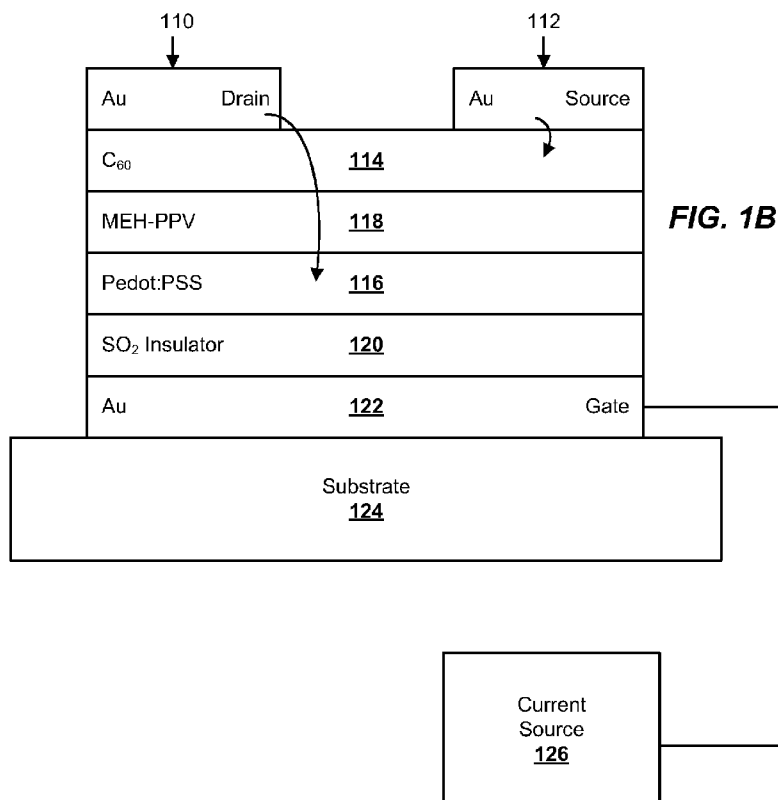




- (51) International Patent Classification:  
*H01L 51/05* (2006.01) *H01L 29/786* (2006.01)
- (21) International Application Number:  
PCT/US2012/026365
- (22) International Filing Date:  
23 February 2012 (23.02.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
61/463,798 23 February 2011 (23.02.2011) US
- (71) Applicant (for all designated States except US): **UNIVERSITY OF UTAH RESEARCH FOUNDATION** [US/US]; 615 Arapen Drive, Suite 310, Salt Lake City, UT 84108 (US).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): **BOEHME, Christoph** [US/US]; 11594 S. Broadview Way, Sandy, UT 84092 (US).
- (74) Agents: **ERICKSEN, Erik, S.** et al.; Thorpe North & Western, LLP, PO Box 1219, Sandy, UT 84091-1219 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,

[Continued on next page]

(54) Title: ORGANIC SPIN TRANSISTOR



(57) Abstract: An organic spin transistor device can include an active stack with an organic material having a spin-dependency (116). The device can include a back contact (122) including an electrical contact electrically coupled to a back of the active stack and a front contact (110, 112) including an electrical contact electrically coupled to a front of the active stack. A pulsed electrical source (126) can be coupled to at least one of the front (110, 112) and back contacts (122) configured to manipulate a spin state of charge carriers in the active stack.

**WO 2013/043225 A1**



---

SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, **Published:**  
GW, ML, MR, NE, SN, TD, TG).

— *with international search report (Art. 21(3))*

## ORGANIC SPIN TRANSISTOR

### **RELATED APPLICATION**

This application claims the benefit of copending U.S. Provisional Patent Application Serial No. 61/463,798, filed February 23, 2011, which is hereby incorporated herein by reference in its entirety.

5

### **GOVERNMENT INTEREST**

This invention was made with government support from the Department of Energy Grant # DESC0000909. The United States government has certain rights to this invention.

### **BACKGROUND**

This present technology relates to electronic devices based on organic semiconducting materials. More specifically, the present technology covers organic spintronic devices relating generally to the fields of electrical engineering, quantum physics, chemistry, materials science, and spintronics.

Spintronic transistors, or spin transistors, are believed to be an improved design on the common transistor invented in the 1940s. The spin transistor exploits the ability of electrons (and other fermions) to naturally exhibit one of two eigenstates of spin: known as "spin up" and "spin down". Unlike conventional transistors which operate on an electric current, spin transistors operate on electrons on a more fundamental level. Spin transistors can use the application of electrons set in particular states of spin to store information.

Spin transistors are magnetically sensitive devices in which electric fields are used to manipulate electron spin states. Manipulation of spin states in these devices can result in manipulation of electric- or spin-currents. Spin transistors have been proposed utilizing low dimensional inorganic semiconductors with strong spin-orbit coupling and ballistic charge and spin transport via delocalized states (e.g. InGaAs/InAlAs quantum wells).

More than two decades have passed since spin transistors were proposed and the potential impact of spin transistors for new, spin-based information technologies and energy saving electronics is great. However, progress on technologically feasible implementations of spin-transistors based on the original device concepts have met with little success since

spin diffusion length, spin lifetimes, and/or electric field controlled spin orbit interactions have not been successfully physically implemented.

## **SUMMARY**

5 An organic spin transistor device in accordance with an example of the present technology can include an active stack with an organic material having electronic transitions with a spin-dependency. The device can include a back contact including an electrical contact electrically coupled to a back of the active stack and a front contact including an electrical contact electrically coupled to a front of the active stack. A pulsed electrical source  
10 can be coupled to at least one of the front and back contacts configured to manipulate a spin state of charge carriers in the active stack.

An organic spin transistor device in accordance with another example of the present technology can include a recombination layer, including a pi-conjugated polymer, and a plurality of injection layers, including at least one injection layer on each side of the  
15 recombination layer for injecting electrons into the recombination layer. A transistor source and a transistor gate can be in contact with one of the plurality of injection layers. An insulating layer can be adjacent to another one of the plurality of injection layers. A transistor gate can be adjacent to the insulating layer on a side of the insulating layer opposite another one of the plurality of injection layers. A pulsed electrical source can be coupled to  
20 the transistor gate and configured to manipulate a spin of the electrons in the recombination layer.

A method of manipulating electron spin in an organic spin transistor device in accordance with an example of the present technology can include applying a voltage across a transistor source and drain, causing an electron injection layer of the organic spin transistor  
25 device to inject charge carriers into a recombination layer comprising an organic material; and pulsing an electric field within the recombination layer using an electric current applied to a transistor gate of the organic spin transistor device to manipulate a spin of the charge carriers in the recombination layer.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

30 FIGs. 1A-1B are block diagrams of organic spin transistor devices in accordance with examples of the present technology;

FIG. 1C is a band diagram for the device of FIG. 1A;

FIGs. 2A-2C illustrate electrical control of spin-exchange within polaron pairs in an organic spin transistor device in accordance with an example of the present technology;

FIG. 3 is a flow diagram of a method of manipulating electron spin in an organic spin transistor device in accordance with an example of the present technology; and

FIG. 4 is a flow diagram of a method of manufacturing an organic spin transistor device in accordance with an example of the present technology.

### **DETAILED DESCRIPTION**

Reference will now be made to the exemplary embodiments illustrated, and specific language will be used herein to describe the same. It will nevertheless be understood that no limitation of the scope of the technology is thereby intended. Additional features and advantages of the technology will be apparent from the detailed description which follows, taken in conjunction with the accompanying drawings, which together illustrate, by way of example, features of the technology.

As used herein, “electrically coupled” refers to a relationship between structures that allows electrical current to flow at least partially between them. This definition is intended to include aspects where the structures are in physical contact and those aspects where the structures are not in physical contact. Typically, two materials which are electrically coupled can have an electrical potential or actual current between the two materials. For example, two plates physically connected together by a resistor are in physical contact, and thus allow electrical current to flow between them. Conversely, two plates separated by a dielectric material are not in physical contact, but, when connected to an alternating current source, allow electrical current to flow between them by capacitive means. Moreover, depending on the insulative nature of the dielectric material, electrons may be allowed to bore through, or jump across the dielectric material when enough energy is applied.

As used herein, “adjacent” refers to near or close sufficient to achieve a desired effect. Although direct physical contact is most common in the structures or volumes of the present invention, adjacent can broadly allow for spaced apart features.

As used herein, the term “substantially” refers to the complete or nearly complete extent or degree of an action, characteristic, property, state, structure, item, or result. The exact allowable degree of deviation from absolute completeness may in some cases depend

on the specific context. However, generally speaking the nearness of completion will be so as to have the same overall result as if absolute and total completion were obtained. The use of "substantially" is equally applicable when used in a negative connotation to refer to the complete or near complete lack of an action, characteristic, property, state, structure, item, or result. For example, a composition that is "substantially free of" particles would either completely lack particles, or so nearly completely lack particles that the effect would be the same as if it completely lacked particles. In other words, a composition that is "substantially free of" an ingredient or element may still actually contain such item as long as there is no measurable effect on the property of interest thereof.

As used herein, the term "about" is used to provide flexibility to a numerical range endpoint by providing that a given value may be "a little above" or "a little below" the endpoint with a degree of flexibility as would be generally recognized by those skilled in the art. Further, the term about explicitly includes the exact endpoint, unless specifically stated otherwise.

As used herein, a plurality of items, structural elements, compositional elements, and/or materials may be presented in a common list for convenience. However, these lists should be construed as though each member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a de facto equivalent of any other member of the same list solely based on their presentation in a common group without indications to the contrary.

Concentrations, amounts, and other numerical data may be expressed or presented herein in a range format. It is to be understood that such a range format is used merely for convenience and brevity and thus should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. As an illustration, a numerical range of "about 1 to about 5" should be interpreted to include not only the explicitly recited values of about 1 to about 5, but also include individual values and sub-ranges within the indicated range. Thus, included in this numerical range are individual values such as 2, 3, and 4 and sub-ranges such as from 1-3, from 2-4, and from 3-5, etc., as well as 1, 2, 3, 4, and 5, individually. This same principle applies to ranges reciting only one numerical value as a

minimum or a maximum. Furthermore, such an interpretation can apply regardless of the breadth of the range or the characteristics being described.

Reference will now be made to the exemplary embodiments illustrated, and specific language will be used herein to describe the same. It will nevertheless be understood that no  
5 limitation of the scope of the technology is thereby intended. Additional features and advantages of the technology will be apparent from the detailed description which follows, taken in conjunction with the accompanying drawings, which together illustrate, by way of example, features of the technology.

With the general examples set forth in the Summary above, it is noted in the present  
10 disclosure that when describing the system, or the related devices or methods, individual or separate descriptions are considered applicable to one other, whether or not explicitly discussed in the context of a particular example or embodiment. For example, in discussing an organic spin transistor device per se, other device, system, and/or method embodiments are also included in such discussions, and vice versa.

15 Furthermore, various modifications and combinations can be derived from the present disclosure and illustrations, and as such, the following figures should not be considered limiting.

An organic spin transistor device is described in accordance with an example of the present technology. The device can include an active stack with an organic material having a  
20 spin-dependency. The device can include a back contact including an electrical contact electrically coupled to a back of the active stack and a front contact including an electrical contact electrically coupled to a front of the active stack. A pulsed electrical source can be coupled to at least one of the front and back contacts configured to manipulate a spin state of charge carriers in the active stack.

25 The spin transistor device can have electronic and spintronic characteristics which are similar to existing (but still not technically feasible) spin transistor concepts, but with working principles departing radically from existing approaches.

The manipulation of spin-states via electric fields in weakly spin-orbital coupled systems can be implemented by a gate controlled exchange interaction on excitonic precursor  
30 pairs, or so-called "polaron pairs." The spin device can operate solely due to spin permutation symmetry, not spin polarization, and is therefore be suitable for room temperature

spintronics. It is noted that use of significant spin polarization is not currently feasible at room temperatures.

The organic spin transistor device opens avenues for organic electronics and spintronics and thus, for the currently very strongly evolving field of organic spintronics. The organic spin transistor device can enable new sensor technologies and new organic microelectronic circuitry, as well as organic quantum information devices.

Experimental use of the technology demonstrates that spin dependent processes exist in an organic semiconductor (such as, MEH-PPV). As an example application, these transitions have been used to experimentally measure magnetic fields in the kGauss range, and also for field sensing in the range 10-3500 Gauss (1 Gauss is approximately the Earth's magnetic field).

The spin of an electron or charge carrier has many properties of an angular momentum intrinsic to the electron that is separate from the angular momentum due to its orbital motion. The electron's spin is  $1/2\hbar$ , implying that the electron acts as a Fermion, where  $\hbar$  represents the reduced Planck constant.

Similar to orbital angular momentum, the spin has an associated magnetic moment, the magnitude of which is expressed as the Bohr magneton  $\mu_B$ .

In a solid the spin of many electrons can act together to affect the magnetic and electronic properties of a material, for example endowing a material with a permanent magnetic moment as in a ferromagnet.

In many materials, electron spins are approximately equally present in both the up and the down state, and no effect due to polarization dependent observables is possible. A spintronic device typically involves generation or manipulation of a spin-polarized population of electrons, or a population in which there is an excess of spin up or spin down electrons.

The polarization can be written as

$$P_X = \frac{X_{\uparrow} - X_{\downarrow}}{X_{\uparrow} + X_{\downarrow}}$$

with  $X_{\uparrow}$  and  $X_{\downarrow}$  denoting the population of spin up and down, respectively.

A net spin polarization can be achieved either through creating a very large energy splitting between spin up and spin down such as putting a material in a large magnetic field (Zeeman effect) or through exchange interaction as it is the case for ferromagnets; or by



forcing the system out of equilibrium. The period of time that such a non-equilibrium population can be maintained is known as the spin relaxation time, or lifetime,  $\tau$ .

$\pi$ -conjugated polymers (also referred to herein as  $\pi$ -conjugated polymers or PCPs) have utility for potential applications such as organic light-emitting devices, organic field-effect transistors, and organic photovoltaic (OPV) devices (a.k.a. organic solar cells). Upon excitation of PCPs, excitons (tightly bound intrachain electron-hole pairs) are usually formed. Dissociation of the generated excitons is facilitated by energy differences between a donor material (the PCP) and an acceptor material (the fullerene). Initially each exciton separates into a loosely-bound polaron pair (PP), an intermediate species that exists at the donor/acceptor interface. Subsequently, some of the PP species separate into “free” electrons and holes that are available for transport. In the blend, the PCP acts as electron donor and hole transporter, whereas the fullerene derivative is an electron acceptor and hole transporter. Thus, the generated holes and electrons can be readily collected at the anode and cathode, respectively. However, if recombination of either the exciton or polaron pair occurs prior to dissociation, there is no contribution to the electrical current.

Similar to inorganic spin transistors, organic spin transistors allow the control of spin-states via electric fields and the control of electric current by electron spin states. However, in contrast to inorganic spin transistors, organic spin transistors are based on spin-dependent transport and recombination processes between localized states in low spin orbit coupled semiconductor materials. The spin states which control current are not polarization states but spin-pair permutation symmetry. The organic spin transistor devices therefore can work even at room temperature where spin polarization is vanishingly small. The spin transistor concept used here is based on an organic bipolar field effect transistor, also referred to herein as an “organic light emitting transistor” (OLET) due to the light emission of recombining charge carriers that occurs under operation conditions. In organic materials, exciton recombination significantly controls the current in OLETs, which in turn, due to spin selection rules, strongly depends on the spin state of the recombining charge carriers. Thus, manipulating the spin-state by application of electric fields can enable the manipulation of the device’s current. A controlled, non-adiabatic exchange interaction between two electron spin states is able to manipulate the spin pair state in a similarly defined manner as magnetic resonance. This concept is applied within this device for the control of electric fields, and, therefore, electric current control in an OLET structure.

Referring to FIG. 1A, a simplified schematic of an organic spin transistor device is illustrated in accordance with an example of the present technology. An OLET is used consisting of two contacts (drain 110 and source 112) and two injection layers 114, 116 for electron and hole polaron injection as well as a recombination layer 118 in between the injection layers. The device consists further of an insulating layer 120 and a gate electrode layer 122 for the electric field control. Under operating conditions (no external magnetic field, room temperature), the spin statistics of recombining charge carriers will be random and due to the longer lifetime of triplet states, high triplet densities of excitonic precursor pairs (so called polaron pairs, PPs) will form due to the longer lifetimes of spin-triplet states compared to the singlet states. The device current is influenced by the ratio of the numbers of PPs which eventually recombine via excitonic states and those which dissociate into unbound charge carriers before they recombine. Thus, manipulation of the spin pairs via electric field induced exchange can govern the ratio of spin states (singlet to triplet) and, therefore, the net device current.

In one example, OLET structures may be based on the pi-conjugated conducting material poly[2-methoxy-5-(20-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) 118, using Fullerene C<sub>60</sub> 114 and poly(3,4-ethylenedioxythiophene) (PEDOT) 116 as electron and hole injectors, respectively. Electric channel current can be controlled by electric field induced spin exchange interaction within PPs. For the verification that current control takes place through *J*-coupling induced spin control (and not through conventional electrostatic fields), an electrically detected spin measurement scheme can be employed which has shown to be viable in the past for pulsed electrically detected magnetic resonance spectroscopy. *J* is a spin exchange parameter which is described briefly in more detail below and which is understood in the art.

The spin transistor can include one or more injection layers 114, 116 in the active stack for charge injection into the active stack. The injection layer can be a plurality of injection layers, such as the C<sub>60</sub> and PEDOT (or PEDOT:PSS) layers described above, in the active stack between the front and back contacts and on either side of the organic material for charge injection into the active stack. The example materials provided here are intended to be non-limiting and a variety of other material may also be suitable. For example, Calcium, Barium, and Strontium are non-limiting example materials which may be used in place of the described C<sub>60</sub> material. Gold (Au) is a non-limiting example material which may be used in

place of the PEDOT material. Various other materials may also be used. The materials can be selected to include injection layers with low and high work functions, respectively.

Suitable work function criteria of the injection material can be relative and may depend on the adjacent pi-conjugated polymer selected for the organic layer. For example, C<sub>60</sub> and

PEDOT work well with MEH-PPV. For the electron injector material, a work function of the material can be sufficient to produce a Fermi level close to, at or slightly above a LUMO (lowest unoccupied molecular orbital) level of the pi-conjugated polymer. For the hole injector material, a work function of the material can be sufficient to produce a Fermi level close to, at or slightly below a HOMO (highest occupied molecular orbital) level of the pi-conjugated polymer. The Fermi energies of the injection contacts can be considered to be “sufficiently close” to the HOMO and LUMO levels, when sufficient holes and electrons, respectively, are injected into the material such that the respective species is a majority carrier within the respective injection region.

The organic material in the device can comprise an organic layer 118. Perturbation of the organic layer can modify at least one of conductivity or luminescence of the organic material as a result of the spin-dependence. The organic material can include at least one of polyphenylenevinylene (PPV), polythiophene, polyfluorene-vinylene (PFV), polyfluorene (PFO), polyacetylene, polypyrrole, polyaniline, cyano-polyphenylene vinylene (CN-PPV), polyphenylene ethynylene (PPE), poly(2,5 pyridine), poly(3,5 pyridine), poly(2,5-bis(3-sulfonatopropoxy)-1,4-phenylene, disodium salt-alt-1,4-phenylene) (PPP), hydrocarbon molecules, porphyrin, and phthalocyanine. In one specific aspect, the organic material can comprise poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV). The thickness of the organic layer can be tailored to maximize or create a change in current sufficient to be measurable. However, as a general guideline, the thickness can range from about 1 nm to about 100,000 nm, and in some cases from about 20 nm to about 200 nm.

The injection layers and/or organic layer or layers can consist of one of, or more than one of, or blends of organic polymers or molecules. These include, but are not limited to, the following materials or materials which include derivatives thereof:

Polyphenylenevinylene (PPV) or derivatives or related materials such as: MDMO-PPV: Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene], MEH-PPV: Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], PSS PPV-co-MEH PPV: [(C<sub>40</sub>H<sub>76</sub>O<sub>14</sub>Si<sub>8</sub>)<sub>x</sub>(C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>)<sub>y</sub>], Poly(1-methoxy-4-(O-disperse Red 1))-2,5-phenylenevinylene,

BTEM-PPV: [Poly[2,5-bis(triethoxymethoxy)-1,4-phenylene vinylene], Poly(2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,4-phenylenevinylene)], Poly(2,5-dihexyloxy-1,4-phenylenevinylene), Poly(2,6-naphthalenevinylene), Poly[(m-phenylenevinylene)-alt-(2,5-dihexyloxy-p-phenylenevinylene)], Poly[1-methoxy-4-(3-propyloxy-heptaisobutyl-PSS)-2,5-phenylenevinylene], Poly[2,5-bis(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene], Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], and PTDPV: Poly[tris(2,5-bis(hexyloxy)-1,4-phenylenevinylene)-alt-(1,3-phenylenevinylene)].

Polythiophene or derivatives or related materials such as: P3BT: Poly(3-butylthiophene-2,5-diyl), P<sub>3</sub>C<sub>4</sub>MT: Poly(3-cyclohexyl-4-methylthiophene-2,5-diyl), P<sub>3</sub>CHT: Poly(3-cyclohexylthiophene-2,5-diyl), Poly(3-decyloxythiophene-2,5-diyl), P3HT: Poly(3-hexylthiophene-2,5-diyl), P3OT: Poly(3-octylthiophene-2,5-diyl), POT-co-DOT: Poly(3-octylthiophene-2,5-diyl-co-3-decyloxythiophene-2,5-diyl), Poly(thiophene-2,5-diyl), PODT: Poly[(2,5-didecyloxy-1,4-phenylene)-alt-(2,5-thienylene)], EDOT: 3,4-Ethylenedioxythiophene, and PEDOT: Poly(3,4-ethylenedioxythiophene).

Polyfluorene-Vinylene (PFV) or derivatives or related materials such as: PFV: Poly(9,9-di-(2-ethylhexyl)-9H-fluorene-2,7-vinylene).

Polyfluorene (PFO) or derivatives or related materials such as: Poly(9,9-di-n-dodecylfluorenyl-2,7-diyl), Poly(9,9-n-dihexyl-2,7-fluorene-alt-9-phenyl-3,6-carbazole), and Poly[9,9-di-(2'-ethylhexyl)fluorenyl-2,7-diyl]. Polyacetylene or derivatives or related

materials. Polypyrrole or derivatives or related materials such as: 1H-Pyrrole-1-propionic acid and EDOP: 3,4-Ethylenedioxyppyrrrole. Polyanilines or derivatives or related materials such as: Camphor-10-sulfonic acid ( $\beta$ ). Cyano-Polyphenylene vinylene (CN-PPV) or derivatives or related materials such as: Poly(2,5-di(hexyloxy)cyanoterephthalylidene), Poly(2,5-di(octyloxy)cyanoterephthalylidene), and Poly(5-(2-ethylhexyloxy)-2-methoxy-cyanoterephthalylidene). Poly(phenylene ethynylene) (PPE) or derivatives or related materials such as: Poly(2,5-di(3',7'-dimethyloctyl)phenylene-1,4-ethynylene), Poly(2,5-dicyclohexylphenylene-1,4-ethynylene), Poly(2,5-di(2'-ethylhexyl)-1,4-ethynylene), Poly(2,5-didodecylphenylene-1,4-ethynylene), and Poly(2,5-dioctylphenylene-1,4-ethynylene). Poly(2,5 pyridine) or Poly(3,5 pyridine) ) or derivatives or related materials.

Poly(fluorenylene ethynylene) (PFE) or derivatives or related materials such as: Poly(9,9-dioctylfluorenyl-2,7-yleneethynylene), Poly[9,9-di(2'-ethylhexyl)fluorene-2,7-yleneethynylene] and Poly[9,9-didodecylfluorenyl-2,7-yleneethynylene]. Poly(2,5-bis(3-

sulfonatopropoxy)-1,4-phenylene, disodium salt-*alt*-1,4-phenylene) (PPP) or other water soluble polymers. Hydrocarbon molecules, such as: Alq<sub>3</sub>: Tris-(8-hydroxyquinoline)aluminium, Ir(piq)<sub>3</sub>: Tris[1-phenylisoquinoline-C2,N]iridium(III), Tris(benzoylacetato) mono(phenanthroline)europium(III), Tris(2,2'-bipyridyl-d8)ruthenium(II) hexafluorophosphate, Rubrene: 5,6,11,12-Tetraphenylnaphthacene, Perylene, Anthracene, Benz[*b*]anthracene, Coumarin 6: 3-(2-Benzothiazolyl)-7-(diethylamino)coumarin, 3-(2-Benzothiazolyl)-*N,N*-diethylumbelliferylamine, TDAB: 1,3,5-Tris(diphenylamino)benzene, TECEB: 1,3,5-Tris(2-(9-ethylcabazyl-3)ethylene)benzene, mCP: 1,3-Bis(N-carbazolyl)benzene, 1,4-Bis(diphenylamino)benzene, CBP: 4,4'-Bis(*N*-carbazolyl)-1,1'-biphenyl, PCBM: [6,6]-Phenyl C<sub>61</sub> butyric acid methyl ester, PCBB: Phenyl-C<sub>61</sub>-Butyric-Acid-Butyl Ester, PCBO: Phenyl-C<sub>61</sub>-Butyric-Acid-Octyl Ester, ThCBM: Thienyl-C<sub>61</sub>-Butyric-Acid-Methyl Ester, and d5-PCBM: Pentadeuterophenyl-C<sub>61</sub>-Butyric-Acid-Methyl Ester. Porphyrin or derivatives or related materials such as: PtOEP: Platinum octaethylporphyrin and H<sub>2</sub>TPP: Tetraphenylporphyrin. Phthalocyanine or derivatives or related materials such as: Copper phthalocyanine, Lead phthalocyanine, Silicon phthalocyanine, 2,3-Naphthalocyanine and Aluminum 2,3-naphthalocyanine chloride.

The device can include an insulator 120 between the front contact (i.e., the drain 110 and source 112) and the back contact (i.e., the gate 122). The insulator can be configured to substantially prevent electrical shorts between the front contact and back contact. The insulating layer can be fabricated of any insulating material compatible with the fabrication method used. For example, silicon dioxide, silicon nitride, other ceramics, plastics, composites, or the like can be suitable.

The front and back contacts may comprise any suitable conductive material. Non-limiting examples of suitable contact materials can include metals, composites thereof, conductive polymers, and the like. Specific non-limiting examples of such materials can include copper, gold, silver, indium tin oxide (ITO), polythiophenes, polyphenylene sulfide, polyphenylene vinylene, polyacetylenes, composites thereof, and combinations thereof. The back contact can be formed adjacent to an optional substrate, the active stack can be formed on top of the back contact, and the front contact can be formed on top of the active stack. The contact layers can be any material with a sufficiently high conductivity to provide current flow to and from the active stack.

The front and/or back contacts may comprise a transparent conductive material. The front and/or back injection layers may comprise at least one blend of organic polymers or molecules. The organic material layer may comprise a plurality of different organic materials. The front and back injection layers may comprise different organic materials.

5 The spin-dependency of the organic material can include all or at least one of: polaron pair recombination or dissociation, triplet-triplet annihilation, triplet-polaron recombination or annihilation, polaron-polaron spin blockade, and triplet-trion recombination.

FIG. 1B is a block diagram of an organic spin transistor device similar to the device of FIG. 1A, further including a substrate 124 upon which the spin transistor stack is formed and an electric current source 126 electrically coupled to the gate 122.

10 The substrate may be any material which a device can be fabricated on and which has the desired mechanical integrity for a given application. The substrate may be rigid or flexible. Non-limiting examples of such materials include metal, semiconductors such as silicon, plastic or glass. Additionally specific, but non-limiting examples of suitable substrates include glass, silicon, silicon dioxide, germanium, gallium arsenide, indium phosphide, aluminum oxide, alloys thereof, and composites thereof. Typically, the substrate can be electrically non-conductive or a semiconductor.

FIG. 1C is a band diagram of an organic spin transistor device illustrating electron energy in the various layers of the device. Electric current of the device is controlled by a spin-dependent polaron pair recombination rate in the recombination layer (MEH-PPV). C<sub>60</sub> and PEDOT:PSS represent materials used in the injection layers described above.

20 FIGs. 2A-2C illustrate the electric field induced spin manipulation. In absence of electric fields (FIG. 2A), PPs (+, -) are weakly spin exchange coupled due to localized electronic states on different polymer chains 205. Once a strong electric field  $E$  is applied, approximately one half of the PPs will dissociate due to their random orientation against the electric field (FIG. 2B). The other approximately one half of the PPs will experience increased exchange interaction (FIG. 2C) which will lead to a switch of the permutation symmetry as long as the electric field is applied non-adiabatically (i.e., abruptly or in pulses).

25 In FIGs. 2A-2C,  $J$  is a spin exchange parameter.  $J$  involves the exchange interaction, which is due to electric repulsion and the Pauli exclusion principle. In general, the direct magnetic interaction between a pair of electrons (due to their magnetic moments) is negligibly small compared to this electric interaction. Normally, exchange interactions are

very short-ranged, confined to electrons in orbitals on the same atom (intra-atomic exchange) or nearest neighbor atoms (direct exchange) but longer-ranged interactions can occur via intermediary atoms.

Referring to FIG. 3, a flow diagram of a method 300 of manipulating electron spin in an organic spin transistor device, such as an electrical field controlled bipolar transistor for example, is illustrated in accordance with an example of the present technology. The method can be performed, for example, at room temperature. The method can include applying 310 a voltage across a transistor source and drain, causing an electron injection layer of the organic spin transistor device to inject charge carriers into a recombination layer comprising an organic material; and pulsing 320 an electric field within the recombination layer using an electric current applied to a transistor gate of the organic spin transistor device to manipulate a spin of the charge carriers in the recombination layer according to spin permutation symmetry. Pulsing the electric field may comprise non-adiabatically applying the electric current.

According to the method, pulsing the electric field to manipulate the spin of the charge carriers may include pulsing the electrical field to govern a ratio of spin states of spin pairs to induce electrical current through the organic spin transistor device. Pulsing the electric field dissociates polaron pairs of approximately one half of the charge carriers and increases exchange interaction with another approximately one half of the charge carriers, as has been described above. The strength of the electric field can be sufficiently high such that a sufficiently high exchange interaction is established as described above. These high fields are expected to occur above field of 1000V/cm but may need to be as high as  $10^6 - 10^7$  V/cm, depending on the materials.

FIG. 4 includes a flow diagram of a method 400 for fabricating an organic spin transistor in accordance with an embodiment of the present technology. The method can include depositing 410 a back contact comprising an electrical contact. The method can also include depositing 420 an active stack comprising an organic material having a spin-dependence, such that a back of the active stack is electrically coupled to the back contact. A front contact can be deposited 430 comprising an electrical contact such that the front contact is electrically coupled to a front of the active stack. The steps of depositing can be performed using any suitable approach. For example, lithography is currently a very effective approach, although other techniques can be used such as, but not limited to, patterned deposition (ink jet

printing and other additive processes), and the like. Lithographic fabrication of the sensor can be at the nanoscale or at larger scales. Lithographic fabrication techniques are known and are not specifically described here. Size or scale of lithographic fabrication of the sensors is practically limited by limits of lithography.

5           The method can further include encapsulating the organic materials to limit degradation.

          The organic spin transistors described establish the foundations for fundamentally new electronic and spintronic device concepts. These devices may become elements for future spintronic circuitry, especially for the currently strongly emerging organic spintronic concepts. Direct, short to intermediate term technological impact is expected on applications such as sensor technologies, mechanically flexible, low cost microelectronics or organic light emitting and organic photovoltaic devices. Furthermore, the ability to electrically control spin pairs of polaron states in organic semiconductors will allow for similar spin quantum bit manipulation experiments that have recently been demonstrated for quantum dots. In contrast to these experiments, the proposed PP systems will allow for these experiments at room temperature. In the long term, the organic spin transistor devices may also be significant for technical concepts of organic room temperature quantum information concepts. Electron spins in organic semiconductors can have extremely long spin coherence times. With the gate voltage induced technique for coherent spin control and detection as described herein, systems can be used for spintronic or quantum information applications.

          The spin transistor described herein and its electrical connections can be designed to be placeable in a pulsed microwave resonator without perturbing the field modes for magnetic resonance experiments. The device is feasible as an organic field effect transistor in which gate voltage controlled drain-source current can be measured as a function of voltage characteristics. The device is feasible as an electric field controlled bipolar transistor by the detection of electroluminescence.

          Pulsed electrically detected magnetic resonance spectroscopy can be carried out as verification method for the electric field induced spin-exchange interaction. This method is a state of the art, highly sensitive coherent spectroscopy which allows the direct measurement of spin-exchange interaction which influences electric currents through spin-selection rules.

          A benefit of the organic spin transistors described herein over regular transistors is that spin states can be detected and altered without necessarily requiring the application of an



electric current. This allows for detection hardware (such as hard drive heads) that are much smaller but even more sensitive than today's devices, which rely on noisy amplifiers to detect the minute charges used on today's data storage devices. One potential end result is devices that can store more data in less space and consume less power, using less costly materials.

- 5 The increased sensitivity of spin transistors is also being used in creating more sensitive automotive sensors, a move being encouraged by a push for more environmentally-friendly vehicles.

Another benefit of a spin transistor is that the spin of an electron is semi-permanent and can be used as means of creating cost-effective non-volatile solid state storage that does not require the constant application of current to sustain. As a result, organic spin transistors may also be useable for Magnetic Random Access Memory (MRAM).

10

While the forgoing examples are illustrative of the principles of the present technology in one or more particular applications, it will be apparent to those of ordinary skill in the art that numerous modifications in form, usage and details of implementation can be made without the exercise of inventive faculty, and without departing from the principles and concepts of the technology. Accordingly, it is not intended that the technology be limited, except as by the claims set forth below.

15

**CLAIMS**

1. An organic spin transistor device, comprising:  
an active stack comprising an organic material having a spin-dependency;  
a back contact comprising an electrical contact electrically coupled to a back  
5 of the active stack;  
a front contact comprising an electrical contact electrically coupled to a front  
of the active stack; and  
a pulsed electrical source coupled to at least one of the front and back contacts  
configured to manipulate a spin state of charge carriers in the active stack.

2. The device of claim 1, wherein the organic material comprises a pi-conjugated  
polymer.

3. The device of claim 1, wherein the organic material comprises at least one of  
15 polyphenylenevinylene (PPV), polythiophene, polyfluorene-vinylene (PFV), polyfluorene  
(PFO), polyacetylene, polypyrrole, polyaniline, cyano-polyphenylene vinylene (CN-PPV),  
polyphenylene ethynylene (PPE), poly(2,5 pyridine), poly(3,5 pyridine), poly(2,5-bis(3-  
sulfonatopropoxy)-1,4-phenylene,disodium salt-alt-1,4-phenylene) (PPP), hydrocarbon  
molecules, porphyrin, and phthalocyanine.

4. The device of claim 1, wherein the organic material comprises poly[2-  
methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV).

5. The device of claim 1, wherein the spin-dependency comprises at least one of:  
25 polaron pair recombination or dissociation, triplet-triplet annihilation, triplet-polaron  
recombination or annihilation, and triplet-trion recombination.

6. The device of claim 1, further comprising a flexible substrate, wherein the  
active stack is supported by the substrate.

7. The device of claim 1, wherein the front contact comprises a plurality of electrical contacts including an electrical source and an electrical drain and the back contact comprises an electrical gate.

8. The device of claim 1, wherein application of the pulsed electrical source creates an electrical field within the organic material to change an interaction between charge carriers within the organic material.

9. The device of claim 8, wherein the application of the pulsed electrical source changes a spin state of the charge carriers.

10. An organic spin transistor device, comprising:  
a recombination layer including a pi-conjugated polymer;  
a plurality of injection layers, including at least one injection layer on each side of the recombination layer for injecting charge carriers into the recombination layer;  
a transistor source and a transistor gate in contact with one of the plurality of injection layers;  
an insulating layer adjacent to another one of the plurality of injection layers;  
a transistor gate adjacent to the insulating layer on a side of the insulating layer opposite the another one of the plurality of injection layers; and  
a pulsed electrical source coupled to the transistor gate and configured to manipulate a spin of the charge carriers in the recombination layer.

11. The device of claim 10, wherein the pi-conjugated polymer comprises at least one of polyphenylenevinylene (PPV), polythiophene, polyfluorene-vinylene (PFV), polyfluorene (PFO), polyacetylene, polypyrrole, polyaniline, cyano-polyphenylene vinylene (CN-PPV), polyphenylene ethynylene (PPE), poly(2,5 pyridine), poly(3,5 pyridine), poly(2,5-bis(3-sulfonatopropoxy)-1,4-phenylene,disodium salt-alt-1,4-phenylene) (PPP), hydrocarbon molecules, porphyrin, and phthalocyanine.

12. The device of claim 10, wherein the pi-conjugated polymer comprises poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV).

13. The device of claim 10, wherein the spin-dependency comprises at least one of: polaron pair recombination or dissociation, triplet-triplet annihilation, triplet-polaron recombination or annihilation, and triplet-trion recombination.

14. A method of manipulating charge carrier spin in an organic spin transistor device, comprising:

10           applying a voltage across a transistor source and drain, causing a charge carrier injection layer of the organic spin transistor device to inject charge carriers into a recombination layer comprising an organic material; and

              pulsing an electric field within the recombination layer using an electric current applied to a transistor gate of the organic spin transistor device to manipulate a spin of the charge carriers in the recombination layer.

15

15. The method of claim 14, wherein pulsing the electric field to manipulate the spin of the charge carriers comprises pulsing the electrical field to govern a ratio of spin states of spin pairs to induce electrical current through the organic spin transistor device.

20

16. The method of claim 14, wherein pulsing the electric field dissociates polaron pairs of approximately one half of the charge carriers and increases exchange interaction with another approximately one half of the charge carriers.

17. The method of claim 14, wherein pulsing the electric field comprises non-adiabatically applying the electric current.

25

18. The method of claim 14, wherein the method is performed at room temperature.

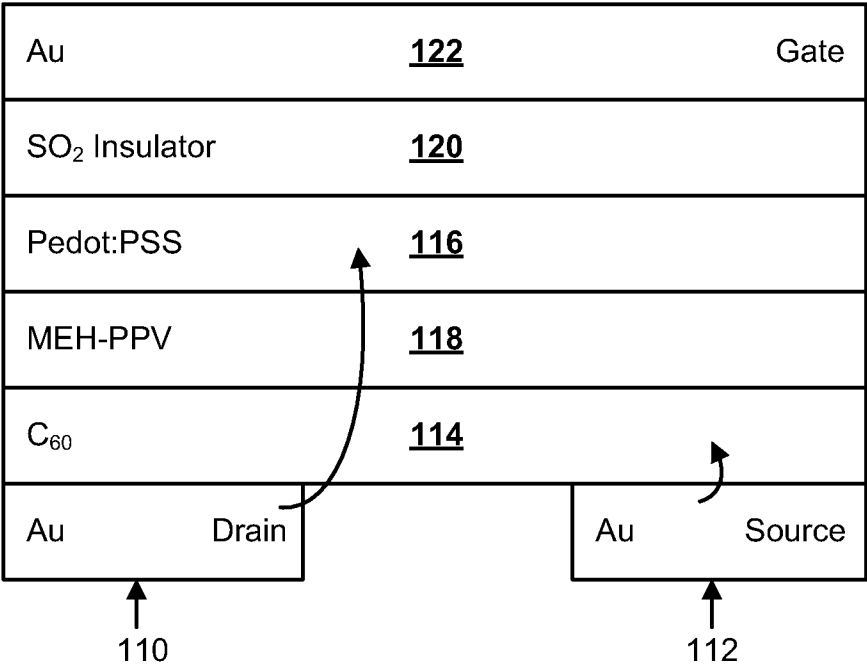
30

19. The method of claim 14, wherein the spin of the charge carriers of manipulated according to spin permutation symmetry.

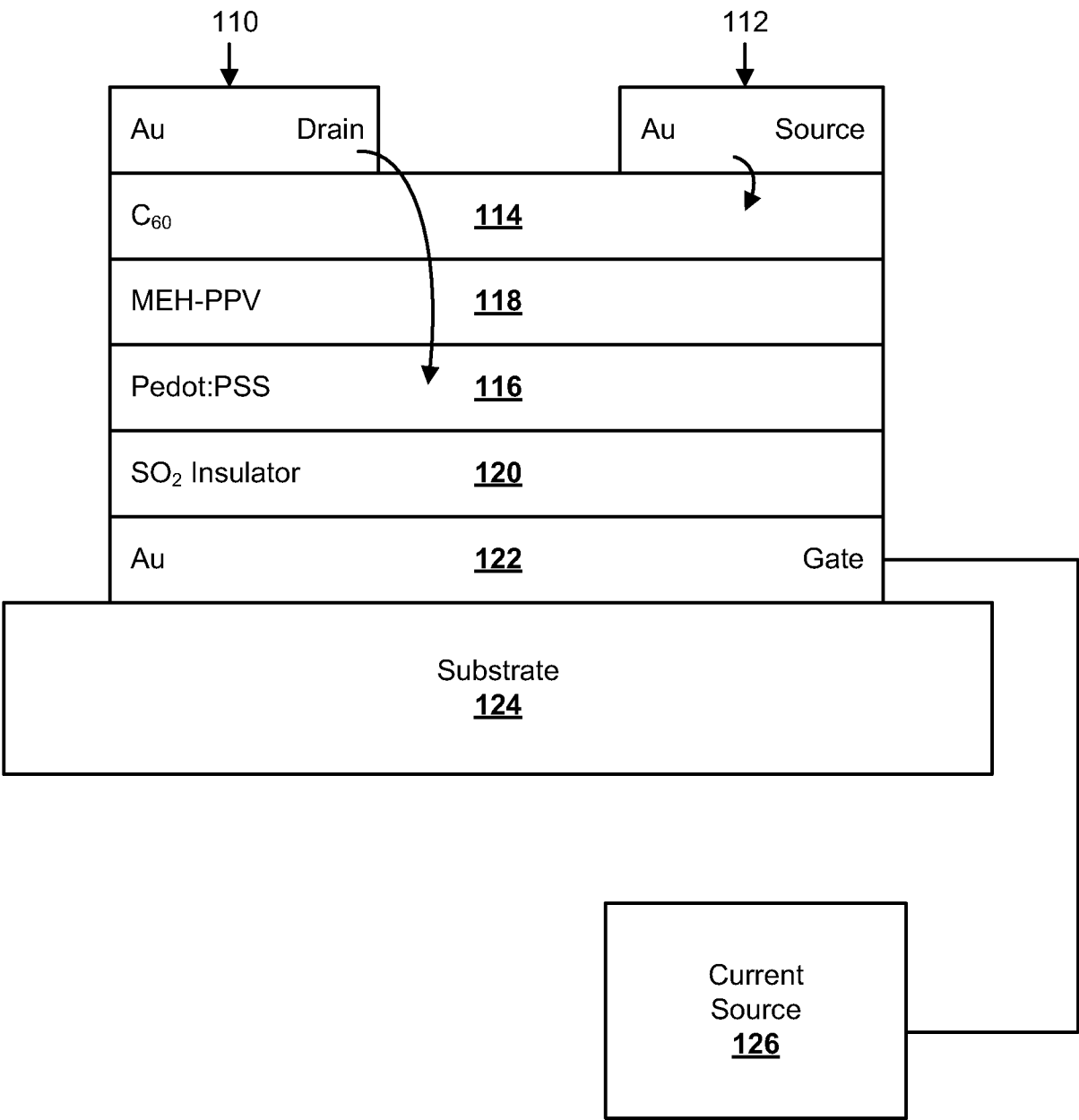
20. The method of claim 14, wherein the organic spin transistor device comprises an electrical field controlled bipolar transistor.

5

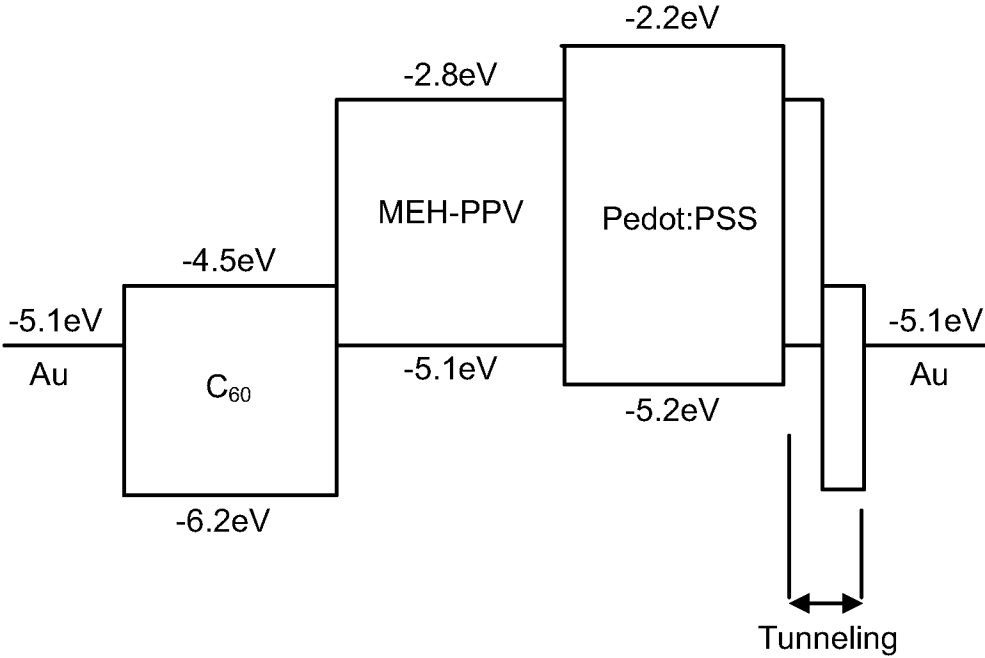
10



**FIG. 1A**

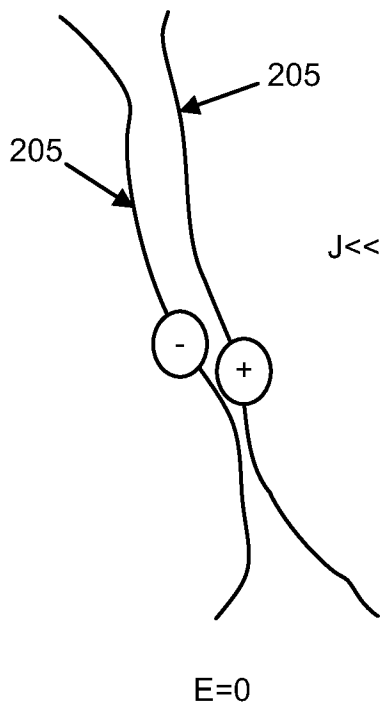


**FIG. 1B**

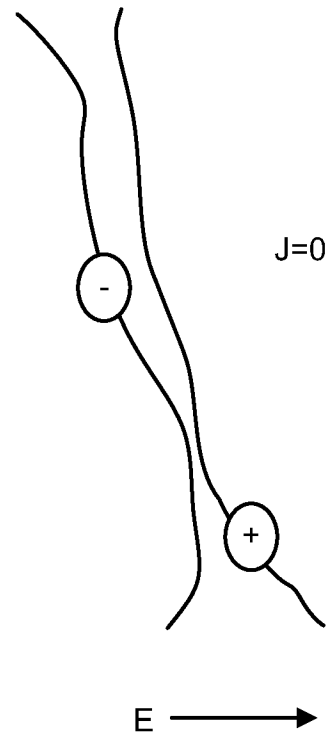


**FIG. 1C**

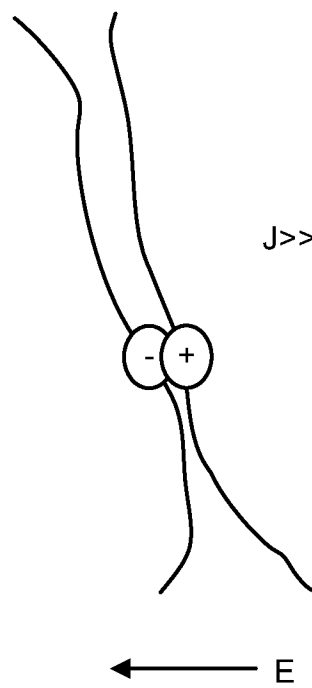




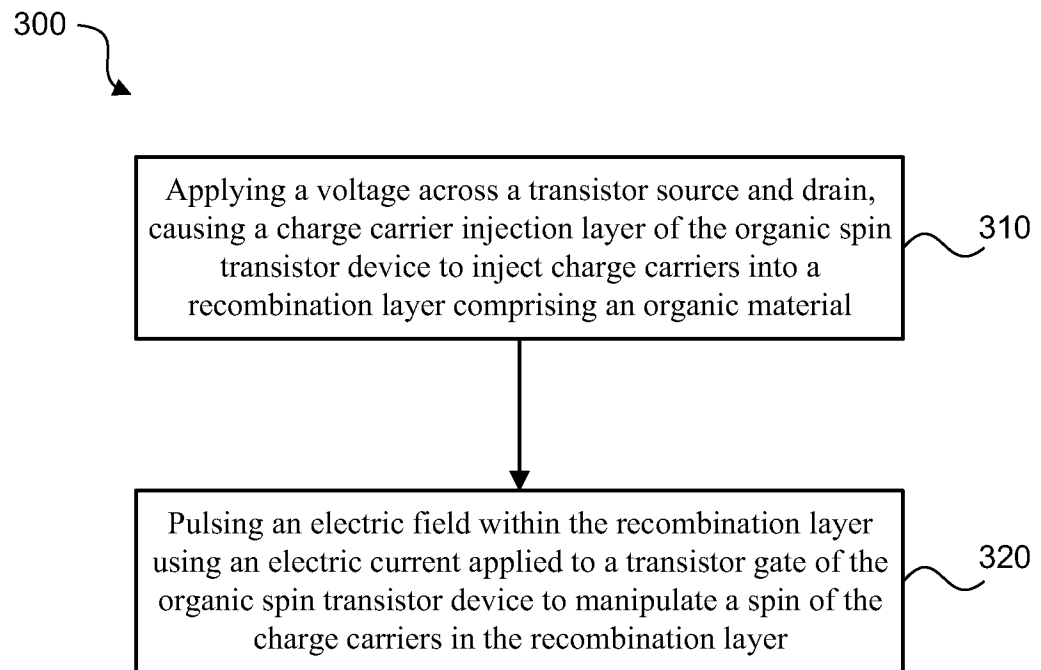
**FIG. 2A**

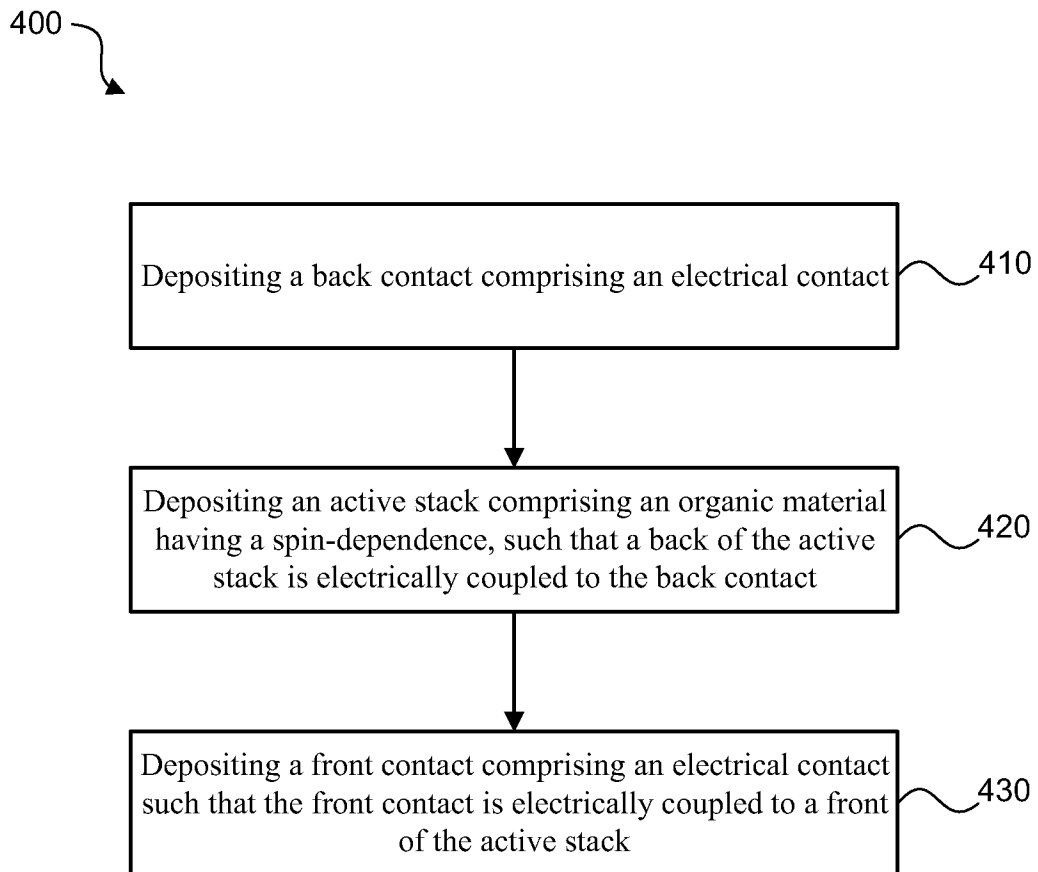


**FIG. 2B**



**FIG. 2C**

**FIG. 3**

**FIG. 4**

**A. CLASSIFICATION OF SUBJECT MATTER*****H01L 51/05(2006.01)i, H01L 29/786(2006.01)i***

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)

H01L 51/05; H01L 51/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) &amp; Keywords:organic spin transistor, spintronics, spin-dependency

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WJM Naber et al., "Organic spintronics", J.Phys.D:Appl.Phys., Vol.40, pp.R205-R228,2007.6.4 See pages R209-R215	1-20
A	US 6621100 B2 (EPSTEIN; ARTHUR J. et al.) 16 September 2003 See abstract,claims 1-12	1-20
A	J. M.Lupton et al., "Coherent spin manipulation in molecular semiconductors: Getting a handle on organic spintornics", ChemPhysChem, Vol.11, pp.3040-3058, 2010.7.2 See pages 3042-3058	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 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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

30 OCTOBER 2012 (30.10.2012)

Date of mailing of the international search report

**30 OCTOBER 2012 (30.10.2012)**

Name and mailing address of the ISA/KR

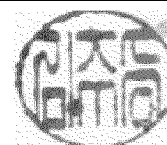
Korean Intellectual Property Office  
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan  
City, 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

Kim, Ju Seung

Telephone No. 82-42-481-8576



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2012/026365**Patent document  
cited in search reportPublication  
datePatent family  
member(s)Publication  
date

US 6621100 B2

16.09.2003

US 2003-001154 A1

02.01.2003