim wherein the depth of the recesses is 300 μm or less.

5. A microelectrode for electrochemical use according to any preceding claim wherein the depth of the recesses is 1 μm or greater.

6. A microelectrode for electrochemical use according to any preceding claim wherein the depth of the recesses is 10 μm or greater.

7. A microelectrode for electrochemical use according to any preceding claim wherein the width the recesses at the first surface is 2000 μm or less.

8. A microelectrode for electrochemical use according to any preceding claim wherein the width of the recess at the first surface of the working electrodes is 1 μm or more.

9. A microelectrode for electrochemical use according to any preceding claim wherein the width of the recess at the first surface of the working electrodes is 10 μm or more.

10. A microelectrode for electrochemical use according to any preceding claim wherein the width of the recess is equal to or greater than the depth of the recess.

11. A microelectrode for electrochemical use according to any preceding claim wherein the separation at the first surface between two working electrodes is 50 mm or less.

12. A microelectrode for electrochemical use according to any preceding claim wherein the separation at the first surface between two working electrodes is 1 μm or greater.

13. A microelectrode for electrochemical use according to any preceding claim wherein the root-mean-square roughness, R_q, of the surface measured across any interface between a working electrode in the first surface and the first surface of the electrically non-conductive diamond plate is 50 nm or less.

14. A microelectrode according to any preceding claim wherein the height difference measured across any interface between a working electrode in

the first surface and the first surface of the electrically non-conductive diamond plate is 10 μm or less.

15. A microelectrode for electrochemical use according to any preceding claim wherein each electrically conductive connection member comprises: a cavity in the electrically conductive diamond plate extending between the second surface of the electrically non-conductive diamond plate and the working electrode.

16. A microelectrode for electrochemical use according to any of claims 1 to 14 wherein any of the at least two electrically conductive connection members extends from the second surface to the first surface, such connection member having a first end at the first surface.

17. A microelectrode for electrochemical use according to claim 16 wherein the microelectrode further comprises a layer of electrically non-conducting material at least partially covering the first end of any contact member having a first end at the first surface, but leaving at least part of the working electrodes uncovered.

18. A microelectrode for electrochemical use according to claim 17 wherein the thickness of the layer of electrically non-conducting material at least partially covering the first ends of the contact members is 10 μm or less.

19. A microelectrode for electrochemical use according to claim 16 or claim 17 wherein the thickness of the layer of electrically non-conducting material at least partially covering the first ends of the contact members is 3 nm or more.

20. A microelectrode for electrochemical use according to any of claims 17 to 19 wherein the electrically non-conducting material at least partially covering the first ends of the contact members is diamond-like carbon.

21. A method of using a microelectrode for electrochemical use for characterising or monitoring an electrochemical reaction or process comprising:

(a) providing a microelectrode comprising:

(i) an electrically non-conductive diamond plate having a first surface containing at least two discrete recesses and an opposed second surface;

(ii) electrically conductive diamond material contained within said recesses and being substantially flush with the first surface of said diamond plate, the electrically conductive diamond material in each of said at least two discrete recesses providing respective working electrodes in use; and

(iii) at least two electrically conductive connection members that extend from the second surface of the electrically non-conductive diamond plate into the electrically non-conductive diamond plate, such that each of the connection members is electrically connected to respective ones of the working electrodes;

(b) connecting the working electrodes of the microelectrode via the connection members within an electrical circuit;

(c) immersing the microelectrode in an electrolyte such that at least part of each working electrode is exposed to the electrolyte;

(d) imposing a potential difference between the working electrodes; and

(e) measuring or monitoring the current flow between the working electrodes.

22. A method of making a microelectrode for electrochemical use comprising the steps of:

(a) providing an electrically non-conductive diamond plate with substantially parallel first and second surfaces;

(b) forming at least two discrete recesses in the first surface;

(c) depositing electrically conductive diamond material in said recesses, the electrically conductive diamond material in said recesses forming working electrodes; and

(d) forming for each working electrode an electrical connection between the second surface of the electrically non-conductive diamond plate the working electrode.

23. A method according to claim 22 wherein the step of depositing electrically conductive diamond material in the recesses also comprises depositing electrically conductive diamond material over at least part of the first surface of the electrically non-conductive diamond plate.

24. A method according to claim 22 or claim 23 wherein, after the deposition of conductive diamond material, the method comprises the step of planarising the deposited electrically conductive diamond material and the electrically non-conductive diamond plate that is on either side thereof so as to expose the working electrodes and the surface of the electrically non-conductive diamond plate on either side of the working electrodes.

25. A method according to any of claims 22 to 24 wherein the depth of the at least two recesses is 300 μm or less.

26. A method according to any of claims 22 to 25 wherein the width of the at least two recesses is 2000 μm or less.

27. A method according to any of claims 22 to 26 wherein the width of the at least two recesses is equal to or greater than the depth of the recess.

28. A method according to any of claims 22 to 27 wherein the electrically conductive diamond material deposited into the at least two recesses is deposited using a chemical vapour deposition (CVD) process.

29. A method according to any of claims 22 to 28 wherein the electrically conductive diamond material is boron doped diamond material.

30. A method according to any of claims 22 to 29 wherein the step of forming an electrical connection between the second surface and each of the working electrodes comprises: for each of the working electrodes forming at least one cavity having a surface that extends from the second surface of the electrically non-conductive diamond plate to the working electrode.

31. A method according to claim 30 wherein forming an electrical connection between the second surface and each of the working electrodes comprises depositing electrically conductive material on the surface of the cavity.

32. A method according to claim 22 to 29 wherein the step of forming an electrical connection between the second surface and each of the working electrodes comprises the steps of forming a cavity that extends between the second surface and the first surface; at least partially filling the cavity with electrically conductive material such that the electrically conductive material at least partially filing the cavity is electrically connected to the working electrode; and depositing a layer of electrically non-conductive material so as to at least partially cover the first ends of the connection members but so as to leave uncovered at least part of the working electrodes.

33. A method according to claim 32 wherein the electrically non-conductive material is electrically non-conductive diamond-like carbon.

34. A method according to claim 33 wherein the thickness of the layer of electrically non-conductive diamond-like carbon is 10 nm or greater.

35. A method according to claim 32 or claim 33 wherein the thickness of the layer of electrically non-conductive material is 2 μm or less.

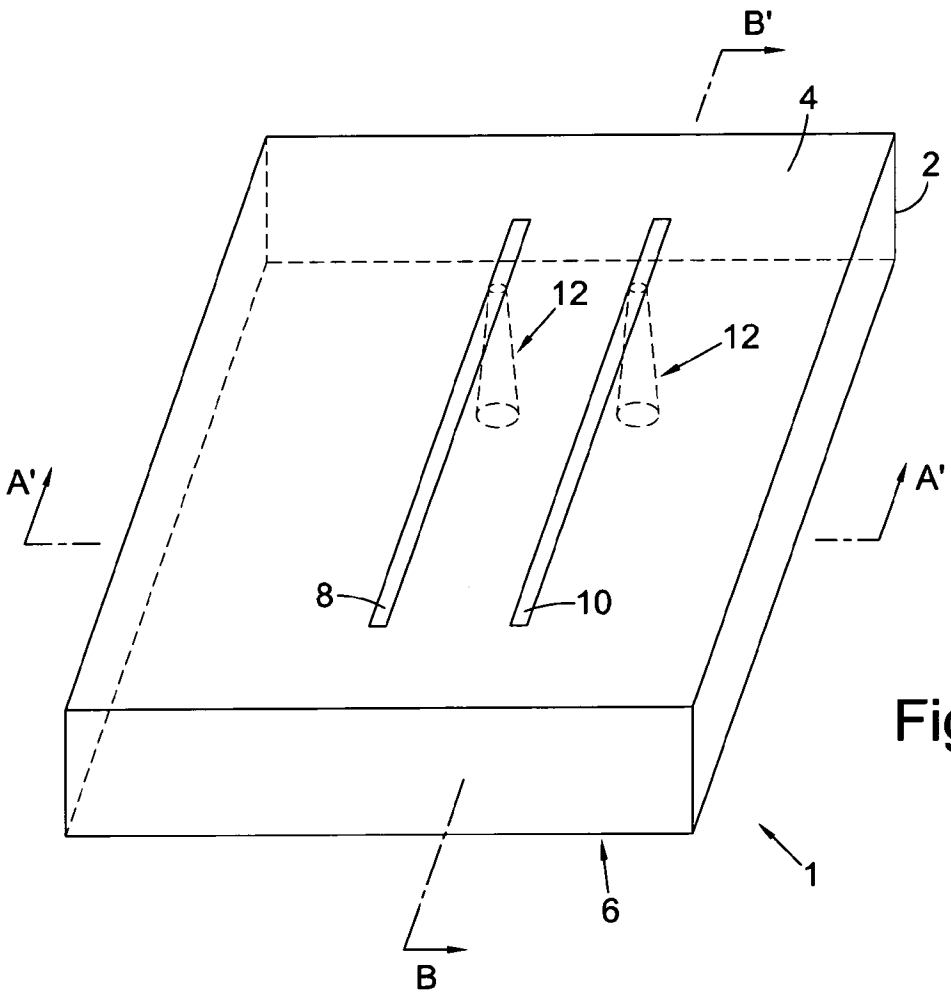


Fig. 1a

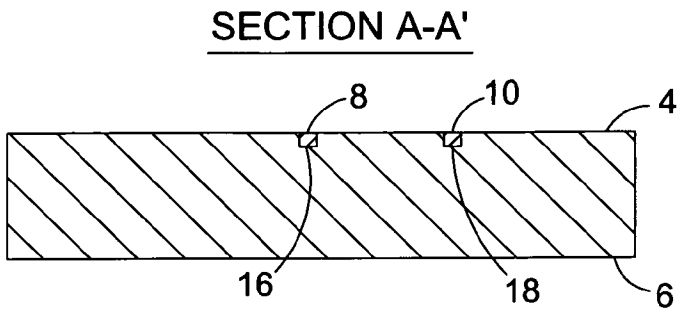


Fig. 1b

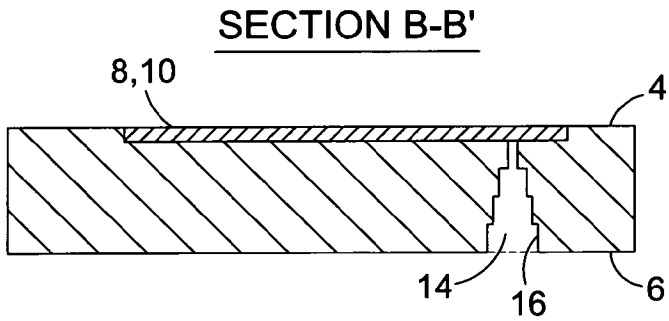


Fig. 1c

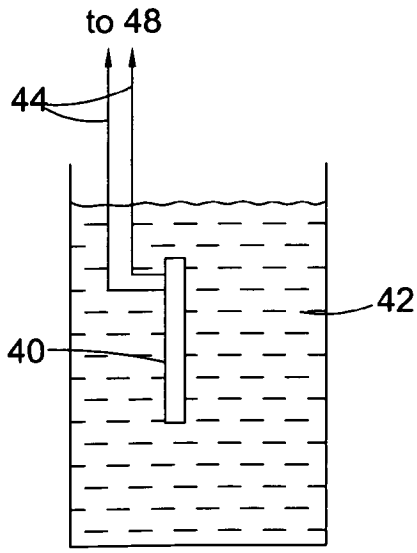


Fig. 2

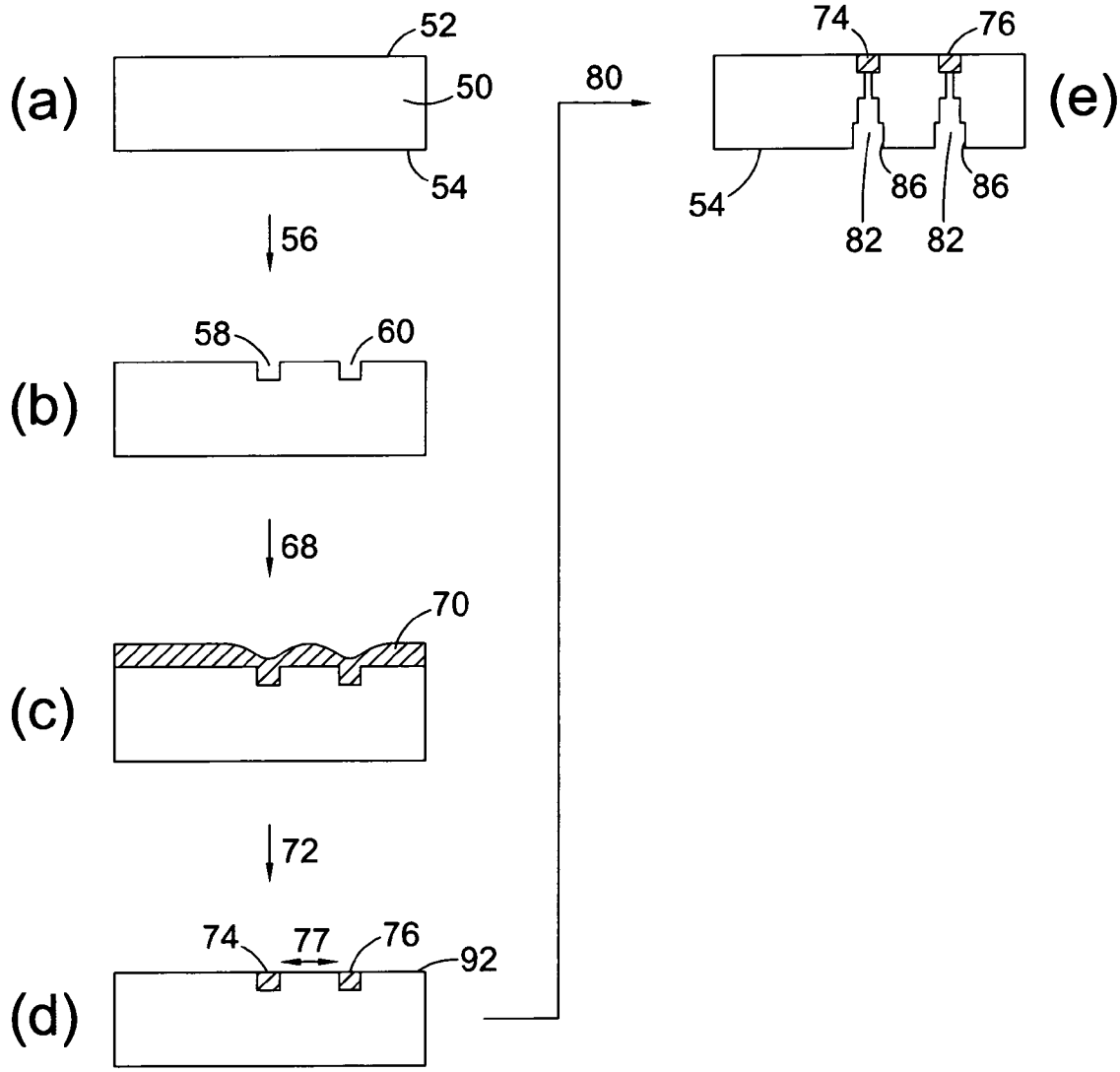


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068213

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/30
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/015435 A1 (SCHLUMBERGER TECHNOLOGY BV [NL]; SCHLUMBERGER HOLDINGS; SCHLUMBERGER C) 7 February 2008 (2008-02-07)	1-22, 25-35
Y	paragraph [0040] - paragraph [0049]; figure 3 claim 18	23,24
Y	WO 2005/012894 A1 (ELEMENT SIX LTD [GB]; PICKLES CHARLES SIMON JAMES [GB]; HALL CLIVE EDW) 10 February 2005 (2005-02-10) page 12, line 22 - line 28	23,24

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 May 2013	03/06/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Purdie, Douglas

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068213

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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