approach is not truly scalable with regard to industrial applications, particularly in roll-to-roll processes.

In contrast to thermal evaporation techniques, sputtering techniques offer the potential to be a more scalable method better suited for industrial application of CIGS materials. However, it is very challenging to supply the needed amount of chalcogen during the sputtering of Cu, In, Ga, and/or Al to form high quality CIGS in one step. As a consequence, CIGS films have been sputtered from one or more metal targets in the presence of selenium and/or sulfur containing gas or vapor from an evaporated source. Using only a gas or vapor as a chalcogen source during sputtering of other components typically requires that enough gas be used to at least supply the desired chalcogen content in the precursor film, often with an additional overpressure of chalcogen. Using so much chalcogen-containing gas or vapor tends to cause equipment degradation and 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 $In_xSe_y$ compounds, lowered overall deposition rates, and the damage of targets due to electrical arcing.

## SUMMARY ~~OF THE INVENTION~~

The present ~~invention~~disclosure provides strategies for making high quality CIGS photoabsorbing compositions from sputtered precursor film(s) that incorporate chalcogen(s) with a sub-stoichiometric concentration, with the option of localizing a sub-layer of this chalcogen-containing layer at a specific location within the precursor film(s). The conversion of these precursors into CIGS photoabsorbing material via a following chalcogenizing treatment (also referred to as "post-chalcogenization," including, e.g., "post-selenization" when Se is used) provides one or more or all of the following benefits: clearly reduced overall void area and size; altered void location within the film such that a majority of voids are not located at the CIGS-back contact interface; improved adhesion; reduced Ga migration upon chalcogenization; improved Ga concentrations in the top region of the post-selenized CIGS film relative to a purely metal precursor film that is post selenized; improved Ga concentrations in the bottom boundary region; and improved film smoothness resulting in fewer device defects via the improvement in conformality of overlying photovoltaic device layers.

TIn one aspect, the present inventiondisclosure relates to a method of making a chalcogen-containing photoabsorbing composition. A precursor of the chalcogen-containing photoabsorber is formed wherein the precursor includes a sub-stoichiometric amount of at least one chalcogen. The precursor is subjected to a chalcogenization treatment.

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

(a) sputtering metals comprising Cu and Ga using at least one first sputtering target in the presence of one or more chalcogens comprising Se to form a Se-containing precursor of the chalcogen-containing photoabsorber, wherein the Se-containing precursor includes a sub-stoichiometric amount of the one chalcogen throughout the precursor in selected areas of the precursor; and

(b) while the precursor comprises Se throughout the precursor or in selected areas of the precursor, subjecting the Se-containing precursor to a thermal treatment in the presence of one or more chalcogens comprising Se to convert the precursor into a chalcogenide photoabsorbing material.

The present inventiondisclosure also encompasses photovoltaic devices made by this method.

TIn another aspect, the present inventiondisclosure relates to a photovoltaic device that comprises a chalcogen-containing photoabsorbing film having a top surface and a bottom surface. The photoabsorbing film comprises a void content of 0.5 to 50%. The film also includes from about 0.1 to about 60 atomic percent Ga at least in a first boundary region proximal to the bottom surface of the photoabsorbing film and/or a second boundary region proximal to the top surface of the photoabsorbing film, wherein the atomic percent Ga is based on the total composition of the corresponding boundary region.

In a second aspect, there is provided a photovoltaic device, comprising a chalcogen-containing photoabsorbing film having a top surface and a bottom surface, said photoabsorbing film comprising:

a void content of 0.5 to 50%; and

0.1 to 60 atomic percent Ga at least in a first boundary region proximal to the bottom surface of the photoabsorbing film and/or a second boundary region proximal to the top surface of the photoabsorbing film, wherein the atomic percent Ga is based on the

total composition of the corresponding boundary region, and wherein at least one additional region is interposed between the first and second boundary regions, wherein the additional region includes a reduced Ga content relative to the first and second boundary regions.

T~~In another aspect t~~he present ~~invention~~disclosure relates to a precursor film of a chalcogen-containing photoabsorbing material. The precursor comprises from about 0.1 to about 60 atomic percent Ga selectively co-incorporated into one or more portions of the precursor with at least one chalcogen based upon the total composition of said portion; and wherein the precursor includes a sub-stoichiometric amount of a chalcogen based upon the overall composition of the precursor film.

In a third aspect, there is provided a precursor film of a chalcogen-containing photoabsorbing material, said precursor comprising from 0.1 to 60 atomic percent Ga selectively co-incorporated into one or more portions of the precursor with at least one chalcogen based upon the total composition of said portion; and wherein the precursor includes a sub-stoichiometric amount of a chalcogen based upon the overall composition of the precursor film, and wherein at least one additional region is interposed between the first and second boundary regions, wherein the additional region includes a reduced Ga content relative to the first and second boundary regions.

## 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 showing how to make a photovoltaic device according to a representative embodiment of the present invention in which a single layer CIGS precursor film is prepared via sputtering from a single target;

Fig. 2 is a schematic diagram showing how to make an alternative embodiment of a CIGS photoabsorbing layer, wherein multiple confocal targets are used to prepare a single layer CIGS precursor film; and