



(43) International Publication Date
1 August 2013 (01.08.2013)

- (51) **International Patent Classification:**
H01L 31/042 (2006.01) *H01L 21/324* (2006.01)
H01L 31/18 (2006.01)
- (21) **International Application Number:**
PCT/US2013/021035
- (22) **International Filing Date:**
10 January 2013 (10.01.2013)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/590,660 25 January 2012 (25.01.2012) US
13/401,206 21 February 2012 (21.02.2012) US
- (71) **Applicant:** THE TRUSTEES OF DARTMOUTH COLLEGE [US/US]; 11 Rope Ferry Road, Room 6210, Hanover, NH 03755 (US).
- (72) **Inventors:** LIU, Jifeng; 11 Rip Road, Hanover, New Hampshire 03755 (US). WANG, Xiaoxin; 11 Rip Road, Hanover, New Hampshire 03755 (US).
- (74) **Agent:** BARTON, Steven, K.; Lathrop & Gage LLP, 4845 Pearl East Circle, Suite 201, Boulder, CO 80301 (US).

(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, 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, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, ML, MR, NE, SN, TD, TG).

Published:

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

(54) **Title:** METHOD OF FORMING SINGLE-CRYSTAL SEMICONDUCTOR LAYERS AND PHOTOVOLTAIC CELL THEREON

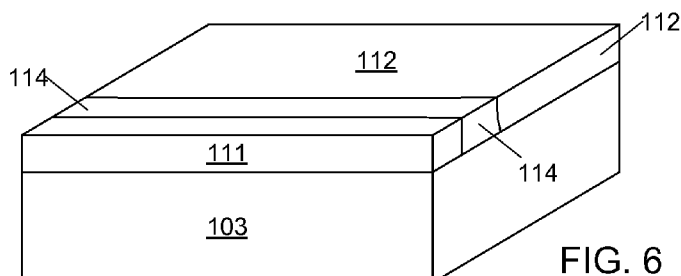


FIG. 6

(57) **Abstract:** A method for forming single crystal or large-crystal-grain thin-film layers deposits a thin-film amorphous, nanocrystalline, microcrystalline, or polycrystalline layer, and laser-heats a seed spot having size on the order of a critical nucleation size of the thin-film layer. The single-crystal seed spot is extended into a single-crystal seed line by laser-heating one or more crystallization zones adjacent to the seed spot and drawing the zone across the thin-film layer. The single-crystal seed line is extended across the thin-film material layer into a single-crystal layer by laser-heating an adjacent linear crystallization zone and drawing the crystallization zone across the thin-film layer. Photovoltaic cells may be formed in or on the single-crystal layer. Tandem photovoltaic devices may be formed using one or several iterations of the method. The method may also be used to form single-crystal semiconductor thin-film transistors, such as for display devices, or to form single-crystal superconductor layers.



METHOD OF FORMING SINGLE-CRYSTAL SEMICONDUCTOR LAYERS AND PHOTOVOLTAIC CELL THEREON

RELATED APPLICATIONS

[0001] This application claims priority to U.S. Patent Application Serial No. 13/401,206 and U.S. Patent Application Serial No. 61/590,660, filed January 25, 2012, the disclosures of which are incorporated herein by reference.

BACKGROUND

[0002] Photovoltaic (PV) cells are made of many materials. Among common PV cells are those having active photon-absorber layers of polycrystalline Silicon, Single-crystal silicon, or amorphous silicon; photovoltaic cells may be made from other semiconductor materials such as Germanium, Gallium Arsenide, Gallium Phosphide, Indium Gallium Phosphide, Cadmium Telluride, Copper-Indium Gallium diSelenide (CIGS), Copper Oxide, Zinc Oxide, Zn_3P_2 , and Indium Gallium Nitride.

[0003] It is well known that PV cells having absorber layers of single-crystal or large-crystal-grain semiconductors are more efficient at converting energy from incident photons into electrical energy than those of polycrystalline, microcrystalline, nanocrystalline, or amorphous materials due to less material defects. Here “single crystal” means the entire semiconductor material has the same crystallographic orientation without any grain boundaries. “Large-crystal-grain” means that the grain size is comparable or larger than the carrier diffusion length such that electron-hole recombination at grain boundaries is negligible. For example, single-crystal silicon cells are typically as much as twice as efficient as polycrystalline or amorphous silicon cells. However, single crystal materials are significantly more expensive than their polycrystalline, microcrystalline, nanocrystalline, or amorphous counterparts, which is a limiting factor for their applications.

[0004] Most single-crystal silicon PV cells available today are made from silicon wafers produced by growing large, single-crystal, boules using the Czochralski process, and sawing slices, or wafers, from the boule. The wafers are then polished and the photovoltaic device formed on and in the wafer. This process is considerably more expensive than forming polycrystalline, microcrystalline, or amorphous thin-

film layers on a substrate such as glass. Single crystal wafers of other semiconductor materials are even more expensive than single crystal Si wafers. For example, GaAs wafers are several times more expensive than Si wafers with the same area. For some semiconductor materials such as CIGS, single crystal wafers are unavailable.

Furthermore, since sawn wafers have a minimum practical thickness and material is lost from sawing, over 100 times more semiconductor material is typically required to create PV cells of a particular surface area from Czochralski wafers than from thin-films. In addition, the sawing and polishing process is expensive, and wafers tend to be stiff and brittle. Although new technologies such as direct wafer casting from molten Si are being developed to reduce material wastes associated with sawing, the wafers produced are multicrystalline instead of single-crystal. Moreover, the direct wafer casting technique is still unlikely to catch up with the low cost of thin-film layers since the wafers are still about 100 times thicker than thin-films while the material growth temperature is nearly 1000 °C higher.

[0005] Layers of polycrystalline, amorphous, and microcrystalline silicon and other semiconductor materials may be deposited on a substrate by various versions of chemical vapor deposition (CVD) and physical vapor deposition (PVD), including plasma-enhanced CVD (PECVD), low pressure CVD (LPCVD), atmosphere pressure CVD (APCVD), ultra-high vacuum CVD (UHV-CVD), thermal evaporation, electron-beam evaporation, sputtering, and laser ablation. Techniques for depositing polycrystalline silicon are well known in the integrated circuit art. Polycrystalline silicon can be deposited on a large variety of substrates, ranging from metal foils to some kinds of glasses, and may also be deposited over conductive metal films previously deposited on some glasses and similar substrates.

[0006] Amorphous, nanocrystalline or microcrystalline silicon layers may be deposited on substrates having softening temperatures of less than 600°C; laser recrystallization has been performed on such layers to produce polycrystalline silicon layers at relatively low-temperature on polyester substrates.

[0007] As previously mentioned, PV cells fabricated from single-crystal or large-grained silicon wafers are twice as efficient yet considerably more expensive than those made with polycrystalline or amorphous silicon thin films. Further, cells

fabricated from Czochralski wafers are fragile, and are usually packaged in inflexible, heavy, and bulky panels for use in fixed solar panel arrays.

[0008] Single-crystal thin-films are an alternative approach to high efficiency PV cells. Conventionally, single-crystal thin films have been grown on single crystal substrates or template layers by epitaxy. However, inexpensive, non-single-crystal substrates such as glass, plastics or metal make it impossible to form single-crystal thin films by conventional epitaxial growth due to lack of single crystal substrate or template. For example, glass and plastics are amorphous, while metals are polycrystalline. Thin films deposited on these substrates are also amorphous, microcrystalline or polycrystalline since there is nothing to guide the crystallographic orientation of thin film growth. An approach to form single-crystal thin-films on non-single-crystal substrates or templates is wafer bonding using a “Smart Cut” process, a technique involving surface oxidation, hydrogen implantation into the single crystal Si wafer, bonding to the desired substrate at high temperatures, and annealing to separate a thin layer of Si from the original single crystal Si wafer. This process is very expensive and cannot be scaled to large area due to the limitation of Si wafer size (currently 12 inch in diameter). In fact, the resulting product such as silicon-on-insulator (SOI) is about 10 times more expensive than single-crystal Si wafers themselves. As a result, they are currently only used for high-end electronics and optoelectronics devices. Clearly, this approach is not applicable to high volume solar cell applications.

SUMMARY

[0009] In an embodiment, a method for forming a single crystal or large-crystal-grain thin-film layer uses a thin-film amorphous, nanocrystalline, microcrystalline, or polycrystalline layer deposited on a substrate or template, and laser-heats a seed spot having size on the order of a critical nucleation size of the thin-film layer. The single-crystal seed spot is then extended into a single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the thin-film layer. The single-crystal seed line is then extended across the thin-film layer into a single crystal plane by laser-heating a

crystallization zone adjacent to the seed line and drawing the crystallization zone across the thin-film layer.

[0010] In an embodiment, a method of fabricating a photovoltaic device involves depositing an electrical contact layer on a substrate or template, and depositing a thin-film semiconductor layer with an initial microstructure selected from the group consisting of amorphous, nanocrystalline, and microcrystalline. A seed spot of the semiconductor layer is laser-heated to a crystallization temperature, the seed spot having size on the order of a critical size of nucleation of the thin-film semiconductor layer, and nucleates into a single-crystal seed. The single-crystal seed spot is extended into a single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the thin-film semiconductor layer. The single-crystal seed line is then extended across the thin-film semiconductor layer into a single crystal plane by laser-heating a linear crystallization zone adjacent to the seed line and drawing the crystallization zone across the thin-film semiconductor layer. A second electrical contact layer is added, and one of the first and second contact layers may be patterned.

[0011] In another embodiment, a method of fabricating a tandem PV cell includes depositing an electrical contact layer on a transparent substrate, depositing a thin-film semiconductor layer having initial microstructure selected from amorphous, nanocrystalline, and microcrystalline, and further having at least a first junction sublayer and a second junction sublayer, each junction sublayer further having a P-type, an Intrinsic, and an N-type sub-sublayer. A seed spot of the thin-film semiconductor layer is then laser-heated to a crystallization temperature, the seed spot having size on the order of a critical size of nucleation of the thin-film semiconductor layer, and thereby nucleates into a single crystal seed. The single crystalline seed spot is extended into a single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the thin-film semiconductor layer. The single-crystal seed line is then extended across the thin-film semiconductor layer into a single-crystal plane by laser-heating a linear crystallization zone adjacent to the seed line and drawing the crystallization zone across the thin-film semiconductor layer, the crystallization zone crystallizing at least

the intrinsic sub-sublayer of the second junction sublayer without crystallizing at least the intrinsic sub-sublayer of the first junction sublayer. A second electrical contact layer is applied.

[0012] A photovoltaic device as such may be formed by the method having a first junction and a second junction, the first and second stacked, the first and second junction formed in a chemically same semiconductor material, the first semiconductor junction having amorphous structure and the second semiconductor junction having single crystalline structure.

[0013] In another embodiment, a method of forming a tandem photovoltaic device includes depositing a first electrical contact layer on a substrate or template. A first thin-film semiconductor layer of a first semiconductor is deposited having an initial microstructure selected from the group consisting of amorphous, nanocrystalline, and microcrystalline. A seed spot of the first thin-film semiconductor layer is laser-heated to a crystallization temperature, the seed spot having size on the order of a critical size of nucleation of the first thin-film semiconductor layer, and nucleating into a single-crystal seed. The single-crystal seed spot is extended into a single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the first thin-film semiconductor layer. The single crystalline seed line is then extended across the first thin-film semiconductor layer into a single crystal plane by laser-heating a crystallization zone adjacent to the seed line and drawing the crystallization zone across the thin-film semiconductor layer. At least a second thin-film semiconductor layer is deposited, the second thin-film semiconductor layer chemically different from the first semiconductor layer. More thin-film semiconductor layers with different chemical compositions can be sequentially deposited. Junctions are formed at each thin-film semiconductor layers, and a second electrical contact layer is added. The electrical contact layers may be patterned.

BRIEF DESCRIPTION OF THE FIGURES

[0014] Fig. 1 is a cross sectional illustration of an amorphous, nanocrystalline, microcrystalline, or polycrystalline semiconductor layer on a, non-single-crystal substrate or template.

[0015] Fig. 2 is a top view of a semiconductor coating on the substrate or template, showing an initial laser focal point and corresponding seed spot for nucleation.

[0016] Fig. 3 is a cross sectional illustration of an initial phase in forming a seed line by heating and nucleating a seed spot in the semiconductor coating, taken at 3-3 in FIG. 2.

[0017] Fig. 3A is a cross sectional illustration of an intermediate phase in forming a seed line in the semiconductor coating.

[0018] Fig. 4 is a top view illustration of an intermediate phase in forming a seed line in the semiconductor coating.

[0019] Fig. 5 illustrates a top view of the seed line prior to extension of single-crystal growth across the remaining semiconductor layer.

[0020] Fig. 6 illustrates a perspective view of heated crystallization zone adjacent to the seed line.

[0021] Fig. 7 illustrates sweeping the heated crystallization zone away from the seed line and across the remaining semiconductor layer on the substrate (top view).

[0022] Fig. 7A is a perspective view illustrating a completed crystallized single-crystal layer.

[0023] Fig. 8 is a flowchart of the method of crystallizing a thin-film material.

[0024] Fig. 9 is a cross-sectional diagram illustrating a tandem photovoltaic device having stacked crystalized and amorphous cells, the cells having distinct bandgaps and fabricated in a single semiconductor material.

[0025] Fig. 10 is a cross-sectional diagram illustrating an alternative tandem photovoltaic device having crystalized cells of differing semiconductor materials with distinct bandgaps.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0026] To achieve single crystal or large-crystal-grain thin film semiconductor layers on non-single-crystal substrates or templates, the key is to control the number of nuclei during the crystallization process. For single crystal thin

film growth, there has to be only one nucleus formed on the substrate, and the rest of the thin film has to be crystallized from this seed nucleus. For large-crystal-grain thin-film semiconductor layers, the number of nuclei has to be limited such that the total substrate area divided by the number of nuclei is comparable or larger than the carrier diffusion area of electrons and holes in the semiconductor material. During the nucleation process, there is a critical size for nucleation, below which no stable nucleus can be formed. Therefore, when the initial crystallization process is localized to a small area in the same order as the critical nucleation size, only one nucleus can be formed. Using this single nucleus as the seed for the crystallization of the rest of the thin-film, a single-crystal thin film is achieved on non-single-crystal substrates or templates. Our invention describes a new technology based on this approach, which is applicable to manufacturing high efficiency thin-film solar cells as well as SOIs at low cost.

[0027] An amorphous, nanocrystalline, microcrystalline, or polycrystalline thin-film layer 101 is fabricated 202 (Fig. 8) on a substrate or template 103 (Fig. 1) using one of a variety of techniques such as evaporation, sputtering, laser ablation, or chemical vapor deposition. In a particular embodiment thin-film layer 101 is an amorphous silicon layer; in an alternative embodiment semiconductor layer 101 is a microcrystalline silicon layer. In alternative embodiments, thin-film layer 101 may be made of another semiconductor material such as Ge, GaAs, GaP, InGaP CdTe, CIGS, CuO, Cu₂O, ZnO, Zn₃P₂, or InGaN. In other alternative embodiments, thin-film layer 101 may be made of a superconductor material such as yttrium barium copper oxide (YBCO) or magnesium diboride (MgB₂) for use in superconducting devices. The substrate is typically a non-single-crystal material such as glass, plastic, metal or ceramic. A template layer is typically a non-single-crystal material such as a silicon oxide SiO_x ($x \leq 2$), a silicon nitride SiN_x ($x \leq 1.33$), silicon oxy-nitride SiON, amorphous silicon (a-Si), or a similar material. In some embodiments, an electrically conductive contact layer, which in some variations is patterned, may be deposited on the substrate and beneath the semiconductor layer.

[0028] A laser beam is focused at the amorphous or microcrystalline layer to heat selected portions of the film at an initial focal point, at which a single-crystal seed spot 104 is to be formed. In a particular embodiment, the laser is configured to

heat the illuminated or heated region at focal point 104 of the amorphous semiconductor layer to a sufficiently high temperature that layer 101 undergoes crystal nucleation and growth in the heated region under laser illumination. In an alternative embodiment, a laser-treated region of a microcrystalline or polycrystalline semiconductor layer is heated by the laser to a temperature where previously existing grain boundaries vanish to allow re-nucleation and recrystallization.

[0029] All materials have a critical nucleation zone size for crystallization. The critical nucleation zone size is dependent on the material and temperature. For heated volumes below the critical nucleation zone size, the surface energy required at a boundary between a crystal nucleus and surrounding non-crystallized material is sufficiently large that crystallization is inhibited, and a crystal nucleus is thermodynamically unstable. For heated volumes above the critical nucleation zone size, the surface energy of boundary between crystal nucleus and surrounding non-crystallized material can no longer dominate the energy release from crystallizing material, such that a crystal nucleus becomes thermodynamically stable and, once a nucleus forms, the nucleus will grow since crystal growth further reduces the energy of the system. Typically, a nucleation zone size will range from one to one thousand nanometers in diameter depending on the particular thin-film material and the substrate.

[0030] A focused laser beam 106 or beams from the laser is initially aimed to heat 204, and crystallizes a single seed spot 104 (Fig. 2 and 3); the seed spot is sized comparable to the critical size of nucleation, i.e., within the same order of magnitude. In a particular embodiment, the seed spot size is not more than twice the critical size of nucleation. Because the seed spot is too small to support more than one nucleation site, under these conditions the seed spot nucleates as a single crystal seed.

[0031] For materials where the critical size of nucleation is below one hundred nanometers, a near-field optical focusing technique, such as metal-coated tapered optical fiber, can be applied to achieve a focal spot, and hence seed spot, size of less than one hundred nanometers diameter. For larger critical sizes of nucleation, and required laser spot sizes, the laser may be an infrared CO₂ laser. For materials with smaller critical sizes of nucleation the laser may have a shorter wavelength. The

laser providing beam 106 can be a continuous-wave laser or may be a pulsed laser with pulse duration between fifty femtoseconds and one hundred microseconds. The peak power density should be greater than ten watts per square centimeter.

[0032] After the nucleation of the single crystal seed spot 104, the laser is redirected (Fig. 3A and 4) as two beams 108, each heating a lateral crystallization zone 110 adjacent to the seed spot 104. The crystallization zones 110 are collinear with the seed spot 104, as the laser or lasers are further redirected to shift crystallization zone 110 laterally away from the seed spot 104 each of the crystallization zones leaves behind a single crystal half seed line 111A that is surrounded by untreated material 112, the half-seed lines 111A together with the seed spot 104 forming a single-crystal seed line 111. Since the crystallization zones 110 are kept at or below the critical size of nucleation, and the beam moves laterally away from the seed spot 104, crystallization in zones 110 extends 206 the single crystal seed spot 104 into a single-crystal seed line 111 having the same crystal orientation as the original seed spot.

[0033] In an alternative embodiment, a single laser beam heats a lateral crystallization zone adjacent to, and on a first side of, the seed spot 104. Heating from the beam forms a single crystallization zone, that is then drawn away from the seed spot leaving half a single-crystal seed line behind. The laser is then redirected to heat a second crystallization zone adjacent to, and located adjacent the seed spot opposite the first crystallization zone, and similarly drawn away from the seed spot leaving a second half single-crystal seed line. The two half-seed lines 111A are collinear with the seed spot 104, and, together with seed spot 104, form a full single crystal seed line 111 surrounded by untreated material 112.

[0034] In another alternative embodiment, the seed spot 104 is located at an edge of the amorphous or microcrystalline layer. A single laser beam heats a lateral crystallization zone adjacent to, and on a side of, the seed spot 104. Heating from the beam forms a single crystallization zone, that is then drawn away from the seed spot towards the opposite edge of the amorphous or microcrystalline layer, leaving behind a single-crystal seed line 111 surrounded by untreated material 112. The single-crystal seed line 111 has the same crystal orientation as, and includes, the original seed spot 104. In a particular embodiment, a laser beam is swept at uniform rate onto,

then across, the amorphous or microcrystalline layer, the seed spot 104 is formed as the beam sweeps onto the layer, the lateral crystallization zone as the beam shifts adjacent to the seed spot, and single-crystal seed line 111 forms and extends across the layer behind the beam.

[0035] In each embodiment, the laser sweep is adjusted (FIG. 4) to move the lateral crystallization zones 110 away from the single-crystal seed line zone 111. Thus, the single crystal seed line zone 111 is extended laterally. The sweep is continually adjusted with the lateral extension zones moving towards edges of the coated substrate until the lateral crystallization zones 110 pass outside the coated substrate. This step forms a single-crystal seed line 111 (Fig. 5) extending across the coated substrate.

[0036] Next, as illustrated in FIG.6 and FIG. 7, the laser beam is adjusted into a line focus that is used to heat 208 a linear heated crystallization zone having shape of a line 114 directly adjacent to and overlapping, but not melting, the seed line 111. In an alternative embodiment, the laser beam that heats linear crystallization zone 114 is provided by a second laser. In a particular embodiment, a cylinder lens is used to diverge the laser beam to heat this linear region.

[0037] In a manner similar to the lateral sweep of the heated crystallization zone, the heated linear crystallization zone 114 is swept perpendicular to, and away from, the single crystal seed line 111 across the untreated material 112 in a direction perpendicular to the seed line 111. Since the laser is directed such that further crystallization is seeded by single-crystal seed line 111, the single-crystal zone 116 now expands into a sheet or layer behind heated crystallization zone 114. This sweep is continued until the entire untreated amorphous or microcrystalline layer 112 has been consumed and single crystal zone 116 expands to cover the entire coated substrate. After the entire substrate passes through the laser line, or the laser line passes over the entire substrate, the crystallization is completed and the initial thin film is converted to a single-crystal thin film 116 (FIG. 7A).

[0038] In an embodiment the sweep of Fig. 7 is performed optically by moving laser beams; in an alternative embodiment the substrate is moved under a stationary laser and optical system at a rate of between one micron and ten millimeters

per second determined by available laser power, the particular thin-film material, width of the coated substrate, and similar factors.

[0039] After the entire substrate passes through the laser line, the crystallization is completed and the initial amorphous or microcrystalline thin film 101 is converted to a single-crystal thin film 116, as shown in Fig. 7A.

[0040] If the starting thin-film material 101 is microcrystalline instead of amorphous, large-crystal-grain semiconductor film can be achieved using the approach described above, although complete single-crystal growth may not be feasible since there are already many tiny crystalline grains in the material.

[0041] Once the thin-film material has been crystallized, or recrystallized if the starting thin-film is microcrystalline, a solar cell is fabricated 210 in the crystallized material using techniques known in the art. In embodiments, these techniques involve forming a junction by diffusing dopants into the crystallized material, growing an epitaxial layer of opposite polarity on top of the crystallized material, or depositing a heterojunction partner layer, as appropriate for the semiconductor material; in embodiments they further include adding a top contact conductor or metallization to provide electrical contact to a top of the junction.

[0042] In a particular embodiment, the method herein described is applied to crystallize a thin-film layer of amorphous silicon into single-crystal silicon.

[0043] The disclosed technology can also be applied to fabricated tandem solar cells, 300 as illustrated in Fig. 9. In one embodiment, amorphous silicon layers with two in-situ doped p-i-n junction structures is deposited on a transparent substrate 302.

[0044] The cell of Fig. 9 is constructed by depositing a layer or grid of low-resistance electrical contact 303 on the substrate 302, then depositing a P-type amorphous-silicon layer 304, an intrinsic (I) silicon absorber layer 306, and an N-type amorphous-silicon layer 308. In some embodiments, an ohmic-contact layer 309 may then be deposited. Another P-type amorphous-silicon layer 310, intrinsic silicon absorber layer 312, and N-type amorphous-silicon layer 314 are then deposited. The first-deposited P-I-N layers 304, 306, 308 form a first, bottom, junction 316, and the second-deposited P-I-N layers 310, 312, 314 form a second, top, junction 318, The two junction structures 316, 318, are vertically stacked. In an alternative

embodiment, the N-type and P-type layers here described are swapped, such that each cell has its N-type amorphous layer deposited before its P-type layer. The structure therefore has a layer of thin-film semiconductor material that is formed of N, P, and I sublayers.

[0045] We then choose a laser wavelength such that the beam's penetration depth is smaller than the total thickness of the amorphous silicon thin films and comparable to the total thickness of the top junction 318. Crystallization as above described is then performed. Since the heated crystallization zones 104, 110 and 114 only penetrate and heat the top junction 318 and heating is fast enough that heat fails to penetrate deeper into the films such that crystallization depth 319 includes only layers of the top junction, and the laser fails to heat the bottom junction sufficiently to cause crystallization in the lower junction 316, only the top layers and associated junction are converted into single crystal Si, while the bottom junction remains amorphous Si. The step of extending 208 the single-crystal seed line into a single-crystal sheet or layer therefore converts only some sublayers of the layer into single-crystal form. Following the crystallization, a back-contact metallization layer 320 is added to complete the device.

[0046] Since amorphous Si has a larger band gap than single-crystal Si, the structure constitutes a tandem solar cell. Sunlight 322 is illuminated from the backside of the transparent substrate in this case.

[0047] In another alternative embodiment of a tandem photovoltaic device 400, as illustrated in Fig. 10, a back-contact layer 404 is deposited on a substrate 402. The contact layers herein described are typically transparent, conductive, metal oxide layers, such as but not limited to indium-tin-oxide, zinc oxide, or tin oxide, where transparency is required, or metal layers where transparency is not required. Contact layers may also be heavily-doped layers of semiconductor material. A first semiconductor absorber layer 406 formed of a first semiconductor material is deposited on the back-contact layer, followed by a junction layer 408, or a heterojunction partner layer, as appropriate for solar cells fabricated from the first semiconductor material. The absorber 406 and junction layers 408 together form a first junction 412. In some embodiments, a contact layer 410, and/or a diffusion barrier layer, is then applied to ensure ohmic conduction between the first junction

layer 408 and a second absorber layer 414, formed of a second semiconductor material. A second junction layer 416, or a second heterojunction partner layer, as appropriate for solar cells fabricated from the second semiconductor material, is next deposited, the second absorber layer 414 and junction layer 416 form a second junction 418; since the semiconductor materials of the first 412 and second 418 junctions differ, these junctions have differing band gaps and spectral sensitivities.

[0048] An electrical conductor layer 420 is deposited over the second junction layer. In some embodiments a grid 422 of conductive metal is formed over the conductor layer 420. At least one of the conductor layers 404 and 420 should be transparent. A passivation or protection layer 424 may be added atop the device. The device 400 will function as a tandem photovoltaic device when exposed to light 426. When the band gaps of the absorber layers from bottom to top are arranged from small to large, the light 426 should be illuminated from the top. Conversely, when the band gaps of the absorber layers from bottom to top are arranged from large to small, the light 428 should be illuminated from the bottom, and the substrate 402 as well as the contact layer 404 should be transparent in this case. Variant embodiments may have additional layers, such as diffusion barrier layers, that are not shown herein. Further, variant embodiments not illustrated herein may have additional layers forming a third or more junction layers of a third or more semiconductor materials. It is anticipated that various embodiments may make use of two, or more, chemically-different semiconductor materials selected from the group consisting of Silicon, Germanium, Gallium Arsenide, Gallium Phosphide, Indium Gallium Phosphide, Cadmium Telluride, Copper Indium Gallium diSelenide, Cupric or Cuprous Oxide, Zinc Oxide, Zinc Phosphide, or Indium Gallium Nitride. The band gaps of the multiple semiconductor absorber layers in the stack should be arranged from large to small, either from top to bottom or bottom to top.

[0049] In an embodiment of the device 400, where the first semiconductor material requires higher temperatures or smaller spot sizes for crystallization than those required by the second semiconductor material, or where the second semiconductor material is unstable at temperatures required for crystallization of the first material, crystallization as above described with reference to Fig. 8 of the first semiconductor material is performed after deposition of first junction layer 408 and

prior to deposition of second absorber layer 414 in order to convert the first junction 412 into single crystal layers. In this embodiment, crystallization of the second semiconductor material may then be performed after deposition of the second junction layer 416 by repeating the process described with reference to Fig. 8 with a laser spot size chosen appropriate to the critical size of nucleation of the second junction layer in order to convert the second junction 418 into single crystal layers. In an alternative embodiment, before depositing top conductor layer 420, a third absorber layer (not shown) of a third semiconductor material, chemically different from both the first and second semiconductor materials, is deposited with appropriate contact, barrier, and junction layers, to form a third junction atop the second junction 418; the third absorber layer may be crystallized by again repeating the process described with reference to Fig. 8 with a laser spot size chosen appropriate to the critical size of nucleation of the third junction layer.

[0050] In an embodiment of the device 400 where both semiconductor materials can be crystalized at similar temperatures and crystallization-zone spot sizes, both materials are crystalized in a single pass of the crystallization process described with reference to Fig. 8 in order to convert the semiconductor absorber layers of both junctions of the entire stack 412 and 418 into single crystal layers.

[0051] In another embodiment, the single-crystal semiconductor layer 116 achieved is used as a template layer to grow tandem cells by epitaxy. In this case no single-crystal substrate is needed so that the fabrication cost is greatly reduced over devices based on Czochralski-process wafers. Furthermore, the material and composition of single-crystal thin film layer 116 can be selected to match the lattice constants of other desired semiconductor materials in the tandem cell structure to minimize defect density. Such materials or composition may or may not be available in the form of single-crystal wafers.

[0052] The herein described method of crystallizing materials as applied to semiconductor materials is useful for fabricating both single-junction and tandem, stacked-junction, solar cells as herein described. The method of crystallizing materials, as applied to semiconductor materials, is also applicable to producing single-crystal thin films for use in electronic applications where insulating, or transparent, non-single-crystal substrates are necessary or desirable. Such electronic

applications may include high-performance display devices or panels, where metal-gate or polysilicon-gate metal-oxide-semiconductor (MOS) transistors having single-crystal channel, source and drain produced in single-crystal thin films, the single-crystal thin films produced according to the herein described method, may prove advantageous over the conventional thin-film transistors currently used for pixel selection and on-panel decoding.

[0053] The herein described method of crystallizing materials is also expected to be useful for producing single-crystal thin films of materials such as MgB₂ and YBCO.

Combinations

[0054] It is expected that various combinations of the above recited elements may be used in one or more embodiments, as follows:

[0055] A method designated A for forming a single-crystal thin-film material layer of a first material includes: depositing a thin-film material layer on a surface selected from a substrate and a template layer on a substrate, the thin-film semiconductor layer having an initial microstructure selected from the group consisting of amorphous, nanocrystalline, microcrystalline, and polycrystalline; laser-heating to a crystallization temperature a seed spot of the thin-film material layer, the seed spot having size on the order of a critical size of nucleation of the thin-film material layer, and thereby crystalizing the seed spot; extending the seed spot into a single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the thin-film material layer; and extending the single crystal seed line across the thin-film material layer by laser-heating a crystallization zone adjacent to the seed line and drawing the crystallization zone across the thin-film semiconductor layer.

[0056] A method designated AB including the method designated A wherein the thin-film material layer comprises a material selected from the group consisting of Silicon, Germanium, Gallium Arsenide, Gallium Phosphide, Indium Gallium Phosphide, Cadmium Telluride, Copper Indium Gallium diSelenide, Cupric or Cuprous Oxide, Zinc Oxide, Zinc Phosphide, and Indium Gallium Nitride.

[0057] A method designated AC including the method designated AB wherein the thin-film material has amorphous initial microstructure.

[0058] A method designated AD including the method designated A, AB or AC wherein the thin-film material comprises primarily silicon.

[0059] A method designated AE including the method designated A, AB, AC or AD wherein the thin-film semiconductor material has amorphous initial microstructure.

[0060] A method designated AF including the method designated A, AB, AC, AD, or AE, wherein said surface is a substrate comprising a non-single-crystal material selected from the group consisting of glass, plastics, metal, or ceramics.

[0061] A method designated AG including the method designated A, AB, AC, AD, or AE,, wherein said surface comprises a template layer comprising a non-single-crystal material from the group consisting of a silicon oxide, silicon nitride, silicon oxynitride, or amorphous silicon.

[0062] A method designated AH including the method designated A, AB, AC, AD, AE, AF, or AG, wherein the seed spot has size between one and one thousand nanometers.

[0063] A method designated AK including the method designated AH, wherein the seed spot has size not greater than twice the critical size of nucleation.

[0064] A method designated AL including the method designated A, AB, AC, AD, AE, AF, or AG, further comprising depositing a second thin-film layer comprising a semiconductor second material chemically different from the first material.

[0065] A method designated AM including the method designated AL wherein the step of laser heating is performed after the step of depositing the second semiconductor material, and both the first and second thin-film layers are crystalized during the step of laser heating.

[0066] A method designated AN including the method designated AL wherein the step of laser heating is performed prior to depositing the second thin-film layer.

[0067] A method designated AP including the method designated AN and further including: a second laser heating to form a second seed spot; extending the

second seed spot into a second single-crystal seed line in the second thin-film semiconductor layer by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the second thin-film layer; and extending the single crystal seed line across the second thin-film layer by laser-heating a crystallization zone adjacent to the seed line and drawing the crystallization zone across the second thin-film layer.

[0068] A method designated AQ including the method designated AL further including depositing a third thin-film layer of a semiconductor third material chemically different from the first and second materials.

[0069] A method designated AR including the method designated AQ further including: a third laser heating to form a third seed spot; extending the third seed spot into a third single-crystal seed line in the third thin-film layer by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the third thin-film layer; and extending the single crystal seed line across the third thin-film semiconductor layer by laser-heating a crystallization zone adjacent to the seed line and drawing the crystallization zone across the third thin-film layer.

[0070] A method designated AS including the method designated A, AB, AC, AD, AE, AF, AG, AH, AK, AL, AM, AN, AP, AQ, or AR wherein the thin-film semiconductor layer has at least a first and a second sublayer, and wherein the step of extending the seed line crystallizes at least the first, but not the second, sublayer.

[0071] A method of fabricating a photovoltaic device designated B including: depositing an electrical contact layer on a surface; depositing a first thin-film semiconductor layer, the first thin-film semiconductor layer having an initial microstructure selected from the group consisting of amorphous, nanocrystalline, and microcrystalline; laser-heating to a crystallization temperature a seed spot of the first thin-film semiconductor layer, the seed spot having size on the order of a critical size of nucleation of the first thin-film semiconductor layer, and thereby crystallizing the first seed spot into a single-crystal seed; extending the seed spot into a first single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the first thin-film semiconductor layer; extending the first single crystal seed line across the thin-film semiconductor

layer by laser-heating a crystallization zone adjacent to the first seed line and drawing the crystallization zone across the first thin-film semiconductor layer; constructing a first junction using the first thin-film semiconductor layer; and applying contact metallization.

[0072] A method designated BA including the method designated B and further including: depositing a second thin-film semiconductor layer, the second thin-film semiconductor layer having an initial microstructure selected from the group consisting of amorphous, nanocrystalline, and microcrystalline; laser-heating to a crystallization temperature a seed spot of the second thin-film semiconductor layer, the seed spot having size on the order of a critical size of nucleation of the second thin-film semiconductor layer, and thereby crystalizing the seed spot into a single-crystal seed; extending the seed spot into a second single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the second thin-film semiconductor layer; extending the second single crystal seed line across the thin-film semiconductor layer by laser-heating a crystallization zone adjacent to the second seed line and drawing the crystallization zone across the second thin-film semiconductor layer; constructing a second junction using the second thin-film semiconductor layer.

[0073] A method designated C of fabricating a tandem photovoltaic device including steps: depositing an electrical contact layer on a transparent substrate; depositing a thin-film semiconductor layer, the thin-film semiconductor layer having an initial microstructure selected from the group consisting of amorphous, nanocrystalline, and microcrystalline, the thin-film semiconductor layer comprising at least a first junction sublayer and a second junction sublayer, each junction sublayer further comprising a P-type, an Intrinsic, and an N-type sub-sublayer.

[0074] While the invention has been particularly shown and described with reference to particular embodiments thereof, it will be understood by those skilled in the art that various other changes in the form and details may be made without departing from the spirit and scope of the invention. It is to be understood that various changes may be made in adapting the invention to different embodiments without departing from the broader inventive concepts disclosed herein and comprehended by the claims that follow.

CLAIMS

What is claimed is:

1. A method for forming a single-crystal thin-film material layer of a first material comprising:
 - depositing a thin-film material layer on a surface selected from a substrate and a template layer on a substrate, the thin-film semiconductor layer having an initial microstructure selected from the group consisting of amorphous, nanocrystalline, microcrystalline, and polycrystalline;
 - laser-heating to a crystallization temperature a seed spot of the thin-film material layer, the seed spot having size on the order of a critical size of nucleation of the thin-film material layer, and thereby crystallizing the seed spot;
 - extending the seed spot into a single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the thin-film material layer; and
 - extending the single crystal seed line across the thin-film material layer by laser-heating a crystallization zone adjacent to the seed line and drawing the crystallization zone across the thin-film semiconductor layer.
2. The method of claim 1 wherein the thin-film material layer comprises a material selected from the group consisting of Silicon, Germanium, Gallium Arsenide, Gallium Phosphide, Indium Gallium Phosphide, Cadmium Telluride, Copper Indium Gallium diSelenide, Cupric or Cuprous Oxide, Zinc Oxide, Zinc Phosphide, and Indium Gallium Nitride.
3. The method of claim 2 wherein the thin-film material has amorphous initial microstructure.
4. The method of claim 2 wherein the thin-film material comprises primarily silicon.

5. The method of claim 4 wherein the thin-film semiconductor material has amorphous initial microstructure.
6. The method of claim 1, wherein said surface is a substrate comprising a non-single-crystal material selected from the group consisting of glass, plastics, metal, or ceramics.
7. The method of claim 1, wherein said surface comprises a template layer comprising a non-single-crystal material from the group consisting of a silicon oxide, silicon nitride, silicon oxynitride, or amorphous silicon.
8. The method of claim 1 wherein the seed spot has size between one and one thousand nanometers.
9. The method of claim 1 wherein the seed spot has size not greater than twice the critical size of nucleation.
10. The method of claim 1, 2, 3, 4, 5, 6, 7, 8, or 9 further comprising depositing a second thin-film layer comprising a semiconductor second material chemically different from the first material.
11. The method of claim 10 wherein the step of laser heating is performed after the step of depositing the second semiconductor material, and both the first and second thin-film layers are crystalized during the step of laser heating.
12. The method of claim 10 wherein the step of laser heating is performed prior to depositing the second thin-film layer.
13. The method of claim 12 further comprising:
 - a second laser heating to form a second seed spot;
 - extending the second seed spot into a second single-crystal seed line in the second thin-film semiconductor layer by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the second thin-film layer; and

extending the single crystal seed line across the second thin-film layer by
laser-heating a crystallization zone adjacent to the seed line and
drawing the crystallization zone across the second thin-film layer.

14. The method of claim 10 further comprising depositing a third thin-film layer of a semiconductor third material chemically different from the first and second materials.

15. The method of claim 14 further comprising:
a third laser heating to form a third seed spot;
extending the third seed spot into a third single-crystal seed line in the third thin-film layer by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the third thin-film layer; and
extending the single crystal seed line across the third thin-film semiconductor layer by laser-heating a crystallization zone adjacent to the seed line and drawing the crystallization zone across the third thin-film layer.

16. The method of claim 1, 2, 3, 4, 5, 6, 7, 8, or 9 wherein the thin-film semiconductor layer comprises at least a first and a second sublayer, and wherein the step of extending the seed line crystallizes at least the first, but not the second, sublayer.

17. A method of fabricating a photovoltaic device comprising:
depositing an electrical contact layer on a surface;
depositing a first thin-film semiconductor layer, the first thin-film semiconductor layer having an initial microstructure selected from the group consisting of amorphous, nanocrystalline, and microcrystalline;
laser-heating to a crystallization temperature a seed spot of the first thin-film semiconductor layer, the seed spot having size on the order of a critical size of nucleation of the first thin-film semiconductor layer, and
thereby crystallizing the first seed spot into a single-crystal seed;

extending the seed spot into a first single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the first thin-film semiconductor layer;
extending the first single crystal seed line across the thin-film semiconductor layer by laser-heating a crystallization zone adjacent to the first seed line and drawing the crystallization zone across the first thin-film semiconductor layer;
constructing a first junction using the first thin-film semiconductor layer; and
applying contact metallization.

18. The method of claim 17 further comprising:
depositing a second thin-film semiconductor layer, the second thin-film semiconductor layer having an initial microstructure selected from the group consisting of amorphous, nanocrystalline, and microcrystalline;
laser-heating to a crystallization temperature a seed spot of the second thin-film semiconductor layer, the seed spot having size on the order of a critical size of nucleation of the second thin-film semiconductor layer, and thereby crystalizing the seed spot into a single-crystal seed;
extending the seed spot into a second single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the second thin-film semiconductor layer;
extending the second single crystal seed line across the thin-film semiconductor layer by laser-heating a crystallization zone adjacent to the second seed line and drawing the crystallization zone across the second thin-film semiconductor layer;
constructing a second junction using the second thin-film semiconductor layer.

19. A method of fabricating a tandem photovoltaic device comprising:
depositing an electrical contact layer on a transparent substrate;
depositing a thin-film semiconductor layer, the thin-film semiconductor layer having an initial microstructure selected from the group consisting of amorphous, nanocrystalline, and microcrystalline, the thin-film

semiconductor layer comprising at least a first junction sublayer and a second junction sublayer, each junction sublayer further comprising a P-type, an intrinsic, and an N-type sub-sublayer.

laser-heating to a crystallization temperature a seed spot of the thin-film semiconductor layer, the seed spot having size on the order of a critical size of nucleation of the thin-film semiconductor layer, and thereby crystallizing the seed spot into a single-crystal seed;

extending the single-crystal seed spot into a single-crystal seed line by laser-heating at least one crystallization zone adjacent to the seed spot and drawing the crystallization zone across the thin-film semiconductor layer, the crystallization zone crystallizing at least one sub-sublayer of the second junction sublayer and without crystallizing at least the intrinsic sublayer of the first junction sublayer; and

applying a contact layer.

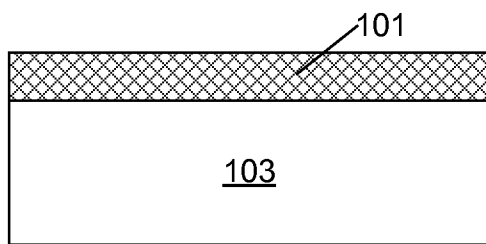


FIG. 1

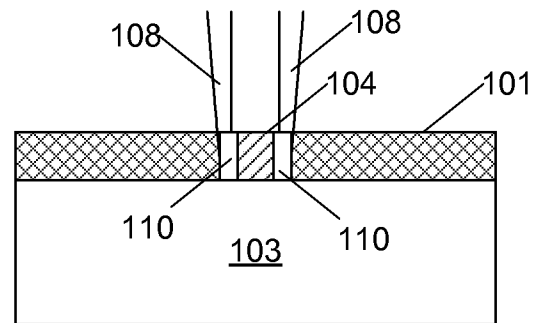


FIG. 3A

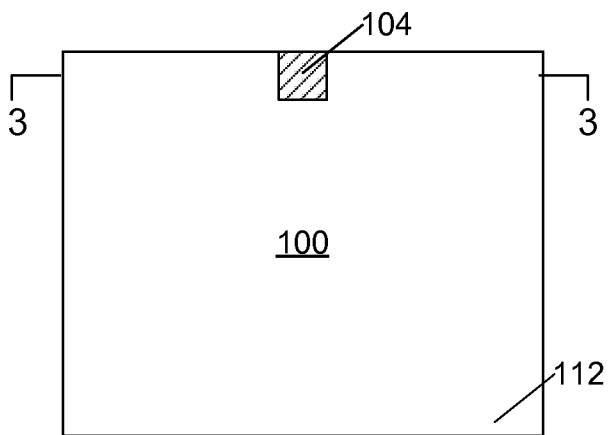


FIG. 2

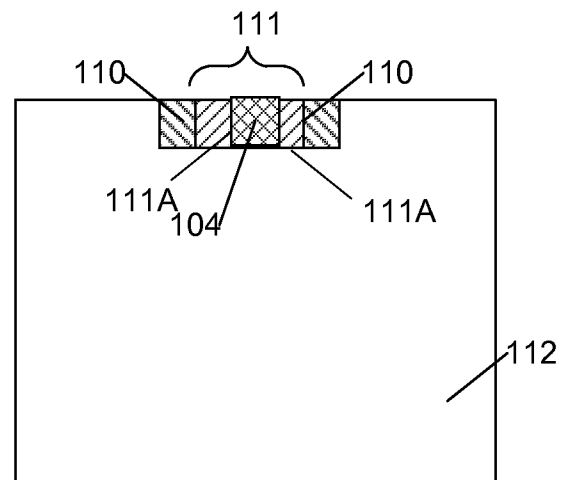


FIG. 4

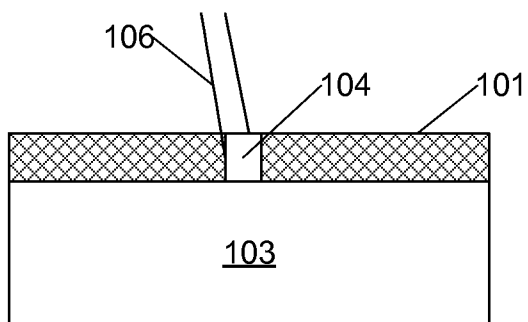


FIG. 3

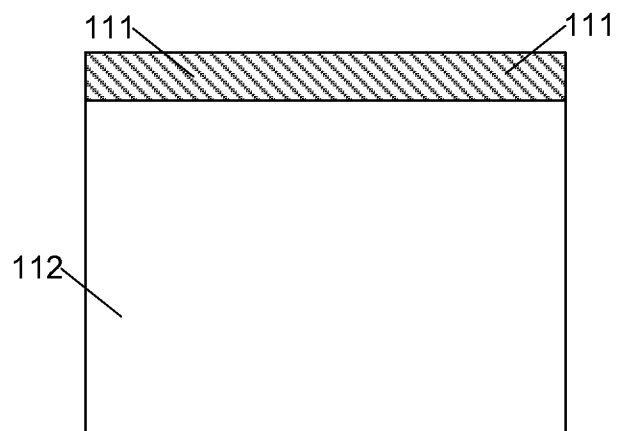
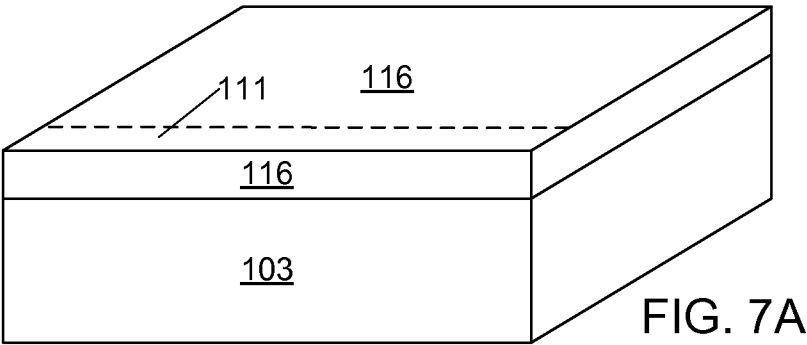
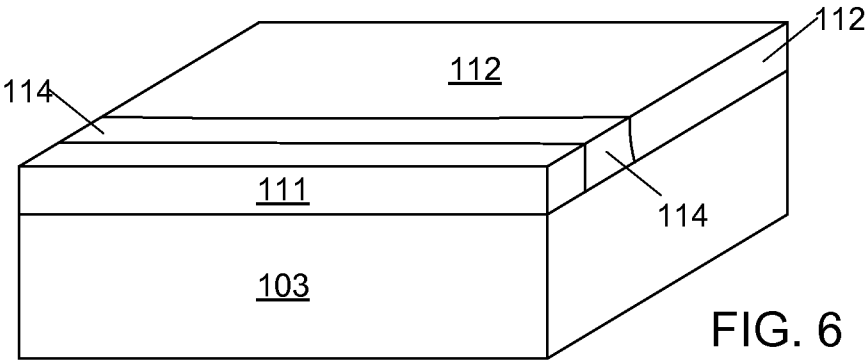


FIG. 5



3/4

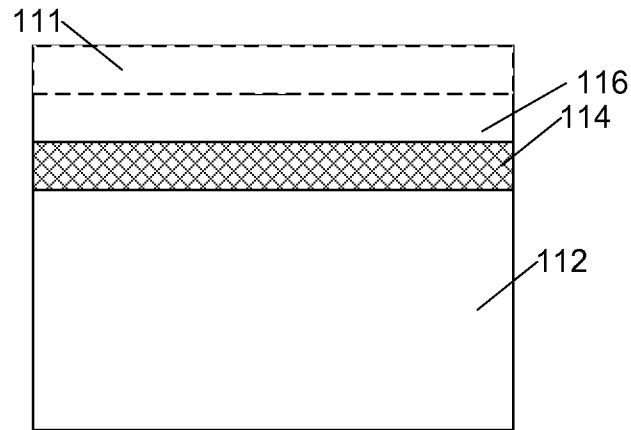


FIG. 7

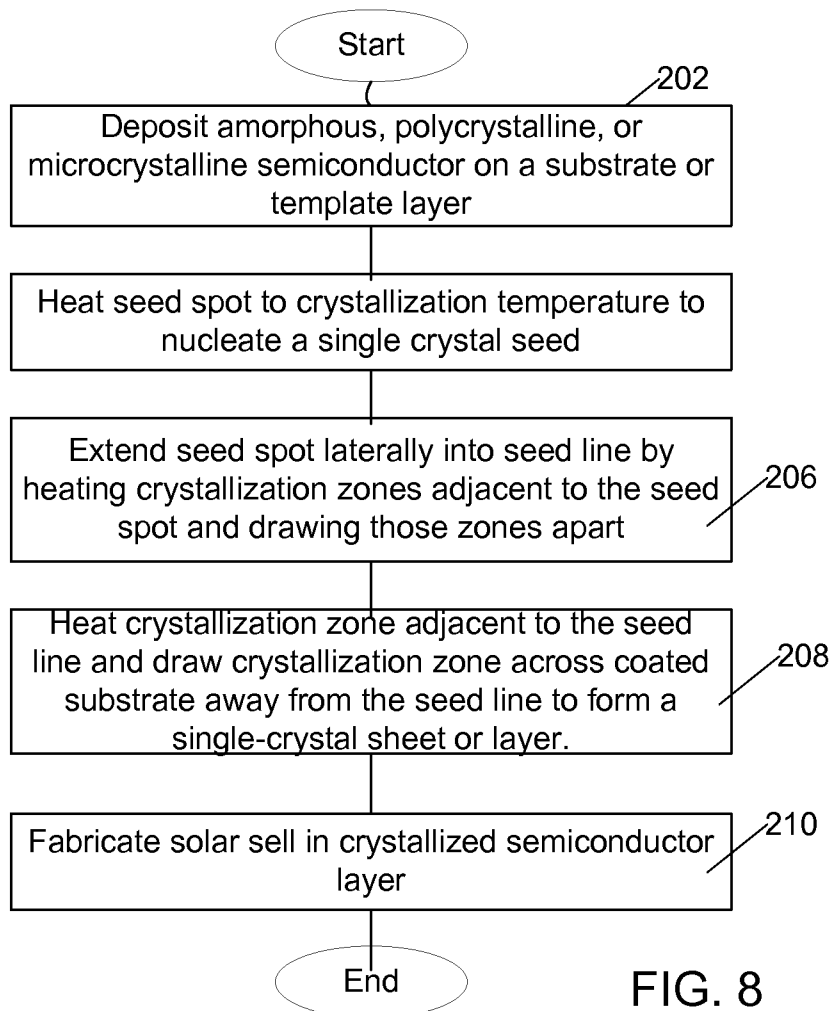
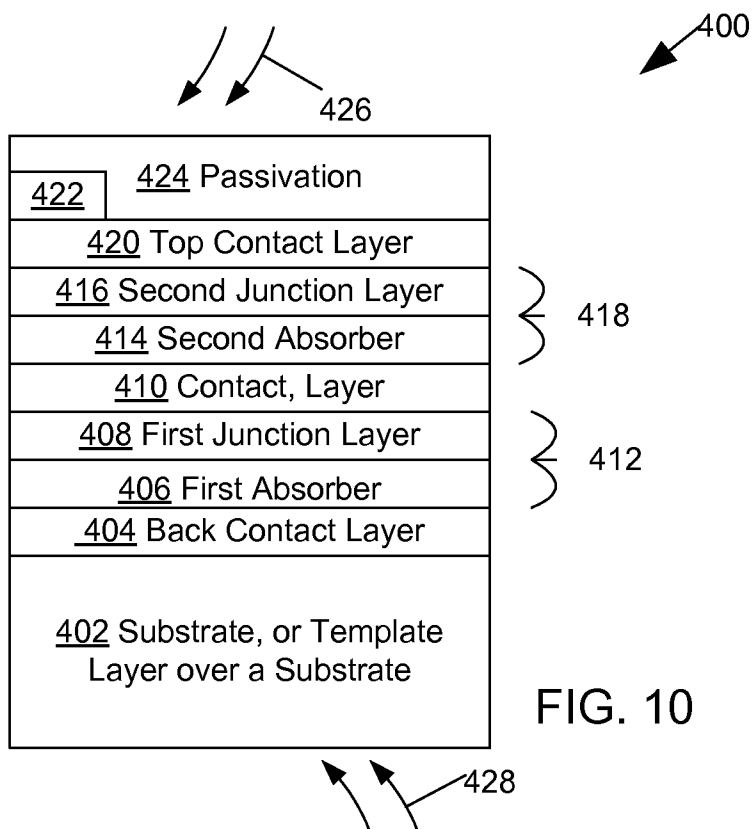
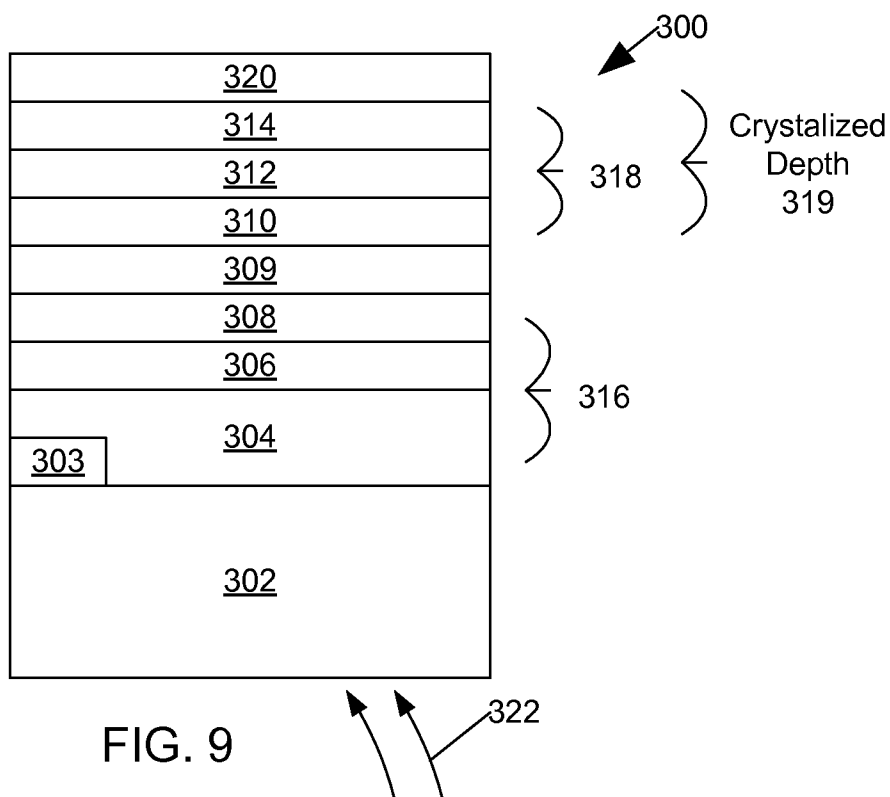


FIG. 8

4/4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/021035**A. CLASSIFICATION OF SUBJECT MATTER*****H01L 31/042(2006.01)i, H01L 31/18(2006.01)i, H01L 21/324(2006.01)i***

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01L 31/042; H01L 21/20; C30B 29/06; C30B 7/00; H01L 31/04; C30B 13/06; C30B 11/02

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: single crystal thin-film material layer, seed spot, crystallization zone

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 99-13136 A1 (SINGLE CRYSTAL SEMICONDUCTOR CORP.) 18 March 1999 See page 4, lines 31-36; page 7, line 5 - page 8, line 13; and figures 3, 4.	1-19
Y	JP 07-240531 A (KURISUTARU DEVICE KK.) 12 September 1995 See paragraphs [0146]-[0208]; and figures 1-22.	1-19
A	US 5893948 A (NORBERT H. NICKEL et al.) 13 April 1999 See column 3, line 38 - column 5, line 59; and figures 3A-3E.	1-19
A	JP 2004-273886 A (HITACHI CABLE LTD.) 30 September 2004 See paragraphs [0044]-[0049]; and figure 1.	1-19
A	JP 2004-091293 A (KYOCERA CORP.) 25 March 2004 See paragraphs [0020]-[0032]; and figure 1.	1-19

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

29 April 2013 (29.04.2013)

Date of mailing of the international search report

29 April 2013 (29.04.2013)

Name and mailing address of the ISA/KR

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

Facsimile No. 82-42-472-7140

Authorized officer

KIM, Do Weon

Telephone No. 82-42-481-5560



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/021035

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 99-13136 A1	18.03.1999	AU 9040198 A US 05800611 A WO 99-13136 A1	29.03.1999 01.09.1998 18.03.1999
JP 07-240531 A	12.09.1995	EP 0659910 A2 EP 0659910 A3 JP 03247262 B2 JP 03272887 B2 JP 07-193152 A JP 07-193254 A JP 07-239482 A JP 07-241088 A JP 07-273232 A JP 2003-177414 A JP 2003-177420 A JP 2003-209055 A KR 10-0262720 B1 US 05738731 A US 06025252 A US 06106734 A US 06137120 A US 6177706 B1 US 6225668 B1 US 6677214 B1	28.06.1995 21.10.1998 02.11.2001 25.01.2002 28.07.1995 28.07.1995 12.09.1995 12.09.1995 20.10.1995 27.06.2003 27.06.2003 25.07.2003 01.11.2000 14.04.1998 15.02.2000 22.08.2000 24.10.2000 23.01.2001 01.05.2001 13.01.2004
US 5893948 A	13.04.1999	JP 04237278 B2 JP 10-050608 A	11.03.2009 20.02.1998
JP 2004-273886 A	30.09.2004	None	
JP 2004-091293 A	25.03.2004	None	