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(54) **RECTIFYING CONTACT TO AN N-TYPE
OXIDE MATERIAL OR A SUBSTANTIALLY
INSULATING OXIDE MATERIAL**

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(57) **ABSTRACT**

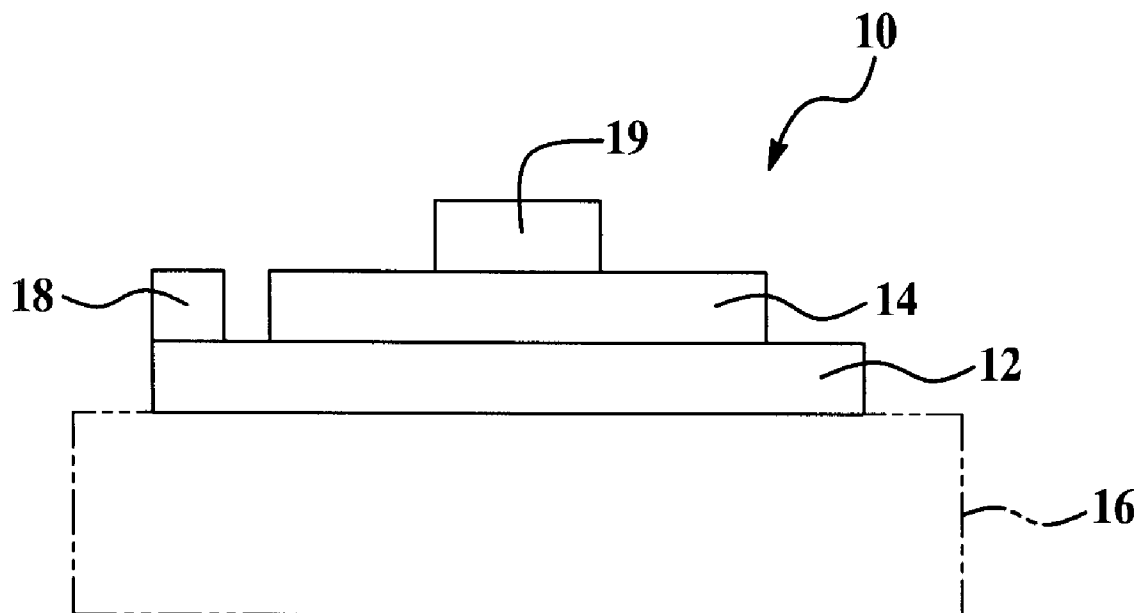
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A rectifying contact to an n-type oxide material and/or a substantially insulating oxide material includes a p-type oxide material. The p-type oxide material includes a copper species and a metal species, each of which are present in an amount ranging from about 10 atomic % to about 90 atomic % of total metal in the p-type oxide material. The metal species is selected from tin, zinc, and combinations thereof.

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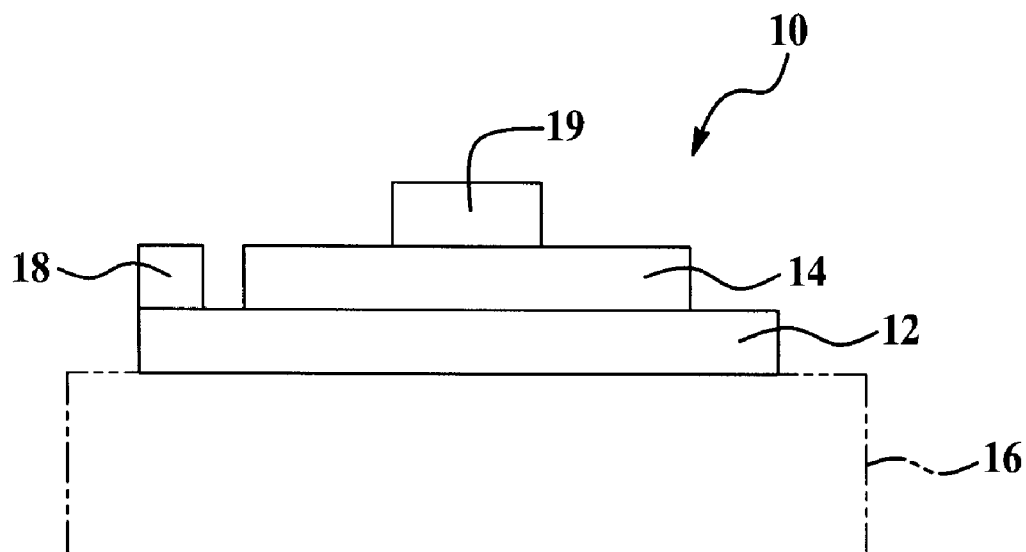


Figure 1A

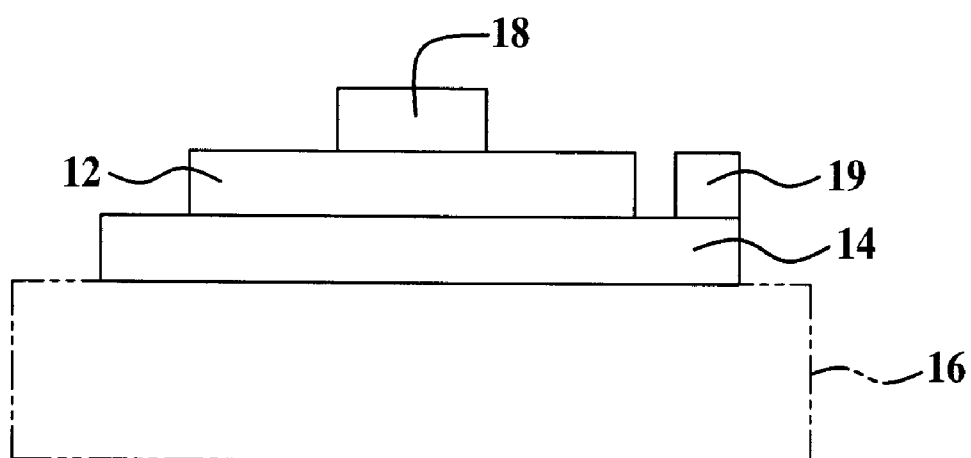


Figure 1B

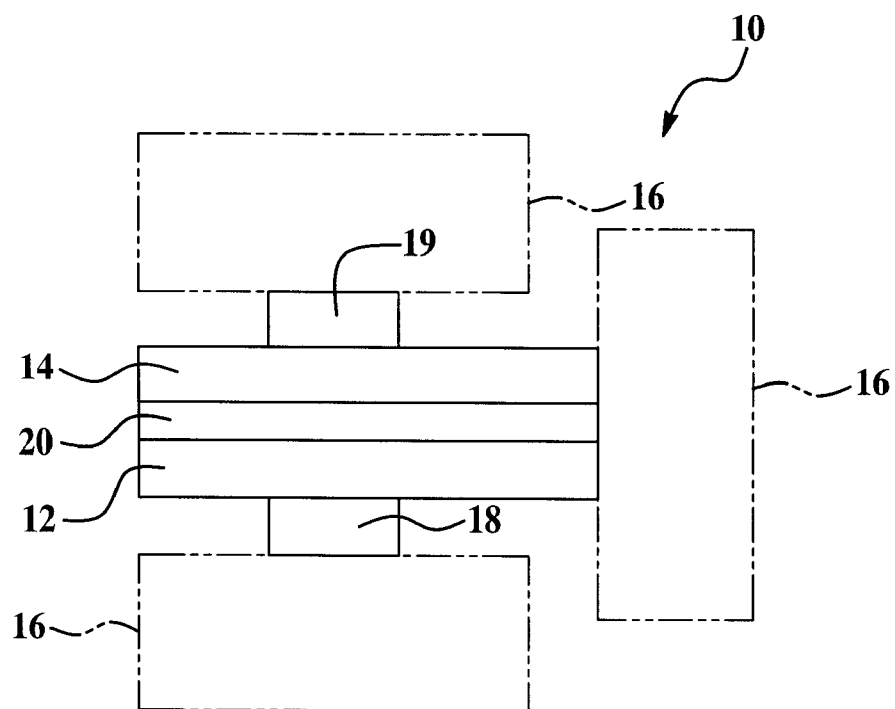


Figure 2

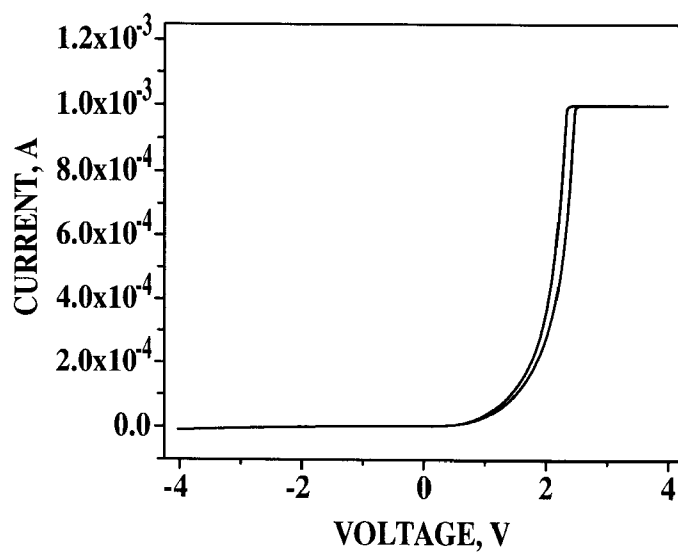


Figure 3

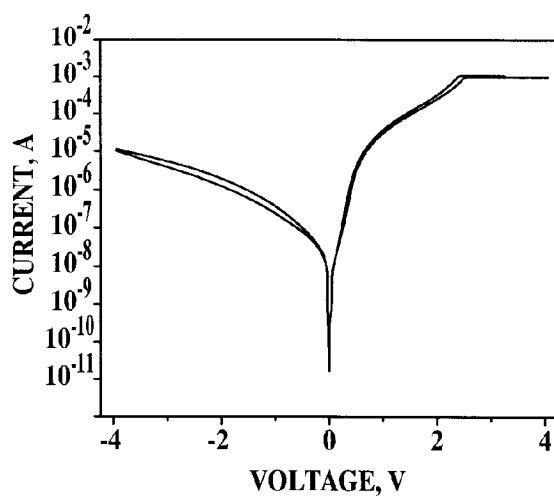


Figure 4

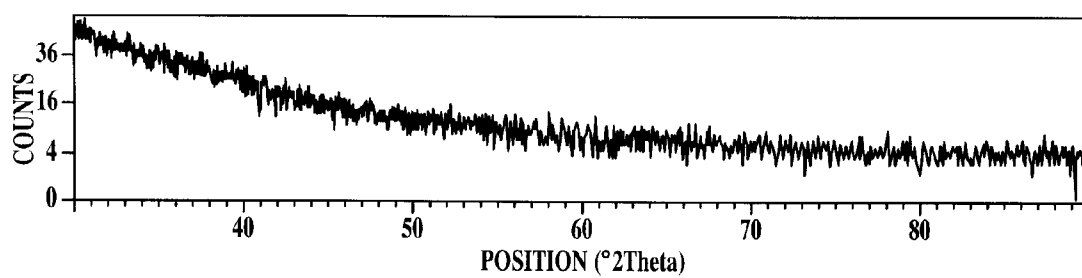


Figure 5

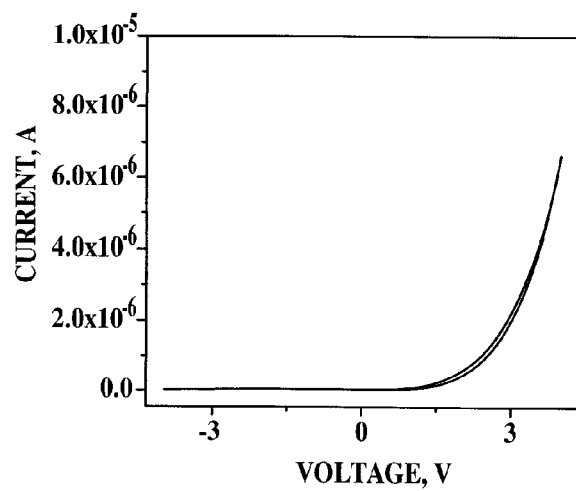


Figure 6

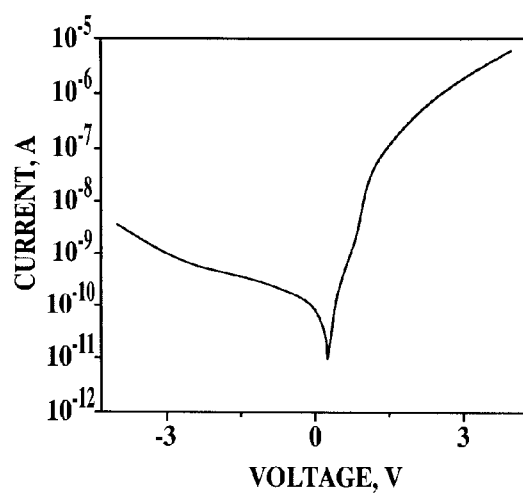


Figure 7

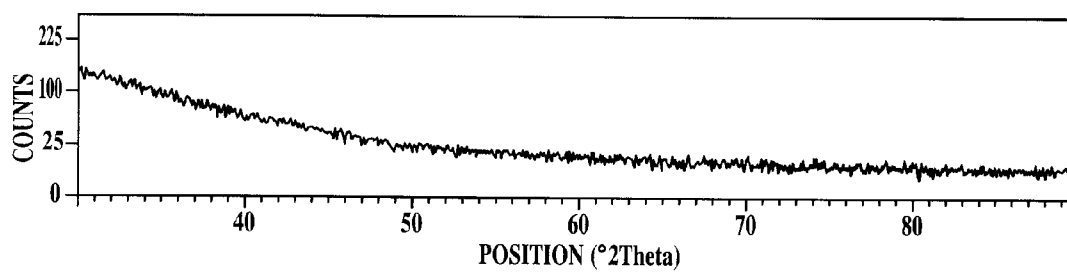


Figure 8

RECTIFYING CONTACT TO AN N-TYPE OXIDE MATERIAL OR A SUBSTANTIALLY INSULATING OXIDE MATERIAL

BACKGROUND

[0001] The present disclosure relates generally to rectifying contacts to an n-type oxide material or a substantially insulating oxide material.

[0002] Many electronic devices are based on oxide semiconductors. Such devices may include thin-film transistors with oxide semiconductor channel layers or diodes incorporating oxide semiconductor materials.

[0003] The formation of high quality rectifying contacts to oxide semiconductors may, in some instances, be difficult. One method for forming a rectifying contact includes doping a material n-type and p-type in adjacent regions to form a diode. This method may, in some instances, not be suitable, as many oxide semiconductors have a tendency toward either n-type or p-type conductivity, with the opposite conductivity being difficult to attain. Many oxides (e.g., ZnO, In₂O₃, and SnO₂) tend strongly toward n-type, and their electron affinity is relatively large (~4-5 eV). As such, a p-type material or metal suitable for formation of a rectifying contact should have a relatively large work function and/or suitable interface properties so as to provide a sufficient barrier to charge injection into the n-type layer when the rectifying contact is biased in the negative direction (i.e., with a relative positive potential applied to the n-type layer). Where a rectifying contact may be obtained, complex surface preparation and low-energy deposition processes may be necessary.

[0004] As such, it would be desirable to provide a p-type material that is capable of forming a rectifying contact to n-type oxides.

SUMMARY

[0005] A rectifying contact to an n-type oxide material and/or a substantially insulating oxide material is disclosed. The rectifying contact includes a p-type oxide material. The p-type oxide material includes a copper species and a metal species, each of which are present in an amount ranging from about 10 atomic % to about 90 atomic % of total metal in the p-type oxide material. The metal species is selected from tin, zinc, and combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Objects, features and advantages will become apparent by reference to the following detailed description and drawings, in which like reference numerals correspond to similar, though not necessarily identical components. For the sake of brevity, reference numerals having a previously described function may not necessarily be described in connection with subsequent drawings in which they appear.

[0007] FIG. 1A is a schematic view of an embodiment of a diode;

[0008] FIG. 1B is a schematic view of an alternate embodiment of a diode;

[0009] FIG. 2 is a schematic view of an embodiment of a diode including a substantially insulating oxide material;

[0010] FIG. 3 is a graph depicting current vs. voltage for a diode containing a copper zinc oxide p-type oxide material;

[0011] FIG. 4 is a graph depicting current vs. voltage for a diode containing a copper zinc oxide p-type oxide material;

[0012] FIG. 5 is a graph depicting the x-ray diffraction analysis of a copper zinc oxide p-type material;

[0013] FIG. 6 is a graph depicting current vs. voltage for a diode containing a copper tin oxide p-type oxide material;

[0014] FIG. 7 is a graph depicting current vs. voltage for a diode containing a copper tin oxide p-type oxide material; and

[0015] FIG. 8 is a graph depicting the x-ray diffraction analysis of a copper tin oxide p-type material.

DETAILED DESCRIPTION

[0016] Several copper-based p-type oxides are known, including SrCu₂O₂, CuAlO₂, CuGaO₂, CuInO₂, and CuYO₂. Some of these p-type oxides are capable of forming rectifying contacts to n-type oxides, such as, for example zinc oxide. The fabrication of rectifying contacts based on these materials generally includes targeting a specific composition that corresponds to a specific crystal structure (e.g., Cu:Al:O₂ 1:1:2 (atomic) to provide CuAlO₂) and metal oxidation state (e.g., Cu(I) to provide CuAlO₂). Targeting such a specific composition generally requires precisely controlled and developed process conditions.

[0017] Embodiments of the rectifying contacts disclosed herein, which are based on copper zinc oxide and/or copper tin oxide materials, do not necessarily correspond to a particular chemical compound and/or crystalline phase; rather they may include substantially amorphous and/or mixed-phase crystalline films. As such, embodiments of the p-type oxide materials discussed in further detail below are fabricated with relatively simple deposition and processing techniques, without complicated surface preparation and/or cleaning processes. Still further, embodiments of the p-type oxide materials may advantageously provide rectifying contacts for various oxide materials, including n-type materials and substantially insulating oxide materials.

[0018] Referring now to FIGS. 1A and 1B, embodiments of diodes 10, each including an embodiment of the p-type oxide material 12, are shown. Generally, the diodes 10 include an n-type (i.e., a material in which electrons are the majority carrier type) oxide material 14 electrically coupled to a p-type (i.e., a material in which holes are the majority carrier type) oxide material 12. In each of these embodiments, a p-n junction is formed between the p-type oxide material 12 and the n-type oxide material 14. It is to be understood that, in these embodiments, the p-type oxide material 12 provides a rectifying contact to the n-type oxide material 14.

[0019] The p-type oxide material 12 and the n-type oxide material 14 may be established on a suitable substrate 16 in any suitable configuration (different embodiments of which are shown in FIGS. 1A and 1B). Non-limitative examples of suitable substrate materials include glass, silicon, quartz, sapphire, PLEXIGLAS (which is commercially available from Rohm and Haas Co., located in Philadelphia, Pa.),

polyamides, metals (a non-limitative example of which includes stainless steel), polyarylates (PAR), polyimides (PI), polyestersulfones (PES), polyethylene naphthalates (PEN), polyethylene terephthalates (PET), polyolefins, and/or combinations thereof.

[0020] The p-type oxide material **12** includes a copper species present in an amount ranging from about 10 atomic % to about 90 atomic % of total metal in the p-type oxide material **12**. Non-limitative examples of the copper species are copper I oxide and copper II oxide.

[0021] The p-type oxide material **12** also includes a metal species present in an amount ranging from about 10 atomic % to about 90 atomic % of total metal in the p-type oxide material **12**. The metal species may include a species of tin, zinc, and/or combinations thereof. Specific non-limitative examples of the metal species include tin oxide, zinc oxide, and/or combinations thereof.

[0022] Some non-limitative examples of the p-type oxide materials **12** include copper zinc oxide, copper tin oxide, and copper zinc tin oxide. In an embodiment, the p-type oxide material may also include gallium, indium, and/or combinations thereof. Examples of the p-type oxide material **12** including indium and/or gallium include, but are not limited to copper zinc indium oxide, copper zinc gallium oxide, copper zinc gallium indium oxide, copper tin indium oxide, copper tin gallium oxide, copper tin gallium indium oxide, copper zinc tin gallium oxide, copper zinc tin indium oxide, copper zinc tin gallium indium oxide, or the like.

[0023] As defined herein, it is to be understood that the term copper/metal "species" may encompass an oxide of the corresponding metal. For example, "copper species" may encompass copper oxide materials; and "metal species" may encompass metal oxide materials.

[0024] It is to be understood that the combination of the copper species and the metal species may be formulated so that the p-type oxide material **12** is substantially homogeneous, substantially heterogeneous, or so that portions of the material **12** are homogeneous while other portions are heterogeneous.

[0025] In one non-limitative example, the p-type oxide material **12** includes about 50 atomic % of the copper species and about 50 atomic % of the metal species. In another non-limitative example, the p-type oxide material **12** includes from about 25 atomic % to about 75 atomic % of the copper species and from about 25 atomic % to about 75 atomic % of the metal species.

[0026] Embodiments of the p-type oxide material **12** are adapted to provide rectifying contacts to suitable oxide semiconductors, including the n-type oxide materials **14**. Non-limitative examples of n-type oxide materials **14** include oxides of zinc, tin, indium, gallium, and/or combinations thereof. Some specific examples of the n-type oxide materials **14** include, but are not limited to zinc oxide, tin oxide, indium oxide, zinc tin oxide, zinc indium oxide, gallium indium oxide, zinc indium gallium oxide, zinc tin gallium oxide, and/or the like, and/or combinations thereof.

[0027] The p-type oxide materials **12** disclosed herein may be substantially amorphous materials and/or mixed-phase crystalline materials.

[0028] The p-type oxide materials **12** disclosed herein may also be at least semi-transparent. When the materials are operatively disposed in a diode **10**, it is to be understood that the transparency of the material may be increased by decreasing the thickness of the established material.

[0029] The diode **10** may also include a contact **18**, **19** in electrical contact with one of the other elements **12**, **14** in the device **10**. Examples of suitable contacts **18** for the p-type oxide material **12** include, but are not limited to high-work function metals (non-limitative examples of which include gold, iridium, nickel, palladium, platinum, rhenium, rhodium, or combinations thereof), p-type conductive oxides (non-limitative examples of which include CuAlO_2 , CuGaO_2 , CuYO_2 , SrCu_2O_2 , Cu_2O), sulfides (a non-limitative example of which includes BaCu_2S_2), halides (a non-limitative example of which includes BaCuSF), or combinations thereof. Examples of suitable contacts **19** for the n-type oxide material **14** include, but are not limited to n-type conductive oxides (non-limitative examples of which include ZnO , In_2O_3 , indium tin oxide (ITO), SnO_2 , or the like), metals (non-limitative examples of which include aluminum, silver, chromium, titanium, or the like), or combinations thereof. In an embodiment, each of the contacts **18**, **19** has a thickness of about 100 nm.

[0030] Referring now to FIG. 2, another embodiment of the diode **10** includes a substantially insulating layer **20** positioned between the p-type and n-type oxide materials **12**, **14**, respectively. In this embodiment, a p-i-n junction is formed in the diode **10**, and the p-type oxide material **12** provides a rectifying contact to the substantially insulating layer **20**.

[0031] If desirable, the embodiment of the diode **10** shown in FIG. 2 may be established on a substrate **16**. It is to be understood that the substrate **16** may be established in contact with either of the two contacts **18**, **19** or with one or more of the materials **12**, **20**, **14**.

[0032] Non-limitative examples of the substantially insulating oxide material **20** include zinc tin oxide, zinc indium oxide, zinc oxide, zinc gallium oxide, zinc indium gallium oxide, indium gallium oxide, and/or the like, and/or combinations thereof.

[0033] Acting as a rectifying contact to either an n-type oxide material **14** (FIGS. 1A and 1B) and/or to a substantially insulating oxide material **20** (FIG. 2), the p-type oxide material **12** may provide a rectifying contact which exhibits a forward-to-reverse current ratio greater than about 10. In another embodiment, the rectifying contact may exhibit a forward-to-reverse current ratio equal to or greater than about 100. In still another embodiment, the rectifying contact may exhibit a forward-to-reverse current ratio greater than about 1000.

[0034] Methods for forming the diode(s) **10** include establishing the p-type oxide material **12** in electrical contact with the n-type oxide material **14**. It is to be understood that the materials **12**, **14** may be established on a substrate **16** in any suitable order and/or arrangement (e.g., vertical to the substrate surface, horizontal to the substrate surface, angled (at any desired angle) with respect to the substrate surface etc.). Furthermore, in an embodiment in which the diode **10** is established on the substrate **16**, either one or all of the materials **12**, **14** may be established directly on the substrate

16. For example, the n-type oxide material 14 may be established directly on the substrate 16 (see FIG. 1B), the p-type oxide material 12 may be established directly on the substrate 16 (see FIG. 1A), one of the contacts 18, 19 may be established directly on the substrate 18 (see FIG. 2), or both the n-type and p-type materials 14, 12 may be established directly on the substrate 16 (see FIG. 2).

[0035] Further, the substantially insulating layer 20 may be established between the p-type oxide material 12 and the n-type oxide material 14, and a contact 18, 19 may be respectively established in electrical contact with the p-type oxide material 12 and the n-type oxide material 14.

[0036] In an embodiment, establishing the materials 12, 14 is accomplished by low temperature deposition techniques and low temperature post-processing techniques. The materials 12, 14 may be established via sputter deposition techniques at ambient temperatures. In other embodiments, the materials 12, 14 may be established via evaporation (e.g., thermal, e-beam, or the like), physical vapor deposition (PVD) (e.g., dc reactive sputtering, rf magnetron sputtering, ion beam sputtering, or the like), chemical vapor deposition (CVD), atomic layer deposition (ALD), pulsed laser deposition, spin coating, spray coating, dip coating, chemical bath deposition, ink-jet printing, gravure printing, liquid electro-photography, dry electro-photography, or the like. It is to be understood that the p-type oxide material 12, that is capable of providing a rectifying contact to an n-type oxide material 14 and/or a substantially insulating oxide material 20, may be obtained without relatively complicated surface preparation, relatively expensive single crystal substrates, and/or relatively complicated cleaning processes.

[0037] It is to be understood that the contacts 18, 19 may be established via any suitable technique, including, but not limited to dc sputter deposition.

[0038] In embodiments of the method, the p-type oxide material 12, the n-type oxide material 14, and the optional substantially insulating layer 20 may be established having a thickness ranging from about 10 nm to about 1000 nm. In another embodiment, the thickness ranges from about 150 nm to about 200 nm.

[0039] To further illustrate embodiment(s) of the present disclosure, the following examples are given. It is to be understood that these examples are provided for illustrative purposes and are not to be construed as limiting the scope of embodiment(s) of the present disclosure.

EXAMPLE 1

[0040] A p-n diode structure was formed with a copper zinc oxide p-type oxide material and a zinc indium oxide n-type oxide material. An indium tin oxide (ITO, acting as a contact for the n-type oxide material) coated glass was used as the substrate. A 150 nm thick zinc indium oxide (ZIO) layer was sputter deposited from a ZnO/In₂O₃ (1:2 molar ratio) target through a shadow mask at ambient temperature on the ITO layer of the substrate. The ZIO acted as an n-type semiconductor. It is believed that good ohmic (i.e., low resistance) contact between ITO and ZIO may be formed without thermal treatments (e.g., annealing). A 150 nm thick layer of copper zinc oxide (CZO) was sputter deposited from a Cu₂O/ZnO (1:1 molar ratio) target at ambient temperature on the ZIO layer to form the p-type oxide material. A gold contact was deposited on top of the CZO to form the device.

[0041] FIGS. 3 and 4 depict graphs of current vs. voltage for the p-n diode structure formed. The current vs. voltage relationship is plotted as linear-linear plot and log-linear plot for FIGS. 3 and 4, respectively. The voltage reference used here assigns the p-type oxide material as the positive terminal. The data was obtained by scanning from negative voltage to positive voltage, and then back down to negative voltage. The data is plotted for both directions of the measurement sweep, and very little hysteresis is observed. Clear rectification in the device is observed where the I_{on}/I_{off} ratio (forward-to-reverse current ratio) at a potential of ± 2 V is over 200. The region where the current level remains constant above about 2.4 V is due to the compliance limit (1 mA) set on the test instrumentation.

[0042] FIG. 5 depicts an X-ray diffraction analysis of a copper zinc oxide p-type oxide material formed using process conditions substantially the same as those used to fabricate the diode in this example. No measurable diffraction was detected, suggesting that the degree of crystallinity in the film is relatively small (i.e., the material is substantially amorphous or weakly crystalline). The X-ray diffraction analysis was performed using a Philips MRD system employing Cu K α radiation (1.54056 angstroms). A grazing angle geometry was employed, using the following conditions:

Parameter	Value
Incident Optic	XRM - 0.5°
Incident Beam Mask	10 mm
Detector Optic	PPC
Soller Slit	Diffacted Beam - 0.04 Rad
Omega angle	0.15°

EXAMPLE 2

[0043] A p-i-n diode structure was formed with an indium tin oxide n-type oxide material, a zinc tin oxide substantially insulating layer, and a copper tin oxide p-type oxide material. An indium tin oxide (ITO, acting as a contact for the n-type oxide material) coated glass was used as the substrate, and the indium tin oxide acted as the n-type oxide material. A 200 nm thick zinc tin oxide (ZTO) layer was sputter deposited from a ZnO/SnO₂ (1:1 molar ratio) target through a shadow mask at ambient temperature on the ITO layer of the substrate, to form the substantially insulating layer of the p-i-n diode. The zinc tin oxide layer was annealed at about 300° C. A 200 nm thick layer of copper tin oxide (CTO) was sputter deposited from a Cu₂O/SnO₂ (1:1 molar ratio) target at ambient temperature on the ZTO layer to form the p-type oxide material. A gold contact was deposited on top of the CTO to form the device.

[0044] FIGS. 6 and 7 depict graphs of current vs. voltage for the diodes formed. The current vs. voltage relationship is plotted as linear-linear plot and log-linear plot for FIGS. 6 and 7, respectively. The data was obtained by scanning from negative voltage to positive voltage, and then back down to negative voltage. The data is plotted for both directions, and very little hysteresis is observed. Clear rectification in the device is observed where the I_{on}/I_{off} ratio (forward-to-reverse current ratio) at a potential of ± 2 V is over 800.

[0045] FIG. 8 depicts an X-ray diffraction analysis of a copper tin oxide p-type oxide material formed using process

conditions substantially the same as those used to fabricate the diode in this example. No measurable diffraction was detected, again suggesting that the degree of crystallinity in the films is relatively small (i.e., the material is substantially amorphous or weakly crystalline). The analysis conditions described in Example 1 were used for the X-ray diffraction of the copper tin oxide material.

[0046] Embodiment(s) of the p-type oxide material 12 described herein include, but are not limited to the following advantages. The p-type oxide materials 12 may advantageously provide rectifying contacts for various oxide materials, including n-type materials 14 and substantially insulating oxide materials 20. Furthermore, the compositions of the p-type oxide materials 12 do not necessarily correspond to a particular chemical compound and/or crystalline phase, rather they may include substantially amorphous and/or mixed-phase crystalline films. As such, the p-type oxide materials 12 may advantageously be obtained via low-temperature deposition processes and without complicated surface preparation, expensive single crystal structures, and/or complicated cleaning processes.

[0047] While several embodiments have been described in detail, it will be apparent to those skilled in the art that the disclosed embodiments may be modified. Therefore, the foregoing description is to be considered exemplary rather than limiting.

1-35. (canceled)

36. A method of making a diode, comprising:

providing a rectifying contact having a p-type oxide material, including:

a copper species present in an amount ranging from about 10 atomic % to about 90 atomic % of total metal in the p-type oxide material; and

a metal species present in an amount ranging from about 10 atomic % to about 90 atomic % of total metal in the p-type oxide material, the metal species selected from tin, zinc, and combinations thereof; and

establishing the p-type oxide material in electrical contact with an n-type oxide material, thereby forming a p-n junction.

37. The method as defined in claim 36, further comprising establishing a substantially insulating oxide material between the p-type oxide material and the n-type oxide material, thereby forming a p-i-n junction.

38. The method as defined in claim 36, further comprising establishing the p-n junction on a substrate.

39. The method as defined in claim 36 wherein establishing the p-type oxide material in electrical contact with the n-type oxide material is accomplished via sputter deposition at ambient temperature.

40. A method of using a p-type oxide material, the method comprising:

establishing the p-type oxide material in electrical contact with an n-type oxide material, the p-type oxide material including:

a copper species present in an amount ranging from about 10 atomic % to about 90 atomic % of total metal in the p-type oxide material; and a metal species selected from zinc, tin, and combinations thereof, the metal species present in an amount ranging from about 10 atomic % to about 90 atomic % of total metal in the p-type oxide material;

wherein the p-type oxide material is adapted to provide a rectifying contact to an

41. (canceled)

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