

CHALCOGENIDE-BASED MATERIALS AND METHODS OF MAKING SUCH MATERIALS UNDER VACUUM USING POST-CHALCOGENIZATION TECHNIQUES

PRIORITY

The present nonprovisional patent application claims priority under 35 U.S.C. §119(e) from United States Provisional patent application having serial number 61/346,515, filed on May 20, 2010, by Nichols et al. and titled CHALCOGENIDE-BASED MATERIALS AND METHODS OF MAKING SUCH MATERIALS UNDER VACUUM USING POST-CHALCOGENIZATION TECHNIQUES, wherein the entirety of said provisional patent application is incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates to methods for making chalcogenide-based photoabsorbing materials as well as to photovoltaic devices that incorporate these materials. More specifically, the present invention relates to methods for making chalcogenide-based photoabsorbing materials, desirably in the form of thin films as well as to photovoltaic devices that incorporate these materials, in which a precursor film is prepared and then converted to the desired photoabsorbing composition via a chalcogenization treatment.

BACKGROUND OF THE INVENTION

Both n-type chalcogenide materials and/or p-type chalcogenide materials have photovoltaic functionality (also referred to herein photoabsorbing functionality). These materials absorb incident light and generate an electric output when incorporated into a photovoltaic device. Consequently, these chalcogenide-based photoabsorbing materials have been used as the photovoltaic absorber region in functioning photovoltaic devices. Illustrative p-type chalcogenide materials often include selenides (S), sulfides (also referred to as S; in some embodiments, SS indicates that sulfur is being used in combination with selenium), and/or tellurides (T) of at least one or more of copper (C), indium (I), gallium (G), and/or aluminum (A). Specific chalcogenide compositions may be referred to by acronyms such as CIS, CISS, CIGS, CIGST, CIGSAT, and/or CIGSS compositions, or the like, to represent the constituents of the composition.

Photoabsorbers based upon chalcogenide compositions offer several advantages. As one advantage, these compositions tend to have a very high cross-section for absorbing incident light. This means that a very high percentage of incident light can be captured by chalcogenide-based absorber layers that are very thin. For example, in many devices,

chalcogenide-based absorber layers have a thickness in the range of from about 1 μm to about 2 μm . These thin layers allow devices incorporating these layers to be flexible. This is in contrast to crystalline silicon-based absorbers. Crystalline silicon-based absorbers have a lower cross-section for light capture and generally must be much thicker to capture the same amount of incident light. Crystalline silicon-based absorbers tend to be rigid, not flexible.

Making photoabsorbing chalcogenide compositions with industrially scalable processes is quite challenging. Industry has invested and continues to invest considerable resources in developing this technology. According to one proposed manufacturing technique, evaporative techniques are used to deposit the film constituents at a high substrate temperature such that the film reacts and crystallizes fully during growth. According to an alternative hybrid method the films are formed by sputtering from one or more metal targets in the presence of selenium and/or sulfur containing gas or vapor from an evaporated source. Unfortunately, these conventional evaporation approaches are not easily scalable for industrial applications. Also, using only a gas as a chalcogen source during sputtering typically requires that enough gas be used to supply the desired chalcogen content in the precursor film plus an overpressure of chalcogen. Using so much chalcogen-containing gas tends to cause equipment degradation and chalcogen (e.g. Se) buildup, target poisoning, instabilities in process control (resulting in composition and rate hysteresis), the loss of In from the deposited film due to volatile indium selenide compounds, lowered overall deposition rates, and the damage of targets due to electrical arcing.

An alternative manufacturing approach involves initially forming a precursor film of the desired metal constituents. This film may include one or more layers. Chalcogen(s) are incorporated into the precursor at a later processing stage under conditions effective to incorporate chalcogen into the film and convert it to the desired tetragonal, chalcopyrite phase. Due to the incorporation of chalcogen into the film after precursor formation, this approach may be referred to as a "post-chalcogenization" approach. This approach appears to be easier to integrate into industrial scale processes. Yet, serious challenges remain.

As one challenge, many known approaches tend to practice post-chalcogenization within relatively high pressure regimes, such as on the order of a few torr to atmospheric pressure. Even in these higher pressure regimes, retention of In and Se during post-chalcogenization is a problem widely recognized in the industry. It has been challenging to carry out the post-chalcogenizing treatment without undue loss of one or both of these materials.

It is believed that one loss mechanism occurs when In and/or Se react to form volatile species that are lost to evaporation. The formation of volatile species is consistent with the observation that retention problems tend to become more severe at lower pressures. Frustratingly, the post-chalcogenization techniques practiced with reasonable success at higher pressures often are not directly translatable to use at lower pressures. For instance, undue In loss may still result when practicing a process strategy at a lower pressure even though that same technique provides acceptable In retention at a pressure in the range from about 10 torr to 760 torr.

SUMMARY OF THE INVENTION

The present invention provides strategies for making high quality chalcogenide-based, photoabsorbing compositions from sputtered precursor film(s). The precursors are converted into the chalcogenide photoabsorbing material via a chalcogenizing treatment (also referred to as "post-chalcogenization," including, e.g., "post-selenization" when Se is used and/or "post-sulfurization" when S is used) using techniques that allow the post-chalcogenizing treatment to occur under atypically and surprisingly low pressure conditions without significant indium loss. Consequently, the strategies of the invention are readily incorporated into batch processes or continuous processes such as roll-to-roll process occurring under vacuum. The present invention is useful at lab, pilot plant, and industrial scales.

In one aspect, the present invention provides a method of making a chalcogen-containing photoabsorbing composition, comprising the steps of:

- a) forming a workpiece comprising a precursor of the chalcogen-containing photoabsorber;
- b) forming a cap on the precursor, said cap comprising at least one chalcogen;
- c) heating the capped workpiece to cause chalcogenization at a pressure of below about 300 millitorr (mT).

In a preferred aspect of the invention, heating is carried out in the presence of at least one gas or vapor that comprises a chalcogen. Preferably, the gas or vapor comprises H_2S or H_2Se . In still another preferred aspect of the invention, heating is carried out in an inert gas. In yet another preferred aspect of the invention, a solid cap incorporates a chalcogen in elemental form. In yet another preferred aspect of the invention, a process according to the invention occurs in a continuous and/or semicontinuous roll-to-roll manufacturing process. Such preferred aspects may be practiced singly, or two or more of these may be practiced in combination.

BRIEF DESCRIPTION OF THE DRAWINGS

The above mentioned and other advantages of the present invention, and the manner of attaining them, will become more apparent and the invention itself will be better understood by reference to the following description of the embodiments of the invention taken in conjunction with the accompanying drawings, wherein:

Fig. 1 is a schematic diagram of an illustrative photovoltaic device that incorporates principles of the present invention;

Fig. 2 is a schematic diagram showing an exemplary structure for a substrate that may be used in the device of Fig. 1; and

Fig. 3 is a schematic diagram illustrating how the principles of the present invention may be used to fabricate a chalcogen-containing photoabsorbing layer useful in the device of Fig. 1.

DETAILED DESCRIPTION OF PRESENTLY PREFERRED EMBODIMENTS

The embodiments of the present invention described below are not intended to be exhaustive or to limit the invention to the precise forms disclosed in the following detailed description. Rather the embodiments are chosen and described so that others skilled in the art may appreciate and understand the principles and practices of the present invention. All patents, pending patent applications, published patent applications, and technical articles cited herein are incorporated herein by reference in their respective entireties for all purposes.

Fig. 1 schematically shows an illustrative embodiment of a photovoltaic device 10 that is prepared according to principles of the present invention. Device 10 desirably is flexible to allow device 10 to be mounted to surfaces incorporating some curvature. In preferred embodiments, device 10 is sufficiently flexible to be wrapped around a mandrel having a diameter of 50 cm, preferably about 40 cm, more preferably about 25 cm without cracking at a temperature of 25°C. Device 10 includes a light incident face 12 that receives light rays 16 and a backside face 14.

Device 10 includes a chalcogenide-containing photovoltaic absorber region 20 formed on an underlying substrate 18. Substrate 18 generally refers to the body on which the CIGS precursor film is formed and often incorporates multiple layers. One illustrative embodiment of a multilayer structure for substrate 18 is shown in Fig. 2. In the illustrative embodiment of Fig. 2, substrate 18 generally includes support 22, barrier region 23, and backside electrical contact region 24. Support 22 may be rigid or flexible, but desirably is

flexible in those embodiments in which the photovoltaic device may be used in combination with non-flat surfaces.

Support 22 may be formed from a wide range of materials. These include glass, quartz, other ceramic materials, polymers, metals, metal alloys, intermetallic compositions, woven or non-woven fabrics, combinations of these, and the like. Stainless steel is preferred. The support 22 desirably is cleaned prior to use to remove contaminants, such as organic contaminants. A wide variety of cleaning techniques may be used. As one example, plasma cleaning, such as by using RF plasma, would be suitable to remove organic contaminants from metal-containing supports. Other examples of useful cleaning techniques include ion etching, wet chemical bathing, and the like.

The barrier region 23 helps to isolate the photovoltaic absorber region 20 from the support 22 to prevent contamination. For instance, barrier region 23 can help to block the migration of Fe and other constituents from a stainless steel support 22 into the absorber region 20. The barrier region 23 also can protect the support 22 against Se migration if Se is used in the formation of the photovoltaic absorber region 20. Desirably, the barrier region 23 also helps to promote adhesion between the support 22 and overlying layers of device 10. Barrier region 23 can be formed from one or more of a wide range of materials. Exemplary materials include Nb, Cr, and Al_2O_3 , combinations of these, and the like. A film comprising Nb desirably has a thickness of at least about 30 nm, preferably at least about 50 nm, and more preferably at least about 100 nm. The thickness of such a film desirably is less than about 1000 nm, preferably less than about 400 nm and more preferably less than about 300 nm. In one embodiment, a Nb barrier having a thickness of about 150 nm would be suitable.

The backside electrical contact region 24 provides a convenient way to electrically couple the device 10 to external circuitry (not shown). The backside electrical contact region 24 also helps to isolate the photovoltaic absorber region 20 from the support 22 to minimize cross-contamination. As is the case with any of the regions of device 10, region 24 may be formed from a single layer or multiple layer using a wide range of electrically conductive materials, including one or more of Cu, Mo, Ag, Al, Cr, Ni, Ti, Ta, Nb, W combinations of these, and the like. Conductive compositions incorporating Mo may be used in an illustrative embodiment.

Region 24 optionally may incorporate one or more agents such as Na, Li, H, combinations of these, and the like. Na, for instance, is believed to favorably impact the growth of crystalline grains in the formation of the photovoltaic absorber region 20. It also is believed that the Na acts as a Se flux and/or mobilizing agent to facilitate the formation of

high quality chalcogen-containing photoabsorber materials. Na might also contribute favorably to the electronic performance of the chalcogen-containing photoabsorbing materials.

Materials such as Na, Li, and/or the like may be incorporated into region 24 in a variety of ways. According to one approach, a separate layer incorporating NaF, Na-doped metals, or the like may be incorporated into region 24. This layer may exist on the top of region 24, be buried at any other location in region 24, or mixed evenly within the layer. According to another approach, a Na-containing target may be co-sputtered or otherwise concurrently supplied with one or more electrically conductive materials to incorporate Na into at least a portion of the resultant sputtered region 24. For instance, a target containing 97 atomic percent Mo and 3 atomic percent Na can be sputtered to form a suitable film having a thickness of at least about 30 nm, preferably at least about 50 nm. Such a film desirably has a thickness of less than about 2000 nm, preferably less than about 500 nm. In one embodiment, such a target is sputtered to provide a film that is about 350 nm thick.

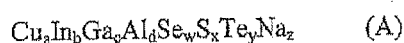
Referring again mainly to Fig. 1, chalcogenide-containing photovoltaic absorber region 20 absorbs light energy embodied in the light rays 16 and then photovoltaically converts this light energy into electric energy. Region 20 can be a single integral layer as illustrated or can be formed from one or more layers.

The chalcogenide absorber region 20 preferably incorporates at least one IB-IIIB-chalcogenide, such as IB-IIIB-selenides, IB-IIIB-sulfides, and/or IB-IIIB-selenides-sulfides that include at least one of copper, indium, and/or gallium. In many embodiments, these materials are present in polycrystalline form. Some embodiments include sulfides or selenides of copper and indium. Additional embodiments include selenides or sulfides of copper, indium, and gallium. Specific examples include but are not limited to copper indium selenides, copper indium gallium selenides, copper gallium selenides, copper indium sulfides, copper indium gallium sulfides, copper gallium sulfides, copper indium sulfide selenides, copper gallium sulfide selenides, and copper indium gallium sulfide selenides. In some embodiments, such chalcogenide materials optionally may include aluminum, tellurium, and the like. Aluminum could be used, for instance, instead of or in addition to gallium. Such chalcogenide materials also may be doped with other materials, such as Na, Li, H or the like, to enhance performance. In many embodiments, CIGS materials have p-type characteristics.

Oxygen (O) is technically a chalcogen according to its placement in the periodic table of the elements. However, oxygen is deemed not to be a chalcogen for purposes of the present invention inasmuch as oxygen does not contribute to photoabsorbing functionality to

the extent of the other chalcogens such as S and/or Se. Even though oxygen does not promote photoabsorbing functionality to the same degree and/or in the same manner as Se or S, oxygen may still be incorporated into chalcogenide photoabsorbing materials purposefully for other reasons such as to contribute to electronic properties, as an artifact of manufacture, and/or the like. Indeed, many chalcogen materials incorporate at least some oxygen, e.g., from 0 atomic percent to about 5 atomic percent based on the total composition of the region 20.

One preferred class of chalcogenide photoabsorbing materials may be represented by the formula



wherein, if "a" is defined as 1, then:

"(b+c+d)/a" = 1 to 2.5, preferably 1.05 to 1.65

"b" is 0 to 2, preferably 0.8 to 1.3

"c" is 0 to 0.5, preferably 0.05 to 0.35

d is 0 to 0.5, preferably 0.05 to 0.35, preferably d = 0

"(w+x+y)" is 1 to 3, preferably 2 to 2.8 (note, (w+x+y) < 2 for substoichiometric precursor films)

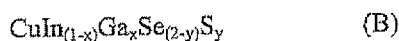
"w" is 0 or more, preferably at least 1 and more preferably at least 2 to 3

"x" is 0 to 3, preferably 0 to 0.5

"y" is 0 to 3, preferably 0 to 0.5

"z" is 0 to 0.5, preferably 0.005 to 0.02

The copper indium selenides/sulfides and copper indium gallium selenides/sulfides are preferred. Illustrative examples of such photoelectronically active chalcogenide materials may be represented by the formula



where x is 0 to 1 and y is 0 to 2. As measured and processed, such films usually include additional In, Ga, Se, and/or S.

Advantageously, the chalcogen-containing, photoabsorbing materials exhibit excellent cross-sections for light absorption that allow region 20 to be very thin and flexible. In illustrative embodiments, a typical absorber region 20 may have a thickness of at least about 1 μm , preferably at least about 1.5 μm . Region 20 desirably has a thickness of less than about 5 μm , preferably less than about 3 μm .

The principles of the present invention are used to form high quality, chalcogenide-based photovoltaic materials for use in region 20. These principles allow these materials to

be formed at low pressure in a manner that is compatible with continuous roll to roll manufacturing strategies that occur under vacuum. The methodologies of the invention include at least three main stages that can be practiced sequentially or at least partially co-currently with one or more of the other stages. These stages include forming a precursor of the desired chalcogenide photoabsorbing composition, forming a chalcogen-containing cap on the precursor, and then converting the capped precursor into the desired photoabsorbing material.

A preferred methodology incorporating at least these three stages is schematically illustrated in Fig. 3. Referring now to Fig. 3, an initial stage 100 involves preparing a precursor film 112. In many embodiments, this is accomplished by using one or more targets to sputter the constituents onto substrate 18 to form precursor film 112. Sputtering may occur in one step or in a sequence of two or more steps. If multiple sputtering steps are used, these may occur sequentially, concurrently, or in overlapping fashion. The resultant precursor film structure may include one or more layers. If the precursor film 112 has multiple layers, the interfaces between layers may be distinct or can be graded transitions. The constituents of precursor film 112 may be incorporated into the same and/or different layers.

For purposes of illustration, a single target 110 is used in stage 100 to form a precursor film 112 with a single layer structure. Generally, the precursor film includes the desired metal constituents and optionally at least a portion of the desired chalcogen content. Consequently, target 110 would have a composition that is effective to deposit at least the metal constituents of the desired region 20 in the desired proportions. For instance, if the resultant region 20 (Fig. 1) is to include Cu, In, and Ga as metal constituents, target 110 of this illustrative embodiment generally would include copper, indium, and gallium in proportions effective to form precursor film 112 including these elements. One such suitable target 110 may include about 35 to about 50 atomic percent Cu, about 50 to about 65 atomic percent In, and about 0 to about 30 atomic percent Ga. Other targets having other proportions of the constituents may also be used.

A specific embodiment of an exemplary target of this type includes 45 atomic percent Cu, 42 atomic percent In, and 13 atomic percent Ga. In one exemplary mode of practice suitable for incorporation in a roll to roll manufacturing strategy that occurs in its substantial entirety under vacuum, such a target can be used to form a precursor film 112 including Cu, In, and Ga having a thickness of at least about 0.75 μm , preferably at least about 0.8 μm . Such a film desirably has a thickness of less than about 2 μm , preferably less than about 1 μm . Such a film 112 in many embodiments may have a target mass of about

65 mg to about 75 mg of CIG material per 4 inch x 4 inch area of the substrate 18. The target containing 45:42:13 atomic percent C:In:Ga could be pre-sputtered for a suitable time period, such as about 3 minutes, to pre-condition the target.

The precursor film 112 may be formed at any suitable pressure. For incorporation into a roll-to-roll process, a suitable pressure may be at least about 1 millibar (mBar), preferably at least about 3 mBar. Such a pressure desirably is less than about 10 mBar, preferably less than about 5 mBar. A pressure of about 4 mBar would be suitable for instance. Sputtering desirably occurs in the presence of a suitable sputtering gas supplied at a suitable flow rate to establish the desired pressure. An exemplary sputtering gas is argon. It is understood that the flow rate(s) used are a function of a number of factors including pumping speed and the configuration of the chamber. Sputtering occurs for a suitable time period, such as for about 28 minutes at a suitable sputtering power, such as about 125W to form a precursor film 112.

Additional constituents such as Na, Li, Te, and/or the like may also be incorporated into precursor film 112 via sputtering or other techniques as well. If sputtered, these can be incorporated into the same target 110 or supplied from additional target(s) (not shown). Optionally, such additional constituents or even a portion of the metal constituents can be supplied via other sources, such as by sputtering in the presence of one or more suitable gases or vapors.

According to alternative embodiments, precursor film 112 could be formed from multiple targets such as a pair of confocal targets. Using this strategy, for instance, a CuGa target and an In target could be used confocally to form a C:I:G precursor film. Alternatively, the precursor film may be formed from multiple targets by passing the substrate through a plurality of sputtering zones.

Confocal target or other multiple-target strategies such as this are also useful in some embodiments to pre-incorporate at least a portion of the chalcogen content of the desired region 20 (Fig. 1) into at least a portion of the precursor film 112.

For example, according to this strategy, a precursor film incorporating overall a substoichiometric amount of selenium (i.e., the film includes less than one chalcogen atom for each metal atom included in the composition) is formed from confocal first and second targets, wherein the first target includes the composition Cu_xSe_y , wherein x is approximately 2 and y is approximately 1, and the second target incorporates Cu, In, and Ga according to the formula $\text{CuIn}_p\text{Ga}_{(1-p)}$, wherein p desirably is in the range from about 0.5 to about 1. Details of incorporating chalcogen into precursor film 112 are further described in Assignee's co-pending U.S. Provisional Patent Application Serial No. 61/314,840, filed

March 17, 2010, titled "CHALCOGENIDE-BASED MATERIALS AND IMPROVED METHODS OF MAKING SUCH MATERIALS" by Gerbi et al the entirety of which is incorporated herein by reference for all purposes. Multilayer embodiments of precursor film 112 also are further described in U.S. Provisional Patent Application Serial No. 61/314,840, filed March 17, 2010, bearing Attorney Docket No. DOW0027/P1, in the names of Jennifer E. Gerbi, Marc G. Langlois, Robert T. Nilsson.

Still referring to Fig. 3, a chalcogen-containing film also referred to herein as a cap 114 is formed in stage 102 over the precursor film 112. Desirably, the cap 114 is in the form of a solid cap including one or more chalcogens. In preferred modes of practice, the cap 114 incorporates Se, Te, and/or S. Se and/or S are preferred. Se is most preferred. If both Se and S are used, the atomic ratio of Se to S in illustrative embodiments may be in the range from about 1000:1 to about 1000:100, preferably about 1000:10 to about 1000:50. The chalcogens can be present in cap 114 as compounds and/or in elemental form. The elemental form is preferred.

The amount of chalcogen(s) incorporated into the cap 114 relative to the stoichiometric amount needed to complete region 20 can vary over a wide range. However, if the amount of chalcogen(s) in the cap is too low, lesser amounts of In and/or Se may be incorporated into the resultant region 20 than might be desired. Also, the reproducibility of the stage 102 may be less than desired. Generally, it is desirable that the cap 114 includes at least the stoichiometric amount (1x) of chalcogen(s) needed to convert substantially the entirety of the precursor film 112 to the desired tetragonal photoabsorbing phase, taking into account chalcogen content that might already be present in the precursor film 112. More preferably, it is desirable that at least 2x, and more preferably at least about 5x the stoichiometric amount of chalcogen(s) are incorporated into the cap 114.

From a theoretical perspective, there generally is no upper limit on the amount of chalcogen(s) used in the cap 114. Indeed, using greater stoichiometric excess is more desirable and provides multiple benefits. First, using a greater excess tends to produce more uniform chalcogenide photoabsorbing materials over time as the process is carried out more consistently. Additionally, the reproducibility of tetragonal formation is less sensitive to temperature fluctuations in the course of subsequent chalcogenization. However, as a practical matter, using excessively greater amounts of chalcogen(s) in cap 114 than is required for stoichiometry can be wasteful without providing sufficient incremental benefit. Consequently, it is preferred that the cap incorporates no more than about 100x, preferably no more than about 60x, preferably no more than about 30x, of the stoichiometric amount of chalcogen(s). In illustrative embodiments, using a cap with 1.0x, 1.5x, 2.0x, 2.5x, 10x, 25x,

or 50x of the stoichiometric amount of chalcogen(s) would be suitable. The stoichiometric amount of chalcogen can be calculated based upon the relative amounts of metal constituents in the precursor.

Often, a cap 114 with a suitable stoichiometric excess of chalcogen(s) has a thickness in the range from about 15 μm to about 20 μm . The target mass desirably involves depositing an amount of chalcogen(s) effective to provide the stoichiometric quantity (1x) relative to the precursor or the desired excess of chalcogen(s) (e.g., about 2X to about 50X in illustrative embodiments) relative to the precursor.

The cap 114 may be formed by evaporation from a resistively heated stainless steel boat or ceramic crucible. The pre-weighed substrate is suspended facedown over the crucible. Based on calibration, the amount of selenium needed to achieve the desired cap is loaded into the crucible. The chamber is pumped to a base pressure of less than about 10^{-4} mBar, and then the crucible is heated to greater than about 300°C (based on a temperature reading from a thermocouple immersed in the molten chalcogen). The full selenium load is evaporated.

In some modes of practice, it may be desirable to form a cap 114 from multiple layers in view of factors including to enhance uniformity, to accommodate equipment limitations, to prevent radiative heating of the substrate over extended deposition times, and/or the like. For example, in cases of larger caps, the crucible may be loaded two or more times to form the cap in two or more steps. To promote uniformity, it can be desirable to rotate the workpiece between growths. For instance, if forming cap 114 from two elemental layers, rotating the workpiece 180° between growths may be desirable.

In a further stage 104, the capped precursor film 108 is subjected to chalcogenization conditions effective to convert the precursor film 112 and cap 114 to the desired final form of region 20. This stage also may be referred to as a "post-chalcogenization" treatment to connote that at least a portion of the treatment occurs after precursor formation. For example, if Se is being incorporated into the precursor, the stage 104 can be referred to as a post-selenization treatment. Likewise, if S is being incorporated in the precursor, the stage 104 can be referred to as a post-sulfurization. Generally, this stage 104 occurs under thermal conditions effective to also anneal the capped film 108, thereby converting the precursor film 112 to the desired tetragonal, chalcopyrite phase to the extent the capped precursor does not already have that crystal structure at this stage. Consequently, stage 104 also may be referred to as an annealing treatment to recognize the conversion of the precursor film 112 into the desired chalcopyrite, tetragonal phase.

Chalcogenization generally occurs by positioning the capped film 108 in a suitable processing chamber (not shown) in which the capped film 108 is exposed to thermal conditions effective to convert the precursor into the photoabsorbing region 20. The chamber can be the same or different from the chamber(s) used to form other layers of the capped film 108. In a continuous roll-to-roll process occurring under vacuum, the capped film 108 generally is transferred from a capping station to one or more dedicated, downstream stations at which chalcogenization occurs. The sample temperature desirably is maintained at a suitably low temperature during the transfer to avoid undue loss of In and/or Se. As exemplary guidelines, the sample temperature may be about 150°C or less, more preferably about 100°C or less during the transfer. In an exemplary mode of practice, a transfer temperature of about 80°C would be suitable.

The temperature of the capped film 108 is then increased to an annealing temperature effective to cause the desired conversion. The rate at which the temperature is increased to the annealing temperature can impact the incorporation of In and/or Se into the resultant product. If the temperature ramp rate is too low, undue loss of In and/or Se may occur. On the other hand, if the ramp rate is too fast, undue loss of In, Se, and/or Ga could occur. Other problems that may be encountered include pinholing of the final film. It could also be possible that damaging microbursts could result from volatilization of constituents of the capped precursor film 108. Balancing these concerns, it is desirable that the temperature ramp rate is at least about 1°C/min, preferably at least about 20°C/min, more preferably at least about 30°C/min, and most preferably at least about 60°C/min. Additionally, the temperature ramp rate is desirably less than about 500°C/min, preferably less than about 400°C/min, and most preferably less than about 200°C/min. In one illustrative embodiment, a ramp rate of about 30°C/min to about 60°C/min would be suitable. In another illustrative embodiment, a ramp rate of 100 °C/min to 150°C/min would be suitable.

A wide range of annealing temperatures can be used. If the annealing temperature is too low, poor incorporation Se could be observed. Additionally, the conversion of the precursor film to the desired tetragonal phase may be less complete than is desired due to unreacted starting materials or formation of stable byproducts including binary chalcogens. On the other hand, constituents of the precursor film 112 and/or the substrate 18 could be unduly lost or degraded if the annealing temperature is too high. Balancing these concerns, the annealing temperature desirably is at least about 450°C, preferably at least about 500°C, and less than about 600°C, more preferably less than about 550°C.

Significantly, preferred modes of practice allow annealing to occur at atypically low temperatures. Thus, in another example, an annealing temperature of about 350°C would be

suitable such as when annealing with a Se cap in the presence of a chalcogen containing gas such as H_2Se .

Annealing generally occurs for a time sufficient to chalcogenize the film and to convert the film to the tetragonal phase to the desired degree. In many embodiments, annealing occurs for a time period of at least about 1 minute, preferably at least about 5 minutes, but less than about 36 hours, preferably less than about 3 hours.

Desirably, a suitable control strategy is implemented in order to maintain the annealing temperature at a steady level during the course of annealing. Feedback control using PID strategies would be suitable.

Advantageously, stage 104 can occur in a low-pressure regime that is compatible with continuous roll-to-roll processes occurring under vacuum. It is quite significant to find process conditions that work under such low pressure inasmuch as process strategies that work at higher pressures do not necessarily translate to vacuum processes. Generally, the risk of In loss increases if the pressure at stage 104 is too low. On the other hand, if the pressure is too high, it could be harder to practically and economically integrate stage 104 into a continuous roll-to-roll process occurring under vacuum. Balancing these concerns, stage 104 desirably occurs at a pressure no greater than about 300 millitorr (4e^{-1} mBar), preferably no greater than about 100 millitorr (1e^{-1} mBar), more preferably no greater than about 50 millitorr (6e^{-2} mBar), and most preferably no greater than about 15 millitorr (2e^{-2} mBar). Preferably the pressure is at least about 0.1 millitorr (1e^{-4} mBar), more preferably at least about 1 millitorr (1e^{-3} mBar), and most preferably at least about 3 millitorr (1e^{-3} mBar). In an exemplary embodiment, a pressure of about 5 millitorr (7e^{-3} mBar) would be suitable. In another exemplary embodiment, a pressure of about 10 millitorr (1e^{-2} mBar) would be suitable.

One or more gases can be introduced into the reaction vessel in order to help establish the desired pressure during the course of chalcogenization and annealing. A wide variety of strategies can be used to accomplish this. According to one strategy, annealing and chalcogenization occur in the presence of a flow of an inert gas such as Ar, or the like, introduced into the chamber. For instance, annealing at 505°C in the presence of 136 sccm Ar would be suitable. In a typical processing chamber, this flow rate of Ar corresponds to a pressure of about 10^{-3} millibarr. According to another mode of practice, annealing and chalcogenization occur in the presence of one or more gases or vapors incorporating one or more chalcogens introduced into the chamber. These gases may serve as additional sources of chalcogen to be incorporated into region 20. Exemplary gases of this type include H_2S , H_2Se , mono or dialkylated S, mono or dialkylated Se, combinations of these and the like.

Combinations of these strategies also may be used. For instance, annealing can occur in the presence of a combination of one or more inert gases and one or more chalcogen-containing gases.

Gases containing Se require more careful handling than gases including S. Yet, it is still desirable to incorporate selenium into region 20. Accordingly, a preferred mode of practice involves capping the precursor film 112 with a Se cap 114 while annealing in the presence of a sulfur containing gas such as H_2S . This approach is believed to yield tetragonal CIGSS ($Cu:In:Ga:Se:S$) and offers significant advantages. First, the Se cap provides sufficient Se to selenize the film while the H_2S supplies sulfur to sulfurize the film, increasing bandgap. Second, the sulfur-containing gas is much easier to handle than a Se-containing gas. Third, conversion of the capped precursor to CIGSS using this strategy has been observed to occur at lower temperatures, e.g., as low as $350^\circ C$.

One factor impacting chalcogenization in some embodiments may be whether the reactor walls are chilled or cooled. As non-limiting examples, either hot-walled or cold-walled chambers can be used to accomplish selenization. Cold-walled reactors are desirably used when the stoichiometric excess of chalcogen(s) in a cap is greater than about 5X, preferably greater than about 7X, more preferably greater than about 10X. Cooling of at least a portion of the reactor walls can be accomplished in any desired fashion. Water-cooling is one suitable technique. In a typical mode of practice, the cooled walls may be maintained at a temperature in the range of about 10 to about $25^\circ C$, preferably 15 to about $22^\circ C$. As the capped sample is heated, at least a portion of the selenium in the cap is expected to evaporate. Evaporated selenium generally would not be expected to be incorporated into the final film in a chamber with chilled walls, but rather would be generally expected to be plated out on the cooled walls of the chamber. A benefit of using cold-wall reactors is that the excess selenium is condensed onto the chilled-walls thereby preventing it from entering the pumping system or other system components and causing corrosion or damage to them.

Hot-walled reactors are desirably used when the stoichiometric excess (if any) of chalcogen(s) in the cap is below about 5x, preferably below about 4x, more preferably below about 3x. In a hot wall reactor, at least some of the reactor walls are at temperatures above the sublimation/evaporation points of the selenium. This is expected to create a dynamic selenium annealing atmosphere. Selenium that evaporates from the surface of the capped precursor generally would not be expected to plate against the heated walls of the chamber but instead may contribute to a gaseous selenium environment which then

contributes to the evaporation vs. reaction dynamics of the selenium at the CIGS surface during formation.

Annealing and chalcogenization convert the capped precursor film 108 into the desired photoabsorber region 20. After this stage 104 is completed, the workpiece 108 can be cooled down, or allowed to cool down, and then subjected to further processing to complete device 10. Generally, this involves cooling the sample down to about 200°C. It has been discovered that if the cooling rate is too rapid relative to Se in the surrounding atmosphere, elemental Se could condense at the surface of region 20, which could unduly impair device function. On the other hand, if the substrate cools too quickly relative to Se in the atmosphere, Se can evolve from the surface of the substrate which may unduly impair device function. Balancing these concerns, it is preferred to allow the workpiece to cool passively before transferring it from the chalcogenization chamber.

The cap 114 and the temperature ramp to the annealing temperature singly or in combination can help allow chalcogenization and annealing to occur at low pressure in a manner that is compatible with roll-to-roll manufacturing strategies occurring under vacuum. In the absence of cap 114 and/or by practicing ramp rates that are too slow or too fast, subsequent chalcogenization is much more difficult to carry out effectively. Indium incorporation is poor, and the resultant region 20 may be severely deficient with respect to In if chalcogenization and annealing occur at low pressure, e.g., at a pressure below about 300 millitorr, preferably below about 100 millitorr, more preferably below about 50 millitorr. This is believed to be attributable at least in part to the formation of volatile Indium-containing species, such as InSe and/or InS, that easily volatilize and are lost at low pressure. Additionally, Se incorporation also is poor, so that the resultant region 20 independently may be deficient with respect to Se.

In contrast, use of cap 114, optionally with an appropriate temperature ramp rate, are features that singly and in combination enable chalcogenization and annealing of CIGS precursor films to occur at low pressures feasible for continuous vacuum roll to roll processes. By using a cap and/or appropriate temperature ramp rate under low pressure chalcogenization conditions, In loss is significantly reduced, and incorporation of both In and Se into the resultant region 20 is greatly improved.

For example, in the absence of a cap 114, it was found that carrying out chalcogenization of a C:I:G film precursor at 350°C in the presence of H₂Se or H₂S gas at 5 milliTor (7e⁻³ mBar) can result in In losses of almost 50% per analysis of Cu/In ratios using ICP (inductively coupled plasma optical emission spectroscopy) techniques. Carrying out

chalcogenization at 500°C on a precursor film with no chalcogen cap has been observed to result in a complete loss of In per ICP analysis.

In contrast to this data, capping a C:I:G precursor film (i.e., a precursor film containing Cu, In, and Ga) with elemental Se prior to annealing in H₂Se or H₂S gas substantially reduced the loss of Indium. For example, a precursor film with an initial In/Cu ratio of about 1.3 capped with 2 times the stoichiometric amount of elemental Se required to form a CIGS photoabsorbing material was annealed at 350°C in 5 milliTorr H₂Se. The resultant CIGS material had an In/Cu ratio of greater than 1 per ICP analysis. The same process carried out at 10 milliTorr produced a CIGS material with an In/Cu ratio greater than 0.9. When the same processes were carried out at 5 and 10 millitorr, respectively, using a 25X cap of elemental selenium, the In/Cu ratio was greater than 1 for the resultant films. Similar data for In retention was obtained when H₂S was used to carry out chalcogenization of precursor films containing Cu, In, and Ga capped with 50X elemental selenium. Annealing occurred in 5 millitorr H₂S at 150°C, 350°C, and 500°C. In all samples, the In/Cu ratio of the resultant CIGS material per ICP analysis was greater than 1.2.

Data obtained from annealing the precursor films containing Cu, In, and Ga, and capped with 50X selenium also showed that the annealing temperature profile impacts the amount of chalcogen that remains on or integrates into the film 112. For example, when annealed at 150°C, the resultant region 20 had a Se/Cu ratio of only about 0.5. This is indicative of poor Se incorporation for a Se cap that included 50X times the stoichiometric amount of Se needed to convert the precursor into a photoabsorbing CIGS material. An annealing temperature of 150°C is generally too low to successfully convert the precursor film to the desired tetragonal CIGS material in any event. In contrast, when annealing under otherwise identical conditions at 350°C, Se incorporation improves. The resultant region 20 showed a Se/Cu ratio of 1.6, and XRD analysis indicated the presence of the desired tetragonal CIGS phase. Se incorporation improves further when annealing under otherwise identical conditions at 500°C. The resultant region 20 showed a Se/Cu ratio of 2.5. The region 20 was in the form of the pure, tetragonal CIGS phase.

After forming photoabsorbing region 20 on substrate 18, additional layers and features can be formed to complete the device as shown in Fig. 1. For example, buffer region 28 generally comprises an n-type semiconductor material with a suitable band gap to help form a p-n junction between the absorber region 20 and the buffer region 28. An optional window region 26 also may be present. Optional window region 26 can help to protect against shunts. Window region 26 also may protect buffer region 28 during

subsequent deposition of the transparent conductive layer 30. Each of these regions is shown as a single integral layer, but can be a single integral layer as illustrated or can be formed from one or more layers.

One or more electrical conductors are incorporated into the device 10 for the collection of current generated by the absorber region 20. A wide range of electrical conductors may be used. Generally, electrical conductors are included on both the backside and light incident side of the absorber region 20 in order to complete the desired electric circuit. On the backside, for example, backside electrical contact region 24 provides a backside electrical contact in representative embodiments. On the light incident side of absorber region 20 in representative embodiments, device 10 incorporates a transparent conductive layer 30 and collection grid 36. Optionally an electrically conductive ribbon (not shown) may also be used to electrically couple collection grid 36 to external electrical connections.

A protective barrier system 40 desirably is provided. The protective barrier system 40 is positioned over the electronic grid 36 and helps to isolate and protect the device 10 from the environment, including protection against water degradation. The barrier system 40 optionally also may incorporate elastomeric features that help to reduce the risk of damage to device 10 due to delamination stresses, such as might be caused by thermal cycling and or localized stress such as might be caused by impact from hail and or localized point load from the weight of an installer or dropped tools during installation.

Additional details and fabrication strategies for making layers and features 26, 28, 30, 36, and 40 are described in U.S. Provisional Patent Application Serial No. 61/258,416, filed November 5, 2009, by Bryden et al., entitled MANUFACTURE OF N-TYPE CHALCOGENIDE COMPOSITIONS AND THEIR USES IN PHOTOVOLTAIC DEVICES; U.S. Provisional Patent Application Serial No. 61/294,878, filed January 14, 2010, by Elowe et al., entitled MOISTURE RESISTANT PHOTOVOLTAIC DEVICES WITH EXPOSED CONDUCTIVE GRID; U.S. Provisional Patent Application Serial No. 61/292,646, filed January 6, 2010, by Popa et al., entitled MOISTURE RESISTANT PHOTOVOLTAIC DEVICES WITH ELASTOMERIC, POLYSILOXANE PROTECTION LAYER; U.S. Provisional Patent Application Serial No. 61/302,667, filed February 9, 2010, by Feist et al., entitled PHOTOVOLTAIC DEVICE WITH TRANSPARENT, CONDUCTIVE BARRIER LAYER; and U.S. Provisional Patent Application Serial No. 61/302,687, filed February 9, 2010, by DeGroot et al., entitled MOISTURE RESISTANT PHOTOVOLTAIC DEVICES WITH IMPROVED ADHESION OF BARRIER FILM, each

of which is independently incorporated herein by reference for all purposes in its respective entirety.

The present invention will now be described with reference to the following illustrative examples.

Examples

Example 1 – Fabrication of CIGS solar cell in a roll-to-roll tool

- Substrate preparation:

A roll of 430 series stainless steel is loaded into a continuous roll-to-roll vacuum sputtering system. This active side of the web is first cleaned with ion etching and then is coated by magnetron sputtering with a Nb barrier layer, a dual layer of Mo for a back contact and a NaF layer to act as a sodium source. The back side of the web is coated with Cr as an adhesion layer and Mo to act as a sacrificial layer during the selenization process.

- Target arrangement

The web is then translated into a Cu:In:Ga precursor sputtering chamber. Seven pulsed DC magnetrons are arranged in four zones. Each zone has individual gas control. The web is transported sequentially through the four zones. Each of the first, third, and fourth zones has 2 magnetrons. The second zone has a single magnetron. In this example, all magnetrons are adjusted to sputter parallel to the web. The web moves from magnetron number 1 through 7 where magnetrons 1 (Zone 1), 2 (Zone 1), 3 (Zone 2), 5 (Zone 3), and 7 (Zone 4) have targets of composition 45:32:13 Cu:In:Ga and magnetrons 4 (Zone 3) and 6 (Zone 4) have compositions of 35:46:20 Cu:In:Ga. In stationary tests where the web is not moving, the paired targets show a ~15% overlap in the sputter deposition while the four zones are completely separate.

- Deposition of CIGS precursor

The precursor film containing Cu, In, and Ga (CIG film) is sputtered between 6e-3 to 8e-3 mBar (4.5 to 6 mTorr) in Argon with a maximum web temperature of ~80°C. The flow rates of the Argon and throttling of the pumping system are used to maintain the pressure range in each individual sputter zone. Depending upon the configuration of each zone, it may be desirable to adjust flow rates,

pump settings, or the like, in order to maintain desired pressure(s) in the zones. In this example the flow rates (throttling) Ar of the individual zones are 380 sccm (90° throttle or full open) in zone 1, 600 sccm (25° open throttle) in zone 2, 650 sccm (25° throttle) in zone 3 and 400 sccm (90° throttle or open) in zone 4. The targets are sputtered at 600 watts with no pulsing (straight DC). The final film stoichiometric ratio for the precursors ranges from In/Cu 0.95-1.01 and Ga/Cu 0.32-0.34, as measured by ICP on representative calibrations runs.

- Cap formation on precursor

The web carrying the CIG precursor film is translated into a selenium evaporation unit for application of a selenium cap. The selenium evaporation unit includes a stainless steel boat with a effusion slit at the top with the slit being ~1-2 cm from the CIG-coated web face. The web temperature is not actively controlled. The slit has enough width such that the unit can be considered open-source configuration (i.e. no pressure of selenium vapor is building up inside the unit). The selenium melt is heated to 300-305°C. In this experiment, ICP data shows an average Se/Cu ratio for the cap is 14 (i.e. 7Xstoichiometric excess of selenium) with deviations in Se/Cu from 11 to 17 (6.5X to 8.5X stoichiometric excess of selenium). The resultant product is a web carrying a CIG-Se stack.

- Annealing

After application of the selenium cap, the resultant web carrying the CIG-Se stack is translated into a hot-wall oven. Within this oven, the pressure is estimated to be 1-10e-3 mBar (0.75 to 7.5 mTorr) based upon a pressure gauge outside the furnace zone but in the same chamber. Adjacent chamber pressures are maintained at 1e-3 mBar to 8 e-3 mBar(0.75 to 6 mTorr). The heating zones are set to achieve a maximum ramping rate of ~60°C/min to an average web temperature of 580-585°C. This temperature range is estimated based on previous calibration of the system and not actively measured due to the dynamic configuration intrinsic to the continuous roll-to-roll process. The web is maintained at an average temperature of 580-585°C for ~20 minutes before being cooled to ~425°C at 60 °C/min and then further to <300°C at a reduced rate of 20°C/min.

- Data

The completed CIGS films are then transferred into additional process chambers (all within the same vacuum system) for deposition of buffer and window layers before being wound onto a final core. After removal of the core from the continuous roll-to-roll system, the CIGS films are analyzed by ICP. Final In/Cu ratios ranged from 0.86 to 0.97 while Ga/Cu range from 0.27 to 0.33 giving final III/Cu ratios from 1.13 to 1.30. Se/Cu ratios ranged from 2.48 to 2.91 – as sample preparation for the ICP digestion is not specific to the active side vs. the back side, it is likely that some of the stoichiometric excess of selenium is not in the CIGS film but rather in the form of elemental or reacted coatings on the back side of the substrate. Upon application of a Ni-Ag grid and mechanical scribing to form a 0.47 cm² test cell, photoactivity of the material was demonstrated with efficiencies typically ranging from 5-8%.

Example 2 – Fabrication of tetragonal CIGS in the presence of H₂S gas (H₂S) on a cluster tool at 6.6e-3 mBar and 350C

- Substrate preparation:

A stainless steel coupon is first cleaned by sonication in solvent baths and dried with dry N₂ gas and loaded into a multi-chamber vacuum deposition system. The face of the substrate is further cleaned using 300W RF plasma etching in Argon. The substrate is then transferred under vacuum to a second chamber where a niobium adhesion layer and molybdenum back contact layer are deposited by sputtering. The sample is removed from vacuum.

- Targets

The substrate is later introduced into a precursor sputtering chamber comprising a single, commercially available Cu:In:Ga alloy target tilted off-axis with respect to the substrate to give a more uniform coating thickness. The target is 45:42:13 Cu:In:Ga. The sample is rotated during deposition.

- Deposition conditions The CIG precursor film is sputtered at 75 Watts, in ~4e-3 mBar in Argon at ambient temperature. The final film stoichiometric ratio for the precursors ranges from In/Cu 0.90-1.3 and Ga/Cu 0.27-0.30, as measured by ICP on representative calibrations runs.

- Cap formation on precursor

The substrate bearing the CIG film is removed from vacuum and loaded into a selenium evaporation chamber for application of a selenium cap. The selenium evaporation unit includes an open-top ceramic cup nested in a resistive heating element. The substrate is mounted face-down over the cup on a metal frame, and 22 g of shot is loaded to give a 25x cap. The system is evacuated to $<5 \times 10^{-6}$ Torr (7×10^{-6} mBar). The selenium crucible is heated to $>300^\circ\text{C}$ for sufficient time to allow the full aliquot of shot to be evaporated. The system is allowed to cool and then vented for loading of a second 22g aliquot of selenium shot. The sample is rotated to improve film thickness uniformity before evaporation of the second full aliquot. The process yields a 50x cap.

- Anneal conditions.

After application of the selenium cap, the substrate bearing the CIG-Se stack is removed from vacuum and transferred to a selenization chamber. In this chamber, the substrate is suspended face down and heated from the back-side with a radiative graphite element. The system has water-cooled walls ($<25^\circ\text{C}$ recirculating loop). The base pressure is 3×10^{-7} mBar prior to the run. The pressure in the system is increased to 6.6×10^{-3} mBar using 100% H_2S gas prior to heating. The substrate ramped up at $60^\circ\text{C}/\text{min}$ to about 400°C and then at about $3\text{--}5^\circ\text{C}/\text{min}$ to a final temperature $>500^\circ\text{C}$ (estimated to be about 515°C) by setting the power supply for the graphite heater at a previously determined power duty cycle value. The temperature of the substrate is maintained at $>500^\circ\text{C}$ for 30 minutes at which time the power supply is turned off. The resulting film is allowed to cooled to $<80^\circ\text{C}$ before transferring to a vacuum load-lock chamber for removal.

- Data.

The substrate bearing the completed CIGS film is removed from the system and analyzed by ICP for elemental composition. The In/Cu ratio of the film is 1.3 ((In+Ga)/Cu 1.6) while the Se/Cu is 1.7. Sulfur is not detected in the film by ICP. Analysis of the X-ray diffraction pattern of the film shows tetragonal CIGS, InSe, Cu, Mo, Nb, and Fe.

Example 3— Formation of CIGS in H₂Se at 10mT, 25x cap, 350C

- Substrate preparation
The substrate is prepared as in Example 2.
- Target arrangement.
Targets are used according to Example 2.
- Deposition conditions
Deposition of a CIG precursor on the substrate is carried out as in Example 2.
- Description of cap formation on precursor
A Se cap is formed on the CIG precursor as in Example 2.
- Anneal conditions.
After application of the selenium cap, the substrate bearing the CIG-Se stack is removed from vacuum and transferred to a selenization chamber. In this chamber, the substrate is suspended face down and heated from the back-side with a radiative graphite element. The system has water-cooled walls (<25°C recirculating loop). The base pressure is 3e-7 mBar prior to the run. The pressure in the system is increased to 1.4e-2 mBar using 100% H₂Se gas prior to heating. The substrate ramped up to >350°C at 20°C/min by setting the power supply for the graphite heater at a previously determined power duty cycle value. The temperature of the substrate is maintained at >300°C for 20 minutes at which time the power supply is turned off. The resulting film is allowed to cool to <80°C before transferring to a vacuum load-lock chamber for removal.
- Data.
The substrate bearing the completed CIGS film is removed from the system and analyzed by ICP for elemental composition. The In/Cu ratio of the film is 1.1 ((In+Ga)/Cu 1.4) while the Se/Cu is 1.31. Analysis of the X-ray diffraction pattern of the film shows tetragonal CIGS, InSe, Cu, Mo, Nb, and Fe.

Example 4a— Annealing of CIG film in Argon demonstrating baseline for annealing CIG in vacuum

- Substrate Preparation.
As in example 2
- Nature of target/targets – arrangement
As in example 2
- Deposition conditions
As in example 2
- Description of cap formation on precursor
No cap is used.
- Anneal conditions.
The substrate bearing the sputtered CIG precursor is transferred to a chalcogenization chamber under vacuum. In this chamber, the substrate is suspended face down and heated from the back-side with a radiative graphite element. The system has water-cooled walls (<25°C recirculating loop). The base pressure is 6e-7 mBar (4.5e-4 mTorr) prior to the run. The pressure in the system is increased to 6.6e-3 mBar (5 mT) using 100% Ar gas prior to heating. The substrate ramped up to >350°C (at 30°C/min (highest temperature estimated 400°C) by setting the power supply for the graphite heater at a previously determined power duty cycle value. The temperature of the substrate is maintained at >350°C for 30 minutes at which time the power supply is turned off. The resulting film is cooled to <80°C before transferring to a vacuum load-lock chamber for removal.
- Data.
The substrate bearing the completed CIGS film is removed from the system and analyzed by ICP for elemental composition. The In/Cu ratio of the film is 1.05 while the Se/Cu was 0.04.

Example 4b— Annealing of CIG film in H₂Se demonstrating loss of indium from surface when annealing in toxic gas

- Substrate preparation
As in example 2.
- Nature of target/targets – arrangement
As in example 2.
- Deposition conditions
As in example 2.
- Description of cap formation on precursor
No cap is used.
- Anneal conditions - pressure, temperature ramp
The substrate bearing the sputtered CIG precursor material is transferred to a chalcogenization chamber under vacuum. In this chamber, the substrate is suspended face down and heated from the back-side with a radiative graphite element. The system has water-cooled walls (<25°C recirculating loop). The base pressure is 6e-7 mBar (4.5e-4 mT) prior to the run. The pressure in the system is increased to 6.6e-3 mBar (5mT) using 100% H₂Se gas prior to heating. The substrate ramped up to >350°C at 30°C/min (highest temperature estimated to be about 400°C) by setting the power supply for the graphite heater at a previously determined power duty cycle value. The temperature of the substrate is maintained at >350°C for 30 minutes at which time the power supply is turned off. The resulting film is allowed to cool to <80°C before transferring to a vacuum load-lock chamber for removal.
- Data.
The substrate bearing the completed CIGS film is removed from the system and analyzed by ICP for elemental composition. The In/Cu ratio of the film is 0.61 while the Se/Cu is 0.12.

Example 4c— Annealing of CIG film w/2x cap in H₂Se demonstrating improved indium retention when annealing a film with a 2x cap but no CIGS formation yet

- Substrate preparation.
As in example 2.
- Nature of target/targets – arrangement
As in example 2.
- Deposition conditions
As in example 2.
- Description of cap formation on precursor
The substrate bearing the CIG precursor film is removed from vacuum and loaded into a selenium evaporation chamber for application of the selenium cap. The selenium evaporation unit includes an open-top ceramic cup nested in a resistive heating element. The substrate is mounted face-down over the cup on a metal frame and 1.2 g of shot is loaded to give a 1x cap. The system is evacuated to 2e-6 Torr (3e⁻⁶ mBar). The selenium crucible is heated to 360°C for sufficient time to allow the full aliquot of shot to be evaporated. The system is allowed to cool and then vented for loading of a second 1.2 g aliquot of selenium shot and rotation of the substrate to improve uniformity of the selenium film thickness. The evaporation process is repeated (base pressure 2e-6 Torr (3e⁻⁶ mBar), maximum temp 331°C) to yield a 2x cap.
- Anneal conditions - pressure, temperature ramp
The substrate bearing the CIG/Se stack is transferred to a chalcogenization chamber under vacuum. In this chamber, the substrate is suspended face down and heated from the back-side with a radiative graphite element. The system has water-cooled walls (<25°C recirculating loop). The base pressure is 6e-7 mBar (4.5e⁻⁴ mTorr) prior to the run. The pressure in the system is increased to 6.6e-3 mBar (5 mT) using 100% H₂Se gas prior to heating. The substrate ramped up to >350°C (at 30°C/min (highest temperature estimated to be about 400°C) by setting the power supply for the graphite heater at a previously determined power duty cycle value. The temperature of the substrate is maintained at

>350°C for 30 minutes at which time the power supply is turned off. The resulting film is allowed to cool to <80°C before transferring to a vacuum load-lock chamber for removal.

- Data.

The substrate bearing the completed CIGS film is removed from the system and analyzed by ICP for elemental composition. The In/Cu ratio of the film is 1.02 while the Se/Cu is 0.37. X-ray diffraction analysis of this film included peaks for a cubic CIG phase, InSe, In₄Se₃, In, and Cu.

Example 5

A sample is provided including a CIG precursor film formed on a substrate. The precursor film is capped with 25x Se. Thermal annealing of the sample takes place in a vacuum quartz tube oven (VQTO). The oven includes an 8" diameter X 54" long quartz tube inserted in a 38" long tube furnace. The furnace has three heat zones (left, right, and center) that are individually controlled by Watlow controllers. The ends of the tubes have stainless steel caps that are sealed to the tube ends via o-rings. A vacuum rough pump in conjunction with a vacuum turbo pump provide pressures measured down to 0.1 millitorr (1.3e-4 mBar). A mass flow controller (MFC) connected to an argon gas cylinder provides pressure control between 0.1 and 50 millitorr (1.3e-4 to 6.7 e-2 mBar). A liquid nitrogen trap located between the turbo pump and the tube traps selenium vapor. Pressure is measured with a Baratron gauge at a point along a 2-inch diameter line between the quartz tube and the selenium trap.

The configuration includes a stainless steel carrier rack that holds multiple samples, although only a single sample is used in each run of this example. The rack can be inserted from the cold end of the tube to the heated zone via a hook coupled magnetically to the outside of the tube. Conversely, the sample can be removed to cool rapidly with the same device. Two flexible thermocouples are placed directly in contact with the backside of the sample for accurate temperature monitoring. Static thermocouples are also located at various spots in the tube oven to give the temperature profile of the oven. All thermocouples are type "K". Controller and static oven temperatures and pressure are recorded on a computer using Agilent data collecting software. Temperatures connected directly to the samples are recorded using an Omega S309 system. Data from these two sources are then combined into an Excel spreadsheet.

In this example, the sample bearing the CIG-Se stack is placed on a stainless steel carrier, which is then placed in the center of the oven. With the mass flow controller set to zero flow, the endplate is attached and the tube is evacuated via the rough and turbo pump to about 0.1 millitorr. The furnace temperature setpoints are entered into the controllers and the recorders are simultaneously started. The controller power to the heaters is turned on and the tube is heated. The pressure is maintained at about 0.1 mtorr. The substrate is heated at a rate of about 20C/min. to 520C for 35 min. then the carrier with the samples is removed to the cool end of the tube outside the furnace and the power turned off. The sample is cooled overnight to room temperature.

The efficiencies of four resultant CIGS cells on the substrate are measured, and these give efficiencies of 7.12, 6.54, 5.72, and 6.85%.

Example 6

An additional sample is processed identically as in example 5, except that the capped sample is heated at a rate of 5C/min to the annealing temperature.

The efficiencies of four resultant CIGS cells on the substrate are measured, and these give efficiencies of 6.84, 6.54, 6.62, and 6.89%.

Other embodiments of this invention will be apparent to those skilled in the art upon consideration of this specification or from practice of the invention disclosed herein. Various omissions, modifications, and changes to the principles and embodiments described herein may be made by one skilled in the art without departing from the true scope and spirit of the invention which is indicated by the following claims.

WHAT IS CLAIMED IS:

1. A method of making a chalcogen-containing photoabsorbing composition, comprising the steps of:

- 5 a) forming a workpiece comprising a precursor of the chalcogen-containing photoabsorbing composition, said precursor optionally comprising a chalcogen content comprising at least one chalcogen;
- b) forming a solid cap on the precursor, said solid cap and precursor together comprising at least a stoichiometric amount of at least one chalcogen to convert the precursor to the chalcogen-containing photoabsorbing composition;
- 10 c) heating the capped workpiece to cause chalcogenization at a pressure of below about 300 millitorr.

2. The method of claim 1, wherein the process occurs in a roll-to-roll manufacturing process.

3. The method of any of the previous claims, wherein the heating occurs in the presence of an inert gas.

4. The method of any of the preceding claims, wherein the cap incorporates at least one chalcogen in elemental form.

5. The method of claim 4, wherein the cap comprises elemental Se.

6. The method of any of claims 1, 2, 4, 5, wherein at least the heating step occurs in the presence of at least one gas comprising a chalcogen.

7. The method of claim 6, wherein at least the annealing step occurs in the presence of a gas comprising H_2S or H_2Se .

8. The method of any preceding claim, wherein the heating temperature is in the range from about 300°C to about 600°C.

9. The method of any preceding claim, wherein at least the heating step occurs at a pressure of less than about 100 millitorr.

10. The method of any preceding claim, wherein the precursor film comprises Cu, In, and Ga.

11. The method of any preceding claim, wherein the precursor comprises a sub-stoichiometric amount of at least one chalcogen.

12. The method of any preceding claim, wherein the heating occurs at a rate in the range from about 5°C/minute to about 400°C/minute.

13. The method of any preceding claim, wherein the heating occurs at a rate having a substantially linear profile.

14. The method of any preceding claim, wherein the workpiece is maintained at one or more temperatures below about 100°C prior to the heating step.

5 15. The method of any preceding claim, wherein the step of forming the workpiece comprises (a) cleaning a metallic support under conditions effective to remove organic impurities and (b) forming the workpiece on a substrate incorporating the cleaned metallic support.

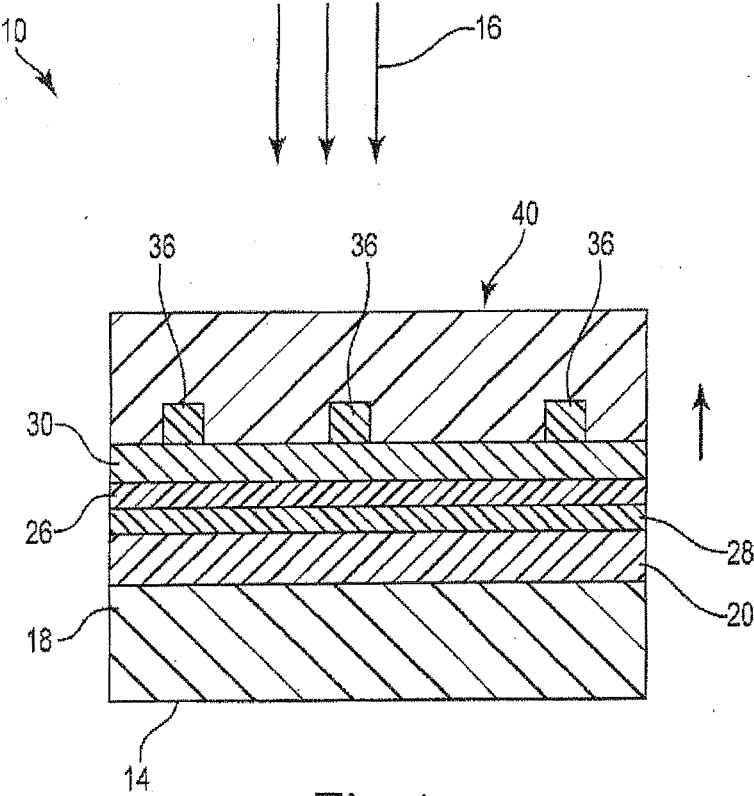


Fig. 1

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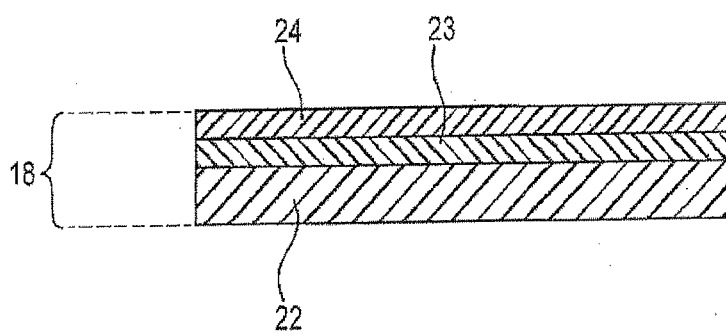


Fig. 2

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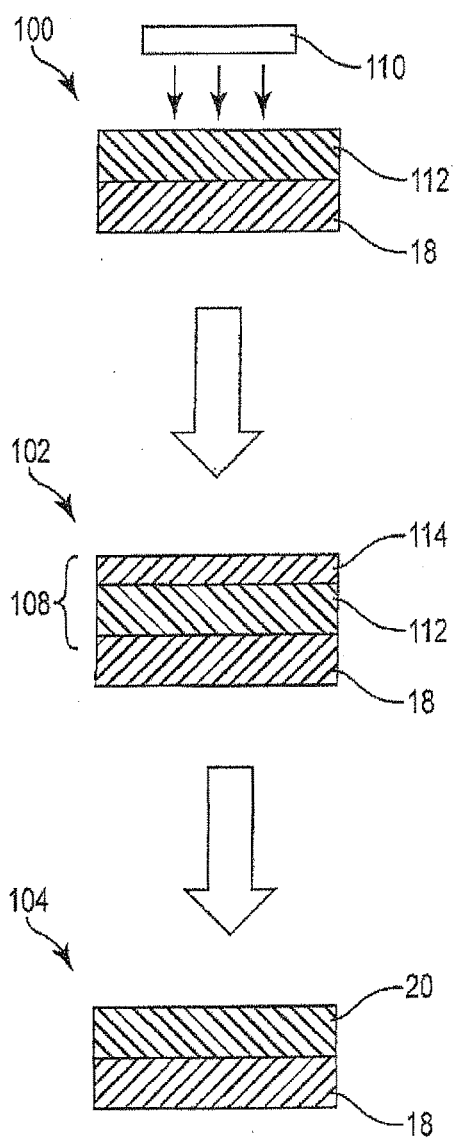


Fig. 3