PHOTOVOLTAIC MODULES WITH WAVELENGTH SHIFTING PHOSPHOR-GLASS COMPOSITE LAYER

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority under 35 U.S.C. § 119 of U.S. Provisional Application No. 63/569,379 filed March 25, 2024, the content of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This disclosure pertains to solar cells or panels having a photovoltaic (PV) cell or layer and a phosphor-glass composite layer that shifts the wavelength (frequency) of at least some incident light to a frequency that generates electrical power more efficiently when the light from the phosphor-glass composite layer is incident on the PV cell.

BACKGROUND

[0003] Various types of photovoltaics (solar cells) have been utilized in the solar energy market. Known silicon solar cells may convert about 20% of the incident solar energy to electricity, which may be referred to as a 20% conversion efficiency. However, existing solar cells may have at least some drawbacks.

SUMMARY

[0004] An aspect of the present disclosure is a photovoltaic ("PV") module including a phosphor-glass composite layer for wavelength shifting of UV light into visible light, thereby increasing the power efficiency and output of a solar cell or panel. Phosphor particles may be embedded in a glass encapsulant material to form a phosphor-glass composite layer in which the glass encapsulant material may be substantially refractive indexed matched to the phosphor particles to reduce or eliminate scattering that could otherwise result from differences in the refractive indices of the glass encapsulant and phosphor particles. The photovoltaic module may optionally include a silicon ("Si") photovoltaic cell layer that has reduced efficiency with regards to converting the UV portion of the sun's spectrum into electrical power. Alternately or additionally, the photovoltaic module may include a polymer bonding layer such as ethylene-vinyl acetate (EVA), wherein the polymer bonding layer absorbs UV light, either intrinsically or due to UV absorbing additives to the polymer. UV absorbers may be added to polymer bonding layers such as EVA in solar applications to extend their useful life through reduced UV degradation. An aspect of the present disclosure involves converting at least some

of the UV portion of sunlight into visible wavelengths at which a SiPV cell is more efficient (relative to UV light), and/or converting at least some of the UV portion of sunlight that would be absorbed by the polymer bonding layer into visible wavelengths that are transmitted through the polymer bonding layer or only weakly absorbed by the polymer bonding layer. This may involve utilizing wavelength-shifting materials such as phosphors, which can absorb UV or blue light and re-emit light at longer wavelengths (also called luminescence). In accordance with some aspects of the present disclosure, various factors may be considered at the module level, such as: 1) quantum efficiency of the luminescence process, which is preferably high; 2) optical scattering or absorption in the luminescent material due to refractive index mismatch between the luminescent material and its surrounding, which refractive index mismatch is preferably low; 3) thermal, chemical, and UV durability of the luminescent material; and 4) mechanical stresses (such as caused by Coefficient of Thermal Expansion ("CTE") mismatch) between the luminescent material and the other module components.

[0005] An aspect of the present disclosure is a photovoltaic module that includes a phosphor-glass composite layer for wavelength shifting of UV light into visible light to thereby increase the power efficiency and/or electrical power output of the photovoltaic module and/or a solar panel including one or more photovoltaic modules. Phosphor particles are embedded in a glass encapsulant material that is preferably substantially refractive index matched to the phosphor particles to reduce or prevent scattering of light due to differences in refractive indices. During fabrication, the phosphor-in-glass composite layer may be formed by coating a glass frit including phosphor particles onto a rear surface of a solar module cover glass. The cover glass may comprise, for example, a low-iron soda lime glass, a borosilicate glass, or an aluminosilicate glass. The cover glass layer may contribute significantly to the mechanical and/or environmental durability of the combined system (i.e. the PV module). Preferred glass encapsulant materials for the phosphor-glass composite layer may include, for example, low-Tg glasses with refractive indices from about 1.65-1.85 that are free of lead and fluorine. The glass encapsulant may preferably comprise tin-containing or SnO-containing glasses, including tin phosphates, tin silicates, tin borates, tin borosilicates, and tin borophosphates. The glass encapsulant materials may comprise low-Tg glass to facilitate sintering of the glass encapsulant together with the phosphor particles to minimize voids that could otherwise generate light scattering, while also allowing the sintering temperature to be below about 700° C, or more preferably below about 500° C, so as not to degrade the phosphor particles. The Tg of the encapsulant glass may also be less than the Tg of the cover glass whereby the composite frit

utilized to form the phosphor-glass composite can be sintered after the composite frit has been deposited on the cover glass without adversely affecting the properties of the cover glass.

[0006] Preferred phosphor materials may have broad UV absorption in the 300-400 nm wavelength range, low visible and near-IR absorption, and efficient conversion to visible or near IR light. For example, preferred phosphor materials may have quantum efficiency greater than 50%, 60%, 70%, 80%, or 90%. Examples of preferred phosphors include barium magnesium silicates, which may be doped with Eu^{2+} and Mn^{2+}. Preferred phosphors may also include willemite (Zn_2SiO_4), calcium magnesium silicates and strontium magnesium silicates and mixed orthosilicates $(Ba,Sr,Ca)_2SiO_4$, which may be doped with Eu^{2+}, Eu^{3+}, Mn^{2+}, Dy^{3+}, Tb^{3+}, Ce^{3+}, Sm^{3+}, Yb^{3+}, Yb^{2+}, Nd^{3+}, Pr^{3+} and other rare earth dopants. Alkaline earth silicates can also be doped with N (Si_3N_4) to red shift the emission.

[0007] Another aspect of the present disclosure is a photovoltaic module including a layer of cover glass and a phosphor-glass composite layer disposed below the layer of cover glass, wherein the phosphor-glass composite comprises phosphor particles embedded in a glass encapsulant material. The phosphor particles may have a refractive index that is matched or nearly matched to the refractive index of the glass encapsulant material. The phosphor particles preferably absorb light in the at least 250-400 nm wavelength range, and re-emit light at wavelengths longer than 400 nm. The glass encapsulant material may be substantially free of lead and fluorine and may have a refractive index of about 1.60 to about 1.90, or about 1.65 to about 1.85. The glass encapsulant material has a sufficiently low glass transition temperature (Tg) to permit sintering of the glass encapsulant material together with the phosphor particles to minimize voids in the glass encapsulant material without significantly degrading the phosphor particles. The photovoltaic module may also include a photovoltaic cell or layer disposed below the phosphor-glass composite layer whereby, in use, at least some light in the visible range that is re-emitted from the phosphor-glass composite layer is converted into electricity by the photovoltaic cell.

[0008] The photovoltaic cell may comprise one or more materials selected from the group consisting of amorphous silicon, cadmium telluride, and a perovskite material.

[0009] The photovoltaic cell or layer may optionally comprise a crystalline silicon material, which may be either polycrystalline silicon or monocrystalline silicon.

[0010] The phosphor particles may be selected to minimize absorption of light in the wavelength range of about 400 nm to about 1100 nm.

[0011] The phosphor particles may optionally comprise at least one material selected from the group consisting of barium magnesium silicates, calcium magnesium silicates, and strontium magnesium silicates.

[0012] The phosphor particles may optionally comprise $Ba_{3-x}Mg_{1-y}Si_2O_8:Eu^{2+}_x$, Mn^{2+}_y.

[0013] The phosphor-glass composite layer may be formed from a composite frit comprising glass encapsulant particles, phosphor particles, and organic additives, and the Tg of the glass encapsulant material may be sufficiently high to allow for volatilization and escape of the organic additives utilized in the composite frit through open pores in the frit during sintering of the frit.

[0014] The Tg of the glass encapsulant material may be greater than about 300 °C.

[0015] The Tg of glass encapsulant material may be sufficiently low to permit the phosphor particles to retain one or more of their composition, crystal structure, and quantum efficiency.

[0016] The Tg of the glass encapsulant material may be less than about 550 °C.

[0017] The Tg of the glass encapsulant material may be from about 360 °C-450 °C, and may have a glass softening temperature that is from about 400 °C-550 °C, wherein the glass softening temperature is a temperature at which the glass encapsulant material has a viscosity of about $10^{\wedge 6.7}$ Pa·S.

[0018] The glass encapsulant material may comprise a material selected from the group consisting of tin-containing glasses (e.g. glasses containing one or more of SnO, Sn2, or Sn4+).

[0019] The glass encapsulant material may include 1) tin silicates with about 25 mol% < SnO < about 60 mol%; and about 40 mol% < SiO_2 < about 75 mol%, or 2) tin borophosphates with about 0 mol% < B_2O_3 < about 30 mol%; about 30 mol% < SnO < about 70 mol%; and about 30 mol% < P_2O_5 < about 60 mol%.

[0020] The glass encapsulant material may include $xB_2O_3 \cdot (100\text{-}x)(66.7SnO–33.3P_2O_5)$, with x = about 5 to about 25mol% having a refractive index in the range of about 1.74 to about 1.78, and the phosphor particles may include $Ba_{3-x}Mg_{1-y}Si_2O_8:Eu^{2+}_x$, Mn^{2+}_y.

[0021] A difference in the refractive indices of the phosphor particles and the glass encapsulant material may be less than about 0.05.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] In the Drawings:

[0023] FIG. 1 is a partially schematic cross-sectional view of a photovoltaic module according to an aspect of the present disclosure;

[0024] FIG. 2 is a partially schematic cross-sectional view of a photovoltaic module according to another aspect of the present disclosure;

[0025] FIG. 3 is a partially schematic cross-sectional view of a photovoltaic module according to another aspect of the present disclosure;

[0026] FIG. 4 is a graph showing the results of a ray tracing model for the photovoltaic module of FIG. 1 showing absorption of external sunlight versus triangular groove elevation angle;

[0027] FIG. 5 is a graph showing the results of a ray tracing model for the photovoltaic module of FIG. 2 showing absorption of the external sunlight versus the aspect ratio of the rectangular grooves; and

[0028] FIG. 6 depicts a schematic flow chart of an embodiment of a method or process for forming a photovoltaic module, as set forth in one or more of the aspects described herein.

DETAILED DESCRIPTION

[0029] In the following detailed description, for purposes of explanation and not limitation, example embodiments disclosing specific details are set forth to provide a thorough understanding of various principles of the present disclosure. However, it will be apparent to one having ordinary skill in the art, having had the benefit of the present disclosure, that the present disclosure may be practiced in other embodiments that depart from the specific details disclosed herein. Moreover, descriptions of well-known devices, methods and materials may be omitted so as not to obscure the description of various principles of the present disclosure. Finally, wherever applicable, like reference numerals refer to like elements.

[0030] Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. As used herein, the term "about" means that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but may be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. When the term "about" is used in describing a value or an endpoint of a range, the disclosure should be understood to include the specific value or endpoint referred to. Whether or not a numerical value or endpoint of a range in the specification recites "about," the numerical value or endpoint of a range is intended to include two embodiments: one modified by "about," and one not modified by "about." It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[0031] The terms "substantial," "substantially," and variations thereof as used herein are intended to note that a described feature is equal or approximately equal to a value or description. For example, a "substantially planar" surface is intended to denote a surface that is planar or approximately planar. Moreover, "substantially" is intended to denote that two values are equal or approximately equal. In some embodiments, "substantially" may denote values within about 10% of each other, for example within about 5% of each other, or within about 2% of each other.

[0032] As used herein, the term "dispose" includes coating, depositing and/or forming a material onto a surface. The disposed material may constitute a layer, as defined herein. The phrase "disposed on" includes the instance of forming a material onto a surface such that the material is in direct contact with the surface and also includes the instance where the material is formed on a surface, with one or more intervening material(s) between the disposed material and the surface. The intervening material(s) may constitute a layer, as defined herein.

[0033] Directional terms as used herein – for example up, down, right, left, front, back, top, bottom – are made only with reference to the figures as drawn and/or to any specific orientation described herein and are not intended to imply absolute orientation.

[0034] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps, or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is in no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including: matters of logic with respect to arrangement of steps or operational flow; plain meaning derived from grammatical organization or punctuation; the number or type of embodiments described in the specification.

[0035] As used herein, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a "component" includes embodiments having two or more such components, unless the context clearly indicates otherwise.

[0036] With reference to FIGS. 1-3, photovoltaic (PV) modules 1, 1A, and 1B according to aspects of the present disclosure include cover glass 2 which may be in the form of a layer. An anti-reflective coating or texture 3 may be disposed on a sun-facing side 4 of photovoltaic module 1 (e.g., on cover glass 2) whereby reflection of sunlight L is reduced or eliminated. The sun-facing side 4 of module 1 may be referred to herein as the "upper" side of module 1. However, it will be understood that the photovoltaic module 1 and the components thereof may

have virtually any orientation. As discussed below, the photovoltaic module 1A (FIG. 2) may also include an AR coating or texture 3, and photovoltaic module 1B (FIG. 3) may include AR protrusions 16. It will be understood that the materials and features of the PV modules 1, 1A, and 1B are not mutually exclusive, but rather may be utilized in any combination. For example, a PV module according to the present disclosure may include a light extraction layer 18 comprising some triangular or pyramidal protrusions 19 and triangular grooves 21 (FIGS. 1 and 3) and may also include some rectangular protrusions 24 and rectangular grooves 26 (FIG. 2) (e.g., protrusions 19 and 24 in first and second regions of the PV module). Similarly, a PV module according to the present disclosure may include an AR coating 3 (FIGS. 1 and 2), and may also include protrusions 16 (FIG. 3) (e.g., AR coating 3 in a first region, and protrusions 16 in a second region).

[0037] Photovoltaic modules 1, 1A, 1B further include a phosphor-glass composite layer 5, an ethylene-vinyl acetate (EVA) or polymer bonding layer 6, and a photovoltaic (PV) device or layer 8. A light extraction layer 18 on a lower side of composite layer 5 may be utilized to direct at least some light towards bonding layer 6 and PV cell or layer 8. As discussed in more detail below, the PV device 8 may comprise a crystalline silicon solar cell or other suitable PV material such as amorphous silicon, cadmium telluride, or perovskite materials. As also discussed below, the phosphor-glass composite layer 5 may comprise a low Tg glass encapsulant material with phosphor particles embedded in the glass whereby the phosphor particles shift UV light in sunlight L into visible light that is transmitted through the bonding layer 6 to PV layer 8 whereby the visible light from the phosphor particles generates electrical power. As discussed in more detail below in connection with FIG. 6, during fabrication layers 2, 10, 18, and optionally layer 6 may form an upper structure 28 that is bonded to one or more PV cells or layers 8.

[0038] The phosphor-glass composite layer 5 preferably includes phosphor particles that are embedded in a glass encapsulant material that is substantially refractive index-matched to the phosphor particles. In general, the refractive index of the glass encapsulant material of the composite layer 5 is preferably about the same as the refractive index of the phosphor materials of the phosphor particles in composite layer 5 to minimize scattering of light due to differences in the refractive indices. However, it will be understood that the relative indices to not necessarily need to be identical, and some scattering of light in composite layer 5 may be acceptable, provided the scattering does not have a significant negative effect with regards to the efficiency of PV module 1, 1A, 1B.

[0039] As discussed in more detail below, during fabrication of photovoltaic module 1, 1A, 1B, the phosphor-in glass layer may be formed by coating a composite frit paste or slurry onto a rear surface 10 of cover glass 2. The cover glass 2 may comprise, for example, a low-iron soda lime glass having suitable mechanical and environmental durability. As also discussed in more detail below, preferred glass encapsulant materials of composite layer 5 may include low-Tg glasses with refractive indices from about 1.65 to about 1.85 that are preferably free of lead and fluorine, and may preferably comprise tin-containing glasses, including tin phosphates, tin silicates, tin borates, tin borosilicates, and tin borophosphates. Preferred phosphor materials for composite layer 5 include materials with broad UV absorption in the 300-400 nm wavelength range, low visible and near-IR absorption, and efficient conversion to visible or near IR light (e.g., quantum efficiency greater than 50%, 60%, 80% or 90%). Preferred phosphors for composite layer 5 may include barium magnesium silicates, which may be doped with Eu^{2+} and Mn^{2+}. Preferred phosphors may also include willemite (Zn_2SiO_4), barium magnesium silicates, calcium magnesium silicates and strontium magnesium silicates and mixed orthosilicates $(Ba,Sr,Ca)_2SiO_4$ or mixed magnesium silicates $(Ba,Sr,Ca)_xMg_ySiO_4$, which may be doped with Eu^{2+}, Eu^{3+}, Mn^{2+}, Dy^{3+}, Tb^{3+}, Ce^{3+}, Sm^{3+}, Yb^{3+}, Yb^{2+}, Nd^{3+}, Pr^{3+} and other rare earth dopants. Alkaline earth silicates can also be doped with N (Si_3N_4) to red shift the emission.

[0040] Referring again to FIG. 1, if PV layer 8 comprises crystalline silicon and cover glass 2 comprises soda lime glass, the preferred UV absorption range (photoluminescence excitation range) for the phosphor materials of composite layer 5 may be from about 250 to about 400 nm or from about 300 to about 400 nm. Sunlight L in these preferred UV absorption ranges is largely (preferably) transmitted through the cover glass layer 2, and comprise wavelengths that may not be converted to electricity with high efficiency in the PV layer 8, or would otherwise be strongly absorbed within the polymer bonding layer 6.

[0041] According to other aspects of the present disclosure, a photovoltaic module 1, 1A, 1B may utilize a photovoltaic material 8 other than crystalline silicon, such as amorphous silicon, cadmium telluride, or perovskite materials. In the case of alternative PV materials 8, the preferred absorption spectrum for the phosphor materials/particles of composite layer 5 may be adjusted, for example to be from about 250 to about 450 nm or from about 300 to about 450 nm. Preferred re-emission wavelengths (photoluminescent wavelengths) for the phosphor materials may be from about 400 to about 1100 nm, from about 450 to about 1050 nm, from about 500 to about 1000 nm, or from about 550 to about 900 nm.

[0042] Preferred phosphor materials may include those with broad UV absorption in a wavelength range of about 300 to about 400 nm, low visible and near-IR absorption, and efficient conversion to visible or near IR light (e.g., quantum efficiency greater than about 60%, about 80%, or about 90%). Preferred phosphors include barium magnesium silicates, which may be doped with Eu^{2+} and Mn^{2+}. Preferred phosphors may also include calcium magnesium silicates and strontium magnesium silicates, which may be doped with Eu^{2+}, Eu^{3+}, Mn^{2+}, Dy^{3+}, Tb^{3+}, Ce^{3+}, Sm^{3+}, Yb^{3+}, Yb^{2+}, Nd^{3+}, Pr^{3+} and other rare earth dopants. Preferred phosphor hosts may also include calcium, strontium, and barium aluminates, which may be doped with the same rare earth dopants listed above. Preferred phosphor hosts may further include calcium silicates, barium silicates, and strontium silicates, doped with the same rare earth dopants listed above. Preferred phosphors may comprise oxides which are lead-free and fluorine-free, for low toxicity and for good chemical durability and UV stability, thereby providing long lifetimes in outdoor solar applications. However, some embodiments may include phosphor-like materials that contain lead, including perovskite materials such as $CsPbCl_3$ which has been reported to achieve 'quantum cutting' photoluminescence with greater than 100% quantum efficiency.

[0043] Preferred glass encapsulant materials of composite layer 5 may also be lead-free and fluorine-free, for low toxicity and for good chemical durability and UV stability, thereby providing long lifetimes in outdoor solar applications. The glass encapsulant material of composite layer 5 is preferably highly transparent in the UV and visible wavelength ranges from about 300 to about 1100 nm. The glass of composite layer 5 preferably has a refractive index that can be tuned in the range from about 1.60 to about 1.90 to permit index matching with the preferred phosphor materials. Other preferred ranges for the refractive index of the glass composite layer 5 may include about 1.65 to about 1.88, and about 1.70 to about 1.85. The glass of the composite layer 5 may contain tin oxide and may comprise a tin phosphate glass or a tin borophosphate glass. The glass of composite layer 5 may be a $SnO\text{-}ZnO\text{-}P_2O_5$ glass, which may also be doped with Mn or other elements listed here, where the glass itself may demonstrate UV photoluminescence with quantum efficiencies as high as 88%.

[0044] Preferred glasses for composite layer 5 may have a Tg below about 550° C and softening temperatures below about 650° C. The Tg is preferably low enough to enable sintering of a powder/slurry/paste composite frit mixture into a transparent phosphor-glass composite at temperatures low enough to allow the phosphor materials to retain their composition, crystal structure, and quantum efficiency. To achieve highly transparent sintered frit-phosphor combinations in composite layer 5, it may be helpful, at least in some cases, to maintain a glass transition temperature for the glass encapsulant above about 300° C, above

about 320° C or above about 360° C, as required for a particular application. In general, maintaining the glass transition temperature above about 300° C preferably permits complete or substantially complete volatilization and removal of organic additives that may be in the composite frit. The composite frit may include organic additives to enable efficient and uniform coatings or cast films to be formed using suitable fabrication processes such as screen printing, tape casting, slot coating, knife coating, doctor blading, gravure coating, or the like. In general, during sintering of composite layer 5, the glass encapsulant preferably remains solid initially and does not start sintering until the frit reaches temperatures greater than about 300° C. This permits escape of volatile organic species through open pores in the frit, whereby the organics are not trapped in closed pores which can be created when the glass of the composite frit used to form composite layer 5 begins to sinter. Experiments demonstrated that tin borophosphate glasses with Tg's in the range of 260°-270° C are not preferred for combination with certain organic frit additives, because the Tg of these glasses is not high enough to allow for full volatilization of the organic frit additives before the glass starts to soften and create closed porosity. However, it will be understood that glasses with Tg's in the range of 260°-270° C may be utilized in composite frits that can be sintered at lower temperatures without trapping organics or other frit additives.

[0045] Thus, a preferred range of glass transition temperatures (which may be measured using known techniques such as differential scanning calorimetry) of the glass of composite layer 5 may be from about 300° C to about 550° C, from about 320° C to about 500° C, or from about 360° C to about 450° C. Preferred glass softening temperature ranges (which may be defined as the temperature where the glass has a viscosity of approximately $10^{\wedge 6.7}$ Pa·S or $10^{\wedge 7.7}$ poise) of the glass composite layer 5 may be from about 300° C to about 650° C, from about 350° C to about 600° C, from about 400° C to about 550° C, or from about 400° C to about 600° C.

[0046] Preferred glass systems for combination with phosphors in composite layer 5 may preferably comprise tin-containing or SnO-containing glasses, including tin phosphates, tin silicates, tin borosilicates, tin borophosphates, and tin borophosphosilicates. Preferred additives to these glasses may include Zn, Al, Mg, or Ca, which may be present in the glass as ZnO, Al_2O_3, MgO, or CaO species. It will be understood that variations in oxidation state and coordination may exist in these materials. In these glass systems, it may be preferred that the majority of the tin is present in the Sn2+ oxidation state, or as SnO in the oxide form (e.g., the SnO/SnO_2 ratio in the glass is greater than 1). In certain embodiments, the SnO content may be greater than about 10 mol%, greater than about 20 mol%, greater than about 30 mol%,

greater than about 40 mol%, greater than about 50 mol%, or greater than about 60 mol%. In some preferred glass compositions, the high SnO/SnO_2 ratio may facilitate achieving the target T_g and/or glass softening temperature range, as well as providing glass compositions that are resistant to moisture ingress.

[0047] A preferred combination of phosphor particle and glass encapsulant materials for composite layer 5 includes the phosphor $Ba_{2.9}Mg_{0.9}Si_2O_8:Eu^{2+}_{0.1}$, $Mn^{2+}_{0.1}$ or more generally written, $Ba_{3-x}Mg_{1-y}Si_2O_8:Eu^{2+}_x$, Mn^{2+}_y. This phosphor has a refractive index of about 1.77, broad UV absorption from about 300 to about 400nm, and low light absorption from about 430 to about 1000 nm. The quantum efficiency of this material has been reported to be about 86%. Another phosphor which may also be suitable is $Ba_2SiO_4:Eu^{2+}$, which is reported to have a quantum efficiency of about 93% and a refractive index of about 1.79 and also has broad UV absorption. However, the absorption band of this phosphor extends further into the visible range to about 480 nm, which may be less desirable for systems using crystalline silicon PV cells due to absorption of visible light that would otherwise be incident on PV layer 8 where it would generate electrical power. Nevertheless, this phosphor may be suitable for alternate PV materials as mentioned above.

[0048] Examples of preferred glass compositions utilized in composite layer 5 may comprise tin silicates with about 25 mol% < SnO < about 60 mol%; and about 40 mol% < SiO2 < about 75 mol%. A specific example is the binary glass 49 SnO – 51 SiO2. These glasses have a Tg in the range of about 400 to about 500° C, softening temperatures in the range of about 450 to about 550° C, and refractive indices in the range of about 1.65 to about 1.75.

[0049] Additional examples of preferred glass for composite layer 5 include Tin borophosphates with about 0 mol% < B_2O_3 < about 30 mol%; about 30 mol% < SnO < about 70 mol%; and about 30 mol% < P_2O_5 < about 60 mol%. A particularly preferred range of B_2O_3 content in this glass system is from about 5 to about 30mol%, which has been shown to result in Tg values from about 300 to about 370° C. A specific example glass composition includes $xB_2O_3 \cdot (100\text{-}x)(66.7SnO–33.3P_2O_5)$, with x = about 5 to about 25mol% which has been shown to have refractive index in the range of about 1.74 to about 1.78, which is a close match to the $Ba_3\text{-}xMg_1\text{-}_ySi_2O_8:Eu^2+_x$, Mn^{2+}_y phosphor described above. These tin borophosphate glass compositions have also been shown to have good UV light transmission for wavelengths longer than ~330nm, and good chemical durability compared to binary tin phosphate glasses.

[0050] ZnO additions to any of the above-mentioned glasses of composite layer 5 may preferably be in the range of about 0 to about 40 mol%.

[0051] Al_2O_3 additions to any of the above-mentioned glasses of composite layer 5 may preferably be in the range of about 0 to about 10 mol%.

[0052] Further tuning of the chemical durability and thermal expansion of tin borophosphate glass systems may involve the addition of dopants to the glass such as ZnO or Al_2O_3, replacement of B_2O_3 with ZnO, and other compositional changes within the general tin phosphate glass family. Filler particles (including the phosphor particles of composite layer 5) may be added to glass frits to tune (adjust) the thermal expansion of the frit and resulting glass. Preferably, the coefficient of thermal expansion for the phosphor glass composite layer 5 is tuned (adjusted) so it is close to (or equal to) the coefficient of thermal expansion of the cover glass 2. If cover glass 2 comprises a low-iron soda lime glass, the coefficient of thermal expansion (CTE) of the glass 2 is about 70-100 x 10^{-7} / °C in the 0-100° C temperature range, and the CTE of the glass of composite layer 5 may be tuned to match the CTE of cover glass 2 within a predefined range such that differences in the CTEs of cover glass 2 and composite layer 5 do not cause either or both layers to degrade when subject to a range of temperatures during use in an outdoor environment. For example, the CTEs of cover glass 2 and composite layer 5 may be sufficiently matched to permit a PV module 1, 1A, 1B to be at temperatures ranging from 0.0° F to 150° F without degradation of cover glass 2 and/or composite layer 5. Further compositions of tin phosphates and filler particle combinations can be found in Morena, R. (2000), "Phosphate glasses as alternatives to Pb-based sealing frits", Journal of non-crystalline solids, 263, 382-387, and in U.S. Patent 5,246,890, September 21, 1993 entitled "Non-Lead Sealing Glasses" the entire contents of both are hereby incorporated herein by reference.

[0053] As discussed above, the refractive indices of the phosphor particles and the glass material of composite layer 5 may be closely matched to maximize light transmission and minimize backscattering. However, there may be a relatively small refractive index difference between the refractive indices of the phosphor particles and the glass encapsulant. For example a difference of less than about 0.01 or about 0.02 or about 0.05, which may result in some forward scattering (which is generally acceptable) with minimal backscattering (which is undesirable due to reflecting external solar energy and preventing it from reaching the PV cell layer 8. If a refractive index difference of less than about 0.05, less than about 0.02, or less than about 0.01 between the phosphor and glass encapsulant of composite layer 5 does exist, the refractive index difference may preferably occur at wavelengths in the range of about 500 to about 900 nm, where Si PV cell efficiency is typically maximized. In some embodiments, the phosphor and glass encapsulant may have a refractive index difference which is minimized

(e.g., less than about 0.05) in a wavelength range from about 400 to about 1000nm or about 500 to about 900 nm (at any wavelength in the range, or in some cases for all wavelengths in this range). Larger index differences at wavelengths outside this range may be acceptable because the PV cell 8 is less efficient outside this range such that backscattering in wavelengths outside this range may result in minimal reductions in efficiency.

[0054] The phosphor particles and glasses used to form composite layer 5 may both be prepared as powders with particle size (D50) in the range of 1-50 microns or the range of 5-50 microns (e.g. a powder having a particle size distribution including some finer particles and some coarser particles), mixed with organic materials to form a frit paste or slurry, coated onto cover glass 2 using known methods such as tape casting or screen printing, and sintered (with glass 2) under atmospheric pressure or vacuum at a temperature of about 200 to about 650° C. The sintering process may substantially remove air voids and residual organic materials that may be present in the frit prior to sintering. The resulting sintered coating layer (composite layer 5) may have a thickness of about 50 to about 500 microns, and may have a total average light transmission from about 450 to about 1050 nm that is higher than about 75%, about 80%, about 85%, or about 90%.

[0055] In general, the phosphor particles of composite layer 5 may emit light in all directions, including away from the PV cell or layer 8, which is typically not desirable because light that does not reach PV layer 8 does not generate electricity. However, as discussed below in connection with FIGS. 4 and 5, light emitted in the phosphor-glass composite layer 5 can be trapped by total internal reflection at top surface 12 of cover glass 2 (FIGS. 1 and 2) or top surface 12A (FIG. 3) and/or top surface 14 of the phosphor-glass composite layer 5. For example, if the light emission is modeled as an array of point sources within a glass medium with refractive index n, the fraction of light that can escape at a flat air/glass interface, F, is given by:

$$F = \left\{ sin\left[\frac{sin^{-1}\left(\frac{1}{n}\right)}{2} \right] \right\}^2 \quad (1)$$

[0056] This equation ignores the small Fresnel refection of the light within the critical angle. This calculation shows that only about 13% of the light will directly escape the structure while about 87% will be directed towards the PV layer 8 in spite of the fact that the emission is isotropic in all directions.

[0057] Referring again to FIGS. 1 and 2, the anti-reflective (AR) coating or treatment 3 on cover glass 2 may comprise a thin film AR coating, a single quarter-wave AR coating, a multilayer AR coating, or a nanotexture AR coating. The AR coating 3 may comprise, for example, a porous SiO_2 layer, which may comprise a sol-gel coating material. The exterior 12A (FIG. 3) of cover glass 2 may comprise a macro-AR texture including protrusions 16 which may comprise pyramids, triangular prisms, or other suitable surface structure, that may be microns to millimeters in size. Macro-AR textures including protrusions 16 have been shown to increase transmission due to multi-bounce effects when the pyramid angle θ of protrusions 16 is greater than about 45°.

[0058] Cover glass 2 (FIGS. 1-3) may comprise thermally strengthened (tempered) low-iron soda-lime glass having mechanical and chemical durability, relatively high optical transmission, and relatively low cost. Thermal tempering of cover glass 2 may be combined with, or be subsequent to, a thermal sintering of the phosphor-glass composite layer 5. If tempering of glass 2 is combined with sintering of composite layer 5, a composite frit (slurry or paste) may be deposited on glass 2, and the glass 2 and frit of composite layer 5 may be heated simultaneously in a suitable oven/furnace. Cover glass 2 may also comprise a chemically strengthened (tempered) alkali silicate glass that may be strengthened through an ion-exchange process. These cover glasses may comprise, for example, an alkali aluminosilicate glass have 2 mol% or more of either Al_2O_3 or ZrO_2 in the glass composition.

[0059] As discussed above, a PV module according to the present disclosure may include a phosphor-glass composite layer 5 (FIGS. 1-3). In the PV modules of FIGS. 1-3, the phosphor-glass composite layer 5 may absorb at least some UV light that could otherwise lead to degradation and reduced optical transmission in bonding layer 6. Thus, in addition to converting UV light to visible light that is utilized by PV layer 8 to generate electrical power, the phosphor particles of composite layer 5 may also reduce UV degradation of bonding layer 6.

[0060] The purpose of the light extraction layer 18 is to frustrate total internal reflection (TIR) at the bottom interface of the phosphor-glass composite layer 5 (which has a higher refractive index than the cover glass 2 or the bonding layer 6), allowing more of the light emitted by the phosphor particles to reach the PV cell layer 8. Total internal reflection is typically not problematic at the top surface 14 of the phosphor-glass composite layer 5, and total internal reflection may be desirable at top surface 14 of composite layer 5. The total internal reflection may also be desirable at the top surface 12 of cover glass 2 at the interface with AR coating 3, as these contribute to trapping light emitted in the phosphor-glass composite layer.

[0061] Referring again to FIGS. 1-3, photovoltaic modules 1, 1A, 1B may include a light extraction layer 18. The light extraction layer 18 may be substantially index-matched to the phosphor-glass composite layer 5. For example, the light extraction layer 18 may comprise the same glass used in the phosphor-glass composite layer 5, with or without the phosphor particles. Dashed line 20 represents an interface between phosphor-glass composite layer 5 and light extraction layer 18. However, interface 20 may not comprise a physical interface (e.g., if composite layer 5 and light extraction layer 18 comprise identical materials).

[0062] The light extraction layer 18 may comprise triangular protrusions or prisms 19 and grooves 21 (FIG. 1) or rectangular protrusions 24 and rectangular grooves 26 (FIG. 2), or a more random rough layer. In addition to preventing detrimental internal reflection at the bottom surface of the layer (that is, directing light out of the cell), the geometry of the light extraction layer 18 may preferably be tuned (configured) to allow the highest possible transmittance for external solar light, most importantly for normal incidence angle solar rays L (FIGS. 1-3). The triangular and rectangular geometries shown in FIGS. 1 and 2 are configured to maximize normal incidence light transmission, which may dominate PV cell generation, especially in applications where sun-tracking systems are employed.

[0063] Although sub-wavelength diffractive structures may be used in the light extraction layer 18, in some cases it may be preferable to use larger features that can be formed by screen printing, gravure offset printing, and other suitable methods, thereby generating feature sizes in the 1-100 micron size range. During production, the light extraction layer 18 may optionally be screen printed or otherwise printed as a second layer over the first phosphor-glass composite layer 5 (e.g. composite layers 5 may be rotated 180° relative to the orientation of FIGS. 1-3). In these cases, it may be beneficial in some embodiments to choose a light extraction layer 18 with a refractive index that is intermediate between the refractive index of the phosphor-glass composite layer 5 and the refractive index of the bonding layer 6.

[0064] With further reference to FIGS. 4 and 5, the relative transmission and light trapping characteristics of the triangular and rectangular grooved interfaces between the phosphor-glass composite layer 5 and bonding layer 6 (FIGS. 1 and 2) were evaluated using a ray tracing optical model (computer program), the results of which are shown in FIGS. 4 and 5. In this modeling, it was assumed that both the bonding layer 6 and cover glass 2 have an index of 1.5, and it was also assumed that the phosphor-glass composite layer 5 has an isotropic, homogenous index of 1.77. The absorption of the Si layer 8 was calculated with variation of angle of the triangular grooves (FIGS. 1 and 4) and the aspect ratio of the rectangular grooves (FIGS. 2 and 5). The transmission of external direct sun, the transmission of diffuse

Lambertian light from the sky, and the multi-bounce trapping of light reflected from the Si layer 8 were also considered in the computer model. The triangular groove angle (FIGS. 1 and 4) is measured relative to the horizontal (e.g., plane "H"), such that an angle of zero degrees in FIG. 4 corresponds to a flat interface between composite layers and bonding layer 6. With reference to FIG. 4, preferred ranges of triangular groove elevation angle for the structure of FIG. 1 may include from about 15 degrees to about 30 degrees and from about 65 degrees to about 75 degrees. Preferred ranges of rectangular groove aspect ratio for the structure shown in FIG. 2 may include from about 0.5 to about 1.5 and from about 2.7 to about 4.0.

[0065] A method or process 50 for forming a photovoltaic module is shown in FIG. 6. It will be understood that the steps shown in the flowchart of FIG. 6 do not necessarily need to occur in any specific sequence. Process 50 includes forming the cover glass at step 52. As discussed above, cover glass 2 (FIGS. 1-3) may comprise a low-iron soda-lime glass, preferably including an anti-reflective (AR) coating or surface on at least a first (sun-facing) side of the cover glass 2. It will be understood that the AR surface or layer may be formed on cover glass 2 prior to or after forming phosphor-glass composite layer 5 and/or other layers are formed.

[0066] Referring again to FIG. 6, at step 54 a glass/phosphor frit paste or slurry is formed. As discussed above, the frit may comprise particles having a size in the range of about 1 to about 50 μm or about 5 to about 50 μm. The glass/phosphor composite frit includes phosphor particles, particles of encapsulant glass, and one or more organics that facilitate the formation of a slurry or paste that can be cast or printed onto surface 10 of cover glass 2. As discussed above, the phosphor particles and particles of encapsulant glass of the composite frit preferably have similar refractive indices to reduce scattering of light in the composite layer 5. As shown at step 55, the glass/phosphor composite frit may be coated onto surface 10 of cover glass 2 using a process such as casting or screen printing (It will be understood that surface 10 of glass 2 may face upwardly at the time the composite frit is deposited on surface 10 and sintered). Although casting or printing may be used, the glass/phosphor composite frit may be formed on surface 10 of glass 2 utilizing virtually any suitable process, and the present disclosure is not limited to casting or screen printing. Examples of suitable frit formulations include the following:

Frit 1:

- Tin borophosphate (or other glass) frit – 53 wt%
- PVA solution (10 wt%) - 30.7 wt%
- Citric acid ammonium salt – 0.4 wt%
- Glycerol – 4.5 wt%
- DI Water – 11.4 wt%

Frit 2:

- Tin borophosphate (or other glass) frit – 54 wt%
- Collodion (98 wt% Amyl Acetate, 2 wt% Nitrocellulose) - 46 wt%

In the frit formulations above, the glass is present in a particulate form, and may be substituted with e.g. 0.1 – 20 wt% of phosphor particles. It will be understood, however, that the present disclosure is not limited to these examples of suitable frits.

[0067] At step 56, diffractive structures may be formed on the glass/phosphor composite frit surface opposite the cover glass 2 by, for example, hot pressing the frit during sintering of the composite frit utilizing a die having surface features that are configured to form the desired refractive structures. As discussed above in connection with FIGS. 1-3, the diffractive structures may comprise triangular protrusions 19 and grooves 21, rectangular protrusions 24 and rectangular grooves 26, or other suitable diffractive structures that increase diffraction, refraction, or reflection to direct light towards the photovoltaic device layer.

[0068] Referring again to FIG. 6, at step 57 the glass/phosphor frit is sintered. The glass/phosphor composite frit may be sintered at about 200 °C to about 650 °C as required for the specific glass/phosphor composite frit composition. Sintering may optionally include initially raising a temperature of the glass/phosphor composite frit to a temperature below a glass transition temperature (Tg) of the encapsulant glass to permit escape of volatile organic species through open pores in the frit prior to completion of sintering at a higher temperature. At least a portion of the sintering is preferably done at a temperature that is high enough to remove air voids and residual organic materials from the phosphor-glass composite material, but below a temperature that would alter the desired light absorbing and light emitting properties of the phosphor particles in the composite frit. The sintered composite layer 5 may preferably have 1) a thickness of about 5 to about 500 microns; and 2) a total average light transmission from about 450 nm to about 1050 nm, wherein the average light transmission is preferably greater than about 75%, about 80%, about 85%, or about 90%.

[0069] The cover glass 2 may be thermally tempered after sintering (step 57) as shown at step 58 (FIG. 6). However, the cover glass 2 may also be tempered during sintering of the glass/phosphor composite frit at step 57. As discussed above, cover glass 2 may comprise thermally strengthened low-iron soda-lime glass, which may be chosen for its mechanical and chemical durability, relatively high optical transmission, and low cost. In general, the thermal tempering step 58 may be combined with, or be subsequent to, a thermal sintering step 57 of

the phosphor-glass composite layer. For example, if the sintering temperature of the glass/phosphor frit (step 57) is suitable for thermally tempering cover glass 2, steps 57 and 58 (FIG. 6) may be combined.

[0070] At step 60 (FIG. 6), the photovoltaic cell or layer 8 is bonded to the sintered composite layer 5 utilizing a suitable process and material. For example, a layer of ethylene vinyl acetate (EVA) may be positioned between the composite layer 5 and the photovoltaic cell layer 8, and the materials may be laminated at elevated pressure and/or temperature utilizing known processes. The photovoltaic cell layer may comprise a series of silicon wafers that can be joined together by wires or other electrical contacts either before or after bonding step 60. At steps 62 and 64, the structure may be segmented or cut to form individual photovoltaic modules 1 and electrical contacts may be formed if required. Alternatively, a plurality of individual (e.g., spaced apart) cells 8 may be bonded to a larger upper structure 28 (FIGS. 1-3), wherein structure 28 comprises cover glass 2, AR layer or surface 3, composite layer 5, and light extraction layer 18, and a plurality of separate bonding layers 6 may optionally have perimeter sizes that substantially match the perimeter sizes of the individual cells 8. Still further, a plurality of individual upper structures 28 may be formed and bonded to individual cells 8 having matching perimeter sizes. The photovoltaic panel may be completed with an additional bonding step, which for example may use EVA or another polymer bonding agent to attached a second glass, polymer, or metal backing sheet to the bottom side of the photovoltaic module.

[0071] Many variations and modifications may be made to the above-described embodiments/aspects of the disclosure without departing substantially from the spirit and various principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

CLAIM(S)

What is claimed is:

1. A photovoltaic module comprising:

a layer of cover glass;

a phosphor-glass composite layer disposed on a lower side of the layer of cover glass, wherein the phosphor-glass composite layer comprises phosphor particles embedded in a glass encapsulant material, wherein the phosphor particles have a refractive index that is within 0.05 of the refractive index of the glass encapsulant material, and absorb at least some light in a 250-400 nm wavelength range, and re-emit at least some light at wavelengths longer than 400 nm;

wherein the glass encapsulant material is substantially free of lead and fluorine and has a refractive index of 1.60-1.90 and a sufficiently low glass transition temperature (Tg) to permit sintering of a composite frit comprising particles of the glass encapsulant material and phosphor particles whereby the glass encapsulant material can be sintered together with the phosphor particles to reduce voids in the phosphor-glass composite layer without degrading the phosphor particles;

a photovoltaic cell disposed below the phosphor-glass composite layer whereby at least some light that is re-emitted from the phosphor-glass composite layer is converted into electricity by the photovoltaic cell.

2. The photovoltaic module of claim 1, wherein:

the photovoltaic cell comprises one or more materials selected from the group consisting of amorphous silicon, cadmium telluride, and perovskite material.

3. The photovoltaic module of claim 1, wherein:

the photovoltaic cell comprises a crystalline silicon solar cell.

4. The photovoltaic module of any of claims 1 to 3, wherein:

a majority of light in a wavelength range of 400nm-1,100nm is not absorbed and re-emitted by the phosphor particles.

5. The photovoltaic module of claim 4, wherein:

the phosphor particles comprise at least one material selected from the group consisting of barium magnesium silicates, calcium magnesium silicates, and strontium magnesium silicates.

6. The photovoltaic module of claim 5, wherein:

the phosphor particles comprise $Ba_{3-x}Mg_{1-y}Si_2O_8:Eu^{2+}_x$, Mn^{2+}_y.

7. The photovoltaic module of any of claims 1 to 6, wherein:

the Tg of the glass encapsulant material is sufficiently high to allow for volatilization and escape of organic additives utilized in a composite frit through open pores in the frit during sintering of the composite frit to form the phosphor-glass composite layer.

8. The photovoltaic module of claim 7, wherein:

the Tg of the glass encapsulant material of the phosphor-glass composite layer is greater than 300° C.

9. The photovoltaic module of any of claims 7 or 8, wherein:

the Tg of the glass encapsulant material of the phosphor-glass composite layer is sufficiently low to permit the phosphor particles to retain one or more of their composition, crystal structure, and quantum efficiency during sintering of a composite frit to form the phosphor-glass composite layer.

10. The photovoltaic module of claim 9, wherein:

the Tg of the glass encapsulant material of the phosphor-glass composite layer is less than 550° C.

11. The photovoltaic module of claim 9, wherein:

the Tg of the glass encapsulant material of the phosphor-glass composite layer is from 360° C-450° C, and a glass softening temperature of the glass encapsulant material is from 400° C-600° C, wherein the glass softening temperature is a temperature at which the glass encapsulant material of the phosphor-glass composite layer has a viscosity of about $10^{\wedge 6.7}$ Pa·S.

12. The photovoltaic module of any of claims 1 to 11, wherein:

the glass encapsulant material of the phosphor-glass composite layer comprises a material selected from the group consisting of tin-containing glass and SnO-containing glass.

13. The photovoltaic module of claim 12, wherein:

the glass encapsulant material of the phosphor-glass composite layer includes 1) tin silicates with 25 mol% < SnO < 60 mol%; and 40 mol% < SiO_2 < 75 mol%, or 2) tin borophosphates with 0 mol% < B_2O_3 < 30 mol%; 30 mol% < SnO < 70 mol%; and 30 mol% < P_2O_5 < 60 mol%, or a combination thereof.

14. The photovoltaic module of claim 13, wherein:

the glass encapsulant material of the phosphor-glass composite layer comprises $xB_2O_3 \cdot (100\text{-}x)(66.7SnO–33.3P_2O_5)$, with x = 5-25mol% having a refractive index in the range of 1.74-1.78;

the phosphor particles comprise $Ba_{3-x}Mg_{1-y}Si_2O_8:Eu^{2+}_x$, Mn^{2+}_y.

15. The photovoltaic module of claims 1 to 14, wherein:

the glass encapsulant material has a refractive index of 1.65-1.85.

16. A method of making a photovoltaic module, the method comprising:

forming a composite frit including particles of encapsulant glass, phosphor particles, and organic species, wherein the phosphor particles absorb at least some UV light and emit at least some visible light;

depositing the composite frit on a layer of cover glass;

sintering the composite frit to form an intermediate structure comprising a phosphor-glass composite layer and the layer of cover glass;

bonding a photovoltaic material to the intermediate structure.

17. The method of claim 16, wherein:

sintering the composite frit includes causing the organic species to escape from pores in the composite frit.

18. The method of claim 16 or claim 17, wherein:

the encapsulant glass has a glass transition temperature (Tg) that is less than a Tg of the cover glass;

at least a portion of the composite frit is in contact with the cover glass when the composite frit is sintered.

19. The method of any of claims 16 to claim 18, wherein:

the encapsulant glass defines a first refractive index;

the phosphor particles define a second refractive index; and

a difference between the first and second refractive indices is less than 0.05

20. The method of any of claims 16 to 19, wherein:

the phosphor particles comprise at least one material selected from the group consisting of barium magnesium silicates, calcium magnesium silicates, and strontium magnesium silicates;

the phosphor particles absorb at least some light in a 250-400 nm wavelength range, and re-emit at least some light at wavelengths longer than 400 nm;

the glass encapsulant material is substantially free of lead and fluorine and has a refractive index of 1.65-1.85; and

the photovoltaic cell comprises a crystalline silicon solar cell.