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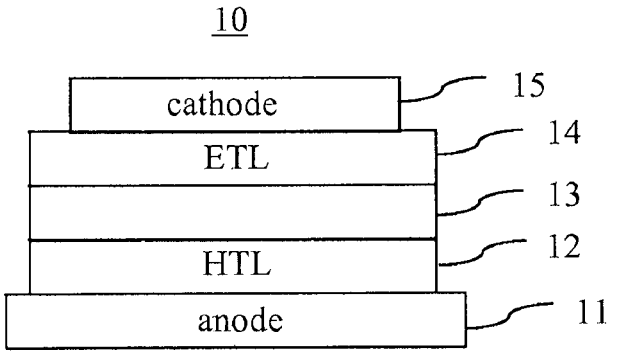

FIG. 1

(57) Abstract: Doping metal oxide charge transport material with an organic molecule lowers electrical resistance while maintaining transparency and thus is optimal for use as charge transport materials in various organic optoelectronic devices such as organic photovoltaic devices and organic light emitting devices.

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METAL OXIDE CHARGE TRANSPORT MATERIAL DOPED WITH ORGANIC MOLECULES

TECHNICAL FIELD

[0001] The present disclosure relates to the field of organic semiconductors and more particularly to organic films for use in organic electronic devices.

BACKGROUND

[0002] Optoelectronic devices rely on the optical and electronic properties of materials to either produce or detect electromagnetic radiation electronically or to generate electricity from ambient electromagnetic radiation. Optoelectronic devices that make use of organic semiconductor materials are becoming more desirable because of their potential for cost advantage over inorganic semiconductor materials and certain beneficial inherent properties organic materials, such as their flexibility.

[0003] Photosensitive optoelectronic devices convert electromagnetic radiation into an electrical signal or electricity. Solar cells, also called photovoltaic ("PV") devices, are a type of photosensitive optoelectronic devices that are specifically used to generate electrical power. An organic photosensitive device comprises at least one photoactive region in which light is absorbed to form an exciton, which may subsequently dissociate into an electron and a hole. The photoactive region will typically comprise a donor-acceptor heterojunction, and is a portion of a photosensitive device that absorbs electromagnetic radiation to generate excitons that may dissociate in order to generate an electrical current. The donor-acceptor heterojunction can be a planar heterojunction, bulk heterojunction, or hybridized mixed-planar heterojunction. A hybridized mixed-planar heterojunction comprises a first organic layer comprising a mixture of an organic acceptor material and an organic donor material; and a second organic layer comprising an unmixed layer of the organic acceptor material or the organic donor material of the first organic layer. Such hybridized mixed-planar heterojunction is described in United States patent application Publication No. 2005/0224113 of Xue, *et al.*, published on October 13, 2005, the contents of which are incorporated herein by reference in its entirety.

[0004] An organic photosensitive optoelectronic device may also comprise transparent charge transfer layers, electrodes, or charge recombination zones. A charge transfer layer may be organic or inorganic, and may or may not be photoconductively active. A charge transfer layer is similar to an electrode, but does not have an electrical connection external to

the device and only delivers charge carriers from one subsection of an optoelectronic device to the adjacent subsection. A charge recombination zone is similar to a charge transfer layer, but allows for the recombination of electrons and holes between adjacent subsections of an optoelectronic device. Charge recombination zones are described, for example, in U.S. Patent No. 6,657,378 to Forrest *et al.*; Published U.S. Patent Application 2006-0032529 Al, entitled "Organic Photosensitive Devices" by Rand *et al.*, published February 16, 2006; and Published U.S. Patent Application 2006-0027802 Al, entitled "Stacked Organic Photosensitive Devices" by Forrest *et al.*, published February 9, 2006; each incorporated herein by reference for its disclosure of recombination zone materials and structures. A charge recombination zone may or may not include a transparent matrix layer in which the recombination centers are embedded. A charge transfer layer, electrode, or charge recombination zone may serve as a cathode and/or an anode of subsections of the optoelectronic device. An electrode or charge transfer layer may serve as a Schottky contact.

[0005] For additional background explanation and description of the state of the art for organic photosensitive devices, including their general construction, characteristics, materials, and features, U.S. Patent Nos. 6,972,431, 6,657,378 and 6,580,027 to Forrest *et al.*, and U.S. Patent No. 6,352,777 to Bulovic *et al.*, are incorporated herein by reference in their entireties.

[0006] In the context of organic materials, the terms "donor" and "acceptor" refer to the relative positions of the Highest Occupied Molecular Orbital ("HOMO") and Lowest Unoccupied Molecular Orbital ("LUMO") energy levels of two contacting but different organic materials. If the HOMO and LUMO energy levels of one material in contact with another are lower, then that material is an acceptor. If the HOMO and LUMO energy levels of one material in contact with another are higher, then that material is a donor. It is energetically favorable, in the absence of an external bias, for electrons at a donor-acceptor junction to move into the acceptor material.

[0007] As used herein, a first HOMO or LUMO energy level is "higher than" a second HOMO or LUMO energy level if the first energy level is closer to the vacuum energy level and the first HOMO or LUMO energy level is "lower than" a second HOMO or LUMO energy level if the first energy level is further away from the vacuum energy level. A higher HOMO energy level corresponds to an ionization potential having a smaller absolute energy relative to a vacuum level. Similarly, a higher LUMO energy level corresponds to an electron affinity having a smaller absolute energy relative to vacuum level. On a

conventional energy level diagram, with the vacuum level at the top, the LUMO energy level of a material is higher than the HOMO energy level of the same material.

[0008] A significant property in organic semiconductors is carrier mobility. Mobility measures the ease with which a charge carrier can move through a conducting material in response to an electric field. In the context of organic photosensitive devices, a material that conducts preferentially by electrons due to high electron mobility may be referred to as an electron transport material. A material that conducts preferentially by holes due to a high hole mobility may be referred to as a hole transport material. A layer that conducts preferentially by electrons, due to mobility and/or position in the device, may be referred to as an electron transport layer. A layer that conducts preferentially by holes, due to mobility and/or position in the device, may be referred to as a hole transport layer. Preferably, but not necessarily, an acceptor material is an electron transport material and a donor material is a hole transport material.

[0009] As used herein, the term "organic" includes polymeric materials as well as small molecule organic materials that may be used to fabricate organic opto-electronic devices. "Small molecule" refers to any organic material that is not a polymer, and "small molecules" may actually be quite large. Small molecules may include repeat units in some circumstances. For example, using a long chain alkyl group as a substitute does not remove a molecule from the "small molecule" class. Small molecules may also be incorporated into polymers, for example as a pendent group on a polymer backbone or as a part of the backbone. Small molecules may also serve as the core moiety of a dendrimer, which consists of a series of chemical shells built on the core moiety. The core moiety of a dendrimer may be a fluorescent or phosphorescent small molecule emitter. A dendrimer may be a "small molecule." In general, a small molecule has a defined chemical formula with a molecular weight that is the same from molecule to molecule, whereas a polymer has a defined chemical formula with a molecular weight that may vary from molecule to molecule. As used herein, "organic" includes metal complexes of hydrocarbyl and heteroatom-substituted hydrocarbyl ligands.

[0010] An example of organic optoelectronic devices that produce electromagnetic radiation electronically include organic light emitting devices (OLEDs). OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED materials and configurations are

described in U.S. Pat. Nos. 5,844,363, 6,303,238, and 5,707,745, the disclosures of which are incorporated herein by reference in their entireties.

[0011] OLED devices are often configured to emit light through at least one of the electrodes, and one or more transparent electrodes may be useful in an organic opto-electronic devices. For example, a transparent electrode material, such as indium tin oxide (ITO), may be used as the bottom electrode. A transparent top electrode, such as disclosed in U.S. Pat. Nos. 5,703,436 and 5,707,745, which are incorporated herein by reference in their entireties, may also be used. For a device intended to emit light only through the bottom electrode, the top electrode does not need to be transparent, and may include a thick and reflective metal layer having a high electrical conductivity. Similarly, for a device intended to emit light only through the top electrode, the bottom electrode may be opaque and/or reflective. This is because, where an electrode does not need to be transparent, using a thicker layer may provide better conductivity, and using a reflective electrode may increase the amount of light emitted through the other electrode, by reflecting light back towards the transparent electrode. Fully transparent devices may also be fabricated, where both electrodes are transparent.

[0012] In many color display applications, three OLEDs, each emitting light of one of the three primary colors, blue, green and red, are arranged in a stack, thereby forming a color pixel from which any color can be emitted. Examples of such stacked OLED ("SOLED") structures can be found described in PCT International Application WO 96/19792 and U.S. Pat. No. 6,917,280, the disclosures of which are incorporated herein by reference in their entireties.

[0013] In such a stacked structure, a pair of electrode layers are provided, one at the bottom and another at the top of the SOLED stack. In one variation of SOLEDs, an intermediate electrode layer that is externally connected can be provided between each of the OLED units in the stack. In other variations of SOLEDs, a charge generating layer ("CGL") that injects charge carriers but without direct external electrical connection is provided between each of the OLED units in the stack.

[0014] As used herein, "top" means furthest away from the optoelectronic device's substrate, while "bottom" means closest to the substrate. For example, for a device having two electrodes, the bottom electrode is the electrode closest to the substrate, and is generally the first electrode fabricated. The bottom electrode has two surfaces, a bottom surface closest to the substrate, and a top surface further away from the substrate. Where a first layer is

described as "disposed over" a second layer, the first layer is disposed further away from substrate but not necessarily in physical contact with the second layer. There may be one or more other layers between the first and second layers, unless it is specified that the first layer is "in physical contact with" the second layer. For example, a cathode may be described as being "disposed over" an anode, even though there are various layers in between.

SUMMARY

[0015] The present disclosure provides a charge transport material for use in an optoelectronic device comprising a metal oxide doped with an organic compound. According to an embodiment of the present disclosure, some examples of the organic material for doping are 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ), acridine orange base (AOB), and chloroboron subphthalocyanine (SubPc).

[0016] According to another embodiment, an optoelectronic device incorporating such charge transport material is disclosed. Such device can be a photosensitive device comprising a first electrode, a second electrode, a photoactive region disposed between the first electrode and the second electrode and electrically connected to the first and second electrodes, and a charge transport layer disposed between the photoactive region and at least one of the first and second electrodes, wherein the charge transport layer comprises a metal oxide material that is doped with an organic dopant material.

[0017] The metal oxide material doped with organic compounds having decreased resistivity can be used as either a hole-transport layer ("HTL"), an electron transport layer ("ETL"), or both, in organic photovoltaic devices ("OPV"). The metal oxide material can also be used as a recombination zone in tandem OPVs, or as charge transport layers in OLEDs or CGLs in SOLEDs.

[0018] According to an embodiment, an OLED comprises an anode, a cathode, and at least one emissive layer and at least one charge transport layer disposed between the anode and the cathode. In this embodiment, the at least one charge transport layer comprises a metal oxide material doped with an organic dopant material.

[0019] In another embodiment, a SOLED comprises an anode, a cathode, a plurality of emissive regions disposed between the anode and the cathode, and a CGL disposed between successive emissive regions. In this embodiment, the CGL comprises a metal oxide material doped with an organic dopant material.

[0020] The present invention also provides a method of making the disclosed charge transport material for use in an optoelectronic device comprising a metal oxide and an organic dopant material. Examples of making such doped metal oxide compositions include vacuum thermal evaporation, solution deposition, spin casting, spray coating, doctor-blading, and other solution processing techniques.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] **FIG. 1** is a cross-sectional view of an organic photovoltaic device according to an embodiment.

[0022] **FIG. 2** is a cross-sectional view of an organic photovoltaic device according to another embodiment.

[0023] **FIG. 3** is a cross-sectional view of a two layer organic light emitting device.

[0024] **FIG. 4** is a cross-sectional view of a three layer organic light emitting device.

[0025] **FIG. 5** is a cross-sectional view of a stacked organic light emitting device.

[0026] **FIG. 6** Resistivity of MoO_3 films doped with AOB, measured from ITO/MoO_3:AOB/Au sandwich-type devices.

[0027] **FIGS. 7a** and **7b** show absorption coefficients of various doped MoO_3 films deposited on quartz.

[0028] **FIGS. 8a** and **8b** show dark (8a) and one-sun illuminated (8b) plots of the J-V characteristics of OPVs incorporating MoO_3 layers doped with Ag, F_4TCNQ, and AOB.

[0029] **FIGS. 9a** and **9b** show one-sun illuminated J-V characteristics (9a) and performance parameters (9b) of OPV devices as a function of AOB doping concentration.

[0030] **FIGS. 10a** and **10b** show dark J-V characteristics (10a) and series resistance (10b) of OPV devices as a function of AOB doping concentration.

[0031] **FIGS. 11a** and **11b** show one-sun illuminated J-V characteristics (11a) and performance parameters (11b) of OPV devices comparing different buffer layers.

[0032] Except where noted otherwise, all drawings are schematic and are not drawn to scale and are not intended to necessarily convey actual dimensions.

DETAILED DESCRIPTION

[0033] New metal oxide charge transport materials doped with organic molecules to increase the conductivity of the metal oxide thin films is disclosed. The resulting charge transport material exhibit increased conductivity, optical transparency, light absorption, and

chemical resistance suitable for optoelectronic devices. They can be used for either a HTL, an ETL, or both, in an OPV device or OLED devices. Other applications of the disclosed composition include uses as a recombination zone in tandem OPVs, or as a charge generation layers in SOLEDs.

[0034] As described herein, "metal oxide" may be any transition metal oxide which have favorable energy level alignment, electric conductivity, optical transparency, and chemical robustness. The metal oxides are suitable as charge transport layers in organic and molecular electronics. They may have abilities to provide good energy level alignment with a wide range of materials to improve carrier injection and extraction. Their optical transparency may allow their use as optical spacers. They are compatible with a wide range of deposition processes such as vacuum evaporation, solution deposition, spin casting, spray coating, doctor-blading, and other solution processing techniques. They also have chemical resistance allowing the subsequent solvent-based deposition of subsequent layers. Examples of the metal oxide material include MoO_3, CrO_3, V_2O_5, WO_3, NiO, Cr_3O_4, Cr_2O_3, CuO, RuO_2, TiO_2, Ta_2O_5, SnO_2, Cu_2O, and other transition metal oxide. A transition metal oxide having high electrical conductivity, optical transparency and chemical robustness is preferred.

[0035] The organic dopant as described herein may be an organic semiconducting material, which have suitable energy alignment with the metal oxide host described above. The organic dopant may exist in the form of small molecules, oligomers or polymers. The small molecules are preferred. Examples of such small molecule organic dopant include 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ), acridine orange base (AOB) and chloroboron subphthalocyanine (SubPc).

[0036] An organic dopant can be selected to provide either *n*-type doping or *p*-type doping based on the following principles. When the HOMO of the dopant is similar to or smaller than (*i.e.*, closer to the vacuum energy level) the LUMO of the metal oxide host, *n*-type doping occurs. Conversely, when the LUMO of the dopant is similar to or larger (*i.e.*, further from the vacuum energy level) than the HOMO of the host, *p*-type doping occurs. As used herein, "similar to" means within ~5 kT, or 0.2 eV.

[0037] For example, a wide range of organic materials can be used for *n*-type doping because the LUMO of MoO_3 is very high (~6 eV). Examples of suitable organic dopants for *n*-type doping of MoO_3 include: acridine orange base (AOB) (~3 eV), pentacene (5.0 eV), tetracene (5.2 eV), copper phthalocyanine (CuPc) (5.2 eV), N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPD) (5.3 eV), diindenoperylene (DIP) (5.5 eV), chloroboron

subphthalocyanine (SubPc) (5.6 eV), and tris(8-hydroxyquinolinato) aluminium (Alq3) (5.8 eV).

[0038] This *n*-type doping also applies to other metal oxides with similar energy levels such as CrO_3, V_2O_5, and WO_3. Acridine orange base (AOB) having low HOMO (~3 eV) may act as an n-type dopant for a wide range of metal oxides, including MoO_3, CrO_3, V_2O_5, WO_3, NiO, Cr_3O_4, Cr_2O_3, CuO, RuO_2, TiO_2, Ta_2O_5, SnO_2, and Cu_2O. For the metal oxides with smaller HOMO levels such as CuO at -5.2 eV, organic molecules such as F_4TCNQ, whose LUMO level is -5.2 eV is suitable as a *p*-type dopant.

[0039] The HOMO/LUMO levels of various transition-metal oxides such as MoO_3, CrO_3, V_2O_5, WO_3, NiO, Co_3O_4, MoO_2, Cr_2O_3, CuO, TiO_2, Ta_2O_5, Cu_2O, and CoO are provided in Greiner *et al.*, "Universal energy-level alignment of molecules on metal oxides," NATURE MATERIALS, Vol. 11, (January 2012), the disclosure of which is incorporated herein by reference in its entirety. The HOMO/LUMO levels of organic materials F_4-TCNQ, NTCDA, TCNQ, PTCDA, BCP, CBP, F_{16}-CuPC, PTCBI, Alq3, α-NPD, CuPC, ZnPC, Pentacene, and α-6T are provided in Kahn *et al.*, "Electronic Structure and Electrical Properties of Interfaces between Metals and π-Conjugated Molecular Films," JOUR. OF POLY. SCI.: PART B: POLYMER PHYSICS, Vol. 41, 2529-2548 (2003), the disclosure of which is incorporated herein by reference in its entirety.

[0040] The organic dopant may be introduced into the metal oxide host through a gas, solution or solid processing technique. Examples of making such doped metal oxide composition include vacuum thermal evaporation, solution deposition, spin casting, spray coating, doctor-blading, and other solution processing techniques. As for doping of metal oxide films deposited from solution with organic molecules, a solvent in which both materials are soluble or dispersed, is chosen. The organic dopant is about 1 to 20 vol.%, more preferably 5-10 vol.%, of the whole composition.

[0041] The benefits of the doped metal oxide charge transport materials were verified by the inventors using the specific examples of MoO_3 doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) or acridine orange base (AOB). With both dopants, the resulting materials have a significantly reduced electrical resistivity while still maintaining transparency of the charge transport material. Because of their high resistance, undoped metal oxides are generally limited for use in very thin film (<20 nm) applications. But, the organic molecule doped metal oxides according to the present disclosure are suitable as

charge transport material for applications requiring charge transport layers of 150 nm or even higher in thickness.

[0042] According to an embodiment, an organic photosensitive device is disclosed. The device comprises a first electrode, a second electrode, a photoactive region disposed between the first electrode and the second electrode, and a charge transport layer disposed between the photoactive region and at least one of the first and second electrodes, wherein the charge transport layer comprises a metal oxide host material that is doped with an organic dopant material.

[0043] **FIG. 1** shows an example of an OPV device **10** according to an embodiment of the present disclosure. The device **10** comprises an anode **11** (e.g. ITO), a cathode **15**, and a photoactive region **13** disposed between the two electrodes. The OPV device **10** can further include a charge transport layer **12**, **14** disposed between the photoactive region **13** and at least one of the two electrodes **11**, **15**, where the charge transport layer comprises a metal oxide material doped with an organic dopant material. The charge transport layer **12** disposed between the photoactive region **13** and the anode **11** is a HTL and the charge transport layer **14** disposed between the photoactive region **13** and the cathode **15** is an ETL. The photoactive region **13** generally includes at least one organic electron donor material and at least one organic electron acceptor material that form a donor-acceptor heterojunction. Various types of donor-acceptor heterojunctions are possible as described herein.

[0044] **FIG. 2** shows another example of an OPV device **20** according to another embodiment. The OPV device **20** is a tandem device and can comprise an anode **21**, a cathode **26** and multiple photoactive subcells **22**, **24** provided in series between the two electrodes. Each of the subcells **22**, **24** can comprise at least one organic electron donor material and at least one organic electron acceptor material that form a donor-acceptor heterojunction in the subcell. A thin layer of electron-hole recombination zone **23** is provided between the individual subcells separating the subcells. According to the present disclosure, the electron-hole recombination zone **23** comprises a metal oxide material doped with an organic dopant material. The recombination zone 23 serves to prevent the formation of an inverse heterojunction between the acceptor material of the anode-side subcell and the donor material of the cathode-side subcell. The recombination zone allows the electrons approaching from the anode-side subcell and the holes approaching from the cathode-side subcell to recombine.

[0045] Another application of the charge transport material of the present disclosure is in organic light emitting devices (OLEDs). In one embodiment, the metal oxide material doped with organic molecules can be used as one or both types of the charge transport layers in OLEDs. In other words, the novel charge transport material can be used for hole transport layers and/or electron transport layers in OLEDs.

[0046] **FIG. 3** shows an example of a two-layer OLED **30** comprising an emissive layer **32** and an electron transport layer **33** disposed in between two electrodes, an anode **31** and a cathode **34**. According to an embodiment, the electron transport layer **33** can comprise the metal oxide doped with organic molecules. **FIG. 4** shows an example of a three-layer OLED **40** comprising an emissive layer **43**, a hole transport layer **42**, and an electron transport layer **44** that are disposed in between an anode **41** and a cathode **44**. According to another embodiment, one or both of the charge transport layers **44** and **42** can comprise the metal oxide doped with organic molecules. Various methods of fabricating OLEDs having these architecture are known to those skilled in the art.

[0047] Another application of the charge transport material of the present disclosure is in stacked light emitting devices (SOLEDs), where multiple active layers are combined monolithically. In SOLEDs, two or more individual emissive regions are stacked in vertical arrangement, the successive emissive regions being separated by an intermediate layer. The intermediate layers are also referred to as charge generation layers (CGLs) because of their charge carrier generating or injecting function in the device. A CGL is a layer that injects charge carriers but does not have direct external electrical connection. When a voltage is applied across the SOLED, the CGLs inject holes into the emissive region on the cathode side of the CGL, and electrons into the emissive region on the anode side of the CGL.

[0048] **FIG. 5** shows an example of a SOLED **300** having two emissive regions. The SOLED **300** comprises an anode **310**, two organic emissive regions **320** and **330**, a CGL **350**, and a cathode **340**. Organic emissive regions **320** and **330** can comprise multiple layers, such as hole injection layers, electron injection layers, and emissive layers. As will be appreciated by one skilled in the art, the emissive regions can include other layers such as electron blocking layers, hole blocking layer, etc. The CGL **350** is disposed between the two emissive regions **320** and **330**. In a preferred embodiment, the CGL **350** comprises a metal oxides material doped with organic molecules described herein. When voltage is applied across the device, the CGL **350** may inject holes into the emissive region **330** and electrons into the

emissive region **320**. Due to the charge carrier injection properties of the CGL **350**, the device **300** may have improved efficiencies.

[0049] In one embodiment of such SOLEDs, a CGL consisting of doped organic/MoO_3 has been used by Kanno *et al.* (Adv. Mater. 18, 339–342 (2006)). When voltage is applied to the device, the CGL generates an electron on the organic side and a hole on the MoO_3 side, which then contribute to light emission. As this process is dependent on the availability of free charges (Qi *et al.* J. Appl. Phys. 107, 014514 (2010)), it is likely that doping the MoO_3 layer with an organic molecule, thereby increasing the free charge density, would lead to improved performance.

[0050] In another embodiment, the OLEDs and SOLEDs described above are phosphorescent organic light emitting devices ("PHOLED") that utilize emissive materials that emit light from triplet states ("phosphorescence"). But the improved charge transport material of the present disclosure can be applied to PHOLEDs as well as fluorescent OLEDs. The organic emissive materials for PHOLEDs and fluorescent OLEDs are known in the art.

EXAMPLES

[0051] Specific representative embodiments of the invention is now described. It is understood that the specific methods, materials, conditions, process parameters, apparatus and the like are merely examples and do not necessarily limit the scope of the invention.

Experimental Methods:

[0052] The inventors prepared and tested examples of OPV devices according to the following experimental procedures. Substrates consisting of indium tin oxide-coated glass ("ITO") (150 nm, <15Ω, Prazisions Glas & Optik GmbH) quartz (qtz), or silicon were cleaned sequentially in Tergitol, deionized water, acetone, trichloroethylene, acetone, and isopropanol. C_{60} (MER, 99.9% sublimed) and AOB (Aldrich, 75%) were purified once and SubPc (Aldrich, 85%) was purified three times by thermal gradient sublimation at $<1x10^{-7}$ Torr. Other materials were used as received. The ITO substrates were subjected to a UV-ozone treatment for 600 seconds and transferred into a nitrogen glovebox with <0.1 ppm O_2 and H_2O. The substrates were loaded into a high-vacuum chamber with base pressure $<1.0x10^{-6}$ Torr. The metal oxide host and organic dopant materials were evaporated at 0.10 nm/s. Squaraine films were deposited from solution via spin coating in a nitrogen environment. All rates were measured by quartz crystal monitor and calibrated by spectroscopic ellipsometry.

[0053] The device performance of the sample OPV devices were measured in a nitrogen glovebox with <1.0 ppm O_2 and <0.1 ppm H_2O by an Agilent semiconductor parameter analyzer under illumination by a 150W Xe lamp with AM1.5G filters (Oriel). Lamp intensity was varied by using neutral density filters and measured using an NREL-calibrated Si photodiode. Incident light intensity was determined by using the spectral correction factor, determined from the lamp intensity and device and detector responsivities.

Experimental Results:

[0054] Single-layer "sandwich-type" devices having the structure glass/ITO/MoO_3/Au were fabricated. The current-voltage (*I-V*) characteristics of these devices were measured and the resistivity ($\rho=RA/t$) was calculated, where R is the resistance, A is the device area, and t is the layer thickness, by using the Mott-Gurney relation:

$$I = \frac{V}{R} + \frac{9A\varepsilon\mu V^2}{8t^3}$$

[0055] First, the *I-V* characteristics of 90 nm MoO_3 layers doped with various concentrations of AOB were measured. As shown in **FIG. 6**, for the neat MoO_3 film, the resistivity ρ was 1.6 MΩcm and decreased to below 800 kΩcm when the MoO_3 film was doped with 7 vol. % AOB. Next, the absorption coefficient α of the doped metal oxide films was measured. As seen in **FIGS. 7a** and **7b**, increased doping led to increased α at longer wavelengths. Additionally, the emergence of a new absorption peak at higher doping concentrations of AOB appear near 530 nm. This absorption does not correspond to that of neat AOB, but may reflect energy transfer from the organic dopant to the metal oxide host. This new absorption peak near 530 nm does not appear when doping with SubPc, indicating that energy transfer is not occurring.

[0056] Next, the doped MoO_3 films were incorporated into sample OPV devices. The device structure consisted of glass/ITO/40 nm MoO_3:dopant/9 nm MoO_3/13 nm SubPc/40 nm C_{60}/8 nm bathocuproine (BCP)/100 nm Ag. A control device with no MoO_3 layers was also included for comparison. The dopants in these working OPV examples were AOB, F_4TCNQ or SubPc, as compared to the control without any dopant, or the MoO_3 film doped with silver. The 9 nm MoO_3 buffer layer was incorporated into the sample devices to ensure that the organic dopants in the 40 nm MoO_3 are not affecting MoO_3/SubPC interface (e.g. causing exciton quenching, etc.). The inventors have found that this is not a problem.

[0057] **FIGS. 8a** and **8b** show the dark (8a) and one-sun illuminated (8b) plots of the *J*-V characteristics of these sample OPV devices incorporating MoO_3 layers doped with Ag,

F_4TCNQ, and AOB. R_s was then calculated from the dark *J-V* curves at forward bias by using a simplified version of the ideal diode equation, $J = J_s\{\exp[q(V - JR_s)/nk_bT] - 1\}$, where J_s is the reverse saturation current, q is the electron charge, n is the ideality factor, k_b is Boltzmann's constant, and T is absolute temperature.

[0058] **Table I** summarizes the results of the calculated *Rs* of the OPVs from these un-doped and doped MoO_3 layers. While *Rs* increases from 112±1 Ωcm^2 for undoped case, it is reduced to 4.3±0.1 Ωcm^2 when doped with 1 vol.% Ag and reduced to 6.5±0.1 Ωcm^2 when doped with 10 vol.% AOB, which is near the value of 4.4±3 Ωcm^2 obtained without a MoO_3 layer. R_S also decreases when F_4TCNQ is used, though to a lesser degree—this is unexpected, as F_4TCNQ is typically used as a *p*-type dopant for organic materials and MoO_3 is considered by most to be an *n*-type material. It is possible that, because the ionization potential of MoO_3 is larger, F_4TCNQ in this case is acting as a weak *n*-type dopant.

[0059] **Table I.** Comparison of the series resistance for OPVs with different buffer layers.

Buffer	Dopant	Ratio (vol%)	R_S (Ωcm^2)
None	n/a	n/a	4.4±0.3
MoO_3	None	0	112±1
MoO_3	Ag	1	4.3±0.1
MoO_3	F_4TCNQ	10	29.8±0.4
MoO_3	AOB	10	6.5±0.1
MoO_3	SubPc	4	70.7±0.3

[0060] Similar OPV devices were fabricated with 90 nm MoO_3 layers and varying concentrations of AOB as the dopant. **FIGS. 9a, 9b** show one-sun illuminated *J-V* characteristics (9a) and performance parameters (9b) of the sample OPV devices as a function of AOB doping concentration. As shown in **FIGS. 10a, 10b**, *Rs* decreased from 46 Ωcm^2 for the neat case to 8 Ωcm^2 for 15.6 vol.% AOB.

[0061] Similar devices were also fabricated using SubPc as the dopant. In this case, a thick MoO_3 layer was doped with 0.7 vol.% Ag, 4.0 vol.% SubPc, or undoped. **FIGS. 11a,**

11b show the performance of such device. The doping with SubPc doping increases the device performance, compared to the undoped case.

[0062] The use of metal oxide doped with organic compounds is likely to be beneficial in other devices. For example, metal oxide films doped with organic molecules could be used for either the hole-transport layer, the electron transport layer, or both.

[0063] It may also be possible to dope oxide films which are deposited from solution. Although all data shown here utilizes MoO_3 deposited by vacuum thermal evaporation, it is also possible to deposit MoO_3 from solution via spincasting, spray coating, doctor-blading, or other techniques. Doping of oxide films deposited from solution with organic molecules is also possible, if a solvent is chosen which both materials are soluble in.

[0064] The foregoing description and examples have been set forth merely to illustrate the invention and are not intended to be limiting. Each of the disclosed aspects and embodiments of the present disclosure may be considered individually or in combination with other aspects, embodiments, and variations of the invention. In addition, unless otherwise specified, none of the steps of the methods of the present disclosure are confined to any particular order of performance. Modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art and such modifications are within the scope of the present invention.

[0065] Those skilled in the art may appreciate that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the attached claims.

What is claimed is:

1. A metal oxide charge transport material for use in an optoelectronic device comprising:

a metal oxide material; and

an organic dopant material.

2. The metal oxide charge transport material of claim 1, wherein the organic dopant material is selected from 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ), acridine orange base (AOB), and chloroboron subphthalocyanine (SubPc).

3. The metal oxide charge transport material of claim 1, wherein the metal oxide material is selected from MoO_3, CrO_3, V_2O_5, WO_3, NiO, Cr_3O_4, Cr_2O_3, CuO, RuO_2, TiO_2, Ta_2O_5, SnO_2, and Cu_2O.

4. The metal oxide charge transport material of claim 1, wherein the HOMO of the organic dopant is similar to or smaller than the LUMO of the metal oxide material.

5. The metal oxide charge transport material of claim 1, wherein the LUMO of the organic dopant is similar to or larger than the HOMO of the metal oxide material.

6. The metal oxide charge transport material of claim 1, wherein the metal oxide material is doped with 1 to 20 vol.% of the organic dopant material.

7. The metal oxide charge transport material of claim 1, wherein the metal oxide material is doped with 10 vol.% of the organic dopant material.

8. An organic photosensitive device comprising:

a first electrode;

a second electrode;

a photoactive region disposed between the first electrode and the second electrode; and

a charge transport layer disposed between the photoactive region and at least one of

the first and second electrodes, wherein the charge transport layer comprises a metal oxide material doped with an organic dopant material.

9. The device of claim 8, wherein the organic dopant material is selected from 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ), acridine orange base (AOB), and chloroboron subphthalocyanine (SubPc).

10. The device of claim 8, wherein the metal oxide material is selected from MoO_3, CrO_3, V_2O_5, WO_3, NiO, Cr_3O_4, Cr_2O_3, CuO, RuO_2, TiO_2, Ta_2O_5, SnO_2, and Cu_2O.

11. The device of claim 8, wherein the HOMO of the organic dopant is similar to or smaller than the LUMO of the metal oxide material.

12. The device of claim 8, wherein the LUMO of the organic dopant is similar to or larger than the HOMO of the metal oxide material.

13. The device of claim 8, wherein the metal oxide material is doped with 1 to 20 vol.% of the organic dopant material.

14. The device of claim 8, wherein the metal oxide material is doped with 10 vol.% of the organic dopant material.

15. The device of claim 8, wherein the photoactive region comprises an organic donor material and an organic acceptor material forming a donor-acceptor heterojunction.

16. An organic photosensitive device comprising:

an anode;

multiple subcells in series, each subcell comprising:

an electron donor layer, and an electron acceptor layer in contact with the electron donor layer forming a donor-acceptor heterojunction, an electron-hole recombination zone separating the subcells; and

a cathode,

wherein the electron-hole recombination zone comprises a metal oxide material doped with an organic dopant material.

17. The device of claim 16, wherein the organic dopant material is selected from 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ), acridine orange base (AOB), and chloroboron subphthalocyanine (SubPc).

18. The device of claim 16, wherein the metal oxide material is selected from MoO_3, CrO_3, V_2O_5, WO_3, NiO, Cr_3O_4, Cr_2O_3, CuO, RuO_2, TiO_2, Ta_2O_5, SnO_2, and Cu_2O.

19. The device of claim 16, wherein the HOMO of the organic dopant is similar to or smaller than the LUMO of the metal oxide material.

20. The device of claim 16, wherein the LUMO of the organic dopant is similar to or larger than the HOMO of the metal oxide material.

21. The device of claim 16, wherein the metal oxide material is doped with 1 to 20 vol.% of the organic dopant material.

22. The device of claim 16, wherein the metal oxide material is doped with 10 vol.% of the organic dopant material.

23. An organic light emitting device comprising:

an anode;

a cathode; and

at least one emissive layer and at least one charge transport layer disposed between the anode and the cathode, wherein the at least one charge transport layer comprises a metal oxide material doped with an organic dopant material.

24. The device of claim 23, wherein the organic dopant material is selected from 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ), acridine orange base (AOB), and chloroboron subphthalocyanine (SubPc).

25. The device of claim 23, wherein the metal oxide material is selected from MoO_3, CrO_3, V_2O_5, WO_3, NiO, Cr_3O_4, Cr_2O_3, CuO, RuO_2, TiO_2, Ta_2O_5, SnO_2, and Cu_2O.

26. The metal oxide charge transport material of claim 23, wherein the HOMO of the organic dopant is similar to or smaller than the LUMO of the metal oxide material.

27. The metal oxide charge transport material of claim 23, wherein the LUMO of the organic dopant is similar to or larger than the HOMO of the metal oxide material.

28. The device of claim 23, wherein the metal oxide material is doped with 1 to 20 vol.% of the organic dopant material.

29. The device of claim 23, wherein the metal oxide material is doped with 10 vol.% of the organic dopant material.

30. The device of claim 23, wherein the at least one charge transport layer is an electron transport layer in direct contact with the at least one emissive layer and disposed between the at least one emissive layer and the cathode.

31. The device of claim 23, wherein the at least one charge transport layer is a hole transport layer in direct contact with the at least one emissive layer and disposed between the at least one emissive layer and the anode.

32. A stacked organic light emitting device comprising:

an anode;

a cathode;

a plurality of emissive regions disposed between the anode and the cathode; and

a charge generation layer disposed between successive emissive regions,

wherein the charge generation layer comprises a metal oxide material doped with an organic dopant material.

33. The device of claim 32, wherein the organic dopant material is selected from 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ), acridine orange base (AOB), and chloroboron subphthalocyanine (SubPc).

34. The device of claim 32, wherein the metal oxide material is selected from MoO_3, CrO_3, V_2O_5, WO_3, NiO, Cr_3O_4, Cr_2O_3, CuO, RuO_2, TiO_2, Ta_2O_5, SnO_2, and Cu_2O.

35. The metal oxide charge transport material of claim 32, wherein the HOMO of the organic dopant is similar to or smaller than the LUMO of the metal oxide material.

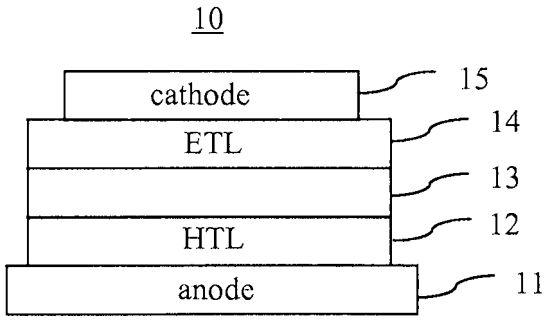
36. The metal oxide charge transport material of claim 32, wherein the LUMO of the organic dopant is similar to or larger than the HOMO of the metal oxide material.

37. The device of claim 32, wherein the metal oxide material is doped with 1 to 20 vol.% of the organic dopant material.

38. The device of claim 32, wherein the metal oxide material is doped with 10 vol.% of the organic dopant material.

39. The device of claim 32, wherein the at least one charge transport layer is an electron transport layer in direct contact with the at least one emissive layer and disposed between the at least one emissive layer and the cathode.

40. The device of claim 32, wherein the at least one charge transport layer is a hole transport layer in direct contact with the at least one emissive layer and disposed between the at least one emissive layer and the anode.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11

FIG. 1

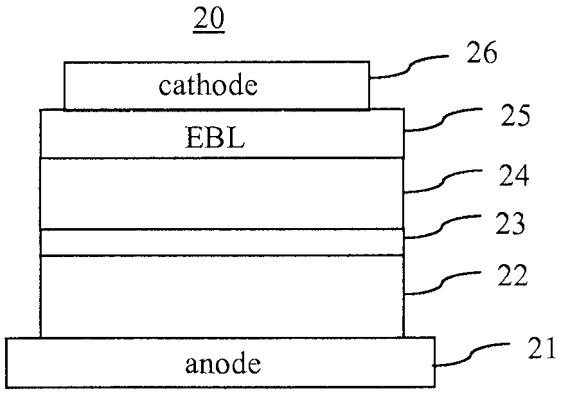
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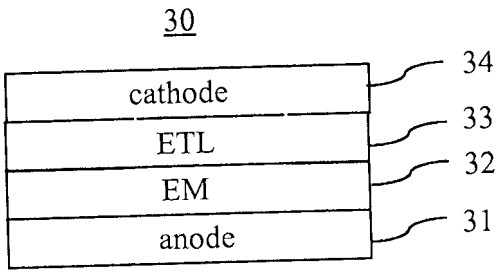
FIG. 2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anode
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FIG. 3

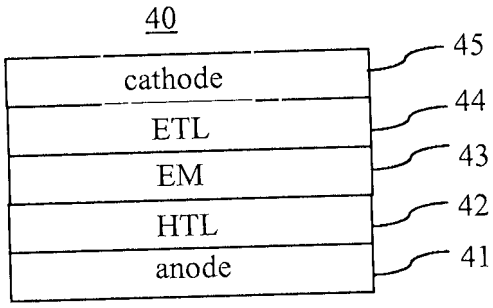
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FIG. 4

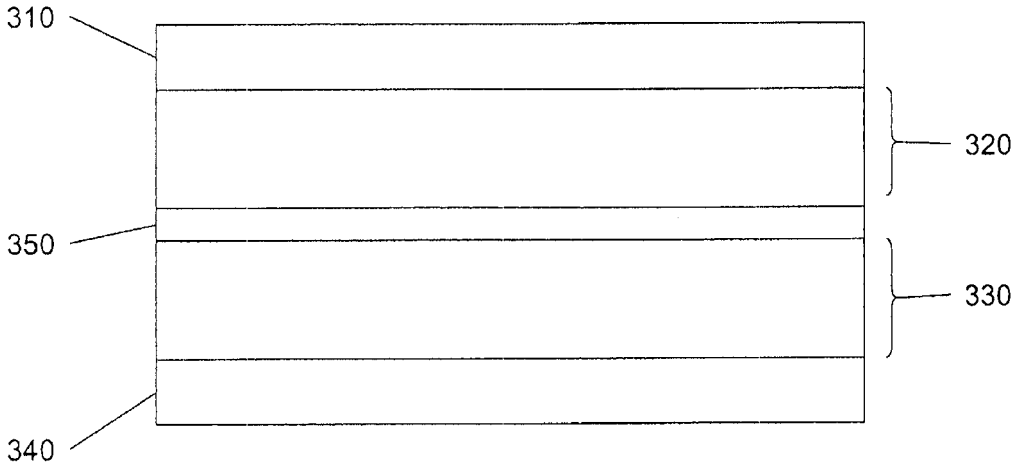

FIG. 5

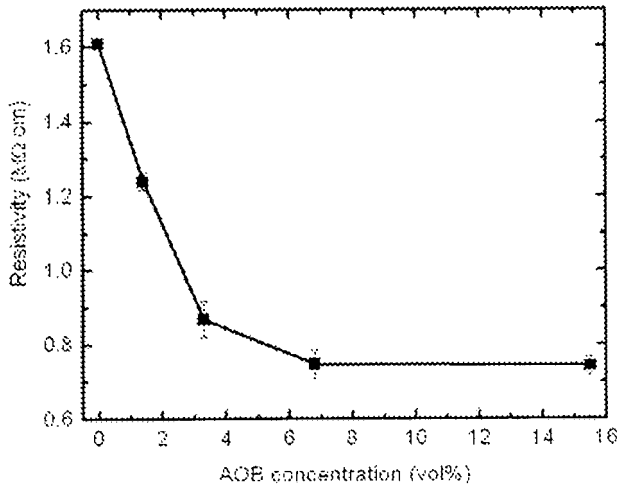

FIG. 6

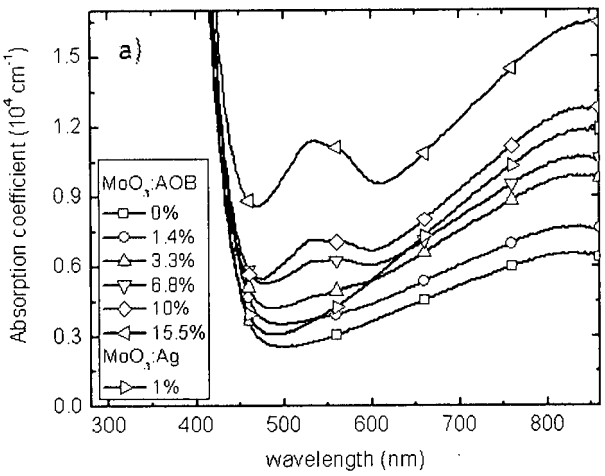

FIG. 7a

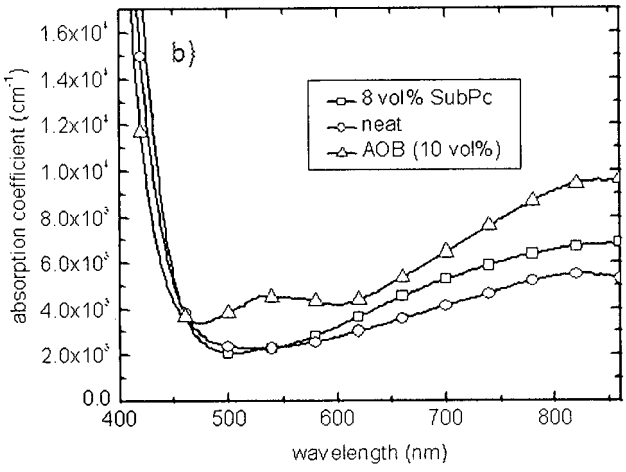

FIG. 7b

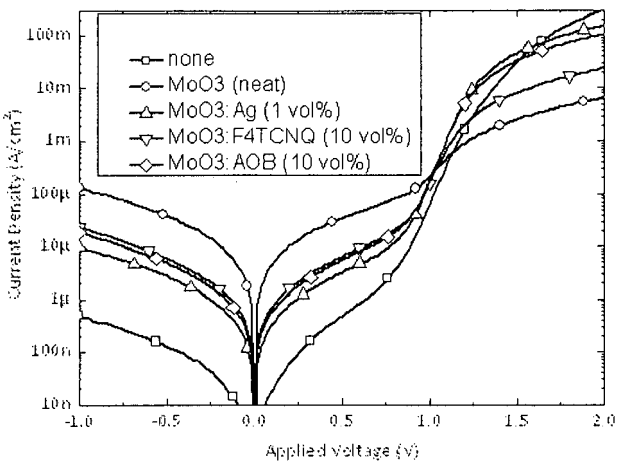

FIG. 8a

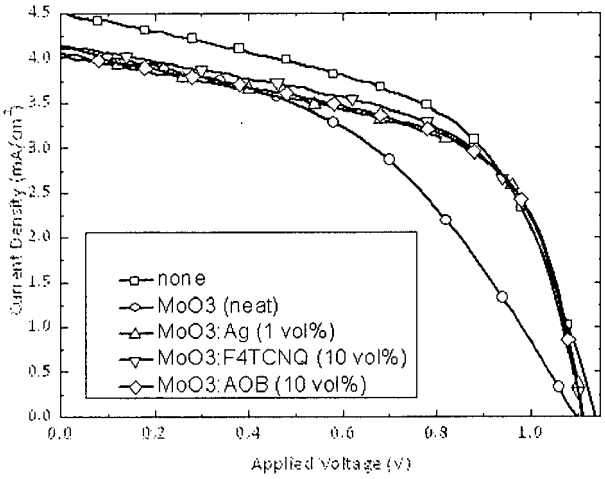

FIG. 8b

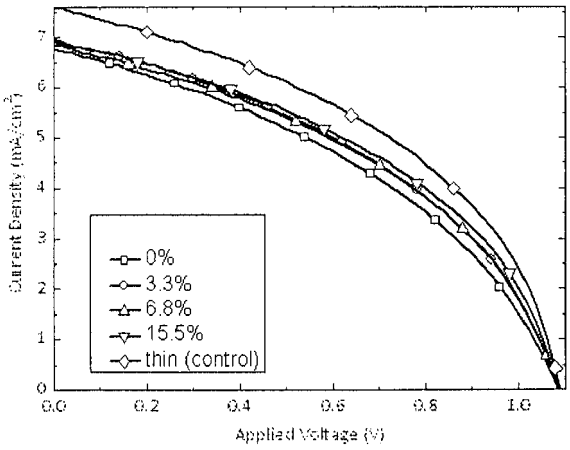

FIG. 9a

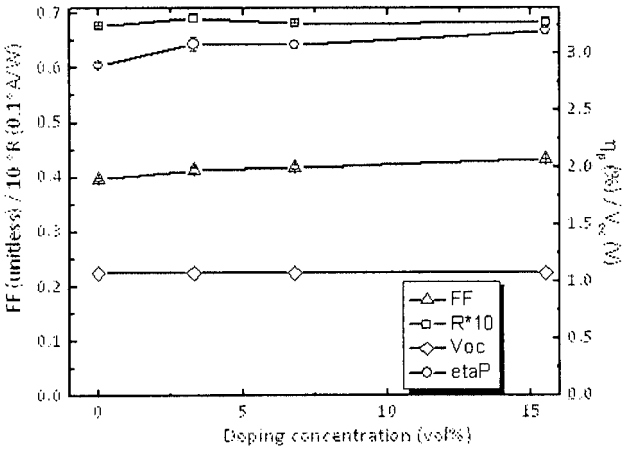

FIG. 9b

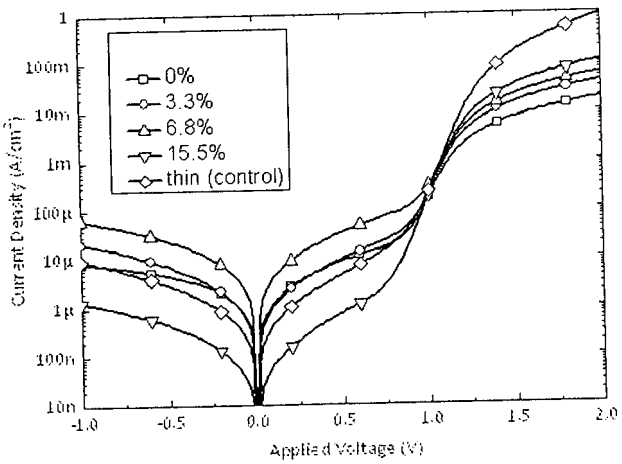

FIG. 10a

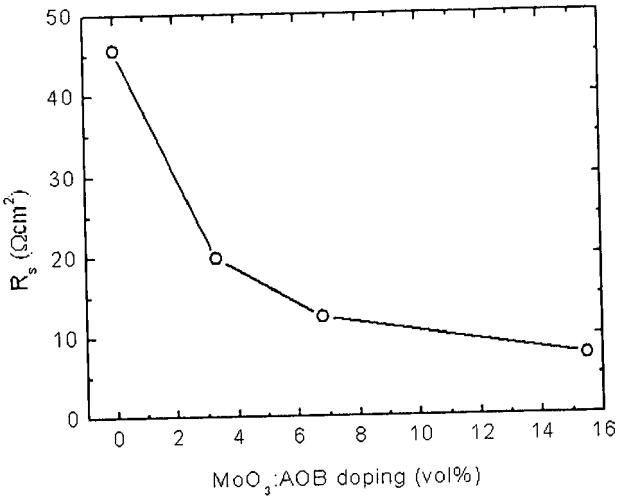

FIG. 10b

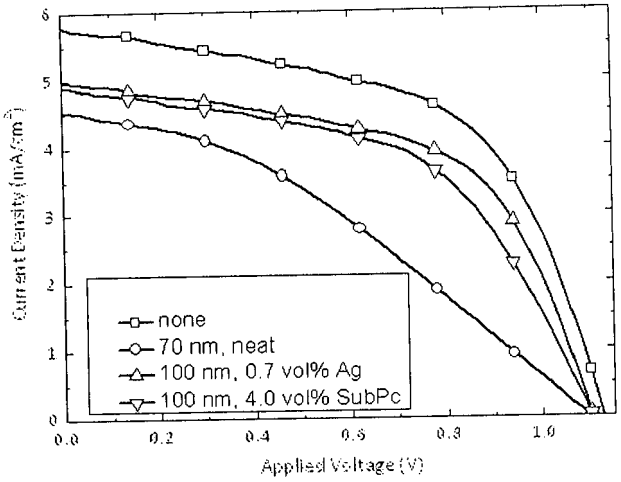

FIG. 11a

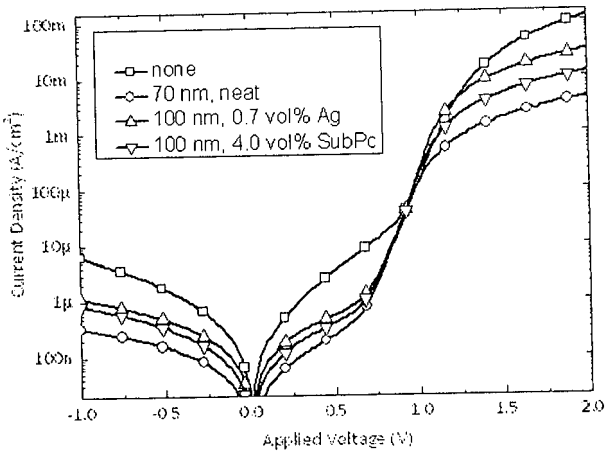

FIG. 11b

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/029305

A. CLASSIFICATION OF SUBJECT MATTER

H01L 51/54(2006.01)i, H05B 33/14(2006.01)i, H01L 51/52(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 51/54; H01L 51/42; H01J 1/62; H01L 31/04; C07D 339/08; H01L 29/66; H01L 51/50; H01L 51/44; H05B 33/14; H01L 51/52

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) & Keywords: organic, metal oxide, transport, and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009-070534 A1 (KONARKA TECHNOLOGIES GMBH) 4 June 2009 See abstract; page 1, lines 22-23, page 4, line 1 - page 5, line 34, page 6, lines 1-30, page 9, lines 3-13, page 21, line 1 - page 22, line 30; claim 1; and figure 1.	1-29,32-38
Y		30,31,39,40
Y	US 2007-0043222 A1 (YOSHIMOTO, TAKUJI et al.) 22 February 2007 See abstract; and paragraphs [0045]-[0047], [0111].	30,31,39,40
A	US 2010-0132770 A1 (BEATTY, PAUL H.J. et al.) 3 June 2010 See abstract; paragraphs [0051]; and figure 1.	1-40
A	US 2008-0054783 A1 (XIA, CHUANJUN) 6 March 2008 See abstract; paragraphs [0040]-[0041]; and figure 2.	1-40
A	US 2010-0289008 A1 (JANG, JUN-GI et al.) 18 November 2010 See abstract; paragraphs [0009]-[0019]; claim 1; and figure 1.	1-40

☐ 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
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"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
29 July 2013 (29.07.2013)	**29 July 2013 (29.07.2013)**

Name and mailing address of the ISA/KR
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/029305

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(43)申请公布日 2014.11.26

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2014.09.12
(86)PCT国际申请的申请数据
PCT/US2013/029305 2013.03.06
(87)PCT国际申请的公布数据
WO2013/138132 EN 2013.09.19
(71)申请人 密执安州立大学董事会
地址 美国密执安
(72)发明人 S·R·弗里斯特 B·E·拉西特
(74)专利代理机构 中国国际贸易促进委员会专利商标事务所 11038
代理人 王海宁
(51)Int.Cl.
H01L 51/54(2006.01)
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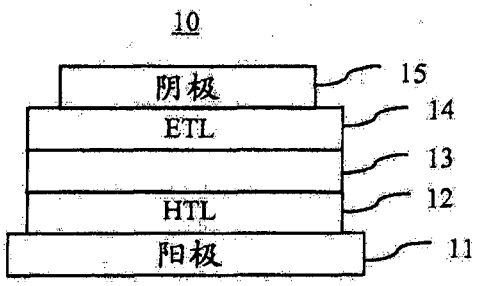
(54)发明名称

掺杂有机分子的金属氧化物电荷传输材料

(57)摘要

用有机分子掺杂金属氧化物电荷传输材料降低电阻同时维持透明度，并且因此在各种有机光电器件中用作电荷传输材料是最佳的，例如有机光伏器件和有机发光器件。



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1. 用于光电器件的金属氧化物电荷传输材料，该材料包含：

金属氧化物材料；和

有机掺杂剂材料。

2. 权利要求 1 的金属氧化物电荷传输材料，其中所述有机掺杂剂材料选自 2,3,5,6-四氟-7,7,8,8-四氰基醌二甲烷（F_4TCNQ）、吖啶橙碱（AOB）和氯硼亚酞菁（SubPc）。

3. 权利要求 1 的金属氧化物电荷传输材料，其中所述金属氧化物材料选自 MoO_3、CrO_3、V_2O_5、WO_3、NiO、Cr_3O_4、Cr_2O_3、CuO、RuO_2、TiO_2、Ta_2O_5、SnO_2 和 Cu_2O。

4. 权利要求 1 的金属氧化物电荷传输材料，其中所述有机掺杂剂的 HOMO 类似于或小于所述金属氧化物材料的 LUMO。

5. 权利要求 1 的金属氧化物电荷传输材料，其中所述有机掺杂剂的 LUMO 相似于或大于所述金属氧化物材料的 HOMO。

6. 权利要求 1 的金属氧化物电荷传输材料，其中所述金属氧化物材料掺杂有 1 至 20 体积%的所述有机掺杂剂材料。

7. 权利要求 1 的金属氧化物电荷传输材料，其中所述金属氧化物材料掺杂有 10 体积%的所述有机掺杂剂材料。

8. 有机光敏器件，该器件包括：

第一电极；

第二电极；

设置在所述第一电极和所述第二电极之间的光活性区域；和

设置在所述光活性区域与所述第一和第二电极中的至少一个电极之间的电荷传输层，其中所述电荷传输层包含掺杂有机掺杂剂材料的金属氧化物材料。

9. 权利要求 8 的器件，其中所述有机掺杂剂材料选自 2,3,5,6-四氟-7,7,8,8-四氰基醌二甲烷（F_4TCNQ）、吖啶橙碱（AOB）和氯硼亚酞菁（SubPc）。

10. 权利要求 8 的器件，其中所述金属氧化物材料选自 MoO_3、CrO_3、V_2O_5、WO_3、NiO、Cr_3O_4、Cr_2O_3、CuO、RuO_2、TiO_2、Ta_2O_5、SnO_2 和 Cu_2O。

11. 权利要求 8 的器件，其中所述有机掺杂剂的 HOMO 类似于或小于所述金属氧化物材料的 LUMO。

12. 权利要求 8 的器件，其中所述有机掺杂剂的 LUMO 类似于或大于所述金属氧化物材料的 HOMO。

13. 权利要求 8 的器件，其中所述金属氧化物材料掺杂有 1 至 20 体积%的所述有机掺杂剂材料。

14. 权利要求 8 的器件，其中所述金属氧化物材料掺杂有 10 体积%的所述有机掺杂剂材料。

15. 权利要求 8 的器件，其中所述光活性区域包含形成施主-受主异质结的有机施主材料和有机受主材料。

16. 有机光敏器件，该器件包含：

阳极；

多个串联的子单元，每个子单元包含：

电子施主层，和与所述电子施主层接触的电子受主层，从而形成施主-受主异质结，分

隔所述子单元的电子 - 空穴复合区 ;和

阴极,

其中所述电子 - 空穴复合区包含掺杂有机掺杂剂材料的金属氧化物材料。

17. 权利要求 16 的器件,其中所述有机掺杂剂材料选自 2,3,5,6- 四氟 -7,7,8,8- 四氰基醌二甲烷 (F_4TCNQ)、吖啶橙碱 (AOB) 和氯硼亚酞菁 (SubPc)。

18. 权利要求 16 的器件,其中所述金属氧化物材料选自 MoO_3、CrO_3、V_2O_5、WO_3、NiO、Cr_3O_4、Cr_2O_3、CuO、RuO_2、TiO_2、Ta_2O_5、SnO_2 和 Cu_2O。

19. 权利要求 16 的器件,其中所述有机掺杂剂的 HOMO 类似于或小于所述金属氧化物材料的 LUMO。

20. 权利要求 16 的器件,其中所述有机掺杂剂的 LUMO 类似于或大于所述金属氧化物材料的 HOMO。

21. 权利要求 16 的器件,其中所述金属氧化物材料掺杂有 1 至 20 体积 % 的所述有机掺杂剂材料。

22. 权利要求 16 的器件,其中所述金属氧化物材料掺杂有 10 体积 % 的所述有机掺杂剂材料。

23. 有机发光器件,该器件包含 :

阳极 ;

阴极 ;和

设置在所述阳极和所述阴极之间的至少一个发射层和至少一个电荷传输层,其中所述至少一个电荷传输层包含掺杂有机掺杂剂材料的金属氧化物材料。

24. 权利要求 23 的器件,其中所述有机掺杂剂材料选自 2,3,5,6- 四氟 -7,7,8,8- 四氰基醌二甲烷 (F_4TCNQ)、吖啶橙碱 (AOB) 和氯硼亚酞菁 (SubPc)。

25. 权利要求 23 的器件,其中所述金属氧化物材料选自 MoO_3、CrO_3、V_2O_5、WO_3、NiO、Cr_3O_4、Cr_2O_3、CuO、RuO_2、TiO_2、Ta_2O_5、SnO_2 和 Cu_2O。

26. 权利要求 23 的金属氧化物电荷传输材料,其中所述有机掺杂剂的 HOMO 类似于或小于所述金属氧化物材料的 LUMO。

27. 权利要求 23 的金属氧化物电荷传输材料,其中所述有机掺杂剂的 LUMO 类似于或大于所述金属氧化物材料的 HOMO。

28. 权利要求 23 的器件,其中所述金属氧化物材料掺杂有 1 至 20 体积 % 的所述有机掺杂剂材料。

29. 权利要求 23 的器件,其中所述金属氧化物材料掺杂有 10 体积 % 的所述有机掺杂剂材料。

30. 权利要求 23 的器件,其中所述至少一个电荷传输层是与所述至少一个发射层直接接触的电子传输层并且设置在所述至少一个发射层和所述阴极之间。

31. 权利要求 23 的器件,其中所述至少一个电荷传输层是与所述至少一个发射层直接接触的空穴传输层并且设置在所述至少一个发射层和所述阳极之间。

32. 堆叠的有机发光器件,该器件包含 :

阳极 ;

阴极 ;

设置在所述阳极和所述阴极之间的多个发射区；和

设置在邻接发射区之间的电荷产生层，

其中所述电荷产生层包含掺杂有机掺杂剂材料的金属氧化物材料。

33. 权利要求 32 的器件，其中所述有机掺杂剂材料选自 2,3,5,6- 四氟 -7,7,8,8- 四氰基醌二甲烷 (F_4TCNQ)、吖啶橙碱 (AOB) 和氯硼亚酞菁 (SubPc)。

34. 权利要求 32 的器件，其中所述金属氧化物材料选自 MoO_3、CrO_3、V_2O_5、WO_3、NiO、Cr_3O_4、Cr_2O_3、CuO、RuO_2、TiO_2、Ta_2O_5、SnO_2 和 Cu_2O。

35. 权利要求 32 的金属氧化物电荷传输材料，其中所述有机掺杂剂的 HOMO 类似于或小于所述金属氧化物材料的 LUMO。

36. 权利要求 32 的金属氧化物电荷传输材料，其中所述有机掺杂剂的 LUMO 类似于或大于所述金属氧化物材料的 HOMO。

37. 权利要求 32 的器件，其中所述金属氧化物材料掺杂有 1 至 20 体积％的所述有机掺杂剂材料。

38. 权利要求 32 的器件，其中所述金属氧化物材料掺杂有 10 体积％的所述有机掺杂剂材料。

39. 权利要求 32 的器件，其中所述至少一个电荷传输层是与所述至少一个发射层直接接触的电子传输层并且设置在所述至少一个发射层和所述阴极之间。

40. 权利要求 32 的器件，其中所述至少一个电荷传输层是与所述至少一个发射层直接接触的空穴传输层并且设置在所述至少一个发射层和所述阳极之间。

掺杂有机分子的金属氧化物电荷传输材料

技术领域

[0001] 本发明公开涉及有机半导体领域，其更具体地涉及用于有机电子器件的有机膜。

背景技术

[0002] 光电器件依靠材料的光学和电子性质来以电子方式产生或检测电磁辐射，或者由周围电磁辐射产生电能。利用有机半导体材料的光电器件正变得越来越合意，因为它们相比于无机半导体材料具有成本优势潜力以及有机材料的某些有益的固有性质，例如它们的柔性。

[0003] 光敏光电器件将电磁辐射转变成电信号或电力。太阳能电池，也被称作光伏（"PV"）器件，是专门用于产生电能的一类光敏光电器件。有机光敏器件包含至少一个光活性区域，其中吸收光从而形成激子，该激子可随后离解成电子和空穴。为了产生电流，光活性区域将典型地包括施主－受主异质结，并且是吸收电磁辐射以产生可以离解的激子的光敏器件的一部分。施主－受主异质结可以是平面异质结、本体异质结或杂化的混合平面异质结。杂化的混合平面异质结包括：包含有机受主材料和有机施主材料的混合物的第一有机层；以及包含第一有机层的有机受主材料或有机施主材料的非混合层的第二有机层。于2005年10月13日公开的Xue等人的美国专利申请公开第2005/0224113号中描述了这种杂化的混合平面异质结，通过引用将其内容整体并入本文。

[0004] 有机光敏光电器件也可以包括透明电荷传输层、电极、或电荷复合区。电荷传输层可以是有机的或无机的，并且可以是或不是光电导活性的。电荷传输层与电极类似，但不具有至器件外部的电连接并且仅将载流子从光电器件的一个子部分（subsection）传递到邻近的子部分。电荷复合区与电荷传输层类似，但在光电器件的相邻子部分之间允许电子与空穴的复合。例如，下述文献中描述了电荷复合区：Forrest等人的美国专利第6,657,378号；2006年2月16日公开的Rand等人的题为"Organic Photosensitive Devices"的公开美国专利申请2006-0032529A1；和2006年2月9日公开的Forrest等人的题为"Stacked Organic Photosensitive Devices"的公开美国专利申请2006-0027802A1；通过引用将每一篇的关于复合区材料和结构的公开内容并入本文。电荷复合区可包括或可以不包括其中嵌入复合中心的透明基质层。电荷传输层、电极、或电荷复合区可充当光电器件的子部分的阴极和/或阳极。电极或电荷传输层可充当肖特基接触部。

[0005] 关于有机光敏器件的现有技术的另外背景说明和描述，包括它们的一般构造、特性、材料和特征，通过引用将Forrest等人的美国专利6,972,431、6,657,378和6,580,027以及Bulovic等人的美国专利6,352,777整体并入本文。

[0006] 在有机材料的背景中，术语"施主"和"受主"是指两种接触但不同的有机材料的最高占据分子轨道（"HOMO"）和最低未占分子轨道（"LUMO"）能级的相对位置。如果一种材料（其与另一种材料接触）的HOMO和LUMO能级较低，那么该材料是受主。如果如果一种材料（其与另一种材料接触）的HOMO和LUMO能级较高，那么该材料是施主。在没有外加偏压的情况下，这在能量上有利于施主－受主结处的电子移动至受主材料中。

[0007] 如本文所使用的，如果第一能级更接近真空能级，那么第一 HOMO 或 LUMO 能级“高于”第二 HOMO 或 LUMO 能级，以及如果第一能级更远离真空能级，那么第一 HOMO 或 LUMO 能级“低于”第二 HOMO 或 LUMO 能级。较高的 HOMO 能级对应于相对于真空能级具有较小绝对能量的电离势。类似地，较高的 LUMO 能级对应于相对真空能级具有较小绝对能量的电子亲和性。在常规能级图上，真空能级处于顶部，材料的 LUMO 能级高于同一材料的 HOMO 能级。

[0008] 有机半导体的重要性质是载流子迁移率。迁移率度量载流子可以响应电场而移动通过导电材料的容易程度。在有机光敏器件的背景下，由于高的电子迁移率而优先通过电子导电的材料可被称作电子传输材料。因高的空穴迁移率而优先通过空穴导电的材料可被称作空穴传输材料。因在器件中的迁移率和 / 或位置而优先通过电子导电的层可被称作电子传输层。因在器件中的迁移率和 / 或位置而优先通过空穴导电的层可被称作空穴传输层。优选地但不一定，受主材料是电子传输材料而施主材料是空穴传输材料。

[0009] 如本文所使用的，术语“有机”包括可用于制作有机光电器件的聚合物材料以及小分子有机材料。“小分子”是指不是聚合物的任何有机材料，并且“小分子”实际上可能相当大。在一些情形中，小分子可以包括重复单元。例如，使用长链烷基作为取代基不会将分子从“小分子”类别中排除。小分子也可被纳入聚合物中，例如作为聚合物主链上的侧基或作为主链的一部分。小分子还可以充当树枝状分子 (dendrimer) 的核心结构部分，该树枝状分子由一系列构建在该核心结构部分上的化学外壳组成。树枝状分子的核心结构部分可以是荧光或磷光性小分子发光体。树枝状分子可以是“小分子”。通常，小分子具有分子量从分子到分子相同的限定化学式，而聚合物具有分子量从分子到分子可能变化的限定化学式。如本文所使用的，“有机”包括烃基配体和杂原子取代的烃基配体的金属络合物。

[0010] 以电子方式产生电磁辐射的有机光电器件的一个例子包括有机发光器件 (OLED)。OLED 利用当跨器件施加电压时发光的有机膜。对于诸如平板显示、照明和背光应用中的使用，OLED 正在变为日益令人感兴趣的技术。美国专利 US5,844,363、US6,303,238 和 US5,707,745 中描述了几种 OLED 材料和构造，通过引用将其公开内容整体并入本文。

[0011] OLED 器件通常被构造为通过至少一个电极发射光，并且在有机光电器件中一个或多个透明电极可以是有用的。例如，透明电极材料，如氧化铟锡 (ITO)，可用作底部电极。还可以使用透明顶部电极，例如美国专利 US5,703,436 和 US5,707,745 中所公开的，通过引用将它们整体并入本文。对于意图仅通过底部电极发射光的器件，顶部电极不必是透明的，并且可包括具有高导电性的厚且反射的金属层。类似地，对于意图仅通过顶部电极发射光的器件，底部电极可以是不透明的和 / 或反射的。这是因为，当电极不必是透明时，使用较厚的层可提供较好的导电性，并且使用反射性电极，可以通过将光反射回透明电极而增加通过另一电极发射的光量。还可以制造全透明的器件，其中两个电极都是透明的。

[0012] 在许多彩色显示应用中，堆叠排列三种 OLED，每种发射三基色（蓝、绿和红）中的一种光，由此形成可发射任何颜色的彩色像素。这种堆叠 OLED（“SOLED”）结构的例子可见于 PCT 国际申请 WO96/19792 和美国专利 US6,917,280 中的描述，通过引用将它们的公开内容整体并入本文。

[0013] 在这种堆叠结构中，提供一对电极层，一个在 SOLED 堆叠体的底部，而另一个在 SOLED 堆叠体的顶部。在 SOLED 的一种变体中，可在堆叠体中的每个 OLED 单元之间提供外部连接的中间电极层。在 SOLED 的其它变体中，在堆叠体中的每个 OLED 单元之间提供电荷

产生层（“CGL”），该电荷产生层注入载流子但没有直接外部电连接。

[0014] 如本文所使用的，“顶部”是指最远离光电器件的基底，而“底部”是指最接近基底。例如，对于具有两个电极的器件，底部电极是最接近基底的电极，并且通常是制造的第一个电极。底部电极具有两个表面，底表面最接近基底，而顶表面更远离基底。当第一层被描述为“设置在”第二层“上方”时，所述第一层被设置为更远离基底，但不一定与第二层物理接触。在第一和第二层之间可以有一个或多个其它层，除非指定第一层与第二层“物理接触”。例如，阴极可被描述为“设置在”阳极“上方”，即使它们之间有各种层。

[0015] 发明概述

[0016] 本发明提供了一种用于光电器件的电荷传输材料，该电荷传输材料包含掺杂有机化合物的金属氧化物。根据本发明的一种实施方案，用于掺杂的有机材料的一些例子是 2,3,5,6- 四氟 -7,7,8,8- 四氰基醌二甲烷 (F_4TCNQ)、吖啶橙碱 (AOB)、和氯硼亚酞菁 (SubPc)。

[0017] 根据另一种实施方案，公开了一种包含这种电荷传输材料的光电器件。这样的器件可以是光敏器件，该光敏器件包含第一电极、第二电极、设置在第一电极和第二电极之间并与第一和第二电极电连接的光活性区域、和设置在光活性区域与第一电极和第二电极中的至少一个电极之间的电荷传输层，其中该电荷传输层包含掺杂有机掺杂剂材料的金属氧化物材料。

[0018] 具有降低的电阻率的掺杂有机化合物的金属氧化物材料可以用作有机光伏器件（“OPV”）中的空穴传输层（“HTL”）、电子传输层（“ETL”）、或它们两者。金属氧化物材料也可以用作级联 OPV 中的复合区，或用作 OLED 中的电荷传输层或 SOLED 中的 CGL。

[0019] 根据一种实施方案，OLED 包含阳极、阴极以及设置在阳极和阴极之间的至少一个发射层和至少一个电荷传输层。在该实施方案中，所述至少一个电荷传输层包含掺杂有机掺杂剂材料的金属氧化物材料。

[0020] 在另一种实施方案中，SOLED 包含阳极、阴极、设置在阳极和阴极之间的多个发射区、以及设置在邻接发射区之间的 CGL。在该实施方案中，所述 CGL 包含掺杂有机掺杂剂材料的金属氧化物材料。

[0021] 本发明还提供了一种制备所公开的用于光电器件的包含金属氧化物和有机掺杂剂材料的电荷传输材料的方法。制备这种掺杂的金属氧化物组合物的例子包括真空热蒸发、溶液沉积、旋涂、喷涂、刮刀涂布和其它溶液加工技术。

[0022] 附图简述

[0023] 图 1 是根据一种实施方案的有机光伏器件的横截面视图。

[0024] 图 2 是根据另一种实施方案的有机光伏器件的横截面视图。

[0025] 图 3 是两层有机发光器件的横截面视图。

[0026] 图 4 是三层有机发光器件的横截面视图。

[0027] 图 5 是堆叠的有机发光器件的横截面视图。

[0028] 图 6 示出了从 ITO/MoO_3:AOB/Au 夹层型器件测得的掺杂 AOB 的 MoO_3 膜的电阻率。

[0029] 图 7a 和 7b 示出了沉积在石英上的不同掺杂的 MoO_3 膜的吸收系数。

[0030] 图 8a 和 8b 示出了包含掺杂 Ag、F_4TCNQ、和 AOB 的 MoO_3 层的 OPV 的黑暗 (8a) 和一太阳光照射 (8b) 的 J-V 特征曲线。

[0031] 图 9a 和 9b 示出了 OPV 器件的随 AOB 掺杂浓度变化的一太阳光照射的 J-V 特征 (9a) 和性能参数 (9b)。

[0032] 图 10a 和 10b 示出了 OPV 器件的随 AOB 掺杂浓度变化的黑暗 J-V 特征 (10a) 和串联电阻 (10b)。

[0033] 图 11a 和 11b 示出了 OPV 器件的一个太阳光照射的 J-V 特征 (11a) 和性能参数 (11b)，比较了不同缓冲层。

[0034] 除非另有说明，所有的附图都是示意性的，并且不是按比例尺绘制并且不意图一定表达实际的尺寸。

[0035] 详细描述

[0036] 公开了用有机分子掺杂以增加金属氧化物薄膜传导性的新型金属氧化物电荷传输材料。所得到的电荷传输材料展示出适合于光电器件的提高的传导性、透光性、光吸收、和耐化学性。它们可用于 OPV 器件或 OLED 器件中的 HTL、ETL 或其两者。所公开组合物的其它应用包括作为级联 OPV 中的复合区或作为 SOLED 中的电荷产生层的用途。

[0037] 如本文所使用的，“金属氧化物”可以是具有有利的能级排列、导电性、透光性和化学稳定性的任何过渡金属氧化物。所述金属氧化物适合作为有机和分子电子器件中的电荷传输层。它们可具有提供与宽广范围的材料的良好能级排列从而改善载流子注入和提取的能力。它们的透光性可允许它们用作光学间隔物。它们与宽广范围的沉积方法相容，例如真空蒸发、溶液沉积、旋涂 (spin casting)、喷涂、刮刀涂布、和其它溶液加工技术。它们还具有允许随后的基于溶剂沉积后续层的化学耐受性。所述金属氧化物材料的例子包括 MoO_3、CrO_3、V_2O_5、WO_3、NiO、Cr_3O_4、Cr_2O_3、CuO、RuO_2、TiO_2、Ta_2O_5、SnO_2、Cu_2O、和其它过渡金属氧化物。优选具有高导电性、透光性和化学稳定性的过渡金属氧化物。

[0038] 本文描述的有机掺杂剂可以是有机半导体材料，其与上述的金属氧化物主体具有合适的能级排列。该有机掺杂剂可以按小分子、低聚物或聚合物的形式存在。优选小分子。此类小分子有机掺杂剂的例子包括 2,3,5,6- 四氟 -7,7,8,8- 四氰基醌二甲烷 (F_4TCNQ)、吖啶橙碱 (AOB) 和氯硼亚酞菁 (SubPc)。

[0039] 可基于以下原则选择有机掺杂剂以提供 n 型掺杂或 p 型掺杂。当掺杂剂的 HOMO 类似于或小于 (即更接近真空能级) 金属氧化物主体的 LUMO 时，发生 n 型掺杂。相反地，当掺杂剂的 LUMO 类似于或大于 (即更远离真空能级) 主体的 HOMO 时，发生 p 型掺杂。如本文所使用的，“类似于”是指在～ 5kT 或 0.2eV 之内。

[0040] 例如，由于 MoO_3 的 LUMO 很高 (～ 6eV)，因此宽广范围的有机材料可用于 n 型掺杂。用于 MoO_3 的 n 型掺杂的合适有机掺杂剂的例子包括 : 吖啶橙碱 (AOB)(～ 3eV)、并五苯 (5.0eV)、并四苯 (5.2eV)、酞氰铜 (CuPc)(5.2eV)、N,N' - 二 (萘 -1- 基)-N,N' - 二 (苯基)- 联苯胺 (NPD)(5.3eV)、二茚并芘 (DIP)(5.5eV)、氯硼亚酞菁 (SubPc)(5.6eV)、和三 (8- 羟基喹啉) 铝 (Alq3)(5.8eV)。

[0041] 这种 n 型掺杂也适用于具有类似能级的其它金属氧化物，例如 CrO_3、V_2O_5 和 WO_3。具有低 HOMO(～ 3eV) 的吖啶橙碱 (AOB) 可充当宽广范围的金属氧化物的 n 型掺杂剂，包括 MoO_3、CrO_3、V_2O_5、WO_3、NiO、Cr_3O_4、Cr_2O_3、CuO、RuO_2、TiO_2、Ta_2O_5、SnO_2、和 Cu_2O。对于具有较小 HOMO 能级的金属氧化物，如 -5.2eV 的 CuO，有机分子诸如 F_4TCNQ(其 LUMO 能级为 -5.2eV) 适合作为 p 型掺杂剂。

[0042] Grenier 等人,“Universal energy-level alignment of molecules on metal oxide”,NATURE MATERIALS, 第 11 卷 (2012 年 1 月) 中提供了多种过渡金属氧化物的 HOMO/LUMO 能级,例如 MoO_3、CrO_3、V_2O_5、WO_3、NiO、Co_3O_4、MoO_2、Cr_2O_3、CuO、TiO_2、Ta_2O_5、Cu_2O 和 CoO,通过引用将其公开内容整体并入本文。Kahn 等人,“Electronic Structure and Electrical Properties of Interfaces between Metals and π-Conjugated Molecular Films”, JOUR. OF POLY. SCI. :PART B:POLYMER PHYSICS, 第 41 卷,第 2529-2548 页 (2003) 中提供了有机材料 F_4-TCNQ、NTCDA、TCNQ、PTCDA、BCP、CBP、F_{16}-CuPC、PTCBI、Alq3、α-NPD、CuPC、ZnPC、并五苯和 α-6T 的 HOMO/LUMO 能级,通过引用将其公开内容整体并入本文。

[0043] 可通过气体、溶液或固体加工技术将有机掺杂剂引入金属氧化物主体。制造这种掺杂的金属氧化物组合物的例子包括真空热蒸发、溶液沉积、旋涂、喷涂、刮刀涂布、和其它溶液加工技术。对于用有机分子掺杂从溶液沉积的金属氧化物膜,选择两种材料都可溶或分散于其中的溶剂。有机掺杂剂占整体组合物的约 1 至 20 体积%,更优选 5 至 10 体积%。

[0044] 本发明人使用掺杂 2,3,5,6- 四氟 -7,7,8,8- 四氰基醌二甲烷 (F_4TCNQ) 或吖啶橙碱 (AOB) 的 MoO_3 的具体实例证实了掺杂的金属氧化物电荷传输材料的益处。使用这两种掺杂剂,所得到的材料具有显著降低的电阻率而仍然维持电荷传输材料的透明性。由于它们的高电阻,未掺杂的金属氧化物通常被限制用于非常薄的膜 (<20nm) 应用。但是,根据本发明的有机分子掺杂的金属氧化物适合作为需要 150nm 或甚至更高厚度的电荷传输层的应用中的电荷传输材料。

[0045] 根据一种实施方案,公开了一种有机光敏器件。该器件包含第一电极、第二电极、设置在第一电极和第二电极之间的光活性区域、以及设置在光活性区域与第一和第二电极中的至少一个电极之间的电荷传输层,其中电荷传输层包含掺杂有机掺杂剂材料的金属氧化物主体材料。

[0046] 图 1 示出了根据本发明一种实施方案的 OPV 器件 10 的例子。器件 10 包含阳极 11(例如 ITO)、阴极 15、和设置在两个电极之间的光活性区域 13。OPV 器件 10 可进一步包括设置在光活性区域 13 与两个电极 11、15 中至少一个电极之间的电荷传输层 12、14,其中电荷传输层包含掺杂有机掺杂剂材料的金属氧化物材料。设置在光活性区域 13 和阳极 11 之间的电荷传输层 12 是 HTL,而设置在光活性区域 13 和阴极 15 之间的电荷传输层 14 是 ETL。光活性区域 13 通常包括形成施主 - 受主异质结的至少一种有机电子施主材料和至少一种有机电子受主材料。如本文所描述的,各种类型的施主 - 受主异质结是可能的。

[0047] 图 2 示出了根据另一种实施方案的 OPV 器件 20 的另一个例子。OPV 器件 20 是级联器件并且可包含阳极 21、阴极 26 和在两个电极之间串联提供的多个光活性子单元 22、24。每个子单元 22、24 可包含至少一种有机电子施主材料和至少一种有机电子受主材料,这些材料在子单元中形成施主 - 受主异质结。在独立子单元之间提供电子 - 空穴复合区 23 的薄层从而分隔所述子单元。根据本发明,电子 - 空穴复合区 23 包含掺杂有机掺杂剂材料的金属氧化物材料。电子 - 空穴复合区 23 用于防止在阳极侧的子单元的受主材料与阴极侧的子单元的施主材料之间形成反向异质结。复合区允许来自阳极侧的子单元的电子与来自阴极侧的子单元的空穴接近。

[0048] 本发明的电荷传输材料的另一种应用在有机发光器件 (OLED) 中。在一种实施方案中,掺杂有机分子的金属氧化物材料可用作 OLED 中的一类或两类电荷传输层。换句话

说，该新型电荷传输材料可用作 OLED 中的空穴传输层和 / 或电子传输层。

[0049] 图 3 示出了一种两层 OLED 30 的例子，该 OLED 30 包含设置在两个电极即阳极 31 和阴极 34 之间的发射层 32 和电子传输层 33。根据一种实施方案，电子传输层 33 可包含掺杂有机分子的金属氧化物。图 4 示出了一种三层 OLED 40 的例子，该 OLED 40 包含设置在阳极 41 和阴极 44 之间的发射层 43、空穴传输层 42 和电子传输层 44。根据另一种实施方案，电荷传输层 44 和 42 之一或两者可包含掺杂有机分子的金属氧化物。制备具有这些构造的 OELD 的各种方法对于本领域的技术人员是已知的。

[0050] 本发明的电荷传输材料的另一种应用在堆叠发光器件 (SOLED) 中，其中使多个活性层单片组合。在 SOLED 中，两个以上的独立发射区以竖直排列方式堆叠，通过中间层分隔接连的发射区。中间层也被称作电荷产生层 (CGL)，因为它们在器件中的载流子产生或注入作功能。CGL 是注入载流子但不具有直接外部电连接的层。当跨 SOLED 施加电压时，CGL 向 CGL 的阴极侧的发射区中注入空穴，并且向 CGL 的阳极侧的发射区中注入电子。

[0051] 图 5 示出了具有两个发射区的 SOLED 300 的例子。SOLED 300 包含阳极 310、两个有机发射区 320 和 330、CGL 350、以及阴极 340。有机发射区 320 和 330 可包含多个层，如空穴注入层、电子注入层、和发射层。正如本领域的技术人员将理解的，发射区可包括其他层，如电子阻挡层、空穴阻挡层等。CGL 350 设置在两个发射区 320 和 330 之间。在优选的实施方案中，CGL 350 包含本文所述的掺杂有机分子的金属氧化物材料。当跨器件施加电压时，CGL 350 可向发射区 330 中注入空穴并且向发射区 320 中注入电子。由于 CGL 350 的载流子注入性质，器件 300 可具有改善的效率。

[0052] 在此类 SOLED 的一种实施方案中，由掺杂的有机物 /MoO_3 组成的 CGL 已被 Kanno 等人使用 (Adv. Mater. 18, 339-342(2006))。当向器件施加电压时，CGL 在有机物侧产生电子并且在 MoO_3 侧上产生空穴，该电子和空穴然后有助于发光。由于该过程依赖于自由电荷的可利用性 (Qi 等人，J. Appl. Phys. 107, 014514(2010))，因此用有机分子掺杂 MoO_3 层，由此增加自由电荷密度，将有可能导致改善的性能。

[0053] 在另一种实施方案中，上述的 OLED 和 SOLED 是磷光有机发光器件 (“PHOLED”)，该器件利用从三重态发光 (磷光) 的发光材料。但本发明的改善的电荷传输材料可应用于 PHOLED 以及荧光 OLED。用于 PHOLED 和荧光 OLED 的有机发光材料在本领域中是已知的。

实施例

[0054] 现在描述本发明的具体代表性实施方案。应当理解，具体的方法、材料、条件、工艺参数、设备等仅仅是示例并且不一定限制本发明的范围。

[0055] 实验方法：

[0056] 根据下面的实验程序，本发明人制备并测试了 OPV 器件的实施例。由涂覆氧化铟锡的玻璃 (“ITO”)(150nm, <15Ω, Prazisions Glas & Optik GmbH)、石英 (qtz) 或硅组成的基底依次在 Tergitol、去离子水、丙酮、三氯乙烯、丙酮和异丙醇中进行清洗。通过以 $<1\times10^{-7}$ 托的热梯度升华将 C_{60}(MER, 99.9% 升华) 和 AOB(Aldrich, 75%) 纯化一次，并且将 SubPc(Aldrich, 85%) 纯化三次。其它材料按原样使用。使 ITO 基底经受 600 秒的紫外线 - 臭氧处理并转移到具有 <0.1ppm O_2 和 H_2O 的氮气手套箱中。将基底装入基准压力 $<1.0\times10^{-6}$ 托的高真空室中。金属氧化物主体和有机掺杂剂材料以 0.10nm/s 蒸发。在氮

气环境中通过旋涂从溶液沉积方酸(squaraine)膜。所有的速率通过石英晶体检测仪测量并通过椭圆偏振光谱仪校准。

[0057] 在具有<1.0ppm O_2和<0.1ppm H_2O的氮气手套箱中,并在具有AM1.5G滤光片(Oriel)的150W氙灯照射下通过Agilent半导体参数分析仪测量样品OPV器件的器件性能。通过使用中性密度滤光片改变灯强度并使用NREL-校准的Si光电二极管测量灯强度。通过使用由灯强度以及器件和检测仪响应率确定的光谱校正因子来确定入射光强度。

[0058] 实验结果

[0059] 制造了具有玻璃/ITO/MoO_3/Au结构的单层"夹层型"器件。测量了这些器件的电流-电压(I-V)特性并计算电阻率($\rho = RA/t$),其中R是电阻,A是器件面积,以及t是层厚度,通过使用Mott-Gurney关系式:

[0060] $$I = \frac{V}{R} + \frac{9A\varepsilon\mu V^2}{8t^3}$$

[0061] 首先,测量掺杂不同AOB浓度的90nm MoO_3层的I-V特性。如图6所示,对于纯MoO_3膜,电阻率ρ是1.6kΩcm,并且当MoO_3膜掺杂7体积%的AOB时降低至800MΩcm以下。接下来,测量掺杂的金属氧化物膜的吸收系数α。在图7a和7b中可见,提高的掺杂在更长的波长时导致增加的α。另外,在较高AOB掺杂浓度下,在530nm附近出现新的吸收峰。该吸收并不对应于纯AOB,但可以反映从有机掺杂剂向金属氧化物主体的能量转移。当掺杂SubPc时,在530nm附近没有出现该新吸收峰,这表明未发生能量转移。

[0062] 接下来,将掺杂的MoO_3膜纳入样品OPV器件中。该器件结构由玻璃/ITO/40nm MoO_3:掺杂剂/9nm MoO_3/13nm SubPC/40nm C_{60}/8nm浴铜灵(BCP)/100nm Ag组成。还包括没有MoO_3层的对照器件用于比较。与没有任何掺杂剂的对照器件相比,这些工作OPV实施例中的掺杂剂是AOB、F_4TCNQ或SubPc,或掺杂Ag的MoO_3膜。向样品器件中纳入9nm的MoO_3缓冲层以确保40nm MoO_3中的有机掺杂剂不影响MoO_3/SubPc界面(例如引起激子猝灭等)。本发明人已发现这不是问题。

[0063] 图8a和8b示出了包含掺杂Ag、F_4TCNQ、和AOB的MoO_3层的这些样品OPV器件的黑暗(8a)和一个太阳光照(8b)的J-V特征曲线。随后使用理想二极管方程的简化型式,$J = J_s\{\exp[q(V-JR_s)/nk_bT]-1\}$,由正向偏压下的黑暗J-V曲线计算$R_s$,其中$J_s$是反向饱和电流,q是电子电荷,n是理想因子,$k_b$是玻尔兹曼常数,以及T是绝对温度。

[0064] 表I汇总了这些未掺杂和掺杂的MoO_3层的OPV的R_s的计算结果。尽管对于未掺杂的情形R_s由112±1Ωcm^{2}增加,当掺杂1体积%的Ag时其降低至4.3±0.1Ωcm^{2}并且当掺杂10体积%的AOB时降低至6.5±0.1Ωcm^2,这接近在没有MoO_3层时获得的值4.4±0.3Ωcm^2。当使用F_4TCNQ时R_s也降低,然而程度较小—这是出乎预料的,因为F_4TCNQ典型地被用作有机材料的p型掺杂剂,并且大多数人认为MoO_3是n型材料。因为MoO_3的电离势较大,因此F_4TCNQ在该情形中充当弱n型掺杂剂是有可能的。

[0065] 表I 具有不同缓冲层的OPV的串联电阻的比较

[0066]

缓冲层	掺杂剂	比率 (体积%)	R_s (Ωcm^2)
无	n/a	n/a	4.4 ± 0.3
MoO_3	无	0	112 ± 1
MoO_3	Ag	1	4.3 ± 0.1
MoO_3	F_4TCNQ	10	29.8 ± 0.4
MoO_3	AOB	10	6.5 ± 0.1
MoO_3	SubPc	4	70.7 ± 0.3

[0067] 制造了具有 90nm 的 MoO_3 层和变化的 AOB 掺杂剂浓度的类似 OPV 器件。图 9a、9b 示出了随 AOB 掺杂浓度变化的样品 OPV 器件的一个太阳光照的 J-V 特征 (9a) 和性能参数 (9b)。如图 10a、10b 所示，R_s 由纯 (neat) 情形的 46 Ωcm^2 降低至掺杂 15.6 体积% AOB 时的 8 Ωcm^2。

[0068] 还制备了使用 SubPc 作为掺杂剂的类似器件。在该情形中，厚的 MoO_3 层掺杂有 0.7 体积%的 Ag、4.0 体积%的 SubPc，或未掺杂。图 11a、11b 示出了这种器件的性能。与未掺杂的情形相比，用 SubPc 掺杂剂掺杂提高了器件性能。

[0069] 掺杂有机化合物的金属氧化物的使用可能在其它器件中是有益的。例如，掺杂有机分子的金属氧化物膜可用于空穴传输层、电子传输层或其两者。

[0070] 也有可能掺杂从溶液沉积的氧化物膜。尽管此处所示的所有数据均利用由真空热蒸发沉积的 MoO_3，然而也可能通过旋涂、喷涂、刮刀涂布、或其它技术从溶液沉积 MoO_3。如果选择两者材料都可溶于其中的溶剂，也可能用有机分子掺杂从溶液沉积的氧化物膜。

[0071] 已阐述了前述说明和实施例，仅仅是为了说明本发明而不意图限制。本发明所公开的方面和实施方案可单独考虑或与本发明的其它方面、实施方案和变体组合。此外，除非另外指出，本发明方法的任何步骤均不限于任何特定的实施顺序。本领域的技术人员可想到包含本发明精神和实质的公开实施方案的修改，并且这样的修改在本发明的范围内。

[0072] 本领域的技术人员可理解，在不背离本发明的广义发明概念的情况下，可对上述实施方案进行改变。因此应理解，本发明不限制于所公开的具体实施方案，而是意图覆盖如所附权利要求书定义的本发明的精神和范围内的修改。

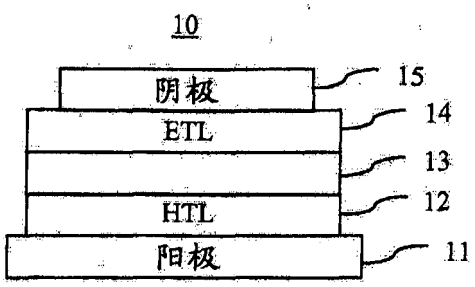
10
阴极
15
ETL
14
13
HTL
12
阳极
11

图 1

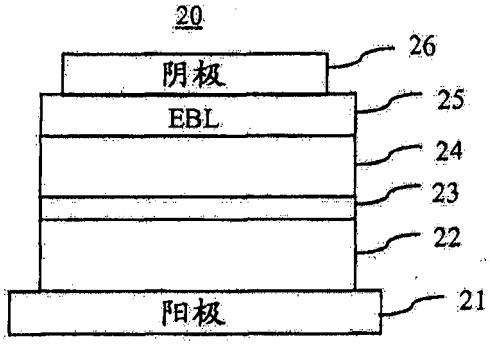
20
阴极
26
EBL
25
24
23
22
阳极
21

图 2

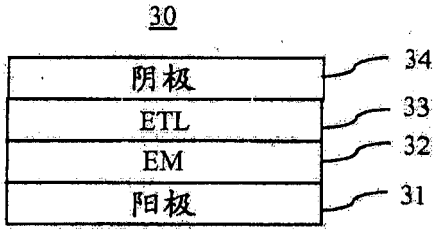
30
阴极
34
ETL
33
EM
32
阳极
31

图 3

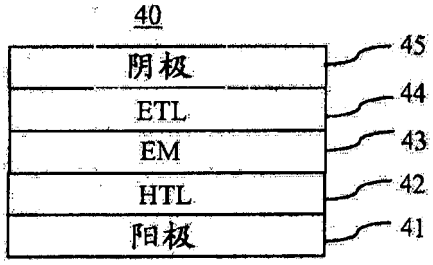
40
阴极
45
ETL
44
EM
43
HTL
42
阳极
41

图 4

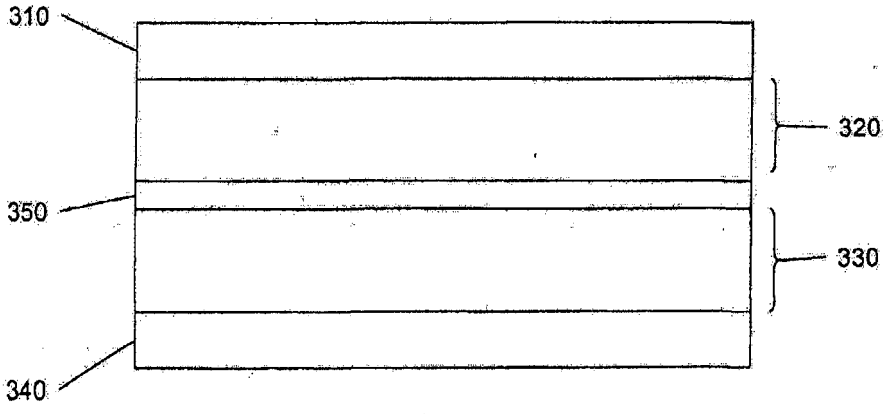
310
320
350
330
340
300

图 5

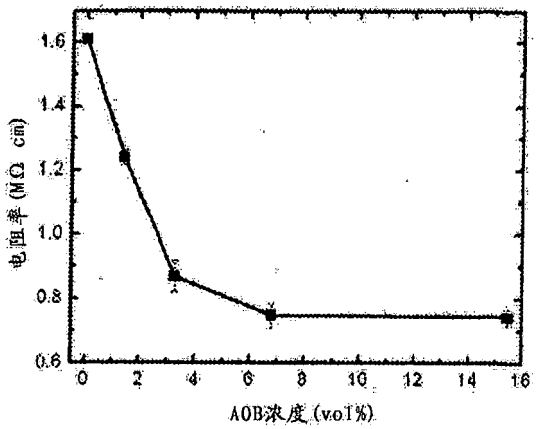

图 6

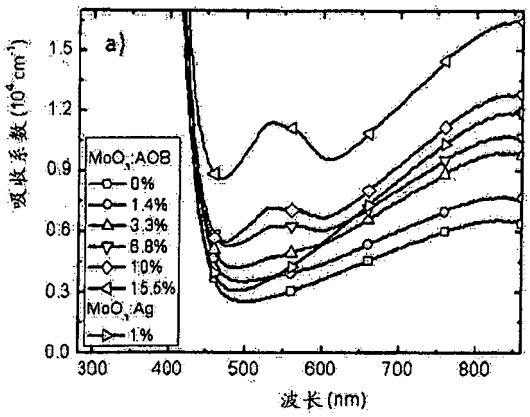

图 7a

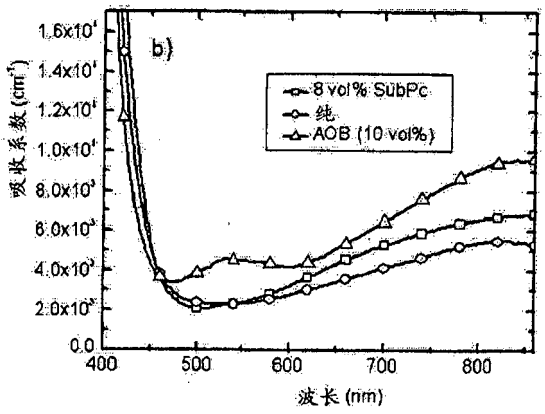

图 7b

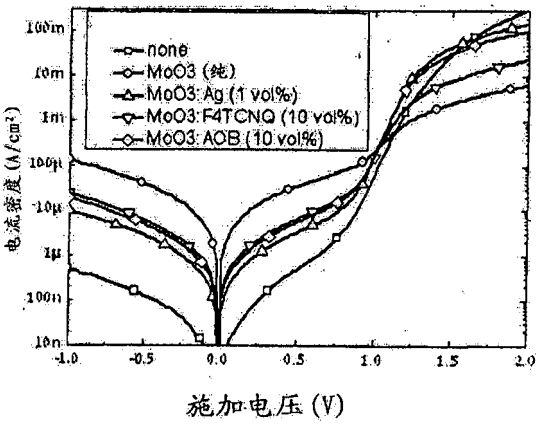

图 8a

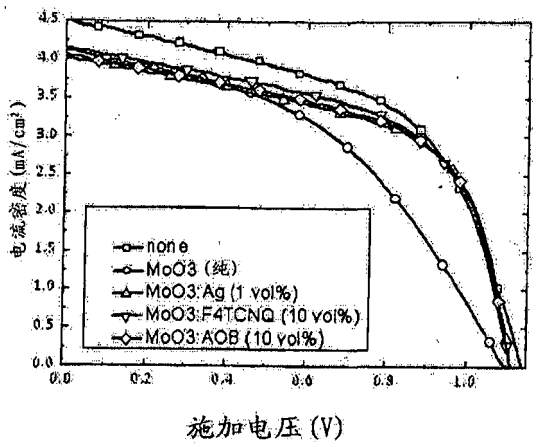
电流密度 (mA/cm²)
none
MoO3 (纯)
MoO3:Ag (1 vol%)
MoO3:F4TCNQ (10 vol%)
MoO3:AOB (10 vol%)
施加电压 (V)

图 8b

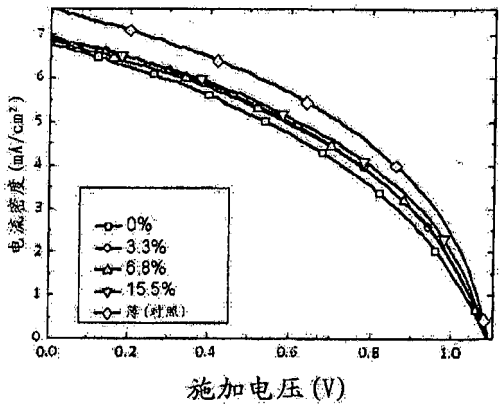
电流密度 (mA/cm²)
0%
3.3%
6.8%
15.5%
施加电压 (V)

图 9a

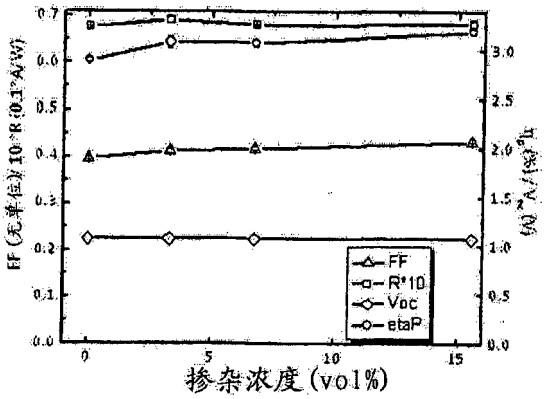
FF
R*10
Voc
etaP
掺杂浓度 (vol%)

图 9b

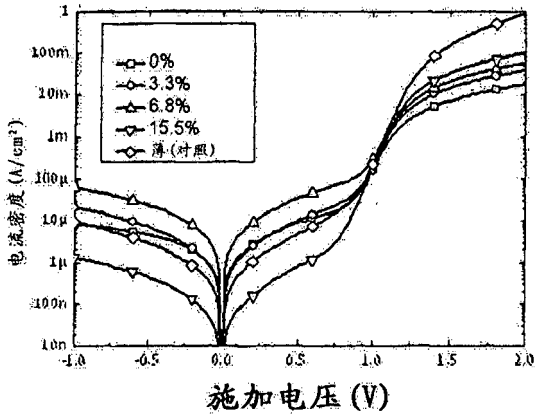

图 10a

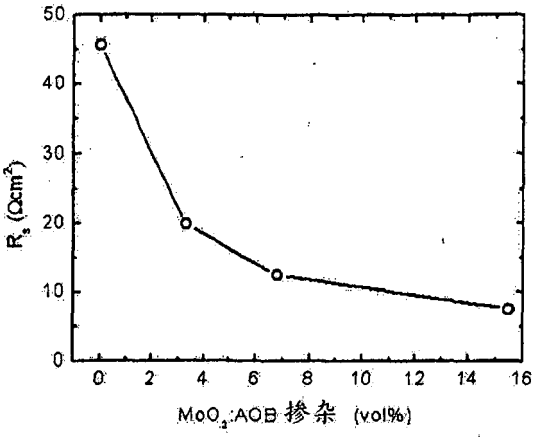

图 10b

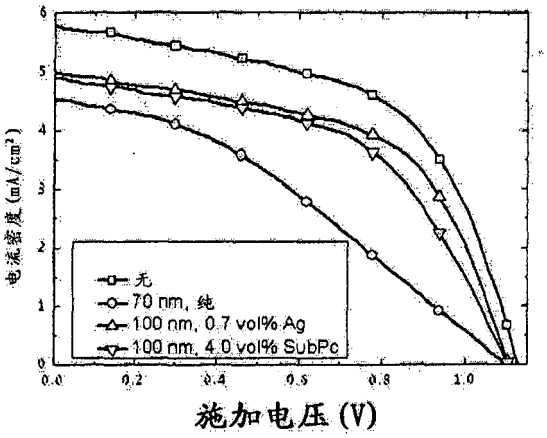

图 11a

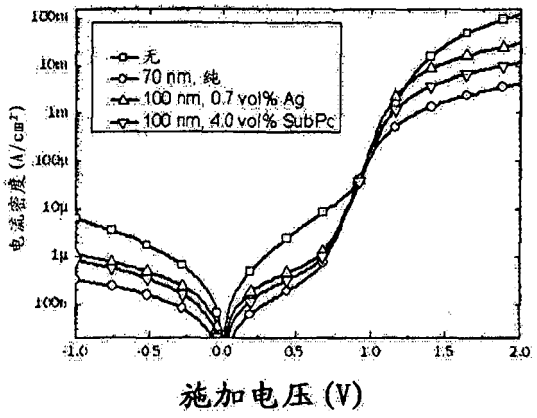

图 11b