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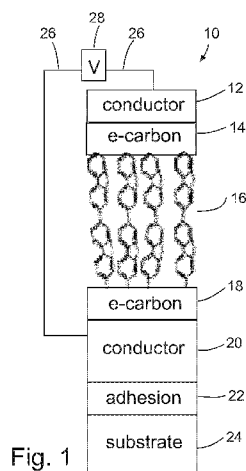


Fig. 1

(57) Abstract: An electronic device may have one or more intermediate layers between contacts each comprising an e-beam deposited carbon (e-Carbon) layer and a metal layer. The e-Carbon layers may be contacting the adjacent intermediate layers. The one or more intermediate layers may comprise a molecular or oxide layer. One or more of the contacts may be sufficiently thin to allow at least partial transparency to light. The device may be deposited on a flexible substrate and be sufficiently thin to allow the substrate to flex without damaging the device.



DEVICES WITH FLAT CONDUCTING SURFACES

TECHNICAL FIELD

[0001] Conducting surfaces in electronic devices.

BACKGROUND

[0002] Electronic devices including molecular electronic devices often involve thin layers (e.g. 1-10 nm) between conducting "contact" surfaces. The contact surface roughness generally must be less than the molecular layer thickness in order to provide a well-defined molecular layer with reasonably constant thickness. Preparation of sufficiently flat carbon or metal surfaces is difficult with vapour deposition and conventional fabrication methods, due to diffusion of deposited metal and island formation.

[0003] The best substrate to date for molecular electronics is pyrolyzed photoresist film (PPF). However, PPF has relatively low conductivity (200 S/cm) and is not readily amenable to current manufacturing processes. Avoiding the high temperature required to make PPF and increasing substrate conductivity would significantly expand the range of applications, provided the ability to lithographically pattern the substrate and the very flat substrate surface of PPF are retained.

[0004] Electron beam (e-beam) deposited carbon ("e-C" or "e-Carbon") has been used on top of pyrolyzed photoresist to make electronic junctions, but this application did not involve a metal substrate. [*ACS Appl. Mater. Interfaces* **2010**, 2, 3693-3701.]

[0005] A metal "underlayer" followed by e-beam carbon has been used to make partially transparent substrates for spectroscopy. The e-Carbon itself did not have sufficient conductivity due to the thin film required for transparency. A platinum/e-C bilayer provided sufficient conductivity to permit electronic characterization of a molecular layer on the e-Carbon. Although this work involved a metal/carbon bilayer, the flat surface was not necessary due to relatively thick molecular and oxide layers [Bonifas, A. P.; McCreery, R. L.; *Chem Mater.* **2008**, 20, 3849-3856.; *Anal. Chem.* **2012**, 84, 2459-2465].

SUMMARY

[0006] There is provided an electronic device and a method of making an electronic device, the device comprising an intermediate layer formed between upper and lower conducting contacts, each conducting contact comprising a carbon layer and a conductor, the carbon layers being formed by e-beam deposition.

[0007] In various embodiments, there may be included any one or more of the following features: the carbon layers of the upper and lower contacts may be in contact with the intermediate layer. The roughness of the surface of the lower contact in contact with the intermediate layer may be less than 0.88 nm rms. The intermediate layer may be a functional layer comprising one or more molecular or oxide layers, and the device may be arranged in a circuit to act as a molecular junction. The intermediate layer may comprise an insulating layer, and the device may be arranged in a circuit to act as a capacitor. The intermediate layer may comprise two redox-active layers which undergo a redox reaction with respect to one another to change respective redox states of the layers in the presence of an applied voltage, at least one of the redox-active layers having conductivity that depends on the redox state of the layer, and the device may be arranged in a circuit to act as a memory element. The redox reaction may be at least partially reversible by the application of an opposite voltage, and the device may be arranged in a circuit to act as a rewritable memory element. The intermediate layer may comprise at least two layers having different molecular energy levels to create a preferred direction of current flow, and the device may be arranged in a circuit to act as a rectifying diode. The intermediate layer may comprise at least one light sensitive layer which energizes charge carriers in response to light, and the device may be arranged in a circuit to act as a photodetector, or as a photovoltaic energy source. The at least two layers having different molecular energy levels may comprise materials selected to cause production of light in response to electrical current flowing between the layers, and device may be arranged in a circuit to act as a light-emitting element. One or more of the conducting contacts and the intermediate layer may be at least partially transparent to light.

BRIEF DESCRIPTION OF THE FIGURES

[0008] Embodiments will now be described with reference to the figures, in which like reference characters denote like elements, by way of example, and in which:

[0009] Fig. 1 is a schematic cross-section of an embodiment of a device comprising electron beam deposited carbon (e-Carbon);

[0010] Fig. 2 is a schematic cross-section of an embodiment of a capacitor;

[0011] Fig. 3 is a schematic cross-section of an embodiment of a rectifier;

[0012] Fig. 4 is a schematic cross-section of an embodiment of a photodetector;

[0013] Fig. 5 is a schematic cross-section of an embodiment of a light emitting junction;

[0014] Fig. 6 is a schematic cross-section of an embodiment of a device comprising three molecular or oxide layers;

[0015] Fig. 7 is a schematic cross-section of an embodiment of a memory device;

[0016] Fig. 8 is a schematic diagram of an e-beam carbon deposition apparatus (prior art);

[0017] Figs. 9A-9F are graphs showing line scans using atomic force microscopy (AFM) on a series of surfaces made with e-beam deposition on a Silicon surface with a 280 nm thick SiO_x layer, in respect of: an initial Si/SiO_x surface, shown in Fig. 9A, a similar surface coated with ~1 μm thick pyrolyzed photoresist film (PPF), shown in Fig. 9B, a Si/SiO_x coated with a 15 nm thick Au layer (by mass), shown in Fig. 9C; a 15 nm Au layer on 3 nm of Chromium, shown in Fig. 9D ; 15 nm of Au on e-Carbon on Si/SiO_x, shown in Fig. 9E; and a Si/SiO_x/Au surface initially similar to that of Fig. 9C after deposition of 10 nm of e-Carbon, shown in Fig. 9F;

[0018] Figs. 10A-10F are graphs showing line scans of the same surfaces shown in Figs. 9A-9F respectively, but at an expanded X-axis scale

[0019] Figs. 11A-11C are graphs showing AFM line profiles of surfaces made with e-C on top of Au (Fig. 11B), and both under and on top of Au (Fig. 11A), and of Au deposited on SiO_x without e-C (Fig. 11C).

DETAILED DESCRIPTION

[0020] Immaterial modifications may be made to the embodiments described here without departing from what is covered by the claims.

[0021] Fig. 1 is a schematic cross-section of an embodiment of a device comprising e-beam deposited carbon (e-carbon). As shown in Fig. 1, the device 10 comprises an intermediate layer 16 formed between conducting contacts, each conducting contact comprising a carbon layer and a conductor, the carbon layer being formed by electron beam (e-beam) deposition and being in contact with the intermediate layer. In the embodiment shown, an upper conductor layer 12 lies on an upper e-carbon layer 14, which lies on a molecular layer or oxide layer 16 (shown as a molecular layer in Fig. 1), which lies on a lower e-Carbon layer 18 on lower conductor 20. Lower conductor 20 may lie on an adhesion layer 22 which lies on substrate 24. The lower conductor may also lie directly on the base. In this embodiment, electrical leads 26 connect a voltage-inducing circuit component 28 to the upper conductor layer and lower conductor layer to form a circuit, the layers shown comprising a molecular junction in the circuit in this embodiment.

[0022] The upper conductor layer 12 and lower conductor layer 20 can be any conductor, though with resistivity $< 0.002 \Omega\text{-cm}$ for the bottom layer 12, including Au, Ag, Cu, Pt, Pd, Al, Ni, also Titanium nitride, Tungsten/Titanium alloy, Tantalum nitride, conducting polymers such as polypyrrole, poly(ethylenedioxy thiophene), polythiophene. The device may be formed on a substrate 24, possibly flexible, made of any of various materials including Si/SiO_x, plastics such as polyethylene, polyvinylchloride, polystyrene and related plastics, glass, silicon, quartz, and H-terminated silicon. It is used as a base on which the other structures are built.

[0023] E-beam deposited carbon (e-Carbon) as currently deposited is amorphous, consisting of a random mixture of sp^2 and sp^3 hybridized carbon atoms.

[0024] There may optionally be an adhesion layer 22, e.g. Cr, e-Carbon, Al, Ti, Co, Ta between substrate 24 and the other layers described. The optional layer provides adhesion to the substrate, which may not be needed depending on the materials.

[0025] There may also be an adhesion layer (not shown in the figures) between the lower conductor 20 (e.g. metal) and the lower e-Carbon layer 18. This adhesion layer may

comprise for example Titanium carbide, titanium nitride, etc, applied between the e-beam deposition of lower conductor 20 and e-Carbon, without breaking vacuum. Such a layer improves adhesion of the e-Carbon to the underlying metal, with minimal effect on roughness or electronic properties. An example of a full “stack” made this way is: SiO_x/Cr/Au/TiC/e-C/molecule/eC/Au.

[0026] In an embodiment, suitable for example for use as a molecular junction, and shown in Fig. 1, the intermediate layer may be a functional layer comprising a molecular or oxide layer. The structure could apply to any molecule or oxide layer. In particular the molecular or oxide layer may comprise, for example:

- a. aromatic molecules deposited by reduction of diazonium reagents,
e.g. azobenzene, biphenyl, anthraquinone, thiophene oligomers
- b. organic molecules deposited using physical vapor deposition, e.g. anthraquinone (AQ), anthracene, pentacene
- c. organic molecules deposited by radical mediated reactions, such as atom transfer radical polymerization (ATRP)
- d. Oxides of Si, Al, Ti, Ta, W, Mo, Ha made by oxidizing metal films
- e. Oxides of Si, Al, Ti, Ta, W, Mo, Ha deposited with atomic layer deposition
- f. Oxides of Si, Al, Ti, Ta, W, Mo, Ha made by physical vapor deposition
- g. the molecular layer may comprise two or more successive layers with different chemical structures
- h. The intermediate layer may also comprise successive layers of molecules and oxides, for example anthraquinone and aluminum oxide.

[0027] The device may have more than a single molecular layer of homogeneous composition. There may be intermediate layers with two or more successive layers having different composition, such as two molecular layers each 10 nm thick, or a molecular layer followed by an oxide layer, even a multilayer with various combinations.

[0028] An example is a photodetector, where a bilayer of different molecules would introduce an asymmetry of energy levels causing charge carriers to move in a preferred direction within the bilayer to create a net current when energized by light. Also, a light emitter may have two very thin (<50 nm) molecular layers. These cases would all share the

conductor/e-C/functional layer/e-C/conductor structure, but would allow multiple functional layers.

[0029] A molecular junction as described above can be used in, for example, a clipped amplifier as disclosed in WO/2015/021552 or in other applications of molecular junctions.

[0030] The device has further applications other than molecular junctions, for example:

- a. capacitors
- b. photodetectors
- c. light emitting junctions
- d. memory devices
- e. rectifying diodes

[0031] For the purposes of this document including the claims, “diode” is a generic term for a 2-terminal device, and “rectifying diode” means a diode that has a tendency to conduct current in only one direction. For the purposes of this document including the claims, rectifying diodes need not act only as rectifiers, that is they can be used for more purposes than converting non-DC current to DC current.

[0032] Embodiments suitable for the additional applications listed above are shown in Figs. 2-7.

[0033] The term light as used herein means electromagnetic radiation, particularly including ultraviolet, visible and near infrared light. The device is expected to have particular utility in the range of wavelengths 200 nm to 2000 nm.

[0034] As shown in Fig. 2, an insulator can be used as the intermediate layer 16 in a device as disclosed here to produce a capacitor. Any insulator could be used. Contacts 30 connect to the upper conductor layer 12 and lower conductor layer 20 to charge and discharge the capacitor.

[0035] A metal/e-Carbon lower contact may be attractive for metal-insulator-metal (“MIM”) devices with a very thin insulator layer. The flatness and covalent properties of e-C permit thinner insulator films than conventional contacts. See, for example, US 8969169. MIM devices are widely used in DRAM, and thinner devices permit higher capacitance and

stored charge density, thus increasing data density. E-Carbon is likely to outperform amorphous metals since eC is covalent, very flat, difficult to oxidize, and not subject to electromigration. A chapter by Conley and Alimardani states “It is shown here that bottom electrode roughness can have a dominant impact on the electrical characteristics of MIM diodes, overwhelming the trends expected based on metal electrode work function differences. It is also shown that as electrode roughness decreases, the percentage yield of well-functioning devices trends higher.”

[0036] As shown in Fig. 3, the intermediate layer may comprise at least two layers having different molecular energy levels to create a preferred direction of current flow. The different energy levels allow one of the layers to act as an electron donor with respect to the other. This allows the device to act as a rectifying diode (i.e., a device that allows current to travel in one direction through the device and blocks current from traveling the opposite direction). A device that converts AC to DC is also known as a rectifier; a conventional silicon or germanium diode can be used for this purpose. The embodiment shown in Fig. 3 can be used as a rectifying diode generally and also specifically as a rectifier. In the embodiment shown electron donor layer 16A is an upper intermediate layer and electron acceptor layer 16B is a lower intermediate layer.

[0037] A material that responds electrically to light can be used as the intermediate layer to produce a photodetector or a light-emitting device (shown in Figs. 4 and 5 respectively). As shown in Fig. 4, the intermediate layer may comprise a light absorbing layer 16D which generates charges when exposed to light and an electron acceptor layer 16C which accepts electrons energized by light 32 absorbed by the light absorbing layer to produce a current. These layers may be molecular layers. Oxide and molecular layers shown in Figs. 1-7 are generic, and may comprise either oxide or molecular layers or both, including multiple layers, , e.g. successive layers consisting of two or more different molecular structures. An example of a light absorber is polythiophene; an example of an electron acceptor is C60. As in Fig. 3 the layers in Fig. 4 have different energy levels creating a preferred direction for the current. An alternative embodiment could have an electron donor layer to fill holes energized in a light absorbing layer. One or both conductor/e-Carbon contacts may be partially transparent, and light may enter from more

than one direction. Ammeter 34 detects the current generated by the device, and thus the light entering the device to generate the current. The device of Fig. 4 may also be used as a photovoltaic energy source, with ammeter 34 replaced by a load.

[0038] As shown in Fig. 5, the intermediate layer may comprise a hole transporter layer 16E and an electron transporter layer 16F, an externally supplied current passing through the layers causing production of light at a light producing zone at or near an interface between the layers. Depending on the embodiment, the light emitting zone may include part of one or both layers or the whole of one or both layers. As in Fig. 3 the layers have different energy levels creating a preferred direction for the current. One or both conductor/e-Carbon contacts may be partially transparent, and light may exit the device in more than one direction. The light emission from the device, and the efficiency and frequency of the light emission may depend on the materials used in the hole transporter and electron transporter layers.

[0039] As shown in Fig. 6, a device may have more than two layers, and the arrangement, number and types of layers may be chosen depending on the desired properties of the device. In this embodiment there is an upper molecular layer 16G, middle oxide layer 16H and lower molecular layer 16J, but as in other figures the oxide and molecular layers shown are generic, and may occur in various orders to realize different electronic properties.

[0040] As shown in Fig. 7, two redox-active layers 16K and 16L can be used as the intermediate layer. A voltage applied to the contacts produces a voltage between the redox-active layers triggering a redox reaction. If at least one of the layers has conductance depending on redox state, the overall resistance between the contacts will depend on the redox state allowing the redox state to be detected. This allows the device to be used as a memory element. If the redox reaction is at least partially reversible, for example by the application of an opposite voltage, the memory element can be erased and rewritten, allowing it to act as a rewritable memory element.

[0041] The embodiments of Figs. 3-7 incorporate bilayers or trilayers (or may include additional layers), and asymmetry is derived from the order of molecular (or oxide) layers. In all cases the devices have the disclosed conductor/e-Carbon contacts, and e-Carbon may be deposited on top of or below molecular or conducting layers.

[0042] E-Carbon (e-C) means carbon deposited by an electron beam (e-beam), as shown in Fig. 8. As shown in Fig. 8, a DC power source 50 energizes a negative terminal 52 providing an electron beam and a positive terminal 54 connecting to, for example, a piece of polycrystalline graphite 55. Any form of elemental carbon could be used, including graphite, fullerenes, glassy carbon or diamond. An electron beam 56 is accelerated by the voltage difference between the terminals, for example 7 kV. In the apparatus shown in Fig. 8 the electron beam 56 follows a curved path due to the application of a magnetic field. The impact of the electron beam on the polycrystalline graphite causes carbon atoms or clusters of carbon atoms 58 to be ejected from the polycrystalline graphite. They may be deposited on a surface at a rate of, for example, 1 Å/sec. In the apparatus shown a substrate 60 is provided with a molecular layer 62 already applied to the substrate. A shadow mask or conventional photolithographic mask 64 may be used to control where the e-Carbon layer forms. The apparatus shown operates in a vacuum, for example at a pressure of 2×10^{-6} torr. Further disclosure of e-beam deposition can be found in McDermott, et al.; Anal. Chem. 2004, 76, 2544 and Mattson, J. S.; Smith, C. A. Anal. Chem. 1975, 47 1122-1125 (OTE), which are incorporated by reference herein.

[0043] E-beam deposition is a known process. Vapor deposited metals diffuse to form rough "islands" when deposited by most methods, including e-beam. However, carbon does not diffuse due to rapid formation of C-C bonds, which are hard to break. It is known that e-C surfaces, not associated with a second conducting layer, can be relatively smooth, but it has now been found that e-beam carbon either on top of a rough metal surface or underneath a metal surface makes it smoother, with the improvement of smoothness due to depositing e-Carbon on top of an already deposited rough metal surface being a particularly unexpected result.

[0044] The layers of the device not formed as e-carbon may be formed by any of various methods, including vapour or electrochemical deposition.

[0045] At any point in fabrication of the multilayer structure, a protective coating may be applied by e-beam evaporation, including inorganic salts such as NaCl, KCl, SiO₂, Al₂O₃, etc. These coatings could be applied at any point in formation of the "stack", in the same vacuum used to deposit the layers, so that the sample may be removed and further

processed without exposure to air. E-beam deposition of a protective layer without breaking vacuum may have significant consequences for air-sensitive materials.

[0046] In one embodiment, there is disclosed the combination of e-beam carbon with a conductive metal layer, with the bilayer having flatness below 0.88 nm rms and higher conductivity than e-carbon alone. The carbon is usually the top layer of the resulting assembly, such as Si/SiOx/Au/e-C.

[0047] It was unexpected that e-C on Au has low roughness (< 0.88 nm), and that this fact enabled successful molecular junction fabrication. The structure provides a flat, conducting, transparent substrate, for use with any molecular or oxide layer layer. e-C provides an interface between a metal and a molecular (or oxide) layer, which improves flatness and reduces electromigration. e-C also improves adhesion between metal and SiOx (or plastic) surfaces.

[0048] Devices of several layer arrangements were tested with the following results:

Failures: (yield was $< 15\%$, meaning that $> 85\%$ were short circuits):

- i) SiOx/Au/AQ/e-C/Au
- ii) SiOx/Cr/Au/AQ/e-C/Au
- iii) SiOx/e-C/Au/AQ/e-C/Au

Successes ($< 10\%$ short circuits, $> 90\%$ functional):

- iv) SiOx/Au/e-C/AQ/e-C/Au
- v) SiOx/Cr/Au/e-C/AQ/e-C/Au
- vi) SiOx/e-C/Au/e-C/AQ/e-C/Au

[0049] Some comparative examples for the roughness of various surfaces obtained in tests are shown in the following table:

Films on SiOx	RMS roughness (Rq)
SiOx/Au	1.19 nm
SiOx/Cr/Au	0.831 nm
SiOx/e-C/Au	0.658 nm
SiOx/Au/e-C	0.431 nm
SiOx/PPF	0.425 nm

[0050] Electron beam deposited carbon (e-C) combined with e-beam deposition of a metal in the same chamber produces thin bi- or tri-layer films with high conductivity and low roughness. For example, e-C may be between the SiO_x substrate and a metal layer, or e-C can be on top of a metal layer. Figs. 9A-9F are graphs showing line scans using atomic force microscopy (AFM) on a series of surfaces made with e-beam deposition on a Silicon surface with a 280 nm thick SiO_x layer. E-beam Deposition rates were 0.03 nm/sec for Au and Cr, and 0.02 nm/sec for e-C. Horizontal scale is in μm , vertical is nm. These figures provide a visual indication of roughness of the indicated films, all deposited on SiO_x using e-beam deposition. Note that the Y axis is greatly magnified relative to the X axis. Since molecular layers deposited on these surfaces can be as little as 1 nm thick, roughness greater than that dimension makes it very difficult to form a junction by deposition of another conductor on top of the molecular layer. As shown in Fig. 9A, a 280 nm thick SiO_x layer surface grown on a silicon wafer has a very flat surface (0.15 nm rms roughness), and $\sim 1 \mu\text{m}$ thick pyrolyzed photoresist film (PPF) formed on SiO_x, which is acceptable for making molecular junctions, is slightly rougher (Fig. 9B, $< 0.5 \text{ nm rms}$). Deposition of 15 nm of Au (by mass) on SiO_x results in unacceptable roughness (Fig. 9C, 1.2 nm rms) due to island formation by diffusion of Au after deposition. A standard existing method for making flat Au surfaces is the use of a thin "adhesion layer" of Cr or Ti between the substrate and Au layers. Fig. 9D shows a 15 nm Au layer on 3 nm of Chromium. Comparing figure 9C to 9D, it is apparent that a Cr layer reduces the roughness of the Au surface, but there are still height variations of $\pm 2 \text{ nm}$ and rms roughness of 0.83 nm. Substituting e-C for Cr (fig 9E) further reduces roughness with peak to peak variation of approximately $\pm 1 \text{ nm}$ (0.6 nm rms), significantly better than that of Cr/ Au. Furthermore, 10 nm of e-C on top of a rough Au film initially similar to that of Fig. 9C also reduces roughness (Fig. 9F). Note that the rough surface of Au in figure 9C is significantly flatter after e-C is deposited on the Au (Fig. 9F). Figs. 10A-10F shows line profiles for the same series of surfaces, plotted with an expanded lateral scale to show more detail.

[0051] In addition to providing smoother surfaces, e-beam deposition of carbon can also provide a conducting carbon film on top of a metal surface suitable for bonding of molecular layers. Aryl diazonium ion reduction on carbon surfaces produces a strong C-C

surface bond important to electronic applications, and not available using diazonium reduction directly on metals. Fig. 11A is a graph showing an AFM line profile for Si/SiO_x/e-C(5nm)/Au(15 nm)/e-C(10nm) and Fig. 11B is a graph showing an AFM line profile for Si/SiO_x/Au(15nm)/e-C(10nm). Fig. 11C is a graph showing an AFM line profile for Si/SiO_x/Au for comparison. The e-C improves or retains the flatness of the underlying substrate, whether deposited under or on top of the metal layer. Not only does e-C provide an excellent surface for electrochemical modification with diazonium reagents, but it also is believed not to be subject to the electromigration of metals common in high electric fields. The e-C/Au/e-C layer arrangement also has much higher lateral conductivity (in the plane of the Au/e-C interface) than either e-C or PPF alone, due to the high conductivity of Au compared to either e-C or PPF. The electrical current through the device need only traverse the low conductivity e-C through its short dimension, resulting in negligible resistance.

[0052] Scanning electron micrographs were obtained of surfaces prepared with e-beam deposition. An electron micrograph of Si/SiO_x/Au showed clearly visible cracks, but electron micrographs of Si/SiO_x/e-C/Au and Si/SiO_x/e-C/Au/e-C appeared much smoother. Cyclic voltammograms were obtained accompanying electrochemical reduction of a diazonium reagent made from anthraquinone (anthraquinone diazonium salt in acetonitrile), for each of the layer arrangements SiO_x/Au/e-C, SiO_x/Pt/e-C and SiO_x/PPF. The cyclic voltammograms scanned from 0.4 V to -0.55 V at a scan rate of 0.4 V/s and a sample interval of 0.001 V. The voltammograms showed sharper, better defined peaks on the e-C surfaces indicating enhanced electrochemical activity and reduced ohmic losses, compared to PPF.

[0053] Current density/voltage plots were obtained for anthraquinone molecular junctions made with different layer arrangements below the anthraquinone, three of which involve e-C and one on PPF for comparison. SiO_x/Cr/Au/e-C/AQ/e-C/Au showed a slightly tighter peak than for SiO_x/PPF/AQ/e-C/Au, though it also widened more at higher absolute values of bias voltage. SiO_x/Au/e-C/AQ/e-C/Au and SiO_x/e-C/Au/e-C/AQ/e-C/Au showed slightly wider peaks. The similarity of these curves indicates that e-C may be used without PPF to make molecular junctions, with high yield and good reproducibility.

[0054] Certain embodiments of e-C/metal or e-C/metal/e-C surfaces may have one or more of the following advantages:

1. e-beam deposition is an established method in the microfabrication industry.
2. e-C and subsequent layers may be deposited through a conventional photolithographic pattern or a shadow mask.
3. e-C/metal (e.g. e-C/Au) surfaces are flatter than those from alternative methods, and e-C on top of a rough metal surface can yield a smoother e-C surface.
4. An e-C/Au/e-C or Au/e-C substrate can have much higher conductivity than e-C or PPF alone.
5. e-C is a covalent conductor, therefore not prone to electromigration.
6. e-C is an excellent substrate for subsequent molecular layer deposition, and the underlying metal reduces ohmic potential errors during electrochemical deposition.
7. Devices made with e-C substrates and top contacts have higher voltage and temperature range than those with metallic conductors.
8. e-C is less electrochemically active than metals, hence less prone to oxidation or other electrochemical processes which might degrade performance.
9. e-C/metal layers made with e-beam deposition can be thin enough to be partially transparent, for use in possible photonic applications and spectroscopy.
10. Unlike PPF, e-C may be deposited on flexible substrates at ambient temperature, thus permitting fabrication of molecular electronic devices on temperature-sensitive, plastic or transparent materials.
11. e-C improves adhesion between layers of other vapour deposited materials, by providing strong, possibly covalent, interactions between metals and other metals, carbon, metal oxides, etc.

[0055] In the claims, the word “comprising” is used in its inclusive sense and does not exclude other elements being present. The indefinite articles “a” and “an” before a claim feature do not exclude more than one of the feature being present. Each one of the individual features described here may be used in one or more embodiments and is not, by virtue only of being described here, to be construed as essential to all embodiments as defined by the claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An electronic device comprising an intermediate layer formed on a lower conducting contact and an upper conducting contact formed on the intermediate layer, each conducting contact comprising a carbon layer and a conductor, the carbon layers being formed by e-beam deposition.
2. The electronic device of claim 1 in which the carbon layers of the upper and lower contacts are in contact with the intermediate layer.
3. The electronic device of claim 1 or 2 in which the surface roughness of the surface of the lower contact in contact with the intermediate layer is less than 0.88 nm rms.
4. The electronic device of any one of claims 1-3 in which the intermediate layer is a functional layer comprising one or more molecular or oxide layers.
5. The electronic device of claim 4 arranged in a circuit to act as a molecular junction.
6. The electronic device of any one of claims 1-3 in which the intermediate layer comprises an insulating layer.
7. The electronic device of claim 6 arranged in a circuit to act as a capacitor.
8. The electronic device of any one of claims 1-3 in which the intermediate layer comprises two redox-active layers which undergo a redox reaction with respect to one another to change respective redox states of the layers in the presence of an applied voltage, at least one of the redox-active layers having conductivity that depends on the redox state of the layer.

9. The electronic device of claim 8 arranged in a circuit to act as a memory element.
10. The electronic device of claim 8 in which the redox reaction is at least partially reversible by the application of an opposite voltage.
11. The electronic device of claim 10 arranged in a circuit to act as a rewritable memory element.
12. The electronic device of any one of claims 1-4 in which the intermediate layer comprises at least two layers having different molecular energy levels to create a preferred direction of current flow.
13. The electronic device of claim 12 arranged in a circuit to act as a rectifying diode.
14. The electronic device of claim 12 in which the intermediate layer comprises at least one light sensitive layer which energizes charge carriers in response to light.
15. The electronic device of claim 14 arranged in a circuit to act as a photodetector.
16. The electronic device of claim 14 arranged in a circuit to act as a photovoltaic energy source.
17. The electronic device of claim 12 in which the at least two layers having different molecular energy levels comprise materials selected to cause production of light in response to electrical current flowing between the layers.
18. The electronic device of claim 17 arranged in a circuit to act as a light-emitting element.

19. The electronic device of any one of claims 1-18 in which one or more of the conducting contacts and the intermediate layer is at least partially transparent to light.
20. The electronic device of any one of claims 1-19 in which one or both carbon layers comprise an amorphous random mixture of sp² and sp³ hybridized carbon atoms.
21. A method of making an electronic device, comprising forming a lower conducting contact, an intermediate layer in contact with the lower conducting contact, and an upper conducting contact in contact with the intermediate layer, each conducting contact comprising a carbon layer formed by e-beam deposition and a conductor.
22. The method of claim 21 in which the carbon layers of the upper and lower conducting contacts are formed to be in contact with the intermediate layer.
23. The method of claim 21 or claim 22 in which the lower conducting contact is formed to have a surface roughness less than 0.88 nm rms.
24. The method of any one of claims 20-22 in which the intermediate layer is a functional layer comprising one or more molecular or oxide layers.
25. The method of claim 24 further comprising arranging the electronic device in a circuit to act as a molecular junction.
26. The method of any one of claims 21-23 in which the intermediate layer comprises an insulating layer.
27. The method of claim 26 further comprising arranging the electronic device in a circuit to act as a capacitor.

28. The method of any one of claims 21-23 in which the intermediate layer comprises two redox-active layers which undergo a redox reaction with respect to one another to change respective redox states of the layers in the presence of an applied voltage, at least one of the redox-active layers having conductivity that depends on the redox state of the layer.
29. The method of claim 28 further comprising arranging the electronic device in a circuit to act as a memory element.
30. The method of claim 28 in which the redox reaction is at least partially reversible by the application of an opposite voltage.
31. The method of claim 30 further comprising arranging the electronic device in a circuit to act as a rewritable memory element.
32. The method of any one of claims 21-24 in which the intermediate layer comprises at least two layers having different molecular energy levels to create a preferred direction of current flow.
33. The method of claim 32 further comprising arranging the electronic device in a circuit to act as a rectifying diode.
34. The method of claim 32 in which the intermediate layer comprises at least one light sensitive layer which in operation energizes charge carriers in response to light.
35. The method of claim 34 further comprising arranging the electronic device in a circuit to act as a photodetector.
36. The method of claim 34 further comprising arranging the electronic device in a circuit to act as a photovoltaic energy source.

37. The method of claim 32 in which the at least two layers having different molecular energy levels comprise materials selected to cause production of light in response to electrical current flowing between the layers.
38. The method of claim 37 further comprising arranging the electronic device in a circuit to act as a light-emitting element.
39. The method of any one of claims 21-38 in which one or more of the conducting contacts and the intermediate layer is at least partially transparent to light.
40. The method of any one of claims 21-39 in which one or both carbon layers comprise an amorphous random mixture of sp^2 and sp^3 hybridized carbon atoms.

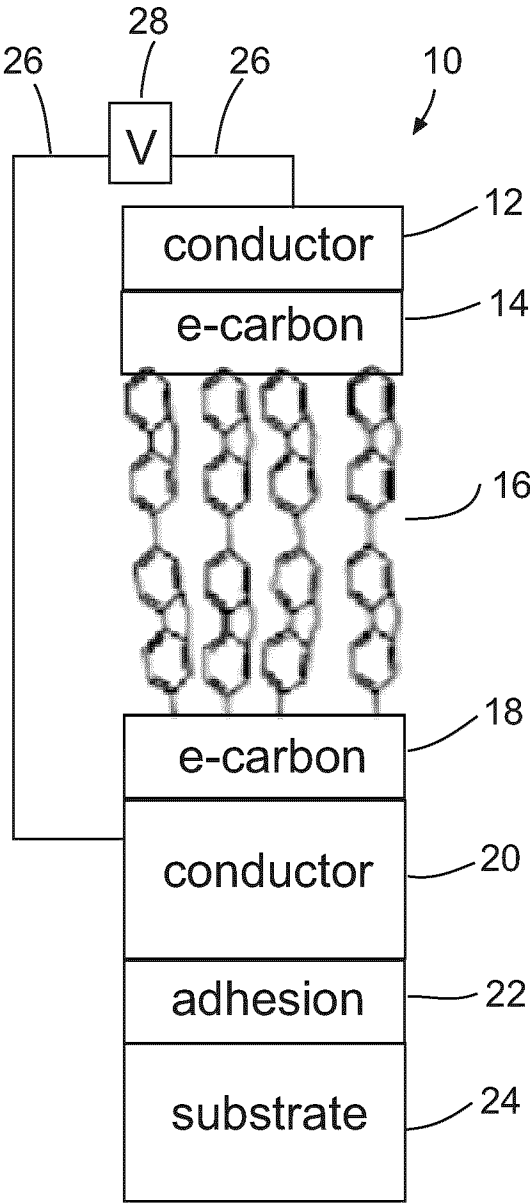


Fig. 1

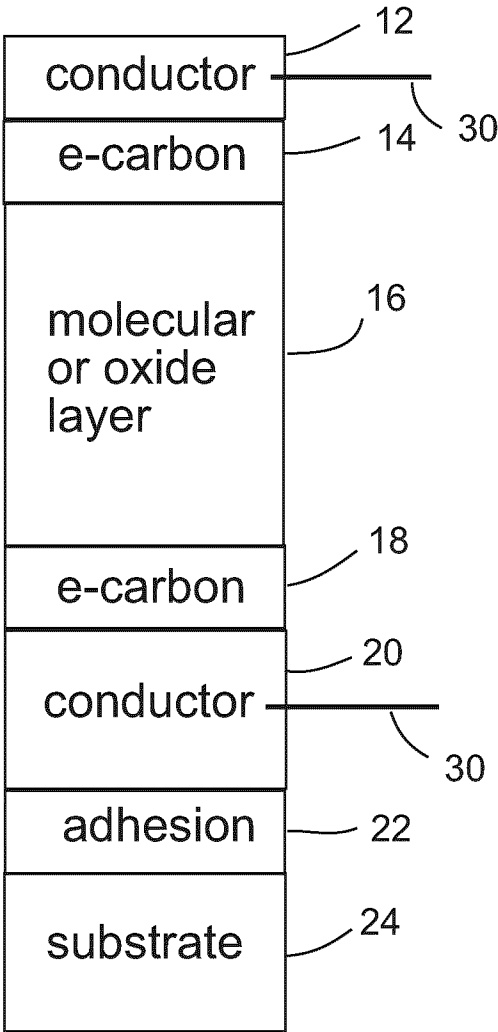


Fig. 2

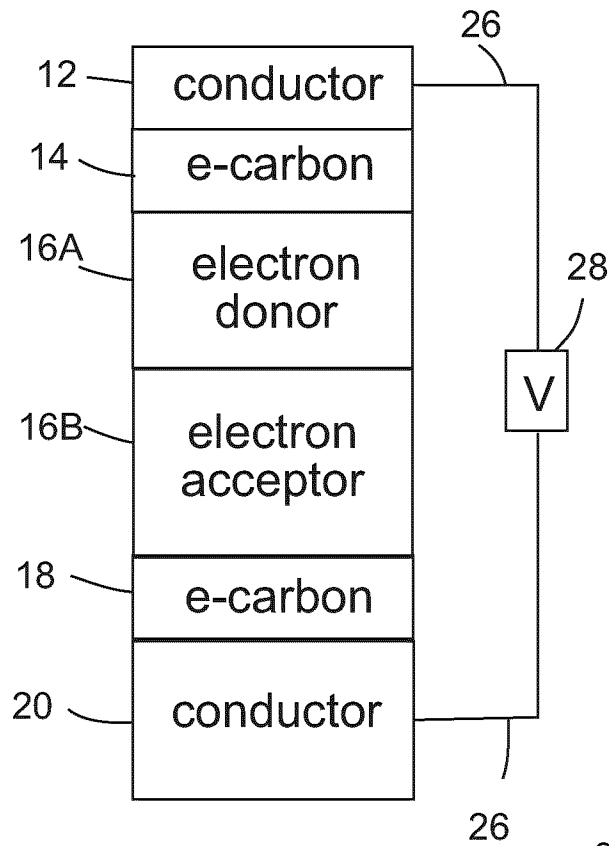


Fig. 3

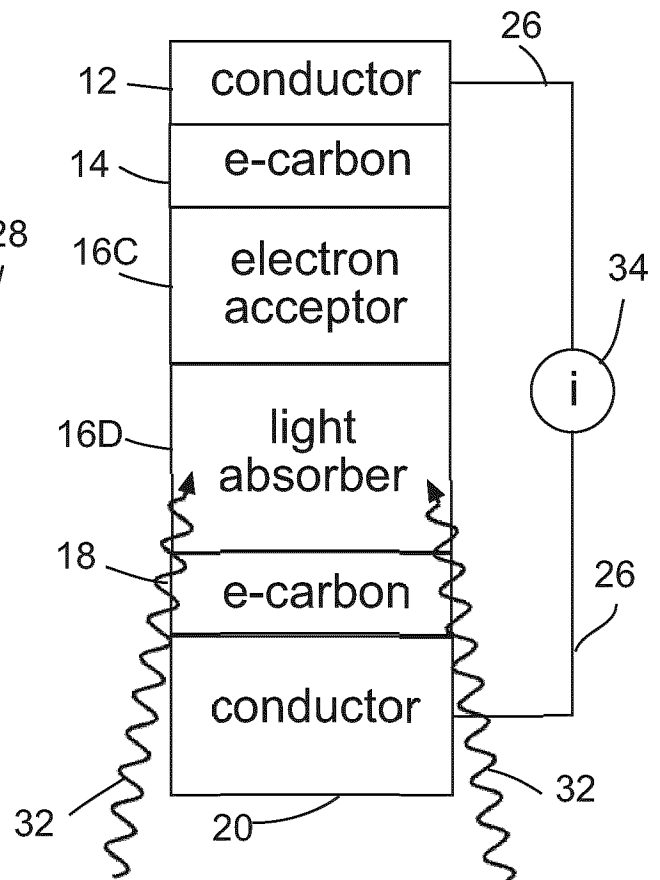


Fig. 4

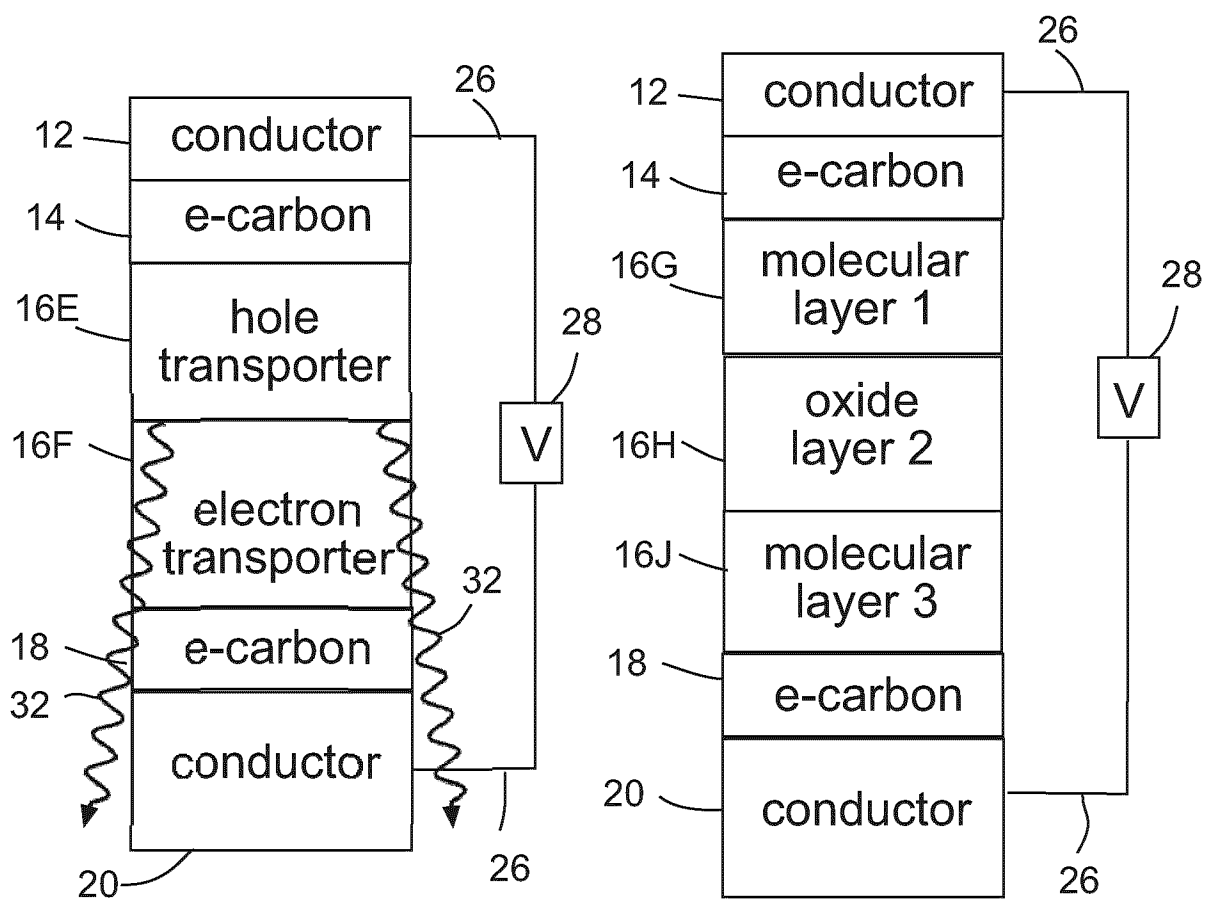


Fig. 5

Fig. 6

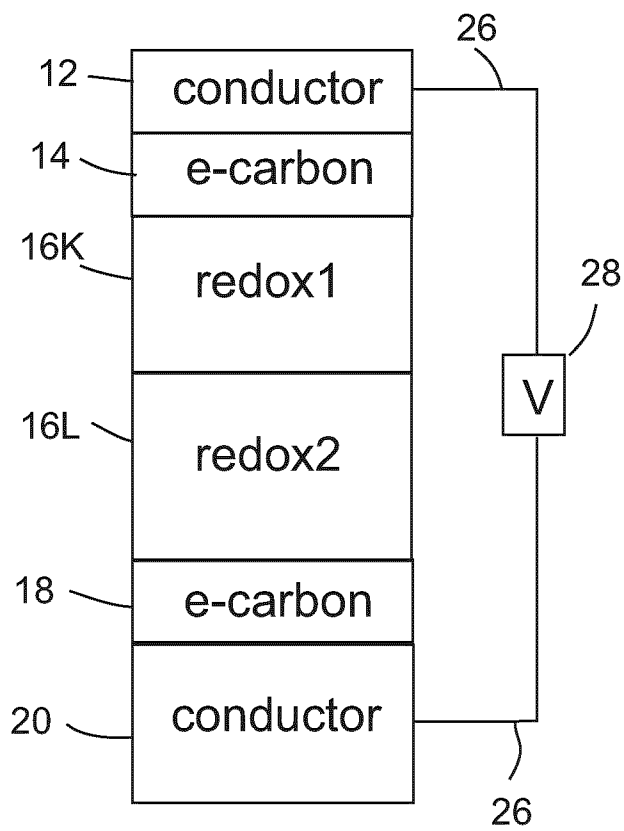


Fig. 7

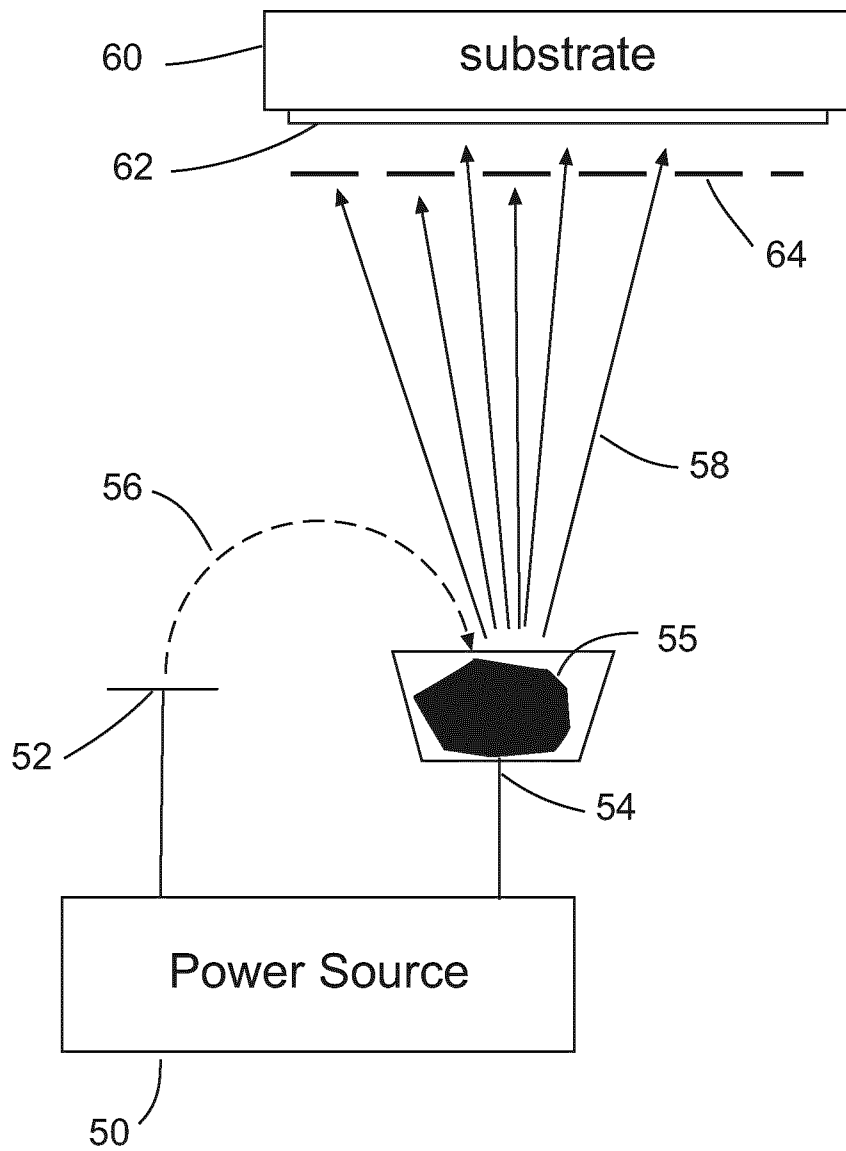


Fig. 8 (prior art)

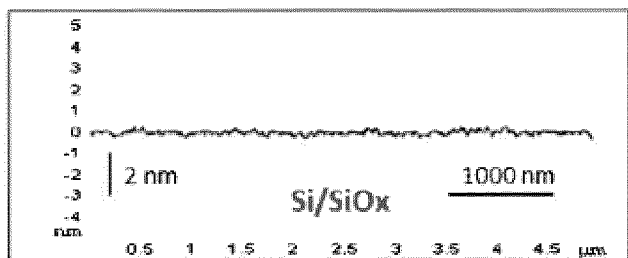


Fig. 9A

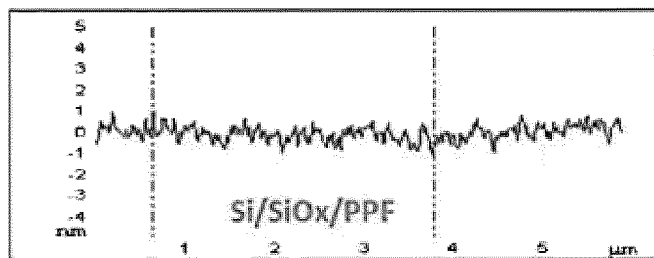


Fig. 9B

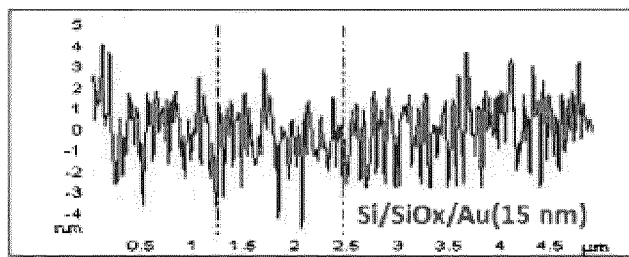


Fig. 9C

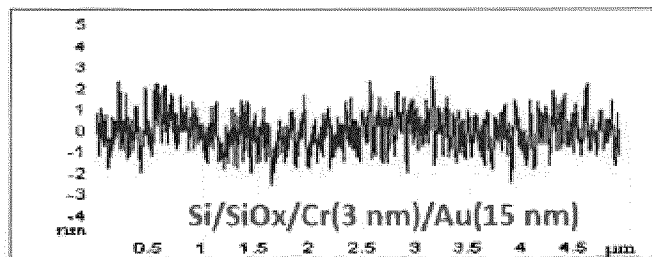


Fig. 9D

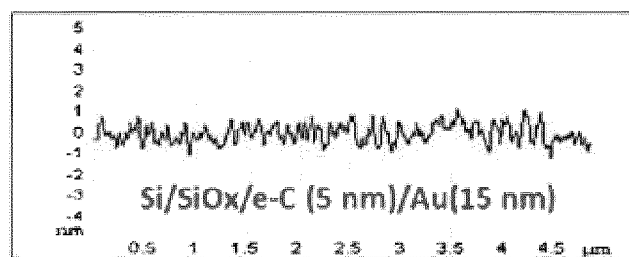


Fig. 9E

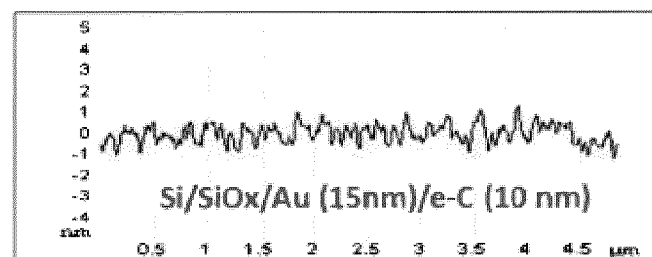


Fig. 9F

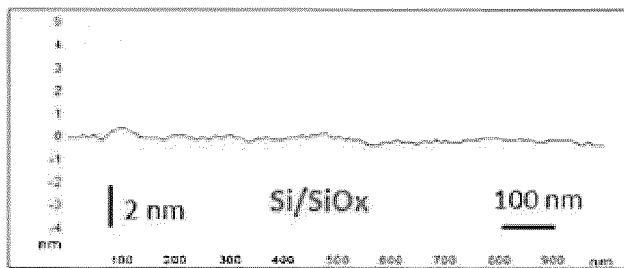


Fig. 10A

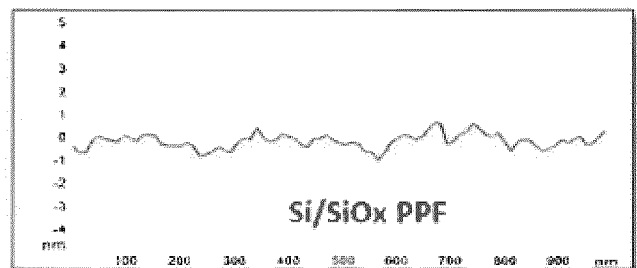


Fig. 10B

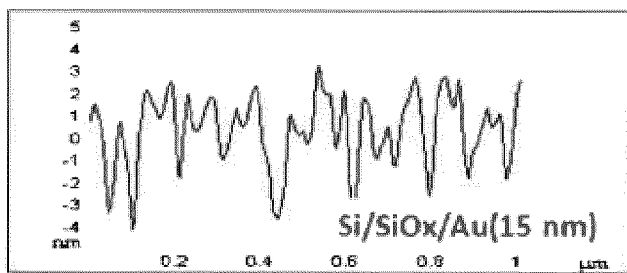


Fig. 10C

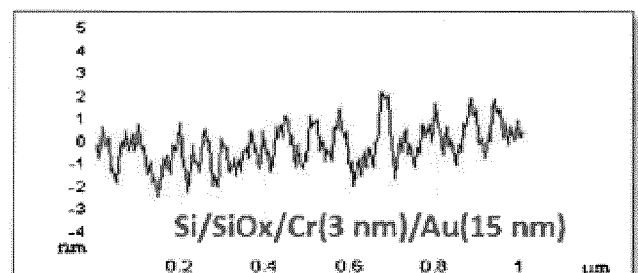


Fig. 10D

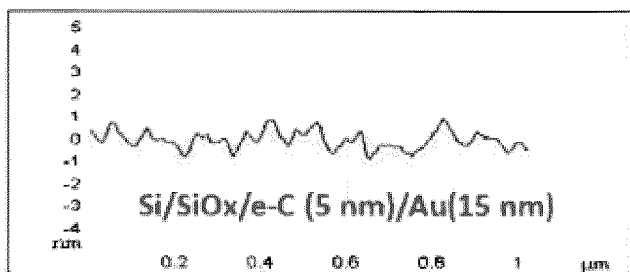


Fig. 10E

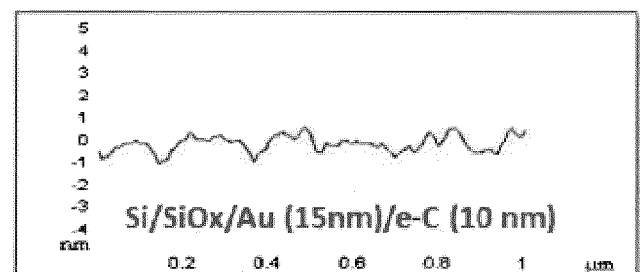


Fig. 10F

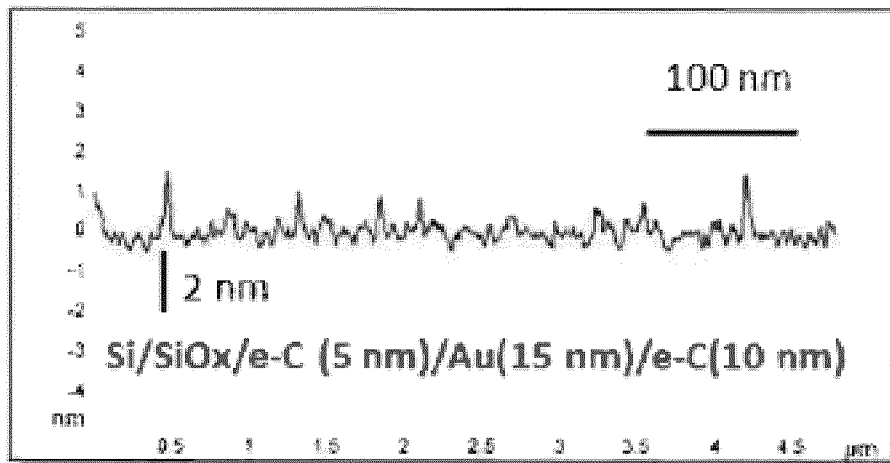


Fig. 11A

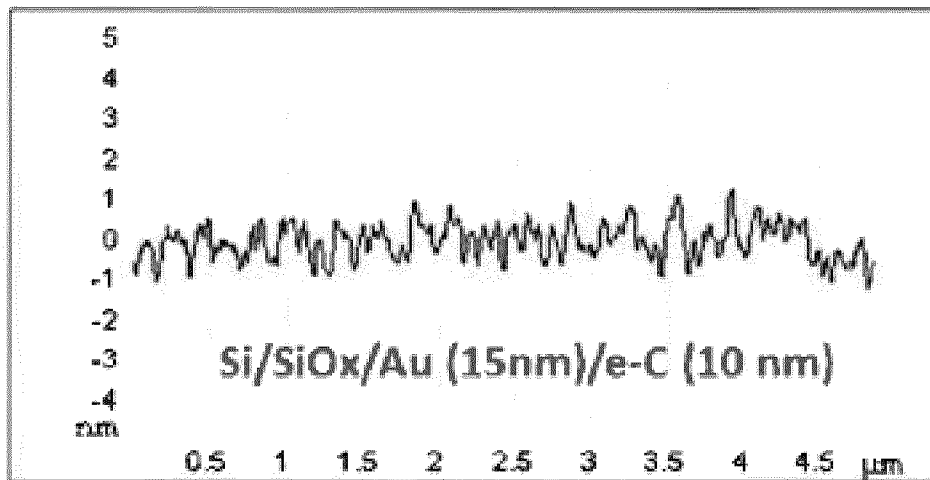


Fig. 11B

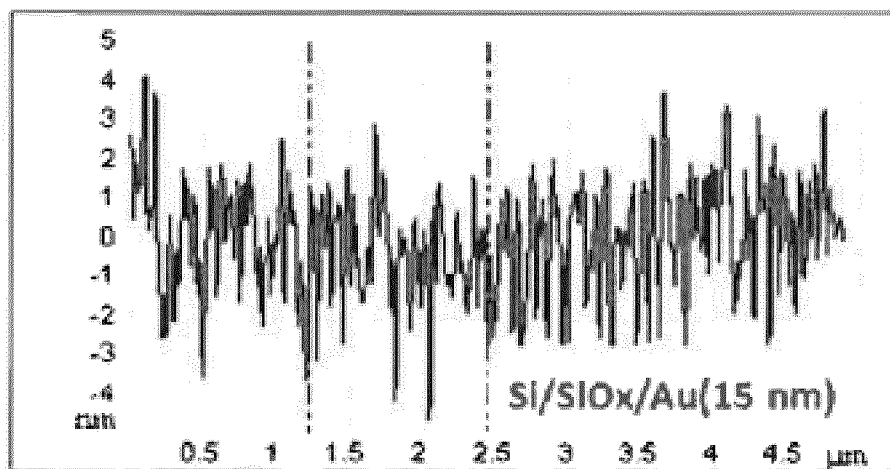


Fig. 11C

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050592

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **H01L 21/441** (2006.01), **H01L 23/48** (2006.01), **H01L 29/12** (2006.01)

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: **H01L 21/441** (2006.01), **H01L 23/48** (2006.01), **H01L 29/12** (2006.01)

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

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

Databases: Questel Orbit, IEEEExplore

Keywords: electron beam deposition, e-carbon, electron beam, carbon, molecular junction, contact, photovoltaic, stack

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KIM et al., " <i>Fabrication of an UltraLow-Resistance Ohmic Contact to MWCNT-Metal Interconnect Using Graphitic Carbon by Electron Beam-Induced Deposition (EBID)</i> ". IEEE Trans. on Nanotechnology, November 2012 (11-2012), Vol. vol. 11, no. 6, pp. pp. 1223-1230, [online] [retrieved on 10 August 2016 (10-08-2016)]. Retrieved from the Internet: <URL: http://ieeexplore.ieee.org/stamp/stamp.jsp?tp=&arnumber=6323037&isnumber=6355725 >	1-7, 9-27, 29-40 -- 8, 28
A	ARAI et al., " <i>Electron-Beam-Induced Deposition of Conductive Nanostructures with Carbon Nanotube Emitters</i> ". 3rd IEEE Con. on Nanotechnology, IEEE-NANO 2003, 14 August 2003 (14-08-2003), Vol. vol. 2, pp. pp. 811-814, [online] [retrieved on 10 August 2016 (10-08-2016)]. Retrieved from the Internet: <URL: http://ieeexplore.ieee.org/stamp/stamp.jsp?tp=&arnumber=1231038&isnumber=27574 >	1-40
A, P	WO2015197834 (GOLZHAUSER et al.) 30 December 2015 (30-12-2015)	1-40
A	EP0390523 (ISODA et al.) 3 October 1990 (03-10-1990)	1-40

Further documents are listed in the continuation of Box C.

See patent family annex.

* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international filing date 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) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	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 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 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
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Date of the actual completion of the international search
01 September 2016 (01.09.2016)Date of mailing of the international search report
01 September 2016 (01-09-2016)Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 819-953-2476

Authorized officer

Coralie Gill (819) 639-3176

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050592

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y - A	WO03081638 (MCCREERY) 2 October 2003 (02-10-2003)	1-7, 9-27, 29-40 -- 8, 28
A	SE1151096 (JAFRI) 19 May 2013 (19-05-2013)	1-40

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2016/050592

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
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EP0390523A2	03 October 1990 (03-10-1990)	EP0390523A2 EP0390523A3 EP0390523B1 DE69024394D1 DE69024394T2 JPH02257675A JP2752687B2 US5211762A	03 October 1990 (03-10-1990) 23 January 1991 (23-01-1991) 27 December 1995 (27-12-1995) 08 February 1996 (08-02-1996) 14 August 1996 (14-08-1996) 18 October 1990 (18-10-1990) 18 May 1998 (18-05-1998) 18 May 1993 (18-05-1993)
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