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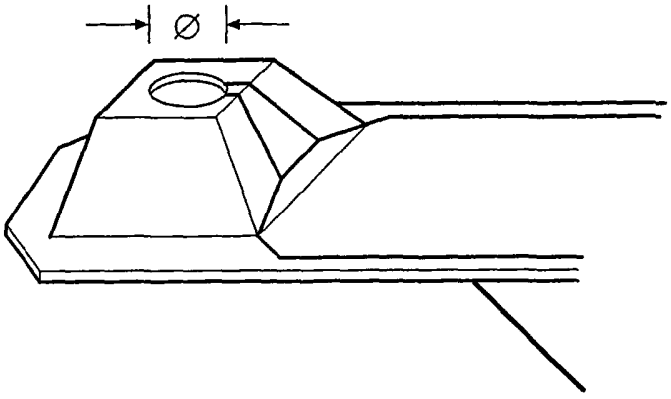
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(54) Title: SCANNING ELECTROCHEMICAL MICROSCOPE PROBE



(57) Abstract: Probe for use in the imaging of a substrate, its use and manufacturing method, the probe comprising an electrically insulated probe body and extending therefrom a cantilever from which extends an imaging tip, the probe further comprising an electrically conducting material which extends substantially along the length of the cantilever and which includes a region where it is exposed through the insulator to provide an electrochemical sensor, wherein the width of the electrically conducting material is substantially less than the width of the cantilever itself.

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SCANNING ELECTROCHEMICAL MICROSCOPE PROBE

Field of the invention

The invention relates to probes for use in imaging substrates, methods of manufacture and uses thereof.

Background to the invention

The scanning electrochemical microscope (SECM) is a scanned probe microscope that has proven to be a powerful instrument for the quantitative investigation of a number of processes that occur at interfaces. The probe of the SECM is a ultramicroelectrode (UME), with the amperometric or potentiometric response of the UME being recorded as the probe is scanned either normal to the interface of interest or over the interface, typically at a fixed height.

The atomic force microscope (AFM) maps the topography of a substrate with nanometer vertical resolution, by monitoring the interaction force between the sample and a sharp tip, which is attached to the end of a cantilever.

Macpherson[1] *et al*, 2000, have described a SECM-AFM probe capable of imaging in air and under fluids, and simultaneously acquiring topographical, electrical and electrochemical measurements with high spatial resolution. The hand-fabricated probe, possessing dual electrochemical and force sensing capabilities, was fabricated by coating flattened and etched platinum wires with insulating, electrophoretically deposited paint. The flattened portion of the probe provided a flexible cantilever (force sensor) whilst the coating procedure acts to insulate the wire, such that the tip

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(electrode) remains exposed to solution. This probe was capable of recording submicrometer electrochemical information and correlating with surface topography measurements, at high resolution, under aqueous solution.

There are however many problems associated with the hand-microfabrication technique. The tip fabrication process, including the etching process for sharpening the platinum wire and the insulation step does not facilitate the reproducible fabrication of geometrically well-defined UMEs.

Kranz *et al*, 2001 acknowledged the limitations of the hand-microfabricated probes and developed a method of fabrication which allowed integration of an electroactive area, within a commercial AFM probe in order to obtain electrochemical information at an exactly defined distance above the end of the tip. Subsequent remodelling of the original AFM tip by focused ion beam, enabled simultaneous high resolution topographical imaging. A complete separation of topographical and electrochemical signal was thus possible. However this fabrication method and resultant probe has a number of limitations associated with it. The probe comprises a flat top with a sharp point (imaging tip) protruding from the centre of a square or ring electrode. This imaging tip can impede the movement of species away from the sample surface for subsequent detection at the electrode. Furthermore, each probe is made individually, and the process is thus extremely time-consuming and prone to irreproducibility.

In both of the aforementioned probes, a layer of insulating material (approx 1 μm thickness) is required to cover the electrical conducting material, with removal of the insulating material at a pre-determined location(s) exposing the electrochemical

sensor or as it may also be referred, the electrode. There is however often a tendency for so called "pin-holes" to develop within the insulating material. The formation of these 'pin-holes' result in undesired electrodes located across the probe. This 'pin-hole' phenomena leads to difficulties in the quantitative analysis of electrochemical species, as the number of electrodes is unknown. The larger the area of metal which needs coating with insulator, the greater the likelihood of unwanted electrodes arising from 'pin-hole' formation.

We have identified a micro-fabrication process for the manufacture of SECM-AFM probes which overcomes a number of the problems identified in the prior art.

Statements of the invention

According to a first aspect of the invention there is provided a probe for use in the imaging of a substrate, the probe comprising an electrically insulated probe body and extending therefrom a cantilever from which extends an imaging tip, the probe further comprising an electrically conducting material which extends substantially along the length of the cantilever and which includes a region where it is exposed through the insulator to provide an electrochemical sensor, wherein the width of the electrical conducting material is substantially less than the width of the cantilever itself..

In a preferred embodiment of the invention the width of the electrical conducting material is about 10 μm or less. Even more preferably the width of the electrical conducting material is about 5 μm or less. Even more preferably still the width of the electrical conducting material is in the range of between 1-2 μm.

The use of an electrical conducting material in the aforementioned width ranges has a number of technical advantages. As described above, there is an identified problem in the art of 'pin-holes' forming in the insulating material, which results in a plurality of electrochemical sensors being exposed on a probe and making quantification of results problematic. The use of the aforementioned widths of electrical conducting material means that if 'pin-holes' do form in the insulating layer the likelihood of them forming over an area of electrical conducting material is significantly reduced.

Furthermore, when the insulator is laid down at sub-micrometer thicknesses (approx 0.1μm), onto electrical conductive material having a width of above 10μm, it has been found that insulating material does not adhere satisfactorily to the electrical conductive material and has a tendency to peel off into solution during the final stages of the manufacturing process. When, for example, gold and silicon dioxide are used as the electrical conductive and insulating materials respectively, whilst they are electrochemically inert in the environments in which the probe is used to image, this inertness reduces their ability to adhere to each other. This problem has been overcome by using electrical conductive material having a width of less than 10μm.

In a preferred embodiment of the invention the electrical conductive material which forms the electrochemical sensor is a metal.

The metal is preferably any metal which is compatible with electron beam lithography (EBL), can be evaporated and is not attacked by the KOH release etch. Preferably the metal is a transition metal selected from the Group VIII, for example Pt, Ag, Au or

mixtures thereof. Alternatively the metal is a transition metal selected from the Group IX, for example, Ir.

By using the probes of the invention as substrates for further modification, highly specialised electrochemical sensors are possible, for example: (i) Hg thin film UMEs, formed by the controlled reduction of Hg_2^{2+} onto Pt, Ag or Au, (ii) High resolution pH (potentiometric) probes, by depositing iridium onto a Pt substrate and electrochemically oxidising to form iridium oxide (iii) electrochemically oxidising silver in the presence of chloride ions to form silver chloride, which is capable of detecting chloride ion concentrations, for example in cystic fibrosis or in corrosion studies (iv) polymer modified electrodes

In a further embodiment of the invention the insulating material, which is non-electrical conducting is, for example, an oxide, nitride or carbide of silicon, and may be selected from the group consisting of SiO_2, Si_3N_4 or SiC. Alternative materials can be used, and thickness can be varied. The only requirements being a compatibility with the KOH etch release and an ability to be dry etched and minimal film stress to prevent probe bending.

Microfabrication (e.g EBL) enables the pattern of the shape and area of the exposed metal forming the electrochemical sensor to be precisely defined and sector-shaped electrochemical sensor geometries of sub-micrometre dimensions down to approximately 50 nm are possible. The patterning can alter electrode size, shape, number and position. The capability of defining the geometry of the metal stripes has the advantage of minimising the amount of metal that needs coating in insulator.

Surprisingly it has also been found that coating only one side of the imaging tip with metal does not significantly impair performance. It may also be desired to coat both sides of the imaging tip in metal, with an electrode being exposed on each side. It has been found that this probe may be particularly useful for conductivity measurements (in air) and does not perturb significantly the concentration profile of the species that is being measured.

In an alternative embodiment of the invention the imaging tip is substantially pyramidial. In a still further preferred embodiment of the invention, as described in Example 2, the imaging tip is substantially frusto-pyramidial, being provided with a substantially square apical surface. Preferably at least one zone of electrical conductive material is exposed on this apical surface to provide the electrochemical sensor. This zone may be, for example, located substantially centrally on the apical surface.

The height of the imaging tip may be in the range of from about 1-100μm. Preferably the height is in the range of from about 1-50μm. Even more preferably the height in the range of from about 10-25μm and more preferably still in the range of from about 15-18μm.

According to a second aspect of the invention there is provided the use of a probe according to the invention for the imaging of a substrate. In a preferred embodiment of the invention the imaging is topographical imaging. In a more preferred embodiment of the invention the imaging is electrochemical imaging. In a still further preferred embodiment of the invention the imaging is topographical and

electrochemical imaging. This topographical and electrochemical imaging is preferably simultaneous although alternatively it may be sequential. When using the probe described in Example 1, it is preferable to simultaneously image topographical and electrochemical parameters. When using the probe described in Example 2, it is preferable to firstly undertake topographical imaging of the substrate and then position the probe at a defined distance above the substrate surface and undertake electrochemical imaging.

It will be understood to those skilled in the art that the topographical imaging using this probe may be within the contact or tapping modes.

There is a vast array of uses of the probe of the invention within a wide range of disciplines ranging from material sciences to biological based systems.

According to a further aspect of the invention there is provided a method of imaging a substrate comprising the steps of;

(i) bringing into contact a probe according to any of Claims 1 to 12 with a substrate to be imaged;

(ii) collecting imaging data; and, optionally

(iii) storing and/or analysing and/or presenting the data.

According to a still further aspect of the invention there is provided a process for the manufacture of a probe according to the invention comprising electron beam lithography. Alternatively photolithography may also be used to provide the probe of the invention. Even more preferably, a combination of photolithography and electron beam lithography is used in the micro-fabricating process.

Micro-fabrication also enables batch manufacture of the probes which increases the reproducibility of the probe structure, particularly the electrode geometry, thereby leading to increased reliability and reproducibility of results.

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According to a further aspect of the invention there is provided a microscope, comprising a probe of the invention, for use in the imaging of a substrate.

Specific embodiments of the invention

10 Embodiments of the invention will now be described by example only and with reference to the following Figures:

Figure 1: A schematic of a planar disc probe.

Figure 2: A schematic of probe comprising an electrode self-aligned at tip apex.

15 Figure 3: A schematic of a ring-disc probe.

Figures 4-6: Scanning Electron Micrograph (SEM) showing side views of the probe shown in Figure 2.

Figure 7: SEM of probe illustrated in Figure 2, in plan view.

Figure 8: An optical micrograph of the tip of the probe illustrated in Figure 2.

20 Figure 9: An SEM of the tip of the probe illustrated in Figure 2.

Detailed description of the Figures

Figure 1. The probe illustrated in Figure 1(a) is a simple noble metal (Pt, Au or Ag)

25 disc electrode (electron beam evaporated with pattern transfer by lift-off), insulated by

a thin layer of plasma enhanced chemical vapour deposited Si_3N_4 or evaporated SiO_2. These dielectrics are chemically inert over a wide potential window and in a range of solvents. The disc geometry, which is most common in SECM, will be produced by (reactive ion) etching a small hole in the insulator. Such apertures may be defined with sizes (Ø) down to 50 nm (Figure 1(b)). The electrode is situated at the apex of a 20 μm high AFM tip, providing good access to the specimen. If the depth of the recess resulting from the fabrication procedure is sizeable compared to the dimensions of the electrode, the gap will be filled by the electrodeposition of Pt, Au or Ag. By using the above-mentioned probe electrodes as substrates it will also be possible to produce highly specialised electrochemical sensors, for example: (i) Hg thin film UMEs, formed by the controlled reduction of Hg_2^{2+} onto Pt, Ag or Au, (ii) High resolution pH (potentiometric) probes, by depositing iridium onto a Pt substrate and electrochemically oxidising to form iridium oxide (iii) electrochemically oxidising silver in the presence of chloride ions to form silver chloride, which is capable of detecting chloride ion concentrations, for example in cystic fibrosis or in corrosion studies (iv) polymer modified electrodes

Since a decrease in topographical spatial resolution (in both contact and tapping mode), over conventional AFM probes, could result from the flat tip apex of the probe a very sharp, short tip, may be positioned close to the electrode. This is fabricated by the gradual reduction in the size of a circular hole in an undercut bilayer resist during evaporation. Provided the tip is small enough, so as not to impede diffusion to the electrode, and in a defined position, it should be possible to correlate electrochemical and topographical maps of a surface with this device.

Figure 2: The probe as illustrated in Figure 2 is formed by modification of the cantilever, generally manufactured from silicon nitride, such that the end of the probe is a sharp tip. The active region of the probe is defined by a self-alignment process in which the electrode is written over the end of the cantilever. Insulation is then deposited over the probe and a small window opened either at the end of the cantilever, or else adjacent to it. The electrode can therefore be positioned at any point along the length of the cantilever and indeed on one or both sides of the cantilever. Sector-shaped electrode geometries of sub-micrometre dimensions down to 200 nm (limited by alignment accuracy) are predicted using this methodology. Tip radii is controllable to below 30 nm for good topographic resolution. The range of electrode materials identified for Probe 1 are usable for this probe.

Figure 3: The probe as illustrated in Figure 3, is manufactured by the same micro-fabrication method used to fabricate Probe 1, although the method is extended to allow the use of multiple electrodes at the tip apex resulting in a "ring-disc" geometry in which a disc electrode is surrounded by one or more rings. The size of the inner ring is subject to the same lithographic constraints described for Probe 1. Minimum spacing between rings is limited by level-to-level alignment; spacing down to 300 nm should be achievable with good yield. Since this probe will have more than one active connection, a multiple connector probe card will be developed (similar to that used by Digital Instruments in their thermal microscope system). The flexibility provided by the lithographic definition of the ring and disc electrodes will allow the electrodes themselves to be split into individually addressable segments (up to four in the first instance), thereby permitting, simultaneous detection of multiple species on a local scale with the same probe. This design strategy also enables one or more disc electrodes to be situated on the side of the tip or on the cantilever itself, each having

independent connections. Preferably two independent disc electrodes are provided on the tip, preferably being positioned on the apical surface of the tip. Even more preferably four independent disc electrodes are provided on the tip, preferably being positioned on the apical surface of the tip

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2. Kranz, C, Freidbacher, G and Mizaikoff, B (2001) Integrating an ultramicroelectrode in an AFM cantilever:combined technology for enhanced information. Anal. Chem. 2001 72:2491-2500.

Micro-Fabrication of the probe in Example 1

Using 3 inch silicon wafers with 100nm of LPCVD silicon nitride on both sides.

1) Wafer is cleaned in nanostrip for twenty minutes then transferred to deionised water for five minutes, then acetone for five minutes and finally IPA for five minutes before being blown dry with a stream of nitrogen.
2) 100nm of nichrome is evaporated onto one side of the wafer.
3) Wafer is cleaned in acetone for five minutes, followed by IPA for five minutes then blown dry with a stream of nitrogen.
4) Photolithography is carried out on the side of the wafer without nichrome to define alignment marks.
5) This side is then dry etched to remove the silicon nitride exposed by the photolithography.
6) The photoresist is stripped in acetone and the wafer cleaned in nanostrip for twenty minutes followed by deionised water for five minutes.
7) The wafer is then transferred to HF:water 1:4 for one minute before thorough rinsing in water.
8) The wafer is then wet etched in 7M KOH at 80 C for 80 minutes.
9) The wafer is neutralised in H_2SO_4:water 1:4 for one minute followed by a water rinse.
10) Wafer is then cleaned in acetone for five minutes, IPA for five minutes, blown dry with nitrogen, placed in nanostrip for twenty minutes, rinsed in water for five minutes and blown dry with nitrogen.
11) Photolithography is carried out on the side without nichrome to define the AFM probe bodies.
12) The wafer is dry etched as in step 5.
13) The resist is stripped as in step 6.
14) The wafer is deoxidised as in step 7.
15) The wafer is wet etched in 7M KOH at 105 C for 70 minutes.
16) The wafer is neutralised as in step 9.
17) The wafer is cleaned in nanostrip for twenty minutes followed by water for five minutes .
18) The nichrome is removed from the wafer by placing in chrome etch for ten minutes followed by a rinse in water.
19) The wafer is cleaned as in step 1.
20) 8% PMMA is spun on the unetched side of the sample at 5000 rpm for sixty seconds.
21) The sample is baked at 180 C for one hour.
22) 4% PMMA is spun on the same side of the sample at 5000 rpm for sixty seconds.
23) The sample is then baked at 180 C for six hours.
24) The pyramid tops, crack arrestors and markers are written with ebeam lithography.
25) The pattern is developed in MIBK:IPA 1:1 for thirty seconds, transferred to IPA for thirty seconds and blown dry with nitrogen.
26) The wafer is cleaned in an O_2 plasma for 30 seconds.
27) 75nm of NiCr is evaporated over the PMMA pattern.

28) Lift-off is carried out in warm acetone, followed by an IPA rinse and blow dry with nitrogen.
29) The wafer is then dry etched to remove silicon nitride not covered by the NiCr.
30) A calibration sample is cleaned as in step 17.
31) The calibration sample is deoxidised as in step 7.
32) The calibration sample is etched in KOH (20 % by weight):IPA 3:1 at 70 C for 30 minutes.
33) The calibration sample is removed, rinsed in water, neutralised in nanostrip for several minutes and rinsed in water.
34) The calibration sample is then cleaned in acetone for five minutes, IPA for five minutes and blown dry with nitrogen.
35) The etch depth is determined using an optical microscope and the time required to produce pyramids of the appropriate height calculated.
36) The wafer is cleaned as in step 17.
37) The wafer is deoxidised as in step 7.
38) The wafer is etched as in step 32 for the period of time calculated in step 35.
39) The wafer is the neutralised as in steps 9-10.
40) The wafer is then placed in HF:water 1:4 for 1-3 hours until the LPCVD silicon nitride has been completely etched away.
41) The sample is then removed and rinsed in water before being blown dry using nitrogen.
42) 500nm of PECVD stress free silicon nitride is deposited on the pyramid side of the wafer.
43) The wafer is cleaned as in step 34.
44) 80nm of chrome is evaporated onto the pyramid side of the wafer.
45) PMMA is spun on the pyramid side of the wafer as in step 20.
46) The sample is baked as in step 21.
47) A layer of 1.5% PMMA is float coated on to the pyramid side of the wafer (depositing 50nm of resist).
48) The final bake is at 180 C for six hours.
49) The cantilever, including tip is written with ebeam lithography.
50) The pattern is developed as in step 25.
51) The wafer is placed in chrome etch for ten minutes, then rinsed in water.
52) The PMMA is stripped in acetone for five minutes.
53) The wafer is cleaned as in step 34.
54) PMMA is spun onto the pyramid side of the wafer as in step 20.
55) The wafer is baked as in step 21.
56) PMMA is float coated onto the wafer as in step 47.
57) The wafer is baked at 180 C for 30 minutes.
58) Steps 56 and 57 are repeated to deposit the desired resist thickness.
59) The wafer is finally baked as in step 48.
60) A protective cap over the probe pyramid tip is written using ebeam lithography.
61) The pattern is developed as in step 25.
62) The wafer is cleaned as in step 26.
63) 120nm of chrome is evaporated onto the PMMA pattern.
64) Lift-off is carried out as in step 28.
65) The wafer is inspected using an SEM to ensure the chrome dry etch mask is acceptable.

66) The wafer is cleaned in an O_2 plasma for five minutes.
67) The wafer is dry etched to remove any silicon nitride not covered in chrome.
68) The wafer is inspected in an SEM to ensure the silicon nitride has been fully etched through.
69) Steps 66, 67 and 68 are repeated as necessary.
70) The chrome is stripped by placing the wafer in chrome etch for 10 minutes, then rinsed in water.
71) The wafer is cleaned as in step 34.
72) PMMA is spun on the pyramid side of the wafer as in step 20.
73) The sample is baked as in step 21.
74) A layer of PMMA is float coated as in step 47.
75) Steps 46 and 47 are repeated to deposit the desired resist thickness.
76) The final bake is as in step 48.
77) The gold pad, mirror and electrodes are written with ebeam lithography.
78) The pattern is developed as in step 25.
79) The wafer is cleaned as in step 26.
80) 10nm of nichrome and 100nm of gold are evaporated onto the PMMA pattern.
81) Lift-off is carried out as in step 28.
82) The wafer is cleaned as in step 34.
83) 100nm of PECVD stress free silicon nitride is deposited on the gold electrode side of the wafer.
84) PMMA is spun on the pyramid side of the wafer as in step 20.
85) The sample is baked as in step 21.
86) A layer of PMMA is float coated as in step 47.
87) The final bake is as in 48.
88) The outline of the cantilever, contact pads and tip electrode are written using ebeam lithography.
89) The pattern is developed as in step 25.
90) The wafer is cleaned in an O_2 plasma for one minute.
91) The wafer is dry etched to remove any silicon nitride not covered in PMMA.
92) The PMMA is removed using an O_2 plasma for 1 minute, followed by 30 minutes in acetone at 40 C.
93) The wafer is cleaned as in step 34, followed by a 10 minute O_2 plasma clean.
94) The wafer is etched in 7M KOH:IPA 5:1 at 70 C until the crack arrestors are seen to float free, it is then etched for the same time + 10% again before removal.
95) The wafer is rinsed in water and neutralised as in step 9.
96) The wafer is rinsed in methanol for five minutes and allowed to dry in ambient conditions.
97) The wafer is cleaved up into individual probes.

Process summary:-

Steps 1-18 define the bodies of the individual probes into the reverse side of the wafer, whilst providing alignment features to ensure that the eventual devices match up front to back.

Steps 19-42 define the pyramids on the front of the wafer, these will eventually become the tips of the AFM probes. Altering the pattern and KOH etch time in these steps allow the cantilever length and tip height of the eventual devices to be varied. The silicon nitride deposition at this point dictates the thickness of the eventual devices, which can be varied.

Steps 43-70 define the cantilever shape on the front of the wafer. Alteration of the pattern at this stage can change the width of the cantilever although the length is mainly dictated by the pyramid position defined in steps 19-42.

Steps 71-82 define the contact pads, connecting wires and electrode metal. At this stage it is fairly straight forward to change the electrode material. Normally gold is used but platinum or other metals could be substituted. The only requirements are that they can be evaporated and are not attacked by the KOH release etch. Pattern changes at this point can alter the connecting track width and number of individual connections to the tip. If multiple, individually addressable electrodes were desired they could be introduced at this point.

Step 83 is the deposition of the insulating coating over the metal tracks. At this point alternative materials could be used instead of silicon nitride and the thickness can be varied. The only requirements being a compatibility with the KOH release etch an ability to be dry etched and minimal film stress to prevent probe bending.

Steps 84-92 are the tip electrode definition and etching. Pattern changes at this point can alter electrode size, shape, number and position.

Steps 93-97 are the probe release steps. In these stages the silicon is removed from the back of the AFM probes and the silicon nitride cantilevers released to become free standing.

Micro-Fabrication of the probe in Example 2

Using 3 inch silicon wafers with 100nm of LPCVD silicon nitride on both sides.

1) Wafer is cleaned in nanostrip for twenty minutes then transferred to deionised water for five minutes, then acetone for five minutes and finally IPA for five minutes before being blown dry with a stream of nitrogen.
2) 100nm of nichrome is evaporated onto one side of the wafer.
3) Wafer is cleaned in acetone for five minutes, followed by IPA for five minutes then blown dry with a stream of nitrogen.
4) Photolithography is carried out on the side of the wafer without nichrome to define alignment marks.
5) This side is then dry etched to remove the silicon nitride exposed by the photolithography.
6) The photoresist is stripped in acetone and the wafer cleaned in nanostrip for twenty minutes followed by deionised water for five minutes.
7) The wafer is then transferred to HF:water 1:4 for one minute before thorough rinsing in water.

8) The wafer is then wet etched in 7M KOH at 80 C for 80 minutes.
9) The wafer is neutralised in H_2SO_4:water 1:4 for one minute followed by a water rinse.
10) Wafer is then cleaned in acetone for five minutes, IPA for five minutes, blown dry with nitrogen, placed in nanostrip for twenty minutes, rinsed in water for five minutes and blown dry with nitrogen.
11) Photolithography is carried out on the side without nichrome to define the AFM probe bodies.
12) The wafer is dry etched as in step 5.
13) The resist is stripped as in step 6.
14) The wafer is deoxidised as in step 7.
15) The wafer is wet etched in 7M KOH at 105 C for 70 minutes.
16) The wafer is neutralised as in step 9.
17) The wafer is cleaned in nanostrip for twenty minutes followed by water for five minutes .
18) The nichrome is removed from the wafer by placing in chrome etch for ten minutes followed by a rinse in water.
19) The wafer is cleaned as in step 1.
20) 8% PMMA is spun on the unetched side of the sample at 5000 rpm for sixty seconds.
21) The sample is baked at 180 C for one hour.
22) 4% PMMA is spun on the same side of the sample at 5000 rpm for sixty seconds.
23) The sample is then baked at 180 C for six hours.
24) The pyramid tops, crack arrestors and markers are written with ebeam lithography.
25) The pattern is developed in MIBK:IPA 1:1 for thirty seconds, transferred to IPA for thirty seconds and blown dry with nitrogen.
26) The wafer is cleaned in an O_2 plasma for 30 seconds.
27) 75nm of NiCr is evaporated over the PMMA pattern.
28) Lift-off is carried out in warm acetone, followed by an IPA rinse and blow dry with nitrogen.
29) The wafer is then dry etched to remove silicon nitride not covered by the NiCr.
30) A calibration sample is cleaned as in step 17.
31) The calibration sample is deoxidised as in step 7.
32) The calibration sample is etched in KOH (20 % by weight):IPA 3:1 at 70 C for 30 minutes.
33) The calibration sample is removed, rinsed in water, neutralised in nanostrip for several minutes and rinsed in water.
34) The calibration sample is then cleaned in acetone for five minutes, IPA for five minutes and blown dry with nitrogen.
35) The etch depth is determined using an optical microscope and the time required to produce pyramids of the appropriate height calculated.
36) The wafer is cleaned as in step 17.
37) The wafer is deoxidised as in step 7.
38) The wafer is etched as in step 32 for the period of time calculated in step 35.
39) The wafer is the neutralised as in steps 9-10.
40) The wafer is then placed in HF:water 1:4 for 1-3 hours until the LPCVD silicon nitride has been completely etched away.

41) The sample is then removed and rinsed in water before being blown dry using nitrogen.
42) 500nm of PECVD stress free silicon nitride is deposited on the pyramid side of the wafer.
43) The wafer is cleaned as in step 34.
44) 80nm of chrome is evaporated onto the pyramid side of the wafer.
45) PMMA is spun on the pyramid side of the wafer as in step 20.
46) The sample is baked as in step 21.
47) A layer of 1.5% PMMA is float coated on to the pyramid side of the wafer (depositing 50nm of resist).
48) The final bake is at 180 C for six hours.
49) The cantilever (without point) is written with ebeam lithography.
50) The pattern is developed as in step 25.
51) The wafer is placed in chrome etch for ten minutes, then rinsed in water.
52) The PMMA is stripped in acetone for five minutes.
53) The wafer is cleaned as in step 34.
54) PMMA is spun onto the pyramid side of the wafer as in step 20.
55) The wafer is baked as in step 21.
56) PMMA is float coated onto the wafer as in step 47.
57) The wafer is baked at 180 C for 30 minutes.
58) Steps 56 and 57 are repeated to deposit the desired resist thickness.
59) The wafer is finally baked as in step 48.
60) The sharp point and lift-off assisting strip are written using ebeam lithography.
61) The pattern is developed as in step 25.
62) The wafer is cleaned as in step 26.
63) 120nm of chrome is evaporated onto the PMMA pattern.
64) Lift-off is carried out as in step 28.
65) The wafer is inspected using an SEM to ensure the chrome dry etch mask is acceptable.
66) The wafer is cleaned in an O_2 plasma for five minutes.
67) The wafer is dry etched to remove any silicon nitride not covered in chrome.
68) The wafer is inspected in an SEM to ensure the silicon nitride has been fully etched through.
69) Steps 66, 67 and 68 are repeated as necessary.
70) The chrome is stripped by placing the wafer in chrome etch for 10 minutes, then rinsed in water.
71) The wafer is cleaned as in step 34.
72) The wafer is placed in a beaker of 20% by weight KOH in water, at room temperature for 10 minutes.
73) The wafer is removed, neutralised and cleaned as in steps 9-10.
74) PMMA is spun on the pyramid side of the wafer as in step 20.
75) The sample is baked as in step 21.
76) A layer of PMMA is float coated as in step 47.
77) Steps 46 and 47 are repeated to deposit the desired resist thickness.
78) The final bake is as in step 48.
79) The gold pad, mirror and electrodes are written with ebeam lithography.
80) The pattern is developed as in step 25.
81) The wafer is cleaned as in step 26.

82) 10nm of nichrome and 100nm of gold are evaporated onto the PMMA pattern.
83) Lift-off is carried out as in step 28.
84) The wafer is cleaned as in step 34.
85) 100nm of PECVD stress free silicon nitride is deposited on the gold electrode side of the wafer.
86) PMMA is spun on the pyramid side of the wafer as in step 20.
87) The sample is baked as in step 21.
88) A layer of PMMA is float coated as in step 47.
89) The final bake is as in 48.
90) The outline of the cantilever, contact pads and tip electrode are written using ebeam lithography.
91) The pattern is developed as in step 25.
92) The wafer is cleaned in an O_2 plasma for one minute.
93) The wafer is dry etched to remove any silicon nitride not covered in PMMA.
94) The PMMA is removed using an O_2 plasma for 1 minute, followed by 30 minutes in acetone at 40 C.
95) The wafer is cleaned as in step 34, followed by a 10 minute O_2 plasma clean.
96) The wafer is etched in 7M KOH:IPA 5:1 at 70 C until the crack arrestors are seen to float free, it is then etched for the same time again before removal.
97) The wafer is rinsed in water and neutralised as in step 9.
98) The wafer is rinsed in methanol for five minutes and allowed to dry in ambient conditions.
99)The wafer is cleaved up into individual probes.

Process summary:-

Steps 1-18 define the bodies of the individual probes into the reverse side of the wafer, whilst providing alignment features to ensure that the eventual devices match up front to back.

Steps 19-42 define the pyramids on the front of the wafer, these will eventually become the tips of the AFM probes. Altering the pattern and KOH etch time in these steps allow the cantilever length and tip height of the eventual devices to be varied. The silicon nitride deposition at this point dictates the thickness of the eventual devices, which can be varied.

**Steps 43-73 define the cantilever shape on the front of the wafer. The sharp probe tip is also defined. Alteration of the pattern at this stage can change the width of the cantilever although the length is mainly dictated by the pyramid position defined in steps 19-42. The tip angle, shape and length are also dictated by the patterns used at this point, changes such as multiple points could be added at this stage.

**Steps 74-84 define the contact pads, connecting wires and electrode metal. At this stage it is fairly straight forward to change the electrode material. Normally gold is used but platinum or other metals could be substituted. The only requirements are that they can be evaporated and are not attacked by the KOH release etch. Pattern changes at this point can alter the connecting track width and number of individual connections to the tip. If multiple, individually addressable electrodes were desired they could be introduced at this point.

Step 85 is the deposition of the insulating coating over the metal tracks. At this point alternative materials could be used instead of silicon nitride and the thickness can be varied. The only requirements being a compatibility with the KOH release etch an ability to be dry etched and minimal film stress to prevent probe bending.

**Steps 86-94 are the tip electrode definition and etching. Pattern changes at this point can alter electrode size, shape, number and position.

Steps 95-99 are the probe release steps. In these stages the silicon is removed from the back of the AFM probes and the silicon nitride cantilevers released to become free standing.

** indicates the only different processing steps between the point and disc probes. Although the finished probes have very different appearances and characteristics theses differences are mainly the results of changes in the patterns written at these points.

Claims

1. A probe for use in the imaging of a substrate, the probe comprising an electrically insulated probe body and extending therefrom a cantilever from which extends an imaging tip, the probe further comprising an electrically conducting material which extends substantially along the length of the cantilever and which includes a region where it is exposed through the insulator to provide an electrochemical sensor, wherein the width of the electrically conducting material is substantially less than the width of the cantilever itself.

2. A probe according to Claim 1 wherein the width of the electrically conducting material is about 10μm or less.

3. A probe according to Claim 1 or 2 wherein the width of the electrically conducting material is about 5 μm or less.

4. A probe according to any of Claims 1 to 3, wherein the width of the electrically conducting material is in the range of between 1-2μm.

5. A probe according to any of Claims 1 to 4, wherein the electrically conducting material comprises a metal.

6. A probe according to Claim 5, wherein the metal comprises a transition metal.

7. A probe according to Claim 6, wherein the transition metal is selected from the Group VIII transition elements.

8. A probe according to Claim 7, wherein the metal is selected from the group consisting of; Pt, Ag, Au or mixtures thereof.

9. A probe according to Claim 6, wherein the transition metal is selected from the Group IX transition elements.

10. A probe according to Claim 9, wherein the transition metal is Ir.

11. A probe according to any of Claims 1 to 10, wherein insulator comprises a nitride, oxide or carbide of silicon.

12. A probe according to Claim 11, wherein the insulator is selected from the group consisting of; SiO_2, Si_3N_4 or SiC.

13. The use of a probe according to any of Claims 1 to 12 in imaging of a substrate.

14. Use according to Claim 13, wherein the imaging is topographical imaging.

15. Use according to Claim 13, wherein the imaging is electrochemical imaging.

16. Use according to Claim 13, wherein the imaging is topographical and electrochemical imaging.

17. Use according to Claim 16, wherein the topographical and electrochemical imaging are simultaneous.

18. A method of imaging a substrate comprising the steps of;

i) bringing into contact a probe according to any of Claims 1 to 12 with a substrate to be imaged;

ii) collecting imaging data; and, optionally

iii) storing and/or analysing and/or presenting the data.

19. A method according to Claim 18, wherein the imaging is topographical imaging and/or electrochemical imaging of the substrate.

20. A method according to Claim 18 or 19, wherein the topographical and electrochemical imaging is simultaneous.

21. A process for the manufacture of a probe according to any of Claims 1 to 12 comprising electron beam lithography.

22. A microscope comprising a probe according to any of claims 1-12

23. A probe or method as described herein with reference to the examples.

24. A probe according to Claim 1 or a method according to Claim 19 and substantially as described herein.

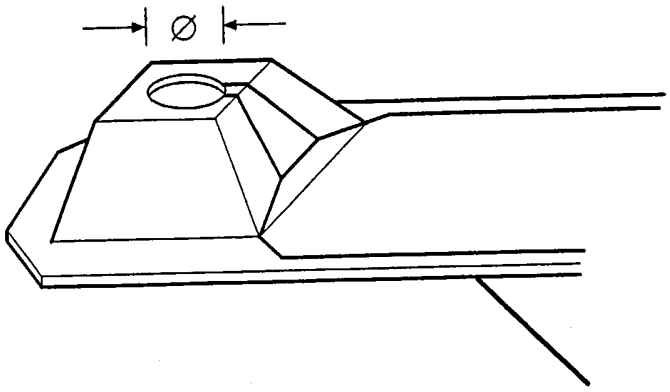


Fig. 1 (a)

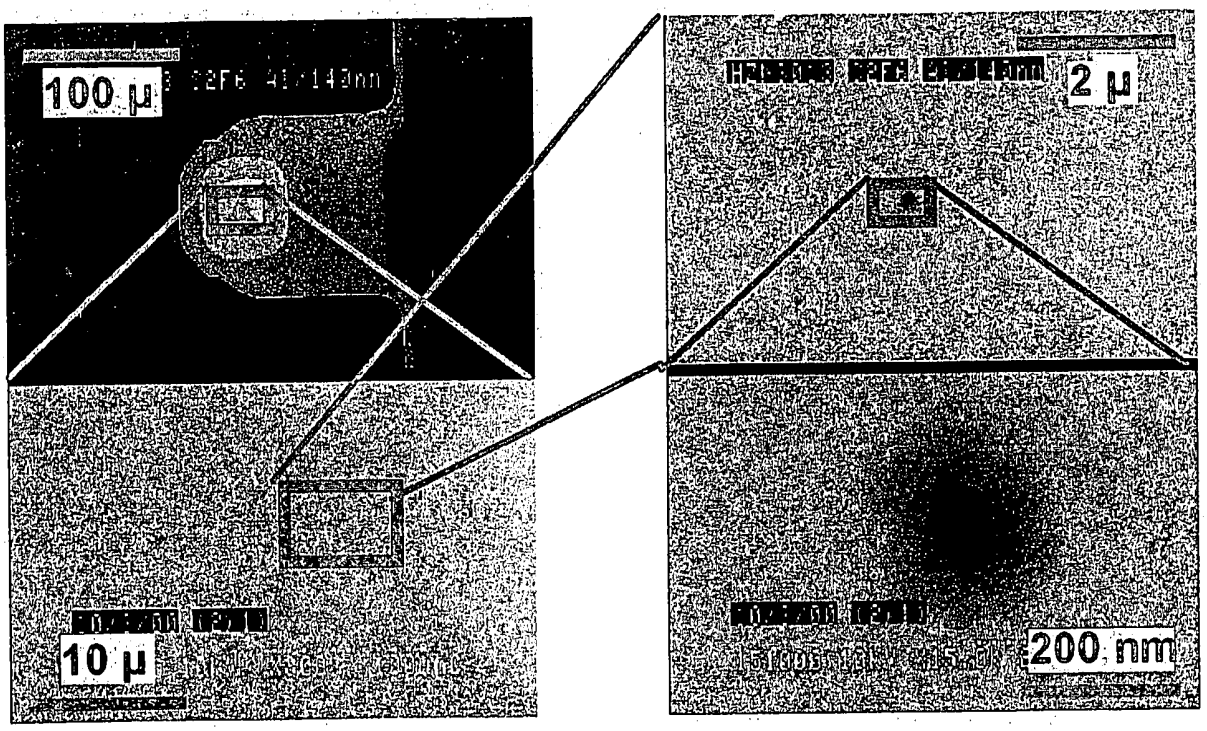


Fig. 1 (b)

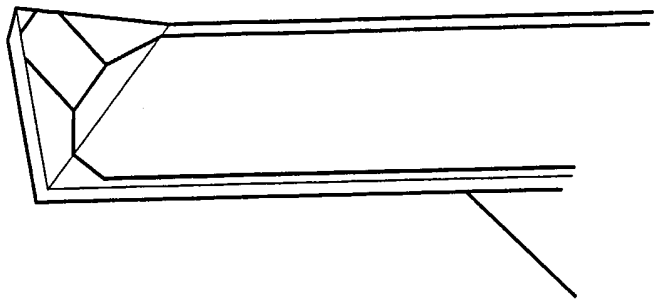


Fig. 2

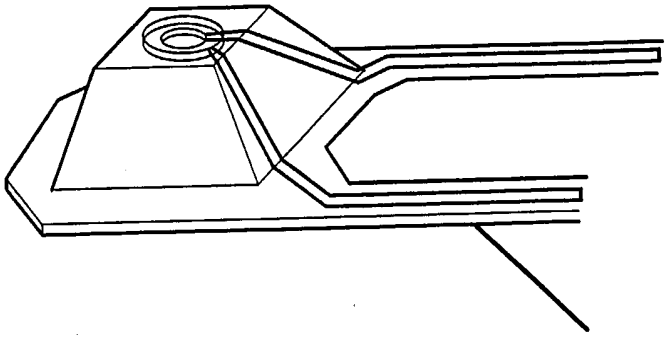


Fig. 3

Figure 4

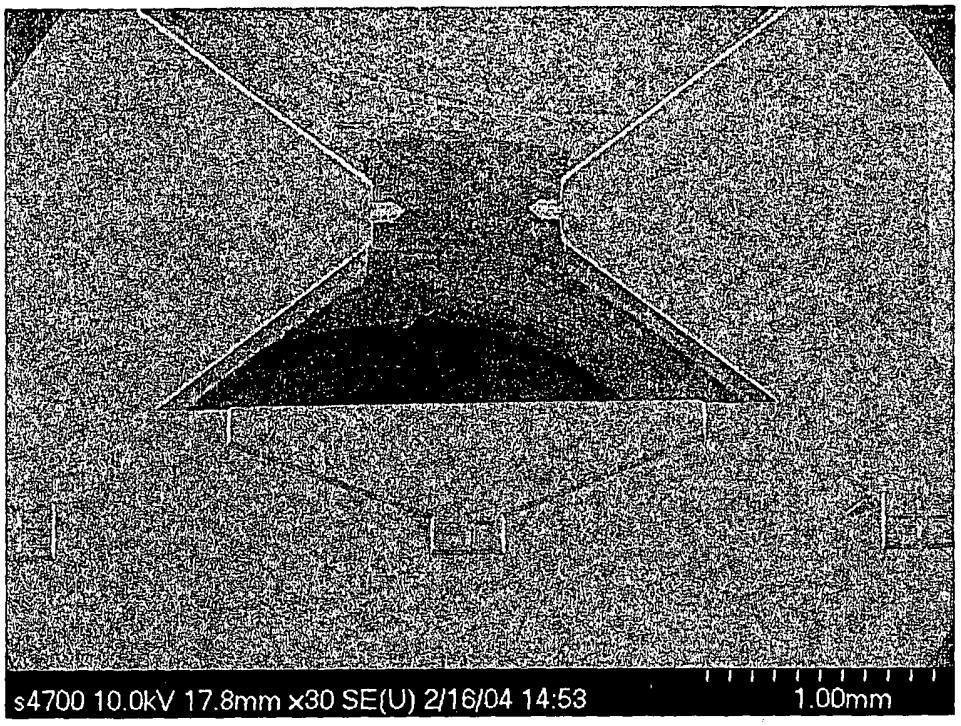


Figure 5

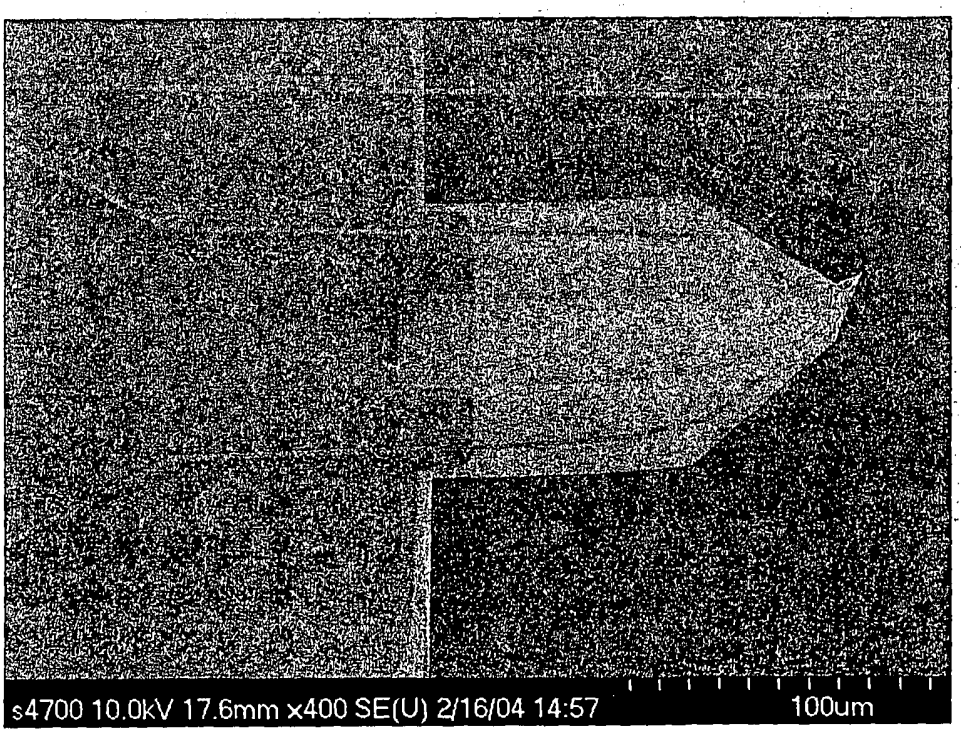


Figure 6

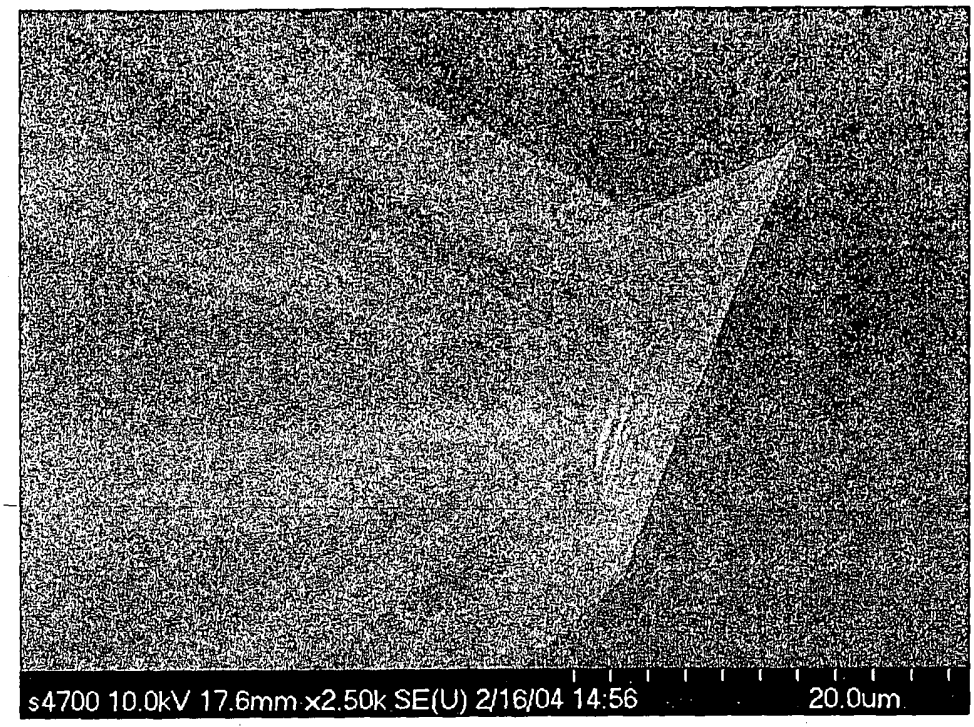


Figure 7

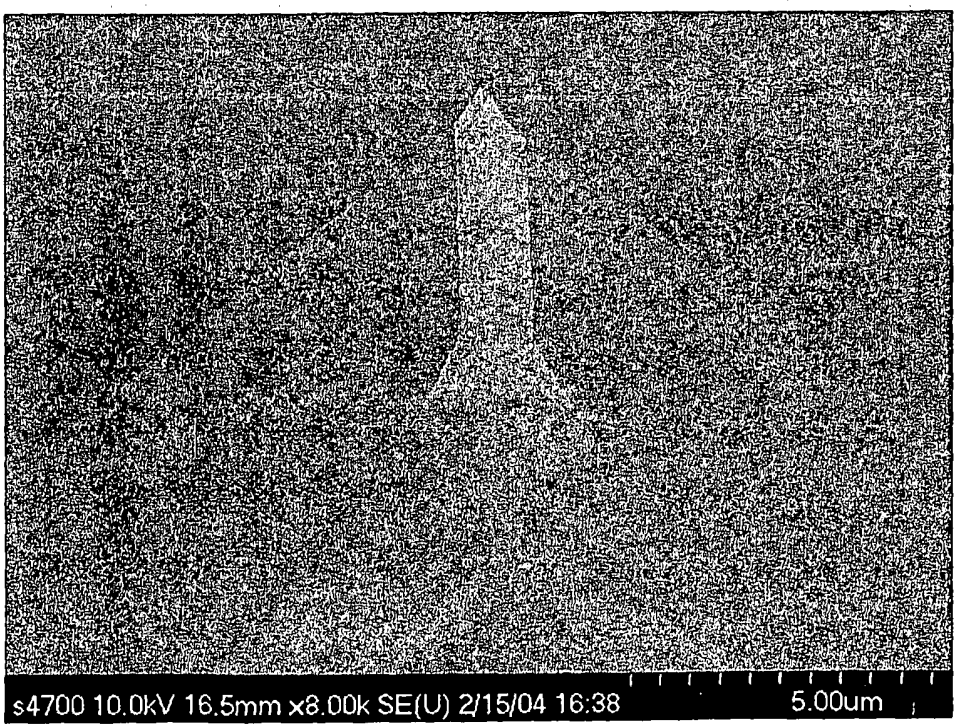


Figure 8

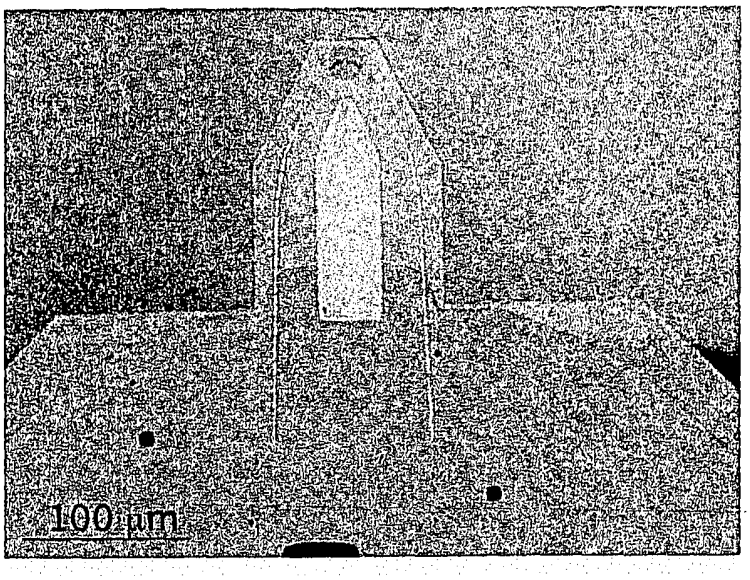
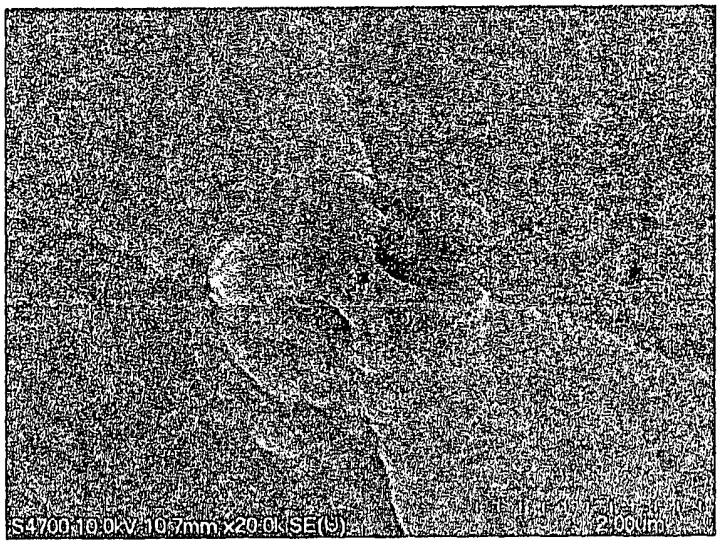


Figure 9



INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT/GB2005/002284

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G12B21/02 G12B21/04 G12B21/08

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)
IPC 7 G12B G01B 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 practical, search terms used)
EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, BIOSIS, EMBASE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/94877 A (INNOVATIONSAGENTUR GESELLSCHAFT M.B.H; KRANZ, CHRISTINE; MIZAIKOFF, BO) 13 December 2001 (2001-12-13) figures 10-19 page 28, line 29 - page 33, line 12	1-22,24
X	WO 01/94926 A (INNOVATIONSAGENTUR GESELLSCHAFT MBH; LUGSTEIN, ALOIS; BERTAGNOLLI, EMM) 13 December 2001 (2001-12-13) figures 1-7 example 1	1-22,24

-/--

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

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 August 2005	05/09/2005

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, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Polesello, P

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB2005/002284

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KRANZ C ET AL: "INTEGRATING AN ULTRAMICROELECTRODE IN AN AFM CANTILEVER: COMBINED TECHNOLOGY FOR ENHANCED INFORMATION" ANALYTICAL CHEMISTRY, AMERICAN CHEMICAL SOCIETY. COLUMBUS, US, vol. 73, no. 11, 1 June 2001 (2001-06-01), pages 2491-2500, XP001081128 ISSN: 0003-2700 cited in the application figures 2-4 paragraph 'RESULTS!	1-22,24
X	MACPHERSON J V ET AL: "IN-SITU IMAGING OF IONIC CRYSTAL DISSOLUTION USING AN INTEGRATED ELECTROCHEMICAL/AFM PROBE" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US, vol. 118, 1996, pages 6445-6452, XP001008882 ISSN: 0002-7863 figure 1 paragraph 'EXPERIMENTAL!	1-20,22, 24
A		21
A	US 5 936 237 A (VAN DER WEIDE ET AL) 10 August 1999 (1999-08-10) figures 1,4-9 column 7, line 10 - column 13, line 19	1-22,24
A	US 6 002 131 A (MANALIS ET AL) 14 December 1999 (1999-12-14) figures 3,4 column 4, line 49 - column 7, line 63	1-22,24

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2005/002284

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 23
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 23

Claim 23 relates to a probe or method as described herein with reference to the examples. According to Rule 6.2(a) of PCT such a claim is not acceptable and has therefore not been searched.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Int nal Application No
PCT/GB2005/002284

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