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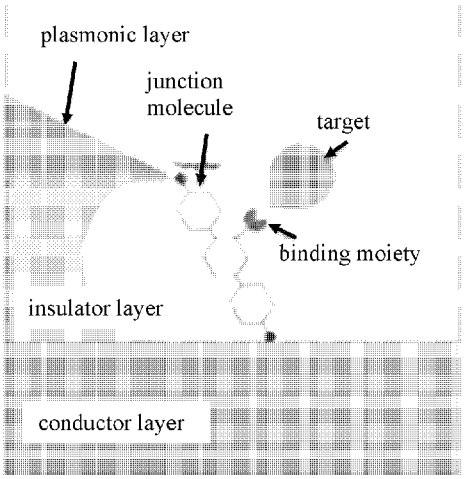

FIG. 1D

(57) Abstract: A nanoplasmonic sensor comprises a plasmonic layer configured to produce surface plasmon polaritons (SPPs) for creating hot carriers upon exposure to light; a conducting layer configured to receive an injection of hot carriers; a dielectric layer positioned between the plasmonic layer and the conducting layer, the dielectric layer configured to form a gap between the plasmonic layer and the conducting layer; and a conductive junction molecule electrically coupled to the plasmonic layer and the conducting layer so as to form a molecular junction, wherein the junction molecule is configured to receive the hot carriers from the plasmonic layer and inject the hot carriers to the conducting layer, thereby creating an injected current, wherein the injected current is modulated upon contact of the junction molecule with a target molecule.

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NANOPLASMONIC SENSOR

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 62/754,751 filed November 2, 2018, which is hereby incorporated by reference in its entirety.

BACKGROUND

Field of the Invention

[0002] Embodiments generally concerns compositions and devices related to sensors and nanosensor. In particular, various embodiments are directed to sensors or devices comprising a nano-plasmonic sensor.

Description of the Related Art

[0003] Different approaches have been attempted to fabricate sensors for biomolecules in an integrated scale for emerging optoelectronic devices. These research endeavors have not successfully exploited the current of hot carriers induced by plasmon decay across a molecular junction. Various studies report the phenomenon of generation of hot carriers from plasmonic decay, due to potential research implications. Most of the applied research endeavors have been devoted to the validity and suitability of these devices as efficient energy converters for light harvesting in solar energy applications and as enhancers of photocatalytic processes. Molecular biosensors with high level of selectivity and sensitivity have only been demonstrated using optical identification mechanism. Surface Enhanced Raman Spectroscopy (SERS) is typically used as the detection method. Miniaturization and integration of this technology into the envisioned applications is difficult due to the inherent complexity of the optical detection system.

[0004] There remains a need for sensors capable of sensing target molecules with high selectivity and sensitivity, in particular using current of excited carriers induced by plasmon decay across a molecular junction.

SUMMARY

[0005] Certain problems related to the sensing of a molecule or biomolecule are addressed by the fabrication of a sensor using hot carrier induced current through a molecular junction for sensing. Embodiments of this disclosure are directed to sensors capable of detection of

presence of target molecules and their concentrations in a sample. The target molecule can be a biomolecule, bio-hazard specimen, environmental polluting agents, etc. In certain embodiments the sensor is integrated in a wearable or portable electronic device.

[0006] Certain embodiments are directed to a sensor comprising, a plasmonic layer (first conducting layer) configured to produce surface plasmon polaritons (SPPs) for creating hot carriers; a conducting layer configured to receive an injection of hot carrier; a dielectric layer positioned between the plasmonic layer and the conducting layer, the dielectric layer configured to form a gap between the first (plasmonic layer) and second conducting layer (conductor layer); and a junction molecule or bridge electrically coupled to the plasmonic layer and the conductor layer forming a molecular junction, wherein the junction molecule is configured to receive the hot carrier from the plasmonic layer and inject the hot carrier to the conducting layer creating an injected current, the injected current is capable of being modulated upon direct or indirect contact of the junction molecule with a target molecule.

[0007] Certain embodiments are directed to a method of detecting a target molecule, the method including contacting a sensor with a sample comprising the target molecule, wherein the sensor includes a plasmonic layer configured to produce surface plasmon polaritons (SPPs) for creating hot carriers; a conducting layer configured to receive an injection of hot carrier; a dielectric layer positioned between the plasmonic layer and the conducting layer, the dielectric layer configured to form a gap between the plasmonic layer and the conducting layer; and a junction molecule electrically coupled to the plasmonic layer and the conducting layer forming a molecular junction, wherein the junction molecule is configured to receive the hot carrier from the plasmonic layer and inject the hot carrier to the conducting layer creating an injected current, wherein the injected current is modulated upon binding of the target molecule, either directly or indirectly, to the junction molecule.

[0008] Certain embodiments are directed to a wearable device having a sensor with a plasmonic layer configured to produce surface plasmon polaritons (SPPs) for creating hot carriers; a conducting layer configured to receive an injection of hot carrier; a dielectric (insulator) layer positioned between the plasmonic layer and the conducting layer, the dielectric layer configured to form a gap between the plasmonic layer and conductor layer; and a junction molecule electrically coupled to the plasmonic layer and the conductor layer forming a molecular junction, wherein the junction molecule is configured to receive the hot carrier from the plasmonic layer and inject the hot carrier to the conductor layer creating an injected current, the injected current is capable of being modulated upon contact of the junction molecule, either

directly or indirectly, with a target molecule. Other embodiments include microfluidic devices configured to supply sample to the sensor, etc.

[0009] In certain aspects, the plasmonic layer comprises one or more grooves configured to couple photons into SPPs when exposed to light. In certain aspects, the plasmonic layer comprises an optical grating configured to couple photons into SPPs when exposed to light. In certain aspects, the plasmonic layer has one or more tapered regions to funnel SPPs to form a focal region with enhanced rate of generation of hot carreirs. In certain aspects the plasmonic layer is or is about 1, 5, 10, 15, 20, 50, 100 to 200, 250, 275, 280, 285, 290, 295, or 300 nm thick, including all values and ranges there between. In particular aspects, the plasmonic layer is 1 to 275, 1 to 280, 1 to 285, 1 to 290, 1 to 295, 1 to 300, 5 to 275, 5 to 280, 5 to 285, 5 to 290, 5 to 295, 5 to 300, 10 to 275, 10 to 280, 10 to 285, 10 to 290, 10 to 295, 10 to 300, 15 to 275, 15 to 280, 15 to 285, 15 to 290, 15 to 295, 15 to 300, 20 to 275, 20 to 280, 20 to 285, 20 to 290, 20 to 295, or 20 to 300 nm thick, including all values and ranges there between. In certain aspects the plasmonic layer is a metal doped, metal, or metal alloy layer. In particular aspects the plasmonic layer is gold, silver, platinum, palladium, copper, aluminum, tungsten or alloys thereof.

[0010] The conducting layer can be a metal doped or metal layer. In certain aspects the conducting layer is gold, silver, platinum, palladium, copper, tungsten, indium tin oxide (ITO) or alloys/combinations thereof. In certain aspects the conducting layer is or is about 1, 1.2, 1.4, 1.6, 1.8 or 2 to 4, 4.2, 4.4, 4.6, 4.8, or 5 nm thick. In particular aspects the conducting layer is 1 to 4, 1 to 4.2, 1 to 4.4, 1 to 4.6, 1 to 4.8, 1 to 5, 1.2 to 4, 1.2 to 4.2, 1.2 to 4.4, 1.2 to 4.6, 1.2 to 4.8, 1.2 to 5, 1.4 to 4, 1.4 to 4.2, 1.4 to 4.4, 1.4 to 4.6, 1.4 to 4.8, 1.4 to 5, 1.6 to 4, 1.6 to 4.2, 1.6 to 4.4, 1.6 to 4.6, 1.6 to 4.8, 1.6 to 5, 1.8 to 4, 1.8 to 4.2, 1.8 to 4.4, 1.8 to 4.6, 1.8 to 4.8, 1.8 to 5, 2 to 4, 2 to 4.2, 2 to 4.4, 2 to 4.6, 2 to 4.8, or 2 to 5 nm thick, including all values and ranges there between.

[0011] The dielectric/insulator layer can be a metal oxide or oxide of a semiconductor. In certain aspect the dielectric layer is silicon oxide, aluminum oxide, hafnium oxide, titaniom oxide, diamond, silicon nitride, and silicates. In certain aspects dielectric breakdown electric field of the dielectric layer is greater than 40, 45, 50, 55 or 60 MV/m. In certain aspects the dielectric layer is or is about 0.5, 1, 1.5, 2, 2.5 or 3 to 17.5, 18, 18.5, 19, 19.5, or 20 nm thick. In particular aspects the dielectric layer is 0.5 to 17.5, 0.5 to 18, 0.5 to 18.5, 0.5 to 19, 0.5 to 19.5, 0.5 to 20, 1 to 17.5, 1 to 18, 1 to 18.5, 1 to 19, 1 to 19.5, 1 to 20, 1.5 to 17.5, 1.5 to 18, 1.5 to 18.5, 1.5 to 19, 1.5 to 19.5, 1.5 to 20, 2 to 17.5, 2 to 18, 2 to 18.5, 2 to 19, 2 to 19.5, 2 to

20, 2.5 to 17.5, 2.5 to 18, 2.5 to 18.5, 2.5 to 19, 2.5 to 19.5, 2.5 to 20, 3 to 17.5, 3 to 18, 3 to 18.5, 3 to 19, 3 to 19.5, or 3 to 20 nm thick, including all values and ranges there between. In certain aspects, the thickness of the dielectric/insulator layer is relative to the length of the junction molecule.

[0012] The junction molecule is a conductive molecule. In certain aspects the junction molecule is a molecule with delocalized electronic orbitals, such as π orbitals, along the whole length of the molecule. In certain particular aspects, the junction molecule is a conductive polymer, a linear conductive organic molecule, or a polyaromatic molecule (e.g., polyphenyl molecular chains, or poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), or other conductive polymers). In certain aspects the junction molecule is bound to the hot carrier focal region of the plasmonic layer. In certain aspects the junction molecule comprises two functional groups, one to bind to the plasmonic layer and a second to bind to the conducting layer. In certain aspects, the functional groups are thiol groups, such as benzene di-thiol or biphenyl di-thiol. Other functional groups include amines, carboxylic, and the like. In certain aspects, the junction molecule comprises a binding moiety. The binding moiety can be directly coupled to the junction molecule or indirectly coupled to the junction molecule via a linker or the like. In certain particular aspects the binding moiety specifically binds the target molecule. In certain aspects the target molecule is a biomolecule. In particular aspects the binding moiety is an antibody, antibody fragment, an aptamer, a peptide, a protein, a nucleic acid, oligonucleotide or other molecule with sufficient affinity for a target.

[0013] A first embodiment, embodiment 1, is directed to a sensor comprising, a plasmonic layer configured to produce surface plasmon polaritons (SPPs) for creating hot carriers; a conducting layer configured to receive an injection of hot carrier; a dielectric layer positioned between the plasmonic layer and the conducting layer, the dielectric layer configured to form a gap between the plasmonic layer and the conducting layer; and a junction molecule electrically coupled to the plasmonic layer and the conducting layer forming a molecular junction, wherein the junction molecule is configured to receive the hot carrier from the plasmonic layer and inject the hot carrier to the conducting layer creating an injected current, the injected current is capable of being modulated upon contact of the sensing moiety with a target molecule.

[0014] Embodiment 2 is directed to embodiment 1, wherein the plasmonic layer comprises one or more grooves, or an optical grating configured to couple photons into SPPs when exposed to light. The grooves are typically straight and parallel. Depth is not crucial but

typically goes the bottom of the plasmonic layer, e.g., the groove is typically as deep as the plasmonic layer is thick.

[0015] The center-to-center distance of the grooves, in order to couple to visible light, is usually in the range from 400nm to 1000nm. The grooves width can be typically half of the value of their center-to-center distance. Typically from 3 to 6-7 grooves are ok for a good coupling.

[0016] Embodiment 3 is directed to embodiment 1 or 2, wherein the plasmonic layer converges to form a hot carrier focal region.

[0017] Embodiment 4 is directed to embodiment 3, wherein the junction molecule is bound to the hot carrier focal region of the plasmonic layer.

[0018] Embodiment 5 is directed to any one of embodiments 1 to 4, wherein the plasmonic layer is 1 to 300 nm thick.

[0019] Embodiment 6 is directed to any one of embodiments 1 to 5, wherein the plasmonic layer is a metal layer.

[0020] Embodiment 7 is directed to embodiment 6, wherein the plasmonic layer is gold, silver, platinum, palladium, copper, aluminum, tungsten or alloys thereof.

[0021] Embodiment 8 is directed to any one of embodiments 1 to 7, wherein the conducting layer is 1 to 5 nm thick.

[0022] Embodiment 9 is directed to any one of embodiments 1 to 8, wherein the conducting layer is a metal layer.

[0023] Embodiment 10 is directed to embodiment 9, wherein the conducting metal layer is gold, silver, platinum, palladium, copper, tungsten, indium tin oxide (ITO) or alloys thereof.

[0024] Embodiment 11 is directed to any one of embodiments 1 to 10, wherein the dielectric layer comprises metal oxide or oxide of a semiconductor, preferably silicon oxide, aluminum oxide, hafnium oxide layer. In certain embodiments dielectric breakdown of the dielectric layer is larger than 40, 45, 50, 55 or 60 MV/m. In certain embodiments the dielectric layer has a dielectric constant, K, ranging from values of K=1 to K=100. In certain embodiments the dielectric layer has a high dielectric constant, K, ranging from values of K=6 to K=100.

[0025] Embodiment 12 is directed to any one of embodiments 1 to 11, wherein the dielectric layer has a thickness of 0.5 to 20 nm, preferably about 1 nm.

[0026] Embodiment 13 is directed to any one of embodiments 1 to 12, wherein the junction molecule comprises functional groups to bind to the plasmonic and the conducting layer.

[0027] Embodiment 14 is directed to any one of embodiments 1 to 13, wherein the junction molecule is a conductive polymer or a linear conductive organic molecule, or a polyaromatic molecule, preferably a polyaromatic molecule.

[0028] Embodiment 15 is directed to any one of embodiments 1 to 14, wherein the junction molecule comprises or is coupled, directly or indirectly, to a binding moiety.

[0029] Embodiment 16 is directed to embodiment 15, wherein the binding moiety specifically binds the target molecule.

[0030] Embodiment 17 is directed to any one of embodiments 1 to 16, wherein the target molecule is a biomolecule.

[0031] Embodiment 18 is directed to any one of embodiments 15 to 17, wherein the binding moiety is an antibody, antibody fragment, or aptamer.

[0032] Embodiment 19 is directed to a method of detecting a target molecule comprising contacting a sensor of any one of embodiments 1 to 18 with a sample comprising the target molecule and detecting the binding of the target molecule to the sensor by monitoring current flowing from the first plasmonic layer to the second conducting layer.

[0033] Embodiment 20 is directed to a wearable device comprising a sensor of any one of embodiments 1 to 18.

[0034] Other embodiments of the invention are discussed throughout this application. Any embodiment discussed with respect to one aspect of the invention applies to other aspects of the invention as well and vice versa. Each embodiment described herein is understood to be embodiments of the invention that are applicable to all aspects of the invention. It is contemplated that any embodiment discussed herein can be implemented with respect to any method or composition of the invention, and vice versa. Furthermore, compositions and kits of the invention can be used to achieve methods of the invention.

[0035] The use of the word "a" or "an" when used in conjunction with the term "comprising" in the claims and/or the specification may mean "one," but it is also consistent with the meaning of "one or more," "at least one," and "one or more than one."

[0036] Throughout this application, the term "about" is used to indicate that a value includes the standard deviation of error for the device or method being employed to determine the value.

[0037] The use of the term "or" in the claims is used to mean "and/or" unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and "and/or."

[0038] As used in this specification and claim(s), the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0039] Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating specific embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

DESCRIPTION OF THE DRAWINGS

[0040] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of the specification embodiments presented herein.

[0041] **FIGs. 1A-D**: Pictorial representation of the device sensor layout. (A) top view of nanpatterned plasmonic surfaces and side view of the device with two metallic electrodes connected; (B) Active device area zone; (C) Bridged organic functional molecule between the two electrodes; (D) Bioconjugation of target molecule to the bridged functional organic junction molecule.

[0042] **FIGs. 2A-H:** A schematic of a process according an embodiment, forming a device containing a conductive layer, a dielectric layer, and a plasmonic layer.

[0043] **FIGs. 3A-M:** A schematic of a process according an embodiment, forming electric contact and connections for a device obtain by the steps depicted in FIG. 2.

[0044] **FIGs. 4A-F:** Drawing (A)-(C) and pictorial representation (E)-(F) of a device containing multiple sensors obtained after process completion of the steps depicted in FIG. 2 and 3.

[0045] **FIGs. 5A-D:** Scanning Electron Microscopy images of the sensors obtained by the steps depicted in FIG. 2 and 3.

[0046] **FIG. 6:** Global view of devices on a 4 inches diameter wafer containing multiple sensors obtained after process completion of the steps depicted in FIG. 2 and 3.

DESCRIPTION

[0047] The following discussion is directed to various embodiments of the invention. The term "invention" is not intended to refer to any particular embodiment or otherwise limit the scope of the disclosure. Although one or more of these embodiments may be preferred, the embodiments disclosed should not be interpreted, or otherwise used, as limiting the scope of the disclosure, including the claims. In addition, one skilled in the art will understand that the following description has broad application, and the discussion of any embodiment is meant only to be exemplary of that embodiment, and not intended to intimate that the scope of the disclosure, including the claims, is limited to that embodiment.

[0048] Free charges in a conductor, such as in a metal, either electrons or holes can induce collective oscillations, bound to the surface of the metal with a dielectric, known as surface plasmons. Surface plasmons can mainly be divided in two types: localized surface plasmons, and propagating surface plasmons, or SPPs. SPPs propagate on metal surfaces.

[0049] Surface plasmon polaritons (SPPs) are infrared or visible-frequency electromagnetic waves that travel along a metal–dielectric or metal–air interface. The term "surface plasmon polariton" indicates that the wave involves both charge motion in the metal ("surface plasmon") and electromagnetic waves in the air or dielectric ("polariton"). They are a type of surface wave, guided along the interface in much the same way that light can be guided by an optical fiber. SPPs are shorter in wavelength than the incident light (photons). Hence, SPPs can have tighter spatial confinement and higher local field intensity. Perpendicular to the interface, they have subwavelength-scale confinement. An SPP will propagate along the interface until its energy is lost either to absorption in the metal or scattering into other directions (such as into free space).

[0050] There are two loss mechanisms associated with the plasmon excitation: radiative loss, *i.e.*, the conversion of plasmons into free-propagating photons, and intrinsic loss, which is due to the electron-electron scattering, and causes a damping of the oscillation energy into energized excited carriers inside the metal. These losses are responsible for the finite

propagation length of SPPs. The intrinsic loss is exploited for the working principle of the sensors described herein.

[0051] Due to electron-electron scattering inside the metal, SPPs decay into hot carriers. Hot carriers refers to holes or electrons that have gained kinetic energy above the Fermi level of the metal. The "hot" stands for the fact that these hot carriers, electrons or holes, have an energy above the Fermi level of the metal. This phenomenon has for long been considered a problem because it limits the propagation length in metal films. Sensors described herein, exploit the current induced by the excitation of this hot carrier, by collecting the hot carrier current, which flows to a junction via a junction molecule that attached to bridge the two electrodes, one with plasmonic excitation (plasmonic layer or first conductor), and the other one as a reference electrode (conductor layer or second conductor). As used herein the term dielectric breakdown, refers to the voltage at which an insulator material would "breakdown" and start conducing electricity.

[0052] Certain embodiments are directed to a sensor shown in Fig. 1. In one embodiment, the sensor can be at least a 3-layer conductor (e.g., metal) – insulator - conductor (e.g., metal) system. The top conductor layer is a plasmonic layer. SPPs induced in the plasmonic layer propagate and decay in the plasmonic layer to create hot carriers. The bottom conductor layer, is a conducting layer. The conducting layer is a reference electrode configured to collect hot carrier current from the plasmonic layer. The middle insulator layer is a dielectric layer. The dielectric layer functions as a spacer between the two conductor layers and is about 1 nm ± 0.5 nm thick. In certain embodiments the dielectric layer is deposited with Atomic Layer Deposition (ALD) technique. In certain embodiments the dielectric layer is chemically etched, leaving an empty physical gap at the edges between the two conductor layers. A junction molecule, a conductive molecule, is deposited across the physical gap, creating a conductive bridge between the top plasmonic layer and the bottom conducting layer. The thickness of the dielectric layer is adjusted to accommodate the length of the junction molecule. The junction molecule is configured to receive the hot carrier from the plasmonic layer and inject the hot carrier to the conducting layer creating a current flow between the plasmonic layer and the conducting layer. The junction molecule comprises two functional groups (at or near the ends of the junction molecule) and a binding moiety. The distal functional groups are designed to tether covalently to the edges of the plasmonic layer and the conducting layer. In certain embodiments the distal functional groups are independently thiol groups. The binding moiety is capable of selectively bind to a target molecule of interest, wherein the current flow between

the plasmonic layer and the conducting layer is modulated upon binding of the target molecule to the binding moiety.

[0053] The plasmonic layer is configured to allow SPP generation and propagation. The plasmonic layer comprises a device or configuration, to couple external light into SPPs, which compensate the momentum mismatch between free light and SPPs and allow energy transfer from an external light source to SPPs. In certain embodiments an optical grating is engraved into the plasmonic layer. The optical grating is configured to couple light at a specific wavelength and from a specific direction into SPPs. In certain other embodiments the plasmonic layer comprises a single groove formed in the plasmonic layer surface or simple rough plasmonic layer metal surfaces. Such device can be capable of coupling natural sunlight, diffuse white light sources, or UV-visible to near infrared sources into SPPs. The light characteristics are selected to couple to SPPs, so it will be the proper wavelength range for the plasmons to propagate. There are many different plasmonic materials which can work at many different wavelength ranges that can be selected and applied.

[0054] Once generated the SPPs propagate along the plasmonic layer surface until the edges of the layer. In certain embodiments the plasmonic layer is tapered and has a lateral size, which slowly decreases down to zero forming an apex. At the apex the plasmons experience an increase in both real and imaginary part of their effective dielectric constant. A large increase of loss of SPPs is experienced towards the apex of the tapered surface with a consequential large enhancement in the efficiency of generation of hot carriers, forming a hot carrier focal region at the apex. The junction molecule is connected to the plasmonic layer at the hot carrier focal region. In certain embodiments a sensor can have a plurality of plasmonic components, each plasmonic component can for a hot carrier focal region providing the sensor with multiple hot carrier focal regions and multiple junction molecules connected to these hot carrier focal regions, which in turn funnels the SPPs energy at their tips where a large rate of generation of hot carriers is obtained. In certain other embodiments, a plasmonic layer surface does not have a tapered geometry but the decay of SPP and hot carrier generation occurs at the edge of the plasmonic layer.

[0055] The plasmonic layer is made of a material having a free-carrier density, and can sustain SPPs in the UV-visible to near infrared range. In certain embodiments the plasmonic layer is gold, silver, platinum, palladium, copper, aluminum, tungsten, or alloys thereof. In certain aspects, materials that can sustain surface plasmon propagation from the NIR to the UV,

e.g., 300 nm to 3000 nm wavelength, the carrier density can be in the range of about $2.5x10^{20}$ to $2.5x10^{22}$ cm^{-3}.

[0056] The bottom conducting layer (the conducting layer can have a resistance below the MOhm range across the full device, a minimum value for conductivity is that of a doped silicon wafer, which is above 100 Siemens/meter) and is capable to being attached directly or indirectly to the junction molecule. In certain embodiments the bottom conducting layer is gold, silver, platinum, palladium, copper, tungsten, indium tin oxide (ITO), or alloys thereof.

[0057] In certain embodiments sensors may not require any external bias voltage, as the electrons are pushed through Schottky barrier at the metal-molecule junction via excitation by SPPs decay. Design configuration of a sensor may not require any bias and therefore avoid the problems created by the bias voltage. Since no bias is applied, there is no risk of dielectric background in the vertical stack or damage to the junction or conductive molecule, even if a small dielectric layer is required. An electric field across a dielectric spacing layer of about 1 nm reaches the range of several MV/cm.

[0058] In certain embodiments the plasmonic layer, dielectric layer and the conducting layer are arranged laterally. The dielectric layer is etched leaving a planar gap at the edges between the plasmonic layer and the conducting layer. The junction molecule is coupled to the plasmonic layer and the conducting layer across the plane gap.

[0059] The junction molecule is a conductive molecule. In certain embodiments the junction molecules is conductive polymer, a linear conductive organic molecule, or a polyaromatic molecule. In certain embodiments the junction molecule comprise thiol or other groups designed to tether covalently to the edges of the plasmonic or conductor layers. In certain embodiments the thickness of the deposited dielectric layer match with the length of junction molecule.

[0060] In certain embodiments the junction molecule comprises a binding moiety capable of selectively binding to a target molecule in a sample and/or a solution. Sensors can be capable of sensing wide range of different target molecules. In certain embodiments the target molecule are molecules relevant to medical monitoring applications; environmental control and pollutants; forensic science in crime detection and contaminations; bioterrorism; or food spoilage with focus on food safety and food supply-chain control. Binding moiety can include diverse functional groups to selectively bind and detect an intended target molecule. The binding interaction between the target molecule and the binding moiety displaces electronic

charge of the junction molecule. Binding interactions include, but are not limited to peptide-peptide interaction, such as antibody-antigen interaction; binding interaction between conjugated polynucleotides; peptide or protein–small molecule interaction, and the like. In certain embodiments sensor is capable of detecting presence and concentration of glucose and/or other metabolites.

[0061] In certain embodiments the sensor further comprises circuitry for electrical readout of the current flowing through the junction molecule, between the plasmonic layer and the conducting layer. In certain instances, amplitude or amplitude modulation (change of amplitude upon binding) of the current is directly correlated to the concentration of the target molecule in a sample and/or solution. The electronic readout signal can be collected either in voltage or in current. The circuitry is designed to read the current in the desired range, for example, but not limited to a picoampere range. The current range depends on factors including but not limited to the device layout, number of junction molecules bridged across the plasmonic layer and the conducting layer, number of subunits of tapered plasmonic components or waveguides are connected in parallel to the same detector, and the current ranges to be detected as well.

[0062] In certain embodiments the sensor is integrated into an existing bio-electronic devices such as a monitor or a wearable monitor, e.g., integration into smart-watches.

[0063] Certain embodiments are directed to methods of fabricating a sensor, such methods can include, but are not limited to depositing a bottom conducting layer, a middle dielectric layer, and/or a top metal layer; patterning the top metal layer to form a plasmonic layer configured to produce surface plasmon polaritons (SPPs) for creating hot carriers; forming a gap, between the plasmonic layer and the conducting layer, in the middle dielectric layer; coupling a junction molecule between the plasmonic layer and the conducting layer across the gap, wherein the junction molecule is configured to receive the hot carrier from the plasmonic layer and inject the hot carrier to the conducting layer creating an injected current, the injected current being modulated upon contact of the junction molecule with a target molecule. In certain embodiments the top metal layer is patterned by lithography. In certain embodiments the gap is formed by wet etching the middle layer.

[0064] In some aspects, a method for fabricating a nanoplasmonic sensor can include the steps as depicted in **FIG. 2** and **3**. The method can include (a) using an insulating substrate **1** (**FIG. 2 A**); (b) depositing a conducting layer **2** on top of the substrate **1** (**FIG. 2 B**); (c) depositing a dielectric layer **3** on the top of the conducting layer **2** (**FIG. 2 C**); (d) spin coating

a polymer resist layer **4** on top of the dielectric layer **3** (**FIG. 2 D**); (e) exposing a plasmonic structure layout on the polymer resist layer (**FIG. 2 E**); (f) developing the polymer resist layer **4** to reveal the plasmonic structure layout **4b** on the dielectric layer **3** and forming a residual resist layer **4a** (**FIG. 2 F**); (g) depositing a plasmonic layer material **5** on top of the residual resist layer **4a** and the revealed plasmonic structure layout **4b** on the dielectric layer **3** (**FIG. 2 G**); (h) performing a lift-off to remove the residual resist layer **4a** and the plasmonic layer material on top of the residual resist layer to form a plasmonic layer **6** with focal regions on top of the dielectric layer **3** (**FIG. 2 H**); (i) forming an electrical connection to the plasmonic layer (**FIG. 3**); (j) removing a portion of the dielectric layer; and (k) connecting a bridge molecule between the plasmonic layer and the conducting layer, wherein from a bottom to top direction the layers of the sensor are arranged as, conducting layer **2** forming the bottom layer, dielectric layer **3** forming the middle layer and the plasmonic layer **6** forming the top layer. The top surface of the conducting layer **2** is in contact with the bottom surface of the dielectric layer **3** and the top surface of the dielectric layer **3** is in contact with the bottom surface of the plasmonic layer **6**.

[0065] In some aspects, the substrate layer **1** can contain silicon nitride on silicon. In some aspects, the conductive layer **2** can contain platinum. The some aspects, in step (b) the conductive layer **2** can be deposited by ALD. In some aspects, the dielectric layer **3** can contain aluminum oxide. In some aspects, in step (c) the dielectric layer **3** can be deposited by ALD. In some aspects, the polymer resist layer **4** can contain PMMA. In some aspects, the polymer resist layer **4** can have a thickness of about 100 nm to 300 nm, or 150 nm to 250 nm. In some aspects, in step (e) the plasmonic structure layout can be exposed by e-beam lithography. In some aspects, the plasmonic layer material **5** can contain gold. In some aspects, in step (g) the plasmonic layer material **5** can be deposited by e-beam evaporation in high vacuum. In some aspects, the lift off in step (h) can be performed with acetone to remove the residual resist layer **4a** and plasmonic layer material on top of the residual resist layer **4a**. In some aspects, in step (j) a portion of the dielectric layer can be removed by tri-methyl ammonium hydroxide.

[0066] In some aspects, the method for forming an electrical connection to the plasmonic layer in step (i) can include the steps as depicted in **FIG. 3**. The method can include the steps of, (I) depositing a negative optical resist layer **7** on top of a device (**FIG. 3 A**) formed after step (h) (**FIG. 3 B**); (II) patterning the negative optical resist layer to define an area of the bottom conduction layer contact to be isolated **2a** (**FIG. 3 C**), forming a covered portion of the dielectric layer **3a** beneath the pattered negative optical resist layer **7a** and an exposed portion

of the dielectric layer **3b**; (III) removing the exposed portion of the dielectric layer **3a** and a portion of the conductive layer beneath **2a** the exposed portion of the dielectric layer **3a** (**FIG. 3 D**); (IV) removing the pattered negative optical resist layer **7a** to form a bottom contact **2a** (**FIG. 3 E**); (V) depositing a positive resist **9** on top of the device (**FIG. 3 F**); (VI) forming small strip regions **10** in the positive resist layer (**FIG. 3 G**); (VII) depositing a dielectric material **11** on top of the positive resist layer **9** and on top of the small strip region **10** (**FIG. 3 H**); (VIII) performing a lift-off to remove the positive resist layer **9** and the dielectric material **11** on top of the positive resist layer **9**, but leaving the dielectric material **11** on the small strip region **10**, forming insulating strip **11a** that insulates the plasmonic layer **6** and conducting layer **2a** (**FIG. 3 I**), two insulating strips **11a1, 11a2** are formed and can be seen from a top view of the device as shown in **FIG. 4C**; (IX) depositing a second positive resist layer **12** on the device (**FIG. 3 J**); (X) creating an area **13** for electrical contact in second positive resist layer **12** (**FIG. 3 K**); (XI) depositing a conductive material **14** on the second positive resist layer **12** and the area for electrical contact **13** (**FIG. 3 L**); and (XII) performing a lift off removing the second positive resist layer **13** and conductive material **14** on the second positive resist layer **12** forming an electrical connection **14a** to the plasmonic layer **6**.

[0067] In some aspects, in step (I) the negative optical resist **7** was deposited by spin coating. In some aspects, in step (III) the exposed portion of the dielectric layer **3b** and the portion of the conductive layer **2b** beneath the exposed portion of the dielectric layer **3b** was removed by argon plasma. In some aspects, in step (VI) the small strip regions **10a, 10b** were created by optical lithography. In some aspects, in step (VII) the dielectric material **11** contains silicon nitride and/or the dielectric material **11** was deposited by Plasma Enhanced Chemical Vapor Deposition. In some aspects, in step (VIII) the lift–off was performed with acetone. In some aspects, in step (X), the area for electrical contact **13** was created by optical lithography. In some aspects, in step (XI) the conductive material **14** contains gold and/or the conductive material **14** was deposited by e-beam evaporation in high vacuum. In some particular aspects, the conductive material **14** of step (X) contains gold and titanium, where titanium was added to promote gold adhesion on the dielectric layer 3a and the insulating strips **11a**.

EXAMPLES

[0068] The present invention will be described in greater detail by way of specific examples. The following examples are offered for illustrative purposes only, and are not intended to limit the invention in any manner. Those of skill in the art will readily recognize a variety of noncritical parameters which can be changed or modified to yield essentially the same results.

Example 1

Nanoplasmonic sensor

[0069] A Nanoplasmonic sensor was formed accordingly to the steps depicted in FIG. 2 and 3. Silicon wafers with silicon nitride was used as the insulating substrate (**FIG. 2 A**). A 10 nm platinum layer was deposited by Atomic Layer Deposition (ALD), to be used as the conductive layer (**FIG. 2 B**). A 2 nm of aluminum oxide layer was deposited by ALD, to be used as the dielectric layer (**FIG. 2 C**). A 200 nm-thick PMMA resist was spin-coated over the dielectric layer (**FIG. 2 D**). A plasmonic structure layout was exposed by e-beam lithography (**FIG. 2E**). The PMMA resist was developed to reveal the plasmonic structure layout (**FIG. 2 F**). 50 nm of gold layer was deposited by e-beam evaporation in high vacuum. (**FIG. 2 G**). Lift-off was performed in acetone to remove undesired gold and resist residuals (**FIG. 2 H**).

[0070] **FIG. 3** depicts a process of forming electric contact and connections of device obtained by the steps depicted in **FIG. 2**. **FIG. 3 A** shows a side cross-sectional view of the device obtained by the steps depicted in **FIG. 2.** A negative optical resist was spin-coated on the sample (**FIG. 3 B**) and patterned to define the area of the bottom contact to be isolated (**FIG. 3 C**). The dielectric and platinum layer was removed everywhere except under the resist by argon plasma (**FIG. 3 D**), then the patterned resist was removed leaving a bottom contact for each independent device (**FIG. 3 E**). Afterwards, a positive resist was spin-coated on the device (**FIG. 3F**) and a region of small insulating stripes was defined in the resist by optical lithography (**FIG. 3G**). A 40 nm dielectric layer of silicon nitride was deposited by Plasma Enhanced Chemical Vapor Deposition (**FIG. 3H**), then lift-off in acetone was performed to remove all the resist and the silicon nitrides everywhere except in the two small regions, creating the insulating ridge that isolates top gold contact from bottom platinum layer (**FIG. 3 I**). Then another layer of positive optical resist was spin-coated on the device (**FIG. 3 J**), where the area of the electrical contact was defined by optical lithography (**FIG. 3 K**). Subsequently, a layer of 80 nm of gold was deposited by e-beam evaporation in high vacuum, adding first a 5 nm layer of titanium to promote gold adhesion on silicon nitride (**FIG. 3 L**). Undesired gold and resist were removed by lift-off in acetone, leading to the final layout represented in **FIG. 3 M**. After these steps an extra layer of aluminum oxide from the dielectric layer was etched away in tri-methyl ammonium hydroxide to reveal the bottom Pt contact and create the small bridges to be used for molecular connection.

[0071] **FIG. 4** shows the device obtained by the steps of FIG. 2 and 3. **FIG. 4 A-C** shows drawing of the device. **FIG. 4 A**: global view of the dice, 10x10 mm in size, comprising a central area 4x4 individual device, each having its 3 electrical connections (that connected to the tips oriented to right, the one for the tips pointing to the left, and the connection to the base conducting layer) which are leading to an independent contact pad, for a total of 48 pads. A common larger pad on the device bottom is connected to the guard ring of all 16 devices. **FIG. 4 B**: detailed view of the 4x4 array of independent devices. **FIG. 4 C**: highlighted view of a single device, as obtained at the end of the process described in **FIG. 2** and **FIG. 3**. The figure shows the 3 independent connections leaving the device from the top and the common guard ring from the bottom realized in the processing steps described in **FIG. 3J-M**, the square area of the bottom conducting layer realized for each device in the processing steps described in **FIG. 3B-E**, the two small dielectric stripes used to insulate the plasmonic and the conducting layers made according to the processing steps described in **FIG. 3F-I**, and in the center the shape of the plasmonic structure, as obtained according to the process described in **FIG. 2**.

[0072] **FIG. 4 D-F** corresponding optical images of the obtained devices, as shown in **FIG 4 A-C** respectively. **FIG. 4 D:** global view of the dice. FIG. 4 E: detail of the central area with the array of devices. **FIG. 4 F:** highlight of one of the 16 devices, with its connections.

[0073] **FIG. 5** shows Scanning Electron Microscopy images of the device obtained by the steps of **FIG. 2 and 3**. **FIG. 5 A** Intermediate image taken during one of the last steps of the process: the lithography for the electrical connections has been defined and gold has been deposited, the production step which is depicted in **FIG. 3L**. After lift-off the underneath device will be revealed. FIG. **5 B**, shows details of one of the structures, it is well visible the central grating area with the plasmonic tapered guides which ends up with a tip. **FIG. 5 C**, shows different examples of a global view of a complete device. **FIG. 5 D** shows, top tilted view of a gold tip, as obtained by e-beam lithography, at the end of the process.

[0074] **FIG. 6** shows global view of a 4 inches diameter wafer after process completion according to steps of **FIG. 2 and 3**. A total of 52 dices can be obtained on a single wafer, e-beam lithography, can be optimized to cover all the devices of such a wafer in about only 3 hours of continuous operation.

CLAIMS

1. A sensor comprising:

a plasmonic layer configured to produce surface plasmon polaritons (SPPs) for creating hot carriers;

a conducting layer configured to receive an injection of hot carrier;

a dielectric layer positioned between the plasmonic layer and the conducting layer, the dielectric layer configured to form a gap between the plasmonic layer and conducting layer; and

a junction molecule electrically coupled to the plasmonic layer and the conducting layer forming a molecular junction, wherein the junction molecule is configured to receive the hot carrier from the plasmonic layer and inject the hot carrier to the conducting layer creating an injected current, the injected current being modulated upon contact of the junction molecule with a target molecule.

2. The sensor of claim 1, wherein the plasmonic layer comprises one or more grooves, or an optical grating configured to couple photons into SPPs when exposed to light.

3. The sensor of claims 1 or 2, wherein the plasmonic layer converges to form a hot carrier focal region.

4. The sensor of claim 3, wherein the junction molecule is bound to the hot carrier focal region of the plasmonic layer.

5. The sensor of claim 1 wherein the plasmonic layer is 1 to 300 nm thick.

6. The sensor of claim 1 wherein the plasmonic layer comprises a plasmonic metal or plasmonic metal alloy.

7. The sensor of claim 6, wherein the plasmonic layer is gold, silver, platinum, palladium, copper, aluminum, tungsten or alloys thereof.

8. The sensor of claim 1, wherein the conducting layer is 1 to 5 nm thick.

9. The sensor of claim 1 wherein the conducting layer is a metal or doped semiconductor layer.

10. The sensor of claim 9, wherein the conducting layer is gold, silver, platinum, palladium, copper, tungsten, indium tin oxide (ITO) or combinations thereof.

11. The sensor of claim 1, wherein the dielectric layer has a thickness of 0.5 to 20 nm, preferably about 1 nm.

12. The sensor of claim 1, wherein the junction molecule comprises functional groups to bind to the plasmonic and the conducting layer.

13. The sensor of claim 1, wherein the junction molecule is a conductive polymer or a linear conductive organic molecule, preferably a polyaromatic molecule.

14. The sensor of claim 1, wherein the junction molecule comprises a binding moiety.

15. The sensor of claim 14, wherein the binding moiety specifically binds the target molecule.

16. The sensor of any one of claim 1 to 15, wherein the targeting moiety is a biomolecule.

17. The sensor of claim 14 or 16 wherein the binding moiety is an antibody, antibody fragment, or aptamer.

18. A method of detecting a target molecule comprising contacting a sensor of any one of claims 1 to 17 with a sample comprising a target molecule and detecting the binding of the target molecule to the sensor by monitoring current flowing from the first plasmonic layer to the second conducting layer.

19. A wearable device comprising a sensor of any one of claims 1 to 17.

20. A microfluidic device comprising a sensor of any one of claims 1 to 17.

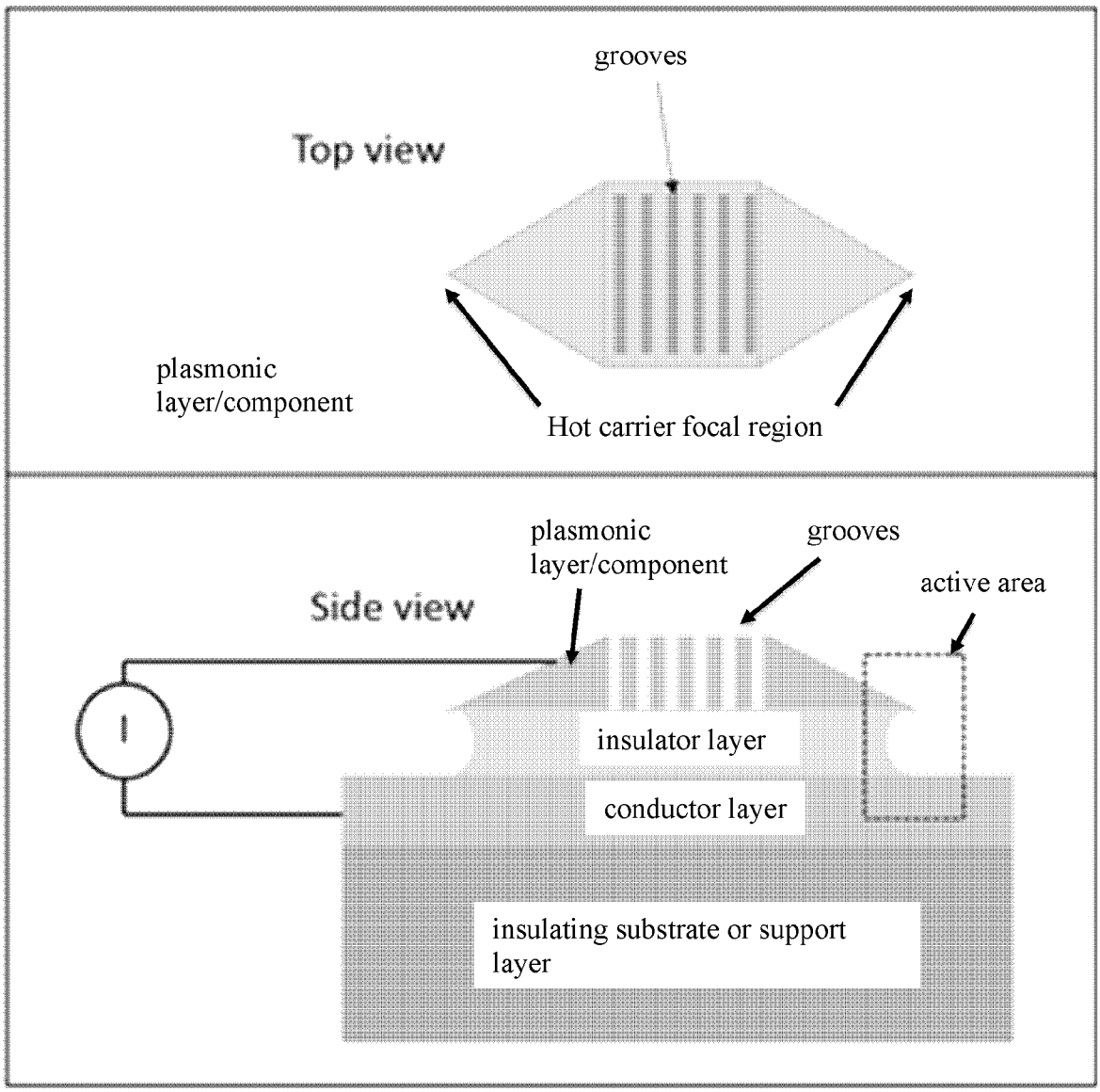

grooves
Top view
plasmonic
layer/component
Hot carrier focal region
plasmonic
layer/component
grooves
active area
Side view
insulator layer
conductor layer
insulating substrate or support
layer

FIG. 1A

FIG. 1B

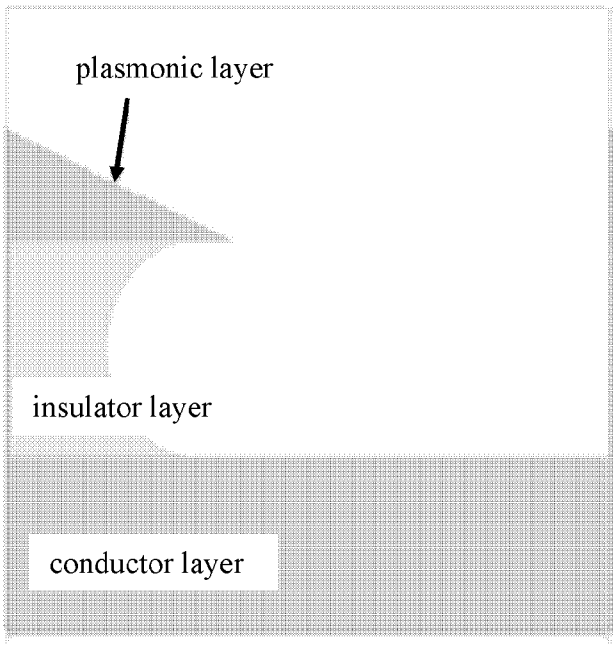
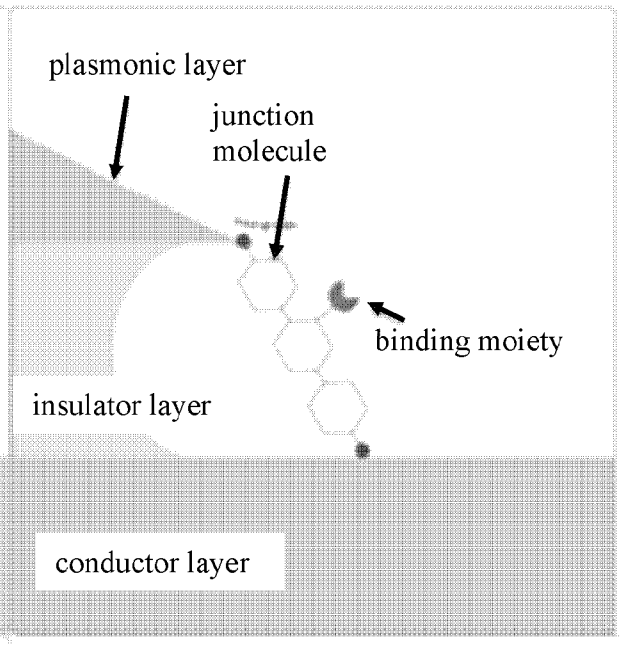


FIG. 1C



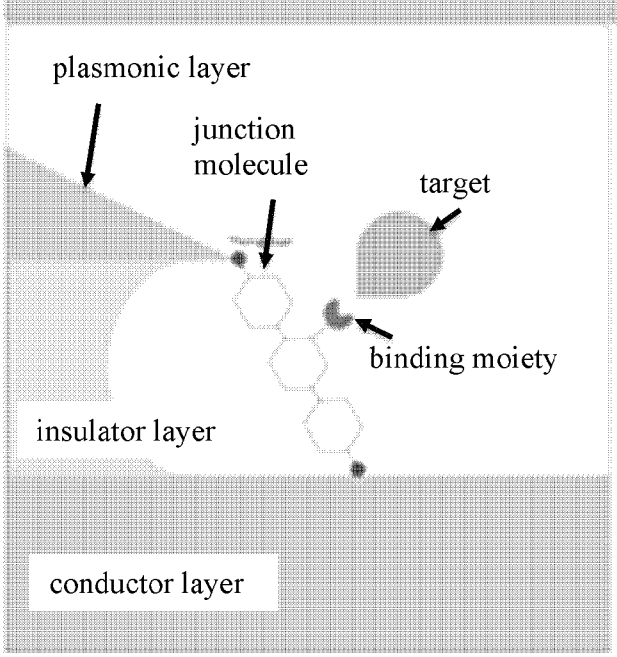


FIG. 1D

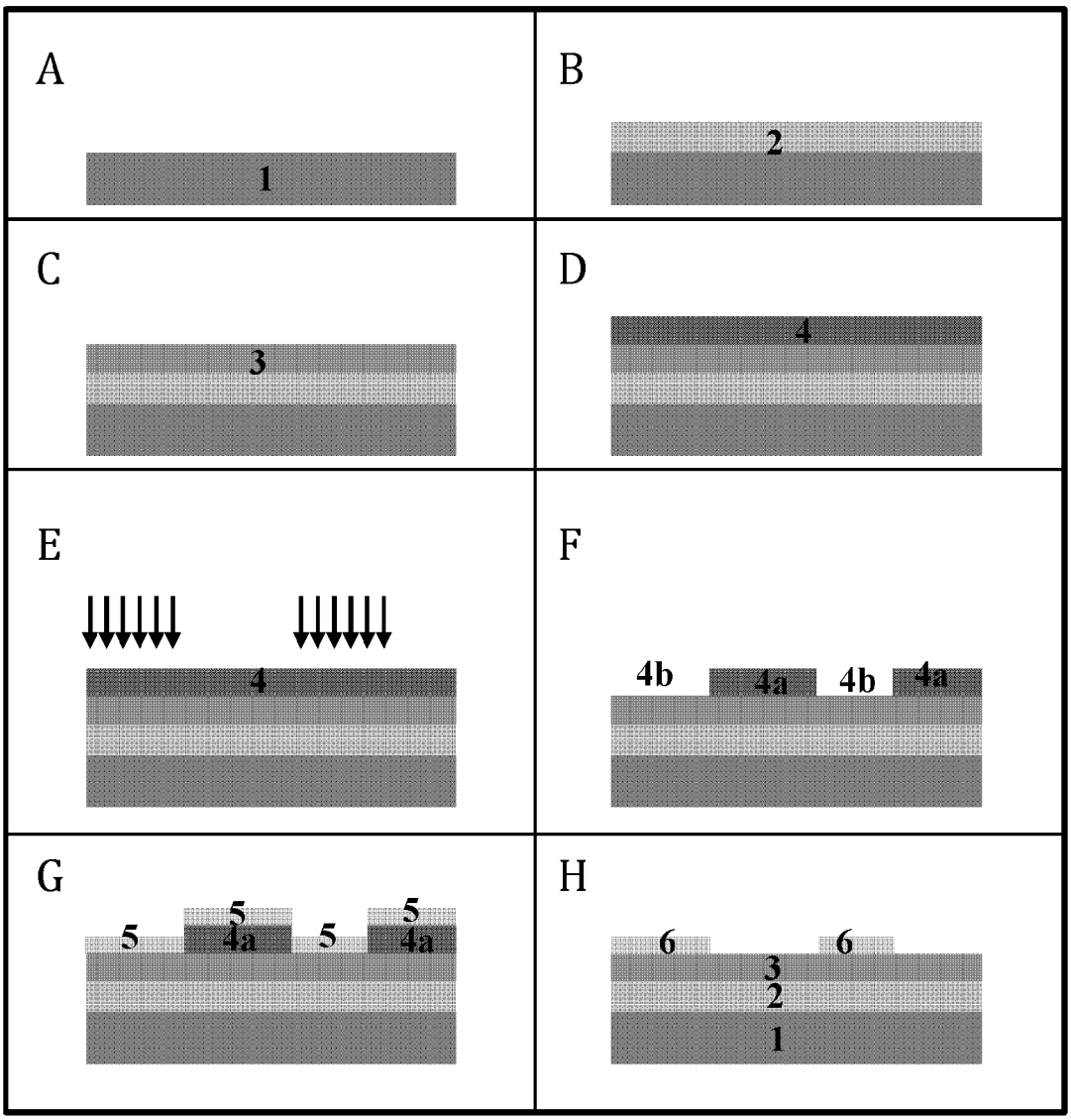


FIG. 2A-H

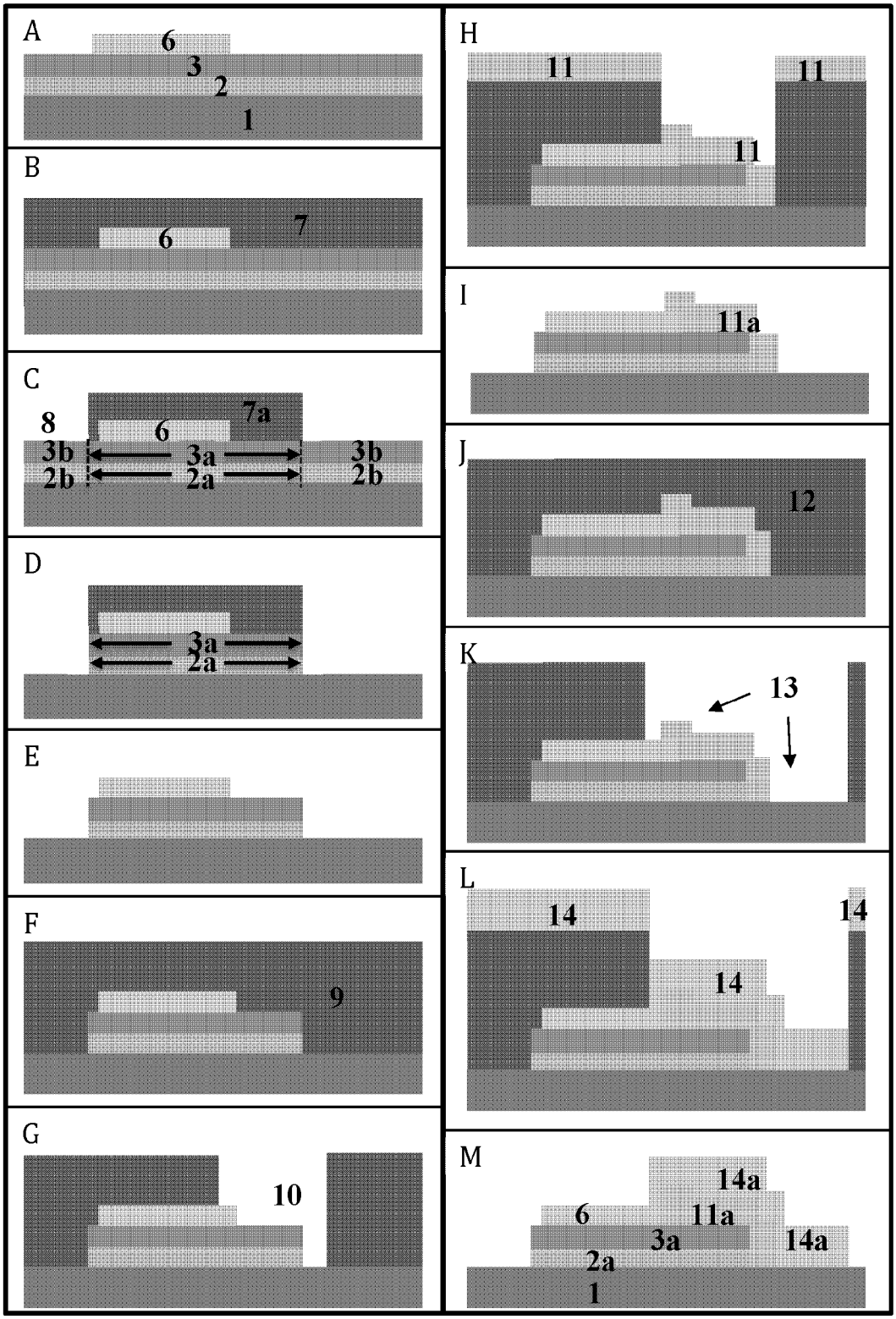

A
6
3
2
1
B
6
7
C
8
7a
6
3b
3a
3b
2b
2a
2b
D
3a
2a
E
F
9
G
10
H
11
11
11
I
11a
J
12
K
13
L
14
14
14
M
14a
6
11a
3a
14a
2a
1

FIG. 3A-M

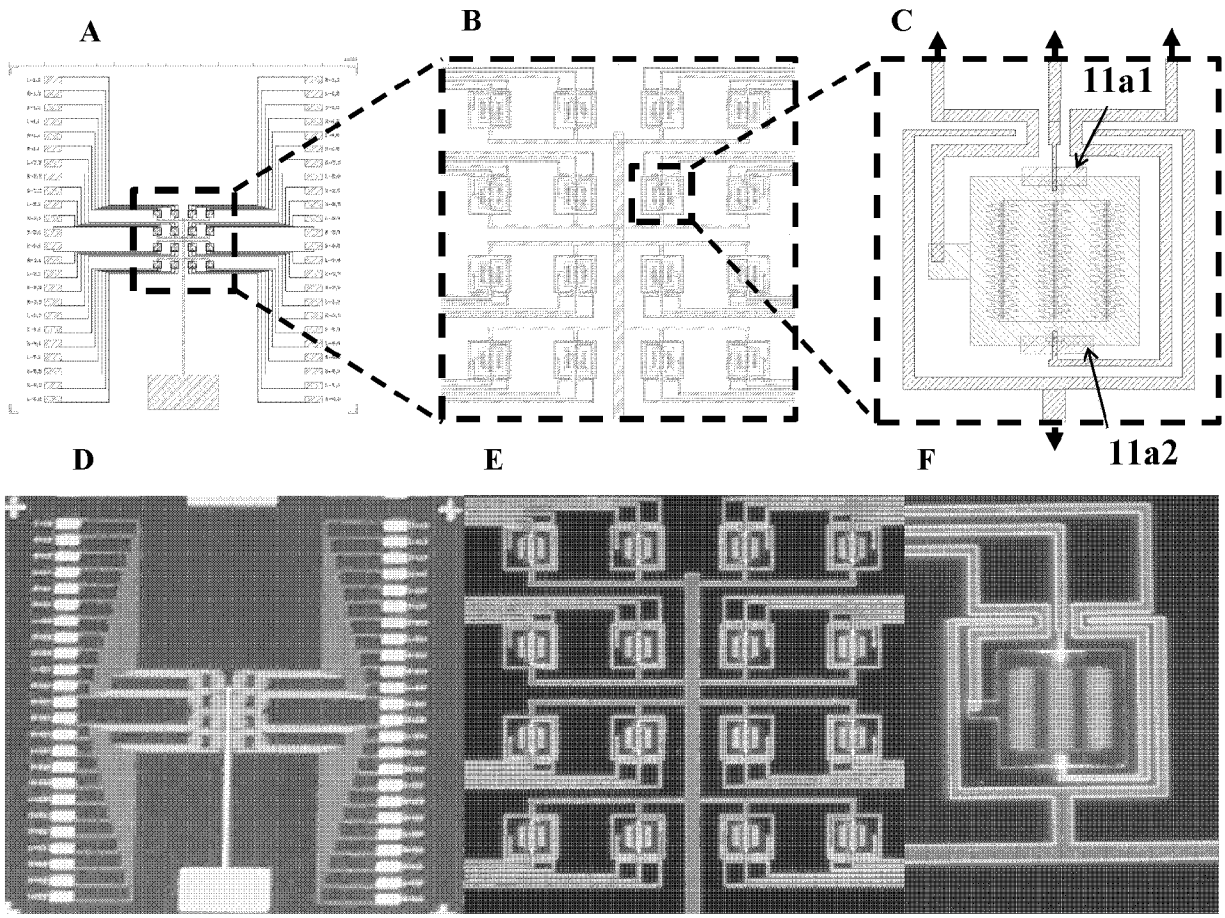


FIG. 4A-F

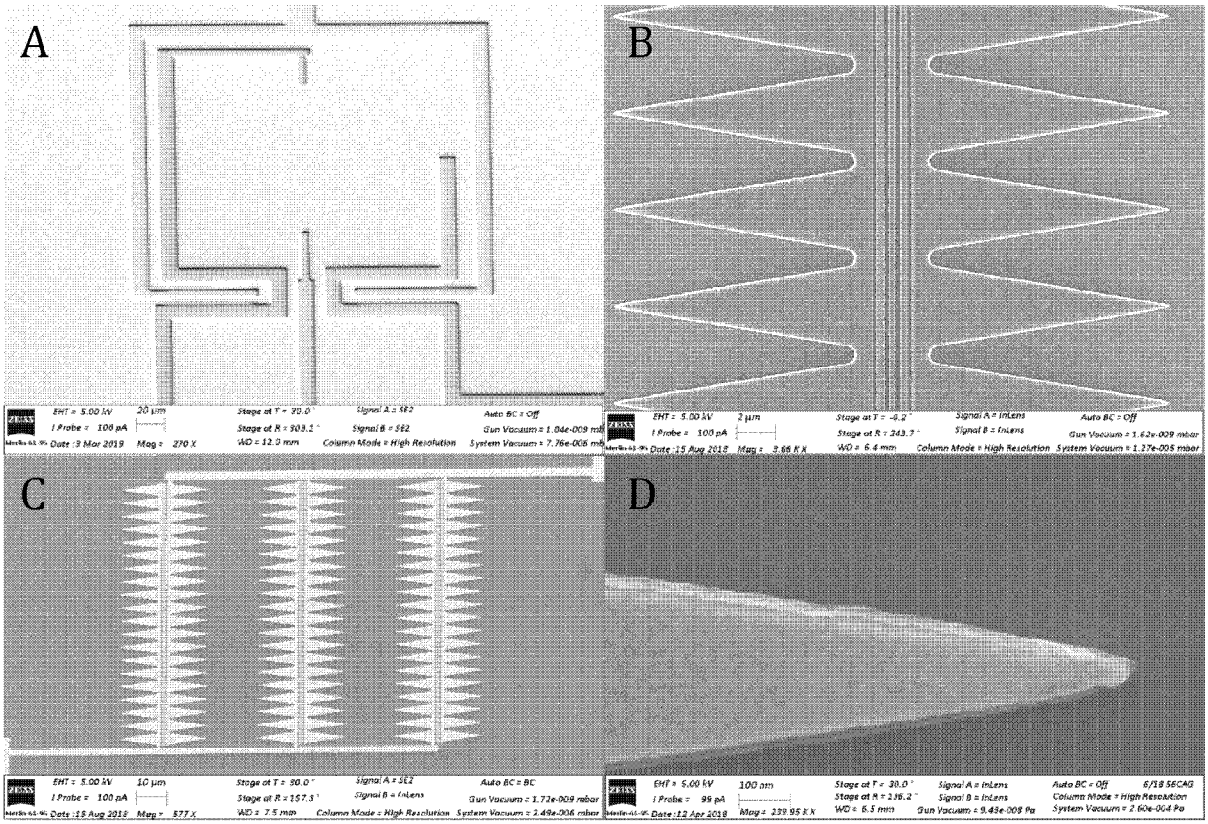


FIG. 5A-D

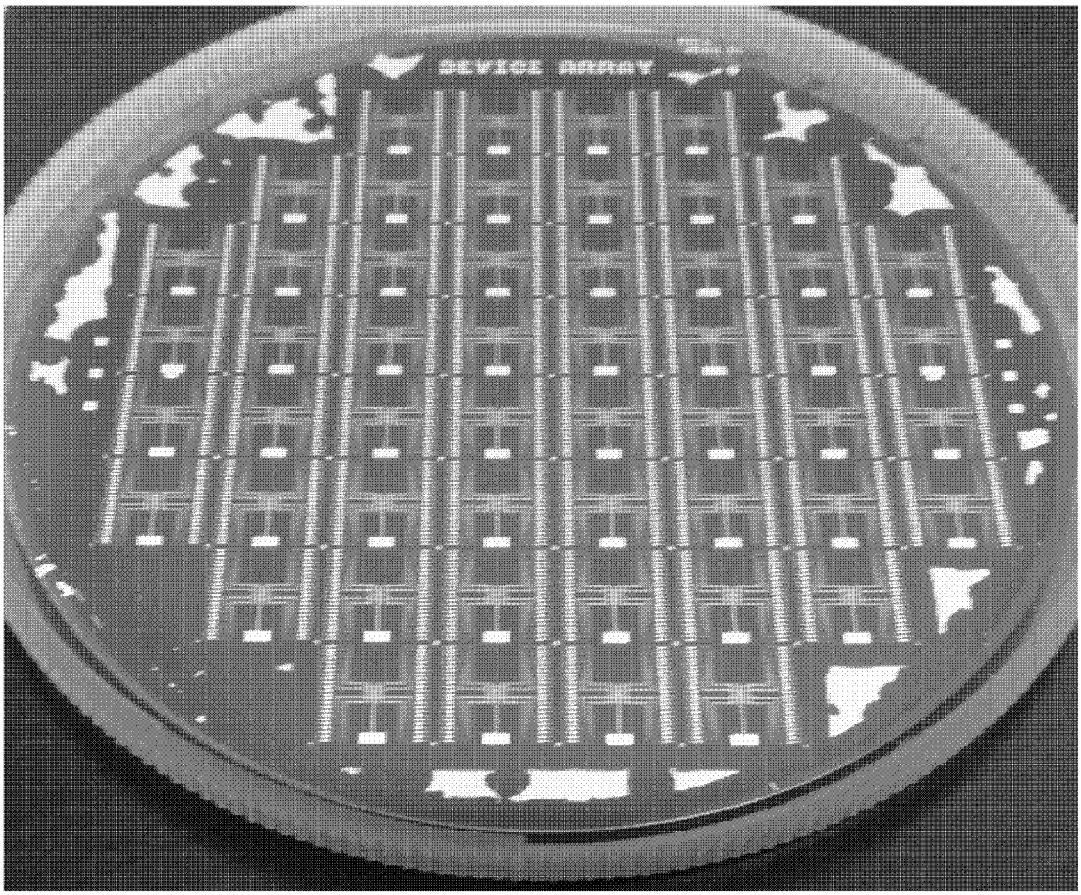


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/059375

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/552 G01N27/12 G01N33/543
ADD.

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

B. FIELDS SEARCHED

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PAWAN TYAGI: "Multilayer edge molecular electronics devices: a review", JOURNAL OF MATERIALS CHEMISTRY, vol. 21, no. 13, 2011, page 4733, XP055654396, GB ISSN: 0959-9428, DOI: 10.1039/c0jm03291c	1,5-20
A	the whole document -----	2-4
A	FUMING WANG ET AL: "Plasmonic Energy Collection through Hot Carrier Extraction", NANO LETTERS, vol. 11, no. 12, 14 December 2011 (2011-12-14), pages 5426-5430, XP055024792, ISSN: 1530-6984, DOI: 10.1021/nl203196z page 5428; figure 4a -----	1-20

☐ 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
19 December 2019	10/01/2020

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