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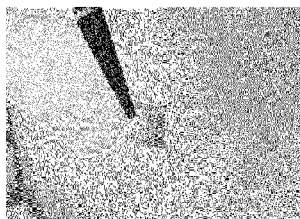


Fig. 1

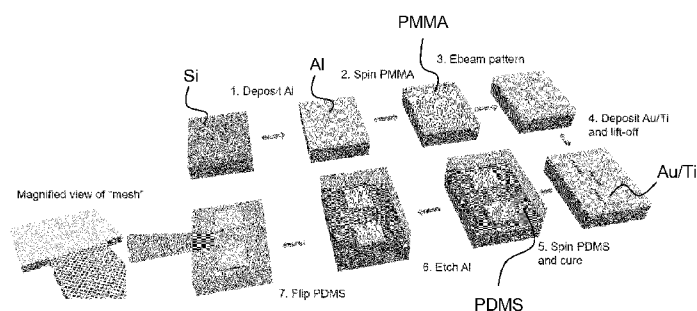


Fig. 6

(57) **Abstract:** A method of forming electrodes on a polymeric body is provided. The method includes: forming a sacrificial layer on a substrate; forming an metal electrode pattern on the exposed surface of the sacrificial layer; attaching a polymeric body to the exposed surface of the metal electrode pattern; and dissolving the sacrificial layer to detach the metal electrode pattern and the polymeric body from the substrate, the metal electrode pattern remaining attached to the polymeric body. The exposed surface of the sacrificial layer has an R_{RMS} roughness which is at least 5% of the thickness of the metal electrode pattern. The metal electrode pattern is formed on the exposed surface of the sacrificial layer such that the metal electrode pattern conforms to the roughness of the exposed surface of the sacrificial layer.

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FORMATION OF ELECTRODES ON A POLYMERIC BODY

Field of the Invention

The present invention relates to a method of forming electrodes on a polymeric body and a polymeric body having a metal electrode pattern attached thereto.

5 Background

It is challenging to fabricate electrodes on soft and stretchable substrates due to the significantly different chemical and physical properties of polymers, such as elastomers, when compared to silicon, glass or foil substrates on which electrodes are more commonly fabricated. These differences generally result in: higher densities of defects, including cracks
10 in the substrate and/or in the electrodes; limited resolutions when using conventional electrode patterning methods; poor adhesion of electrode materials to the substrate; and low surface areas of the electrodes, which can be particularly problematic in the context of bio-sensors and other wearable or implantable bio-electronic devices.

Conventional methods of fabricating electrodes can be grouped into four main categories:

15 lift-off, wet etching, shadow masking and pattern transfer. Lift-off is unsuitable for use on some classes of polymeric substrates (such as elastomeric substrates) with current commercial resists, as differences in coefficient of thermal expansion result in cracks in the protective mask, forming unwanted patterns and shorts in the final device. Wet etching requires the use of toxic agents, such as gold etchants or hydrofluoric acid, which are too
20 readily absorbed by polymers, such as PolyDiMethylSiloxane (PDMS), due to their porous and loose structure. Moreover, dense electrode patterns are problematic to fabricate with this method due to the undercuts formed by the wet etching. Shadow mask-based patterning methods can only provide limited electrode pattern resolutions. Pattern transfer has some promise for forming electrodes on non-planar substrates, as demonstrated by
25 Smythe et al., *A Technique to Transfer Metallic Nanoscale Patterns to Small and Non-Planar Surfaces*, ACS Nano, Vol. 3, No. 1, 2009 pp.59-65, but their method involves stamping which results in the loss of metal features. More recently, Byun et al., *Microcontact Printing Using Flexible Flat PDMS Stamps with Metal Embedment*, Proc. 2012 IEEE Nanotech. Mat. & Dev. Conf., October 16-19, pp.33-33 have developed an alternative pattern transfer
30 technique, but it requires the manual peeling of the PDMS at the end of the process, which can easily cause damage to the elastomer and also places limitations on the thickness of the

same. The technique is thus acceptable for making laboratory prototypes but is not easily scalable for industrial adoption.

Brosteaux et al., *Design and Fabrication of Elastic Interconnections for Stretchable Electronic Circuits*, IEEE Electron Device Letters, Vol. 28, No. 7, July 2007, pp.552-554

5 propose a method for embedding metal interconnections in highly elastic silicone film. A limitation of this method is that the stretchability of the metal interconnections is obtained by a 2-D spring pattern encapsulated in the neutral axis of an elastomeric compound in order to reduce the linear strain applied to the same metallic interconnections. As such, the method is not suitable to develop linearly stretchable interconnects, and neither is it suitable to
10 develop stretchable electrodes that expose a relatively high surface area to the environment, as desirable in applications such as chemical, electro-chemical and bio-sensors. Thus it would be desirable to provide improved techniques for fabricating electrodes on a polymeric body that overcome limitations of known techniques.

Summary

15 Accordingly, in a first aspect, the present invention provides a method of forming electrodes on a polymeric body, the method including:

forming a sacrificial layer on a substrate;

forming an metal electrode pattern on the exposed surface of the sacrificial layer;

attaching a polymeric body to the exposed surface of the metal electrode pattern;

20 and

dissolving the sacrificial layer to detach the metal electrode pattern and the polymeric body from the substrate, the metal electrode pattern remaining attached to the polymeric body;

25 wherein the exposed surface of the sacrificial layer has an R_{RMS} roughness which is at least 5% of the thickness of the metal electrode pattern, and the metal electrode pattern is formed on the exposed surface of the sacrificial layer such that the metal electrode pattern conforms to the roughness of the exposed surface of the sacrificial layer.

Advantageously, by forming the sacrificial layer such that its exposed surface has an R_{RMS} roughness which is at least substantial proportion of, and indeed may be greater than, the
30 thickness of the metal electrode pattern, the metal electrode pattern can be forced to have a substantially equal roughness at its exposed surface which attaches to the polymeric body.

This provides a high surface area on both sides of the metallic electrode layer e.g. for

improved adhesion of the metal electrode pattern to the polymeric body, on one side, and improved sensitivity in sensor applications, on the other side, where the high surface area electrode is used to form the active or working electrode part of a chemical, electrochemical or bio-sensor device. It also helps to make the electrode pattern more tolerant to stretching
5 without loss of conductivity, i.e. the pattern is less susceptible to breakages.

More particularly, the polymeric body can be a stretchable element in order to secure its mechanical compliance with human or animal tissue, such as the outer surface of skin (e.g. for skin-wearable device applications) or inner organs (e.g. heart, brain, muscle, cochlea etc.). Thus desirably the performance of the metal electrode pattern should not substantially
10 change for controlled levels of stretchability of the polymeric body. This can be achieved by controlling the surface roughness of the exposed surface of the sacrificial layer on which the metal electrode pattern is formed according to the proposed method. Similarly, the controlled surface roughness helps to reduce the risk of delamination of the metal electrode pattern due to differential thermal expansion effects.

15 Another advantage of the method is that the roughness of the exposed surface of the sacrificial layer is readily customisable depending on the resolution of the electrode pattern.

A further advantage of the method is that it is compatible with forming a high resolution metal electrode pattern. Indeed, more generally, the method is compatible with conventional lithographic techniques and thus is industrially scalable. Related to this, it is cost effective
20 and reproducible, and can be implemented using a conventional microelectronics manufacturing line. Nonetheless it can overcome limitations of conventional fabrication techniques in regard of electrode fabrication on soft and stretchable substrates, such as polymeric bodies. Also, by attaching the polymeric body to the exposed surface of the metal electrode pattern only after the pattern has been formed, it is possible to avoid having to
25 form (and subsequently remove) a protective layer on the polymeric body.

Surface roughness, otherwise named roughness, is a component of surface texture, which is quantified by the deviations in the direction of the normal vector of a real surface from its ideal form. It is often referred to in terms of average surface roughness, which is the average value of said deviations in the direction of the normal vector of the actual surface
30 from its ideal form. R_{RMS} is a commonly used parameter for characterising average surface roughness. R_{RMS} is the root mean square average of the roughness profile ordinates of a given surface profile, and gives a good general description of height variations in a surface.

Equipment and corresponding techniques that can be adopted to characterize surface roughness in terms of R_{RMS} include mechanical or optical profilometry, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Focused Ion Beam (FIB) microscopy, Transmission Electron Microscopy (TEM), and others.

- 5 The method may have any one or, to the extent that they are compatible, any combination of the following optional features.

10 Preferably the metal electrode pattern is only formed on a surface of the sacrificial layer having the specified R_{RMS} roughness (i.e. at least 5% of the thickness of the metal electrode pattern). That is, preferably no part of the metal electrode pattern is formed elsewhere on the surface of the sacrificial layer which may have a different (and particularly lesser) roughness. In this way, the entirety of the interface between the metal electrode pattern and the polymeric body can benefit from the roughness inherited by the metal electrode pattern from the sacrificial layer.

15 Preferably, the R_{RMS} roughness of the exposed surface of the sacrificial layer is measured by AFM.

The polymeric body can be an elastomeric body.

Preferably the exposed surface of the sacrificial layer has an R_{RMS} roughness which is at least 10% or 50 % of the thickness of the metal electrode pattern.

20 The exposed surface of the sacrificial layer may have an R_{RMS} roughness which is at most 150%, and preferably at most 100%, of the thickness of the metal electrode pattern. Thus the R_{RMS} roughness can be of the same order of size, or even greater than the thickness of the metal electrode pattern.

25 Advantageously, the method of forming electrodes allows dense patterns to be created. The metal electrode pattern may have a thickness of at most 10 μm , and preferably of at most 1 μm , 100 nm or 50 nm. The metal electrode pattern may include elongate electrode tracks having a width of at most 50 μm and preferably of at most 10 μm , 1 μm or 100 nm, and/or having a spacing between adjacent tracks of at most 50 μm and preferably of at most 10 μm , 1 μm or 100 nm. The method can be particularly suitable for forming electrodes having low thicknesses (e.g. less than 1 μm) and/or electrode tracks with narrow widths.

Conveniently, the substrate on which the sacrificial layer is formed (e.g. deposited or developed) may be formed of glass, plastic, silicon, mica or another substrate material serving as temporary carrier, during forming (e.g. deposition and patterning) of the metal electrode pattern.

- 5 Conveniently the sacrificial layer is water insoluble. This helps to make the method compatible with fabrication processes (e.g. electrode patterning processes) that employ aqueous solutions. The sacrificial layer may be formed of a metal, such as titanium, chromium, aluminium, zinc or molybdenum, or a metal oxide such as an oxide of aluminium, zinc or molybdenum. Advantageously, a sacrificial layer formed of such a material can be
10 dissolved in a simple acid, base or salt solution (the chemical species of the solution producing a reaction with the sacrificial layer which allows it to dissolve in water).

- Conveniently the sacrificial layer may be formed by Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), electroplating or solution processing. However, this does not exclude the use of other methods known to the skilled person to form the sacrificial
15 layer. Possible PVD techniques are sputtering, thermal evaporation and e-beam evaporation. The roughness of the sacrificial layer can be enhanced, for example by the initial formation of a rough seed sub-layer at the base of the sacrificial layer, and/or by subsequent high temperature annealing of the sacrificial layer.

- The metal of the metal electrode pattern may be deposited on the exposed surface of the
20 sacrificial layer by PVD (e.g. sputtering, thermal evaporation or e-beam evaporation). The patterning of the metal electrode pattern can be produced by lithography, followed by lift-off or wet etching. The metal electrode pattern may be a single layer, e.g. a single gold layer. Another option is to form it as a multi-layer with e.g. a more conductive over-layer (such as gold), and a more adhesive under-layer (such as titanium or chromium) for attachment to the
25 substrate.

- The method may further include surface treating the exposed surface of the metal electrode pattern before the attachment of the polymeric body to improve the adhesion of the polymeric body to the metal electrode pattern. For example, the exposed surface of the electrode pattern may be treated with organosilane, e.g. an alkoxysilane such as 3-
30 mercaptopropyltrimethoxysilane.

The attachment of the polymeric body to the exposed surface of the metal electrode pattern may be performed by pouring or spin coating a polymer onto the exposed surface of the metal electrode pattern and then curing the polymer to form the polymeric body. Another option is to attach the polymeric body to the exposed surface of the metal electrode pattern by mechanically pressing the polymeric body against the exposed surface of the metal electrode pattern. In this case, the method may further include surface treating the polymeric body, e.g. by oxygen plasma treatment, before pressing to improve the adhesion of the polymeric body to the metal electrode pattern. Yet another option is for the polymeric body to be formed through vapour deposition onto the exposed surface of the metal electrode pattern. Approaches such as pouring, spin coating and vapour deposition allow the polymeric body to be moulded around the metal electrode pattern. Therefore, when the sacrificial layer is dissolved, the revealed surfaces of the metal electrode pattern and the polymeric body can be flush with each other. As a result, the metal electrode pattern can end up being located in a matching recess formed in the polymeric body.

The polymeric body may be formed of PolyDiMethylSiloxane (PDMS) or another compound with suitable mechanical, chemical and physical characteristics, such as e.g. PerFluoroPolyEther (PFPE), PolyLacticAcid (PLA), PolyLacticGlycolicAcid (PLGA), Thermoformed PolyUrethane (TPU), poly(para-xylene) (such as Parylene or Parylene-C), and the like. Poly(para-xylene), in particular, can conveniently be formed by vapour deposition.

The method may further include reactive ion etching (e.g. with CF_4 , Ar, O_2 or Cl_2) the outer surface of the metal electrode pattern which faces away from the polymeric body after the dissolution of the sacrificial layer. This can help to clean any remaining material of the sacrificial layer, and/or to change the surface profile of the outer surface.

In a second aspect, the present invention provides a polymeric (e.g. elastomeric) body having a metal electrode pattern attached thereto, the metal electrode pattern having an outer surface facing away from the polymeric body, which outer surface has an R_{RMS} roughness which is at least 5% of the thickness of the metal electrode pattern.

Thus the polymeric body and its metal electrode pattern can be formed by the method of the first aspect.

Typically, the metal electrode pattern has an inner surface which forms an attachment interface with the polymeric body, which inner surface has an R_{RMS} roughness substantially equal to the R_{RMS} roughness of the outer surface. Indeed, preferably the entirety of this inner surface has an R_{RMS} roughness substantially equal to the R_{RMS} roughness of the outer surface. This helps to prevent delamination of the metal electrode pattern in use.

The metal electrode pattern may be located in a matching recess formed in the polymeric body.

The polymeric body and its metal electrode pattern may have any one or, to the extent that they are compatible, any combination of the following optional features.

The outer surface of the metal electrode pattern may have an R_{RMS} roughness which is at least 10% or 50% of the thickness of the metal electrode pattern.

The outer surface of the metal electrode pattern may have an R_{RMS} roughness which is at most 150%, and preferably at most 100%, of the thickness of the metal electrode pattern.

The metal electrode pattern may have a thickness of at most 10 μm , and preferably of at most 1 μm , 100 nm or 50 nm. The metal electrode pattern may include elongate electrode tracks having a width of at most 50 μm and preferably of at most 10 μm , 1 μm or 100 nm, and/or having a spacing between adjacent tracks of at most 50 μm and preferably of at most 10 μm , 1 μm or 100 nm.

The metal electrode pattern may be a single layer, e.g. a single gold layer. Another option is for the metal electrode pattern to be a multi-layer with e.g. a more conductive inner-layer (such as gold), and a more adhesive outer-layer (such as titanium or chromium) for attachment to the substrate.

The polymeric body may be formed of PolyDiMethylSiloxane (PDMS) or another compound with suitable mechanical, chemical and physical characteristics, such as e.g.

PerFluoroPolyEther (PFPE), PolyLacticAcid (PLA), PolyLacticGlycolicAcid (PLGA), Thermoformed PolyUrethane (TPU), poly(para-xylene) (such as Parylene or Parylene-C), and the like.

Brief Description of the Drawings

Embodiments of the invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a photograph of a square polymeric body on which gold electrode patterns have been formed, the polymeric body being held between the tips of a tweezer;

Figure 2 is a micrograph of adjacent gold electrode tracks from one of the patterns of Figure 1, the tracks having a width of 10 μm ;

Figure 3 shows: (A) an AFM image and (B) an SEM micrograph for an aluminium layer sputtered at a 25°C processing temperature, (C) an AFM image and (D) an SEM micrograph for an aluminium layer sputtered at a 100°C processing temperature, and (E) an AFM image and (F) an SEM micrograph for an aluminium layer sputtered at a 200°C processing temperature;

Figure 4 shows representative surface roughness profiles for the three layers of Figure 3 as measured by AFM; and

Figure 5 shows: (A) an AFM image and (B) an SEM micrograph for a sputtered aluminium layer annealed at 200°C, (C) an AFM image and (D) an SEM micrograph for the sputtered aluminium layer annealed at 300°C, and (E) an AFM image and (F) an SEM micrograph for the sputtered aluminium layer annealed at 600°C;

Figure 6 illustrates steps in the transfer of a high resolution gold pattern onto a PDMS elastomer via an aluminium sacrificial layer;

Figure 7A shows a dark field optical image of a gold mesh patterned on PDMS, Figure 7B shows a scanning electron microscope (SEM) image of the gold mesh, Figure 7C shows a magnified SEM view of part of the mesh, and Figure 7D shows an atomic force microscope (AFM) image of the roughness of the gold film which forms the mesh;

Figure 8A shows schematically a gas sensing setup, and Figure 8B shows I-V characteristics of fabricated nano-resistors on respectively PDMS and silicon in ambient conditions;

Figure 9 shows changes in resistance with time normalized to an initial resistance ($t = 0$) of resistors fabricated on PDMS and silicon toward four different vapours being (A) chloroform (B) toluene, (C) isopropyl alcohol and (D) water vapour; and

Figure 10 shows electrical responses of the PDMS device at different concentrations of being (A) chloroform (B) toluene and (C) water vapour.

Detailed Description and Further Optional Features

Overview

The present invention provides a multi-step method of forming electrodes on a polymeric body. These steps are described in detail below.

Step 1 – Formation of sacrificial layer on substrate

A sacrificial layer is deposited by metal deposition techniques or electroplating on e.g. a glass, plastic or silicon substrate. Using such a substrate helps to make the subsequent sacrificial layer removal operation industrially scalable and repeatable. The thickness and roughness of the sacrificial layer (which can be e.g. aluminum, zinc, molybdenum or an oxide of any one thereof) can be easily controlled by process parameters such as deposition time, deposition rate, RF power, pressure and temperature. The roughness can be further increased by an initial deposition of a rough seed sub-layer at the base of the sacrificial layer, or by subsequent high temperature annealing of the sacrificial layer. Preferably the sacrificial layer is water insoluble in order to be compatible with other fabrication processes that employ aqueous solutions.

Step 2 – Formation of metal electrode pattern on sacrificial layer

Metal can be deposited on the exposed surface of the sacrificial layer by techniques such as sputtering, thermal evaporation or e-beam evaporation. A pattern can be formed in the deposited metal by utilizing known lithographic processes such as photolithography or e-beam lithography followed, for example, by lift-off or wet etching. The metal electrodes formed may include a relatively conductive over-layer (typically gold) and also a relatively adhesive under-layer (typically titanium or chromium). The thickness of the deposited metal is such that the R_{RMS} roughness of the exposed surface of the sacrificial layer is at least 5% of that thickness. Moreover the deposited metal conforms to the roughness of the sacrificial layer. This helps to ensure that an equal or similar degree of roughness is formed in the

deposited metal's opposite (exposed) surface. Typically, this surface has an R_{RMS} roughness which is from 10% to 150% of the thickness of the deposited metal. Thus the method allows precise control of the electrode surface roughness as percentage of its thickness, thereby achieving precise control of mechanical, electrical and electrochemical characteristics of the electrode.

Step 3 (optional) – Surface treatment of metal electrode pattern

After the metal electrode pattern is formed on the sacrificial layer, the pattern's exposed surface can be surface treated to improve its subsequent adhesion to the polymeric body. For example, a gold electrode pattern can be treated with an alkoxysilane, such as 3-mercaptopropyltrimethoxysilane. Other metal electrode patterns can also benefit from surface treatment with an organosilane. In particular, silanes can form a strong bond to PDMS polymeric body.

Step 4 – Attachment to polymeric body

The metal electrode pattern formed on the sacrificial layer is then brought into direct contact with a polymeric body. This can be done in various ways. One option is to form the polymer directly on the exposed surface of the metal electrode pattern. For example, PDMS can be poured or spin coated to the desired thickness on the pattern, and then cured. Another option, however, is to mechanically press a sheet of polymer directly against the pattern's exposed surface. In this case, the polymer can benefit from a surface treatment, such as oxygen plasma treatment, to improve its adhesion to the metal of the pattern of the polymer. Other possible polymers are e.g. PFPE, PLA, PLGA, TPU and poly(para-xylene) (e.g. Parylene or Parylene-C). Conveniently, a poly(para-xylene) body can be formed on the exposed surface of the metal electrode pattern by vapour deposition.

Step 5 – Removal of the sacrificial layer

Next the sacrificial layer is removed by dissolution. Preferably this is achieved by dissolving the layer in a non-toxic etching solvent, such as a simple acid, base or salt solution. Preferably the solution is selected to avoid or reduce damage to the pattern and the polymer.

Step 6 (optional) – Reactive ion etching

A final reactive ion etching cleaning step can be performed to ensure complete removal of the material of the sacrificial layer from the metal electrode pattern. For example, a

transition metal such as titanium or chromium maybe used as the sacrificial layer for a gold electrode pattern. These transition metals dissolve in the etching solution used in the previous step, but reactive ion etching with e.g. CF_4 , Ar, O_2 , or Cl_2 can help to remove any residual transition metal.

- 5 Figure 1 is a photograph of a square polymeric body on which gold electrode patterns have been formed by the above method, the polymeric body being held between the tips of a tweezer. Figure 2 is a micrograph of adjacent gold electrode tracks from one of the patterns of Figure 1, the tracks having a width of 10 μm .

The method provides the following advantages:

- 10
- The metal electrode pattern can have a high resolution, with a thickness which may be less than 50 nm, and with tracks having a width and/or a spacing of at most 100 nm. Even at such high resolutions, unwanted patterns and shorts can be avoided. This is made possible by forming the pattern initially on a rigid substrate, enabling the use of known lithographic processes. The metal electrode pattern can thus have a
- 15
- precisely defined footprint, including for example pad and elongated (stretchable) interconnecting structures in a wide range of geometries and sizes.
 - The method does not require the use of toxic etchants.
 - The method is highly scalable. In particular, the sacrificial layer can be etched away easily with complete pattern transfer after process optimization.
- 20
- The method provides good adherence of the metal electrode pattern to the polymeric body.

The method also enables a high degree of control over the roughness of the interface between the metal electrode pattern and the polymeric body, and over the roughness of the outer surface of the pattern (i.e. the surface which was in contact with the sacrificial layer).

- 25 Having a high level of interfacial and outer surface roughness can be exploited for:

- Improved adhesion of the metal electrode pattern onto the substrate.
 - Improved stretchability of the metal electrode pattern. In particular, the surface roughness allows the pattern to “flatten out” on stretching without the propagation of cracks across the full thickness of the electrodes
- 30
- Production of highly active surface areas for enzyme immobilization, which are useful in electrochemical sensing applications.

To illustrate the degree of control that can be exercised over the roughness of the sacrificial layer and thereby over the surface roughness of the metal electrode pattern, aluminium sacrificial layers 800 nm thick were sputtered onto a substrate at three different processing temperature of 25°C, 100°C and 200°C using the following process conditions:

- 5 RF power: 1100 W
- Target power: 900 W
- Pressure: 2.1×10^{-3} mbar
- Target: Al (99.999%)
- Base pressure: 2.5×10^{-5} mbar
- 10 Deposition time: 15 min

Figure 3 shows: (A) an AFM image and (B) an SEM micrograph for the 25°C processing temperature, (C) an AFM image and (D) an SEM micrograph for the 100°C processing temperature, and (E) an AFM image and (F) an SEM micrograph for the 200°C processing temperature. The R_{RMS} roughness values (measured by AFM at different surface locations

15 for each sample layer, and then averaged) for the three different layers, given as absolute values in nm and as percentages of the thickness of the layers, were:

25°C: 6.5 nm, 8.1%
100°C: 9.2 nm, 11.5%
200°C: 16.5 nm, 20.6%

20 Figure 4 then shows representative surface roughness profiles for the three layers as measured by AFM.

Control of roughness can also be exercised through post-sputtering processing. Thus the aluminium layer formed at a processing temperature of 25°C was annealed for 10 minutes under vacuum conditions at different annealing temperatures of 200°C, 300°C and 600°C.

25 Figure 5 shows: (A) an AFM image and ()B an SEM micrograph for the 200°C annealing temperature, (C) an AFM image and (D) an SEM micrograph for the 300°C annealing temperature, and (E) an AFM image and (F) an SEM micrograph for the 600°C annealing temperature. The R_{RMS} roughness values (measured by AFM at different surface locations for each sample layer, and then averaged) for the three different layers, again given as

30 absolute values in nm and as percentages of the thickness of the layers, were:

200°C: 11.6 nm, 14.5%

300°C: 9.8 nm, 12.3%

600°C: 4.9 nm, 6.1%

A polymeric body having a metal electrode pattern fabricated thereon according to the above method can be a form of soft and/or stretchable electronics that can potentially find numerous applications in e.g. healthcare, fitness and entertainment. For example, it can be used to produce wearable health monitors, and new kinds of implantable sensors and molecular (bio)sensors that are mechanically compliant so that they conform well to the body.

Example

Next a more detailed example of fabrication using the method of the present invention is described. The example is the direct fabrication of a high resolution resistor on PDMS for use as a volatile organic compounds (VOC) sensor.

A thin aluminium sacrificial layer was used in the example, the aluminium being compatible with conventional lithographic techniques. The aluminium layer combines ease of removal with low stresses and ease of template stripping. It can also be applied to create a relatively low roughness surface for high resolution patterning. Hence it enables a conducting device (i.e. metal electrode pattern) in the nanometre dimension range to be transferred onto a range of spin casted polymers such as PDMS. The sensor produced by the method accommodates swelling of PDMS. In particular, the conducting device can have a “mesh” design for extended coverage in the vertical and lateral directions. Figure 6 illustrates steps to fabricate high resolution and conductive gold structures onto the PDMS elastomer.

A rigid sacrificial layer of approximately 150 nm thick aluminium was sputtered onto a blank silicon substrate. The electrode pattern used for gas detection was then defined by electron beam lithography (EBL) and a 4 nm thickness of titanium active layer followed by a 50 nm thickness of gold were deposited via e-beam evaporation, the titanium helping to adhere the gold on the aluminium surface. After lift-off, the sample was immersed in 3-mercaptopropyl trimethoxysilane (MPTMS) solution to create a stable bond between gold and PDMS (as reported in Lee, K. J.; Fosser, K. A.; Nuzzo, R. G. *Adv. Funct. Mater.* 2005, 15 (4), 557–566, and Byun, I.; Coleman, A. W.; Kim, B. J. *Micromech. Microeng* 2013, 23, 85016–10). Next, degassed PDMS was spin-casted on the patterned aluminium and the sample cured at room

temperature. Finally, the sacrificial layer was etched in diluted hydrochloric (HCl) solution to release the gold/titanium embedded PDMS with low induced stress.

Figure 7A shows a dark field optical image and Figure 7B shows a scanning electron microscope (SEM) image of the gold mesh patterned on PDMS. This structure remained highly conductive on the PDMS, suggesting that there was little or no breakage of the metallic layer. In particular, as the elastomer was not subjected to heat treatment, wrinkling or buckling of the thin gold metal film on the PDMS was not observed. Figure 7C shows a magnified SEM view of the device, and confirms that width of the tracks making up the gold mesh was about 400 nm. The gold film was observed to have a granular structure (average grain diameter of 111 nm) consistent with the metal being grown directly on the sputtered aluminium. Physical vapour deposition of aluminium is governed by small nucleation and slow island growth, and also the competitive growth of the metallic atoms on the silicon substrate. The aluminium sputtered onto the flat surface of the silicon had an R_{RMS} roughness of about 9.6 nm, as demonstrated by Figure 7D which shows an atomic force microscope (AFM) image of the roughness of the gold film which inherits the roughness of the sacrificial aluminium.

The electrical response (current, I , versus voltage, V) of the fabricated device was characterised under a controlled environment using the setup shown schematically in Figure 8A.

More particularly, the device was connected onto a printed circuit board (PCB) via silver paste and thin copper leads. The device was then loaded in a chamber, which was sealed with O-rings, while the PCB was connected to Keithley™ Source Measurement Units (SMUs) located outside the measurement chamber. Using this set-up, the I - V characteristics of the mesh structure transferred on to PDMS were compared with those of similar devices fabricated directly on silicon. Similar electrical responses were observed between the devices made on PDMS and their silicon counterparts as shown in Figure 8B where values of electrical resistance, R (V/I), of 146 Ω and 150 Ω were measured on PDMS and on silicon respectively.

Using calibrated mass flow controllers (MFCs), gas sensing measurements of chloroform, toluene, isopropyl alcohol (IPA) and water vapour at various concentration were performed, achieved via dry air dilution. In these measurements, a continuous total air/vapour flowrate of 500 sccm into the system was fixed. Without any air dilution, the entire airflow to the

bubbler was directed, as shown Figure 8A, to displace the saturated vapour of chloroform, toluene, IPA and water with respective concentration of 440000 ppm, 38000 ppm, 63530 ppm and 25260 ppm for 30 seconds. The device was then allowed to recover for 10 minutes before the next pulse.

Figure 9 shows the measured changes in resistance with time normalized to the initial resistance ($t = 0$) of the resistor fabricated on PDMS in comparison with a resistor fabricated on silicon toward (A) chloroform, (B) toluene, (C) IPA and (D) water. Consistent electrical responses were obtained across measurements of the same compound, but different behaviours towards the vapours were observed due to the distinct interactions of these molecules with the PDMS active layer.

Thus when subjected to chloroform vapour, the resistance of the device fabricated on PDMS increased by about 43 Ω , whereas no change was detected on the silicon nano-resistor, as illustrated in Figure 9A. This suggests that the nano-resistor on PDMS was mechanically stressed due to the swelling of the elastomer, as chloroform is a halogenated organic solvent with a high solubility parameter of 9.2 cal^{1/2}cm^{-3/2}. Full recovery of the device was also observed, as the value of R dropped back to the baseline within 3 minutes after dry air was flushed through the system. Likewise, the PDMS swelled in the presence of saturated toluene vapour, as a ΔR of about 37 Ω was recorded as shown in Figure 9B. However, not only was the device unable to make a full recovery within 10 minutes, but the baseline R increased after each toluene pulse, as shown in Figure 9B. This can be explained by the high affinity of toluene towards the elastomer and the higher boiling point (b.p.) of toluene (about 110 °C) compared to chloroform (about 61.5 °C), which renders the removal and evaporation of the toluene molecules more difficult once they diffuse through the PDMS. To facilitate the recovery of the sensor, the device can be heated after toluene exposure to promote the diffusion of the toluene molecules from the PDMS. In the case of propanol (Figure 9C), no changes were observed within the 30 seconds pulse intervals. This could be due either to the insignificant stretching of the resistor or the slower swelling response of the PDMS as propanol is more polar in nature, leading to a stronger repulsion of propanol molecules by the hydrophobic PDMS surface. From Figure 9D it was observed that the value of R of the device decreased slightly with water vapour, a ΔR of about -1.5 Ω being measured. This can be explained by the fact that the nano-resistor embedded in the polymeric network was already subjected to stress due to swelling responses which can result in discontinuities in the film. As water vapour was being adsorbed onto the grains of

gold or any residual titanium (which has a strong gettering effect), the conductivity of the VOC sensor will be improved. At each injection point of water vapour into the chamber, the molecules shorted the mesh on the PDMS resulting in a more conductive pathway between the contacts. In contrast, this was not observed with the more rigid silicon reference device, which instead demonstrated a gradual drift in R of $+2\ \Omega$ over the measurement time. The results therefore suggest that PDMS has a preferential selectivity towards compounds of high hydrophobicity and solubility parameter values close to PDMS.

The nano-resistor fabricated on PDMS was then characterized in chloroform, toluene and water vapour at various concentrations as shown respectively in Figures 10A to 10C. The saturated vapour of the corresponding solvent from the bubbler was diluted with dry air at varying flow rates. Chloroform vapour of 75000 ppm was injected into the system until the value of R reached a steady state. The measurements were repeated with lower concentrations of the same vapour at 5000 ppm intervals. Chloroform down to 10000 ppm was detected with an applied voltage of 1 mV. Over the concentration range tested, the nano-resistor exhibited a linear response toward chloroform with a sensitivity of $2.18 \times 10^{-4}\ \Omega/\text{ppm}$ as shown in Figure 10A.

The VOC sensor also responded to toluene vapour at concentrations as low as 1000 ppm. In addition, concentrations as low as 200 ppm of toluene vapour were detected when the signal to noise ratio of the nano-resistor was improved by increasing the applied voltage by a further 0.5 mV to 1.5 mV. A linear response to toluene vapour was observed at concentrations up to 10000 ppm followed by an exponential increase in ΔR as shown in Figure 10B. Despite an earlier study (Choi, J.; Zhang, H.; Du, H.; Choi, J. H. *ACS Appl. Mater. Interfaces* 2016, 8 (14), 8864–8869) reporting that PDMS swells more in chloroform than toluene liquid, the converse was observed when performing the measurements in these two organic vapours. The more sensitive behavior of the nano-resistor on PDMS towards toluene vapour could be correlated to the closer resemblance of Hildebrand value: $\delta = c^{1/2} = (-U/V)^{1/2}$, where c (cal/cm³) represents the cohesive energy value, U represents the molar internal energy (cal/mol) and V represents the molar volume (cm³/mol). Another contributing mechanism is the non-polarity of toluene with an electronegativity value of 3.86 eV compared to 5.51 eV for chloroform, resulting in strong affinity of toluene vapour which produced a stronger interaction with PDMS in these experiments.

Water vapour affected the device electrical responses above a 8000 ppm threshold value, as shown in Figure 10C. However, no clear trend was observed beyond this threshold.

To ascertain that the VOC sensor can be used for real-time monitoring, the effect of temperature on ΔR was also calibrated. The experiments showed that the value of R of the nano-resistor increased by only $\sim 2 \Omega$ for every increase in 10°C of the surroundings, which is negligible compared to the ΔR values observed for chloroform and toluene. However, further optimization may improve the sensitivity and selectivity of the sensor. This can be achieved by changing any one or more of: the polymer composition, the active layer, the metallic layer, the configuration of the resistor, and the structure of the polymeric layer.

The fabrication method can be modified for applications that require a flat interface or standalone structures below 50 nm, such as waveguides, gratings and stamps with embedded metal for nanoimprinting. To achieve such high resolution features, the surface roughness of the sacrificial layer can be reduced by sputtering the aluminium layer directly on freshly cleaved mica instead of silicon for template stripping. In this way, the resulting R_{RMS} roughness of the sacrificial aluminium layer can be reduced by about 80 fold to as low as 0.121 nm. To confirm the viability of the method for high resolution patterning on PDMS, gold/titanium features of about 25 nm in dimensions were successfully fabricated on the flatter aluminium surface and successfully transferred onto PDMS.

While the invention has been described in conjunction with the exemplary embodiments described above, many equivalent modifications and variations will be apparent to those skilled in the art when given this disclosure. Accordingly, the exemplary embodiments of the invention set forth above are considered to be illustrative and not limiting. Various changes to the described embodiments may be made without departing from the spirit and scope of the invention.

All references referred to above are hereby incorporated by reference.

CLAIMS

1. A method of forming electrodes on a polymeric body, the method including:
forming a sacrificial layer on a substrate;
forming an metal electrode pattern on the exposed surface of the sacrificial layer;
5 attaching a polymeric body to the exposed surface of the metal electrode pattern;
and
dissolving the sacrificial layer to detach the metal electrode pattern and the polymeric
body from the substrate, the metal electrode pattern remaining attached to the polymeric
body;
10 wherein the exposed surface of the sacrificial layer has an R_{RMS} roughness which is
at least 5% of the thickness of the metal electrode pattern, and the metal electrode pattern is
formed on the exposed surface of the sacrificial layer such that the metal electrode pattern
conforms to the roughness of the exposed surface of the sacrificial layer.
2. A method according to claim 1, wherein the polymeric body is an elastomeric body.
- 15 3. A method according to claim 1 or 2, wherein the exposed surface of the sacrificial
layer has an R_{RMS} roughness which is at most 150% of the thickness of the metal electrode
pattern.
4. A method according to any one of the previous claims, wherein the metal electrode
pattern has a thickness of at most 10 μ m.
- 20 5. A method according to any one of the previous claims, wherein the metal electrode
pattern includes elongate electrode tracks having a width of at most 50 μ m.
6. A method according to any one of the previous claims, wherein the sacrificial layer is
water insoluble.
7. A method according to any one of the previous claims, wherein the sacrificial layer is
25 formed of a metal or a metal oxide.
8. A method according to any one of the previous claims, wherein the sacrificial layer is
formed by PVD, CVD, electroplating or solution processing.
9. A method according to any one of the previous claims, wherein the attachment of the
polymeric body to the exposed surface of the metal electrode pattern is performed by

pouring or spin coating polymer onto the exposed surface of the metal electrode pattern and then curing the polymer to form the polymeric body.

10. A method according to any one of claims 1 to 8, wherein the attachment of the polymeric body to the exposed surface of the metal electrode pattern is performed by mechanically pressing the polymeric body against the exposed surface of the metal electrode pattern.

11. A method according to any one of the previous claims, further including reactive ion etching the bottom surface of the metal electrode pattern after the dissolution of the sacrificial layer.

12. A polymeric body having a metal electrode pattern attached thereto, the metal electrode pattern having an outer surface facing away from the polymeric body, which outer surface has an R_{RMS} roughness which is at least 5% of the thickness of the metal electrode pattern.

13. A polymeric body according to claim 12, wherein the outer surface of the metal electrode pattern has an R_{RMS} roughness which is at most 150% of the thickness of the metal electrode pattern.

14. A polymeric body according to claim 12 of 13, wherein the metal electrode pattern has a thickness of at most 10 μm .

15. A polymeric body according to any one of claims 12 to 14, wherein the metal electrode pattern includes elongate electrode tracks having a width of at most 50 μm .

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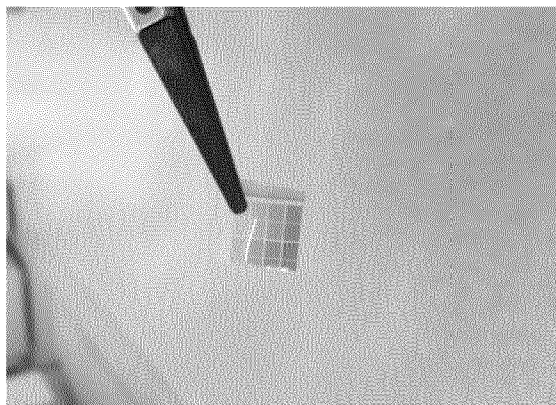


Fig. 1

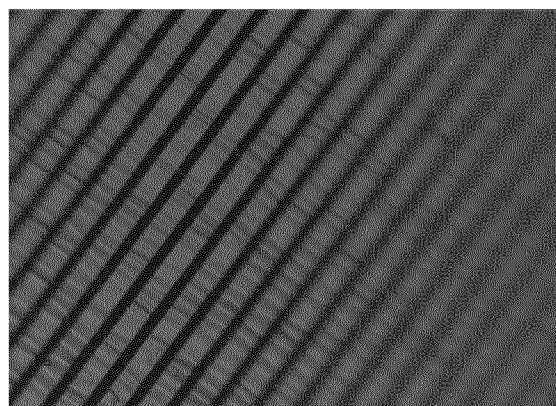


Fig. 2

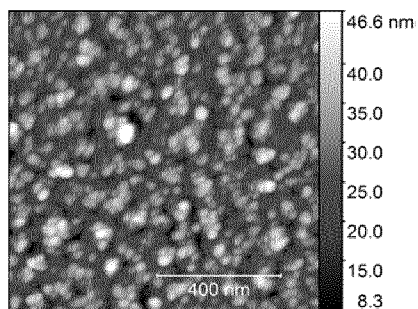


Fig. 3A

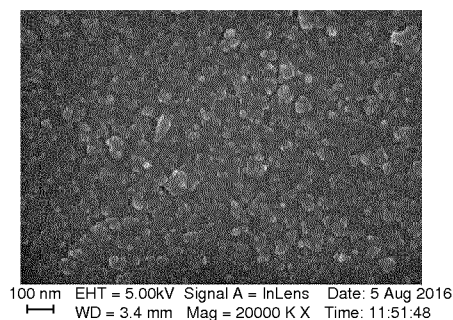


Fig. 3B

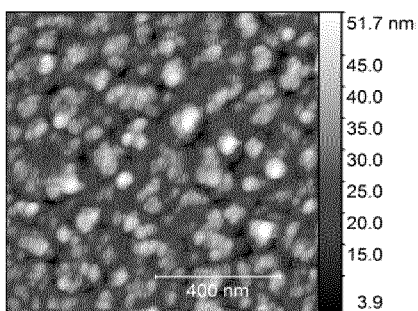


Fig. 3C

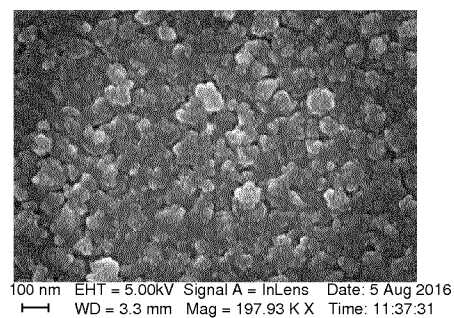


Fig. 3D

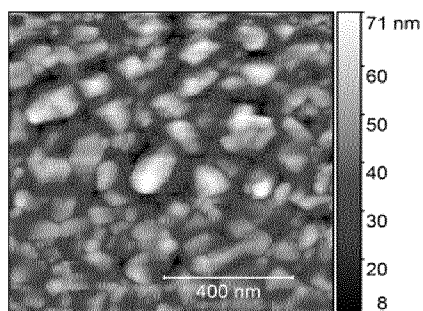


Fig. 3E

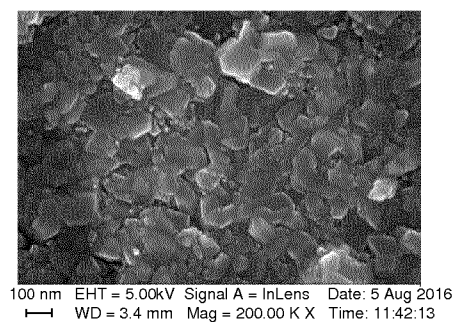


Fig. 3F

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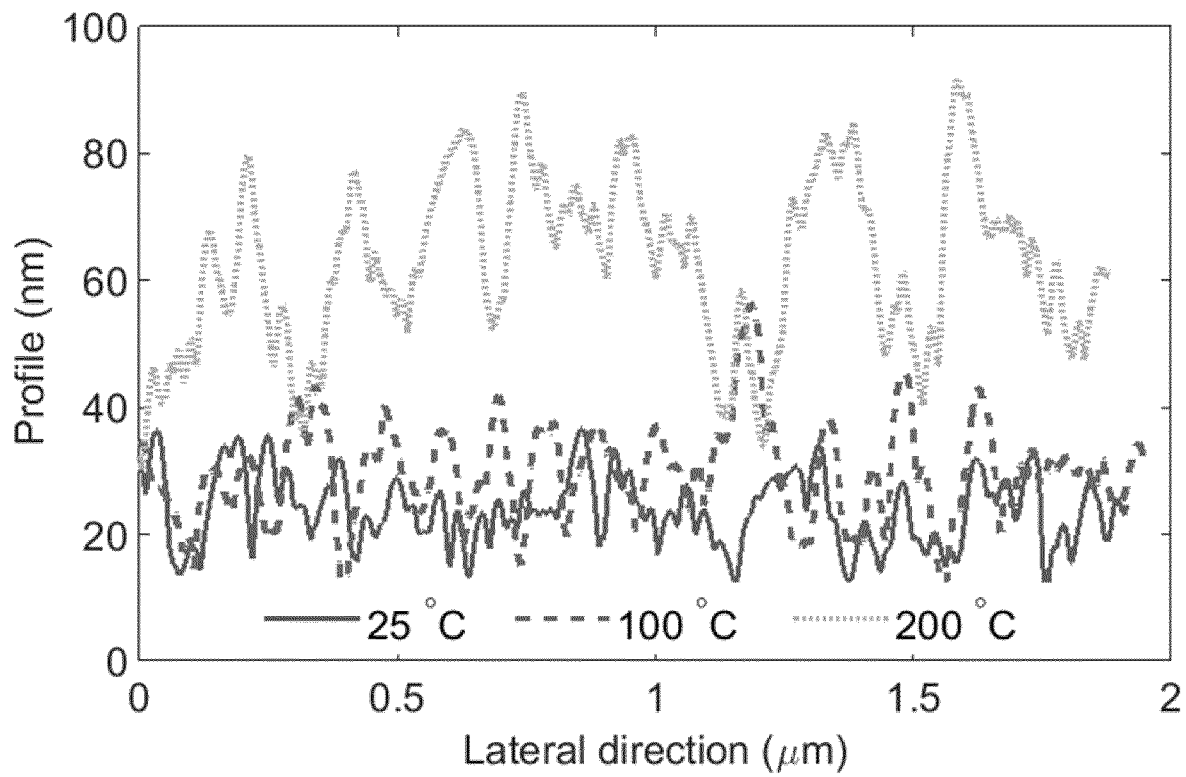


Fig. 4

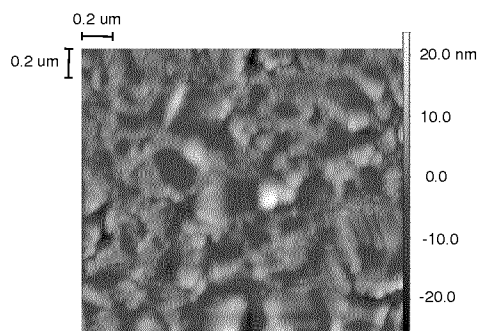


Fig. 5A

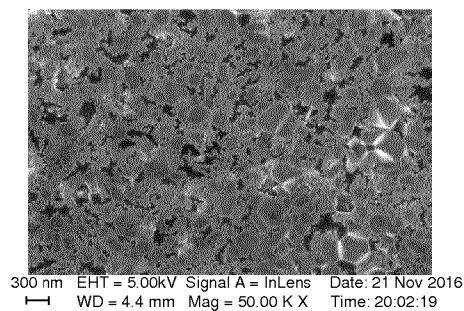


Fig. 5B

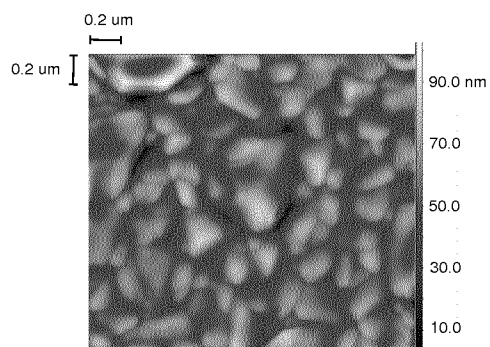


Fig. 5C

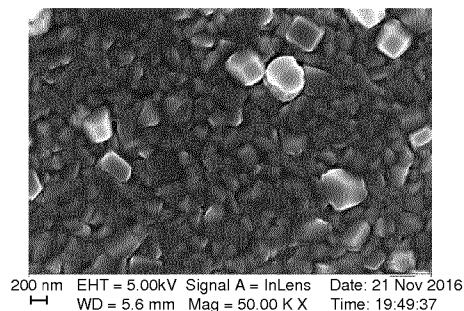


Fig. 5D

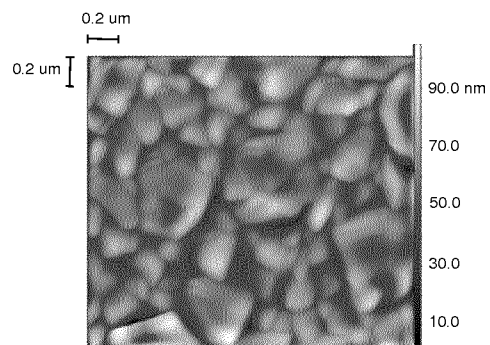


Fig. 5E

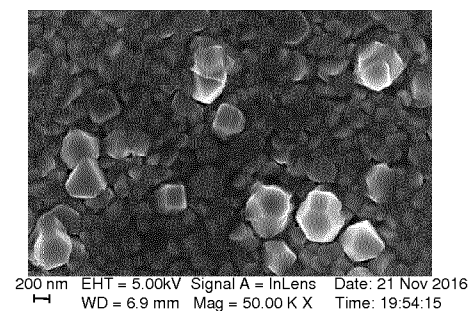


Fig. 5F

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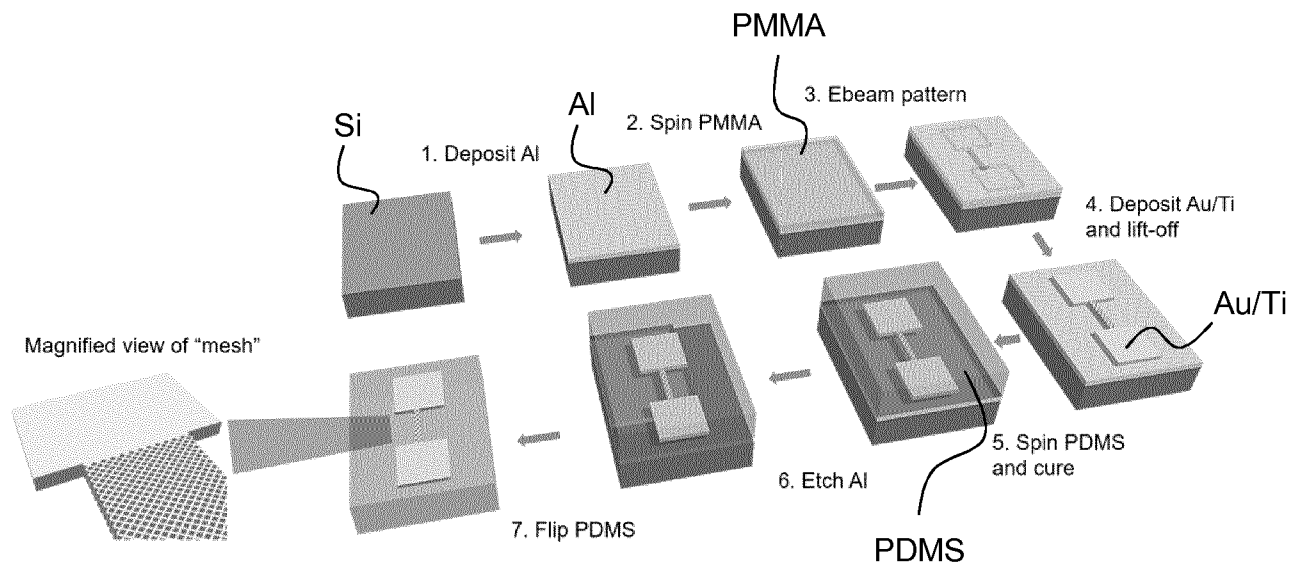


Fig. 6

Fig. 7A

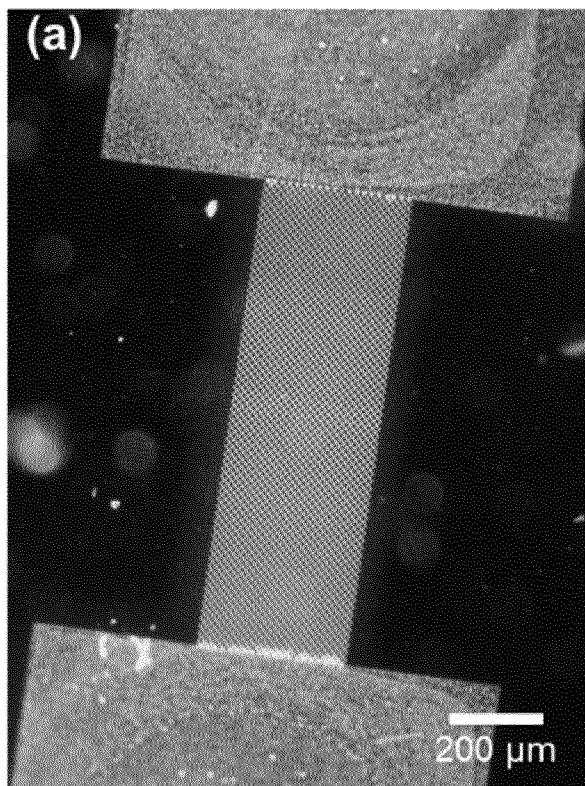


Fig. 7B

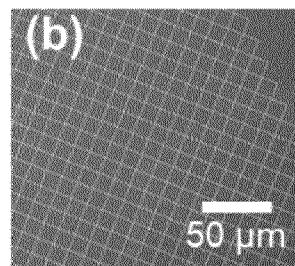


Fig. 7C

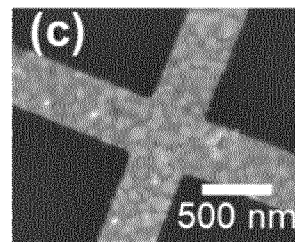
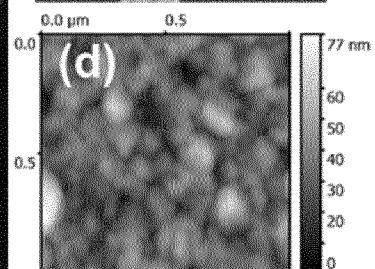


Fig. 7D



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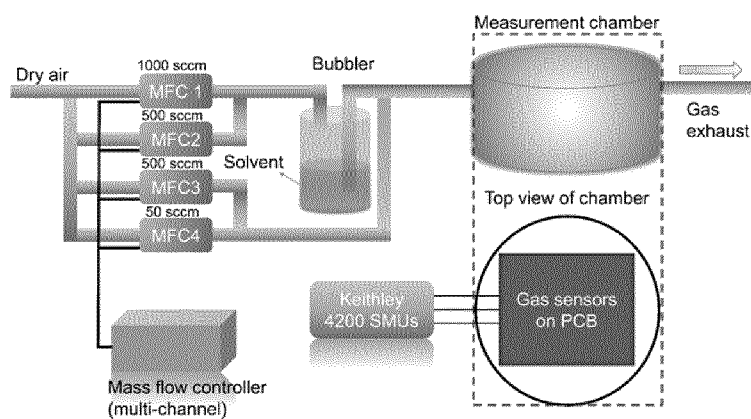


Fig. 8A

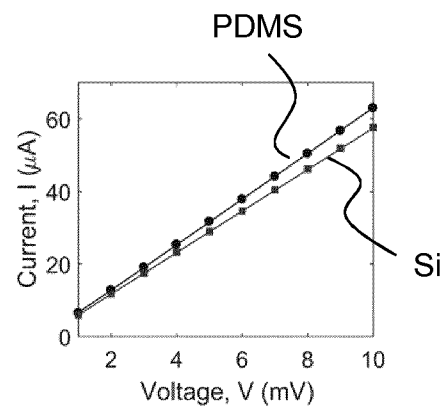


Fig. 8B

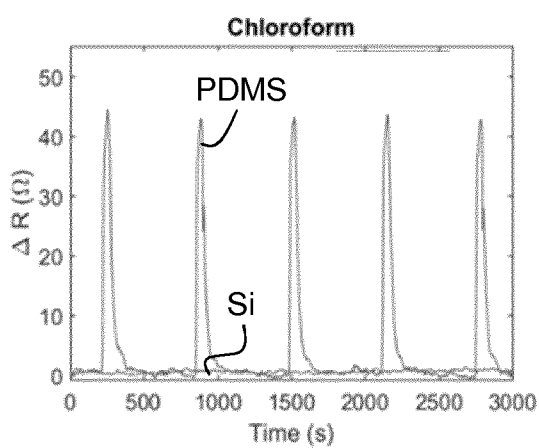


Fig. 9A

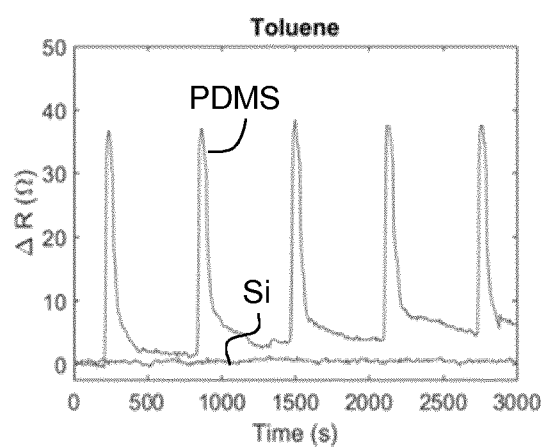


Fig. 9B

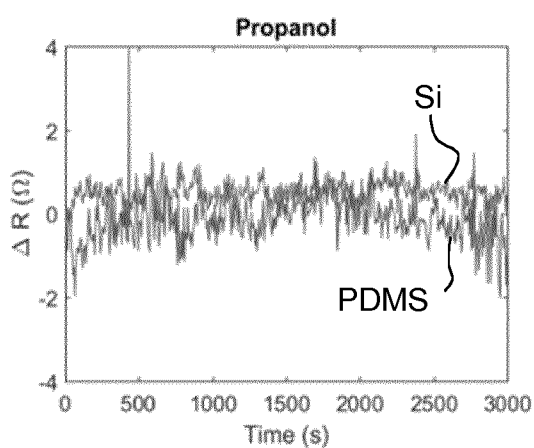


Fig. 9C

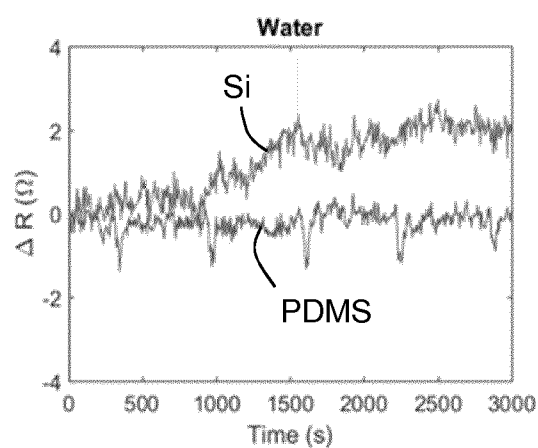


Fig. 9D

Fig. 10A

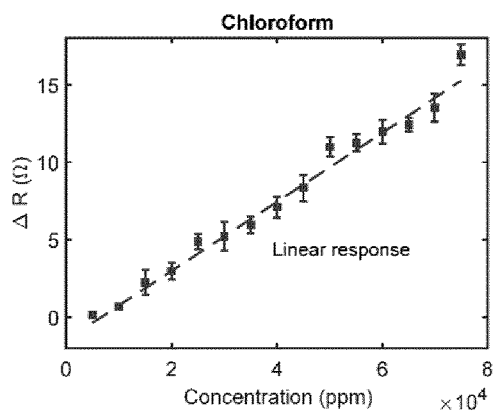


Fig. 10B

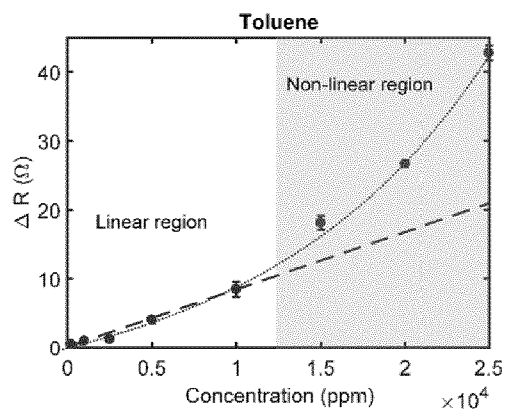
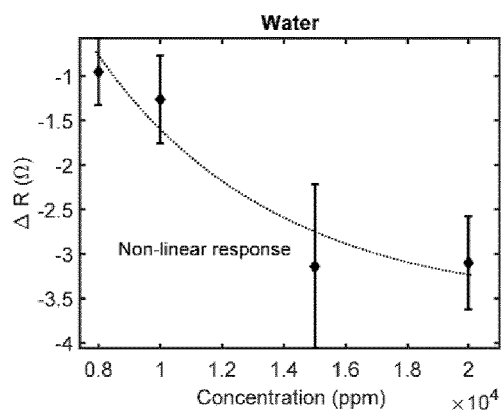


Fig. 10C



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/080330

A. CLASSIFICATION OF SUBJECT MATTER INV. H05K1/11 H05K3/00 H05K3/14 H05K3/38 H01C17/28 H05K3/04 H03H1/00 H03H7/01 H01C1/142 H05K1/02 H05K1/16		
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) H05K H01C H03H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MCLAUGHLIN J A ET AL: "Thin film flexible electrodes based on gold/polytetrafluoroethylene layers", ENGINEERING IN MEDICINE AND BIOLOGY SOCIETY, 1996. BRIDGING DISCIPLINE S FOR BIOMEDICINE., 18TH ANNUAL INTERNATIONAL CONFERENCE OF THE IEEE AMSTERDAM, NETHERLANDS 31 OCT.-3 NOV. 1996, NEW YORK, NY, USA, IEEE, US, vol. 1, 31 October 1996 (1996-10-31), pages 108-109, XP010262609, DOI: 10.1109/IEMBS.1996.656871 ISBN: 978-0-7803-3811-1	12-15
A	the whole document ----- -/--	1-11
☒ Further documents are listed in the continuation of Box C. ☒ See patent family 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 application or patent 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	
27 March 2018	05/04/2018	
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 Frias Rebelo, Artur	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/080330

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	EP 1 988 554 A1 (MITSUI MINING & SMELTING CO [JP]) 5 November 2008 (2008-11-05)	12-15
A	figures 1,2; table 1 -----	1-11
Y	US 2007/098966 A1 (ZHOU ZHANG-LIN [US]) 3 May 2007 (2007-05-03)	12-15
A	paragraph [0016] - paragraph [0026]; claims 19-24; figures 1a-1f -----	1-11
A	BROSTEAUX D ET AL: "Design and Fabrication of Elastic Interconnections for Stretchable Electronic Circuits", IEEE ELECTRON DEVICE LETTERS, IEEE SERVICE CENTER, NEW YORK, NY, US, vol. 28, no. 7, 1 July 2007 (2007-07-01), pages 552-554, XP011186060, ISSN: 0741-3106, DOI: 10.1109/LED.2007.897887 page 552 - page 553; figures 1-3 -----	12-15
A	US 2014/299362 A1 (PARK CHAN WOO [KR] ET AL) 9 October 2014 (2014-10-09) paragraph [0046] - paragraph [0062]; claim 1; figures 3-14 -----	1-15
A	WO 2005/056868 A1 (DOW CORNING [US]; NISHIDA FUMITO [US]; LAUER TIMOTHY [US]; PERNISZ UDO) 23 June 2005 (2005-06-23) paragraph [0009] - paragraph [0025]; claims 1-6 -----	1-15
A	ELIZABETH J. SMYTHE ET AL: "A Technique to Transfer Metallic Nanoscale Patterns to Small and Non-Planar Surfaces", ACS NANO, vol. 3, no. 1, 27 January 2009 (2009-01-27), pages 59-65, XP055330724, US ISSN: 1936-0851, DOI: 10.1021/nn800720r page 59 - page 61; figure 1 ----- -/--	1-15

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MENG YING ET AL: "A flexible dry electrode based on APTES-anchored PDMS substrate for portable ECG acquisition system", MICROSYSTEM TECHNOLOGIES, BERLIN, DE, vol. 22, no. 8, 19 March 2015 (2015-03-19) , pages 2027-2034, XP036004852, ISSN: 0946-7076, DOI: 10.1007/S00542-015-2490-Y [retrieved on 2015-03-19] page 2027 - page 2032; figures 1-4,6-9 -----	1-15

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Information on patent family members

International application No

PCT/EP2017/080330

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			EP 1689906 A1 16-08-2006
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			US 2007082133 A1 12-04-2007
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