very desirable to find a way to modify, reduce or even eliminate total number, size, and even location of these voids in the finished PACB film. It also would be highly desirable to be able to improve the adhesion characteristics of these PACB films. Adhesion problems become even more critical in roll-to-roll processes, particularly when techniques such as screen printing are used to form features such as collection grids.

[11] As another drawback, the raw materials used to form PACB thin films are quite expensive. It is highly desirable to drive down these costs. One way to accomplish this would be to deposit thinner PACB films so that less material is used per device. However, the electronic characteristics of thinner PACB films tend to be seriously compromised and even crippled as the thickness is reduced. It remains desirable to find a way to sputter or otherwise form thinner PACB films that still would offer adequate electronic characteristics.

[12] SUMMARY ~~OF THE INVENTION~~

[13] The present ~~invention~~disclosure provides improved chalcogen-containing, photovoltaic structures as well as related compositions, photovoltaic devices incorporating these structures, methods of making these structures and devices, and methods of using these structures and devices. According to principles of the present ~~invention~~disclosure, the adhesion of PACB compositions is improved through the use of chalcogen-containing tie layers. In a typical approach of the present ~~invention~~disclosure, a tie layer initially is formed on a substrate and then a PACB composition is formed on the tie layer.

[14] The tie layers not only improve adhesion but also improve overall electronic performance of the resultant devices. For example, as compared to otherwise similar devices without tie layers, data have shown that photovoltaic cells incorporating PACB compositions formed on such tie layers tend to have higher average efficiency, less performance variability from device to device, better absorption of light over a large wavelength range, and reduced large scale defects. Significantly, the tie layers also allow thinner, high quality PACB films to be formed that would not be feasible in the absence of the tie layers. The

principles of the present ~~invention~~disclosure are well suited for industrial scale processes, including roll-to-roll processing that may involve screen printing to deposit device features or precursors thereof, such as collection grids.

[15] The tie layers are compositionally similar to PACB compositions in that the tie layers in many embodiments include at least Cu, In, and at least one chalcogen. The tie layers also may include one or more of the other kinds of ingredients included in PACB compositions, including but not limited to gallium (Ga), and/or aluminum (Al), and/or the like. Indeed, in some embodiments, the constituents and optionally the proportions thereof of the tie layer and the PACB layer may be substantially the same. However, the tie layers have a different morphology that favors tie layer functionality. In some embodiments, this is achieved by forming thin, tie layer precursors at lower temperatures. Upon thermal treatment optionally in the presence of chalcogen, these tie layer precursors tend to be converted to a PACB composition comprising a crystal grain structure that on average is much finer than crystalline structures associated with PACB compositions that are more optimized for electronic performance. The fine grain texture has been observed to correlate to improved adhesion. In some embodiments the tie layer precursor composition as deposited is measurably less crystalline than the resultant tie layer formed as a result of post-chalcogenization and/or post-annealing. Without wishing to be bound, it is believed that at least portions of the tie layer precursor PACB composition as deposited might be amorphous.

In a first aspect, there is provided a method of making a chalcogen-containing photoabsorbing structure, comprising the steps of:

(a) using one or more techniques comprising sputtering at least one target at a temperature of less than 350°C to form a first photoactive film precursor comprising at least Cu, In, and at least one chalcogen;

(b) subjecting the first film precursor to annealing and/or chalcogenization treatments under conditions effective to convert the first photoactive film precursor into a first crystalline PACB composition having a first crystalline grain morphology; and

(c) providing a second, photoactive film directly or indirectly on the first crystalline PACB composition or precursor thereof, said second photoactive film comprising at least Cu and In; wherein the second photoactive film has a second crystalline grain morphology, wherein the first crystalline grain morphology has a finer crystalline grain structure than the second crystalline grain morphology; and wherein the annealing and/or chalcogenization treatment of the first photoactive film precursor occurs before, during, and/or after formation of the second photoactive film.

[16] In an embodiment, there is provided ~~one aspect, the present invention relates to~~ a method of making a chalcogen-containing photoabsorbing structure, comprising the steps of:

(a) forming a first photoactive film or a precursor thereof comprising at least Cu, In, and at least one chalcogen; and

(b) forming a second, photoactive film or a film precursor directly or indirectly on the first film, said film comprising at least Cu and In; and

(c) subjecting at least one of the first and second films and/or precursors thereof to an annealing and/or chalcogenization treatment under conditions effective to convert at least one of the first and second films to a crystalline PACB composition.

[17] In an embodiment, there is provided~~another aspect, the present invention relates to~~ a method of making a chalcogen-containing photoabsorbing structure, comprising the steps of:

a) forming at least a portion of a first photoactive film or a precursor thereof comprising at least Cu, In, and at least one chalcogen, wherein at least a portion of said forming occurs at a temperature of less than about 350°C; and

b) forming a second, photoactive film or film precursor thereof directly or indirectly on the first film, said film comprising at least Cu and In; and

c) subjecting at least one of the first and second films and/or precursors thereof to an annealing and/or chalcogenization treatment under conditions effective to form a crystalline PACB composition.

In a second aspect, there is provided a photovoltaic device, comprising:

a) a substrate;

b) a first PACB region formed directly or indirectly on the substrate, wherein the first PACB region comprises Cu, In, and at least one chalcogen, and wherein the first PACB region comprises crystalline grains having a size under 100 nm as measured by XTEM and an average thickness for the region of less than 200 nm; and

c) a second PACB region formed directly or indirectly on the first PACB region, wherein the second PACB region comprises Cu, In, and at least

d) one chalcogen; wherein the combined thickness of first and second regions is less than 1000nm.

[18] In an embodiment, there is provided~~another aspect, the present invention relates to~~ a photovoltaic device, comprising:

a) a substrate;

b) a first PACB region formed directly or indirectly on the substrate, wherein the first PACB region comprises Cu, In, and at least one chalcogen, and wherein at least a major portion of the first PACB region comprises crystalline grains having a size under 100 nm as measured by XTEM and an average thickness for the region of less than about 200 nm; and

c) a second PACB region formed directly or indirectly on the first region, wherein the second region comprises Cu, In, and at least one chalcogen; wherein the combined thickness of first and second regions is less than 1000 nm.

[19] In an embodiment, there is provided~~another aspect, the present invention relates to~~ a photovoltaic device, comprising:

a) a substrate;

b) a first PACB region formed directly or indirectly on the substrate, wherein the first region comprises Cu, In, and at least one chalcogen, and wherein the first region has a thickness under about 200 nm; and

c) a second PACB region formed directly or indirectly on the first PACB region, wherein the second PACB region comprises Cu, In, and at least one chalcogen, wherein the second PACB region has a thickness in the range from about 200 nm to about 1000 nm, and wherein the first PACB region has a smaller average crystalline grain size as measured by XTEM than the second PACB region.

[20] BRIEF DESCRIPTION OF THE DRAWINGS

[21] Fig. 1 is a graph referred to in Example 3 below that shows efficiency results for eight photovoltaic (PV) cells formed with a tie layer (data points on right side of graph) and eight photovoltaic cells formed without a tie layer (data points on left side of graph).

[22] Fig. 2 is a graph referred to in Example 3 below that shows quantum efficiency measurements of the highest performing cell with a tie layer (curve 1) and the highest performing cell without a tie layer (curve 2).

[23] Fig. 3 is a graph that shows an efficiency comparison between samples with and without tie layers.

[24] Fig. 4 is a graph that compares the performance of samples having a 50 nm tie layer to samples with a 200 nm tie layer.

[25] Fig. 5 is a graph that compares samples having an overlying PACB layer with a thickness of about 450 nm to samples having an overlying PACB layer with a thickness of about 1 micron, wherein both sets of samples had tie that were about 50 nm thick.