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(54) Title: MICROELECTRODE FOR MOLTEN SALTS

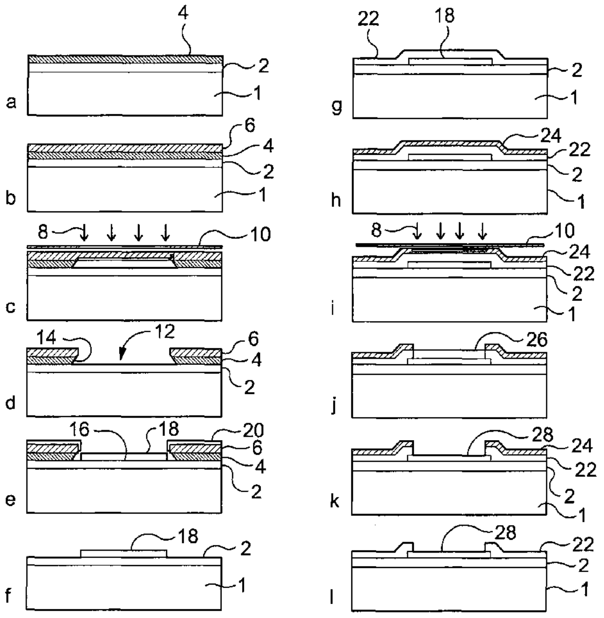

Fig. 1

(57) Abstract: An electrode, in particular a microelectrode, wherein the surface area (48) of conductor material (44) exposed for use is defined by a covering layer (46) comprising a covalent or an intermediate nitride or mixtures thereof is described. The covering layer (46) may comprise a nitride selected from the group consisting of Si, B, Al, Ga, In, P, Mn,Fe, Co, Ni, Te, Tl and Re nitrides or mixtures thereof. Methods of fabrication of the electrode are also provided.

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MICROELECTRODE FOR MOLTEN SALTS

Field of the invention

The present invention relates to electrodes especially microelectrodes suitable for use in harsh environments such as molten salt electrolytes. Methods of manufacture and uses for the electrodes are described.

Background to the Invention

Molten salts have proven to be an ideal medium for the development of a number of electrochemical processes, including extraction and processing of metals and materials and energy technologies. This is largely because molten salts typically provide a non-aqueous solvent with a wide potential window, good complexing ability and anhydrous conditions, which allows the preparation and study of highly reactive species that would not otherwise be accessible in ambient solvent systems. However there is a real need in such processes for techniques to be engineered which are able to sense and analyse the properties of chemical species in the extreme (high temperature and potentially highly corrosive) conditions found in molten salt systems.

Electroanalytical techniques provide an attractive approach to analysis of chemical species under such harsh conditions. Provided suitable electrodes are available, they can be deployed remotely, with data provided in the form of an electrical signal from the circuit employed. However, electrodes in contact with molten electrolytes must be capable of withstanding the conditions. Furthermore macro scale electrodes may have poor signal to noise characteristics, as a consequence of the relative size of the non-Faradaic current (capacitive current) over the Faradaic current and convection processes interfering with the otherwise diffusion controlled processes at the electrode surface. For these reasons microelectrodes, electrodes in which at least one dimension of the conductor material of the electrode is on the micrometre scale have been proposed (ref 1).

However fabrication of microelectrodes suitable for uses such as analysis in molten salts has been shown to be difficult, with variability in size and susceptibility to chemical attack and thermal degradation being encountered. (ref 2).

It is an object of the present invention to provide electrodes that address at least some of the aforementioned difficulties.

Description of the Invention

The present invention provides an electrode wherein the surface area of conductor material exposed for use is defined by a covering layer comprising a covalent or an intermediate nitride or mixtures thereof.

The electrode may be a microelectrode.

Covalent nitrides are insulators and may be selected from the group consisting of B, Al, Ga, In, Te, Si and P nitrides or mixtures thereof. Intermediate nitrides are those that can have semiconductor properties, but can be sufficiently insulating for use in a covering layer of an electrode. They may be selected from the group consisting of Mn, Fe, Co, Ni, Tl and Re nitrides, or mixtures thereof.

The present invention provides an electrode wherein the surface area of conductor material exposed for use is defined by a covering layer comprising a refractory nitride that is covalent or intermediate.

The refractory nitrides are nitrides that are chemically and physically stable at high temperatures and are thus particularly useful in electrodes that are to be employed in harsh environments. For use as a covering layer to the conductor material the refractory nitrides should be selected from those that are insulators or at least sufficiently insulating, under the conditions of use.

Thus the covalent and intermediate nitrides listed above (or mixtures, including mixtures containing at least one covalent nitride and at least one intermediate nitride) can be included in a refractory covering layer for the electrodes described herein.

The covering layer of electrodes of the invention may consist of, or consist essentially of one of the nitrides or mixtures of nitrides described above.

The covering layer may include other components compatible with the intended use.

The surface area of conductor material exposed for use is the surface of conductor material that contacts the electrolyte or other substance or fluid when the electrode is being used. Remaining conductor material, used for example for connecting to a circuit, is covered by the covering nitride layer, thus defining the surface area of conductor material exposed for use. An area of conductor material distal to that which contacts the electrolyte (or other substance or fluid) may be exposed for use as a contact pad with the rest of a circuit.

The electrode provided has the benefits that the surface area of conductor material exposed for use is defined by a covering layer of an insulator layer that is

1. Resistive to attack from the chemicals in the solutions in which it is immersed and / or acts as a barrier to ions
2. Has good adhesion to other dielectric materials and conductor materials.

The covalent or intermediate nitrides, in particular silicon nitride or aluminium nitride, are used advantageously as they can be readily laid down as a covering layer on to conductor material with good bonding.

The covering layer comprising nitride may overlay a portion of conductor material leaving an end or an area of conductor material exposed for use, of selected size and geometry.

An end of conductor material exposed for use may be flush with the covering layer material, defining the surface area of conductor material exposed for use by the visible conductor material surface e.g. an edge of a sheet of conductor material may be exposed, defining the surface area exposed by the thickness of the sheet times its width. Alternatively the end may project beyond the covering layer, and any other layers of insulating material employed in the device, and thus the surface area of conductor material exposed for use will be three dimensional.

The exposed area of conductor material may be exposed through an aperture in the covering layer of insulator (nitride). The layer of insulator may have an array of apertures forming a multi-electrode device, with multiple areas of conductor material exposed. Alternatively a plurality of separate end portions of conductor material may be exposed, each providing the defined area of conductor material for contact with electrolyte or other substance or fluid.

The same approach may be employed to form a single electrode device but with multiple areas of conductor material exposed for use. In that case, for example, an array of apertures exposes conductor material portions that are interconnected, beneath the covering layer of nitride, by conductor material. As an alternative example, a plurality of separate end portions are exposed each providing a defined area of conductor material for contact with electrolyte or other substance or fluid. The exposed end portions are interconnected by conductor material providing a single electrode.

Multiple electrodes, even where multiple areas of conductor material are exposed for use in one or more of the electrodes, may be incorporated in a single device.

Whilst exposing an end of conductor material out of the covering layer of nitride or an area of conductor material through an aperture in the covering layer of a nitride are convenient ways of defining the surface area of conductor material for use, other approaches are possible. For example a portion of conductor material may be laid on top of the covering layer of nitride with connection made to the rest of the circuit by means of conductor material buried in the layer of nitride.

Conveniently the conductor material of the electrode is encapsulated by an insulation comprising the nitrides described above, except for the area exposed for use, at least at the portion of the electrode that is to be immersed or contacted with electrolyte or another substance or fluid when the electrode is used. Conveniently in some examples, all the conductor material of the electrode may be encapsulated by an insulation comprising the nitrides described above except for the area exposed for use and for a distal portion or portions exposed for use as an electrical connection to the rest of a circuit.

The electrodes of the invention provide a well defined surface area of conductor material that is not susceptible to change as the nitride layer or encapsulation provides a sharply defined boundary to the area of exposed conductor material, which is resistant to degradation. Degradation of the material defining boundaries to the surface area of the conductor material can be caused for example by chemical attack and/or other mechanisms such as by high temperatures or cycling of the electrode through fluctuating temperature ranges.

The provision of a well defined and stable surface area for the conductor material in an electrode is of particular value for example when the electrode is to be used as part of a circuit for analytical purposes such as electroanalysis of redox systems. Thus the electrode of the invention is advantageously provided as a microelectrode (wherein at least one dimension of the exposed conductor material is on the µm i.e. micrometre scale, for example 10 to 100 micrometres or even smaller or larger in length/or width, for further example from 1 to 100 micrometres or even from 1 to 500micrometres). In principle the electrodes described herein can be of any size including microelectrodes that are very small and might be described as nanodimension electrodes, with area of conductor material exposed for use as small as 10nm in length and/or width. Such small areas can be produced through known lithography techniques (for example ebeam or optical).

A microelectrode is preferred or at least particularly convenient for analytical procedures in solutions or other electrolytes such as molten salts. Microelectrodes have low resistance per unit area and can operate with low currents. Furthermore they provide results in techniques such as cyclic voltammetry that are time-independent or time-insensitive and not substantially affected by convection processes in the electrolyte. With a technique such as cyclic voltammetry they can operate at fast scan rates to investigate fast redox processes.

A single electrode device with multiple areas of conductor material exposed for use, wherein each area is at the micro scale discussed above, can be advantageous. The total area exposed for use can be at a macro scale but the separate portions of conductor material exposed for use will each behave to the electrolyte or other fluid and its contents as a microelectrode.

The electrodes of the invention can be utilised in sensors. Thus the invention provides a sensor comprising an electrode as described herein.

Conveniently electrodes, especially microelectrodes, can be prepared by making use of the techniques of the semiconductor industry, such as fabrication of the device (electrode in this case) on a planar surface using lithographic based patterning of layers, etching and deposition techniques (including physical and chemical vapour

deposition, evaporation, electrodeposition, electroless deposition and/or electrochemical reaction and layer formation) such as are known in the art
Thus the present invention provides methods of fabricating electrodes of the invention. The present invention also provides electrodes obtainable by the methods described herein.

The method comprises: forming a layer of conductor material on an insulating layer; forming a covering layer comprising covalent or intermediate nitride on the layer of conductor material; and removing a portion of the nitride layer to define a surface area of conductor material exposed for use.

The insulating layer may be a layer provided on a substrate. The insulating layer will be of a non-conducting or a substantially non-conducting material. For example the insulating layer may be a layer of silicon dioxide that may be formed on a substrate of silicon. Silicon e.g. in the form of silicon wafers, provides a particularly convenient substrate for electrodes of the invention. Silicon is widely and inexpensively available, in high quality, well defined form as wafers for semiconductor device manufacture.

Techniques for forming layers on a silicon surface are available; and silicon is itself is a durable material under many conditions. Other substrates may be employed, for example of or comprising a covalent and/or intermediate nitride (e.g. silicon nitride). Other substrates can include silicon carbide, glass, quartz and diamond. Where the substrate is insulating it can be employed as the insulating layer on which the conductor material layer is formed. Where the substrate is conducting e.g. a metal, the substrate can be connected to the layer of conductor material through the insulating layer, for example by conductor material placed in openings (vias) etched in the insulating layer.

The insulating layer may conveniently be of silicon nitride, silicon dioxide, boron nitride or other covalent or intermediate nitride and quartz. A polymer, for example Parylene™ (chemical vapor deposited poly(p-xylylene) polymers) may be suitable for some applications where the selected polymer or its degradation product(s) is serviceable at the temperatures envisaged for the application. These substances can be readily formed as layers on a base layer such as silicon. Mixtures of suitable insulating materials may be employed.

For example, controlled reaction of a silicon base layer (silicon wafer) with oxygen at elevated temperatures produces a silicon dioxide insulating layer. For further example a silicon nitride layer on a silicon substrate can be formed by low pressure chemical vapour deposition (LPCVD) for example using ammonia and dichlorosilane as sources of nitrogen and silicon. Alternative deposition techniques can include PECVD (Plasma Enhanced Chemical Vapour Deposition) and APCVD (Atmospheric Pressure Chemical Vapour Deposition).

Other techniques for producing a nitride layer can include forming a silicon nitride layer by electrochemical oxidation of silicon in ammonia as described for example in WO/1999/034033.

An insulating layer comprising a covalent or intermediate nitride allows the conductor material of the electrode to be encapsulated in insulation comprising nitride, at least at the portion to be immersed or contacted with electrolyte or another substance or fluid when the electrode is used. The nitride insulating layer and the covering layer of nitride form the encapsulation of the conductor material.

However, as discussed hereafter and with reference to a specific embodiment a more robust device may in some circumstances be formed by providing an insulating layer that is not the same as the covering layer of nitride.

The layer of conductor material will typically be a metal, any metal suitable for the intended duty (including the temperature) may be employed. For example the conductor material may be of metals such as silver, gold, platinum, palladium, gallium, titanium, molybdenum, vanadium, niobium, tantalum, tungsten, aluminium, cobalt, nickel, copper and alloys of these or other metals. Examples of liquid electrode materials include mercury, cadmium and bismuth. For further example semiconducting or conducting oxides, nitrides or mixed oxynitrides of metals such as titanium, cobalt, nickel, iron, tin, indium, tantalum, strontium, iron, tungsten, niobium, iridium, molybdenum, hafnium, zinc, gallium, vanadium, aluminium and zirconium and doped versions thereof may also be employed. Conductor material may also be chosen from materials such as carbon, and conducting and semiconducting molecular organics.depending on the conditions of use.

The layer of conductor material can be formed on the insulating layer by methods such as the known sputtering, CVD (chemical vapour deposition), ALD (atomic layer deposition) and electroplating techniques. In some examples adhesion of a selected conductor material may be aided by first forming an adhesion layer of a suitable adhering agent on the insulating layer. It is advantageous if this layer is resistant to attack from the system electrolyte. For example a layer of titanium can aid in adhering a layer of tungsten to an insulating layer of silicon dioxide or silicon nitride. Titanium nitride has also been found to be resistant to attack from some electrolytes while acting as a suitable adhesion layer, for example to adhere a layer of tungsten or platinum to an insulating layer of silicon dioxide or silicon nitride.

The covering layer comprising nitride can then be applied, for example by low pressure chemical vapour deposition (LPCVD) e.g. using ammonia and dichlorosilane as sources of nitrogen and silicon respectively to deposit a layer of silicon nitride. Removal of some covering layer to expose a defined area of conductor material can be achieved by dry etching e.g. reactive ion etching or chemical etching.

Advantageously the removal of the layer comprising nitride is carried out by using photolithographic techniques. For example a method comprising the steps of: covering the layer comprising nitride with a photoresist layer; exposing the photoresist layer to light through a mask to chemically alter an area of photoresist layer corresponding to the area of nitride layer to be removed; removing the exposed area of photoresist; removing the nitride layer where exposed by the removal of the photoresist; and removal of the unexposed photoresist.

Alternative methods may be employed, such as are known in the semiconductor fabricating art. For example using a negative photoresist in which the portion of the photoresist that is exposed to light becomes insoluble to the photoresist developer. The unexposed portion of the photoresist is removed to form the pattern in the known manner. It will be understood that in the methods described herein either negative or positive photoresists may be used with appropriate masks employed to achieve desired patterns.

Conveniently the layer of conductor material does not cover the entire insulating layer, but is formed as a defined area or areas in manufacture by e.g using photolithographic procedures. Such procedures reduce the size (i.e. area) of the conductor material layer which reduces the overall capacitance and can be used for production of appropriate conductive pathways between the portion of conductor material used for contact with electrolyte (or another substance or fluid) when the electrode is used, and a distal portion or portions that may be exposed for use as a connection to the rest of a circuit. In addition, when the covering layer comprising nitride is applied, it seals the edges of the defined area of conductor material. Where the layer of conductor material covers the whole substrate then edges of conductor material may be exposed when discrete electrodes are cut from e.g. a silicon wafer. If these edges are not required as electrodes further processing would be required to cover the exposed parts, e.g. with an insulation comprising nitrides of the types discussed above.

Forming the selected pattern of conductor material layer on a substrate can be carried out by known semiconductor industry techniques.

For example a layer of conductor material can be applied to a substrate e.g. a metal layer applied by sputtering. A layer of photoresist is applied. The photoresist is developed by exposure to light through a mask. The exposed photoresist is removed and unwanted metal, exposed by the removal of photoresist, is removed by reactive ion etching, optionally followed by e.g. an oxygen plasma procedure to further clean the surface where conductor material has been removed.

For further example a lift off resist technique is employed. This technique has been shown to be advantageous in some circumstances, potentially providing a superior quality surface. A lift of resist layer is applied to the substrate. A layer of conventional photoresist may be applied to the lift off resist layer. The photoresist is developed by exposure to light through a mask. The exposed photoresist is removed to leave the desired pattern for the conductor material as a pattern of exposed substrate defined by the remaining resist. A layer of conductor material is then applied e.g. a metal layer applied by sputtering. The remaining resist, photo and lift off is then removed together with its covering layer of conductor material, to leave the desired pattern of conductor material on the substrate.

A number of options and advantages are provided by the above fabrication methods.

A large number of discrete conductor material patterns can be formed on a single substrate layer such as a silicon wafer. The individual electrode arrangements can then be separated into discrete electrodes for use.

Furthermore for some applications an array of electrodes may be provided on a single portion of substrate, with good control of their size and spacing.

If desired an electrode may have more than one defined area of conductor material exposed for use.

Laying down a defined area of conductor material on the insulating layer, rather than completely covering the insulating layer with conductor material has the further advantage of reducing failure or poor performance of electrodes produced. Failure can occur where the layer comprising nitride has a flaw such as a pinhole that allows unwanted contact between conductor material and e.g. electrolyte. Smaller areas of conductor material overlaid by the nitride layer reduce the risk of a pinhole being present on top of an area of conductor material.

Alternative methods may be used to provide an electrode using semiconductor techniques. For example a portion, in the form of a layer, of conductor material can be provided on top of a layer comprising covalent or intermediate nitride. The layer comprising covalent or intermediate nitride covers one or more, vias or conducting tracks of conductor material, or a continuation of the layer of conductor material, which is/are used to connect to the rest of a circuit. The portion of conductor material sitting exposed on top of the layer of the nitride covering layer can be prepared by the same techniques described above for defining the shape of a layer of conductor material.

The electrodes, especially microelectrodes, of the invention can provide a number of uses, especially in analytical procedures.

The electrodes have been shown to be robust in use, even when immersed in electrolytes that are in the form of molten salts, even when the temperature is varied over a wide range, where chemical attack and/or thermal shock might be expected to produce cracking or other damage.

The electrodes may be employed for analytical procedures including as part of a sensor for detecting or quantifying an analyte. Such a sensor can be useful in many applications, especially for remote sensing in corrosive and/or high temperature electrolytes such as molten salts and/or an electrolyte that is toxic or radioactive. Thus the electrodes of the invention may be utilised for process development, analysis and monitoring in aqueous based processing of nuclear fuels and molten salt processing of the same or in metal extraction or forming processes which involve electrodeposition of metals from molten salt systems.

Examples of molten salt systems can include eutectic compositions such as LKE (lithium potassium eutectic, formed by melting together lithium chloride and potassium chloride). An example of an aqueous corrosive electrolyte can be nitric acid solutions. Tests involving such aggressive electrolytes are described hereafter and with reference to specific embodiments of microelectrodes.

In general the various components of the electrodes of the invention can be selected on the basis of the electrolyte and temperature conditions expected in use. LKE provides a good example of a very harsh environment. Testing has shown that microelectrodes constructed on a silicon wafer substrate and having the materials listed in Table A (below) employed in the various layers are notably robust under the harsh conditions of an LKE electrolyte at temperatures of 400-450 ºC or even up to 500ºC, indicating that they may be suitable in a wide range of environments.

Table A

Layer	**Material (thickness)**
Substrate	silicon
Insulating layer	silicon dioxide (100-2000nm)
Adhesion layer	titanium nitride (10-2000nm)
Conductor material	tungsten or platinum (50-2000nm)
Covering layer	Silicon nitride (100-2000nm)

Alternative materials may be employed, even in an LKE environment, but the above combination has been found effective under these harsh conditions. The insulating layer of silicon dioxide has been found to reduce failure due to layer delamination which can occur when e.g. silicon nitride is employed as both the covering layer and the insulating layer. Using silicon dioxide as the insulating layer acts as a stress relieving layer for the silicon nitride covering layer. Typical thicknesses of the layers are shown in the Table above. In general the covering layer needs to be thick enough to prevent electrolyte reaching the conducting material or the underlying insulator, with the upper bound thickness being dependent on the stress levels in the layer and the other materials that form the device when in a particular use. Titanium nitride as the adhesion layer, bonding the conductor material to the insulating layer has been found stable in LKE whereas e.g. titanium metal has a tendency to be subject to electrodissolution. The electrode layer thickness should ideally be thick enough to result in a contiguous conductor that will block the electrolyte from reaching the underlying adhesion layer and/or insulator (at least of the order of 10 nm), but ideally be thicker so that the resistance of the electrode is minimised. The upper bound on the thickness is also dependent on the stress levels in the conductor layer (which typically increase with thickness) and the other materials that form the device.

As far as the use of silicon nitride as the covering layer is concerned tests have shown that using a silicon nitride that is substantially stoichiometric or is stoichiometric in composition (Si_3N_4) is preferred compared with a silicon rich silicon nitride (e.g. $Si_{3.1}N_{3.9}$) which shows decreased chemical resistance in LKE. Aluminium nitride could be used as an alternative covering layer for this duty.

Both tungsten and platinum are suitable conductor materials but platinum dissolves electrochemically at +0.5V in LKE, limiting its use to some extent. Other metals could be employed, for example aluminium.

The present invention provides a method of detecting or quantifying an analyte in a molten salt or other electrolyte, the method comprising:

performing an electronalytical procedure with an electrode of the invention.

The electrode may be used with another electrode of the invention or with other electrode types to form a circuit, in use. For example, when analysing molten salt solutions by cyclic or any other form of potentiometry, voltammetry, galvanometry or chronoamperometry, using a microelectrode of the invention as working electrode, reference and counter electrodes of a macro scale may be employed. For example a conventional silver/silver chloride or a saturated calomel (SCE) reference electrode and conventional tungsten or other suitable metal counter electrode such as might be used with a conventional working electrode.

The method will typically use a microelectrode to provide the advantages discussed above. Exemplary electronalytical techniques include: Linear sweep voltammetry, staircase voltammetry, squarewave voltammetry, cyclic voltammetry, anodic stripping voltammetry, cathodic stripping voltammetry, adsorptive stripping voltammetry, alternating current voltammetry, normal pulse voltammetry, differential pulse voltammetry, potentiometry, coulometry, chronoamperometry, chronocoulometry, electrochemical impedance and dielectric spectroscopy.

Brief Description of the Drawings Figures 1 illustrates schematically the fabrication of an electrode;
Figures 2 illustrate schematically another method of fabrication of an electrode;
Figures 3 show partial microscopic images of electrodes;
Figures 4 to 11 show graphically analytical results obtained using electrodes of the invention in studying the redox reactions of samarium;
Figure 12 shows cyclic voltammagrams obtained when studying silver redox reactions;
Figures 13 to 15 show graphically analytical results obtained using electrodes of the invention when studying processes in nitric acid; and
Figures 16 shows an electrode and a cyclic voltammagram when studying silver redox reactions with the electrode; and
Figures 17 to 20 show further electrode arrangements.

Detailed Description of the Invention

Manufacture of electrodes

Figure 1(a to l) illustrates in schematic cross sections a method of fabricating an electrode, especially a microelectrode of the invention.

This approach has been be used to make exemplary microelectrodes having a layer of tungsten conductor material with a 10x10 to 100x100 μm square surface area exposed for use. Smaller or larger areas, of single or multiple electrodes (arrays) of any selected shape may be prepared.

In this example a silicon wafer substrate 1 is employed, e.g. 100 mm {100} n-type silicon wafers (e.g. from IDB Technologies Ltd). Firstly, a 500 nm silicon nitride layer (as insulating layer) was deposited on the wafer surface using low pressure chemical vapour deposition (LPCVD). The LPCVD furnace was fed with 10sccm (standard cubic centimetres per minute) ammonia (NH_3) and 15sccm dichlorosilane (SiH_2Cl_2), at ambient temperature of 800 °C and pressure of 90mT. After five hours at these conditions, a 500nm layer of silicon-rich, low stress silicon nitride results. This nitride layer 2 provides isolation between the arrays of conductor material and the underlying silicon carrier wafer 1. Alternatively, for example, a silicon dioxide insulating layer may be deposited. Patterned layers of conductor material were then fabricated using a lift off process as outlined below.

A 450 nm layer of lift-off resist 4 (LOR-5B, Microchem, Chestech) was spin deposited onto the wafer 1 (on top of the nitride layer 2) and baked for 5 minutes at 190 °C (Fig. 1a).

This was then followed by spin deposition of a 1 μm layer of standard positive photoresist 6 (Megaposit SPR350, Microchem, Chestech), which was soft-baked for 1 minute at 90 °C (Fig. 1b). Following flood exposure 8 of the resist through the metallization mask plate 10 using a wideband mercury vapour lamp (Fig. 1c), the resist 4,6 was developed (Microposit MF319 Developer, Microchem, Chestech) to give the required electrode pattern 12 complete with an undercut 14 to facilitate the lift off process (Fig. 1d).

This undercut sidewall 14 facilitates the lift-off process, as it ensures a discontinuous film after sputter deposition of the metal layer. The electrode conductor film was produced by first sputter depositing a 5 nm titanium adhesion layer 16, and then depositing a 250 nm film of tungsten 18 (Fig. 1e). The bi-layer resist 4,6 and excess metal 20 is then removed (Microposit 1165 resist remover, Microchem, Chestech) leaving the desired patterns of conductor material (Fig. 1f).

Similar techniques are then used to provide the covering layer of nitride and to expose the conductor for use.

A covering layer of silicon nitride 22 is applied (figure 1 g) in a similar fashion to that described above for the insulating layer 2. Photoresist 24 is then deposited on the covering layer of nitride 22 (figure 1h). Exposure to light 8 through a mask 10 (figure 1 i) allows removal of exposed photoresist. The exposed area of silicon nitride 26 (figure 1 j) is then removed by etching, such as reactive ion etching, to leave a defined area of conductor material 28 (figure 1k) exposed. Unexposed photoresist 24 is then removed to provide the device illustrated by figure 1l.
The finished wafer 1 is then cut into individual devices.

In this case microelectrodes with a square area of exposed conductor material (tungsten) for contacting an electrolyte were produced together with exposed areas distal to the defined squares, for connection with a circuit (see figure 3 for examples).

Figure 2 illustrates schematically an alternative means for preparing the pattern of conductor material on a substrate. In this example a layer of silicon dioxide 36, as insulating layer, has been grown on a silicon wafer 1 (Fig. 2a) and a metal layer 38 deposited by sputter techniques. A conventional resist layer 40 is spun on to the wafer (Fig 2b) and then subsequently exposed to light 8 through a chrome mask plate 10. The areas of resist exposed to light are chemically altered (Fig. 2c), which allows them to be dissolved away in a developer solution leaving the desired pattern defined in the remaining photoresist (Figure 2d). Finally, the metal layer 38 that is not protected by the resist mask is reactively ion etched, which removes unwanted material leaving only the desired metal pattern in the metal. Any excess resist may be removed in an oxygen plasma, leaving the completed electrode metallization (pattern of conductor material on the insulating silicon dioxide - Figure 2e). A silicon nitride covering layer can then be applied as described above for Figure 1 and the subsequent processing of Figures 1(g to l) applied to provide electrodes.

Figures 3 show partial microscopic images of electrodes of the invention, having different areas of conductor material exposed for use. In figure 3a 10 µm square; in figure 3b 20 µm square; and in figure 3c 50 µm square (note the pathway 42 of conductor material 44, visible under the silicon nitride layer, leading to a connection point for a circuit (not shown). In each case the conductor material 44 is overlaid by a silicon nitride layer 46 (which can be of a selected thickness, say from 0.5 to 1 µm or more - a 1 µm thickness is used in these examples) on the insulating layer and a well defined aperture exposes a square of conductor material 48 for use in contacting an electrolyte. The conductor material 44 is visible under the silicon nitride layer in these images.

Performance of Electrodes of the invention

In molten salt electrolytes

The molten salt system under test was lithium potassium eutectic (LKE) which was made up of 55g of potassium chloride and 45 g of lithium chloride. Experiments were performed in the temperature range of 380-500°C.

Electrochemical cell preparation

The chloride melt was prepared by mixing LiCl and KCl (Sigma Aldrich 99.9% and 99.5% anhydrous respectively) in the eutectic composition LiCl:KCl = 58.8:41.2 mol% to a total mass of 100g. The salt was contained in a vitreous carbon crucible and stored in an oven at 398 K for at least 24 hours prior to use. During experiments the electrolyte was fused under vacuum during heating with the temperature held at 723 K. Solutions of Ag(I) were prepared by direct addition of anhydrous AgCl (Sigma Aldrich 99.99% anhydrous) at a concentration of 0.031 mol kg^{-1} in the eutectic. Solutions of Samarium(III) were prepared by adding $Sm(III)Cl_3$ at 0.031molkg^{-1}

Tungsten wires with a diameter of 1.6mm were used as counter electrodes, with microelectrodes also connected using tungsten wires. The reference electrode used was Ag|AgCl and was prepared in a closed-ended Pythagoras tube (Multilab, 6mm OD x 4mm ID x 300mm) by dipping a 2mm diameter silver wire (Sigma Aldrich ≥99.99%) into LiCl-KCl eutectic containing 0.75 mol Kg^{-1}AgCl (Sigma Aldrich 99.9%). The open end of the tube was then sealed with a high-temperature silicone sealant to prevent exposure to moisture.

Electrochemistry

Electrochemical measurements were performed with an Autolab PGSTAT potentiostat/galvanostat controlled by the research software GPES. Heating of the salt was conducted in a vertical tube furnace (Carbolite GVA 12/600), and the temperature controlled using the furnaces built in thermocouple.

In order to execute molten salt experiments in a well contained and controlled manner, a quartz cell was fabricated in which a vitreous carbon crucible containing the molten eutectic is held. This cell was capped with a borosilicate glass lid with either 4 or 5 ports in the top through which the electrodes are supported, and 2 further ports to the sides through which the atmosphere in the cell is controlled. The design of the cell was such, that standard glassware screw connections can be used to seal around the electrode supports, which are also encased in glass so that their outer diameter does not exceed 6mm.

Early cyclic voltammetry experiments with tungsten as conductor material indicated that a passivating layer, most likely an oxide layer could form on the tungsten when the microelectrodes were being heated up, perhaps due to the presence of air of moisture traces in the system.

Cycling the electrode through a cyclic voltammetry (CV) procedure with incremental increase in potential was found to effectively deal with this issue (For a 100x100 μm square of exposed tungsten the potential window was increased in 200mV increments, at a sweep rate of 200mvs^{-1}. The potential was kept between -2.5 v and 1.35V as lithium reduction (plating) can occur at about -2.5 v and chlorine gas evolution at +1.35V.

Cyclic voltammetry with samarium (III) chloride - showing the Sm(III)/Sm(II) redox reaction

The redox activity of samarium (III) chloridewas initially studied in LKE using a 100 μm edge length microsquare device which in these examples use a microelectrode formed as described with respect to figures 1 i.e. with silicon nitride used both as insulating layer and covering layer to encapsulate the conductor material (tungsten) The CV response was found to be wave like, consistent with microelectrode response and the mid potential of the wave was at -1.05 V which shows good agreement with the literature and previous findings from our laboratory (Figure 4). Voltammograms are shown at three different sweep rates (100, 50 and 25 mVs^{-1}). In each as expected for a microelectrode the height of the wave was found to be independent of sweep rate (within experimental error) although there was a greater capacitive contribution in the observed current at higher sweep rates. The calculated Faradaic current density on this particular microelectrode was found to be approximately 20 times higher than that from a tungsten wire macroelectrode at 500°C (0.080 A/cm^2 on micro square vs 0.004 A/cm^2 on macro). This highlights the enhanced diffusive flux at the microelectrode, and the advantages associated with electroanalysis using microelectrodes in terms of the enhanced Faradaic current densities which make the response much less sensitive to convection.

The redox activity of samarium (III) chloride was then studied at 475°C and 500°C and selected data are presented in Figure 5 (sweep rate 25 mVs^{-1}). It can be seen that in particular the limiting current associated with the samarium reduction increased in magnitude as the temperature was increased. The reason for this increase in current is the increase in the diffusion coefficient of samarium ions in the melt as a function of temperature.

Data presented in the previous figures were analysed in order to obtain the diffusion coefficients for samarium (III) chloride in LKE. We have established with aqueous experiment and theory(ref 3)the following analytical expression (eqn. 1) to apply to square microelectrodes:

$$i_L = 4.1nFDcL/\pi^{1/2} \qquad (1)$$

where i_L = limiting current, F = Faraday's constant, D = diffusion coefficient, L = square edge length and c = concentration.

This expression was used to calculate diffusion coefficients for samarium (III) from the limiting current at the variety of temperatures. We were able to compare our results with a paper published on the electrochemical characterisation of samarium (III) chloride in LKE using tungsten macroelectrodes (ref 4). The logarithm of D was plotted against the reciprocal of temperature and a linear relationship was found, as expected from the Stokes-Einstein relationship and the Arrhenius dependence of viscosity on temperature (viscosity depending on the exponential of the inverse of temperature (Figure 6)). The gradient of this plot was used to calculate the activation energy associated with the movement of samarium chloride (III) in LKE and our result was found to differ from previously published data obtained with tungsten macroelectrodes by a factor of two (this is considered a comparable result). The results obtained for the diffusion coefficients of Sm(III) were in the expected range, being of the same order of magnitude as those measured by Cordoba and Caravara (2004) on macroelectrodes(ref 4). Table 1 shows the diffusion coefficients and activation energy values derived from these data.

Table 1.Diffusion coefficients and activation energy for samarium (III) chloride in LKE

Parameter	Cordoba&Caravaca (2004)	Microelectrode values
T/°C	$D/10^{-5}\,cm^2s^{-1}$	$D/10^{-5}\,cm^2s^{-1}$
450	0.41	2.1
475	0.76	3.3
500	1.30	5.1
$E_a/kJ\ mol^{-1}$	-40.27	82.7

In order to confirm the applicability of equation (1), further experiments (cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy) were carried out using a 20 μm edge length microsquare electrode. The CV response (Figure 7) showed that as expected the reduction peak for the Sm(III/II) reaction was smaller at 450°C using the 20 μm square electrode. Chronoamperometry was performed (Figure 8) and the limiting currents at 450°C on a 20 μm vs 100 μm device were found to be 0.79 μA vs 3.8 μA. This is exactly the expected five times smaller current for the 20 μm edge length device, confirming the applicability of eqn. (1) and showing it is possible to make quantitative measurements using the microelectrode systems in the LKE.

Electrochemical Impedance Spectroscopy (EIS) was performed using a 100 μm edge length square electrode at-1.05 V, the half wave potential of the Sm (III/II) couple. Under these conditions it was found that the charge transfer resistance (R_{CT}) was not observable using this electrode (Figures 9A and 9B). This is indicative of extremely fast kinetics at the microelectrode, consistent with a reversible couple. The mass transfer controlled region dominates the impedance response in the form of a 45° line at higher frequency in parallel with the non-linear resistance at lower frequency characteristic of the EIS response from square microelectrodes (ref 6). Using a 20 μm electrode (Figures 10A and 10B) it was possible to observe the effect of a small semicircle at high frequency followed by the 45° line and non linear diffusion typical of the diffusion of redox species to the microsquare electrode. This is because as expected the charge transfer impedance scales inversely with electrode area whereas the non-linear resistance scales inversely with edge length, so the charge transfer resistance becomes a more prominent feature on the smaller electrode. This shows that the smaller microsquare electrode is better able to measure fast charge transfer kinetics (Figure 11).

Voltammetry with silver (I) chloride

Cyclic voltammetry was also performed using silver chloride in LKE at a concentration of 10 g/kg. The recorded response showed a wave like current trace in the region of silver plating (Ag^+ reduction to Ag) with a limiting current of approximately 80 μA (See Figure 12). A relatively sharp silver stripping peak was also observed, and these redox features were centred around 0 V as expected as in this case the concentration of silver chloride in the reference electrode and the melt were similar and the redox reaction is the same for reference and microelectrode. The mass transport limited silver plating was a wave rather than a peak response and appeared to be independent of scan rate, resulting in the oxidative stripping peak area also being largely independent of scan rate. This is again consistent with a microelectrode response.

It is interesting that the diffusion coefficient of 2.6×10^{-4} cm^2s^{-1} obtained for Ag(I) using eqn. (1) from CV measurements at 500°C was 5 times faster than that measured for Sm(III) under the same conditions. This and the difference in the peak areas at the two scan rates suggests dendritic silver plating, with some of the dendrites falling off at the lower sweep rate. This fall off explains the sharp drop in current on the oxidative sweep near -0.75 V at $0.2Vs^{-1}$. Under these conditions, the exact surface area of the electrode becomes uncertain because of the presence of dendritic silver surface growth and so the calculated diffusion coefficient value is likely to be too high.

Microelectrode performance in 3M HNO_3

A study was carried out to assess whether microsquare electrode systems can be designed and used to measure the characteristics of redox-active species in the aqueous solutions relevant to hydrochemical processing (the reprocessing of nuclear fuels using aqueous media), in particular for electroanalysis and on-line sensing applications. In this work, the microelectrode response of fabricated platinum microsquare electrodes (microelectrodes of the invention with platinum as the conductor material) in 3M HNO_3 was first measured. The electrodes are manufactured by similar methods to those described for the tungsten electrodes discussed above with reference to figures 1 to 3. Typical CV scans of the electrode response are shown in Figure 13. The microelectrodes in this example utilised silicon dioxide as insulating layer with a covering layer of silicon nitride. In these CV scans the saturated calomel electrode (SCE) was employed as reference rather than silver/silver chloride.

These CVs show the relatively large reduction current for H^+ to form adsorbed H_2 gas and the associated H_2 reoxidation peak around -0.25V, along with the onset of oxygen adsorption and oxide formation around 1.5V. Each of these is characteristic of clean Pt in strong aqueous acid, and the microamp magnitude currents are characteristic of a microelectrode. Successive CV cycles are shown, which give almost identical responses, characteristic of a stable electrode system.

Silver plating was then studied by adding 10mM of $AgNO_3$ to the 3M HNO_3. The microelectrode was then left in aqueous 3M HNO_3 overnight and the silver plating experiment repeated (Figure 14). The resulting CV responses were comparable, indicating the stability of the microelectrode system to prolonged immersion in 3M HNO_3. Observation under the microscope also showed no obvious signs of degradation of the chip after extended periods of time in the nitric acid. Characteristic silver plating waves were obtained at higher sweep rates, with the onset of silver reduction below 0.3V and the appearance of nucleation loops attributable to enhanced area growth and the fractal deposition of silver at the slowest sweep rates e.g. $1mVs^{-1}$. In all cases, a peak due to silver stripping was observed at 0.4V.

Detection of Nitrous Acid in 3M HNO_3 to Probe Feasibility of Quantitative Electroanalysis in Hydrochemical Reprocessing

During hydrochemical reprocessing, it is desirable to measure the amount of nitrous acid in the nitric acid aqueous solution. Previous work using macroelectrodes (ref 5) has indicated that electrochemical detection of nitrous acid in the range up to 0.1 M concentration is possible through reduction. In particular, a peak is seen on platinized macroelectrodes which is assigned to the 1 proton, 1 electron reduction of HNO_2 (actually in a highly acidic medium mostly present as NO^+) to NO and H_2O with a stated standard reduction potential of 0.983V (0.739 V vs SCE). Solutions of 0.001M, 0.005M, 0.01M, 0.05M and 0.1M nitrous acid in 3M nitric acid were therefore produced by the quantitative addition of $NaNO_2$. CVs of the resulting solutions using the platinum microsquare electrode (Figure 15) showed the onset of a reduction wave below 0.75V which increased in size with increasing amounts of HNO_2, which can be attributed to this reaction. This is seen as a reduction wave, again demonstrating that steady-state responses can be obtained from microelectrodes in these corrosive systems, which makes quantitation feasible. It can be seen from these data that there is a general increase in the size of the wave with increasing concentration of HNO_2. It was subsequently noticed that bubbles were forming on the microelectrode at the higher concentrations, even when no potential or current was being applied to the electrode. In fact the disproportionation reaction of NO_3^- and NO^+ to give gaseous $2NO_2$ is known to occur catalytically on the electrode surface(ref 7), which may explain this observation, why the observed limiting current is not linear with HNO_2 concentration, and why the observed current is also seen to change with time after the addition of HNO_2. In fact the reactions of HNO_2 and HNO_3 are complicated (Ref 5), with NO^+ being required as a catalyst for the reduction of NO_3^- and for HNO to be oxidisable to HNO_3 (which may be the origin of the oxidation peak seen to grow with increasing amounts of added $NaNO_2$).

These results establish the potential for microelectrodes to be used for the identification and quantitation of species present in the aqueous acid reprocessing stream required for hydrochemical processing.

Durability of Microelectrodes of the Invention in a Molten Salt Electrolyte (LKE)

As mentioned above in the Description of the Invention, testing in the aggressive LKE electrolyte has established that an arrangement as described in table A is robust. These tests are described here. It should be noted that a microelectrode with only a limited operating life may nevertheless be useful. Testing for an analyte can be carried out rapidly and the microelectrodes of the invention are expected to be inexpensive in manufacture i.e. they can be considered consumable items in some applications.

Microelectrodes were characterised in 100g of LiCl-KCl (45g of LiCl and 55g of KCl) heated to 500°C in a vitreous carbon crucible. The crucible was placed in a quartz cell and kept under vacuum. Cyclic voltammetry with silver (I) chloride as the redox agent was used to determine the functionality of the devices using a silver/silver chloride reference electrode. The microelectrodes were connected using crocodile clips, crimped to a tungsten wire. The crocodile clip and bond pad were covered in heat-resistant putty prior to use.

Fabrication

For each type of device, with different layer combinations electrodes of edge lengths 10, 20, 30, 50 and 100 μm were fabricated on 100 mm (4 inch) ,<100> P-type silicon wafers. The wafer then had a 500nm underlying insulation layer (silicon dioxide or silicon nitride) grown/deposited on it. The wafer was cleaned and dehydrated in an oxygen plasma for one hour before the surface was pre-treated with HMDS adhesion promoter. A layer of AZ2070-3.5 negative Lift off Resist (AZ Electronic Materials) was spun onto the wafer and baked for 5 minutes at 100°C (Fig 1(1)). The wafer was then exposed to ultraviolet light through a metallisation photomask before being developed (AZ726 MIF, AZ Electronic Materials) to define the pattern. An adhesion layer (titanium or titanium nitride), 20nm thick, was sputtered on to promote adhesion between the electrode metal (conductor material) and the insulation layer. The electrode metal (tungsten or platinum) was then sputtered on. The photoresist was stripped away using resist stripper (ni555 Technistripper, MicroChemicals) at 45°C. A covering layer of 500nm silicon nitride was then grown over the metal to prevent exposure to the salt. Photoresist was applied and exposed through contact mask, which defined the areas to be the contact pad (for connection to the circuit) and the square of exposed conductor material for contact with electrolyte. The wafer was then etched using reactive ion etching for 20 minutes to expose the contact pad and the microsquare, after which the resist was removed and the wafer diced into separate devices.

Devices fabricated

Four types of devices were fabricated, which are described beneath and summarised in table 2:

Device A was fabricated with 500nm silicon nitride underlying insulation layer with a 20nm titanium adhesion layer and 400nm of tungsten. 500nm of Silicon rich silicon nitride, $Si_{3.1}N_{3.9}$, was used as the top insulator.

Device B used 500nm of thermal silicon dioxide as an underlying layer, in place of the silicon nitride.

Device C used 20nm of titanium nitride as an adhesion layer instead of titanium.

Device D had 500nm of stoichiometric silicon nitride, Si_3N_3, as a covering layer.

Device E was the same as device D but used 50nm of platinum instead of tungsten as the electrode metal.

Table 2

Device	Underlying Insulator layer	Adhesion Layer	Electrode Metal	Covering layer
A	Silicon Nitride	Titanium	Tungsten	Silicon-rich Silicon Nitride
B	Silicon Dioxide	Titanium	Tungsten	Silicon-rich Silicon Nitride
C	Silicon Dioxide	Titanium Nitride	Tungsten	Silicon-rich Silicon Nitride
D	Silicon Dioxide	Titanium Nitride	Tungsten	Stoichiometric Silicon Nitride
E	Silicon Dioxide	Titanium Nitride	Platinum	Stoichiometric Silicon Nitride

Devices D and E were found to be the most robust operating successfully in LKE for 30 minutes or more in cyclic voltammetry experiments without noticeable deterioration. The other devices fabricated were more prone to attack in LKE limiting their usefulness in that particular environment, at least reducing their survival time.

Figure 16A shows a schematic plan view of these devices. They were approximately 35mm by 8 mm rectangles with the contact pad 50 for connecting to the circuit (6mm by 4mm) and distal square of conductor material 48 for contact with electrolyte exposed through the covering layer of silicon nitride 46. The extent of the layer of conductor material 44 under the silicon nitride layer 46 is indicated by dashed line.

Figure 16B shows the device of 16A in schematic cross section on A-A, showing the covering layer 46 defining an exposed area of conductor material 44 to form the contact pad 50. The conductor material 44 is adhered by means of adhesion layer 52 to the insulating layer 54 which in turn is laid on the substrate silicon 56.

Figure 16C shows a cyclic voltammogram of silver chloride on a 30 μm edge length device of type E. The current scale is in order of nA as opposed to μA for other devices which is indicative of a correctly defined microelectrode. A diffusion coefficient of 2.55 $\times 10^{-5}$ cm^2s^{-1} was calculated for silver chloride at 450°C. This shows reasonable agreement with literature values, e.g. $2.39\times 10^{-5} cm^2s^{-1}$ at 425°C. The charge passed during silver plating (0.72 μC) is nearly equivalent to that passed during stripping (0.69 μC). Also, the device was cycled using a variety of scan rates and the electrochemical response was independent of scan rate showing that the device performs as predicted for a microelectrode of the defined edge length 30 μm. Finally, the device was cycled in the melt for 30 minutes without change in the electrochemical response. Visual inspection post measurement showed an unblemished top insulating film and the electrode area still defined with the metal present.

Figure 17A shows in schematic plan view an electrode of similar construction to that of figures 16A and 16B except that in this example the layer of conductor material 44 is shaped to a narrow track (dashed line) leading from contact pad 50 to an end 58 of the electrode. As shown in partial cross section (about X-X) end elevation figure 17B the edge 60 of the end 62 of conductor material 44 is flush with the end 58 of the electrode and so edge 60 forms an exposed area of conductor material for contact with electrolyte.

Figure 17C shows an arrangement similar to that of Figure 17B where the end 62 of the conductor material 44 is exposed, projecting beyond end 58 of the electrode providing a three dimensional portion of exposed conductor material.

Figure 18 shows in schematic plan view an electrode similar to that of figure 16A but where multiple, in this case four, squares 48 of conductor material 44 are exposed for use.

Figure 19 shows in schematic plan view an electrode similar to that of figure 16A but where three separate microelectrodes are provided in one device, each having a square 48 of exposed conductor material connected by a separate track of conductor material covered by the covering layer 46 and leading to a separate contact pad 50.

Figure 20A shows in schematic plan view an arrangement where a portion of conductor material 64 in the form of a microsquare layer portion of metal is laid on top of a covering layer 46 of silicon nitride and connects by means of via 66 (filled with conductor material) and a layer of conductor material 44 to contact pad 50 (see cross section elevation 20B, on Y-Y). The portion of conductor material 64 can be deposited and made in square shape by conventional semiconductor fabrication techniques.

It will be understood that the present invention has been described above purely by way of example, and modifications of detail can be made within the scope of the invention.

Each feature disclosed in the description and (where appropriate) the claims and drawings may be provided independently or in any appropriate combination.

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CLAIMS:

1. An electrode wherein the surface area of conductor material exposed for use is defined by a covering layer comprising a covalent or an intermediate nitride or mixtures thereof.

2. The electrode according to claim 1 wherein the electrode is a microelectrode.

3. The electrode according to claim 1 or claim 2 wherein the covering layer comprises a nitride selected from the group consisting of Si, B, Al, Ga, In, P, Mn, Fe, Co, Ni, Te, Tl and Re nitrides or mixtures thereof.

4. The electrode according to claim 1 or claim 2 wherein the covering layer consists of or consists essentially of a covalent or intermediate nitride or mixtures thereof.

5. The electrode according to claim 1 wherein the covering layer consists of or consists essentially of silicon nitride.

6. The electrode according to any preceding claim wherein the covering layer comprising nitride overlays a portion of conductor material leaving at least one end portion of conductor material exposed for use.

7. The electrode according to any one of claims 1 to 5, wherein the exposed area of conductor material is exposed through an aperture formed in the covering layer.

8. The electrode according to claim 7 wherein multiple areas of conductor material are exposed through an array of apertures.

9. The electrode according to any one of claims 1 to 5 wherein a portion of conductor material is provided as a layer on top of the said covering layer comprising a covalent or an intermediate nitride or mixtures thereof; and

one or more of:

vias or conducting tracks of conductor material; or a continuation of the layer of conductor material;

are covered by the covering layer.

10. The electrode according to any preceding claim wherein the conductor material is, except for the portion exposed for use, encapsulated by an insulation comprising a covalent or an intermediate nitride or mixtures thereof, at least at the portion of the electrode that is to be immersed or contacted with electrolyte or another substance or fluid when the electrode is used.

11. The electrode according to any preceding claim wherein the conductor material is selected from the group consisting of:

metals; such as silver, gold, platinum, palladium, gallium, titanium, molybdenum, vanadium, niobium, tantalum, tungsten, aluminium, cobalt, nickel, copper and alloys of these;

semiconducting or conducting oxides, nitrides or mixed oxynitrides of metals such as titanium, nickel, iron, tin, indium, tantalum, strontium, iron, tungsten, niobium, iridium, molybdenum, hafnium, zinc, vanadium, gallium, aluminium and zirconium and doped versions thereof;

carbon; and

conducting and semiconducting molecular organics.

12. The electrode according to any one of claims 1 to 11 comprising:

an insulating layer;

a layer of the conductor material on the insulating layer;

the covering layer comprising a covalent or an intermediate nitride or mixtures thereof, on the layer of conductor material.

13. The electrode according to claim 12 wherein the insulating layer is provided on a substrate.

14. The electrode according to claim 13 wherein the substrate is of silicon.

15. The electrode according to claim 13 or claim 14 wherein the insulating layer comprises at least one of the group consisting of:

silicon dioxide, nitrides of Si, B, Al, Ga, In, P, Mn, Fe, Co, Ni, Te, Tl, Re or mixtures thereof, quartz and polymers, for example chemical vapor deposited poly(p-xylylene) polymers.

16. The electrode according to claim 15 wherein:

the insulating layer is of silicon dioxide and is on a substrate of silicon;

the conductor material layer is selected from the group consisting of tungsten, platinum and aluminium; and

the covering layer is selected from the group consisting of silicon nitride and aluminium nitride.

17. The electrode according to claim 16 wherein the conductor material layer is adhered to the insulating layer by an adhesion layer selected from the group consisting of titanium nitride and titanium

18. A method of fabricating an electrode according to any one of claims 1 to 8 wherein the method comprises:

forming a layer of conductor material on an insulating layer;

forming a covering layer, comprising covalent or intermediate nitride, or mixtures thereof, on the layer of conductor material; and

removing a portion of the covering layer to define a surface area of conductor material exposed for use.

19. The method according to claim 18 wherein the insulating layer is formed on a substrate.

20. The method according to claim 18 wherein the insulating layer is formed on a substrate of silicon.

21. The method according to claim 19 or claim 20 wherein the insulating layer comprises at least one of the group consisting of silicon dioxide, silicon nitride, boron nitride, other covalent or intermediate nitride, quartz, and chemical vapor deposited poly(p-xylylene) polymers.

22. The method according to any one of claims 18 to 21 wherein the removal of the covering layer comprises:

covering the covering layer with a photoresist layer; exposing the photoresist layer to light through a mask to chemically alter an area of photoresist layer corresponding to the area of nitride layer to be removed; removing the exposed area of photoresist; removing the nitride layer where exposed by the removal of the photoresist; and removal of the unexposed photoresist.

23. A method of detecting or quantifying an analyte in a molten salt or other electrolyte, the method comprising:

performing an electronalytical procedure with an electrode according to any one of claims 1 to 17.

24. The method according to claim 23 wherein the electronalytical technique is selected from the group consisting of:

linear sweep voltammetry, staircase voltammetry, squarewave voltammetry, cyclic voltammetry, anodic stripping voltammetry, cathodic stripping voltammetry, adsorptive stripping voltammetry, alternating current voltammetry, normal pulse voltammetry, differential pulse voltammetry, potentiometry, coulometry, chronoamperometry, chronocoulometry, electrochemical impedance spectroscopy and dielectric spectroscopy.

25. An electrode obtainable by the method according to any one of claims 18 to 22.

26. A sensor comprising an electrode according to any one of claims 1 to 17.

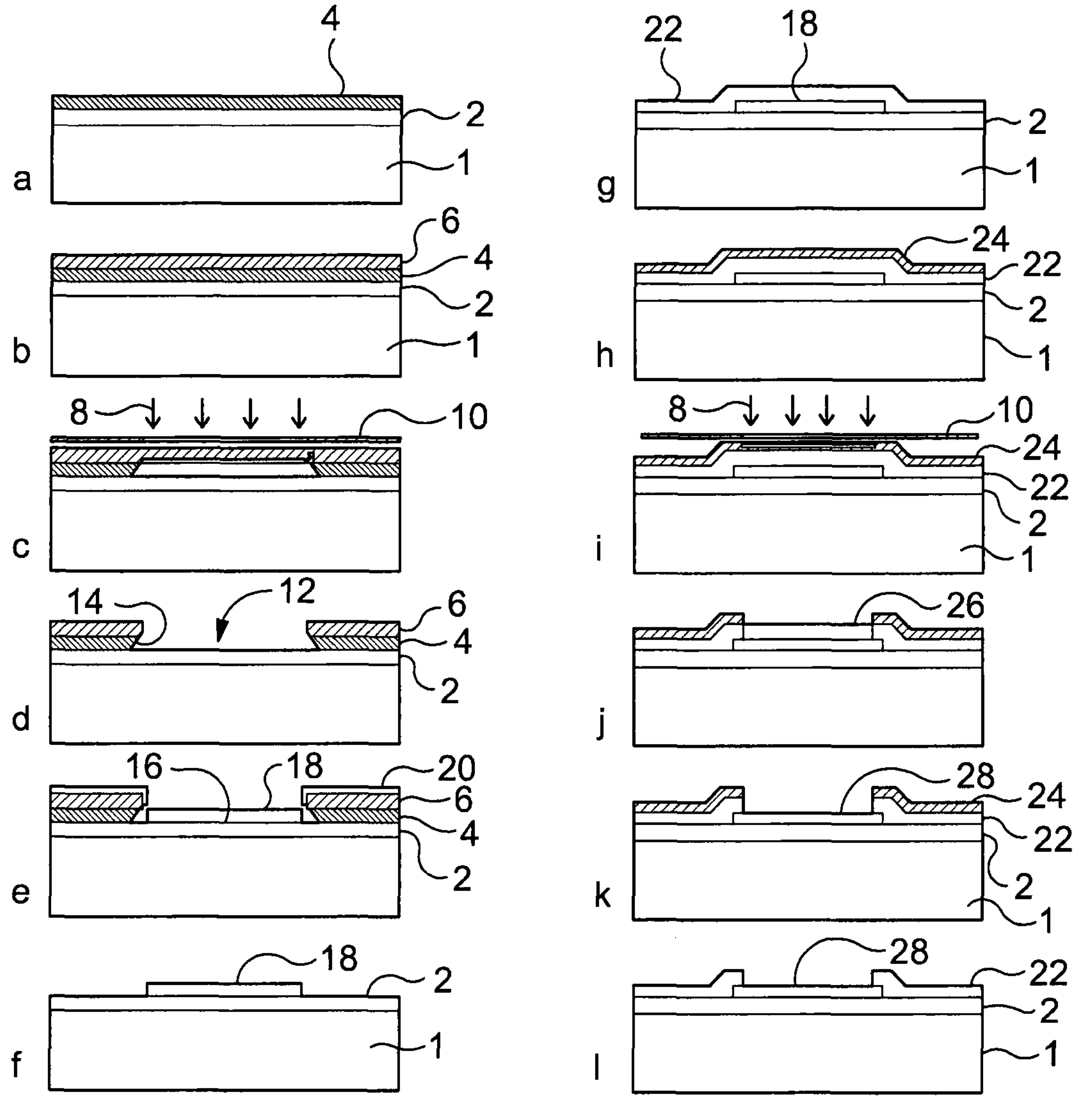


Fig. 1

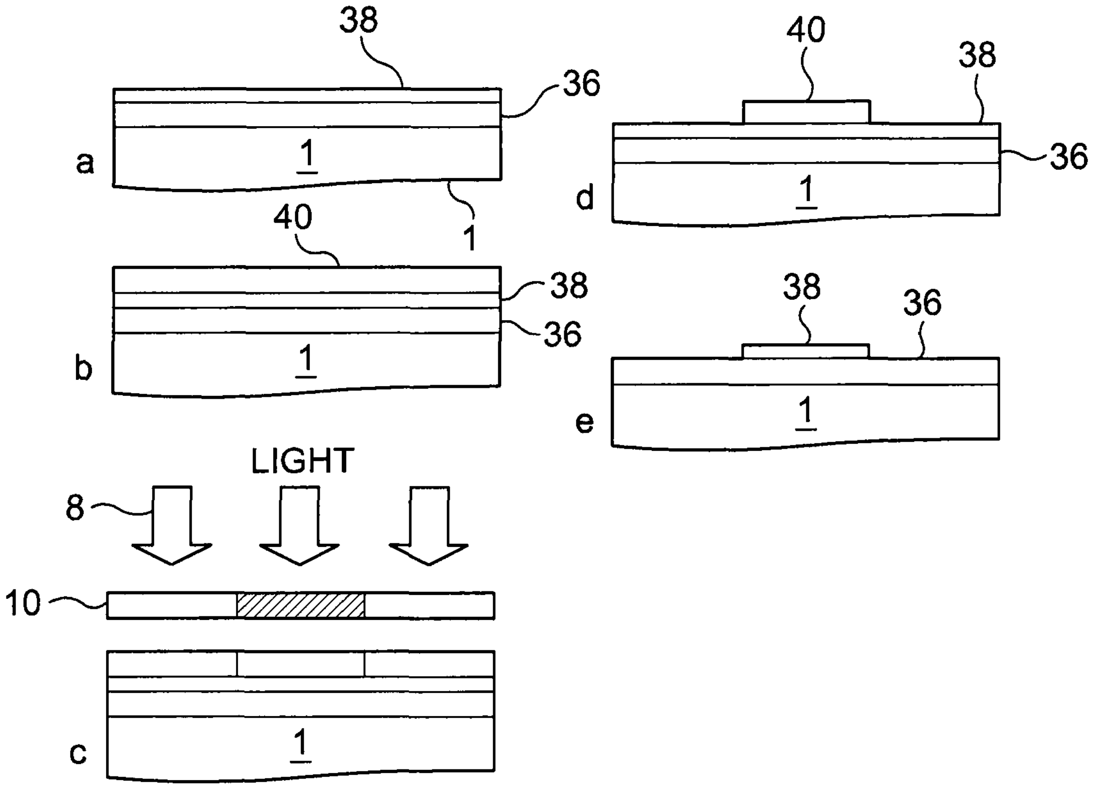
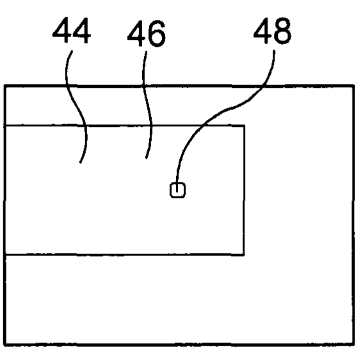
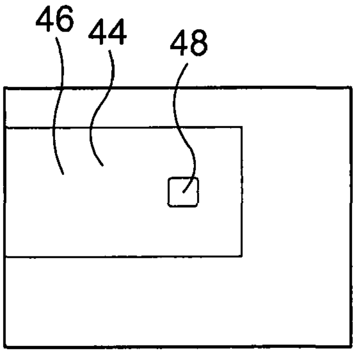


Fig. 2



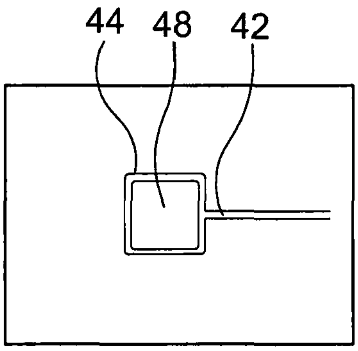
10 μm square

Fig. 3A



20 μm square

Fig. 3B



50 μm square

Fig. 3C

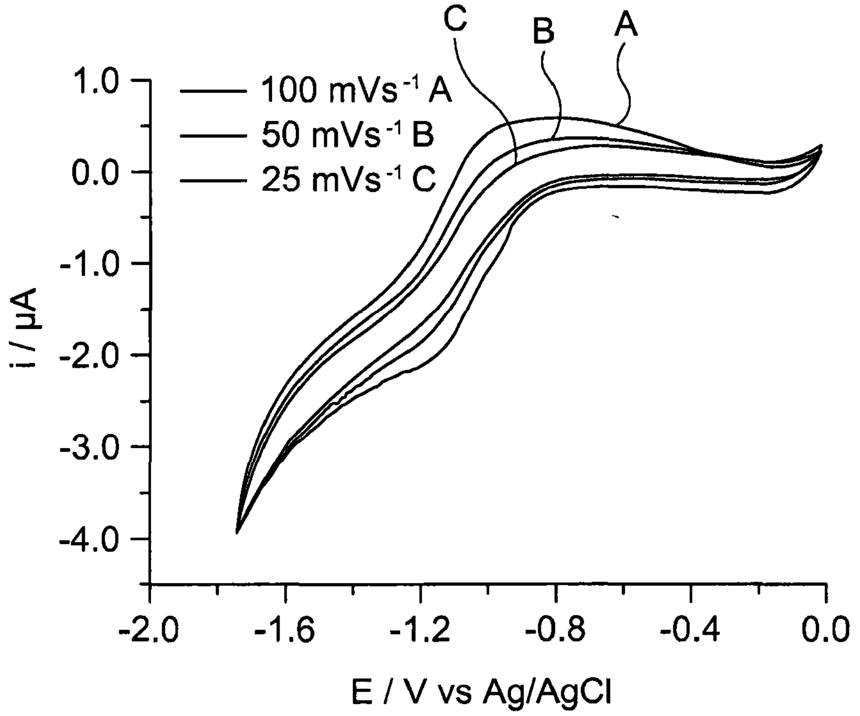
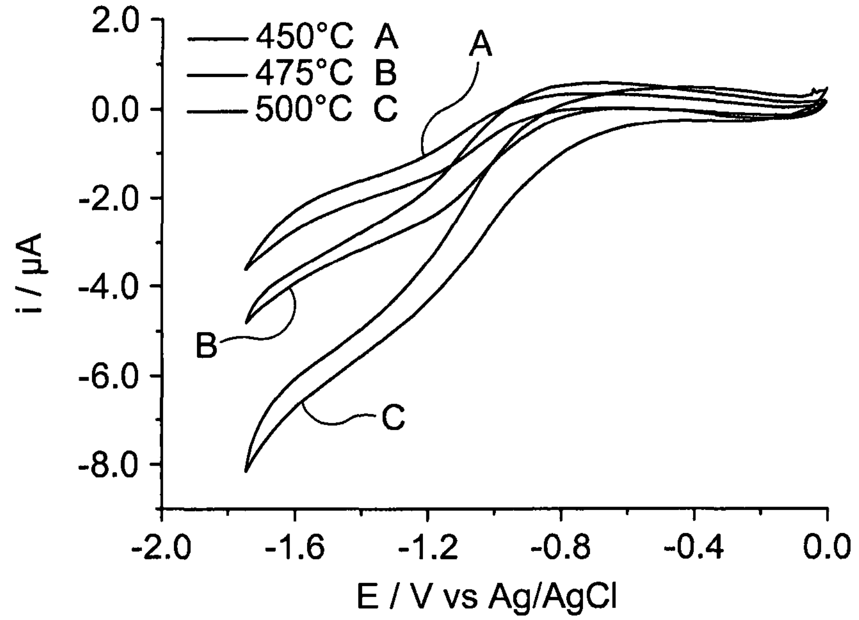


Fig. 4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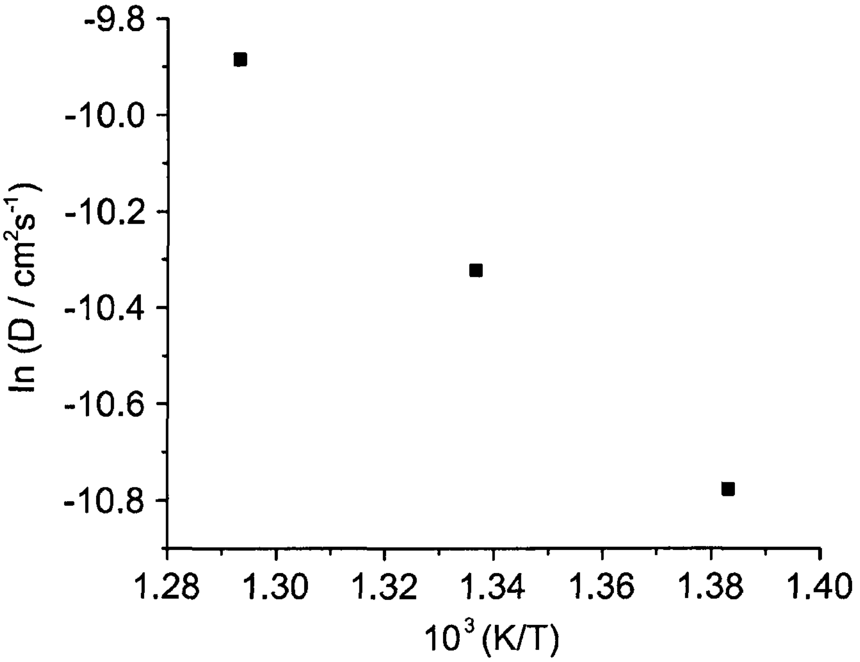
0.0
-2.0
-4.0
-6.0
-8.0
i / μA
-2.0
-1.6
-1.2
-0.8
-0.4
0.0
E / V vs Ag/AgCl
450°C A
475°C B
500°C C
A
B
C

Fig. 5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-10.0
-10.2
-10.4
-10.6
-10.8
ln (D / cm²s⁻¹)
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1.30
1.32
1.34
1.36
1.38
1.40
10³ (K/T)

Fig. 6

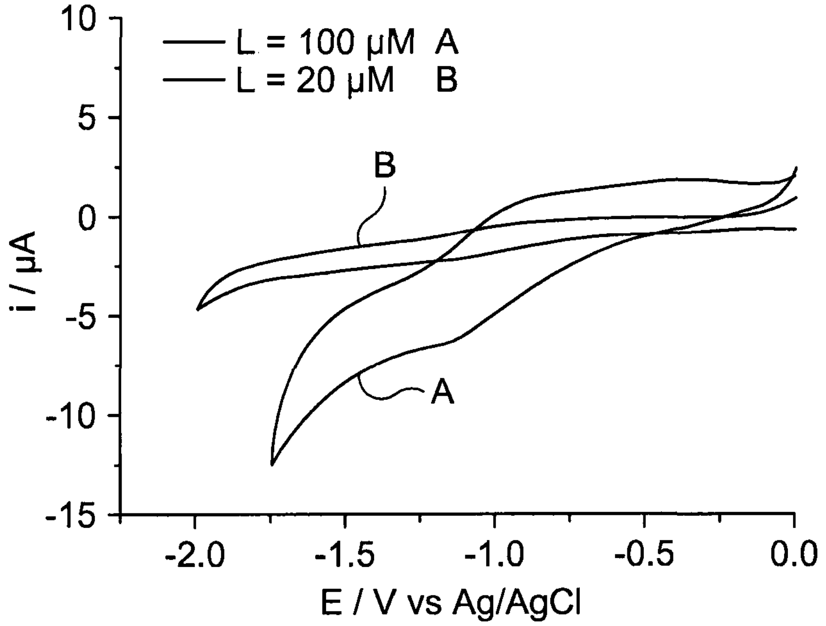
L = 100 µM A
L = 20 µM B
B
A
i / µA
10
5
0
-5
-10
-15
-2.0
-1.5
-1.0
-0.5
0.0
E / V vs Ag/AgCl

Fig. 7

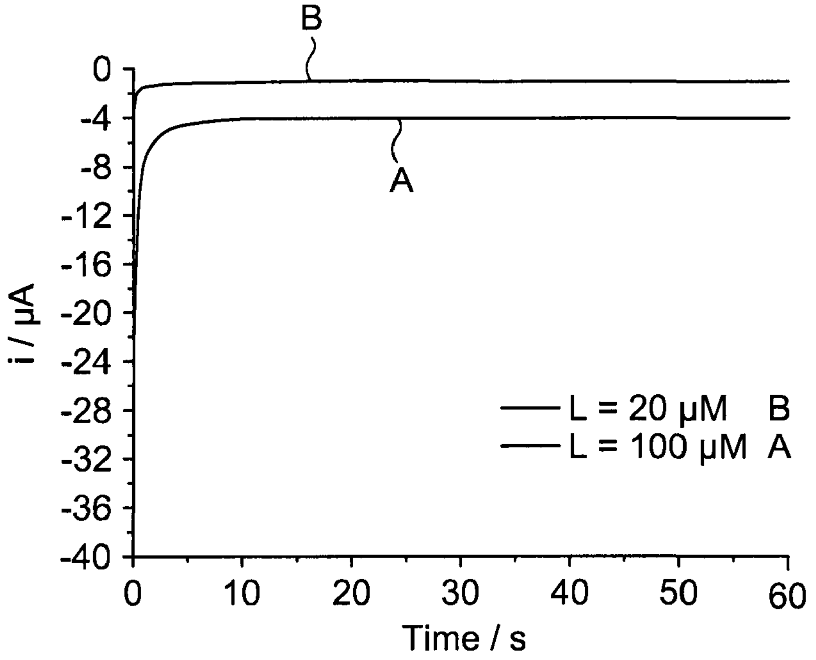
B
A
i / µA
0
-4
-8
-12
-16
-20
-24
-28
-32
-36
-40
L = 20 µM B
L = 100 µM A
0
10
20
30
40
50
60
Time / s

Fig. 8

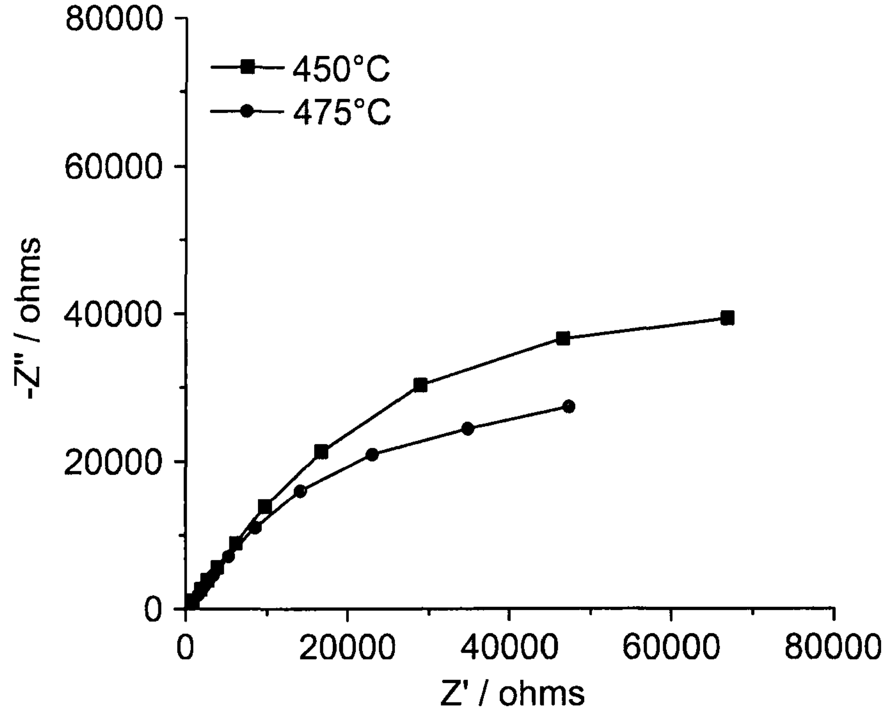
80000
60000
40000
20000
0
-Z" / ohms
450°C
475°C
0
20000
40000
60000
80000
Z' / ohms

Fig. 9A

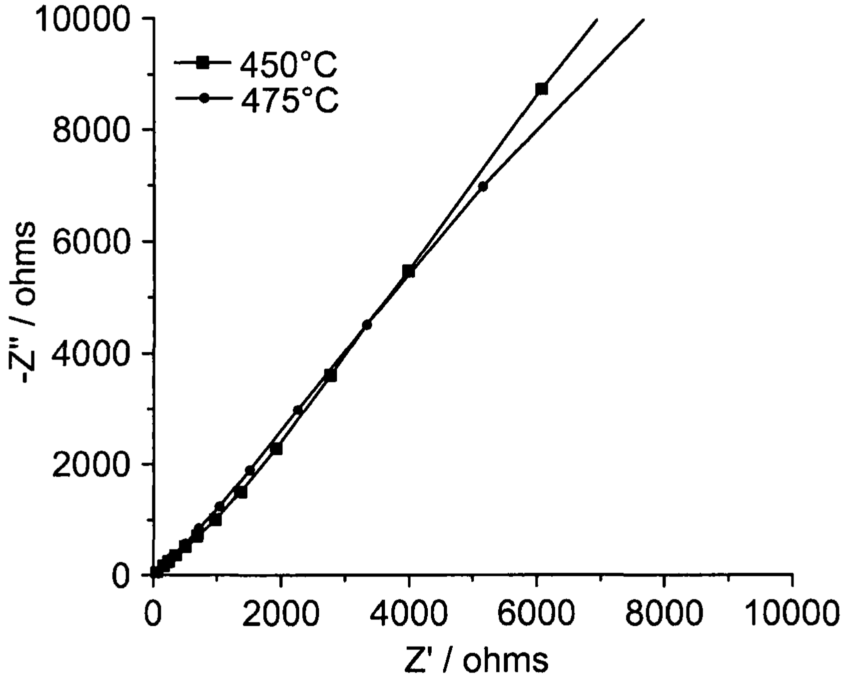
10000
8000
6000
4000
2000
0
-Z" / ohms
450°C
475°C
0
2000
4000
6000
8000
10000
Z' / ohms

Fig. 9B

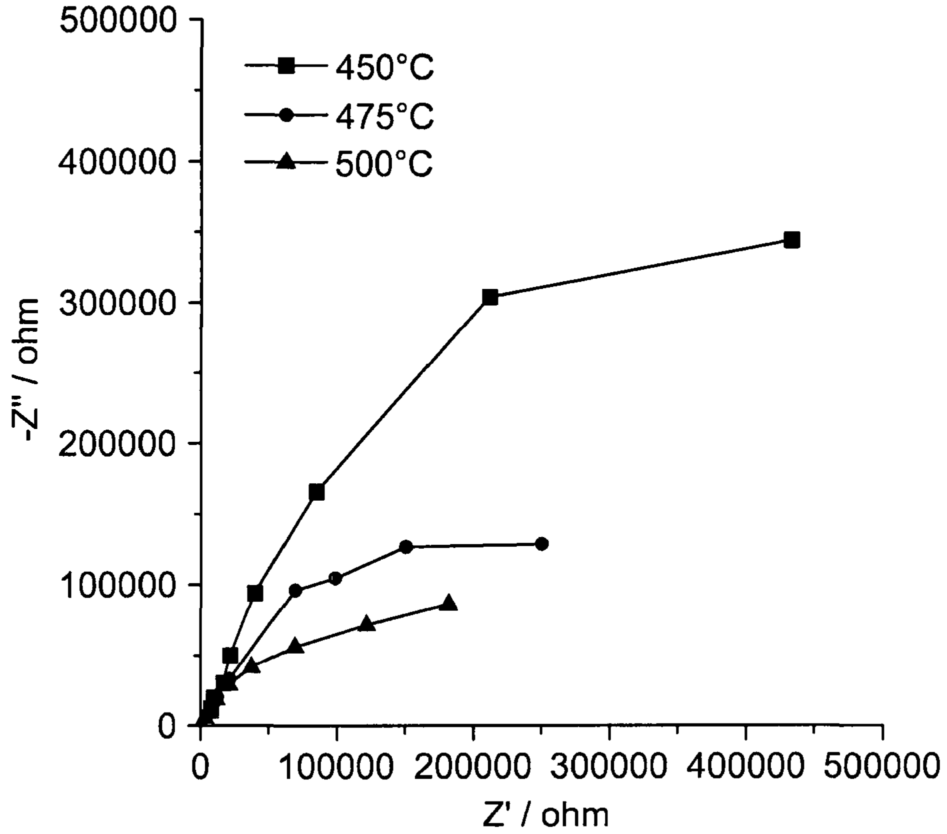

Fig. 10

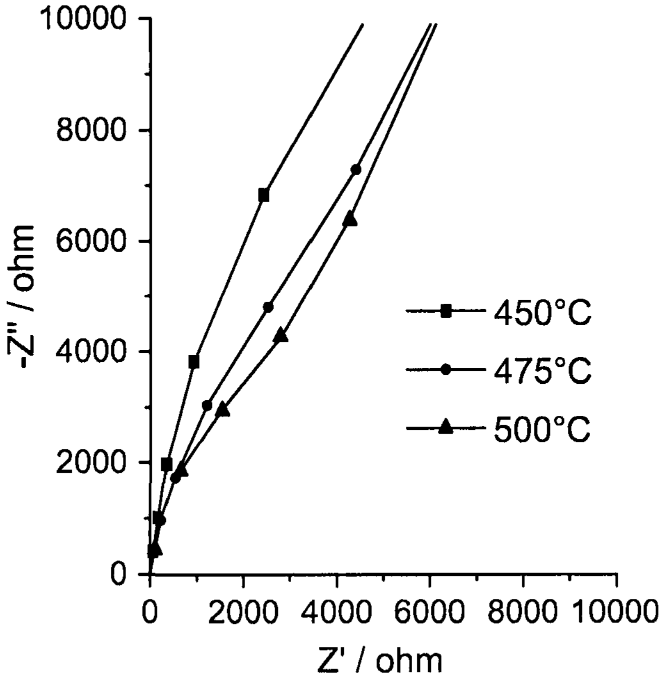

Fig. 10B

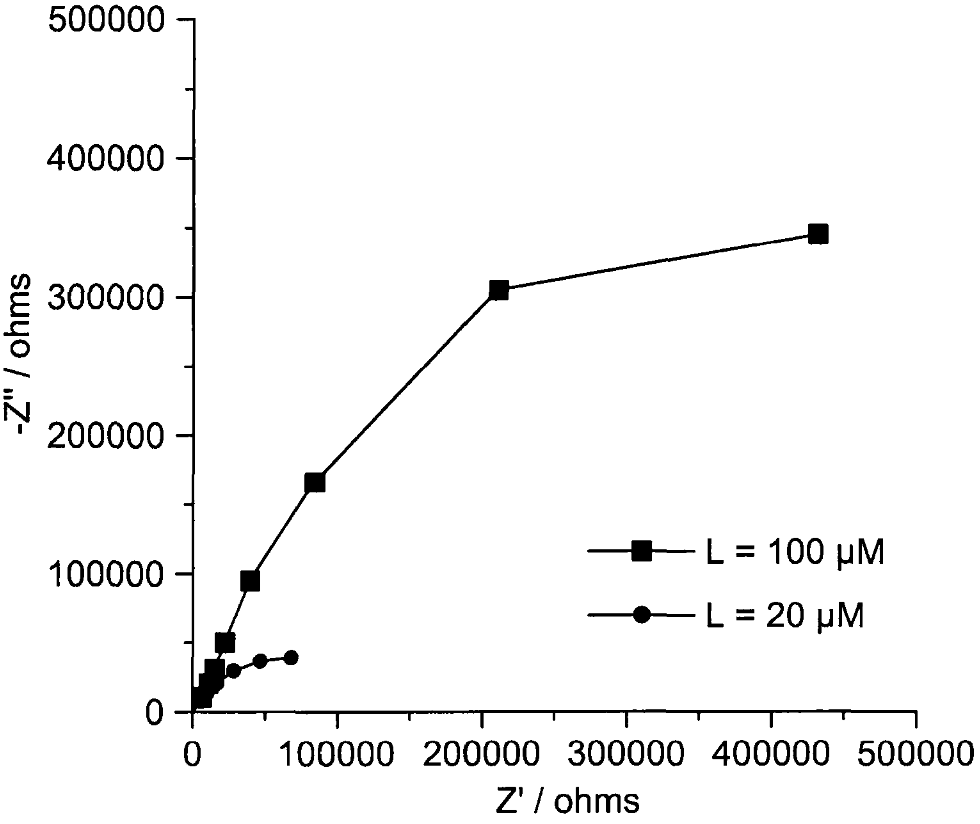
500000
400000
300000
200000
100000
0
-Z" / ohms
0
100000
200000
300000
400000
500000
Z' / ohms
L = 100 μM
L = 20 μM

Fig. 11

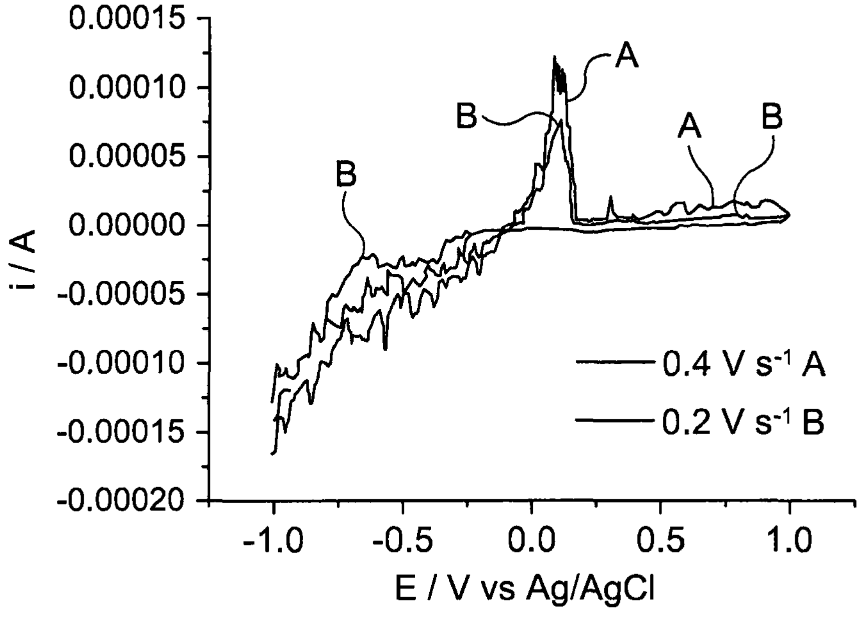
0.00015
0.00010
0.00005
0.00000
-0.00005
-0.00010
-0.00015
-0.00020
i / A
-1.0
-0.5
0.0
0.5
1.0
E / V vs Ag/AgCl
A
B
A
B
B
0.4 V s-1 A
0.2 V s-1 B

Fig. 12

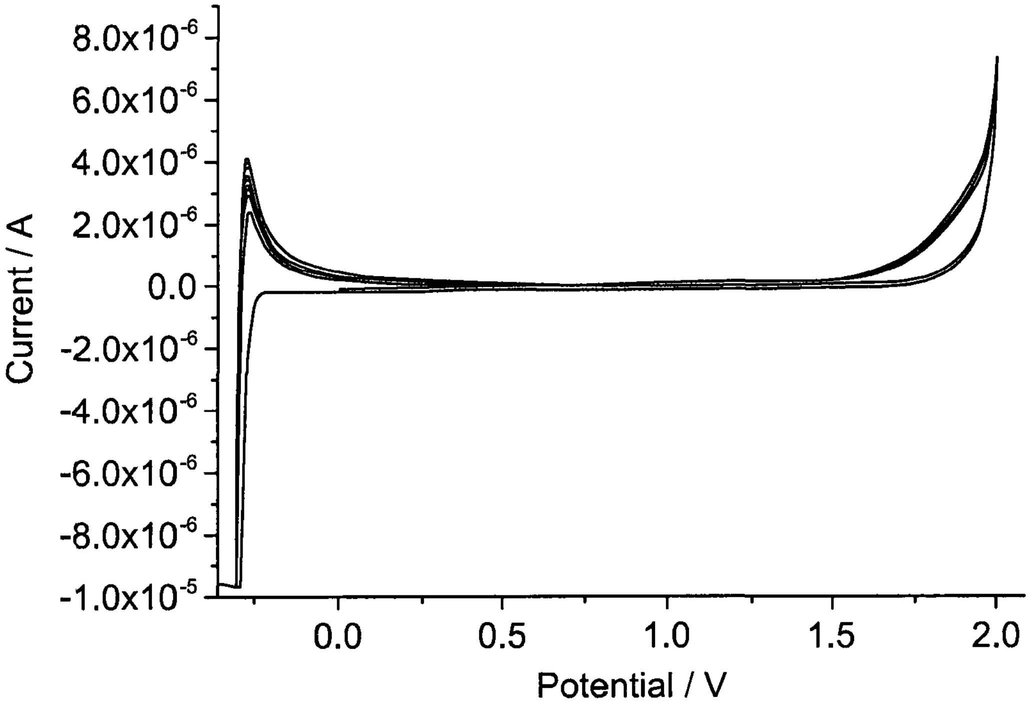
8.0x10^{-6}
6.0x10^{-6}
4.0x10^{-6}
2.0x10^{-6}
0.0
-2.0x10^{-6}
-4.0x10^{-6}
-6.0x10^{-6}
-8.0x10^{-6}
-1.0x10^{-5}
Current / A
0.0
0.5
1.0
1.5
2.0
Potential / V

Fig. 13

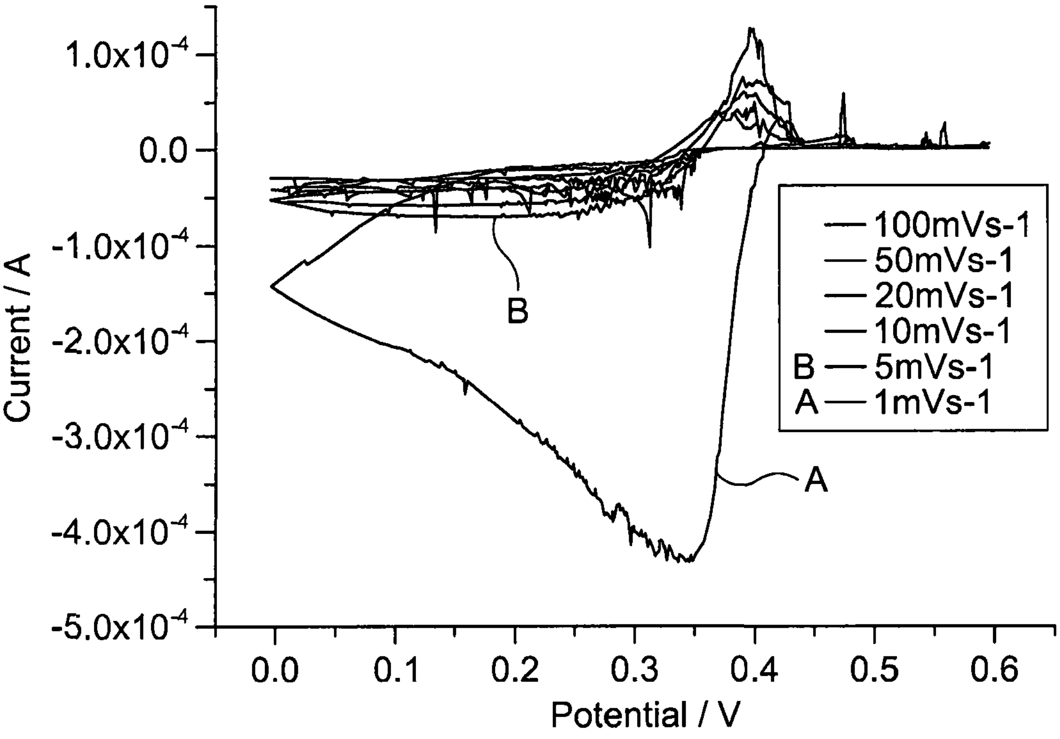
1.0x10^{-4}
0.0
-1.0x10^{-4}
-2.0x10^{-4}
-3.0x10^{-4}
-4.0x10^{-4}
-5.0x10^{-4}
Current / A
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Potential / V
B
A
100mVs-1
50mVs-1
20mVs-1
10mVs-1
B 5mVs-1
A 1mVs-1

Fig. 14

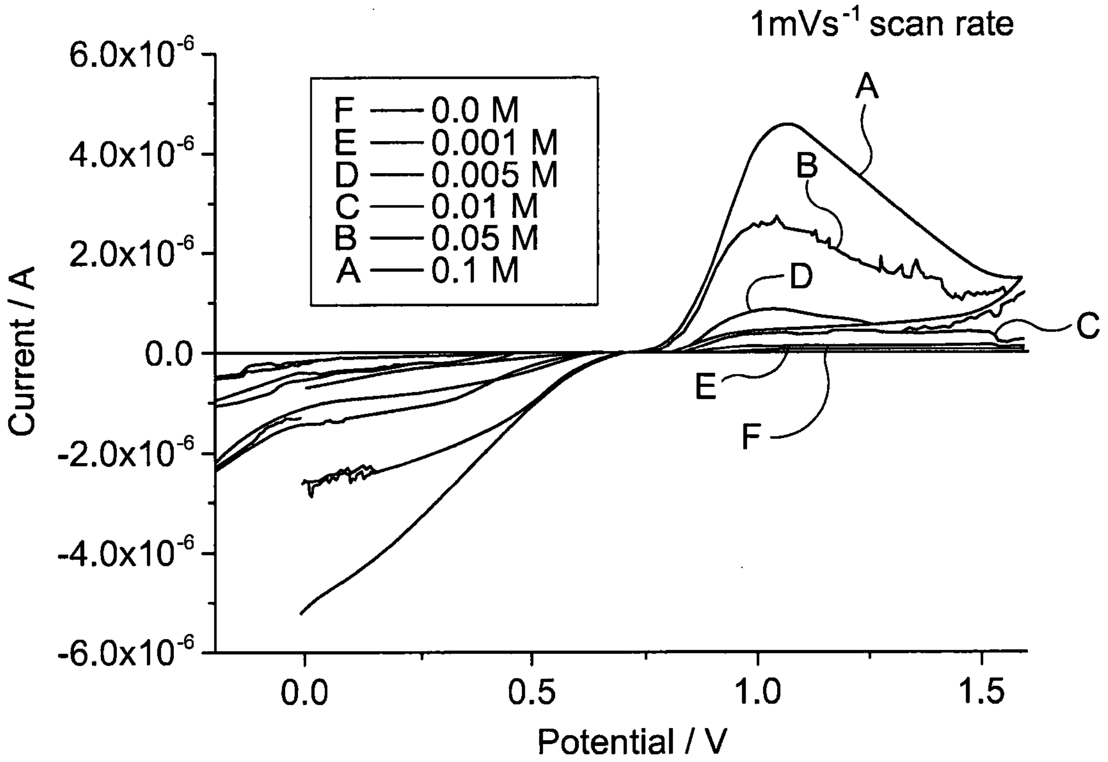
1mVs^{-1} scan rate
F — 0.0 M
E — 0.001 M
D — 0.005 M
C — 0.01 M
B — 0.05 M
A — 0.1 M
A
B
D
C
E
F
6.0x10^{-6}
4.0x10^{-6}
2.0x10^{-6}
0.0
-2.0x10^{-6}
-4.0x10^{-6}
-6.0x10^{-6}
Current / A
0.0
0.5
1.0
1.5
Potential / V

Fig. 15

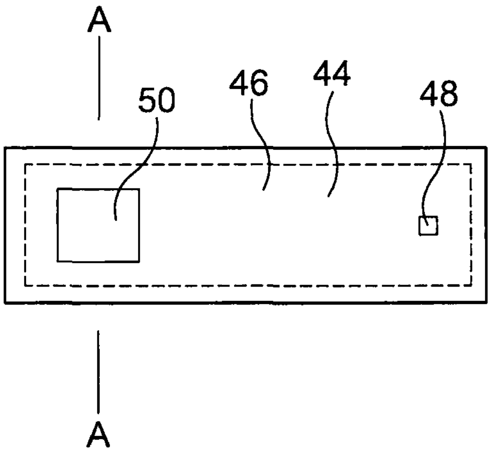

Fig. 16A

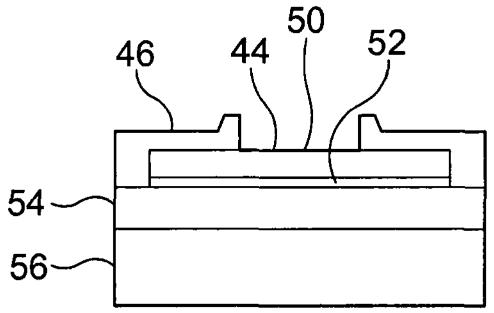

Fig. 16B

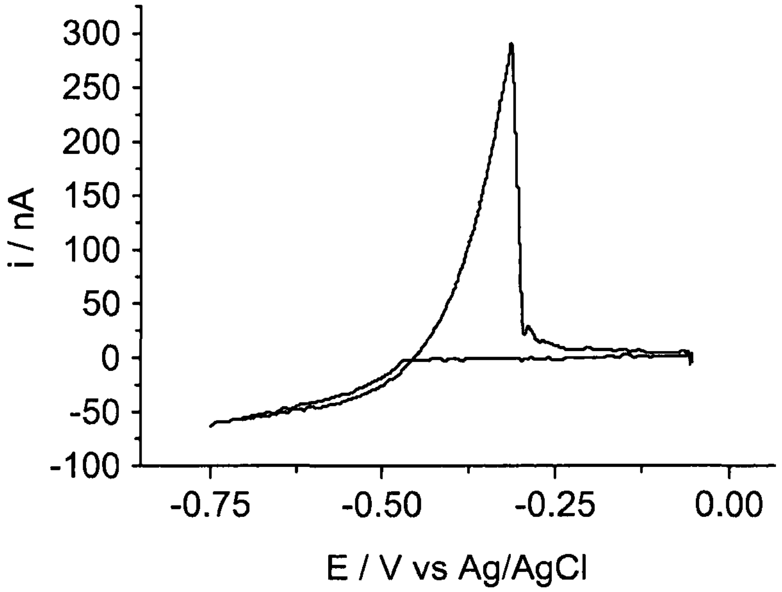

Fig. 16C

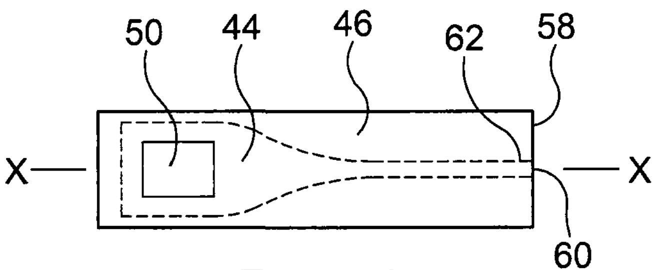

Fig. 17A

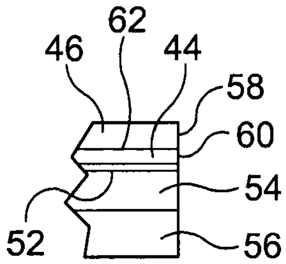

Fig. 17B

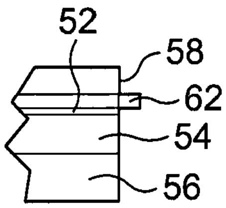

Fig. 17C

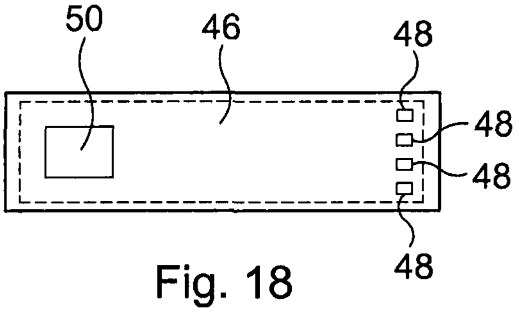

Fig. 18

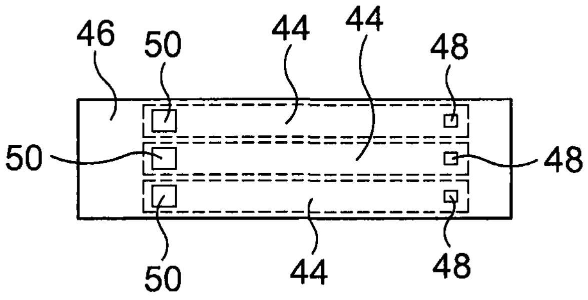

Fig. 19

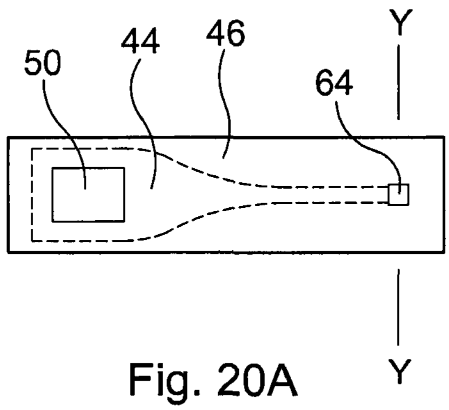

Fig. 20A

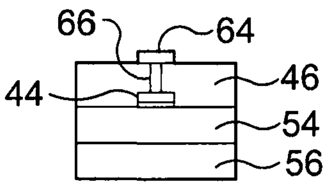

Fig. 20B

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/052596

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, COMPENDEX, INSPEC, 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	NOLAN M A ET AL: "Failure analysis of microfabricated iridium ultramicroelectrodes in chloride media", SENSORS AND ACTUATORS B: CHEMICAL: INTERNATIONAL JOURNAL DEVOTED TO RESEARCH AND DEVELOPMENT OF PHYSICAL AND CHEMICAL TRANSDUCERS, ELSEVIER S.A, SWITZERLAND, vol. 50, no. 2, 31 July 1998 (1998-07-31), pages 117-124, XP004144859, ISSN: 0925-4005, DOI: 10.1016/S0925-4005(98)00164-6	1-8, 10-15, 18-22, 25,26
Y	the whole document	16,17, 23,24
A		9

	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ 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

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"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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Date of the actual completion of the international search 5 December 2013	Date of mailing of the international search report 07/01/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Joyce, David

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/052596

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WITTKAMPF M ET AL: "Characterization of microelectrode arrays by means of electrochemical and surface analysis methods", SENSORS AND ACTUATORS, B: CHEMICAL 1997 MAY 1 ELSEVIER SCIENCE S.A., vol. B40, no. 1, 1 May 1997 (1997-05-01), pages 79-84, XP002717474, figures 1,2 -----	16,17
Y	JIANG K ET AL: "Cyclic voltammetry of solid TiO2 in molten alkali chlorides", ECS TRANSACTIONS - MOLTEN SALTS AND IONIC LIQUIDS 17 2010 ELECTROCHEMICAL SOCIETY INC. USA, vol. 33, no. 7, 2010, pages 273-276, XP002717475, DOI: 10.1149/1.3484784 the whole document -----	23,24
X	WAHL A ET AL: "Nanomolar Trace Metal Analysis of Copper at Gold Microband Arrays", JOURNAL OF PHYSICS: CONFERENCE SERIES, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 307, no. 1, 17 August 2011 (2011-08-17), page 12061, XP020209367, ISSN: 1742-6596, DOI: 10.1088/1742-6596/307/1/012061 the whole document -----	1-8, 10-15, 18-22, 25,26
X	WO 2010/061229 A1 (NANOFLEX LTD [GB]; UNIV EDINBURGH [GB]; FREEMAN NEVILLE JOHN [GB]; MOU) 3 June 2010 (2010-06-03) the whole document -----	1-8, 10-15, 18-24

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2013/052596

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010061229 A1	03-06-2010	EP 2356437 A1	17-08-2011
		JP 2012510615 A	10-05-2012
		US 2012024571 A1	02-02-2012
		WO 2010061229 A1	03-06-2010