



(51) International Patent Classification:
H01L 31/0224 (2006.01)

(21) International Application Number:
PCT/AU2014/001101

(22) International Filing Date:
4 December 2014 (04.12.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2013904714 4 December 2013 (04.12.2013) AU
2013904715 4 December 2013 (04.12.2013) AU
2013904985 19 December 2013 (19.12.2013) AU

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,

[Continued on next page]

(54) Title: A PHOTOVOLTAIC CELL AND A METHOD OF FORMING A PHOTOVOLTAIC CELL

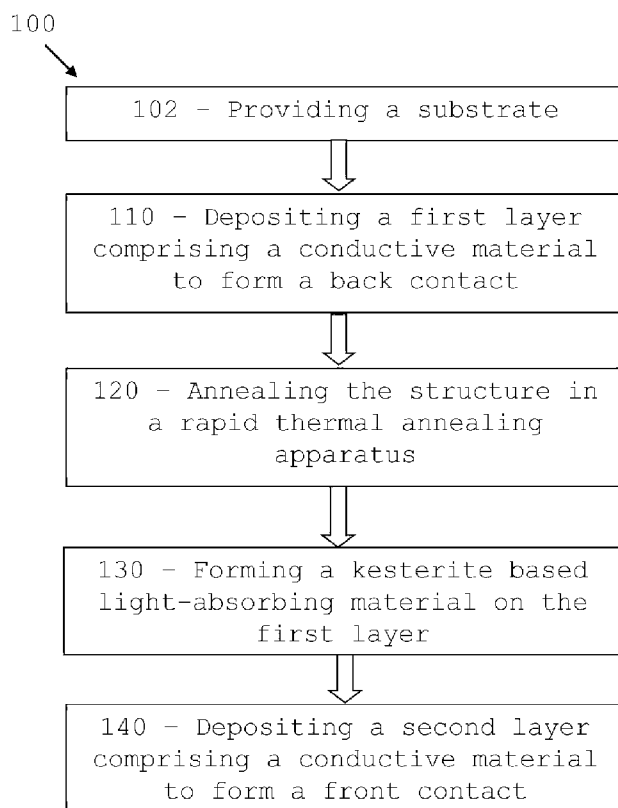


FIGURE 1

(57) Abstract: The present disclosure provides a photovoltaic cell comprising a substrate and a copper based light-absorbing layer. The photovoltaic cell further comprises a first conductive layer that is disposed between the substrate and the light-absorbing layer. The first conductive layer is arranged so as to be electrically coupled to the light-absorbing layer. The photovoltaic cell also comprises a second conductive layer arranged so as to be electrically coupled to the light-absorbing layer. A structure comprising the substrate and the first layer is annealed during formation of the photovoltaic cell.



SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,

DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT,
LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE,
SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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

- 1 -

A PHOTOVOLTAIC CELL AND A METHOD OF FORMING A PHOTOVOLTAIC CELL

Field of the Invention

The present invention generally relates to a photovoltaic cell and a method of forming a photovoltaic cell, such as a photovoltaic cell comprising a copper based chalcogenide light-absorbing material.

Background of the Invention

Thin film solar cells with a copper based chalcogenide light-absorbing material represent an important advancement in thin film photovoltaics technology. Kesterite (CZTS, CZTSe or CZTSSe) based thin film solar cells, for example, use earth abundant materials and inexpensive fabrication techniques. Kesterite is a quaternary compound constituted by copper (Cu), zinc (Zn), tin (Sn) and sulphur (S) or selenium (Se). Kesterite has the chemical formula $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$. Depending on whether the last element is sulphur or selenium the acronyms CZTS or CZTSe are used for Kesterite. By mixing CZTS and CZTSe, absorbers with a direct bandgap, tunable between ~1.0eV and ~1.5eV and a large absorption coefficient can be formed. These properties are ideal for a thin film solar cell absorber.

Current kesterite solar cells are realised on soda lime glass substrates coated with a molybdenum (Mo) layer which functions as a back contact. Generally, a CZTS(Se) absorber layer is formed by annealing a material containing the precursor elements for CZTS(Se). This

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material is usually deposited using PVD, CVD techniques or solution techniques. A front contact consisting of a ZnO/AZO, ITO, BZO layer and a metallic material is normally realised on the absorber layer. Generally,
5 kesterite solar cells also have a CdS intermediate layer between the absorber layer and the front contact.

Although it is widely acknowledged that kesterite solar cells could potentially perform better than other thin film photovoltaic technologies, the current performance of
10 these devices is still below the market average. Record efficiencies of kesterite based solar cells have been reported between 8% and 12.6% compared to, for example, 21.7% for Cu(In, Ga)Se₂ (CIGSe) thin film solar cells.

Some of the causes of the reduced performance of kesterite
15 solar cells are related to structural, chemical and electrical properties of the region between the light-absorbing layer, the back contact and the influence of these properties on the light-absorbing layer.

The propagation of defects from the Mo back contact, to
20 the kesterite absorber layer may reduce the conversion of efficiency of photons into collectable electrical carriers. The Mo layer is generally deposited on the soda lime glass substrate using inexpensive techniques, such as sputtering. Sputtered Mo layers have a high density of
25 structural defect which propagate into the structure affecting the performance of the solar cells.

The chemical instability of the interface between the Mo back contact and the kesterite absorber layer may also be detrimental for the cell performance. This instability can
30 cause decomposition of the absorbing layer or formation of

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MoS₂ and/or MoSe₂ during the annealing of the precursor elements for CZTS(Se). The formation of MoS₂ and/or MoSe₂ generally creates defects deep in the bandgap of the light-absorbing material, causing large current losses.

- 5 There is a need in the art for kesterite based solar cells with improved properties of the region between the light-absorbing layer and the back contact.

Summary of the Invention

Advantageous embodiments of the present invention relate
10 to a copper based chalcogenide solar cell and a method to manufacture a copper based chalcogenide solar cell.
Embodiments of the invention provide a copper based chalcogenide photovoltaic device with a thermally treated back contact structure which provides an improved
15 morphology of the back contact structure and the light-absorbing layer. Embodiments also provide a method for forming a photovoltaic device with a thermally treated back contact structure.

Further advantageous embodiments of the invention provide
20 a copper based chalcogenide photovoltaic device with a back contact structure with an additional intermediate layer which allows reducing the formation of secondary phases, such as metallic sulphide compounds or metallic selenide compounds, in the region between the light-
25 absorbing layer the back contact and/or preserving, or improving, the series resistance of the solar cell.

In accordance with the first aspect, the present invention provides, a photovoltaic cell comprising:

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a substrate;
a copper based light-absorbing layer;
a first conductive layer disposed between the
substrate and the light-absorbing layer, the first
5 conductive layer being arranged so as to be electrically
coupled to the light-absorbing layer; and
a second conductive layer arranged so as to be
electrically coupled to the light-absorbing layer;
wherein a structure comprising the substrate and
10 the first layer is annealed during formation of the
photovoltaic cell.

In accordance with a second aspect, the present invention
provides a photovoltaic cell comprising:

a substrate;
15 a copper based light-absorbing layer;
a first conductive layer disposed between the
substrate and the light-absorbing layer, the first
conductive layer being arranged so as to be electrically
coupled to the light-absorbing layer;
20 an intermediate layer comprising a metallic
material arranged between the light-absorbing layer and
the first conductive layer;
a second conductive layer arranged so as to be
electrically coupled to the light-absorbing layer;
25 wherein the metallic material is selected so as
to reduce the formation of secondary phases such as
metallic sulphide compounds or metallic selenide compounds
in the region between the light-absorbing layer and the
first layer.

30 In accordance with a third aspect, the present invention
provides a photovoltaic cell comprising:

a substrate;

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a copper based light-absorbing layer;
a first conductive layer disposed between the substrate and the light-absorbing layer, the first conductive layer being arranged so as to be electrically
5 coupled to the light-absorbing layer;
an intermediate layer comprising a non-metallic material arranged between the light-absorbing layer and the first conductive layer;
a second conductive layer arranged so as to be
10 electrically coupled to the light-absorbing layer;
wherein the non-metallic material is selected such that a series resistance of the photovoltaic cell is not substantially increased compared to if the photovoltaic cell did not comprise the non-metallic
15 material.

In embodiments, the photovoltaic cell comprises an intermediate layer disposed between the light-absorbing layer and the first layer, the intermediate layer being arranged to reduce the formation of secondary phases such
20 as metallic sulphide compounds or metallic selenide compounds in the region between the light-absorbing layer and the first layer.

The intermediate layer may be further arranged to reduce formation of voids in the region between the light-
25 absorbing layer and the first layer and/or to reduce the series resistance of the photovoltaic cell.

The intermediate layer may comprise a chemically treated surface with an improved surface morphology, when compared with an untreated surface of a similar intermediate layer.

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In some embodiments, the intermediate layer comprises a metallic material and may comprise: an alloy, silver, gold or a gold/silver alloy. The metallic material may have a thickness between 3nm and 50nm.

- 5 In some embodiments, a portion of the metallic material is incorporated in the light-absorbing material during fabrication of the photovoltaic cell. This incorporation may take place during an annealing step of the photovoltaic cell. Further, the atoms of the metallic
10 material in the light-absorbing material may affect the doping concentration of the light-absorbing material.

In embodiments, the intermediate layer comprises a non-metallic material. The non-metallic material may have an electrical resistivity of 100 $\mu\Omega$ cm or less. Further, the
15 non-metallic material may not chemically interact with metallic materials at temperatures below 800°C.

In some embodiments, the non-metallic material comprises a semiconductor material and may comprise titanium diboride or zirconium diboride. In other embodiments, the non-
20 metallic material comprises a conductive oxide material and may comprise a molybdenum oxide layer with a thickness above 5 nm. The non-metallic material may have a thickness between 5 nm and 80 nm.

In embodiments, the photovoltaic cell is fabricated on a
25 substrate and the substrate may comprise soda lime glass, a metallic foil or flexible polyimide.

In embodiments of the invention layers of the photovoltaic cells are thermally treated by annealing. In some embodiments, a structure comprising the substrate and the
30 first layer is annealed using a rapid thermal annealing

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process. In other embodiments a structure comprising the substrate, the first layer and the intermediate layer is annealed during formation of the photovoltaic cell.

The first layer may have a lower density of physical
5 defects when compared to the same layer before annealing of the structure comprising the substrate and the first layer. The first layer may comprise a plurality of nucleation sites developed on the surface of the first layer during annealing.

10 In some embodiments, the substrate comprises sodium and during annealing of the structure comprising the substrate and the first layer sodium diffuses from the substrate to the first layer. The light-absorbing layer may also
15 comprise sodium diffused from the substrate through the first layer. The sodium may diffuse from the first layer to the light-absorbing layer during an annealing process of the light-absorbing layer, such as a sulphurisation process. The light-absorbing layer may comprise about 900 ppm of sodium.

20 In embodiments, the copper based light-absorbing layer is a kesterite based layer. However, the copper based light-absorbing layer may also be a copper-zinc-germanium-tin-chalcogenide based layer or a silver-copper-zinc-tin-chalcogenide based layer.

25 Introducing silver or germanium in the light-absorbing layer provides several advantages, such as a level of controllability of the light-absorbing layer bandgap and improvement of the grain quality and the minority carrier lifetime of the light-absorbing material.

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In embodiments, the photovoltaic cell also comprises a third conductive layer which includes cadmium-sulphide arranged between the light-absorbing layer and the second layer.

- 5 In embodiments, the first material comprises a suitable metallic material or transparent conductive oxide. The first material comprises molybdenum.

In embodiments, the first layer comprises a suitable metallic material and a structure comprising the substrate
10 and the first layer is annealed during formation of the photovoltaic cell and a portion of the first layer is oxidised during annealing.

In some embodiments, the photovoltaic cell has one or a combination of the following properties:

- 15 - an open-circuit voltage higher than 600 mV;
- a short-circuit current density higher than 10 mA/cm²;
- a fill-factor higher than 40%;
- a series resistance lower than 40 Ohm/cm²; and
- a shunt resistance higher than 1.5 kOhm/cm².

20 In accordance with a fourth aspect, the present invention provides a method of forming a photovoltaic cell comprising the steps of:

providing a substrate;

depositing a first conductive material on the
25 substrate,

subsequent the step of depositing the first conductive material, annealing the substrate and the first material;

subsequent the annealing step, forming a copper
30 based light-absorbing material on the first material; and

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depositing a second conductive material such that the second conductive material is electrically coupled to the light-absorbing material.

In accordance with a fifth aspect, the present invention provides a method of forming a photovoltaic cell comprising the steps of:

- providing a first conductive material;
- depositing a metallic material on the first material; subsequent to depositing the metallic material
- 10 forming a copper based light-absorbing material on the metallic material; and
- depositing a second conductive material such that the second material is electrically coupled to the light-absorbing material;
- 15 wherein the metallic material is selected so as to reduce the formation of sulphides and/or selenides at the first material.

In embodiments, the method further comprises the steps of:

- providing a substrate;
- 20 depositing the first material on the substrate;
- and
- subsequent the step of depositing a metallic material on the first material, annealing at least the substrate, the first material and the metallic material.

25 The steps of depositing a metallic material on the first material and forming a copper based light-absorbing material on the metallic material may be performed in a manner such that, during the step of forming a copper based light-absorbing material on the metallic material, a

30 portion of the metallic material is incorporated in the copper based light-absorbing material.

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In embodiments, the method further comprises the steps of:

providing a substrate;

depositing the first material on the substrate;

and

5 subsequent the step forming a copper based light-absorbing material on the metallic material, annealing at least the substrate, the first material, the metallic material and the light-absorbing material.

During the step of annealing at least the substrate, the
10 first material, the metallic material and the light-absorbing material a portion of the metallic material may be incorporated in the copper based light-absorbing material.

In accordance with a sixth aspect, the present
15 invention provides a method of forming a photovoltaic cell comprising the steps of:

providing a first conductive material;

depositing a non-metallic material on the first material; subsequent to depositing the metallic material

20 forming a copper based light-absorbing material on the metallic material; and

depositing a second conductive material such that the second material is electrically coupled to the light-absorbing material;

25 wherein the non-metallic material is selected such that a series resistance of the light-absorbing layer is not substantially increased compared to if the photovoltaic cell did not comprise the non-metallic material arranged between the light-absorbing material and
30 the first material.

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In embodiments, the method further comprises the step of chemically treating the non-metallic material to reduce the density of defects about the interface between the non-metallic material and the light-absorbing material compared to a similar interface where the non-metallic material has not been chemically treated.

In embodiments, the intermediate layer comprises a non-metallic material. The non-metallic material may have an electrical resistivity of $100\ \mu\Omega\ \text{cm}$ or less. Further, the non-metallic material may not chemically interact with metallic materials at temperatures below 800°C .

In some embodiments, the non-metallic material comprises a semiconductor material and may comprise titanium diboride or zirconium diboride. In other embodiments, the non-metallic material comprises a conductive oxide material and may comprise a molybdenum oxide layer with a thickness above 5 nm.

In embodiments, the method further comprises the steps of:
providing a substrate;
depositing the first material on the substrate;
and
subsequent the step of depositing a non-metallic material on the first material, annealing at least the substrate, the first material and the non-metallic layer.

In embodiments, the method of the fifth or sixth aspect further comprises the steps of:
providing a substrate;
depositing the first material on the substrate;
and
subsequent the step of depositing the first

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material on the substrate, annealing at least the substrate and the first material.

In embodiments of the method of the fourth, fifth or sixth aspect, the step of annealing at least the substrate and the first material may be performed in a manner such that sodium diffuses from the substrate to the first layer during annealing. The sodium diffusion may be achieved by controlling the annealing temperature, annealing time or annealing gas flow rate.

10 In embodiments of the method of the fourth, fifth or sixth aspect further comprises the step of forming an oxide layer on a surface of the first conductive material. The oxide layer may be formed during the annealing of the substrate and the first material. The annealing
15 temperature, annealing time or annealing gas flow rate may be controlled to control the thickness of the oxide layer.

The annealing steps of any of the aspects above may comprise the step of placing the photovoltaic cell in an annealing furnace and heating the furnace to a temperature
20 in the range of 500°C to 800°C for a time interval between 5 to 20 minutes.

Brief Description of the Drawings

Features and advantages of the present invention will become apparent from the following description of
25 embodiments thereof, by way of example only, with reference to the accompanying drawings in which:

Figures 1, 8, 13, 15 and 21 show flow diagrams outlining a method of forming a solar cell in accordance with embodiments;

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Figure 2(a) and 2(b) show scanning electron microscope (SEM) images of a solar cell structure as typically realised in the prior art (a), and a kesterite solar cell structure in accordance with an embodiment of the present invention (b) respectively;

Figures 3(a) and 3(b) show SEM images of the back contact surface of the solar cell structures of figures 2(a) and 2(b) respectively;

Figures 4 shows Raman spectra of the solar cell structures of figures 2(a) and 2(b);

Figure 5 shows X-ray diffraction spectra of figures 2(a) and 2(b);

Figures 6(a) and 6(b) show comparative plots of the current-voltage characteristics and external quantum efficiency, respectively, for the solar cell structures of figures 2(a) and 2(b);

Figure 7 and 14 show a schematic representation of a solar cell device in accordance with embodiments;

Figure 9(a), 16(a) and 9(b), 16(b) show SEM images of a solar cell structure as typically realised in the prior art (a), and a solar cell structure in accordance with embodiments of the present invention (b), respectively;

Figures 10(a) and 10(b) show Raman spectra of the solar cell structures of Figures 9(a) and 9(b) respectively;

Figures 11(a) shows X-ray diffraction spectra of the solar cell structures of figure 9; figure 11(b) is a detail of a peak of the spectrum of figure 11(a);

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Figures 12(a) and 12(b) show comparative plots of the current-voltage characteristics and external quantum efficiency, respectively, for the solar cell structures of figure 9;

- 5 Figures 17(a) and 17(b) show electron diffraction spectroscopy plots of the structures shown in figures 16(a) and 16(b) respectively;

Figures 18(a) and 18(b) show Raman spectra of solar cell structures realised according with embodiments;

- 10 Figure 19 shows X-ray diffraction spectra of solar cell structures realised according with embodiments; and

Figure 20 is a comparative plot of the current-voltage performance of a solar cell realised according to embodiments of the present invention and a kesterite solar
15 cell as typically realised in the prior art.

Detailed Description of Embodiments

Embodiments of the present invention relate to photovoltaic cells comprising a copper based chalcogenide light-absorbing material and metallic contacts.

- 20 Advantageous embodiments of the invention are related to a photovoltaic cell comprising a glass substrate covered with a conductive layer which forms a back contact for the cell. An annealing procedure is performed on the substrate and the conductive layer before
25 the copper based chalcogenide light-absorbing material is deposited onto the conductive layer. The annealing procedure improves the structural properties of the back

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contact, thereby reducing the amount of structural defects which propagate to the light-absorbing layer.

According to embodiments of the invention, the substrate and the conductive layer are annealed using a rapid
5 thermal annealing (RTA) process. An RTA process is generally performed in dedicated RTA furnaces and has duration in the order of several minutes. The temperature ramping times in RTA processes are usually also very short. In these embodiments the structure of the back
10 contact is improved; the density of defects in the conductive layer is decreased providing better quality absorbing layers.

Further advantageous embodiments of the invention are related to thin film photovoltaic cells based on a
15 chalcogenide light-absorbing material which have an intermediate metallic layer between a back contact layer and the light-absorbing layer. The metallic layer is arranged to reduce the formation of sulphides and/or selenides in the region between the light-absorbing layer
20 the back contact.

According to embodiments of the invention the intermediate metallic layer has a thickness between 3 nm and 50 nm. The thickness of this layer is suitable to reduce the chemical inter-activity between the back contact and the light-
25 absorbing layer. Only a small amount of metallic material is used to realise this layer, given the reduced thickness. This means that the costs incurred to realise the intermediate layer do not have a major effect on the final cost of the solar cell. Therefore, metallic
30 materials which would not typically be used to realise the entire back contact due to cost, such as silver and/or

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gold, could instead be used for the intermediate metallic layer.

In addition to reducing the detrimental formation of sulphides and/or selenides, the intermediate metallic layer affects the growth properties, and therefore the physical structure, of the light-absorber. This allows obtaining an absorbing layer with a compact structure and a low density of electrically active defects leading to higher carrier generation rates and improved performance.

Solar cells realised according to some embodiments of the present invention may use a Mo based back contact layer. Despite the problems discussed above, Mo appears to be a good material for the back contact as it provides a very good compromise between chemical activity during the cells high-temperature annealing process and cost. However, other conductive material may be used in place of Mo, such as other suitable metallic materials or transparent conductive oxides (TCOs). While the main conductance at the back contact, in these embodiments, is provided by the Mo layer (which should be about 400-800 nm thick to achieve a sheet resistance between 0.2 - 0.5 Ohm/sq), silver (Ag) and gold (Au) layers, for example, may be used to implement the intermediate metallic layer.

In some embodiments, metallic material may be incorporated in the light-absorbing layer during fabrication of the photovoltaic cell. The incorporation may take place during sulphurisation. The sulphurisation step may be controlled, by tuning the temperature, gas concentration or duration, to control the diffusion of the metallic material into the light-absorbing layer. In some embodiments the metallic material of the intermediate layer may be uniformly

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distributed through absorber and be incorporated into the absorber crystal structure such that the intermediate layer is no longer distinguishable.

Additional advantageous embodiments are related to thin
5 film photovoltaic cells based on a chalcogenide light-absorbing material which have an intermediate non-metallic layer between a back contact layer and the light-absorbing layer. The non-metallic layer allows reducing the formation of sulphides and/or selenides at the interface
10 between the back contact and the light-absorber while substantially maintaining, or improving, the series resistance and the fill factor of the solar cell. This is in contrast with some other intermediate non-metallic layers, which have been found to be detrimental for the
15 series resistance and the fill factor of the solar cells.

According to embodiments of the invention the intermediate non-metallic layer has a thickness between 5 nm and 80 nm. The thickness of this layer is suitable to reduce the chemical inter-activity between the back contact and the
20 light-absorbing layer.

The electrical properties of the intermediate non-metallic layer are such that the series resistance of the solar cell is not affected, or is improved, compared to a solar cell with a similar structure which does not have this
25 layer. In order to accomplish this, in some embodiments of the invention, materials which have specific conductivities and are chemically inert during the annealing steps performed for the fabrication of the solar cells are selected.

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The light-absorber layer is grown on the top surface of the intermediate non-metallic layer, instead of the top surface of the metallic back contact layer, as in prior art solar cells. This implies that the structural
5 properties of the copper based chalcogenide absorber layer are affected by the physical properties of the top surface of the intermediate non-metallic layer, in particular the surface morphology.

In some embodiments, this surface is treated in an
10 additional manufacturing step, to improve its structural properties. For example, this surface may be improved using physical treatments, chemical passivation treatments, etching treatments or texturing treatments. The additional manufacturing step is designed to provide
15 an absorbing layer with a compact structure and a low density of electrically active defects leading to higher carrier generation rates and improved performance.

In some embodiments, the improved structure of the back photovoltaic cell back contact also provides enhanced
20 optical performance.

Embodiments of a copper based chalcogenide photovoltaic cell realised in accordance with the present invention is described below. Specific features described below provide details of a copper based chalcogenide photovoltaic cell
25 realised according to the present invention and should not be considered restrictive.

The copper based chalcogenide light-absorbing layer of the embodiments of photovoltaic cells described below is a kesterite light-absorbing layer. However, in alternative
30 embodiments, the light-absorbing layer may comprise

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another copper based chalcogenide material, such as a copper-zinc-germanium-tin-chalcogenide material or a silver-copper-zinc-tin-chalcogenide material.

Referring now to figure 1, there is shown a flow diagram
5 100 outlining a method of forming a kesterite solar cell
in accordance with embodiments of the present invention.
The first step 102 consists in providing a substrate to
deposit the layers of the solar cell upon. This substrate
is generally a soda lime glass substrate. At 110 a
10 conductive layer is then deposited on the soda lime glass.
In this embodiment, a Mo layer with a thickness around
1000 nm is sputtered, using a multi-target sputtering
tool, onto the soda lime substrate to form a back contact.
At 120 the substrate covered with the Mo layer is then
15 transferred into an RTA furnace and annealed for a period
of time between 5 minutes to 20 minutes in a temperature
range between 500°C and 800°C in a chalcogen atmosphere.
In a preferred embodiment, the annealing is performed for
10 minutes at a peak temperature of 650°C. Subsequently,
20 at 130, a kesterite based light-absorbing material is
formed on the Mo layer. In this embodiment, the step 130
of forming the kesterite material comprises two sequential
steps:

- depositing a series of layers containing
25 precursor materials for the kesterite layer
(Zn/Cu/Sn); and
- annealing the entire structure at 575 °C in a S
rich atmosphere for 5 min in a dual zone tube
furnace, with the S zone heating to 300 °C and N₂
30 flowing at 20 sccm.

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At 140, a second conductive layer is successively deposited 140 on the kesterite light-absorber to form the front contact of the solar cell. In this embodiment, the front contact comprises a series of layers which are
5 deposited in sequence on the kesterite layer. Firstly, a CdS layer is formed by using a chemical bath deposition technique. The CdS layer had an opposite polarity to the kesterite absorbing layer. Subsequently, the structure is placed in a multi-target sputtering deposition machine to
10 deposit in sequence:

- an IZO layer with a thickness of about 50 nm; and
- an AZO layer with a thickness of about 300 nm at about 50°C.

Finally, Al contacts are thermally evaporated through a
15 shadow mask to create an Al front electrode. Or alternatively a conductive Ag glue is applied as the top electrode.

The effect of the RTA annealing of step 120 on the physical properties of the kesterite solar cells is
20 analysed below with reference to figures 2 to 6.

Referring now to figure 2(a), there is shown a scanning electron microscope (SEM) 200 image of a kesterite solar cell structure realised in accordance with the prior art method. The SEM picture 200 shows the soda lime glass
25 substrate 202 on which a Mo layer 204 is grown. The Mo layer 204 grows with a 'pillar-like' structure providing a surface 205 with a high density of voids and irregularities for the kesterite absorber 208 to grow upon. The nature of the interface 205 induces defects in
30 the kesterite absorber 208 as can be seen by the irregular

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structure of layer 208 in figure 2(a). The top layer of solar cell structure 200 comprises a stack of layers 210 including a CdS buffer layer, an IZO layer and an AZO layer. These layers follow the irregular morphology of the kesterite absorber 208.

Referring now to figure 2(b), there is shown a SEM image 250 of a kesterite solar cell structure deposited by following the steps of flow diagram 100. Image 250 shows a kesterite absorber layer 258 with a larger grain structure. The Mo layer 254 is more compact and provides improved nucleation islands for the subsequent CZTS grain growth. The structural properties are transferred across solar cell 250 from Mo layer 254, to the kesterite absorbing layer 258, through the Mo/kesterite interface 255, and to the top cell structure 260.

The improved nucleation islands are shown in better detail in figure 3. Figure 3(a) shows a SEM image 300 of the surface of the Mo layer of cell 200. Figure 3(b) shows a SEM image 350 of the surface of the Mo layer of cell 250. Surface 350 shows that grains start to grow in the RTA treated Mo thin film 254. A slight deterioration of the sheet resistance of the RTA annealed Mo layer 254 is observed due to the grains. However, the improved crystallinity of CZTS absorber provides a greater advantage and compensates for the slightly augmented sheet resistance of the Mo layer.

Referring now to figure 4, there is shown a comparison 400 between two Raman plots 402 and 404 respectively acquired from structures 200 and 250. Raman plot 404 shows a higher peak 406 at 337 cm^{-1} indicating a higher crystalline fraction in the kesterite absorber layer when the

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substrate and the Mo layer are annealed by RTA. Figure 4 also shows a substantial enhancement of the Raman signal 404, which is an indication of better subsurface film quality, and an increased formation of SnS_2 .

5 Referring now to figure 5, there is shown a comparison 500 between two XRD plots 502 and 504 respectively acquired from structures 200 and 250. The XRD spectra 502 and 504 agree well with the XRD of tetragonal kesterite (JCPDS No. 026-0575). The increased formation of SnS is confirmed by
10 peak 506.

Referring now to figure 6, there are shown current-voltage (J-V) characteristics 600, figure 6(a), and external quantum efficiency (EQE) and reflection plots 650, respectively acquired from structures 200 and 250. The
15 electrical performance of the solar cell are summarised in the table below.

	η (%)	Voc (mV)	Jsc (mA/cm ²)	FF (%)	R _s (Ω cm ²)	R _{sh} (Ω cm ²)
RTA Mo	3.14	649	11.2	43	23	268
As-dep Mo	1.03	518	7.2	27	44	81

The RTA of the Mo back contact reduces the series resistance. The improved series resistance results in a
20 better fill factor (FF), short circuit current density (Jsc) and conversion efficiency (η). The large grains created during the RTA of the back contact can reduce the defects on grain boundaries due to the reduction of grain interface, which prevents the minority carriers from
25 recombining on the grain boundaries. This is also confirmed by the improved open circuit voltage Voc, which also provides a good indication of the crystal quality of

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the cell. These results are confirmed by the IV curves 600 of figure 6(a).

Figure 6(b) shows an improvement of the external quantum efficiency, due to the RTA of the Mo back contact. The EQE
5 of the cell with an annealed back contact 654 is substantially higher than the EQE of the cell which has not been annealed 652. This is primarily due to the crystallinity improvement of kesterite absorber layer. The band gap energy is calculated from the EQE plots to be
10 approximately 1.45 eV. The improved grain structure allows the solar cell junction to collect the light generated carriers more efficiently.

The enhanced reflection shown in figure 6(b) is due to the smoother layer surfaces of the cells and the reduction of
15 short circuit current is related to the increased SnS_2 .

Figure 6(b) shows an improvement of the external quantum efficiency, due to the RTA of the Mo back contact. The EQE increases from 36% in 652 to 57% in 654. This is primarily due to the crystallinity improvement of kesterite absorber
20 layer. The band gap energy is calculated from the EQE plots to be approximately 1.45 eV. The improved grain structure allows the solar cell junction to collect the light generated carriers more efficiently.

An additional mechanism which limits the performance of
25 kesterite solar cells is the chemical instability of the interface between the Mo back contacts and the kesterite absorber layer. This instability can cause a decomposition of the absorbing layer or formation of MoS_2 and/or MoSe_2 .

The soda lime glass used for the manufacturing of the
30 solar cell contains sodium. In embodiments, method step

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120 is performed so that the sodium from the substrate is allowed to diffuse from the substrate to the first material during the annealing. Once in the first layer the sodium can further diffuse in the light-absorbing material during the formation of the light-absorbing layer. The sodium diffusion may be achieved by controlling the annealing temperature, annealing time or annealing gas flow rate. A longer annealing time generally corresponds to a higher quantity of sodium into the light-absorbing layer. Sodium suppresses the formation of defects into the absorber and passivates electrically active defects, improving the performance of the absorber.

In other embodiments, method step 120 is performed in a manner to form an oxide layer on the surface of the first conductive layer. When molybdenum is used as conductive material, a thin molybdenum oxide layer is formed during step 120 which provides a hole selective membrane and passivates the back surface of the light-absorbing layer. The molybdenum oxide growth may be achieved by controlling the annealing temperature, annealing time or annealing gas flow rate.

Referring now to figure 7, there is shown a schematic representation of a solar cell device 700 in accordance with an embodiment of the present invention. The solar cell consists of a soda lime glass substrate 702 covered with approximately 1000 nm Mo layer 704. An intermediate layer 706 separates the Mo layer 704 and the kesterite based light-absorbing layer 708. In this embodiment, the intermediate layer 706 is a 20 nm Ag layer deposited by thermal evaporation. Similar intermediate layers can be deposited using other PVD or CVD techniques, such as atomic layer deposition (ALD) or sputtering.

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The kesterite based light-absorbing layer 708 is formed on the surface of the Ag layer 706. The formation of the kesterite layer 708 involves a high temperature annealing step. During the annealing, sulphur and/or selenium react with the metal of the back contact 704 forming sulphides or selenides, MoS_2 and/or MoSe_2 in this example, which are detrimental for the performance of the kesterite layer 708. The Ag layer 706 reduces the formation of Mo sulphides and/or selenides affecting the light-absorbing layer 708.

In some embodiments a portion of the Ag from the Ag layer 706 is incorporated in the kesterite layer 708 during fabrication of the photovoltaic cell 700. The incorporation of Ag in the kesterite layer 708 can take place during the sulphurisation step of the precursors of the kesterite layer 708. The sulphurisation step can be controlled, by tuning the temperature, gas concentration or duration, to control the diffusion of Ag into the kesterite layer 708. In some instances the Ag of Ag layer 706 is uniformly distributed through absorber and is incorporated into kesterite crystal structure. Despite no obvious change to the kesterite chemical environment is detectable, the incorporation of Ag reduces the size and amount of voids and reduces the CdS deposited at back contact region. Ag also reduces the amount of planar defects and Cu vacancies in the light-absorber material, improving the performance of the solar cell. Ag may also affect the doping concentration of the light-absorbing material. The doping may take place via Ag ions in the Ag layer 706. Further, the formation of Ag_2S at the interface between the Ag layer 706 and the kesterite layer 708 may provide increased conductivity and enhanced performance.

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In addition, the Ag layer 706 affects the growth and the kesterite layer 708 improving its physical properties and decreasing the density of electrically active defects.

A cadmium sulphide (CdS) buffer layer 710 is deposited
5 between the kesterite layer 708 and a conductive structure which forms the front contact of the solar cell. The CdS layer 710 improves carrier extraction from the kesterite layer 708 and provides electronic band alignment between the kesterite layer 708 and the top contacting layers. In
10 this embodiment, the cadmium sulphide layer 710 is deposited by chemical bath deposition. However, the cadmium sulphide layer 710 could be deposited using other PVD or CVD techniques such as PECVD or ALD.

The front contacting structure of the solar cell 700 is
15 realised with an intrinsic zinc oxide (IZO) layer 712 and an aluminium (Al) doped zinc oxide (AZO) layer 714. These layers are generally formed by sputtering or ALD. Finally an electrical Al contacting structure 716 is deposited on the top surface of the solar cell 700. The Al structure
20 716 is usually deposited by thermal evaporation, but could be deposited by other PVD or CVD techniques.

Referring now to figure 8, there is shown a flow diagram 800 outlining a method of forming a kesterite solar cell in accordance with embodiments of the present invention.
25 The first step 802 consists in providing substrate 802 to deposit the layers of the solar cell upon. This substrate is generally a soda lime glass substrate. A conductive layer is then deposited 810 on the soda lime glass. In this embodiment, a Mo layer with a thickness around 1000
30 nm is sputtered, using a multi-target sputtering tool, onto the soda lime substrate to form a back contact. In

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alternative embodiments a 20 nm thick Zn layer is used. The substrate covered with the Mo layer is then transferred to a thermal evaporator to deposit 820 an intermediate metallic layer onto the Mo sputtered layer.

5 In this embodiment, an Ag layer with a thickness of 20 nm is evaporated. Subsequently, a kesterite based light-absorbing material is formed 830 on the intermediate metallic layer. In this embodiment, the step of forming the kesterite material 830 comprises two sequential steps:

- 10 - depositing a series of layers containing precursor materials for the kesterite layer (Zn/Cu/Sn); and
- annealing the entire structure at 575 °C in a S rich atmosphere for 30 min in a dual zone tube
- 15 furnace, with the S zone heating to 300 °C and N₂ flowing at 20 sccm.

A second conductive layer is successively deposited 840 on the kesterite light-absorber to form the front contact of the solar cell. In this embodiment, the front contact

20 comprises a series of layers which are deposited in sequence on the kesterite layer. Firstly, a CdS layer is formed by using a chemical bath deposition technique. Successively, the structure is placed in a multi-target sputtering deposition machine to deposit in sequence:

- 25 - an IZO layer with a thickness of about 50 nm; and
- an AZO layer with a thickness of about 300 nm at about 50°C.

Finally, Al contacts are thermally evaporated through a shadow mask to create an Al front electrode.

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Referring now to figure 9(a), there is shown a scanning electron microscope (SEM) 900 image of a prior art kesterite solar cell structure which does not include the intermediate metallic layer.

5 The SEM picture shows the soda lime glass substrate 902 with a flat surface on which a Mo layer 904 is grown. The Mo layer 904 grows with compact 'pillar-like' structures providing a surface 905 with a high density of voids and irregularities for the kesterite absorber 908 to grow
10 upon. Chemical reactions take place at the surface 905 during the annealing step when forming the kesterite absorber 908. These reactions create MoS_2 and/or MoSe_2 which are shown as bright areas at the interface 905 in figure 3 and are detrimental to the performance of the
15 kesterite absorber 908. The nature of the interface 905 induces defects in the kesterite absorber 108 as can be seen by the irregular structure of this layer in figure 9(a). The top layer 910 of the solar cell structure 900 of figure 3 comprises: a CdS buffer layer, an IZO layer and
20 an AZO layer. These layers tend to follow the irregular morphology of the kesterite absorber 908. No Al contacting structure is shown in figure 9.

Referring now to figure 9(b), there is shown a SEM image 950 of a kesterite solar cell structure deposited in
25 accordance with an embodiment of the present invention by following the steps of flow diagram 800. The solar cell in the SEM image 950 has the same structure as the cell 700 of figure 7, except for the Al contacts 716. A 20 nm thick Ag layer 956 is evaporated onto the Mo back contact layer
30 954. The kesterite absorber 958 is grown onto the Ag layer surface. The Ag layer 956 reduces the chemical interaction between the kesterite absorber 958 and the Mo back contact

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layer 954. This can be appreciated by the absence of MoS_2 and MoSe_2 around the Ag layer 956 of figure 9(b) in comparison to the interface 905 of figure 9(a). The significant reduction of these chemical reactions, improves the morphology of the Mo back contact layer 954 and the kesterite absorber 958. Furthermore, by growing on the compact Ag layer 956, the kesterite absorber 958 has a lower density of physical electrically active defects, leading to higher carrier generation rates and improved overall performance of the solar cell. An improved morphology can also be seen in the solar cell 950 for the top layers 960 of the solar cell structure (CdS buffer layer, IZO layer and AZO layer). These layers are more regular and have fewer defects than the corresponding layers in figure 9(a).

The reduction of the chemical interaction between the kesterite absorber 708 and the Mo back contact layer 704 due to the Ag layer 706 of figure 7 is further demonstrated by the Raman spectra of figure 10. In figure 10(a) there are shown two Raman spectra measured on the solar cells 900 and 950 of figure 9 respectively. In figure 10(b) there are shown two Raman spectra measured on the same solar cells when the kesterite light-absorber layer 708, and the layers above, have been mechanically removed.

In figure 10(a) trace 154 corresponds solar cell 900 and trace 156 corresponds to solar cell 950. The sharp peak 158 of trace 154 at 312 cm^{-1} shows formation of SnS_2 for the solar cell without the Ag layer 706. Such peak is not present for trace 156, demonstrating reduction sulfurization of the kesterite absorber layer 708.

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In figure 10(b) the trace 164 corresponds solar cell 900 and the trace 166 corresponds to solar cell 950. For these measurements the kesterite absorber layer 708, and the layers above, have been mechanically removed. Plot 160
5 shows peaks associated with MoS_2 at 407 cm^{-1} , 381 cm^{-1} and 285 cm^{-1} . These peaks are more pronounced for trace 164 than for trace 166, demonstrating reduced sulfurization of the Mo back contact layer 704 for these solar cells.

Referring now to figure 11(a), there are shown XRD spectra
10 270 for solar cells 900 and 950. The numbers in brackets in figure 11(a) represent crystal orientations of the measured material. Matching of the spectra of figure 11(a) with library data (JCPDS No. 026-0575) confirm that the measured solar cells contain tetragonal kesterite CZTS
15 material. In figure 11(a) the two traces almost perfectly overlap. However, a closer inspection of the main Mo peak 278 reveals that (detail not shown in figure 11) the solar cell with the Ag layer 706 has a much higher content of Mo in its elemental form. This implies the reduced formation
20 of MoS_2 for the solar cell Ag layer 706. The peak 276 at 15° indicates the presence of SnS_2 and is found only in the solar cell without the Ag layer 706, confirming that the Ag layer 706 promotes the reduction of the SnS_2 phase.

Figure 11(b) is a closer view 280 of the peak 278 of
25 figure 11(a). The left peak 282 has been measured for the solar cell with the Ag layer 706 and is $\sim 0.13^\circ$ shifted towards the left in comparison to the right peak 284 of the solar cell without the Ag layer 706. This indicates the participation of Ag in the formation of $(\text{Cu,Ag})_2\text{ZnSnS}_4$.
30 The left peak 282 is also slightly broader than the right peak 284 suggesting that Ag layer 706 may affect the crystallinity of the solar cell.

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Referring now to figure 12, there are shown current-voltage (J-V) characteristics 360 (figure 12(a)) and external quantum efficiency plots (EQE) 370 (figure 12(b)) for the solar cells with and without the Ag layer 706. The open-circuit voltage (Voc) of the solar cell provides a good indication of the crystal quality of the cell. The J-V curve 362 in figure 12(a) shows a Voc of 0.48 V for the solar cell without the Ag layer 706. The Voc increases, in measurement 364 done for the solar cell with Ag layer 706, to 0.6 V. The short-circuit current (Jsc) increases from 11.2 mA/cm², for the solar cell without Ag layer 706, to 15mA/cm² for the solar cell with Ag layer 706. The FF grows accordingly from 0.41 to 0.49. The enhancement in Voc may be also related to Cu/Ag aggregation at the grain boundary which repels holes and reduces recombination.

The external quantum efficiency data of figure 12(b) can be used to determine the band gap of the kesterite absorber layer 708 and confirm the Jsc of the solar cells. These data are reported in the table below, which also shows the other electrical parameters discussed above. The calculated bandgap of the solar cell with the Ag layer 706 is slightly higher than kesterite material bandgap values reported in the literature. The results show a doping effect due to the Ag layer 706 to the kesterite material. Importantly, the values in the table demonstrate that Ag layer 706 induces a reduction of the series resistance of the solar cell from 16 Ω/cm² to 14.8 Ω/cm².

Structure	Voc (mV)	Jsc (mA/cm ²)	EQE based Jsc (mA/cm ²)	FF	Efficiency η	Rs (Ω·cm ²)	Bandgap (eV)
Mo/Ag/CZTS	0.5977	15.05	14.96	0.492	4.42	14.8	1.59
Mo/CZTS	0.4769	12	11.9	0.407	2.31	16	1.56

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Referring now to figure 13, there is shown a flow diagram 450 outlining a method of forming a kesterite solar cell in accordance with embodiments of the present invention. The flow diagram 450 is similar to the flow diagram 800 of figure 8 except for one additional step 455 which is performed after the deposition of the intermediate metallic layer 820. The step 455 consists in an additional annealing of the structure comprising the substrate, the first conductive layer and the intermediate metallic layer. The step 815 improves the structural and electrical properties of the first conductive layer and the intermediate metallic layer affecting the crystallinity of the subsequently deposited CZTS absorber. The improved crystallinity of CZTS absorber significantly reduces the series resistance and recombination on the grain boundaries, improving the overall cell performance.

Other implications related to annealing step 455 are discussed above with reference to figures 1 to 6.

Referring now to figure 14, there is shown a schematic representation of a solar cell device 550 in accordance with an embodiment of the present invention. The solar cell has a similar structure to solar cell 700 of figure 7 except for intermediate non-metallic layer 556 which separates the Mo layer 554 and the kesterite based light-absorbing layer 558. In this embodiment, the non-metallic intermediate layer 556 is a semiconductor layer, more specifically a titanium boride (TiB_2) layer deposited by sputtering in a multi-target sputtering tool. Similar layers can be deposited using other techniques, such as CVD or atomic layer deposition (ALD). TiB_2 is an extremely hard and chemically stable compound. The TiB_2 layer has a thickness between 5 nm and 80 nm. TiB_2 layers with

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resistivity between 20 and 100 $\mu\Omega\cdot\text{cm}$ have been used in this embodiment.

The kesterite based light-absorbing layer 558 is formed on the surface of the layer 556. The formation of the
5 kesterite layer 108 involves similar steps as discussed above with reference to figure 7. The TiB_2 layer 556 reduces the formation of sulphides and/or selenides by acting as a shielding layer.

The chemical stability of the TiB_2 prevents Ti and/or B
10 ions from leaving the TiB_2 layer 556 to contaminate the light-absorbing layer 558. This is in contrast to other intermediate layer which may provide dopant ions during the annealing step affecting the performance of the light-absorbing layer 558. Further the TiB_2 layer 556 does not
15 react with S and/or Se during the annealing step preventing the formation of other sulphides and/or selenides other than MoS_2 and MoSe_2 and thus not affecting the electrical performance of the kesterite solar cell 550 for example the series resistance.

20 In some embodiments of the invention the top surface of the TiB_2 layer 556 can be appropriately treated to optimise structural and electrical properties. For example, the surface can be treated to optimise the growth of the kesterite layer 558 improving its physical properties and
25 decreasing the density of electrically active defects, or to improve the optical performance of the solar cell 550.

A cadmium sulphide (CdS) buffer layer 560 is deposited above the kesterite layer 558 as discussed with reference to figure 7.

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Referring now to figure 15, there is shown a flow diagram 660 outlining a method of forming a kesterite solar cell in accordance with embodiments of the present invention. The first step 662 consists in providing substrate,
5 generally a soda lime glass substrate. At step 664, a conductive layer is deposited on the soda lime glass.

In some embodiments, the substrate covered with the Mo layer is annealed in an annealing furnace to improve the properties of the Mo layer. This step is optional and is
10 not shown in figure 15. The substrate covered with the Mo layer is then sputtered 666 with a non-metallic material to form an intermediate layer onto the Mo sputtered layer. In this embodiment, a TiB_2 layer with a thickness between 5 nm and 80 nm is sputtered. In some embodiments, a further
15 step 668 to treat the non-metallic layer is performed to optimise its structural and electrical properties. However this step 668 is optional and may not be required in some embodiments of the invention.

Subsequently, a kesterite based light-absorbing material
20 is formed as discussed with reference to figure 8.

A second conductive layer is successively deposited as discussed with reference to figure 8. Finally, Al contacts are thermally evaporated through a shadow mask to create an Al front electrode.

25 Referring now to figure 16, there are shown scanning electron microscope (SEM) images 750 and 770 of a prior art kesterite solar cell structure which does not include the intermediate non-metallic layer and structure including the intermediate layer respectively.

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SEM picture 750 shows MoS_2 and/or MoSe_2 in a dashed area in proximity of the interface 755 in figure 16(a). These are due to chemical reactions take place at the surface 755 during the annealing step while forming the kesterite absorber and are detrimental to the performance of the kesterite absorber.

Referring now to figure 16(b), there is shown a SEM image 770 of a kesterite solar cell structure deposited in accordance with an embodiment of the present invention.

10 Solar cell 370 has the same structure as the illustration 550 of figure 14, except for the Al contacts 566. The soda lime glass substrate 102 is not shown in figure 3. A 30 nm thick TiB_2 layer 775 is evaporated onto the Mo back contact layer 774 and is shown in a dashed line in figure 16(b).

15 The kesterite absorber 778 is grown onto the TiB_2 layer 775 surface. The TiB_2 layer 775 strongly reduces the chemical interaction between the kesterite absorber 778 and the Mo back contact layer 774. This can be appreciated by the absence of MoS_2 and MoSe_2 around the TiB_2 layer 775 of

20 figure 16(b) in comparison to the interface 755 of figure 16(a). The significant reduction of these chemical reactions may also improve the morphology of the Mo back contact layer 774. The absence of substantial growth of MoS_2 and MoSe_2 allows for improved extraction of carriers

25 from the kesterite absorber 778 into the Mo layer 774. This leads to a solar cell with a lower series resistance than the solar cell 750 of figure 16(a).

Referring now to figure 17, there are show two electron diffraction spectroscopy (EDS) plots 850, 870 measured

30 across the samples 750 and 770. The EDS plots show signals from sulphur 852, 872, copper 854, 874, tin 856, 876, zinc 858, 878 and molybdenum 860, 880. The EDS measurements are

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taken along a line starting from the kesterite absorber 778 towards the Mo layer 774. The diffusion of Cu, visible in both figure 17(a) and figure 17(b) is related to the preparation of the TEM specimens. The EDS plot 850 of
5 figure 17(a) shows a substantial confinement of the kesterite precursor materials in the absorber layer 778. The area between the precursor's location and the Mo 860 is separated by a MoS₂ layer. This layer is not apparent in the EDS plot 870 as the Mo back contact is protected by
10 the TiB₂ layer.

The effectiveness of the TiB₂ layer in reducing the formation of MoS₂ is further demonstrated by the Raman spectra of figures 18(a) and 18(b). In figure 18(a) there are shown two Raman spectra 970 measured on the back
15 contact region of solar cells without (972) and with (974) a 30 nm TiB₂ layer. In both cases the absorber layer and the top layers of the cell have been mechanically removed.

The three strong Raman peaks 976 (407 cm⁻¹), 978 (381 cm⁻¹), 979 (285 cm⁻¹) shown that a thick MoS₂ layer covers the Mo
20 back contact of the sample without the TiB₂ layer. The intensity of these peaks is substantially reduced in the Raman spectrum 974 measured for the sample with a 30 nm TiB₂ layer. The presence of the three MoS₂ peaks in the Raman spectrum 974, although attenuated, indicates the
25 presence of minor MoS₂ quantities. The inter-mixing of MoS₂ and TiB₂ provides better recombination velocities and an improved band alignment at the back contact of the solar cell. This allows preserving the increment of the back contact resistance.

30 The intensity of the MoS₂ Raman peaks in relation to the thickness of the TiB₂ layer is shown figure 18(b). Four

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different Raman spectra acquired from samples with a 70 nm TiB₂ layer 982, a 30 nm TiB₂ layer 984, a 10 nm TiB₂ layer 986 and without a TiB₂ layer 988 are shown. The MoS₂ Raman peaks clearly appear in the sample without the TiB₂ layer 988 and constantly decrease with the increasing thickness of the TiB₂ layer. The peaks are hard to differentiate in the Raman spectra 982 of the sample with a 70 nm TiB₂ layer.

Referring now to figure 19, there are shown XRD spectra 170 of the four different samples of figure 18(b). In particular, the XDR spectra have been measured from a sample with a 70 nm TiB₂ 172, a 30 nm TiB₂ 174, a 10 nm TiB₂ 176 and without a TiB₂ layer 178. The numbers in brackets in figure 19 represent crystal planes. Matching of the spectra of figure 19 with library data (JCPDS No. 026-0575) confirm that the measured solar cells contain tetragonal kesterite CZTS material. No peaks related to secondary phases introduced by the TiB₂ layer are shown for any of the samples of figure 19.

Referring now to figure 20, there are shown current-voltage (J-V) characteristics 180 for the solar cells under AM1.5G illumination with (182) and without (184) the TiB₂ layer. The efficiency of the solar cell increases from 3.06% to 4.40% by introducing a 30nm TiB₂ layer. Figure 20 shows a significant improvement of short-circuit current (J_{sc}) and fill-factor (FF) due primarily to the substantial reduction of MoS₂ at back contact region, and secondarily to the decreased density of voids at the absorber layer back interface. The series resistance of the solar cell decreases from 22.0 Ω cm² to 10.3 Ω cm² by introducing a 30nm TiB₂ layer 106. A summary of the principal electrical parameter for solar cells with TiB₂

layers with different thicknesses is given in the table below.

Structure	Voc (mV)	Jsc (mA/cm ²)	FF	Efficiency η	Rs (Ω cm ²)
No TiB ₂	658	9.56	0.49	3.06	22.0
10 nm TiB ₂	608	11.35	0.51	3.51	14.3
30 nm TiB ₂	598	13.21	0.56	4.40	10.3
70 nm TiB ₂	598	13.08	0.54	4.20	10.9

Referring now to figure 21, there is shown a flow diagram
 5 680 outlining a method of forming a kesterite solar cell
 in accordance with embodiments of the present invention.
 The flow diagram 680 is similar to the flow diagram 660 of
 figure 15 except for one additional step 682 which is
 performed after the deposition 666 and treatment 668 of
 10 the intermediate non-metallic layer. The step 682 consists
 in an additional annealing of the structure comprising the
 substrate, the first conductive layer and the intermediate
 non-metallic layer. The step 682 improves the structural
 and electrical properties of the first conductive layer
 15 and the intermediate non-metallic layer affecting the
 structural and electrical properties of the entire solar
 cell. Improved crystallinity due to this additional
 annealing step is beneficial to the series resistance of
 the solar cell and recombination velocity in the absorber
 20 layer and improves the overall cell performance.

Other implications related to annealing step 682 are
 discussed above with reference to figures 1 to 6.

It will be appreciated by persons skilled in the art that
 numerous variations and/or modifications may be made to
 25 the invention as shown in the specific embodiments without
 departing from the spirit or scope of the invention as

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broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

The Claims Defining the Invention are as Follows:

1. A photovoltaic cell comprising:
 - a substrate;
 - a copper based light-absorbing layer;
 - 5 a first conductive layer disposed between the substrate and the light-absorbing layer, the first conductive layer being arranged so as to be electrically coupled to the light-absorbing layer; and
 - a second conductive layer arranged so as to be
 - 10 electrically coupled to the light-absorbing layer;
 - wherein a structure comprising the substrate and the first layer is annealed during formation of the photovoltaic cell.
2. The photovoltaic cell of claim 1 wherein the structure
- 15 comprising the substrate and the first layer is annealed using a rapid thermal annealing process.
3. The photovoltaic cell of claim 1 or 2 wherein the first layer has a lower density of physical defects when compared to the same layer the same first layer before
- 20 annealing of the structure comprising the substrate and the first layer.
4. The photovoltaic cell of any one of the preceding claims, wherein a surface of the first layer comprises a plurality of nucleation sites and the plurality of
- 25 nucleation sites are developed on the surface of the first layer during annealing of the structure comprising the substrate and the first layer.
5. The photovoltaic cell of any one of the preceding claims, wherein the substrate comprises sodium and during

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annealing of the structure comprising the substrate and the first layer sodium diffuses from the substrate to the first layer.

6. The photovoltaic cell of any one of the preceding
5 claims further comprising an intermediate layer disposed between the light-absorbing layer and the first layer, the intermediate layer being arranged to reduce the formation of secondary phases such as metallic sulphide compounds or metallic selenide compounds in the region between the
10 light-absorbing layer and the first layer.

7. The photovoltaic cell of claim 6 wherein the intermediate layer is further arranged to reduce formation of voids in the region between the light-absorbing layer and the first layer.

15 8. The photovoltaic cell of claim 6 or 7 wherein the intermediate layer is further arranged to reduce the series resistance of the photovoltaic cell.

9. The photovoltaic cell of any one of claims 6 to 8 wherein the intermediate layer comprises a chemically
20 treated surface with an improved surface morphology, when compared with an untreated surface of a similar intermediate layer.

10. The photovoltaic cell of any one of claims 8 or 9, wherein a structure comprising the substrate, the first
25 layer and the intermediate layer is annealed during formation of the photovoltaic cell.

11. The photovoltaic cell of any one of claims 6 to 10, wherein the intermediate layer comprises a metallic material.

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12. The photovoltaic cell of claim 11, wherein the metallic material comprises an alloy, silver, gold or a gold/silver alloy.

13. The photovoltaic cell of any one of claims 11 or 12
5 wherein a portion of the metallic material is incorporated in the light-absorbing material during fabrication of the photovoltaic cell.

14. The photovoltaic cell of claim 18 wherein the atoms of the metallic material in the light-absorbing material
10 affect the doping concentration or the defect concentration of the light-absorbing material.

15. The photovoltaic cell of any one of claims 6 to 10 wherein the intermediate layer comprises a non-metallic material.

15 16. The photovoltaic cell of claim 15 wherein the non-metallic material has an electrical resistivity of 100 $\mu\Omega\cdot\text{cm}$ or less.

17. The photovoltaic cell of claim 15 or 16, wherein the non-metallic material does not chemically interact with
20 metallic materials at temperatures below 800°C.

18. The photovoltaic cell of any one of claims 15 to 17 wherein the non-metallic material comprises a semiconductor material.

19. The photovoltaic cell of claim 18, wherein the non-
25 metallic material comprises titanium diboride or zirconium diboride.

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20. The photovoltaic cell of any one of claims 15 to 17 wherein the non-metallic material comprises a conductive oxide material.

21. The photovoltaic cell of claim 20 wherein the non-metallic material comprises a molybdenum oxide layer with a thickness above 5 nm.

22. A photovoltaic cell comprising:

a substrate;

a copper based light-absorbing layer;

10 a first conductive layer disposed between the substrate and the light-absorbing layer, the first conductive layer being arranged so as to be electrically coupled to the light-absorbing layer;

an intermediate layer comprising a metallic material arranged between the light-absorbing layer and the first conductive layer;

a second conductive layer arranged so as to be electrically coupled to the light-absorbing layer;

20 wherein the metallic material is selected so as to reduce the formation of secondary phases such as metallic sulphide compounds or metallic selenide compounds in the region between the light-absorbing layer and the first layer.

23. The photovoltaic cell of claim 22 wherein the intermediate layer is further arranged to reduce formation of voids in the region between the light-absorbing layer and the first layer.

24. The photovoltaic cell of claim 22 or 23 wherein the intermediate layer is further arranged to reduce the series resistance of the photovoltaic cell.

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25. The photovoltaic cell of any one of claims 22 to 24 wherein the intermediate layer comprises a chemically treated surface with an improved surface morphology, when compared with an untreated surface of a similar
5 intermediate layer.

26. The photovoltaic cell of any one of claims 22 to 25, wherein the metallic material comprises an alloy, silver, gold or a gold/silver alloy.

27. The photovoltaic cell of any one of claims 22 to 26
10 wherein a portion of the metallic material is incorporated in the light-absorbing material during fabrication of the photovoltaic cell.

28. The photovoltaic cell of claim 27 wherein the light-absorbing layer is annealed during fabrication of the
15 photovoltaic cell and a portion of the metallic material is incorporated in the light-absorbing layer during annealing.

29. The photovoltaic cell of claims 27 or 28 wherein the atoms of the metallic material in the light-absorbing
20 material affect the doping concentration or the defect concentration of the light-absorbing layer.

30. The photovoltaic cell of any one of claims 22 to 29 wherein the structure comprising the substrate and the first layer is annealed during formation of the
25 photovoltaic cell.

31. The photovoltaic cell of any one of claims 22 to 29 wherein the structure comprising the substrate, the first layer and the intermediate layer is annealed during formation of the photovoltaic cell.

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32. The photovoltaic cell of claim 30 or 31 wherein the annealing is performed using a rapid thermal annealing process.

33. The photovoltaic cell of any one of claims 30 to 32
5 wherein the first layer has a lower density of physical defects when compared to the same layer the same first layer before annealing of the structure comprising the substrate and the first layer.

34. The photovoltaic cell of any one of claims 30 to 33
10 wherein a surface of the first layer comprises a plurality of nucleation sites and the plurality of nucleation sites are developed on the surface of the first layer during annealing of the structure comprising the substrate and the first layer.

15 35. The photovoltaic cell of any one of claims 30 to 34, wherein the substrate comprises sodium and during annealing of the structure comprising the substrate and the first layer sodium diffuses from the substrate to the first layer.

20 36. A photovoltaic cell comprising:

a substrate;

a copper based light-absorbing layer;

a first conductive layer disposed between the substrate and the light-absorbing layer, the first

25 conductive layer being arranged so as to be electrically coupled to the light-absorbing layer;

an intermediate layer comprising a non-metallic material arranged between the light-absorbing layer and the first conductive layer;

30 a second conductive layer arranged so as to be

- 46 -

electrically coupled to the light-absorbing layer;

wherein the non-metallic material is selected such that a series resistance of the photovoltaic cell is not substantially increased compared to if the photovoltaic cell did not comprise the non-metallic material.

37. The photovoltaic cell of claim 36 wherein the intermediate layer is arranged to reduce the formation of secondary phases such as metallic sulphide compounds or metallic selenide compounds in the region between the light-absorbing layer and the first layer.

38. The photovoltaic cell of claim 36 or 37 wherein the intermediate layer is further arranged to reduce formation of voids in the region between the light-absorbing layer and the first layer.

39. The photovoltaic cell of any one of claims 36 to 38 wherein the intermediate layer comprises a chemically treated surface with an improved surface morphology, when compared with an untreated surface of a similar intermediate layer.

40. The photovoltaic cell of any one of claims 36 to 39 wherein the non-metallic material has an electrical resistivity of $100 \mu\Omega \cdot \text{cm}$ or less.

41. The photovoltaic cell of any one of claims 36 to 40 wherein the non-metallic material does not chemically interact with metallic materials at temperatures below 800°C .

- 47 -

42. The photovoltaic cell of any one of claims 36 to 41 wherein the non-metallic material comprises a semiconductor material.

43. The photovoltaic cell of claim 42, wherein the non-metallic material comprises titanium diboride or zirconium diboride.

44. The photovoltaic cell of any one of claims 36 to 43 wherein the non-metallic material comprises a conductive oxide material.

45. The photovoltaic cell of claim 44, wherein the non-metallic material comprises a molybdenum oxide layer with a thickness above 5 nm.

46. The photovoltaic cell of any one of claims 36 to 45 wherein the structure comprising the substrate and the first layer is annealed during formation of the photovoltaic cell.

47. The photovoltaic cell of any one of claims 36 to 45 wherein the structure comprising the substrate, the first layer and the intermediate layer is annealed during formation of the photovoltaic cell.

48. The photovoltaic cell of claim 46 or 47 wherein the annealing is performed using a rapid thermal annealing process.

49. The photovoltaic cell of any one of claims 46 to 48 wherein the first layer has a lower density of physical defects when compared to the same layer the same first layer before annealing of the structure comprising the substrate and the first layer.

- 48 -

50. The photovoltaic cell of any one of claims 46 to 49 wherein a surface of the first layer comprises a plurality of nucleation sites and the plurality of nucleation sites are developed on the surface of the first layer during
5 annealing of the structure comprising the substrate and the first layer.

51. The photovoltaic cell of any one of claims 59 to 63, wherein the substrate comprises sodium and during annealing of the structure comprising the substrate and
10 the first layer sodium diffuses from the substrate to the first layer.

52. The photovoltaic cell of any one of the preceding claims wherein the copper based light-absorbing layer is a kesterite based layer.

15 53. The photovoltaic cell of any one of claims 1 to 51 wherein the copper based light-absorbing layer is a copper-zinc-germanium-tin-chalcogenide based layer

54. The photovoltaic cell of any one of claims 1 to 51 wherein the copper based light-absorbing layer is a
20 silver-copper-zinc-tin-chalcogenide based layer.

55. The photovoltaic cell of any one of the preceding claims, wherein the first layer comprises a suitable metallic material or transparent conductive oxide.

56. The photovoltaic cell of any one of the preceding
25 claims, wherein the first layer comprises a suitable metallic material and a structure comprising the substrate and the first layer is annealed during formation of the photovoltaic cell and a portion of the first layer is oxidised during annealing.

- 49 -

57. The photovoltaic cell of claim 55 or 56 wherein the first material comprises molybdenum.

58. A method of forming a photovoltaic cell comprising the steps of:

5 providing a substrate;

 depositing a first conductive material on the substrate,

 subsequent the step of depositing the first conductive material, annealing the substrate and the first
10 material;

 subsequent the annealing step, forming a copper based light-absorbing material on the first material; and

 depositing a second conductive material such that the second conductive material is electrically coupled to
15 the light-absorbing material.

59. The method of claim 58 wherein the step of annealing the substrate and the first material is performed in a manner such that sodium diffuses from the substrate to the first material during annealing.

20 60. The method of claim 58 or 59 further comprising the step of forming an oxide layer on a surface of the first conductive material.

61. The method of claim 60 wherein the oxide layer is formed during the annealing of the substrate and the first
25 material.

62. The method of claim 61 further comprising the step of controlling annealing temperature, annealing time or annealing gas flow rate to control the thickness of the oxide layer.

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63. A method of forming a photovoltaic cell comprising the steps of:

providing a first conductive material;
depositing a metallic material on the first
5 material; subsequent to depositing the metallic material
forming a copper based light-absorbing material
on the metallic material; and
depositing a second conductive material such that
the second material is electrically coupled to the light-
10 absorbing material;
wherein the metallic material is selected so as
to reduce the formation of sulphides and/or selenides at
the first material.

64. The method of claim 63, wherein the metallic material
15 comprises an alloy, silver, gold, or a silver/gold alloy.

65 The method of any one of claims 63 or 64, further
comprising the steps of:

providing a substrate;
depositing the first material on the substrate;
20 and
subsequent the step of depositing a metallic
material on the first material, annealing at least the
substrate, the first material and the metallic material.

66. The method of any one of claims 63 to 65 wherein the
25 steps of depositing a metallic material on the first
material and forming a copper based light-absorbing
material on the metallic material are performed in a
manner such that, during the step of forming a copper
based light-absorbing material on the metallic material, a
30 portion of the metallic material is incorporated in the
copper based light-absorbing material.

- 51 -

67. The method of any one of claims 63 or 64, further comprising the steps of:

providing a substrate;

depositing the first material on the substrate;

5 and

subsequent the step forming a copper based light-absorbing material on the metallic material, annealing at least the substrate, the first material, the metallic material and the light-absorbing material.

10 68. The method of any one of claim 67 wherein during the step of annealing at least the substrate, the first material, the metallic material and the light-absorbing material a portion of the metallic material is incorporated in the copper based light-absorbing material.

15 69. A method of forming a photovoltaic cell comprising the steps of:

providing a first conductive material;

depositing a non-metallic material on the first material; subsequent to depositing the metallic material

20 forming a copper based light-absorbing material on the metallic material; and

depositing a second conductive material such that the second material is electrically coupled to the light-absorbing material;

25 wherein the non-metallic material is selected such that a series resistance of the light-absorbing layer is not substantially increased compared to if the photovoltaic cell did not comprise the non-metallic material arranged between the light-absorbing material and
30 the first material.

- 52 -

70. The method of claim 69, wherein the non-metallic material is selected such that it has an electrical resistivity of 100 $\mu\Omega$ cm or less.

71. The method of claim 69 or 70, wherein the non-metallic
5 material is selected such that the non-metallic material does not chemically interact with metallic materials at temperatures below 800°C.

72. The method of any one of claims 69 to 71, further comprising the steps of:

10 providing a substrate;
 depositing the first material on the substrate;
and
 subsequent the step of depositing a non-metallic
material on the first material, annealing at least the
15 substrate, the first material and the non-metallic
material.

73. The method of any one of any one of claims 63 to 72, further comprising the steps of:

 providing a substrate;
20 depositing the first material on the substrate;
and
 subsequent the step of depositing the first
material on the substrate, annealing at least the
substrate and the first material.

25 74. The method of claim 73 wherein the step of annealing at least the substrate and the first material is performed in a manner such that sodium diffuses from the substrate to the first layer during annealing.

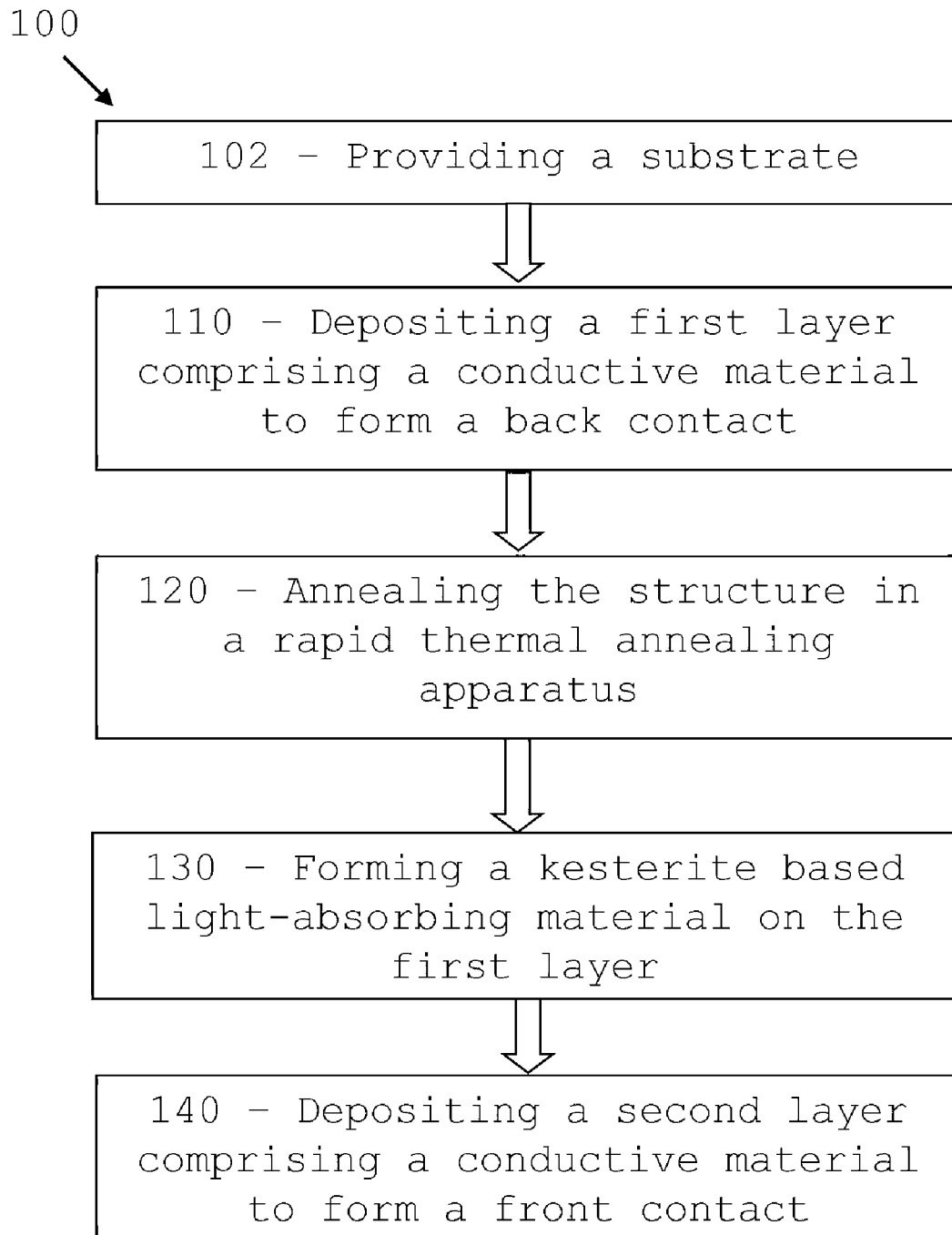
75. The method of any one of claims 58, 62, 65, 67 or 72
30 wherein the annealing step comprises the step of placing

- 53 -

the photovoltaic cell in a an annealing furnace and heating the furnace to a temperature in the range of 500°C to 800°C.

76. The method of claim 75, wherein the annealing step is
5 performed for a time interval between 5 to 20 minutes.

77. The method of claim 75, wherein the annealing step is performed for a time interval between 8 to 15 minutes.

**FIGURE 1**

250



FIGURE 2(b)

200

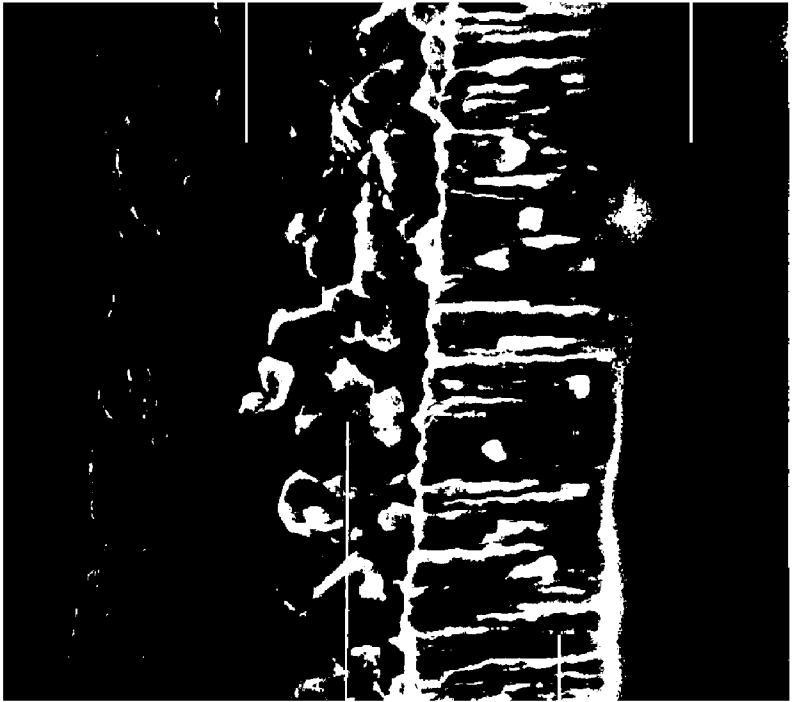


FIGURE 2(a)

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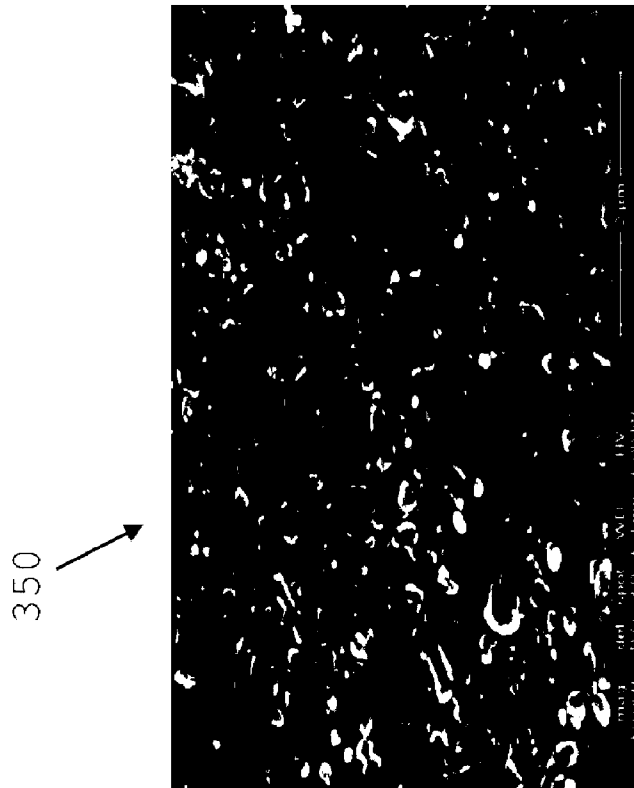
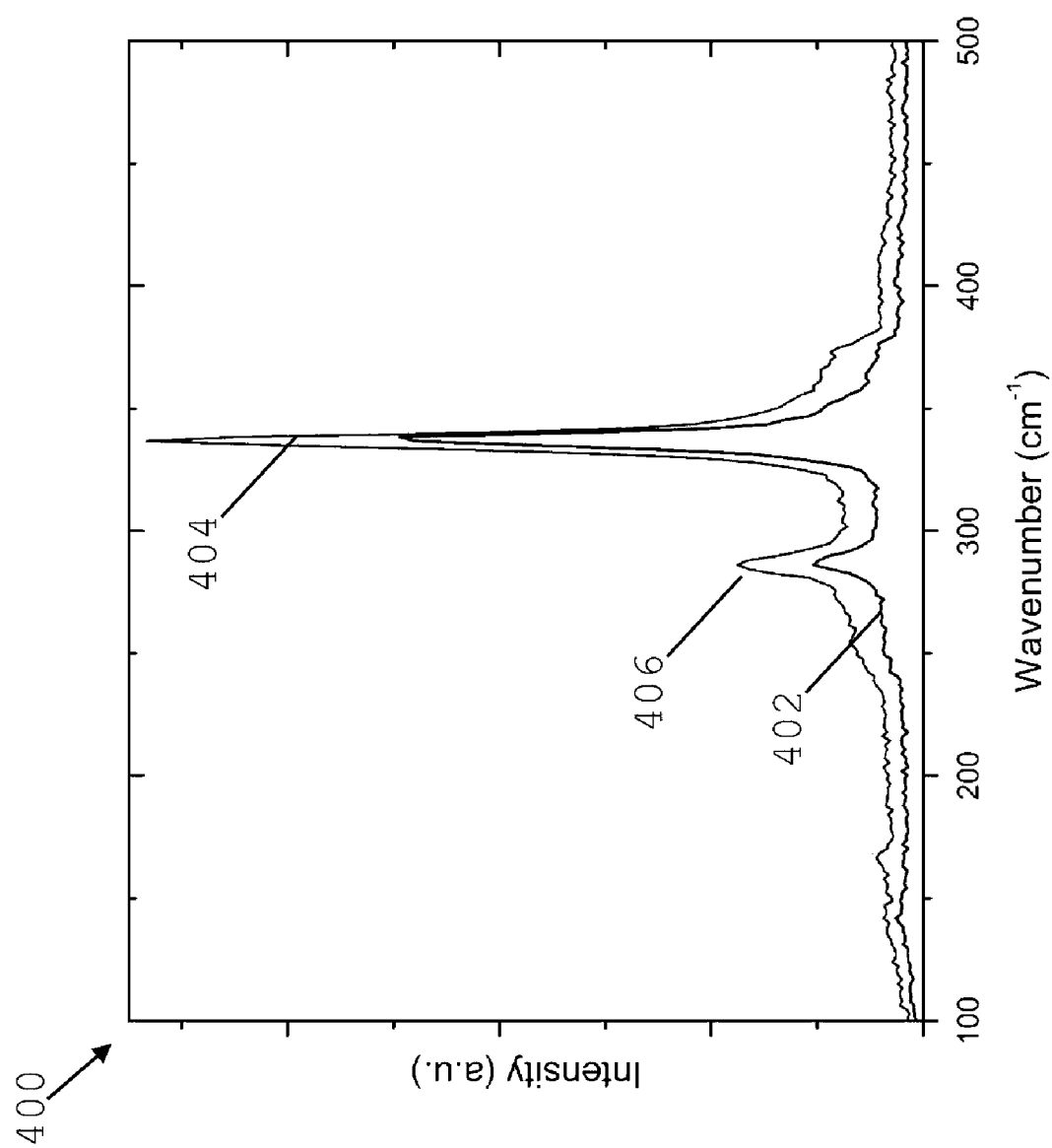


FIGURE 3(b)



FIGURE 3(a)

**FIGURE 4**

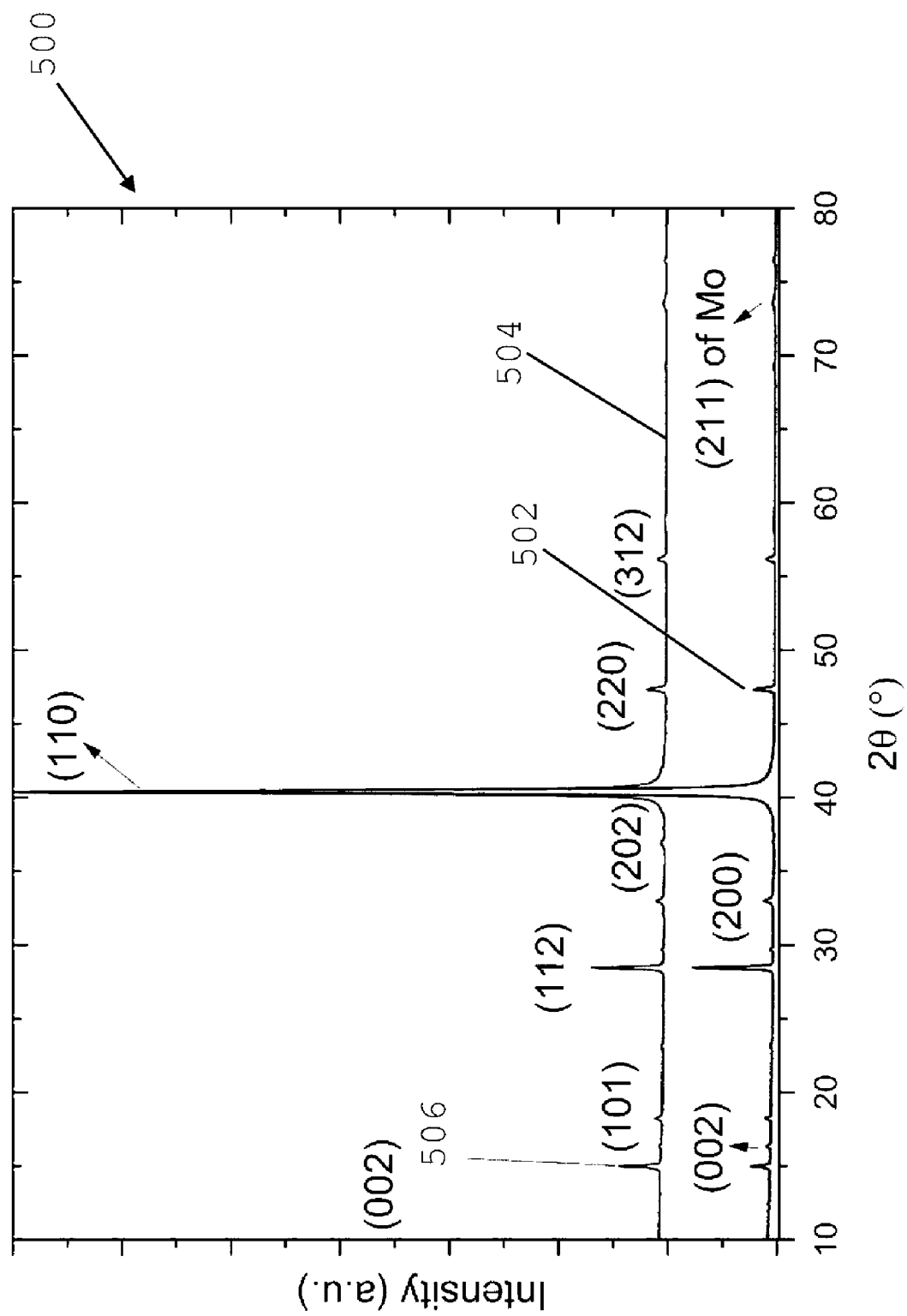


FIGURE 5

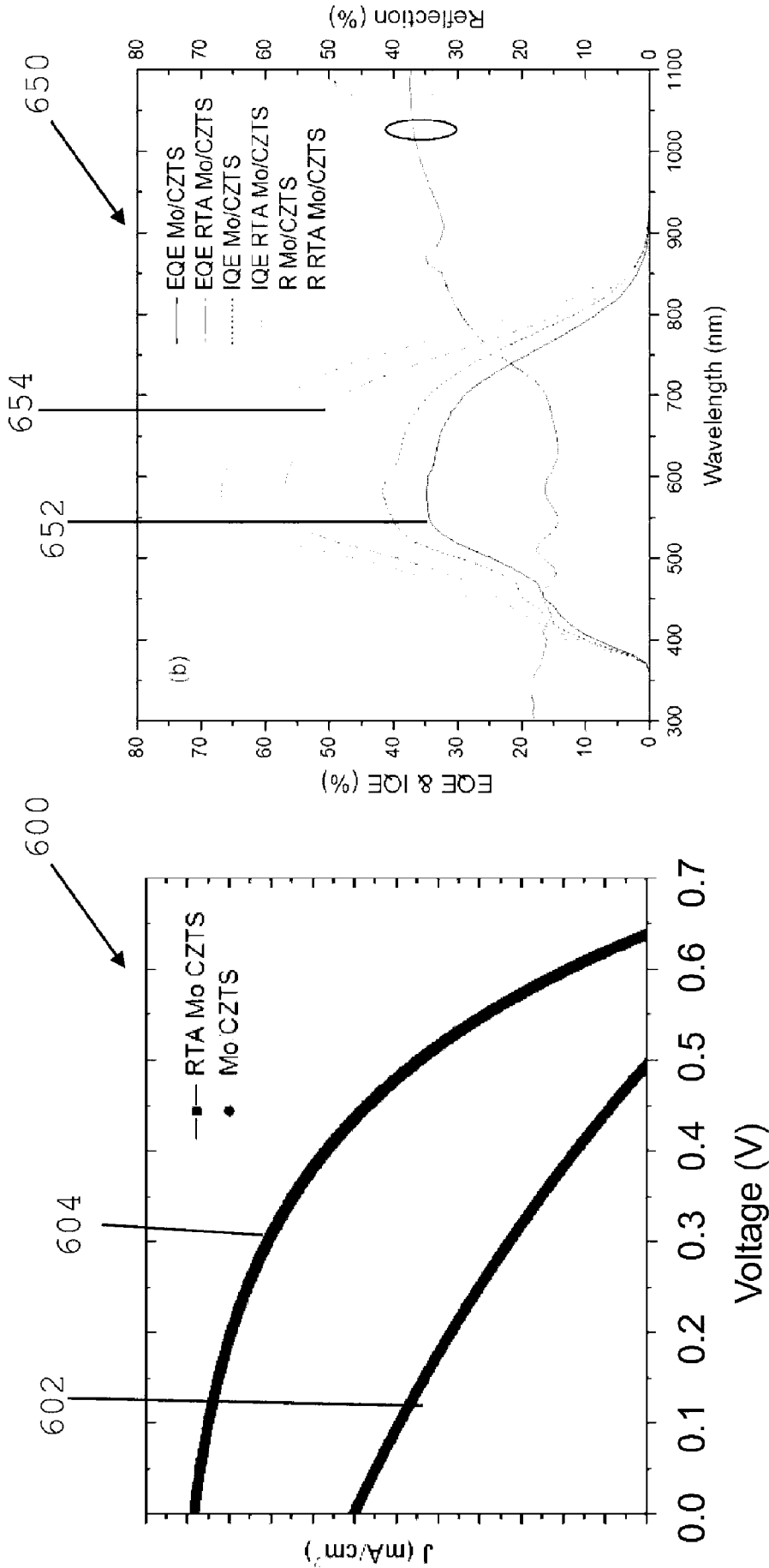


FIGURE 6(a)

FIGURE 6(b)

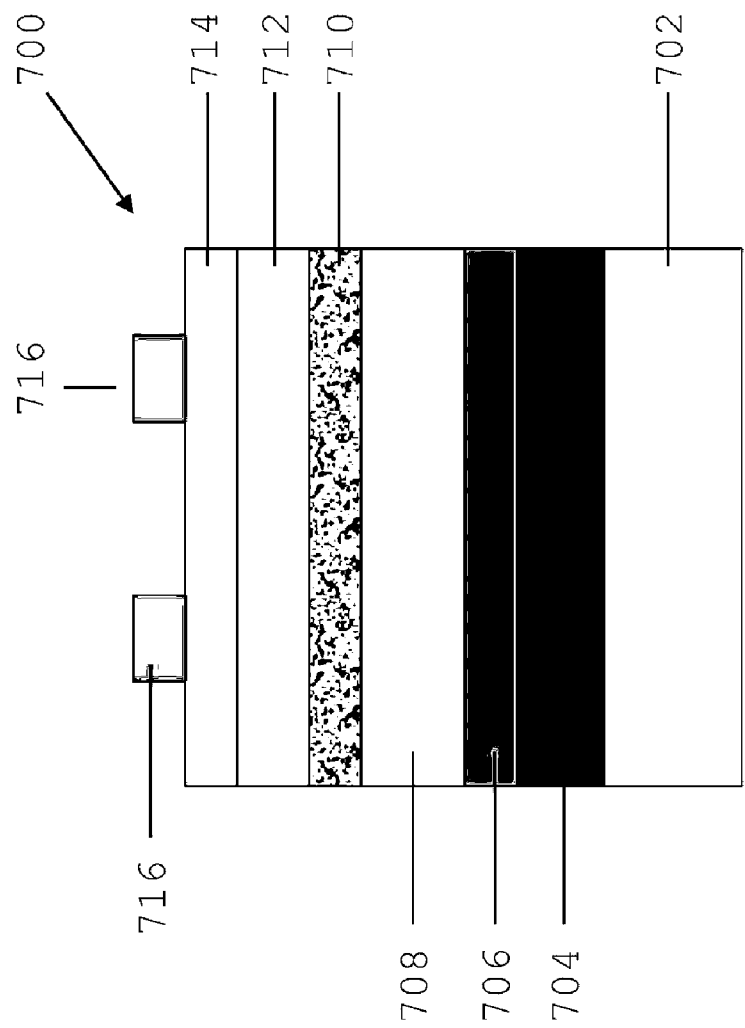
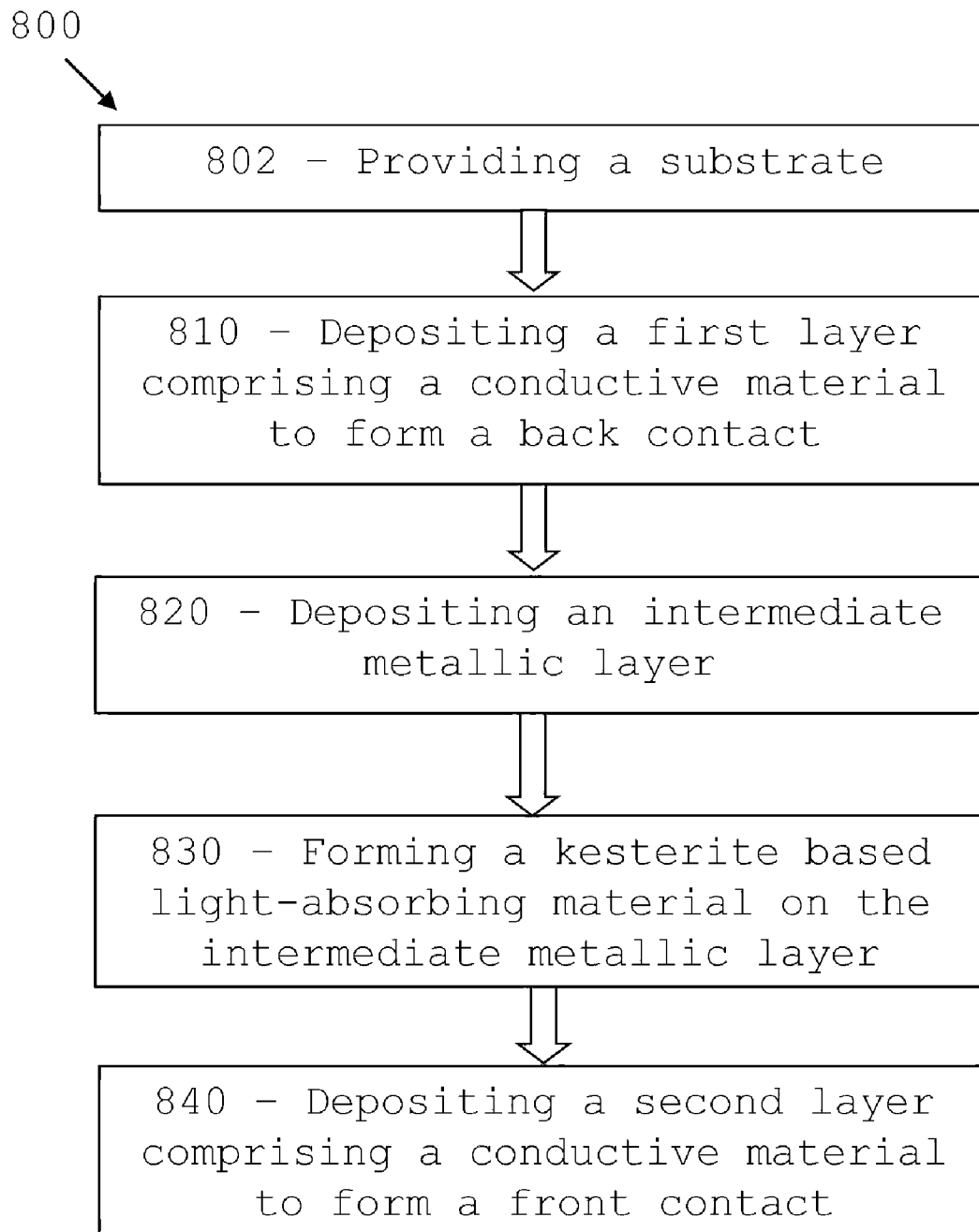


FIGURE 7

**FIGURE 8**

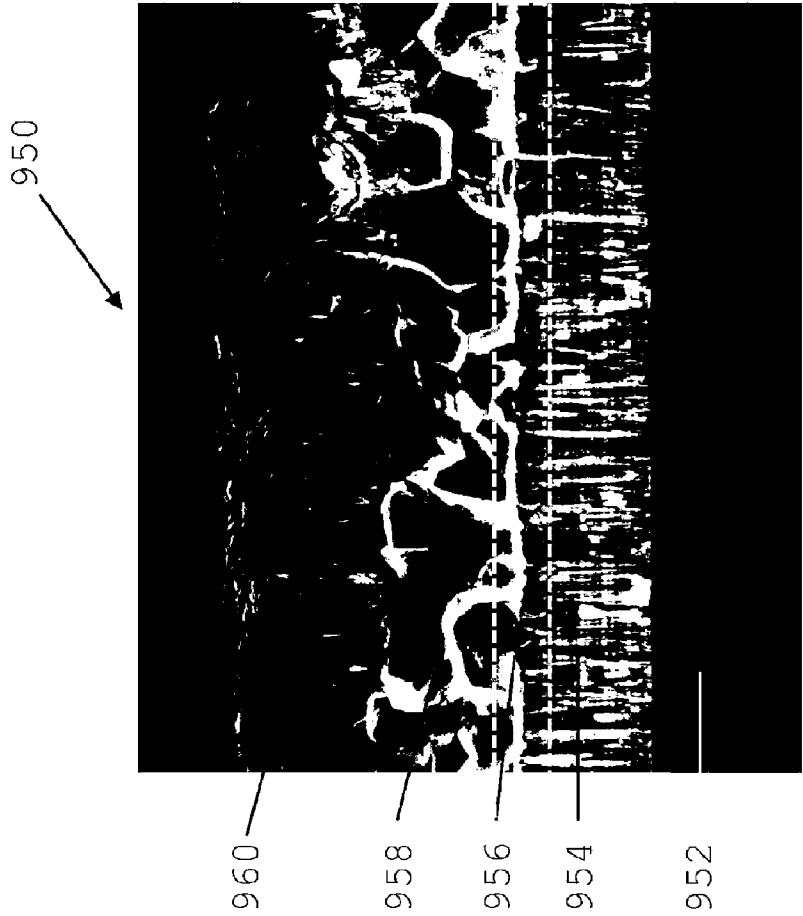


FIGURE 9(b)

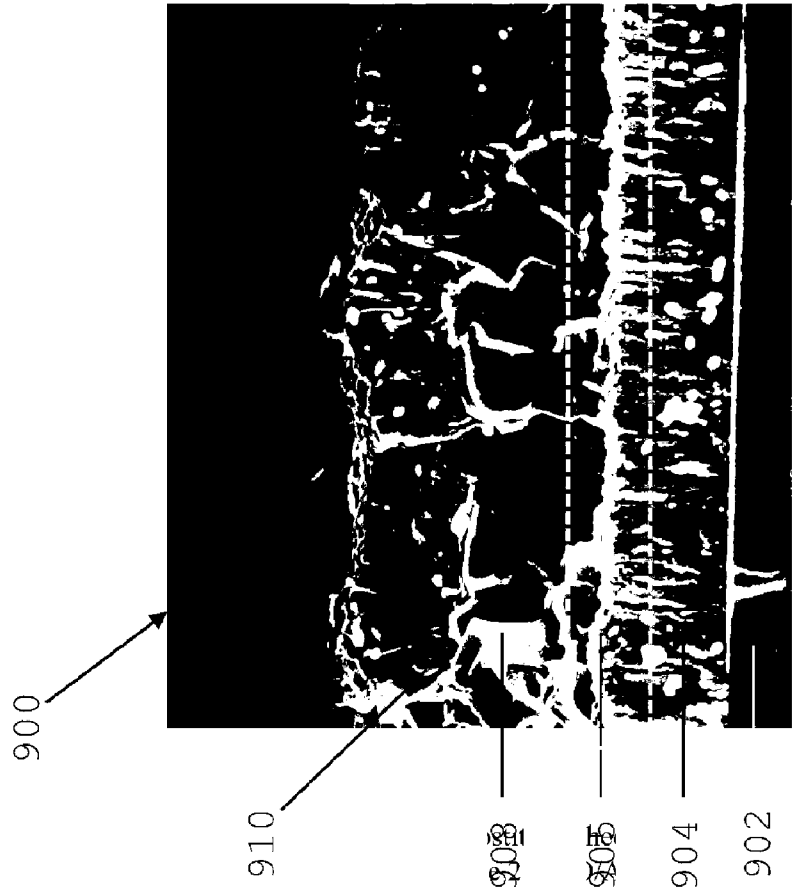


FIGURE 9(a)

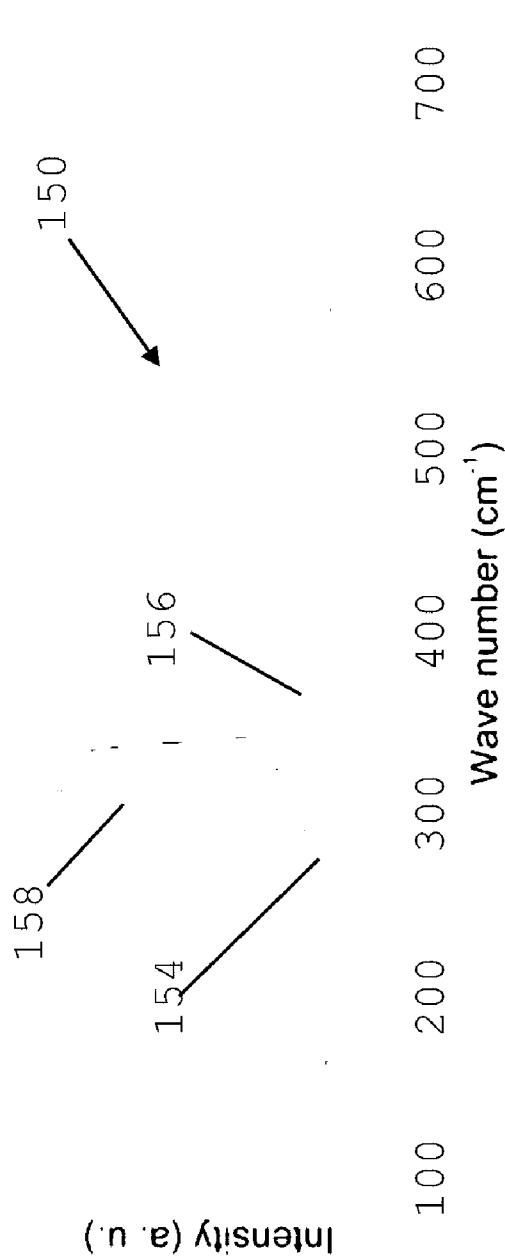


FIGURE 10(a)

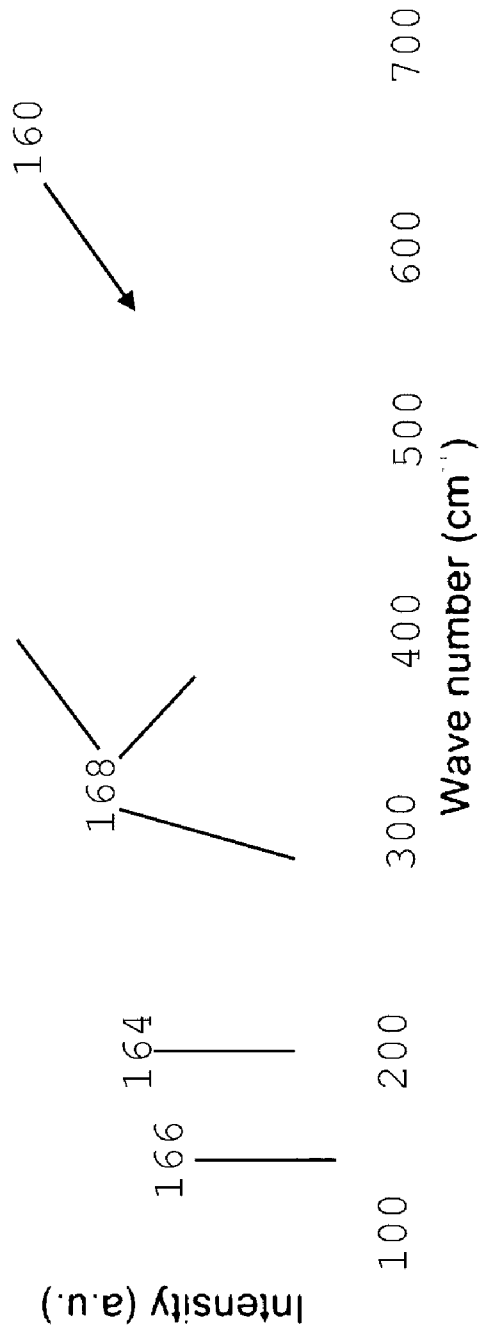


FIGURE 10(b)

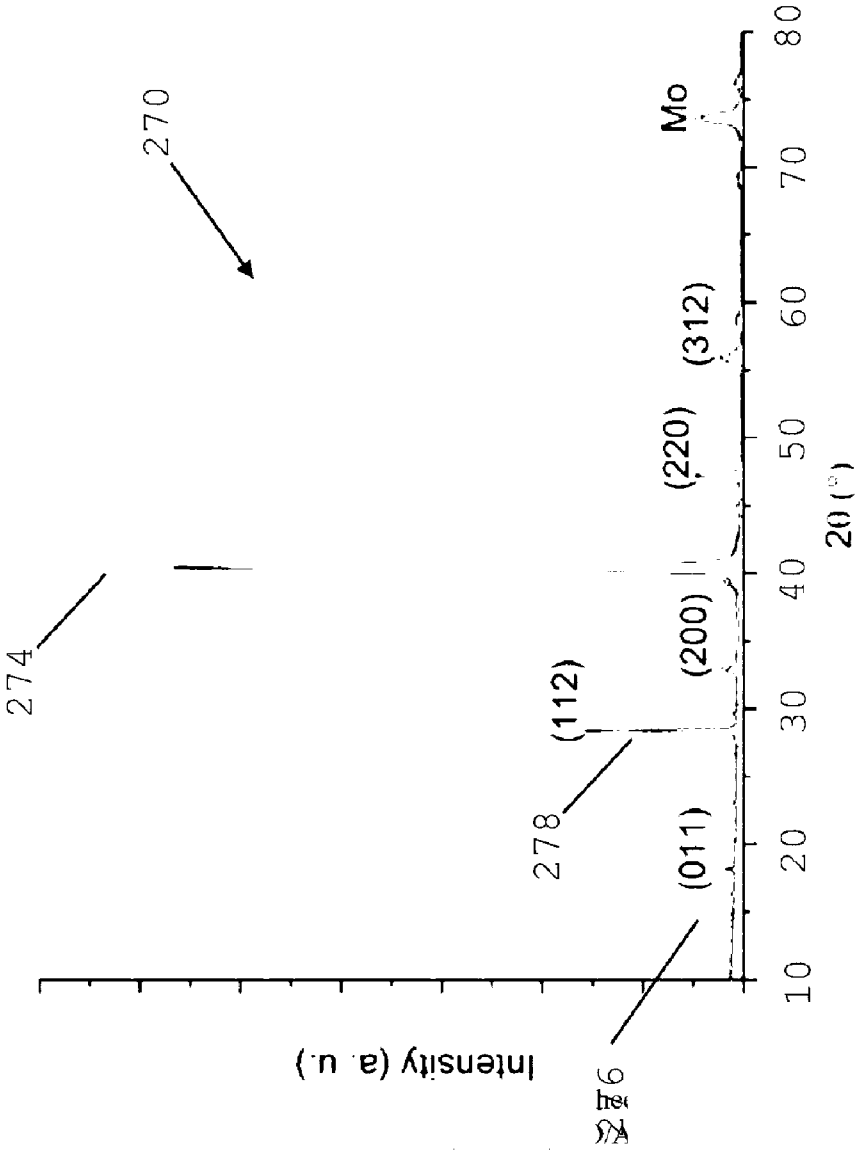


FIGURE 11(a)

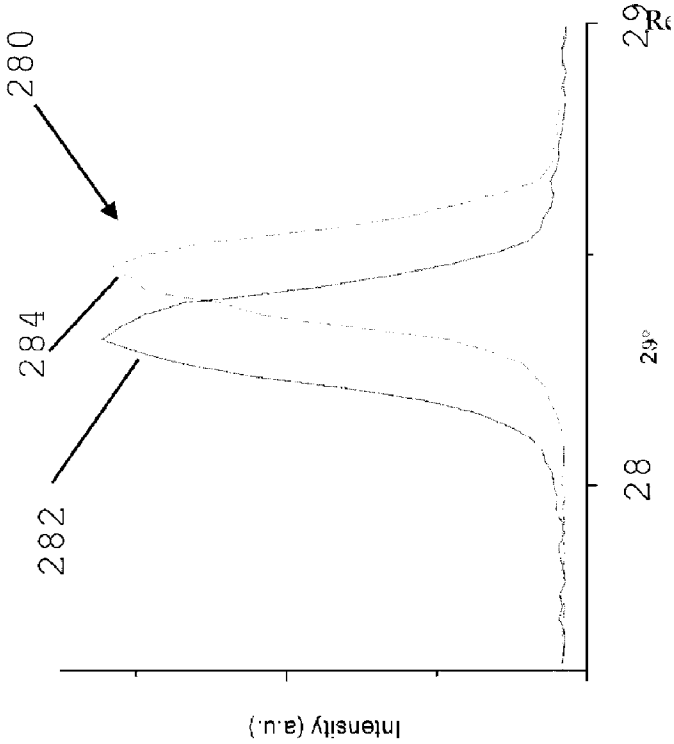


FIGURE 11(b)

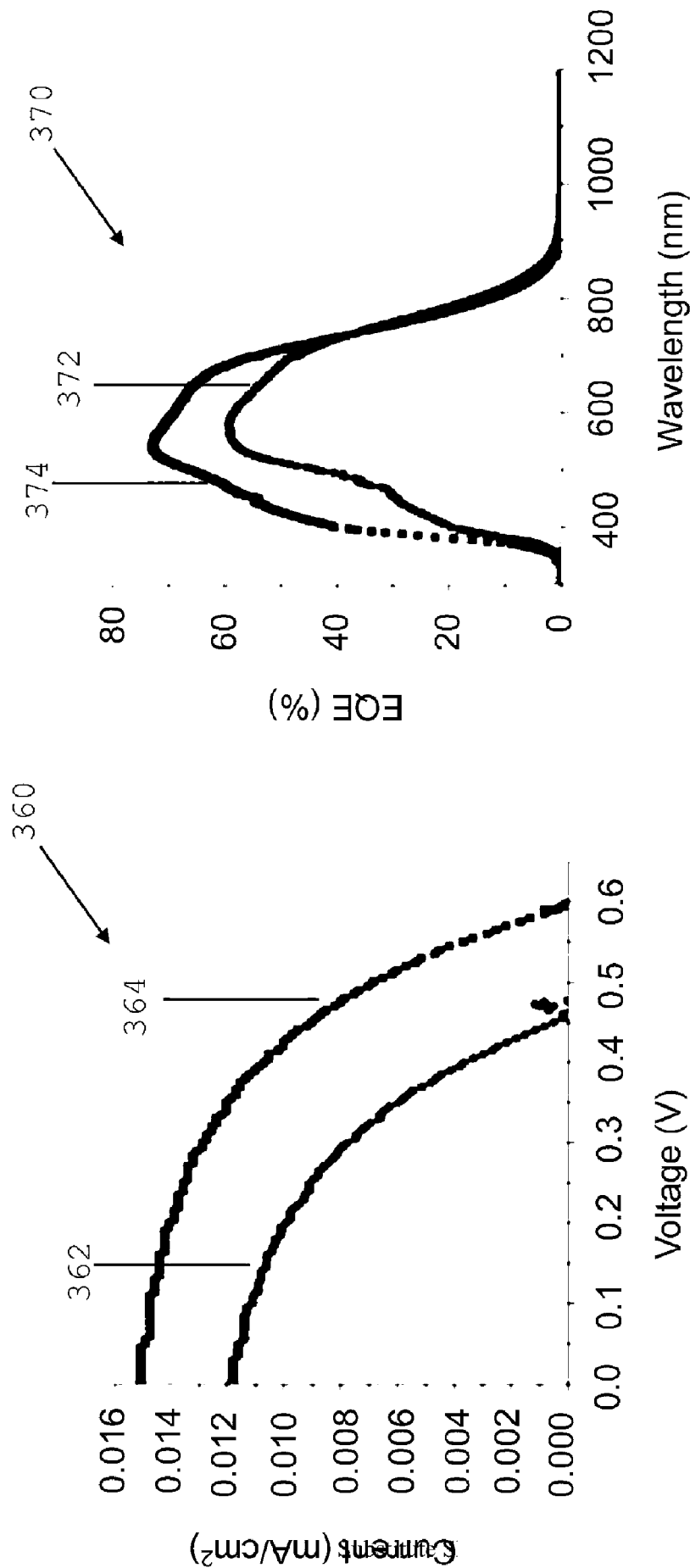


FIGURE 12(b)

FIGURE 12(a)

450

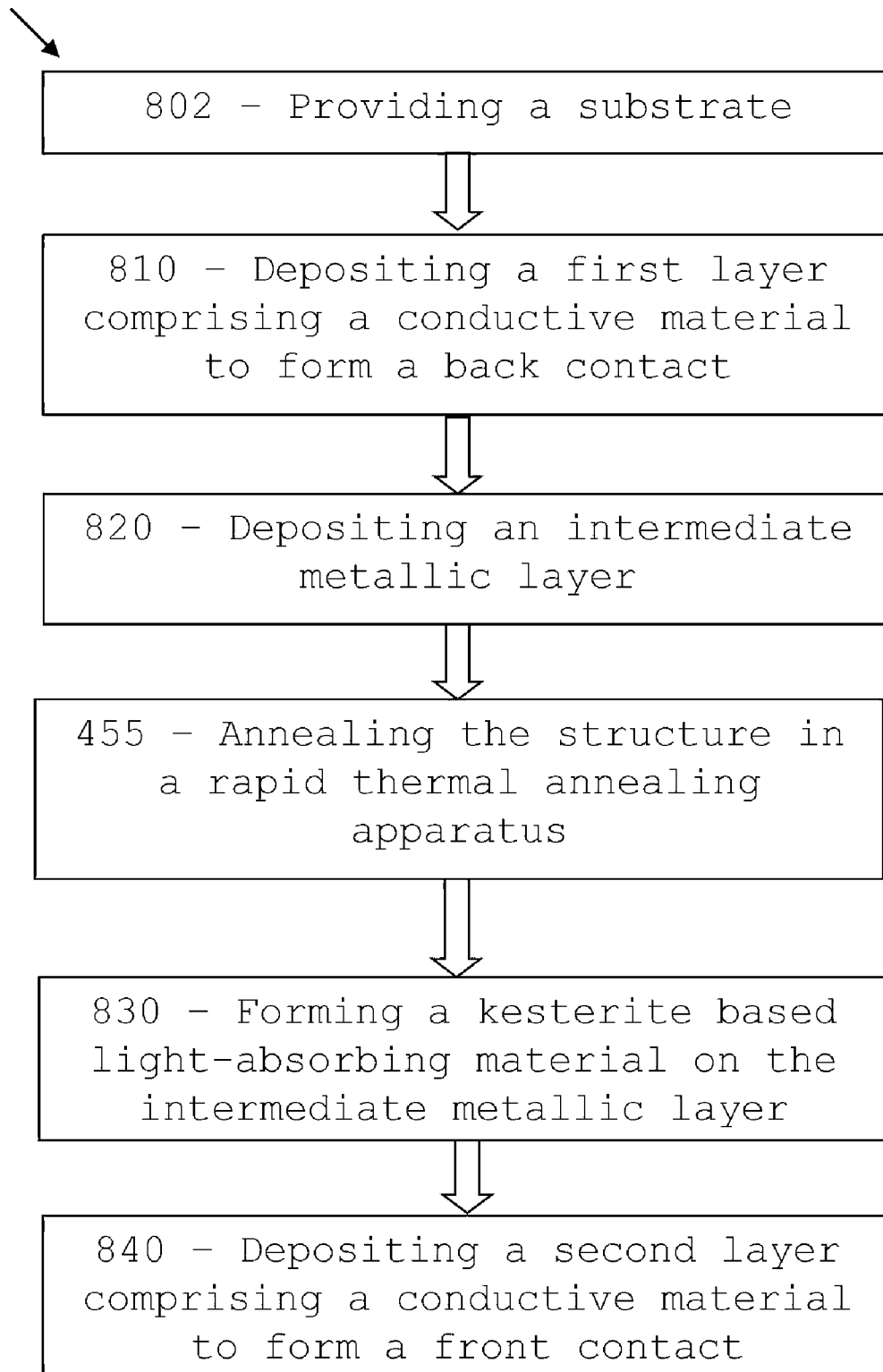


FIGURE 13

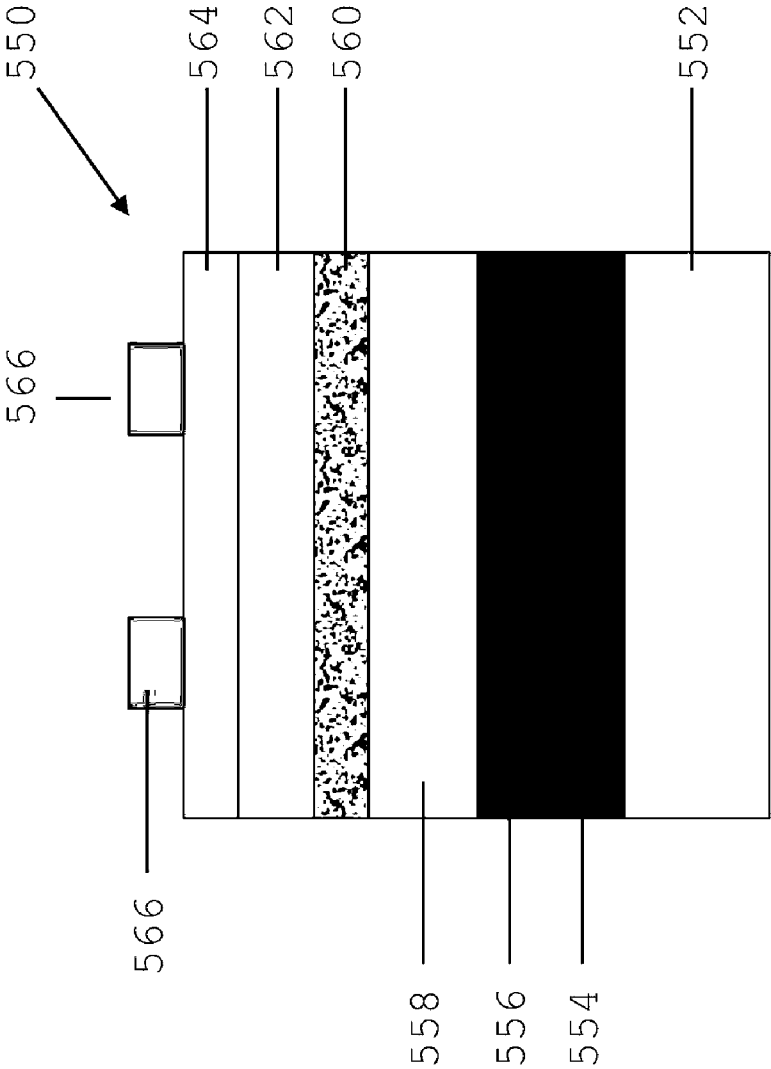


FIGURE 14

660

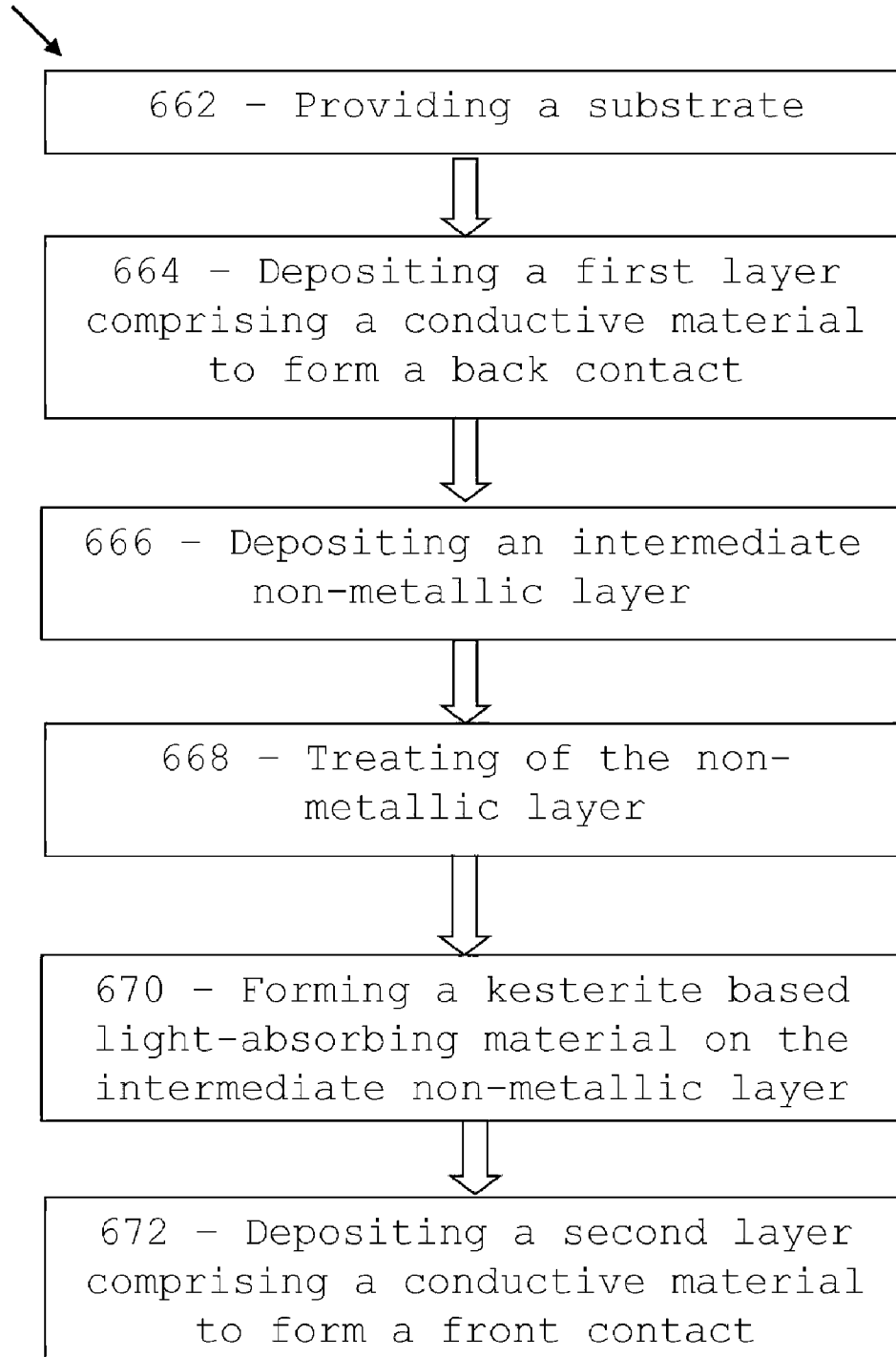


FIGURE 15

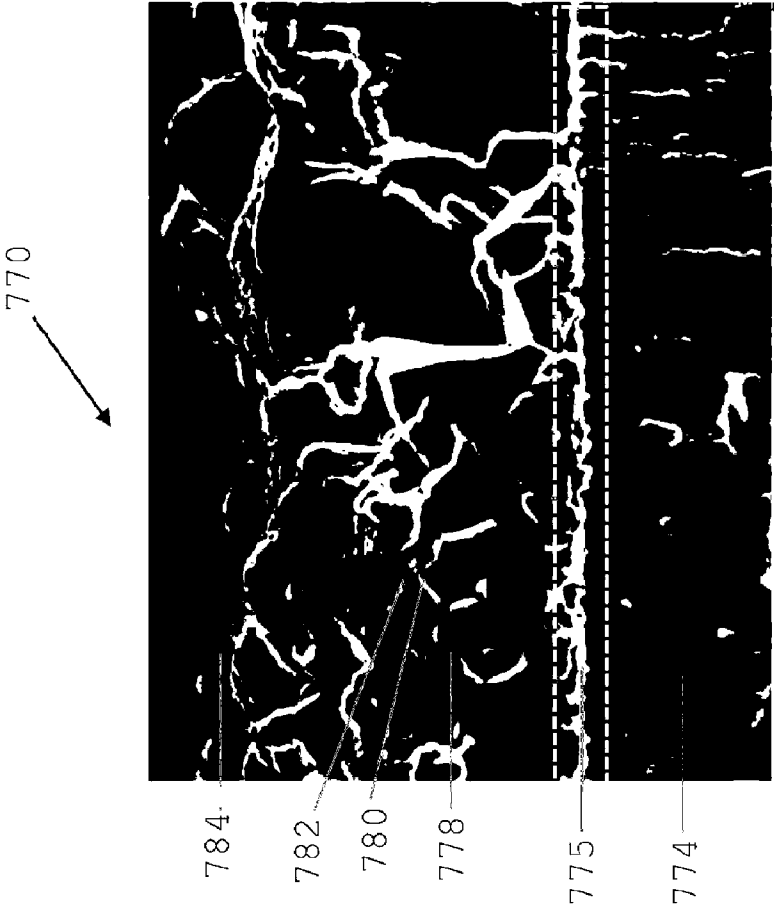


FIGURE 16 (b)

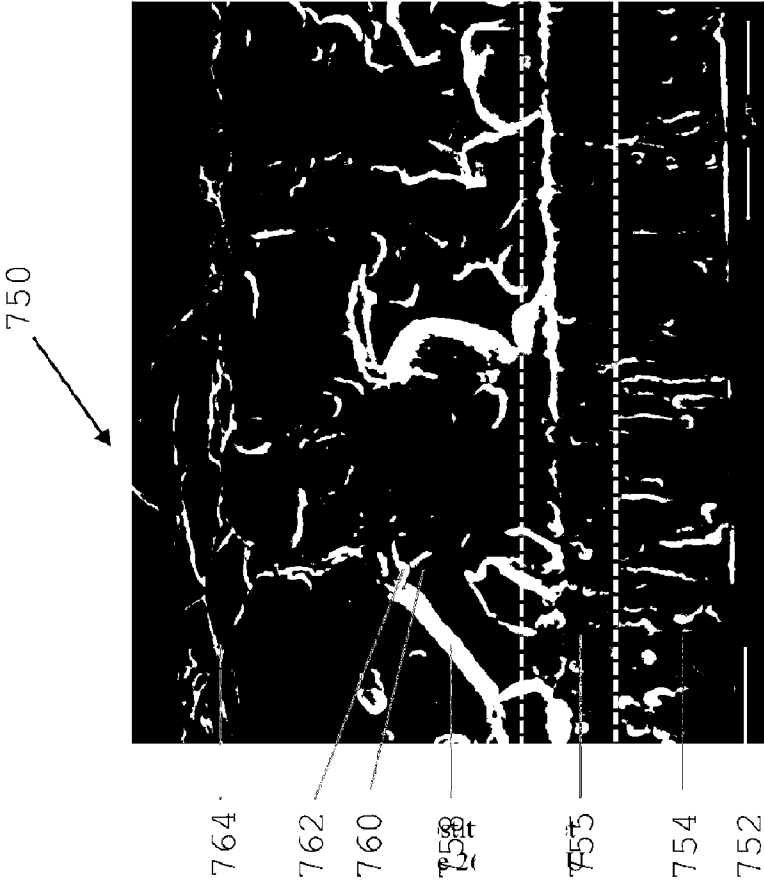


FIGURE 16 (a)

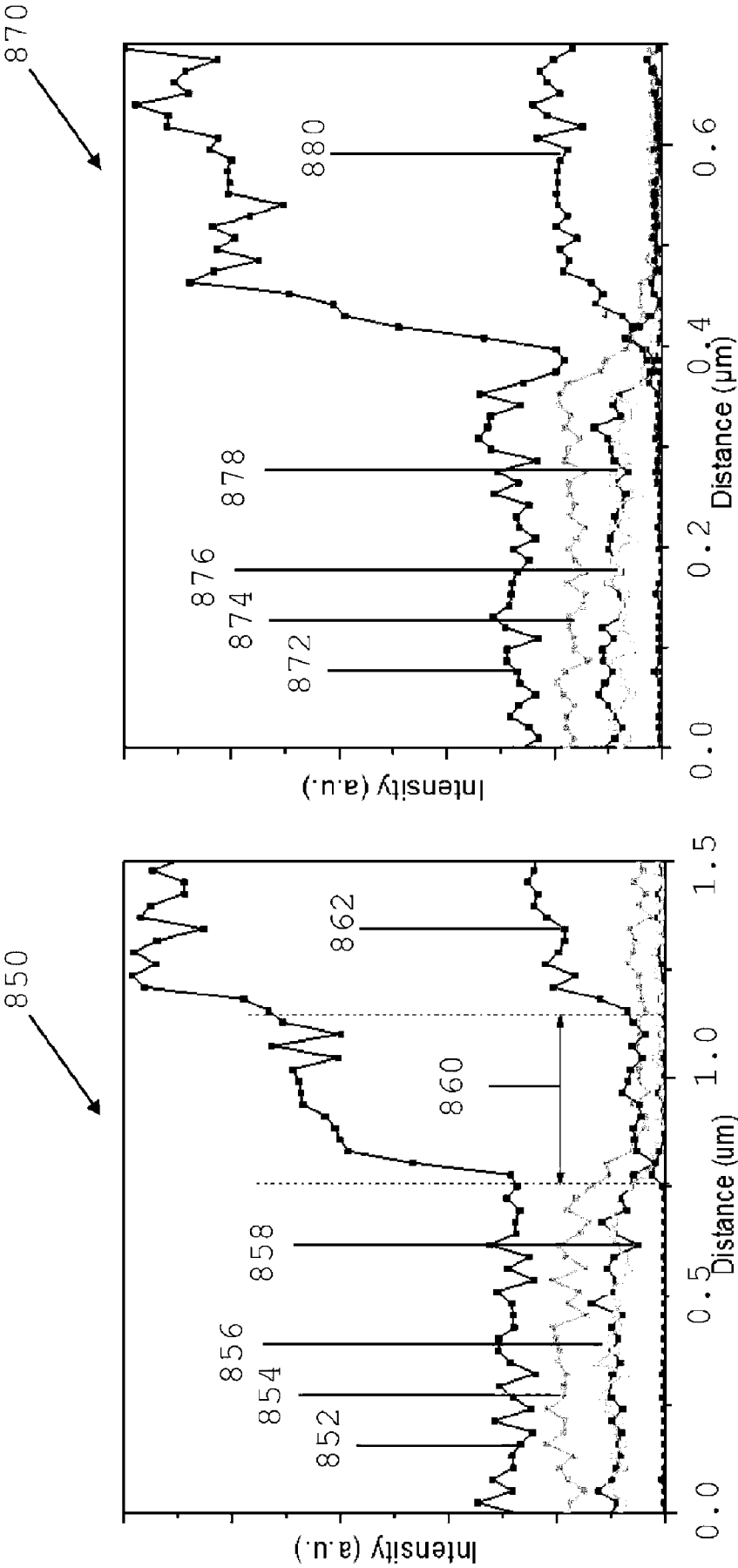


FIGURE 17(b)

FIGURE 17(a)

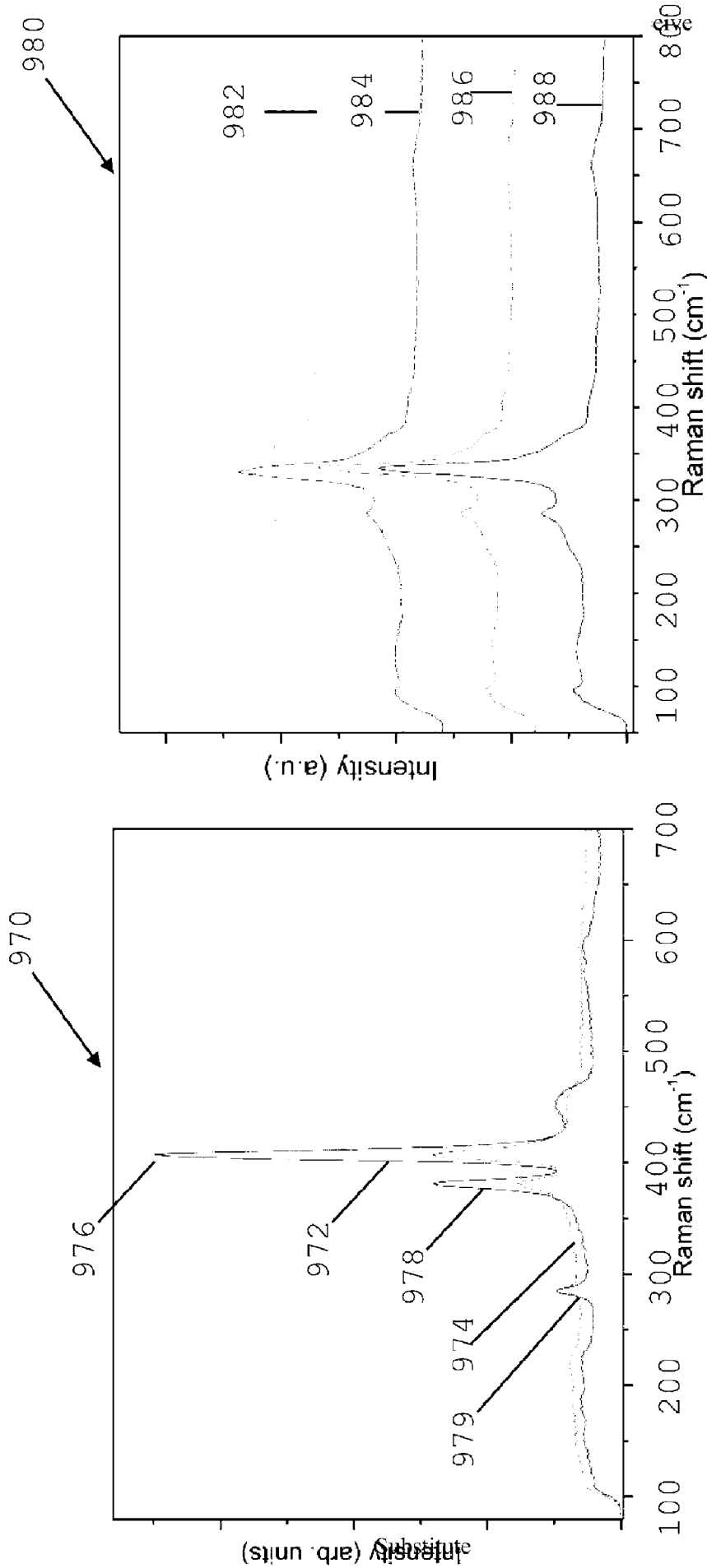


FIGURE 18(a)

FIGURE 18(b)

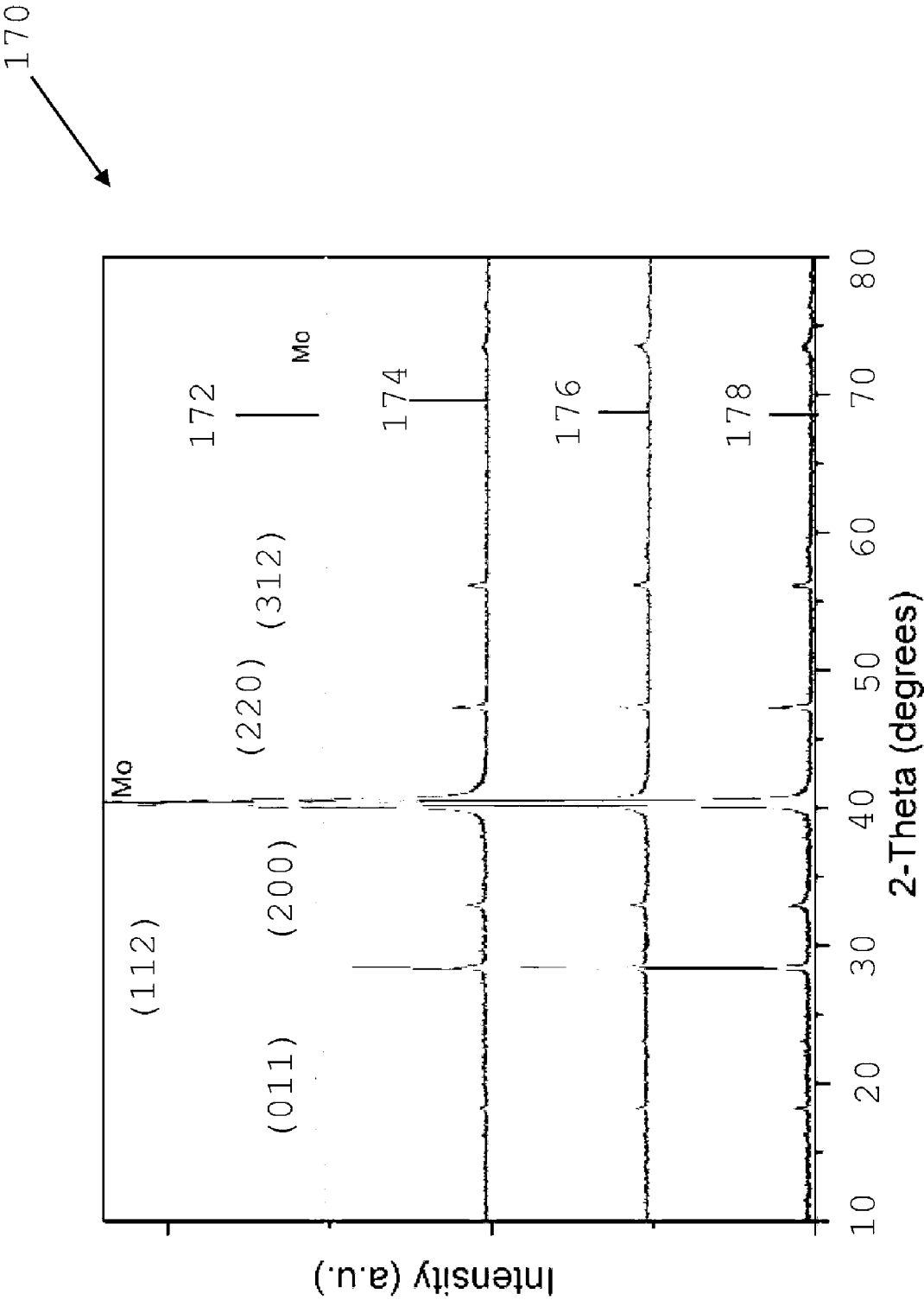


FIGURE 19

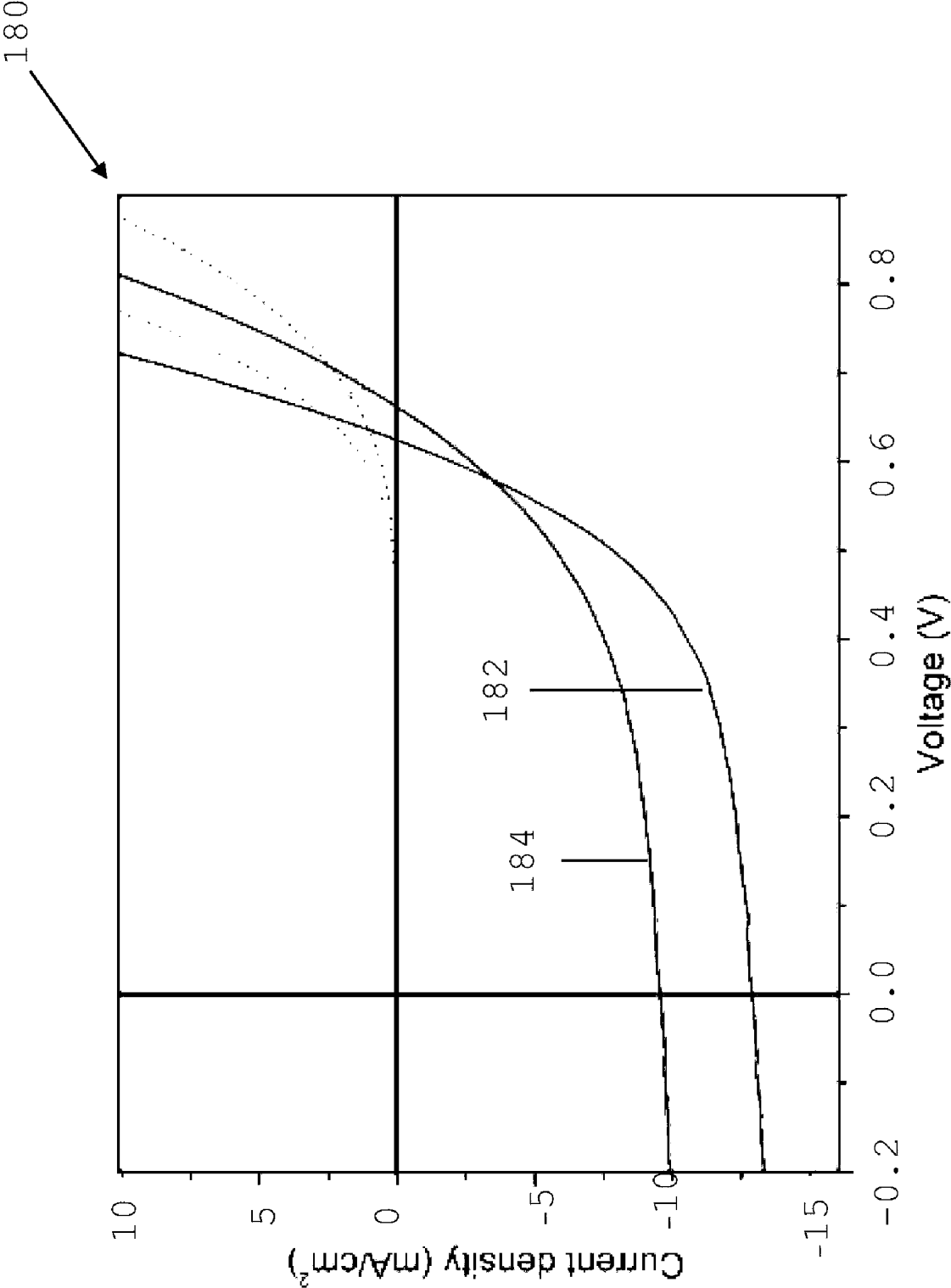


FIGURE 20

680

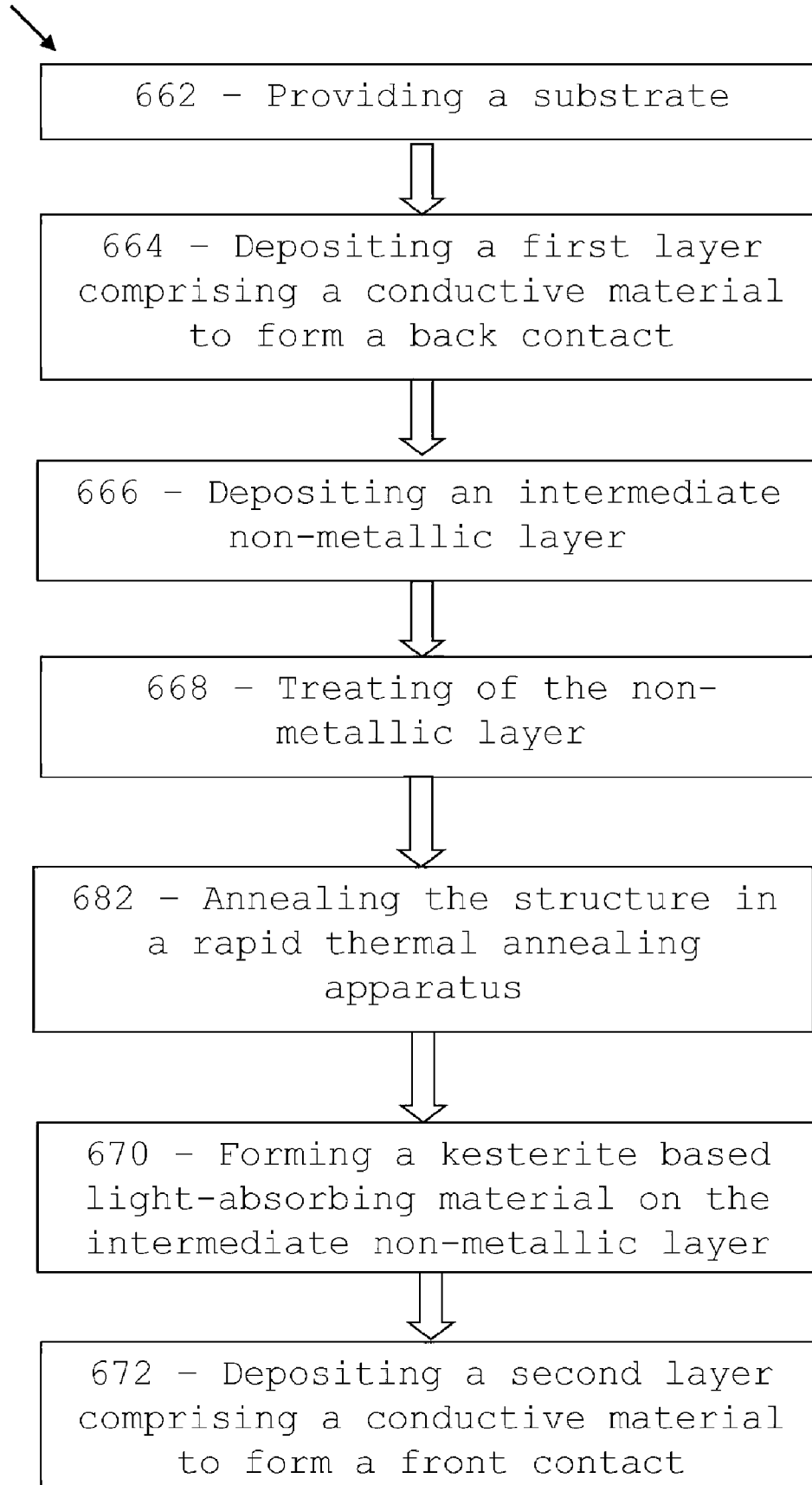


FIGURE 21

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2014/001101

A. CLASSIFICATION OF SUBJECT MATTER

H01L 31/0224 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

Databases: WPI, EPDOC, INSPEC & keywords: solar, PV, photovoltaic, photoelectric, CuInGaSe, CIGSe, CIGS, CZTS, CZTSe, CZTSSe, kesterite, chalcogenide, contact, electrode, conductor, oxide, boride, metal and similar terms.

Google search & keywords: rapid thermal annealing, RTA, contact, electrode, conductive layer and similar terms.

Esp@cenet:NEWSOUTH INNOVATIONS*, GUODIAN NEW ENERGY TECHNOLOGY* and inventors name was searched

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 27 January 2015	Date of mailing of the international search report 27 January 2015
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Jayati Ray AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262223654

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2014/001101
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/0104972 A1 (JEONG ET AL.) 02 May 2013 Fig. 1 and the associated text, paragraphs 0018-0037,	1-35, 58-68
X	US 2012/0006676 A1 (HONECKER ET AL.) 12 January 2012 Fig. 7 and the associated text, paragraphs 0005-0011	22-34, 63-68
X	US 2004/0063320 A1 (HOLLARS) 01 April 2004 Fig. 6 and the associated text, paragraphs 0032-0035, 0055	36-43, 46-57, 69-77
X	US 2008/0308156 A1 (BOYER, JR.) 18 December 2008 Figs. 1, 4, 5 and the associated text, paragraph 0014	1-77

Form PCT/ISA/210 (fifth sheet) (July 2009)

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2014/001101	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2013/0104972 A1	02 May 2013	KR 20130045516 A	06 May 2013
US 2012/0006676 A1	12 January 2012	CA 2803898 A1	12 Jan 2012
		EP 2591133 A2	15 May 2013
		JP 2013536316 A	19 Sep 2013
		TW 201219132 A	16 May 2012
		TW I449581 B	21 Aug 2014
		WO 2012006501 A2	12 Jan 2012
US 2004/0063320 A1	01 April 2004	US 6974976 B2	13 Dec 2005
		AU 2003275239 A1	23 Apr 2004
		CN 1703782 A	30 Nov 2005
		CN 101521249 A	02 Sep 2009
		CN 101521249 B	23 May 2012
		EP 1556902 A2	27 Jul 2005
		TW 200414551 A	01 Aug 2004
		TW I250658 B	01 Mar 2006
		US 2005109392 A1	26 May 2005
		US 7544884 B2	09 Jun 2009
		US 2009145746 A1	11 Jun 2009
		US 7838763 B2	23 Nov 2010
		US 2011259418 A1	27 Oct 2011
		US 8618410 B2	31 Dec 2013
		US 2010276282 A1	04 Nov 2010
		US 2010278683 A1	04 Nov 2010
		US 2014102891 A1	17 Apr 2014
		WO 2004032189 A2	15 Apr 2004
US 2008/0308156 A1	18 December 2008	US 7846750 B2	07 Dec 2010
		BR PI0813443 A2	23 Dec 2014
		EP 2153470 A2	17 Feb 2010
		EP 2153472 A2	17 Feb 2010
		US 2009020157 A1	22 Jan 2009
		US 7875945 B2	25 Jan 2011
		US 2011061730 A1	17 Mar 2011
		US 8133747 B2	13 Mar 2012
		US 2011097841 A1	28 Apr 2011
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2014/001101	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
		US 8415194 B2	09 Apr 2013
		US 2008308147 A1	18 Dec 2008
		WO 2008156521 A2	24 Dec 2008
		WO 2008156556 A2	24 Dec 2008
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			