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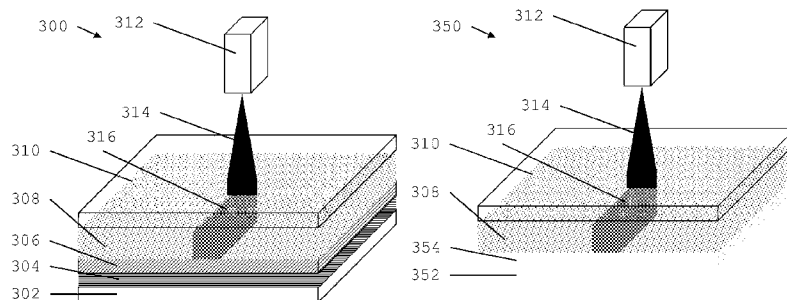


FIGURE 3(a)

FIGURE 3(b)

(57) **Abstract:** The present disclosure provides a method for forming a photovoltaic cell and a photovoltaic cell with a copper-based light-absorbing layer. The method comprises depositing an intermediate layer between the conductive substrate and the light-absorbing layer and depositing a capping layer arranged over at least a portion of the light-absorbing layer. The copper-based light-absorbing layer is exposed to a continuous wave laser light through the capping layer. The intermediate layer is arranged to minimise the energy transferred from the laser light to the conductive substrate and the capping layer is arranged to affect the energy distribution of the laser light through the light-absorbing layer.

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A METHOD OF MANUFACTURING A PHOTOVOLTAIC DEVICE

Field of the Invention

The present invention generally relates to a method for manufacturing a photovoltaic device. In particular, the
5 present invention relates to a method for forming an absorbing material in a thin film photovoltaic device.

Background of the Invention

Advances in thin film photovoltaics have led to the rise in popularity of thin film based solar devices such as
10 CdTe based devices.

One of the drawbacks of CdTe photovoltaic devices is related to the toxicity of Cd which may cause problems once the devices degrade or need to be disposed.

Other thin film photovoltaic technologies have been
15 investigated in recent years to design photovoltaic devices which do not contain toxic materials and, at the same time, can provide competitive market performance.

Solar cells with a copper based chalcogenide light-absorbing material represent an important advancement in
20 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
25 selenium (Se). Kesterite has the chemical formula $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$. Depending on whether the last element is

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5 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 photovoltaic device absorber.

10 Current kesterite photovoltaic devices 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 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
15 normally realised on the absorber layer. Generally, kesterite photovoltaic devices also have a CdS intermediate layer between the absorber layer and the front contact.

20 Although it is widely acknowledged that kesterite solar cells could potentially perform better than other thin film photovoltaic technologies, the current performance of 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,
25 21.7% for Cu(In, Ga)Se₂ (CIGSe) thin film solar cells.

The annealing process used to form the absorber layer in kesterite solar cells has been traditionally performed by sulfurisation of a solid state precursor layer in an annealing furnace. This technique has shown problems
30 associated with the thermal stability of soda lime glass

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substrates, which limits the maximum possible temperature used by conventional furnace or rapid thermal annealing furnaces. The long-time chalcogen annealing is also detrimental to the free carrier transportation due to the increasing of cell's series resistance. Furthermore, during furnace annealing precursors may decompose and react with the back contact layer.

Summary of the Invention

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

providing a substrate comprising a first conductive layer;

depositing an intermediate layer over at least a portion of the conductive layer, the intermediate layer being arranged to be electrically coupled with the first conductive layer;

forming a copper-based light-absorbing layer over at least a portion of the intermediate layer;

depositing a capping layer arranged over at least a portion of the copper-based light-absorbing layer;

exposing the copper-based light-absorbing layer to a continuous wave laser light through the capping layer;

depositing a second conductive layer arranged to be electrically coupled with the copper-based light-

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absorbing layer over at least a portion of the copper-based light-absorbing layer;

wherein the intermediate layer is arranged to minimise the energy transferred from the laser light to the first conductive layer and the capping layer is arranged to affect the energy distribution of the laser light through the copper-based light-absorbing layer.

In an embodiment, the first layer comprises a metallic material or transparent conductive layer.

10 In an embodiment, the intermediate layer and the laser wavelength are selected such that at least 90% of the energy of the laser light that reaches a surface of the intermediate layer is absorbed by the intermediate layer.

In an embodiment, the intermediate layer has a light transmission lower than 10% at a frequency of the continuous wave laser light.

In an embodiment, intermediate layer comprises a metallic material.

In an embodiment, the intermediate layer has a thickness comprised between 10nm and 100nm.

In an embodiment, the intermediate layer comprises one or a combination of Al_2O_x , TiB_2 , TiN , and C.

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

providing a transparent substrate comprising a first transparent conductive layer;

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forming a copper-based light-absorbing over at least a portion of the first transparent conductive layer;

depositing a capping layer arranged over at least a portion of the copper-based light-absorbing layer;

5 exposing the copper-based light-absorbing layer to a continuous wave laser light through the capping layer;

depositing a second conductive layer arranged to be electrically coupled with the copper-based light-
10 absorbing layer over at least a portion of the copper-based light-absorbing layer;

wherein the capping layer is arranged to affect the energy distribution of the laser light through the copper-based light-absorbing layer.

15 In an embodiment, the transparent substrate comprises a TCO covered glass or polymeric substrate or a silicon substrate.

In an embodiment, the step of forming a copper-based light-absorbing layer comprises the steps of:

20 depositing a plurality of precursors to form a solid state layer of precursors, at least one of the precursors comprising a copper-based material; and

annealing a solid state layer of precursors;

wherein the annealing of the solid state layer of
25 precursors occurs during the step of exposing the copper-based light-absorbing layer to a continuous wave laser light through the capping layer.

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In an embodiment, the solid state layer of precursors is exposed to the continuous wave laser light through the capping layer.

5 In an embodiment, the step of exposing the copper-based light-absorbing layer to a continuous wave laser light through the capping layer is performed in a manner such that electrically active defects present in the copper-based light-absorbing layer are annealed while the copper-based light-absorbing layer is formed.

10 In an embodiment, the method further comprises the step of, prior to exposing depositing a second conductive layer, at least partially removing the capping layer.

In an embodiment, the intermediate layer is arranged in a manner such that at least 90% of the energy of the laser
15 light that reaches a surface of the intermediate layer is absorbed by the intermediate layer.

In an embodiment, the capping layer has a light transmission higher than 90% at the wavelength of the continuous wave laser light.

20 In an embodiment, the capping layer comprises one or a combination of ZnS, SiO₂, SnO₂, CdS, In₂S₃, Cd_xZn_(1-x)O_xS.

In an embodiment, the capping layer has a thickness comprised between 10nm and 200nm.

In an embodiment, the capping layer has a bandgap arranged
25 to minimise chemical reactions with the light absorbing layer. The capping layer may be also arranged to improve light trapping of the laser light and therefore optimise the efficiency of the laser annealing process.

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In an embodiment, during the step of exposing the copper-based light-absorbing layer to a continuous wave laser light, the copper-based light-absorbing layer incurs a transition from a first solid phase to a second solid
5 phase.

In an embodiment, during the step of exposing the copper-based light-absorbing layer to a continuous wave laser light at least one of the copper-based light-absorbing layer temporary enters a liquid phase.

10 In an embodiment, the copper based light-absorbing material comprises defects and the method further comprises the step of adjusting one or more parameters of the continuous wave laser light to control the volume density of the defects in the light-absorbing material.

15 In an embodiment, the volume density of defects is controlled while the copper-based light-absorbing material is formed.

In an embodiment, the method further comprises the step of adjusting one or more parameters of the continuous wave
20 laser light to influence the spatial distribution of the defects in the light-absorbing material.

In an embodiment, the intermediate layer comprises defects and the method further comprises the step of adjusting one or more parameters of the continuous wave laser light to
25 influence the volume density of the defects in the intermediate layer.

In an embodiment, the continuous wave laser light has a line-focused beam capable of covering the entire longitudinal extension of the copper-based light-absorbing

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layer and expose the copper-based light-absorbing layer by moving relative to the photovoltaic cell in a single direction.

In an embodiment, the continuous wave laser is scanned
5 across the copper-based light-absorbing layer with a scanning speed in the range of 100-3000 mm/min providing exposure times between 180 μ s to 6 ms.

In an embodiment, the copper based light-absorbing layer is a kesterite based layer.

10 In an embodiment, the copper based light-absorbing layer is a copper-zinc-germanium-tin-chalcogenide based layer

In an embodiment, the copper based light-absorbing layer is a silver-copper-zinc-tin-chalcogenide based layer.

In an embodiment, the second conductive layer comprises
15 cadmium sulphide, In_2S_3 , $\text{Cd}_x\text{Zn}_{(1-x)}\text{O}_x\text{S}$, $\text{Zn}(\text{O},\text{S})$.

In accordance with the third aspect, the present invention provides a photovoltaic cell manufactured in accordance with the method of the first or second aspect.

Advantages of embodiments of the inventions include the
20 reduced annealing duration from several tens of minutes to a few microseconds which can greatly reduce the thermal budget.

The high-power line-focus CW diode laser used in some embodiments can greatly shorten the processing time
25 comparing with conventional RTP process and is a suitable tool to fulfil the requirement for large area processing of thin film. Diode laser annealing has shown improved

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quality of kesterite absorber, which offers a scalable higher throughput version of single junction thin film and multi-junction solar cells technology.

Further, the intermediate layer allows reducing the energy transferred from the laser light to the first conductive layer. At the same time, the capping layer allows controlling and optimising the path of the laser light through the solid state layer of precursors.

Brief Description of the Drawings

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

Figures 1 and 2 are flow diagrams outlining basic steps required to manufacture a photovoltaic device in accordance with embodiments;

Figure 3 schematically shows device being fabricated using methods in accordance with embodiments;

Figures 4 and 5 show Raman spectra of CZTS layers *as-deposited* and annealed at different currents in accordance with embodiments;

Figure 6 shows STEM-EDS maps for Cu, Zn, Sn, and S acquired from CZTS layers *as-deposited* and annealed at different currents in accordance with embodiments;

Figures 7 and 9 shows EQE plots of laser annealed samples with a CdS capping layer and AlO_x intermediate layer respectively, compared to reference samples;

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Figure 8 shows cross-sectional TEM-EDS mapping of reference sample (a) and laser annealed CZTS sample with laser dose of 34J/cm² (b);

Figure 10 shows a steady state PL result (a) and the FWHM of PL peaks (b) of laser annealed samples with AlO_x barrier layer and reference sample for comparison; and

Figure 11 and 12 show Raman spectra and a peak analysis performed using a 785 nm excitation on laser annealed samples and a reference samples.

10 Detailed Description of Embodiments

Embodiments of the present invention relate to a method for manufacturing a thin film photovoltaic device.

Embodiments relate to an annealing method for forming an absorbing material of a thin film photovoltaic device. In particular, embodiments of the method allow improving the quality of CZTS epilayer using a novel laser annealing technique.

Referring now to figure 1, there is shown a flow diagram 100 with steps used to manufacture a photovoltaic device in accordance with embodiments. The steps of method 100 allow forming a device on a rigid substrate, such as stainless steel, or a flexible polymeric substrate. At step 102, a substrate comprising a first conductive layer is provided. An intermediate 'barrier' layer is then deposited on the substrate at step 110. The intermediate layer is in electrical contact with the conductive layer.

The absorption coefficient and the thickness of the intermediate layer are designed so that at least 90% of

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the laser light energy that reaches the intermediate layer is absorbed so that the energy is not transferred to the conductive portion of the substrate. Generally, depending on the material, the intermediate layer has a thickness
5 comprised between 10nm and 100nm.

Subsequently, at step 120, a plurality of precursors comprising a copper-based material is deposited on the intermediate layer to form a copper-based light-absorbing layer. The solid state layer of precursors can be
10 sulphurised and a capping layer is then deposited on the layer of precursors, step 130. The precursors are then exposed to a continuous wave laser light through the capping layer to form a CZTS layer, step 140. In some embodiments a furnace annealing step is performed prior to
15 laser annealing to form CZTS layer and laser annealing step 140 is used to improve the properties of the CZTS layer. The device comprising the substrate, the intermediate layer and the precursors is pre-heated before performing the laser annealing step (140) in order to
20 reduce the thermal mismatch with the CZTS absorbing layer. In some embodiments, the deposited capping layer is chemically removed after laser annealing, in alternative embodiments the capping layer dissolves during laser annealing. After removal of the capping layer a second
25 conductive layer is deposited on the CZTS light absorbing layer, step 150. The second conductive material may comprise CdS, In_2S_3 , $\text{Cd}_x\text{Zn}_{(1-x)}\text{O}_x\text{S}$, $\text{Zn}(\text{O},\text{S})$. Subsequently, a top contacting structure is formed to contact the photovoltaic device. One of the advantages provided by the
30 intermediate layer or 'barrier' layer deposited between the metallic part of the substrate and the CZTS light absorbing layer in method 100 is the reduction of energy

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transferred from the laser light to the first conductive layer. The capping layer, on the other end, allows controlling and optimising the path of the laser light through the solid state layer of precursors.

5 Referring now to figure 2, there is shown a flow diagram 200 with steps used to manufacture a photovoltaic device in accordance with an alternative embodiment. Method 200 allows fabricating a thin film photovoltaic device on a transparent substrate with a transparent conductive layer,
10 such as a TCO covered glass or polymeric substrate. There are a number of advantages associated with depositing the device on a transparent substrate, for example, light may be absorbed by the device through the substrate. In method 200, the layer of precursors is directly deposited onto
15 the conductive portion of the substrate and sulphurised, step 220. A capping layer is deposited at step 230 and the layer of precursors is annealed through the capping layer using a laser (step 240) in a similar manner as in method 100. Method 200 does not permit the use of an intermediate
20 layer between the substrate and the CZTS light absorbing layer. Therefore the annealing step (240) has to be performed in different conditions to annealing step 140.

In some embodiments of the method, during step 140 the precursors incur a transition from a first solid phase to
25 a second solid phase. One or more parameters of the continuous wave laser light can be adjusted to control the volume density or spatial distribution of the defects in the light-absorbing material during the transition.

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In addition, the parameters of the continuous wave laser light can be tuned to influence the volume density of the defects in the intermediate layer.

In the methods described above, the laser is used to
5 anneal the CZTS layer and reduce the density of defect in the grain so that the quality of the material can be improved. The investigation on the phase equilibrium in the Cu_2S - ZnS - SnS_2 system showed that single phase CZTS crystals can only be grown in a very narrow region.
10 Therefore, during the laser annealing process, the input laser power is tuned to heat up the CZTS film below the melting point (990°C of CZTS) to avoid decomposition and forming of second phases. As a result, in advantageous embodiments, the laser annealing process involves only
15 solid-solid phase transition.

Referring now to figure 3, there are shown two devices 300 and 350 being fabricated in accordance with methods 100 and 200 respectively. Both devices are shown while the layer of precursors is being annealed. A silicon substrate
20 302 comprising a conductive molybdenum layer 304 is used to fabricate the device. A layer of Al_2O_x is used as intermediate layer. In alternative embodiments, the intermediate layer can be made of TiN , C and TiB_2 .

Device 350 instead is deposited on a glass substrate 352
25 covered with a TCO layer 354. In both figure 3(a) and figure 3(b) a sulphurised layer of precursors 308 is being annealed by scanning an 808 nm line-focused CW diode laser beam with the dimension of $12 \times 0.27 \text{ mm}^2$ (FWHM) to improve the quality of CZTS epi-layers. The laser annealing is
30 performed through a 150 nm thick ZnS capping layer 310,

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which is sputtered on the layer 308. One of the advantages of ZnS layer 310 is the protection from oxidation, decomposition and evaporation provided to layer 308. Layer 310 is removed by diluted hydrochloric acid after the
5 laser annealing is performed. In alternative embodiments, layer 310 can be made of SiO_2 , SnO_2 , CdS , In_2S_3 , $\text{Cd}_x\text{Zn}_{(1-x)}\text{O}_x\text{S}$.

The annealed portion 316 of layer 308 has improved structural and electrical properties. In particular,
10 portion 316 has a lower concentration of structural and electrical defects in comparison to the remaining portions of layer 318.

Portion 316 has a size similar to the width of laser beam 314. In some alternative embodiments, the laser beam may
15 have a line-focused beam capable of covering the entire longitudinal extension of layer 308 and expose the entire layer 308 by moving once along the layer in a single direction.

The ZnS capping layer 310 is designed to transmit at least
20 90% of the continuous wave laser light and allows minimising chemical reactions with the CZTS absorbing layer 308. In addition to this, ZnS capping layer 310 is designed to improve light trapping of the laser light and therefore optimise the efficiency of the laser annealing
25 process. The refractive index of the ZnS is about 2.3, which is lower than CZTS of 2.6. As a result, the ZnS can act as an ARC layer during the laser annealing process.

Devices were fabricated by the Applicants to investigate the effects of the laser power density, beam speed and
30 substrate temperature on the annealed CZTS absorbing layer

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308. The laser annealing steps were completed in air without S incorporation and the samples were naturally cooled after laser treatment.

Referring now to figure 4, there is shown a plot with
5 Raman curves of CZTS layers *as-deposited* and annealed with different laser powers. The samples were annealed with a fixed substrate heating temperature of 500 °C, scan velocities of 400mm/min and exposure times of 40ms, a 514 nm excitation wavelength was used for the laser with three
10 different power densities: 44.1 W, 45.7 W and 47.3 W.

All of the spectra are characterized by the presence of four main peaks at about 257, 288, 338 and 370 cm^{-1} , which are from CZTS. After laser annealing, the FWHM of the main peak at 338 cm^{-1} , i.e., dominating A mode (m_{1A}), decreases,
15 indicating the improvement in quality of the CZTS epi-layers. Furthermore, the peak at 288 cm^{-1} , i.e., secondary A mode (m_{2A}), is more distinguishable, especially in the spectrum of CZTS annealed at laser power of 45.7 W, which has not been observed in our previous research on post-
20 annealing of CZTS thin films. The variation in m_{2A} after annealing is related to the decrease of Zn/Cu disorder, i.e., the overall random distribution of Cu and Zn at both Cu and Zn sites in the $z=1/4$ and $z=3/4$ planes.

Currently, theoretical and experimental investigations
25 have highlighted the possible negative effects of Cu/Zn disorder on CZTS-based solar cell performance. Cu/Zn disorder accounts for a large part of the voltage deficit with lateral band gap fluctuations. Thus, it is necessary to control Cu/Zn disorder in CZTS. Additionally, it is
30 important to be able to quantify Cu/Zn disorder in the

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type of thin film samples used for solar cells. The intensity ratio between peaks at 288 (m_{2A}) and 303 cm^{-1} (m_{3A}) ($Q = I_{m_{2A}}/I_{m_{3A}}$) can be regarded as an order parameter to estimate the magnitude of random distribution of Cu and Zn. The higher the Q factor, the lower the ability of Cu(Zn) atoms to occupy Zn(Cu) atomic sites in a random way. The Applicants have measured the samples using a 785nm laser excitation line to quantify the disorder-order change.

Referring now to figure 5, there are shown Raman spectra 500 and 550 of CZTS layers that were *as-deposited* and annealed with a laser power of 45.7 W. The Raman spectra were fitted using nine symmetric Lorentz-Gaussian peaks by Renishaw's WiRE (Windows-based Raman Environment) software. All of the peaks correspond to reported kesterite modes. The Q value was increased from 0.94 to 1.51 and the FWHM of m_{1A} decreased from 11.8 to 8.7 cm^{-1} , suggesting a decrease in Cu/Zn disorder and improved symmetry of the crystalline structure. The Raman based study of CZTS thin films showed a critical temperature (T_c) of 533 K for the order and disorder transition. At equilibrium, the material is completely disordered if the temperature is above T_c . Below T_c , the equilibrium ordering degree increases continuously and perfect ordering can be reached only 0K. In this laser annealing process, the substrate temperature is 500 °C This temperature is equal to the substrate temperature used for sputtering CZTS and is also the normal growth temperature for CZTS. Accordingly, in this situation, the ordered kesterite crystal structure cannot exist and the fully disordered structure will form instead. The temperature is much

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higher when the diode laser is applied, which results in the recrystallization of CZTS thin films. Only when the temperature drops below about 533K during post-synthesis cooling can ordering among Cu and Zn begins. The cooling rate effect was also studied. The slowly cooled (10K/h) thin films were found to be more ordered than those that were quickly cooled (quenched in ice water). Further optimization of the diode laser annealing procedure, including power density, substrate heating temperature and cooling rate, is needed in the future.

Referring now to figure 6, there are shown cross sections of samples probed by STEM-EDS. Figure 6 shows STEM-EDS elemental mapping results for Cu(504), Sn (506), Zn (510), S (512) from the TEM specimens of the annealed sample 650 and *as-deposited* sample 600. In Figure 6, a ZnS can be observed and the total thickness of the ZnS and CZTS bilayer has not changed after annealing. In the *as-deposited* sample 600, the ZnS layer is tightly packed over the CZTS layer and Cu, Zn, Sn, S elements are uniformly distributed in the CZTS film. In the annealed sample 650 some voids are present inside the ZnS layer and are adjacent to the interface of CZTS and ZnS. Also, in the Cu mapping 604, there is a Cu-rich neighbouring the interface between the CZTS film and the substrate. However, in the same area, there is no obvious absence of Zn, Sn and S in their elemental mapping images in 650. These observations demonstrate that ZnS is most likely to be incorporated to form a new CZTS layer which is more Zn-rich during annealing, and that the incorporation of Zn may drive Cu to gather at the interface of the CZTS.

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Traditional high-temperature sulfurization, such as tube furnace annealing and rapid thermal annealing (RTA), involves the addition of toxic (N_2+H_2S) gas and sulphur vapour, and the entire substrate must be heated to the
5 required temperature. This places stricter requirements on the substrate material that has to withstand such temperatures and thus limits the maximum available annealing temperature. The diode laser annealing technique proposed by the Applicants is one kind of millisecond
10 annealing that is in thorough use in the microelectronics industry as a replacement for RTA on silicon wafer substrates. The diode laser annealing process heats CZTS thin film over a much shorter time and to a higher temperature than traditional post-sulfurization annealing
15 procedures while allowing the substrate to remain at a much lower temperature and ramp to their peak temperature at a lower rate. In tandem solar cell application, this can prevent the lower cell from being overheated and inducing damage.

20 The fast diode laser annealing process substantially reduces the annealing duration from several tens of minutes to a few microseconds which can greatly reduce the thermal budget. Moreover, more than 90% of the laser energy is absorbed by the CZTS thin film rather than the
25 substrate so the glass substrate can be still kept at a low temperature. CZTS thin films can be heated up quickly to high annealing temperatures, allowing for the removal of the defects at grain boundaries due to crystallographic relaxation, dislocation annihilation through
30 crystallographic glide planes, and microtwins elimination. With the reduction and even removal of these crystallography defects, the structural, electronic

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qualities and associated solar cell performance of the kesterite thin films are expected to be improved.

CdS capping layer

Devices with a 50 nm CdS layer deposited by CBD (chemical bath deposition) were fabricated by the Applicants. The CdS allows protecting the CZTS absorber from oxidation, decomposition and evaporation. Table 1 shows cell performance of samples that received laser annealing compared with a reference cell (without laser treatment). The samples with 24 J/cm² and 29.4 J/cm² laser annealing archived higher cell efficiency of 5.6% and 4.93% compare with 4.55% of the reference. The increase in cell efficiency mainly contributes to the improvement in FF and J_{sc} despites that the V_{oc} shows a decrease compare with the reference sample.

Laser dose	V _{oc}	FF	J _{sc}	Efficiency
[J/cm ²]	[mV]	[%]	[mA/cm ²]	[%]
reference	571.60	54%	14.77	4.55%
24.5	535.50	60%	17.44	5.60%
29.4	537.51	56%	16.29	4.93%
34.3	491.41	51%	15.35	3.83%

Table 1 Device parameters of laser annealed samples with CdS capping layer

Referring now to figure 7, there are shown EQE plots of laser annealed samples with a CdS capping layer compared to a reference sample. All laser annealed samples have a higher J_{sc} than the reference. The better collection

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efficiency in the long wavelength range of 550 nm to 800 nm in EQE indicates an increase in either/both depletion region or/and diffusion length. The decrease in V_{oc} contributes to two possible reasons. One is the decrease of the bandgap caused by Cd diffusion into the absorber from CdS layer during the annealing process. The other is the damage induced by laser power to the interface of CdS/CZTS hetero-junction.

Figure 8 shows the cross-sectional TEM-EDS mapping of the reference sample and the sample received 34 J/cm² laser annealing. No decomposition or changing in the element composition after the laser annealing comparing to the reference, even for the sample with highest laser dose investigated.

15 *AlO_x intermediate layer*

Devices with a sputtered 3nm AlO_x layer between the Mo back contact layer and the CZTS precursor were fabricated by the Applicants. No capping layer was used for these samples and different laser dose was tested by changing the output power the laser beam.

Table 2 shows the result of cell performance of sample received laser annealing with reference cell (without laser treatment) as a comparison. The samples with 24 J/cm² and 34 J/cm² laser annealing archived higher cell efficiency of 7.14% and 7.33% compare with 6.74% of the reference.

Laser Dose	V_{oc}	FF	J_{sc}	Efficiency
[J/cm ²]	[mV]	[%]	[mA/cm ²]	[%]

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24.50	682.9	54.13	19.31	7.14
34.30	664.1	55.99	19.72	7.33
44.10	486.5	44.37	17.50	3.78
reference	674.24	55.51	18.00	6.74

Referring now to figure 9, there are shown EQE plots of laser annealed samples with an AlO_x intermediate layer compared to a reference sample. All laser annealed samples have a higher J_{sc} than the reference. The boost in efficiency mainly contributes to the increase in J_{sc} and the EQE gives more insight of the current enhancement due to the significant improvement at the long wavelength.

Steady State PL and Reman measurement

The Applicants have performed steady state room temperature PL and Resonance Raman measurement on finished device of samples have received laser annealing. Results are shown in figure 10(a) which shows the steady state PL result of laser annealed samples with different laser dose. Comparing with the reference sample, laser annealed samples with lower dose have narrower PL peak. The full width half maximum of each sample is determined and showed in figure 10(b). The figure shows a clear trend which indicates a sharper absorption edge and less severe bandgap fluctuation for the laser annealed samples.

Referring now to figure 11, there are shown Raman spectra obtained using a near-resonant excitation (785 nm) Raman measurement. Figure 11 shows that the intensity ratio between peaks at 288 (m2A) and 303 cm⁻¹ (m3A) ($Q = I_{m2A}/I_{m3A}$)

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m3A) can be regarded as an order parameter to estimate the magnitude of random distribution of Cu and Zn. The higher the Q factor, the lower the ability of Cu (Zn) atoms to occupy Zn (Cu) atomic sites in a random way. Figure 11 presents the 785 nm excitation Raman result of the reference sample and sample annealed with 24 J/cm², 34 J/cm² and 44 J/cm² laser dose.

Figure 12 shows Raman spectra obtained using a 785 nm excitation with peak fitting of laser annealed samples and reference annealed with laser dose 24 J/cm² (a), 34 J/cm² (b), 44 J/cm² (c) and reference sample (d). The Applicant fitted the Raman spectra using 10 symmetric Lorentz peaks by Renishaw's WiRE (Windows-based Raman Environment) software. All of the peaks correspond to kesterite modes reported in the literature. The Q value increased from 1.08 to 1.48 at 24 J/cm² and 1.17 at 34 J/cm², besides, the FWHM of m1A decreased from 6.65 cm⁻¹ to 6.13 cm⁻¹ at 24 J/cm² and 6.35 cm⁻¹ at 34 J/cm², suggesting a decrease in Cu/Zn disorder and improved symmetry of the crystalline structure.

The term "comprising" (and its grammatical variations) as used herein are used in the inclusive sense of "having" or "including" and not in the sense of "consisting only of".

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

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The Claims as defined in the invention are as follows:

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

5 providing a substrate comprising a first
conductive layer;

 depositing an intermediate layer over at least a
portion of the conductive layer, the intermediate layer
being arranged to be electrically coupled with the first
conductive layer;

10 forming a copper-based light-absorbing layer over
at least a portion of the intermediate layer;

 depositing a capping layer arranged over at least
a portion of the copper-based light-absorbing layer;

15 exposing the copper-based light-absorbing layer
to a continuous wave laser light through the capping
layer;

 depositing a second conductive layer arranged to
be electrically coupled with the copper-based light-
absorbing layer over at least a portion of the copper-based
20 light-absorbing layer;

 wherein the intermediate layer is arranged to
minimise the energy transferred from the laser light to
the first conductive layer and the capping layer is
arranged to affect the energy distribution of the laser
25 light through the copper-based light-absorbing layer.

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2. The method of any one of the preceding claims, wherein the first conductive layer comprises a metallic material or a transparent conductive material.

3. The method of any one of the preceding claims wherein
5 the intermediate layer and the laser wavelength are selected such that at least 90% of the energy of the laser light that reaches a surface of the intermediate layer is absorbed by the intermediate layer.

4. The method of any one of the preceding claims wherein
10 the intermediate layer has a light transmission lower than 10% at a frequency of the continuous wave laser light.

5. The method of any one of the preceding claims wherein the intermediate layer comprises a metallic material.

6. The method of any one of the preceding claims wherein
15 the intermediate layer has a thickness between 10nm and 100nm.

7. The method of any one of the preceding claims wherein the intermediate layer comprises one, or a combination, of Al_2O_x , TiB_2 , TiN , and C.

20 8. A method for forming a photovoltaic cell comprising the steps of:

providing a transparent substrate comprising a first transparent conductive layer;

forming a copper-based light-absorbing layer over
25 at least a portion of the first transparent conductive layer;

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depositing a capping layer arranged over at least a portion of the copper-based light-absorbing layer;

exposing the copper-based light-absorbing layer to a continuous wave laser light through the capping
5 layer;

depositing a second conductive layer arranged to be electrically coupled with the copper-based light-absorbing layer over at least a portion of the copper-based light-absorbing layer;

10 wherein the capping layer is arranged to affect the energy distribution of the laser light through the copper-based light-absorbing layer.

9. The method of claim 8 wherein the transparent substrate comprises a TCO covered glass or a polymeric substrate or
15 a silicon substrate.

10. The method of any one of the preceding claims wherein the step of forming a copper-based light-absorbing layer comprises the steps of:

depositing a plurality of precursors to form a
20 solid state layer of precursors, at least one of the precursors comprising a copper-based material; and

annealing a solid state layer of precursors;

wherein the annealing of the solid state layer of precursors occurs during the step of exposing the copper-
25 based light-absorbing layer to a continuous wave laser light through the capping layer.

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11. The method of any one of the preceding claims wherein the solid state layer of precursors is exposed to the continuous wave laser light through the capping layer.

12. The method of any one of the preceding claims wherein
5 the capping layer is arranged to minimise chemical reaction of the precursors with air and evaporation of the precursors.

13. The method of any one of the preceding claims wherein the capping layer is arranged such that at least a portion
10 of the capping layer evaporates during the exposure step.

14. The method of any one of the preceding claims wherein the step of exposing the copper-based light-absorbing layer to a continuous wave laser light through the capping layer is performed in a manner such that electrically
15 active defects present in the copper-based light-absorbing layer are annealed while the copper-based light-absorbing layer is formed.

15. The method of any one of the preceding claims wherein the method further comprises the step of, prior to
20 depositing a second conductive layer, at least partially removing the capping layer.

16. The method of any one of the preceding claims wherein the intermediate layer is arranged in a manner such that at least 90% of the energy of the laser light that reaches
25 a surface of the intermediate layer is absorbed by the intermediate layer.

17. The method of any one of the preceding claims wherein the capping layer has a light transmission higher than 90% at the wavelength of the continuous wave laser light.

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18. The method of any one of the preceding claims wherein the capping layer comprises one or a combination of ZnS, SiO₂, SnO₂, CdS, In₂S₃, Cd_xZn_(1-x)O_xS.

19. The method of any one of the preceding claims wherein
5 the capping layer has a thickness comprised between 10nm 200nm.

20. The method of any one of the preceding claims wherein the capping layer is arranged to improve light trapping of the laser light and optimise the efficiency of the laser
10 annealing process.

21. The method of any one of the preceding claims wherein during the step of exposing the copper-based light-absorbing layer to a continuous wave laser light, the copper-based light-absorbing layer incurs a transition
15 from a first solid phase to a second solid phase.

22. The method of any one of the preceding claims wherein during the step of exposing the copper-based light-absorbing layer to a continuous wave laser light at least one of the copper-based light-absorbing layers temporary
20 enters a liquid phase.

23. The method of any one of the preceding claims wherein the copper based light-absorbing material comprises defects and the method further comprises the step of adjusting one or more parameters of the continuous wave
25 laser light to control the volume density of the defects in the light-absorbing material.

24. The method of claim 23 wherein the volume density of defects is controlled while the copper-based light-absorbing material is formed.

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25. The method of claim 23 or claim 24 wherein the method further comprises the step of adjusting one or more parameters of the continuous wave laser light to influence the spatial distribution of the defects in the light-
5 absorbing material.

26. The method of any one of the preceding claims wherein the intermediate layer comprises defects and the method further comprises the step of adjusting one or more parameters of the continuous wave laser light to influence
10 the volume density of the defects in the intermediate layer.

27. The method of any one of the preceding claims wherein the continuous wave laser light has a line-focused beam capable of covering the entire longitudinal extension of
15 the copper-based light-absorbing layer and expose the copper-based light-absorbing layer by moving relative to the photovoltaic cell in a single direction.

28. The method of claim 27 wherein the continuous wave laser is scanned across the copper-based light-absorbing
20 layer with a scanning speed in the range of 100-3000 mm/min providing exposure times between 180 μ s to 6 ms.

29. The method of any one of the preceding claims wherein the copper based light-absorbing layer is a kesterite based layer.

25 30. The method of any one of claims 1 to 28 wherein the copper based light-absorbing layer is a copper-zinc-germanium-tin-chalcogenide based layer

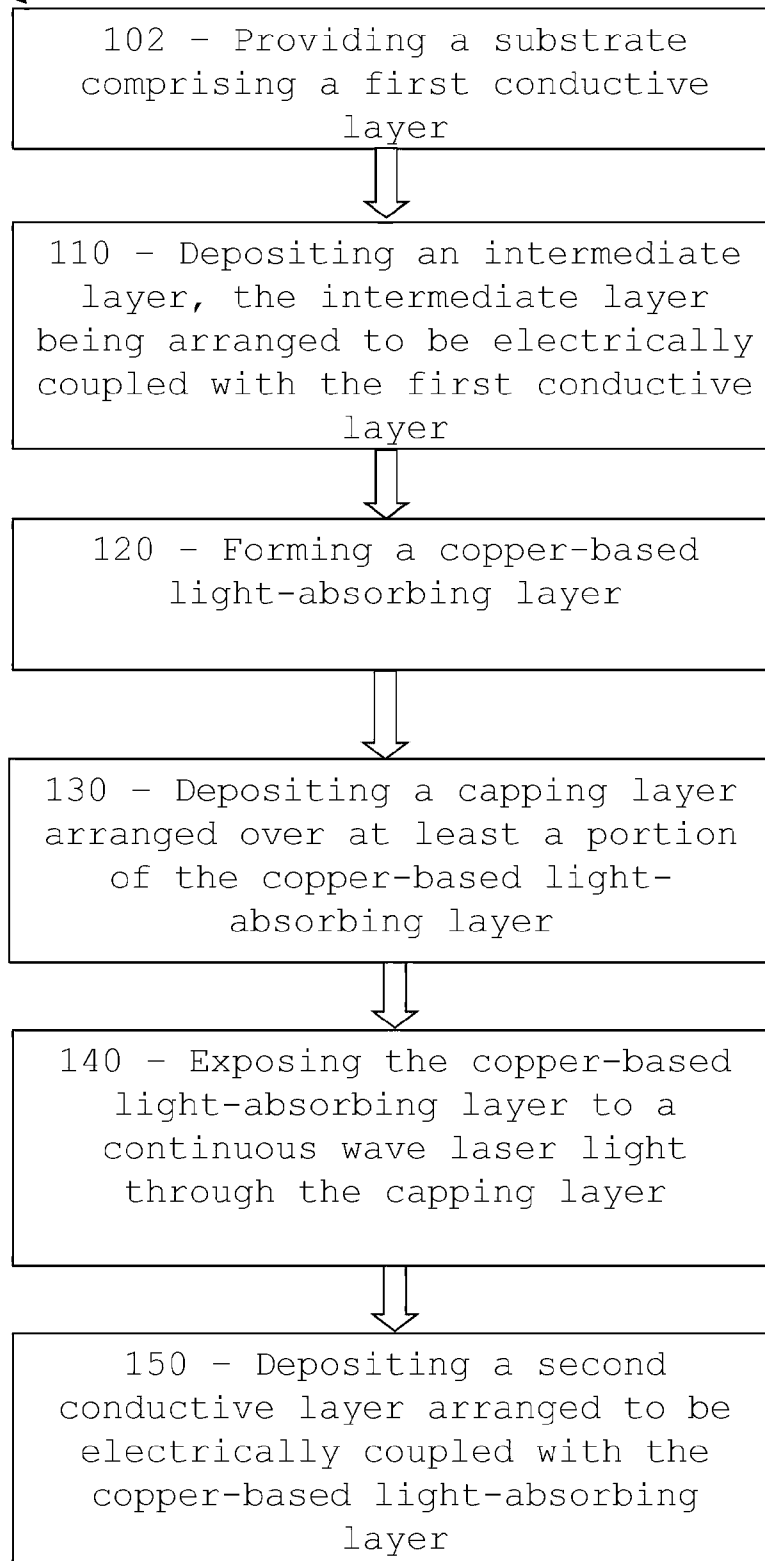
- 29 -

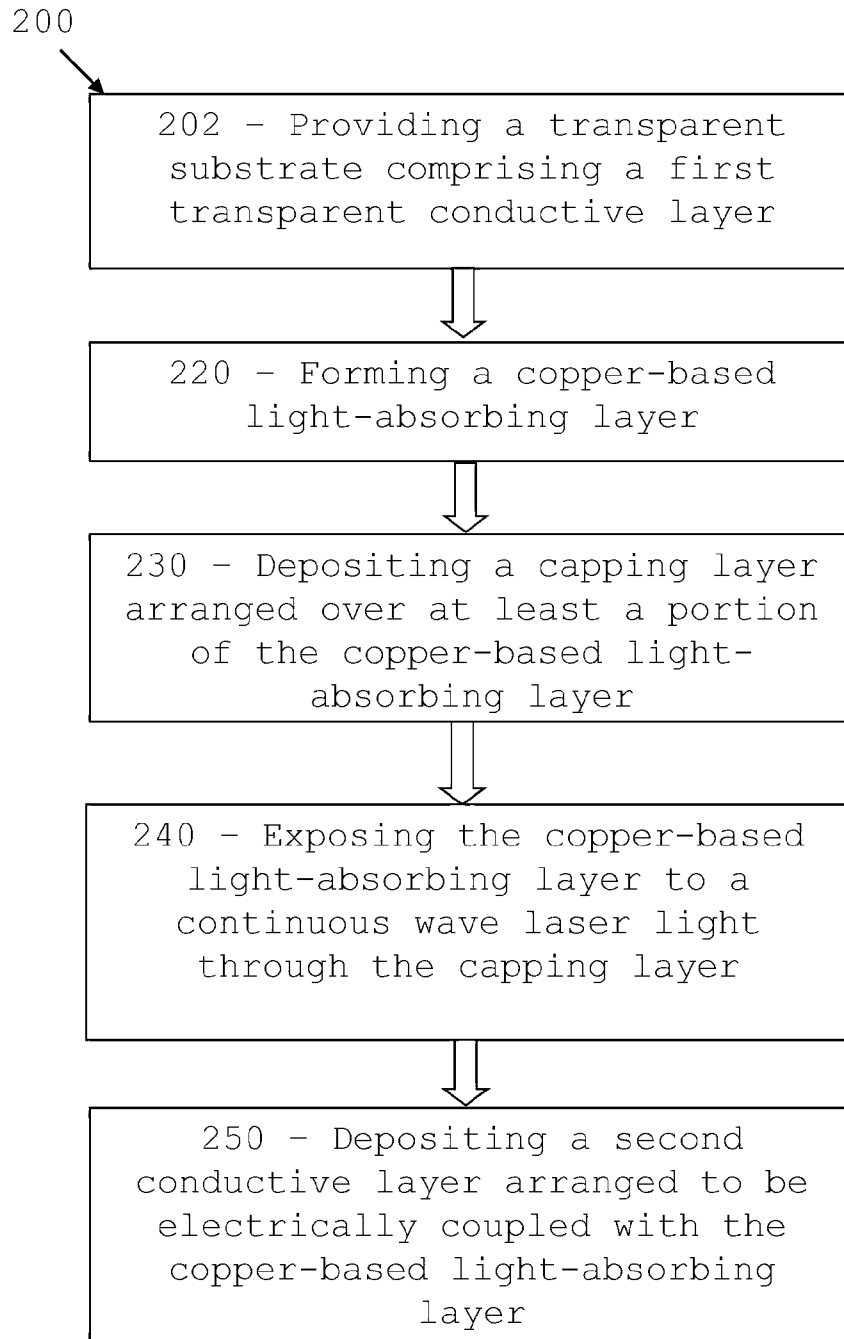
31. The method of any one of claims 1 to 28 wherein the copper based light-absorbing layer is a silver-copper-zinc-tin-chalcogenide based layer.

32. The method of any one of the preceding claims wherein
5 the second conductive layer comprises cadmium sulphide, In_2S_3 , $\text{Cd}_x\text{Zn}_{(1-x)}\text{O}_x\text{S}$, $\text{Zn}(\text{O}, \text{S})$.

33. A photovoltaic cell manufactured in accordance with the method of any one of claims 1 to 32.

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1/12**FIGURE 1**

2/12**FIGURE 2**

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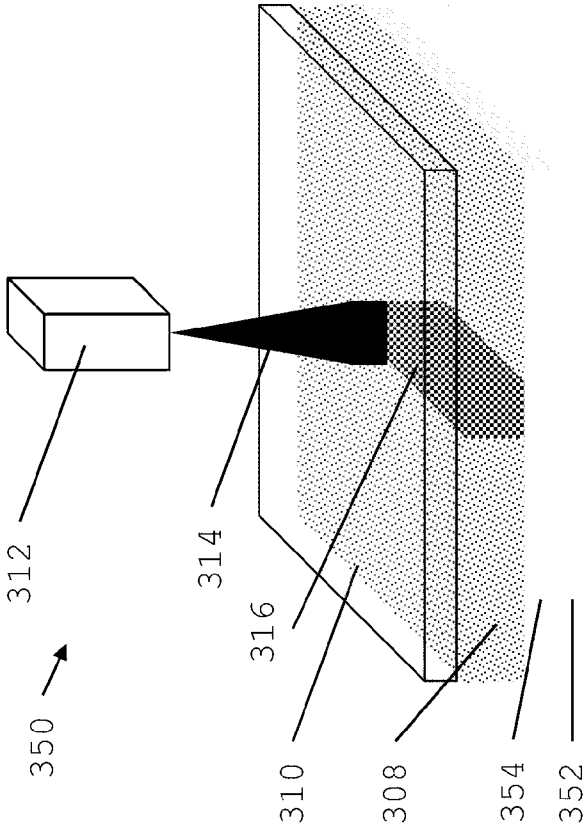


FIGURE 3(b)

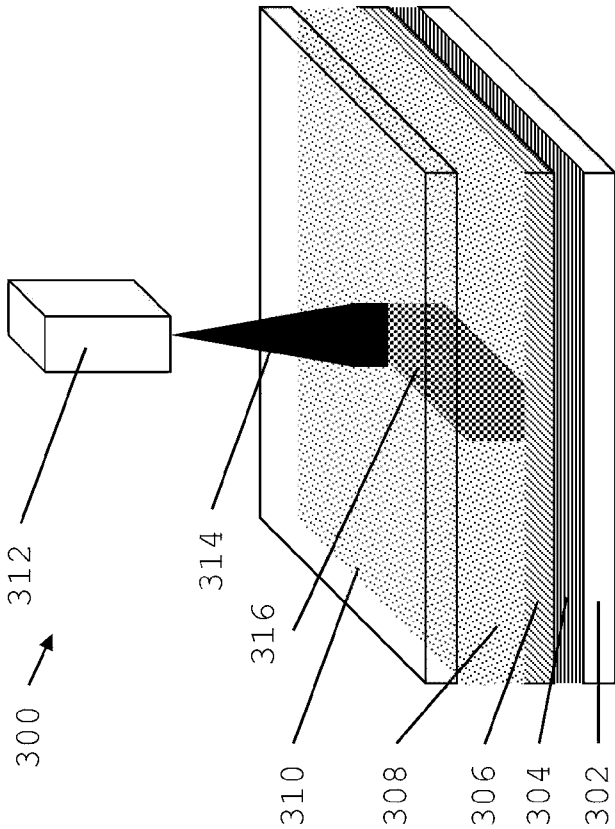
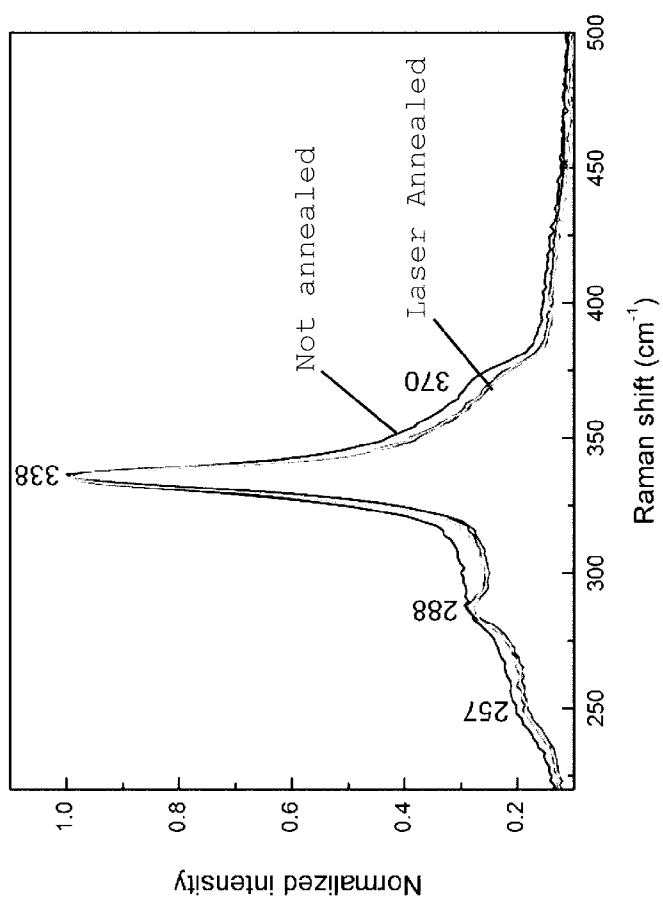


FIGURE 3(a)

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**FIGURE 4**

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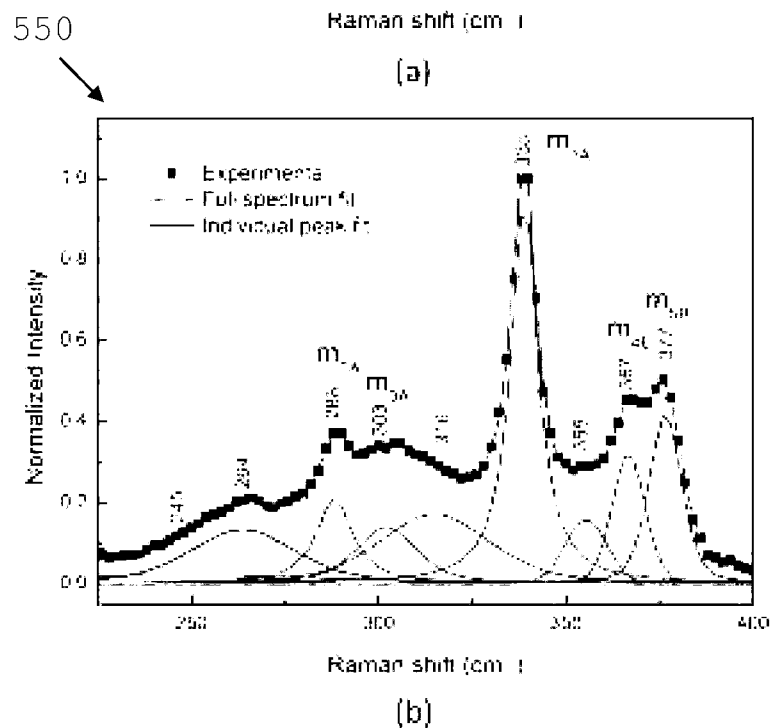
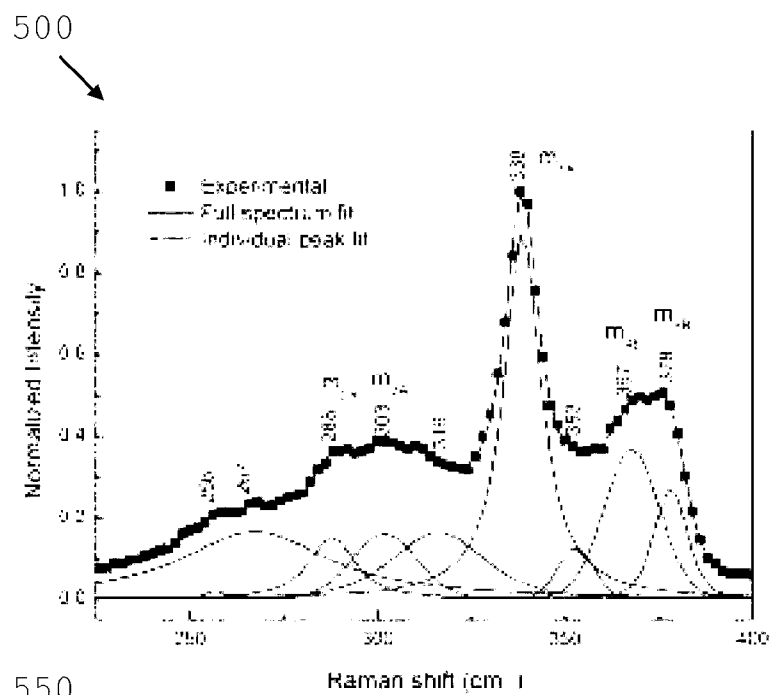


FIGURE 5

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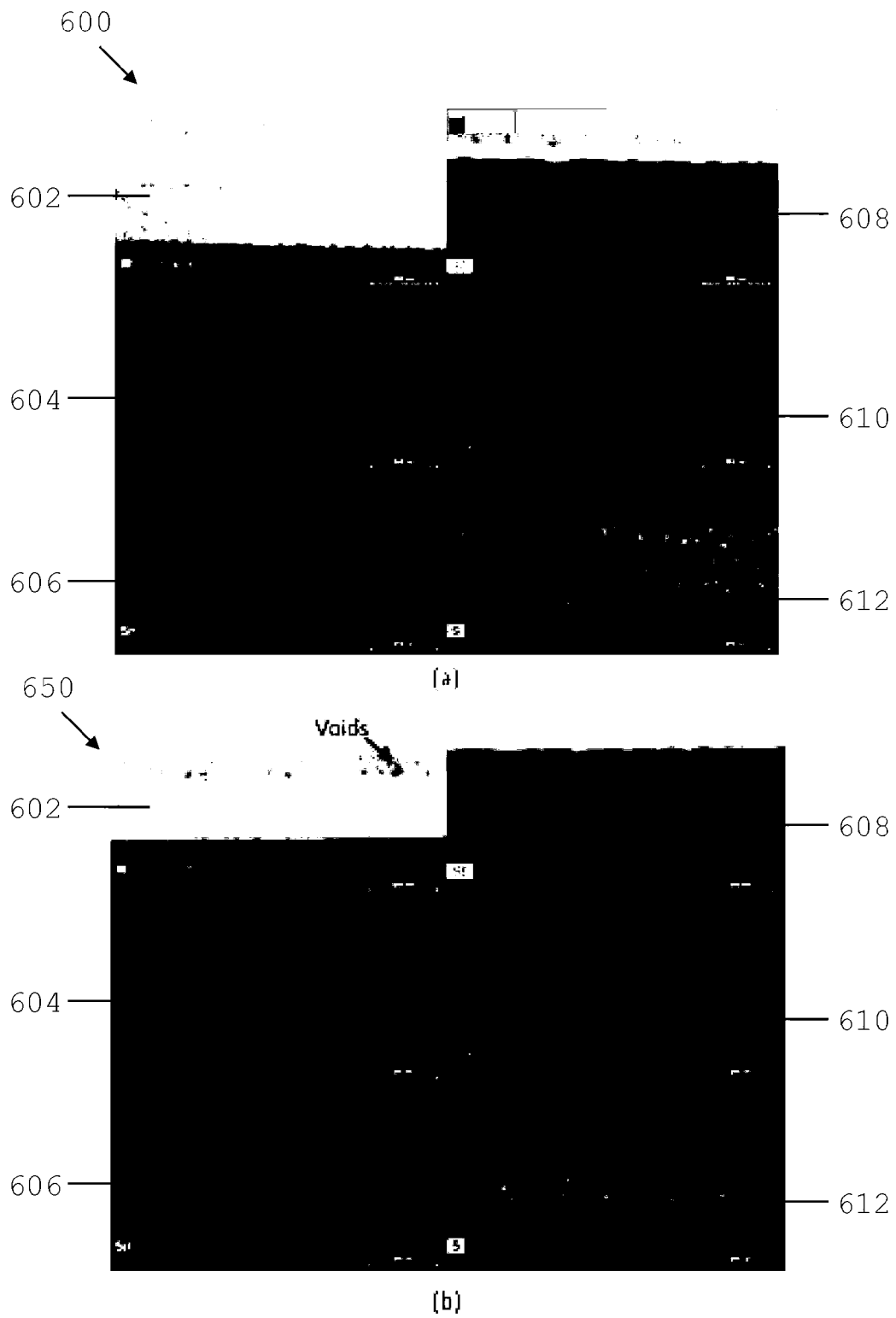


FIGURE 6

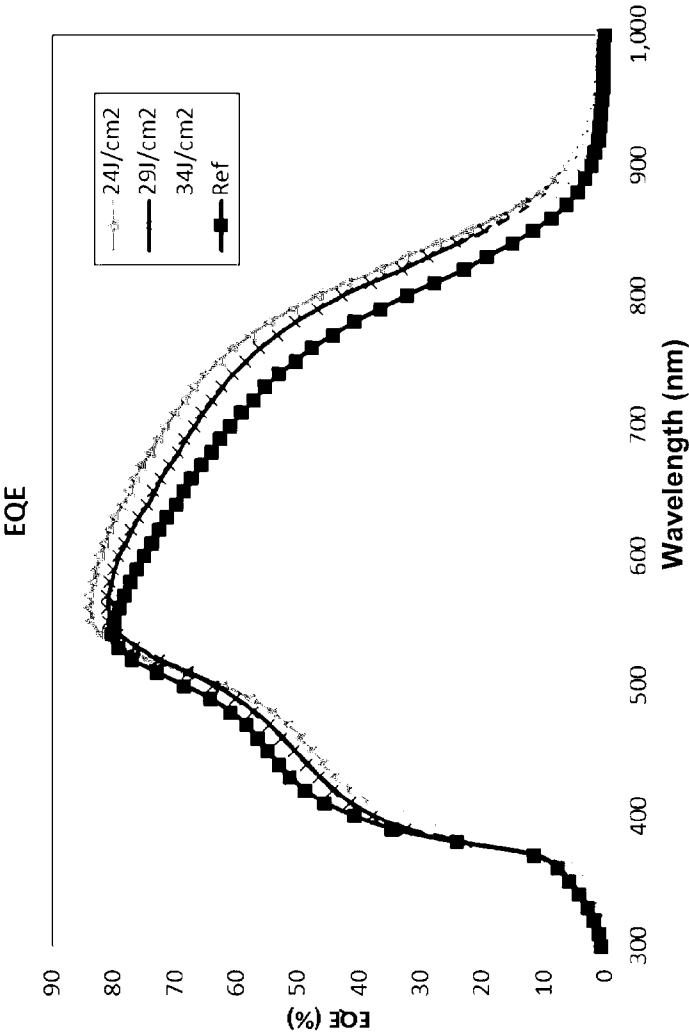


FIGURE 7

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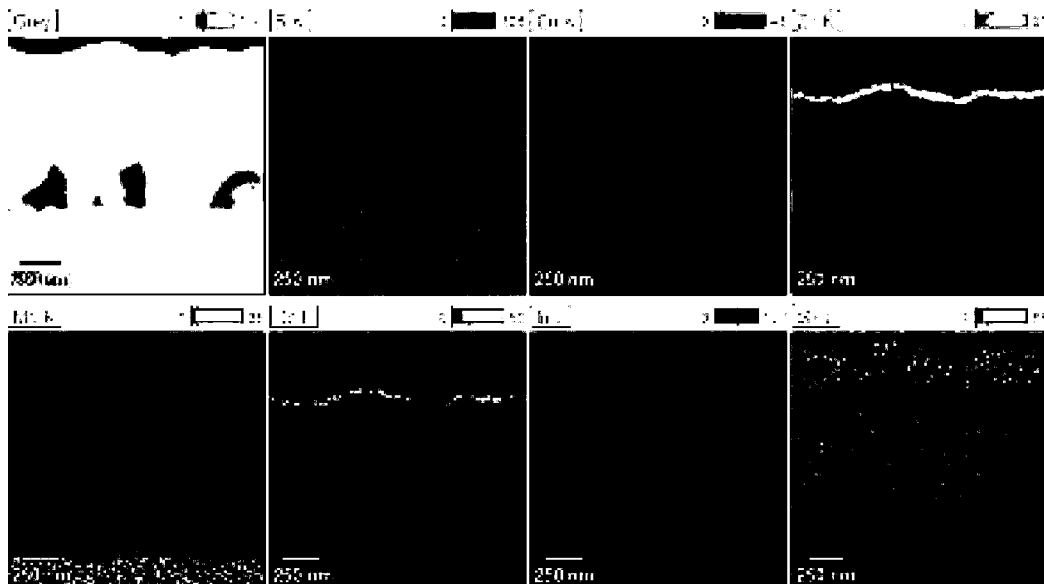


FIGURE 8(a)

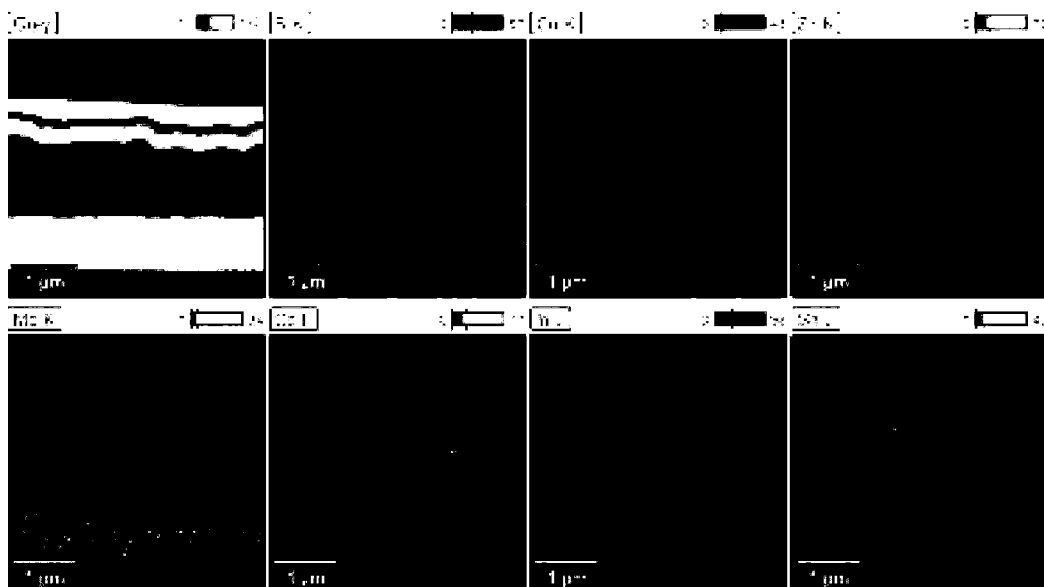


FIGURE 8(b)

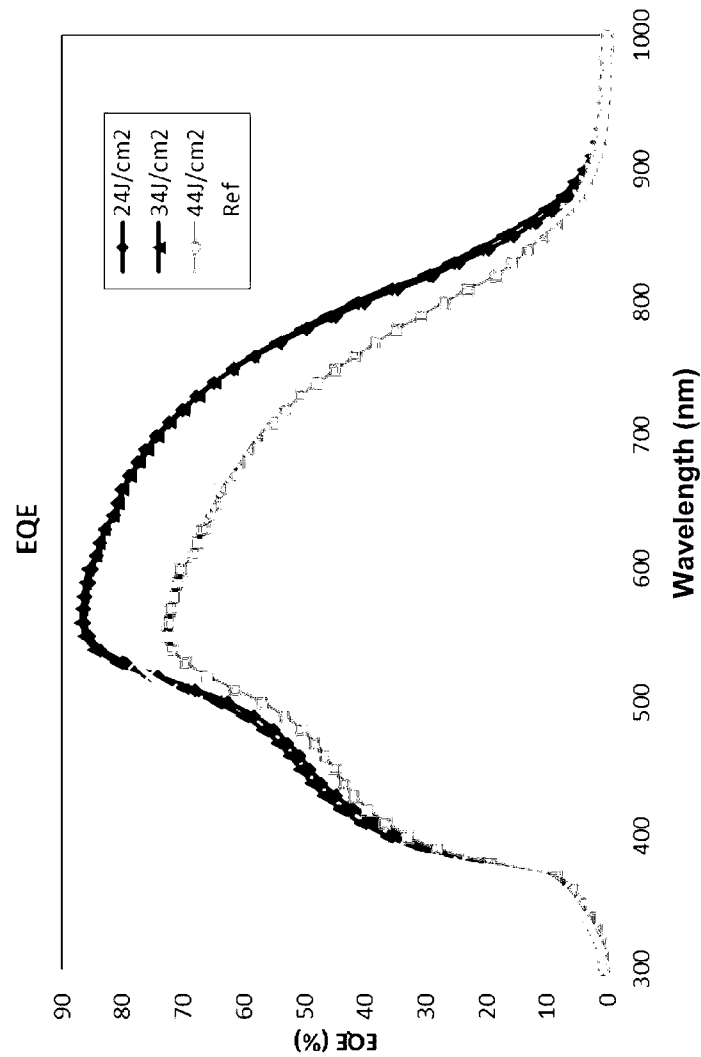


FIGURE 9

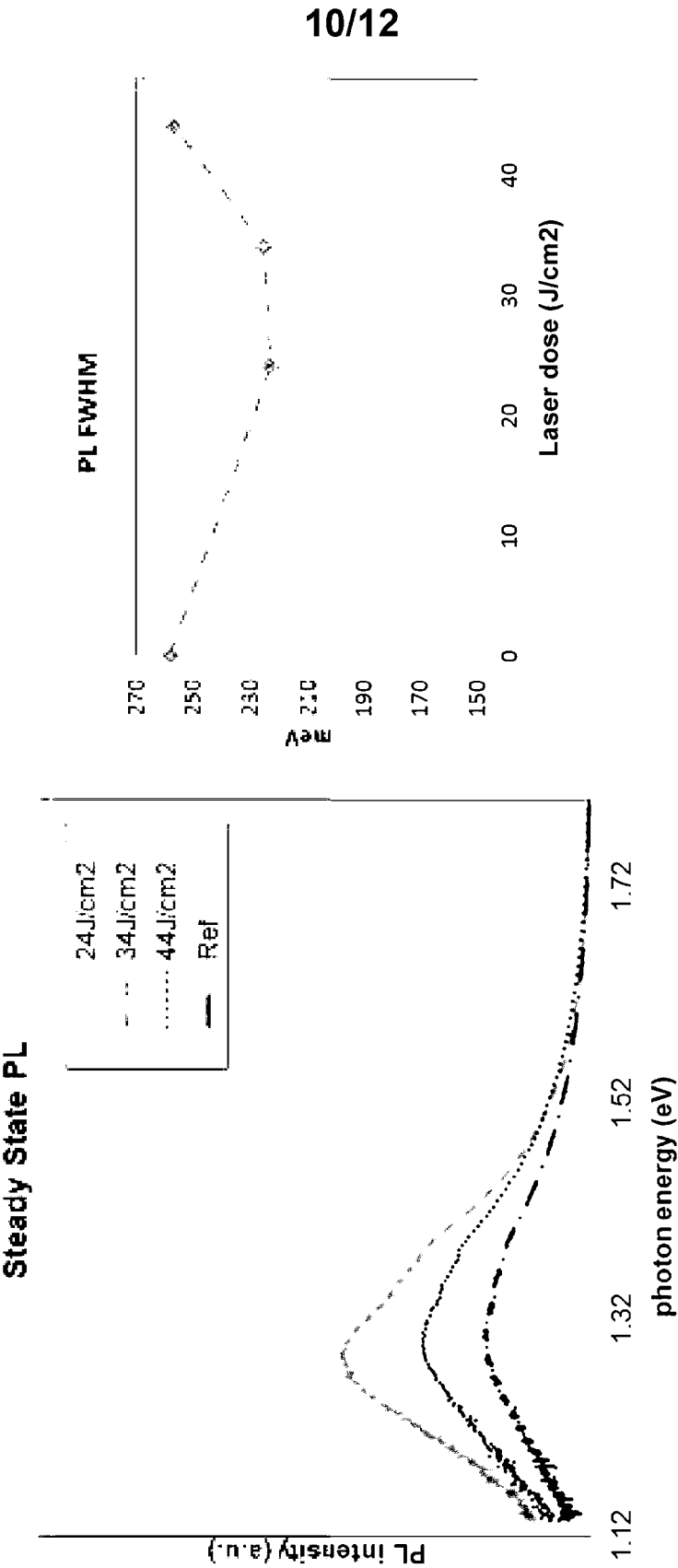


FIGURE 10(b)

FIGURE 10(a)

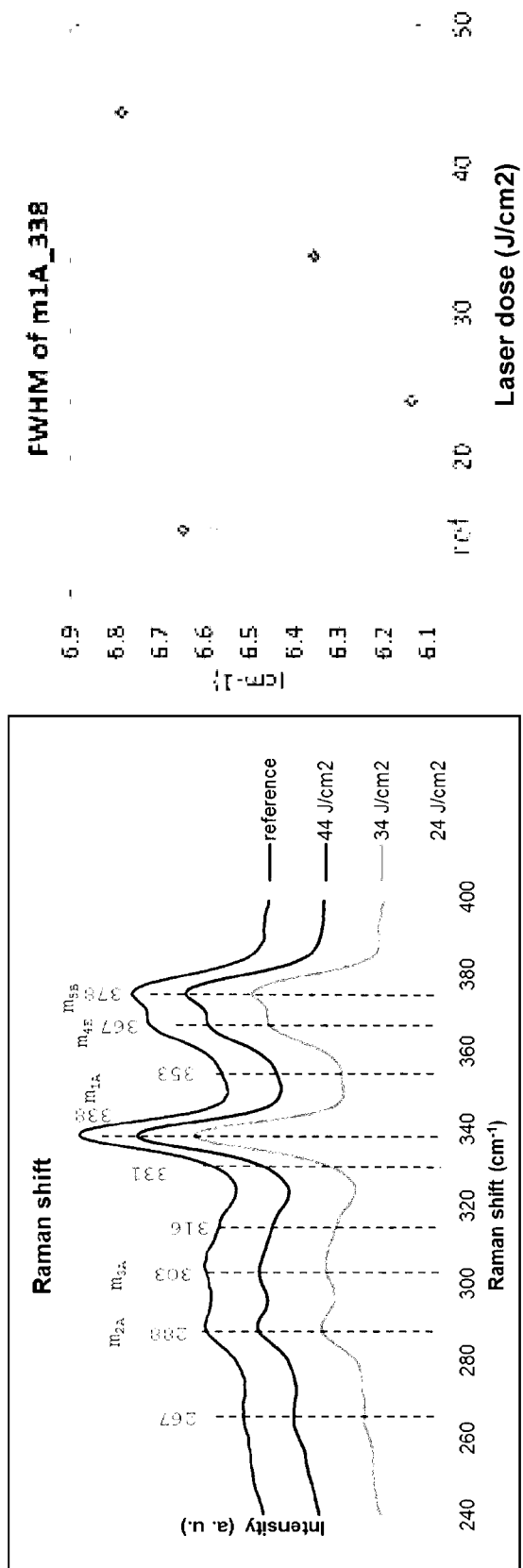


FIGURE 11(a)

FIGURE 11(b)

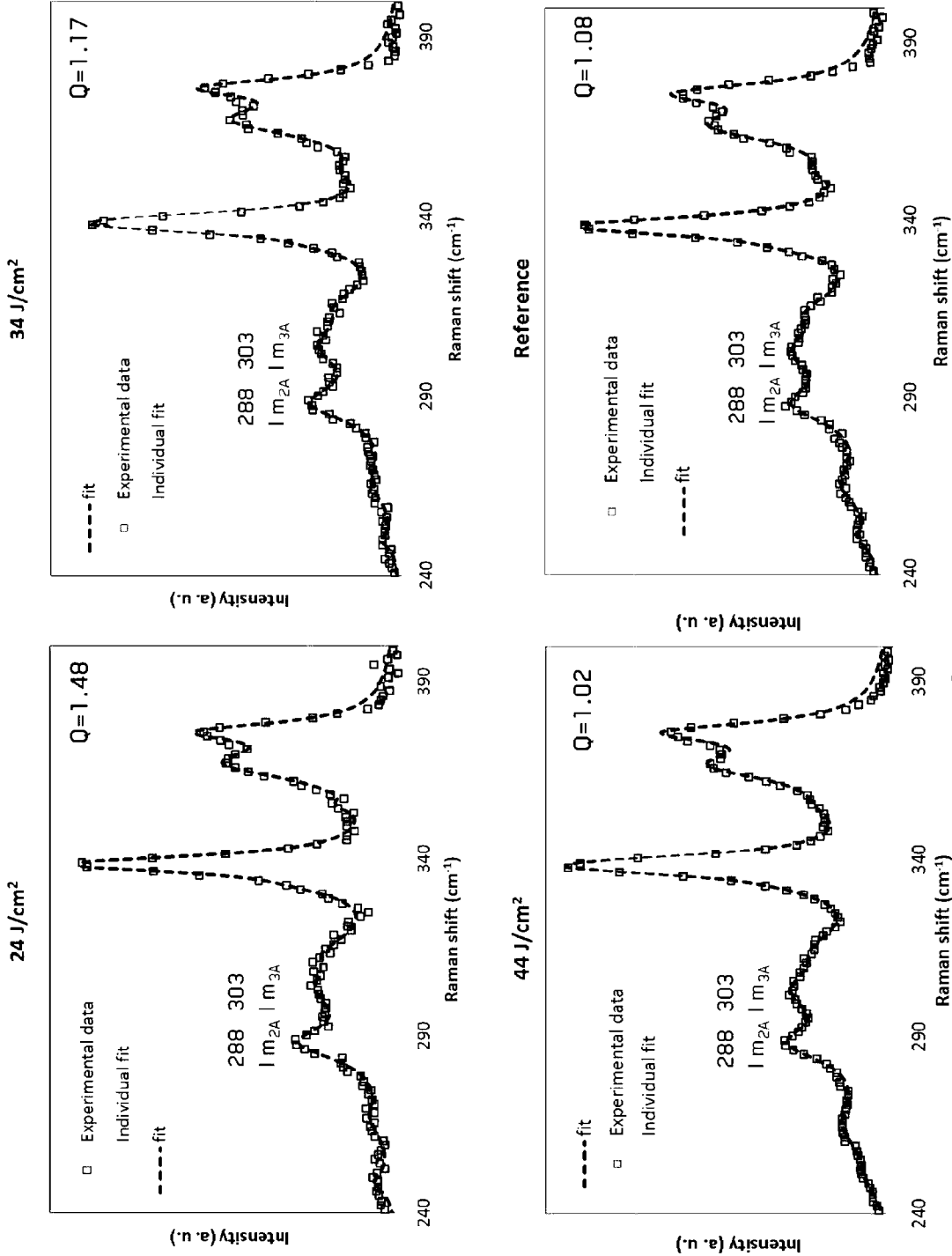


FIGURE 12

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2016/051218

A. CLASSIFICATION OF SUBJECT MATTER

H01L 31/032 (2006.01) H01L 21/02 (2006.01) H01L 31/04 (2014.01)

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)

Searches were performed in Espacenet, Google Patents, Google Scholar, Google Search and Science Direct as well as EPOQUE, using databases EPODOC, WPIAP, TXPEA, TXPEB, TXPEC, TXPEE, TXPEF, TXPEH, TXPEI, TXPEP, TXPEPEA, TXPES, TXPUSE0A, TXPUSE1A, TXPUSEA, TXPUSEB, TXPWOEA, NPL, INSPEC and STN using databases 1MOBILITY, 2MOBILITY, APOLLIT, CAPLUS, CBNB, CEABA-VTB, CIN, COMPENDEX, DKF, ENERGY, IFIALL, INSPEC, INSPHYS, METADEX, MSDS-OHS, PIRA, PQSCITECH, RAPRA, RDISCLOSURE, SCISEARCH, TEMA, TRIBO, USPATFULL, USPATOLD, USPAT2, WELDASEARCH and WSCA. The following symbols and keywords were used: IPC/CPC: H01L21/00/LOW, H01L31/00/LOW, H01L27/14/LOW, Y02E10/50/LOW, Y02P70/521/LOW
 Keywords (along with synonyms and proximity operators): Copper, kesterite, CZTS, CIGS, anneal, laser, solar, thin film.

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 22 February 2017		Date of mailing of the international search report 22 February 2017	
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 Jason Schiemer AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832810	

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. PCT/AU2016/051218
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/0193349 A1 (CALLAHAN) 02 August 2012 Paragraphs [0029], [0036], [0038], [0042], [0044], [0058], [0061]-[0063], [0065]-[0066], [0073], [0075], [0077], [0079]	8-13, 15, 17-18, 21-22, 27-29, 31-33
X	WO 2014/210451 A2 (FIRST SOLAR, INC) 31 December 2014 Paragraphs [0010]-[0011], [0024]-[0026], [0029], [0032], figure 3	8-9, 17-20, 33
A	US 2013/0065355 A1 (LIANG ET AL.) 14 March 2013 Abstract, paragraphs [0009], [0029]-[0031], [0034]-[0037], [0045]	1-33

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2016/051218	
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 2012/0193349 A1	02 August 2012	US 2012193349 A1	02 Aug 2012
		WO 2012103551 A1	02 Aug 2012
WO 2014/210451 A2	31 December 2014	WO 2014210451 A2	31 Dec 2014
		US 2015004743 A1	01 Jan 2015
		US 9406829 B2	02 Aug 2016
US 2013/0065355 A1	14 March 2013	US 2013065355 A1	14 Mar 2013
		US 8551802 B2	08 Oct 2013
		US 2014007938 A1	09 Jan 2014
		WO 2013039912 A1	21 Mar 2013
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)			