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- (71) **Applicant (for all designated States except US):** **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** **SASAKI, Makoto**, [JP/JP]; 33-1, Tamagawadai 2-chome, Setagaya, Tokyo 158-8583 (JP). **AOYAGI, Yasuhiro**, [JP/JP]; 33-1, Tamagawadai 2-chome, Setagaya, Tokyo 158-8583 (JP).
- (74) **Agents:** **NOWAK, Sandra, K.** et al.; 3M Center Office of Intellectual Property Counsel Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

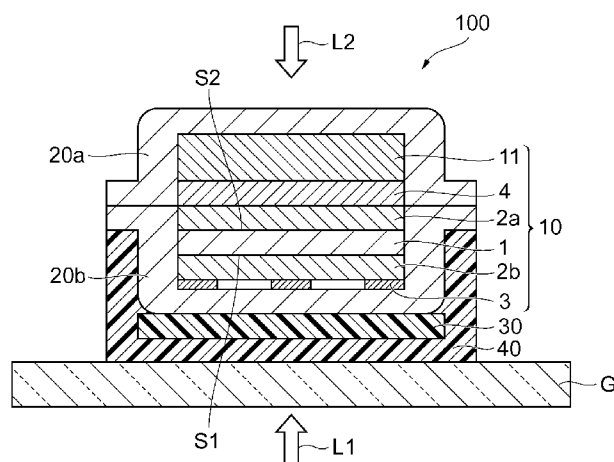
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(54) **Title:** TRANSPARENT IR CUT AND SHATTER RESISTANT SOLAR CELL WINDOW ADHESIVE FILMS



**FIG. 1**

(57) **Abstract:** The present disclosure generally relates to organic photovoltaic films and to photovoltaic cells including such films. In one exemplary embodiment, a multilayer photovoltaic film includes a first plastic film and a second plastic film and a photovoltaic battery positioned between the first and second plastic films. In some embodiments, the photovoltaic battery includes an organic photovoltaic conversion layer containing a fullerene material and at least one of a blue organic dye and a green organic dye. In some embodiments, the multilayer photovoltaic film includes an adhesive layer positioned between the photovoltaic battery and one of the first and second plastic films. In some embodiments, the multilayer photovoltaic film has a visible light transmission between about 20% and about 40%.

## TRANSPARENT IR CUT AND SHATTER RESISTANT SOLAR CELL WINDOW ADHESIVE FILMS

### Technical Field

5           The present disclosure generally relates to organic photovoltaic films and to photovoltaic cells including such films.

### Background

10           Some currently available photovoltaic cells, such as, for example, dye sensitization photovoltaic cells and organic thin layer photovoltaic cells, are relatively thin. Patent Application JP2000-243989 describes a transparent film type photovoltaic cell having increased electric power generation efficiency. This efficiency results from a design that permits light to enter from both sides. Patent Application JP2005-056627 describes a flexible dye sensitization photovoltaic cell in which an electrode film and an electrolyte  
15           solution have been enclosed in the space between two films. Patent Application JP2006-523369 describes a dye sensitization photovoltaic cell in which a patterned photovoltaic battery is placed in the space between two films. The patterned type photovoltaic cell contains a photovoltaic material. Also, a mesh electrode is placed on the side exposed to the sun.

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### Summary

25           Many buildings include glass wall surfaces, glass roofs, or glass ceilings. The inventors of the present disclosure recognized that by adhering a thin form factor organic photovoltaic film to a glass surface, it is possible to generate electrical power powered by sunlight.

30           Currently available photovoltaic cells include a dye compound. However, the inventors of the present disclosure recognized that when the photovoltaic battery is operating, the dye becomes concentrated in an area of the battery. This disadvantageously results in decreased visibility through the portion of the glass surface adjacent to the area of the battery including the concentrated dye. Further, light transmittance through the glass into the inside of the building or automobile is hindered for the portion of the glass surface adjacent to the area of the battery including the concentrated dye. Additionally,

the aesthetic appearance of the building can be negatively affected, as the concentrated dye areas can create a lack of uniformity in the internal and external appearance of the glass.

Additionally, in at least some instances, the dye material in the battery absorbs  
5 light in a specific wavelength range. Consequently, the photovoltaic film itself absorbs heat resulting from the absorbance of sunlight. In some instances, when the photovoltaic film is adhered onto glass and operated, the glass could be heated to such a level that the glass breaks (referred to as “heat break”).

The inventors of the present disclosure discovered a multilayer photovoltaic film  
10 capable of (1) maintaining a high electricity generation efficiency, (2) having sufficient transparency to exhibit excellent visibility and/or light transmittance, and/or (3) having a heat insulation effect that imparts a temperature decrease inside the building and/or reduces the incidence of heat break.

At least some of the multilayer photovoltaic films of the present disclosure  
15 comprise: a first plastic film and a second plastic film; an organic photovoltaic battery positioned between the first and second plastic films, the organic photovoltaic battery including a photovoltaic conversion layer containing a fullerene material and at least one of a blue organic dye and a green organic dye, the organic photovoltaic conversation layer having a thickness of between about 100 nm and about 200 nm; and an adhesive layer  
20 positioned between the photovoltaic battery and one of the first and second plastic films.

At least some of the photovoltaic films of the present disclosure include a first plastic film adjacent to a first side of a photovoltaic battery, a second plastic film adjacent to a second side of the photovoltaic battery; an infrared reflecting layer adjacent to the second plastic film; and an adhesive layer adjacent to the infrared reflecting layer. The  
25 photovoltaic battery comprises (1) a transparent electrode layer; (2) a first electroconductive layer; (3) an organic photovoltaic conversion layer containing a fullerene material and at least one of a blue organic dye and a green organic dye, the organic photovoltaic conversation layer having a thickness of between about 100 nm and about 200 nm; (4) a second electroconductive layer; and (5) a grid electrode.

In some embodiments, the multilayer photovoltaic film has a visible light  
30 transmission between about 20% and about 40%. In some embodiments, the first and second plastic films include at least one of PET and PEN. In some embodiments, the first

and second plastic films include the same materials. In some embodiments, the first and second plastic films include different materials. In some embodiments, the first and second plastic films have a thickness of between about 50 microns and about 500 microns. In some embodiments, the blue organic dye is PB30TP. In some embodiments, the green organic dye is at least one of APFO Green 1 and APFO Green 2. In some embodiments, the photovoltaic film includes blue organic dye and green organic dye. In some embodiments, the photovoltaic conversion layer further includes phenyl – C61 – butyric acid methyl ester. In some embodiments, at least one of the first and second electroconductive layers includes at least one of poly 3, 4 – ethylene dioxy thiophene (PEDOT) and poly 4-styrene sulfonic acid (PSS). In some embodiments, the infrared light reflecting layer is a multi-layer polymer film containing a first polymer layer and a second polymer layer where the first and second polymer layers include different polymers having refractive indices that vary by about 0.05 or less. In some embodiments, the infrared light reflecting layer includes at least one layer of a semi-crystalline type of naphthalene dicarboxylic acid polyester. In some embodiments, the multilayer photovoltaic film further includes a glass substrate adjacent to the adhesive layer. In at least some of the photovoltaic films of the present disclosure, the transmittance coefficient relative to the visible light rays is between about 20% and about 40%. In at least some of the embodiments of the present disclosure, the multilayer photovoltaic film includes a photovoltaic conversion layer that is a bulk hetero junction type photovoltaic conversion layer. In some embodiments of the present disclosure, the multilayer photovoltaic film includes a photovoltaic conversion layer that is a photoelectric conversion layer.

At least some of the multilayer photovoltaic films of the present disclosure further include an infrared reflecting layer between one of the first and second plastic films and the adhesive layer. In such embodiments, infrared light is reflected, which further increases the heat insulation effect.

### **Brief Description of the Drawing**

The present disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying drawing, in which:

Figure 1 is a schematic view showing one exemplary embodiment of a photovoltaic film of a type generally in accordance with the present disclosure.

### Detailed Description

In the following detailed description, reference may be made to the accompanying set of drawings that form a part hereof and in which are shown by way of illustration one specific exemplary embodiment. It is to be understood that other embodiments are contemplated and may be made without departing from the scope or spirit of the present disclosure. The following detailed description, therefore, is not to be taken in a limiting sense. The dimensions and ratios of the dimensions of the photovoltaic film are not limited to those shown in Figure 1.

As used herein, the term “transparent” means that the material allows the transmission of sunlight or artificially generated light in the same wavelength range as sunlight at an average light ray transmittance coefficient of at least 5% relative to the visible light region with a wavelength in the range of approximately 380 nm ~ 780 nm.

In some embodiments, the photovoltaic films of the present disclosure can be adhered to substrates, including, for example, windows, doors, partitions, walls, and ceilings of buildings or automobiles. In some embodiments, the photovoltaic films are adhered to glass substrates. However, the films of the present disclosure can be adhered to any substrate without departing from the teachings herein. In some embodiments, the photovoltaic films described herein advantageously collect and use incident sunlight and ambient light from a room to generate electricity.

Figure 1 is a schematic view of one exemplary embodiment of a multilayer photovoltaic film of the type generally described herein. Multilayer photovoltaic film 100 includes a first plastic film 20a and a second plastic film 20b between which is positioned an organic photovoltaic battery 10. An infrared reflecting layer 30 is positioned adjacent to second plastic film 2b, which is positioned adjacent to an adhesive layer 40 that can be used to adhere photovoltaic film 100 and infrared reflecting layer 30 to a substrate G, such as, for example, glass. Photovoltaic film 100 can have any desired thickness. In some embodiments, the entire multilayer film has a thickness between about 100 microns and about 2000 microns. Some embodiments have a total film thickness between about 180

microns and about 1600 microns. Some embodiments have a total film thickness between about 200 microns and about 500 microns.

Photovoltaic battery 10 includes a photovoltaic (*e.g.*, photoelectric) conversion layer 1 (which has a light receiving surface S1 and a surface opposite the light receiving surface S2). Photovoltaic conversion layer 1 is positioned between two electroconductive layers 2a and 2b. In the embodiment shown in Figure 1, electroconductive layer 2b is positioned adjacent to the light receiving surface S1 of photovoltaic conversion layer 1 and is adjacent to a grid electrode 3. In the embodiment shown in Figure 1, electroconductive layer 2a is positioned adjacent to surface S2 of photovoltaic conversion layer 1 and is positioned adjacent to a transparent electrode layer 4 which is adjacent to a substrate layer 11.

#### The First and Second Plastic Films

Some exemplary materials for use in the first and second plastic films include, for example, syndiotactic polystyrene (SPS), polyphenylene sulfide (PPS), polycarbonate (PC), polyacrylate (Par), polysulfon (PSF), polyester sulfon (PES), polyetherimide (PEI), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), or transparent polyimide (PI0). In some embodiments, the first and second plastic films include the same materials. In some embodiments, the first and second plastic films include different materials.

In some embodiments, any plastic material can be used that has a tensile modulus of a least approximately 100 N/25 mm and an extension coefficient of approximately 60% or greater, both of which assist in scattering prevention.

In some embodiments, at least one of the first and second plastic films 20a and 20b contain polyethylene terephthalate (PET) film or polyethylene naphthalate (PEN) film. In one exemplary implementation, one of the first and second plastic films is a PET film and the other of the first and second plastic films is a PEN film. In another exemplary implementation, both of the first and second plastic films are PET films. In another exemplary implementation, both of the first and second plastic films are PEN films.

There are no particular limitations regarding the thickness of the first and second plastic films. In some embodiments, the first and second plastic films have approximately the same thickness. In some embodiments, the first and second plastic films have

differing thicknesses. In some embodiments, the thickness of at least one of the first and second plastic films is between about 50 microns and about 500 microns. In some embodiments, the thickness of at least one of the first and second plastic films is between about 100 microns about 200 microns. In some embodiments for which glass scattering prevention is important, the thickness of at least one of the first and second plastic films is at least 50 microns.

#### The Organic Photovoltaic Battery

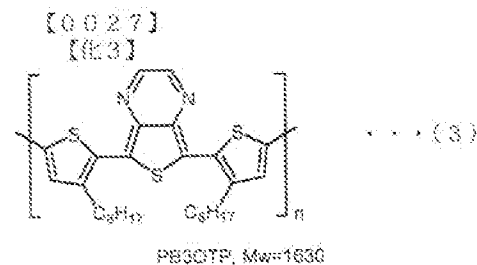
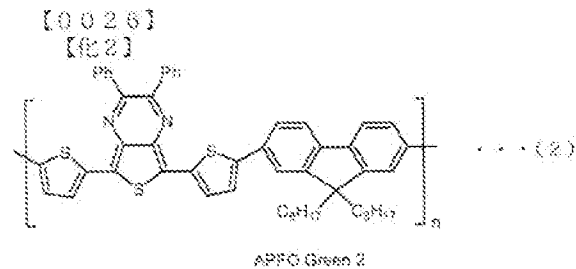
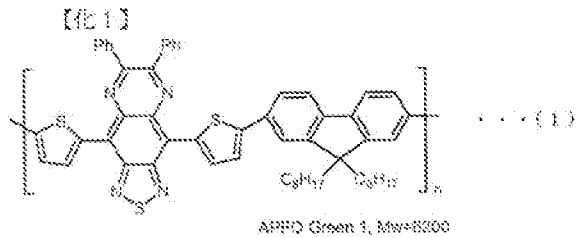
Photovoltaic battery 10 includes a photovoltaic (*e.g.*, photoelectric) conversion layer 1 positioned between two electroconductive layers 2a and 2b. In some embodiments, photovoltaic conversion layer 1 is a bulk hetero junction type photovoltaic conversion layer that has been formed from a mixed material obtained from an electron acceptor material (n-type organic semiconductor material) and an electron donor material (p-type organic semiconductor material). In this specific type of photovoltaic film, the electron donor and acceptor are mixed together, forming a polymer blend.

In some embodiments, the n-type organic semiconductor material is a fullerene derivative material that has a capability as an electron acceptor material. Exemplary fullerene materials include, for example, fullerene (C60) and the fullerene derivative materials that are obtained from fullerene (C60) by substitution. The following are some exemplary substitution radicals that can be used: aryl radicals and aliphatic acid alkyl ester radicals (including, for example, phenyl – C61 – butyric acid methyl ester (PCBM)).

In some embodiments, the p-type organic semiconductor material is at least one of a blue organic dye or a green organic dye. As used herein, the term “blue organic dye” refers to a dye that absorbs light with a wavelength outside of the 450 ~ 495 nm range.

One exemplary blue organic dye is PB30TP, whose chemical structure is shown below.

As used herein, the term “green organic dye” refers to dyes that absorb light with a wavelength outside of the 495 ~ 570 nm range. Some exemplary green organic dyes include APFO Green 1 and APFO Green 2, whose chemical structures are shown below.



The inclusion of the blue and/or green organic dyes in the photovoltaic conversion layer causes absorption of light having a wavelength outside the 450 ~ 495 nm range and/or the 495 ~ 570 nm range. Consequently, the photovoltaic film absorbs the heat from that incident light. As such, the photovoltaic film prevents or minimizes temperature increase inside a room or building that would otherwise result from sunlight transmitted through the glass windows, ceilings, or roofs. The use of a fullerene derivative material in the photovoltaic films further increases the heat insulating effect.

In some embodiments, the photovoltaic conversion layer includes only one of the blue or green organic dyes. In some embodiments, the photovoltaic conversion layer includes both blue and green organic dyes. Other dyes may also be included in the photovoltaic conversion layer. In one exemplary implementation, the photovoltaic conversion layer includes phenyl - C61 - butyric acid methyl ester (PCBM) and PB30TB. In another exemplary implementation, the photovoltaic conversion layer includes phenyl - C61 - butyric acid methyl ester (PCBM) and the APFO Green 1. In another exemplary implementation, the photovoltaic conversion layer includes phenyl - C61 - butyric acid methyl ester (PCBM) and APFO Green 2.

In some embodiments, the photovoltaic conversion layer has a thickness between about 100 nm and about 200 nm. Photovoltaic films having this range of thickness have a high photovoltaic conversion coefficient, good transparency, and good heat insulating properties. In some embodiments, photovoltaic conversion layers having a thickness of less than 100 nm may have an insufficient photovoltaic conversion coefficient, which could negatively affect transparency and heat insulation. In some embodiments, photovoltaic conversion layers having a thickness of greater than 200 nm may have decreased transparency and may experience heat break.

The photovoltaic conversion layer of the present disclosure has a heat insulating effect that exists even in the absence of an infrared reflecting layer. This heat insulating effect can decrease the temperature inside a room and can prevent or minimize the incidence of heat break. Inclusion of an infrared reflecting layer increases the heat insulation of the photovoltaic film because this layer further reduces incidence of infrared light (mainly the light in the range of 850 ~ 1100 nm) on the film.

In some embodiments, the photovoltaic films of the present disclosure are transparent and consequently, light incident on either side of the film (*e.g.*, on S1 or S2) can be effectively received and used for the generation of electricity.

Electroconductive layers 2a and 2b are formed from an electroconductive polymer. In some embodiments, the electroconductive polymers are transparent. Some exemplary materials that can be used in the electroconductive layers include poly 3,4 – ethylene dioxy thiophene (PEDOT) and poly 4-styrene sulfonic acid (PSS). In the specific embodiment shown in Figure 1, electroconductive layers 2a and 2b are positioned on both sides of photovoltaic conversion layer 1. However, in some alternative embodiments, the electroconductive layer 2b on the side of the grid electrode 3 is omitted and the grid electrode 3 is provided directly onto the photovoltaic conversion layer 1.

Grid electrode 3 collects the electric current generated and imparts it external to the photovoltaic film 100. Exemplary materials for use in the grid electrode 3 include, for example, gold (Au), silver (Ag), copper (Cu), cobalt (Co), nickel (Ni), and platinum (Pt). In some embodiments, silver is especially preferred because of its low resistance and cost. Grid electrode 3 can be in any pattern or form, such as, for example, a lattice type pattern (grid) made by a gravure printing method. There are no specific thickness requirements for the lines that form the grid structure, however, in some preferred embodiments, the

thicknesses are between about 10 microns and about 50 microns. There are also no specific grid pitch (the distance of the intra lattice space) requirements, however some embodiments have a grid pitch between about 200 microns and about 300 microns (the distance from the inner side of the grid lines, not including the lines themselves).

5           Transparent electrode layer 4 collects the electric current generated by the battery and transmits it to the external portions/layers of the multilayer photovoltaic film. Materials typically used in organic photovoltaic batteries can be used in the photovoltaic film of the present disclosure. Some exemplary materials include, for example, platinum, gold, silver, copper, aluminum, indium, etc., metals, graphite, carbon black, glassy carbon,  
10       carbon nano tubes, fullarene, carbon materials, TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO, Nb<sub>2</sub>O<sub>5</sub>, indium – lead composite oxides (TO), fluorine doped oxide – lead (FTO), indium chloride zinc (IZO), lead oxide, zinc oxide, and antimonium doped lead chloride. Some preferred implementations include, for example, indium – lead composite oxide (ITO) or indium chloride zinc (IZO). Transparent electrode layer can be, for example, sputtered or vacuum  
15       vapor deposited onto the adjacent layer (*e.g.*, the electroconductive layer).

          In some embodiments, transparent electrode layer 4 has a surface resistance of about 15  $\Omega/\square$  or less. In some embodiments, transparent electrode layer 4 has a surface resistance of about 10  $\Omega/\square$  or less. There are no particular requirements regarding the thickness of transparent electrode layer 4. However, in some embodiments, the thickness  
20       is between about 10 nm and about 150,000 nm. In some embodiments, the thickness is between about 20 nm and about 5000 nm. In some embodiments, the thickness is between about 30 nm and about 500 nm.

#### Additional Layers

25           Substrate material layer 11 is a layer that is formed from the substrate material of the organic photovoltaic battery 10. Any known material can be used to form the substrate material layer 11. In some embodiments, the substrate material layer 11 includes materials used in the first or second plastic films, as described above. There is no required thickness for the substrate material layer. Some exemplary embodiments have a substrate material  
30       layer having a thickness between about 50 microns and about 250 microns.

Infrared light reflecting layer 30 selectively reflects the infrared rays within the sun light. In some preferred embodiments, the infrared light reflecting layer is a multilayer polymer film containing a first polymer layer and a second polymer layer where the first and second layers include differing polymers having refractive indices that vary by about 0.05 or less along the first axis of the 3 mutually orthogonal axes (the axis orthogonal to the surface of the multi-layer polymer film). In some embodiments, the multi-layer polymer film includes at least one layer of a semi-crystalline type of naphthalene dicarboxylic acid polyester layer having a refractive index in at least one axis within the plane that is higher than that of the other polymer layer. One exemplary naphthalene dicarboxylic acid polyester is 2, 6 – poly ethylene naphthalate (“PEN”). An exemplary polymer for inclusion in the other layer is polyethylene terephthalate (“PET”). In some embodiments, the multilayer film is oriented (extended) in at least one direction. In some embodiments, the film has been oriented to a length that is at least 2 times the dimension in that direction. One exemplary commercially available infrared reflecting layer that can be used in the photovoltaic films of the present disclosure is the one described in Japanese Patent Application Number Hei-Sei 11-508380.

Adhesive layer 40 permits the photovoltaic battery and IR reflecting layer to be adhered onto a desired surface, including, for example, a glass surface. Additionally, if the glass surface breaks, due to, for example, an earthquake or other accident, the adhesive layer may prevent flying or falling of glass shards. In some embodiments, the adhesive layer has a separation force of approximately 4.0 N/25 mm or greater measured according to JIS A5759. The adhesive layer can have any desired thickness. Some embodiments include an adhesive layer having a thickness between about 30 microns and about 300 microns.

Known adhesives can be used in adhesive layer 40. Some exemplary adhesives include, for example, acrylic type adhesives, polyester type adhesives, rubber type adhesives, silicone adhesives, and polyurethane type adhesives. In some embodiments, acrylic type adhesives are preferred due to their weather resistance properties. Adhesive layer 40 can be applied using known methods. For example, the adhesive layer can be provided as an adhesive on the surface of a release paper that is dry laminated onto the surface of the infrared light reflecting layer, and then the release paper is removed. In some embodiments, adhesive layer 40 includes a removable liner, which can be removed

at the time of use of the photovoltaic film. Adhesive layer 40 can be positioned, for example, directly adjacent to the photovoltaic battery or can be positioned directly adjacent to the IR reflecting film.

In some embodiments, a scratch damage resisting coating, film, layer, or laminate is provided and acts as a protective film. In some embodiments, decorative or plastic films, laminates, layers, or coatings are provided, as is known in the glass scatter prevention field.

In some embodiments, the transmittance coefficient relative the visible light rays in the direction of the thickness of the multilayer photovoltaic film 100 is between about 20% and about 40%.

Additional advantages and embodiments of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure. In these examples, all percentages, proportions and ratios are by weight unless otherwise indicated.

## Examples

### Example 1

A photovoltaic film 100 with the structure shown in Figure 1 was prepared as follows.

First, the organic photovoltaic battery part (OPB) was prepared as follows. An ITO film (with a surface sheet resistance of  $10 \Omega/\square$ ) was vapor deposited by sputter deposition onto the surface of a 125 micron-thick transparent polyester film to form a transparent electrode layer 4. The resulting sheet was washed with acetone. Next, a PEDOT:PSS (poly (3, 4) – ethylene di oxy thiophene/polystyrene sulfonate) aqueous dispersion (manufactured by Bayer Company, Baytron P) was coated onto the surface of the ITO film. The resulting structure was dried for 10 minutes at a temperature of  $120^\circ \text{C}$  to form an 80 nm thick electroconductive layer (2a of Figure 1). A 1:4 (weight ratio) APFO Green 1:PCBM ([6, 6] – phenyl – C61 butyric acid methyl ester) solution was dissolved in a mixed solution of chloroform and toluene (weight ratio of 1:1). The resulting solution was coated onto the electroconductive layer and the resulting structure

was dried for 10 minutes at a temperature of 90° C to form a photovoltaic conversion layer (1 of Figure 1) having a thickness (after drying) of 100 nm.

A PEDOT:PSS (poly (3, 4) – ethylene di oxy thiophene/polystyrene sulfonate) aqueous dispersion (manufactured by Bayer Company, Baytron P) was coated onto the surface of the photovoltaic conversion layer. The resulting structure was dried for 10 minutes at a temperature of 120° C to form an 80 nm thick (after drying) electroconductive layer (2b of Figure 1). An electroconductive silver ink (manufactured by Toyo Ink Company) was gravure printed onto the electroconductive layer to form a micro grid. The grid had a grid line thickness of 25 microns and a grid pitch (distance on the inner side of the grid lines) of 250 microns.

The photovoltaic film was formed as follows. First, two plies of 50 micron-thick PET film (manufactured by Teijin DuPont Film Company) were obtained. On one surface of each of these films SiO<sub>2</sub> was sputter-deposited (thereby imparting moisture-repelling properties). One of the other surface of the PET film, a polyvinyl butyral solution was applied. The polyvinyl butyral solution included polyvinyl butyral manufactured by Denki Chemical Industries Company, trade name #3000-1 which was dissolved in a mixed solvent media of methyl ethyl ketone (MEK) and toluene (MEK : toluene = 1 : 1 (weight ratio)). The resulting structure was dried to form a 20 micron thick (after drying) adhesive layer. Using the adhesive, each of the two PET films were adhered to opposing sides of the above-described organic photovoltaic battery.

Then, 3M Scotchtint Nano 90 film (which acts as infrared light reflecting layer 30)(manufactured by Sumitomo 3M) was adhered to the PET film on the light receiving surface S1 side of the organic photovoltaic battery by dry laminating a 125 micron thick acrylic type adhesive (adhesive transfer tape, manufactured by 3M).

The electrode was produced through a bus bar from the ITO film (transparent electrode layer) and the micro grid.

### Example 2

The multilayer photovoltaic film of Example 2 was formed exactly as described in Example 1 except that the 3M Scotchtint Nano90 film was not present.

Example 3

The multilayer photovoltaic film of Example 3 was formed exactly as described in Example 1 except that the thickness of the photovoltaic conversion layer was 150 nm.

5      Example 4

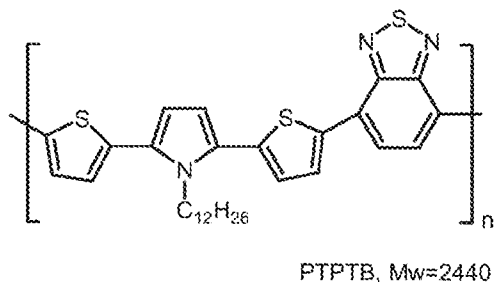
The multilayer photovoltaic film of Example 4 was formed exactly as described in Example 1 except that the thickness of the photovoltaic conversion layer was 200 nm.

Example 5

10      The multilayer photovoltaic film of Example 5 was formed exactly as described in Example 1 except that PB3OTP was used instead of APFO Green 1.

Comparative Example 1

15      The multilayer photovoltaic film of Comparative Example 1 was formed exactly as described in Example 4 except that the p-type semiconductor doped material used was to PTPTB (a red color organic dye material with the chemical formula shown below) instead of APFO Green 1.

20      Comparative Example 2

A 250 micron thick polyester film that had been colored by a gray dye material (colored film manufactured by Toyobo Company) was obtained. An acrylic type adhesive was layer laminated by dry lamination onto the polyester film to form a 125 micron thick adhesive layer.

25

### Comparative Example 3

The multilayer photovoltaic film of Comparative Example 3 was formed exactly as described in Example 2 except the thickness of the photovoltaic conversion layer was 80 nm instead of 100 nm.

5

### Comparative Example 4

A dye sensitization type photovoltaic battery (DSSC) was formed as follows. A laminated layer material formed from a plastic film and a transparent electrode (PECP – IP, manufactured by Peccell technologies Company) was obtained. Using 3M Company's silk screen printing device, a rectangular pattern of 80 mm x 8 mm x 6 rows was silk screen printed at a wet layer thickness of 125 microns onto the laminated layer material. The ink used was a TiO<sub>2</sub> ink (PECC – K1, manufactured by Peccell technologies Company). The resulting printed film was dried at normal temperature for a period of 30 minutes and was then dried in standard drying equipment for 30 minutes at 150° C. The resulting structure was immersed in a dye adhesion solution at a temperature of 40° C for a period of 120 minutes. The dye adhesion solution included 0.357 grams of RU complex dye material (PECD-07, manufactured by Peccell technologies) dissolved in 1000 ml solvent (t-butyl alcohol: ethyl alcohol : aceto nitrile in a 25:25:50 weight ratio). The TiO<sub>2</sub> surface on which the dye was adsorbed was washed using acetonitrile and was then dried.

On the printed surface, a hot melt film (which had been cut out in advance into the same pattern as the described above (80 mm x 8 mm x 6 rows rectangular shape) (TBF-615, manufactured by 3M Company)) was stacked so that the printed pattern and the cut shapes were facing each other. These films were dry laminated. An electrolyte solution (PECE-K01, manufactured by Peccell technologies Company, electric charge transfer layer) was poured and pipette onto the cut out parts of the hot melt film where the printed pattern was exposed. A plastic film was attached via heat seal lamination facing the electrode layer (PECF-CAT, manufactured by Peccell technologies Company) to form the dye sensitization type photovoltaic battery.

To 100 weight parts of an adhesive (AR-2327, manufactured by Big Teknos Company), 1.0 weight parts of isofuron diisocyanate type crosslinker (NV315E, manufactured by Big Teknos Company) was added. The resulting mixture was stirred using a Cowles mixer. The resulting mixture was coated on the surface of a 25 micron

thick (after drying) release-treated PET film (Ceropil, manufactured by Toray Film Manufacturing Company) using a knife coater. The surface of the resulting adhesive was attached to the above-described plastic films. The structure was laminated to form a photovoltaic cell.

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#### Comparative Example 5

The multilayer photovoltaic film of Comparative Example 5 was formed exactly as described in Comparative Example 1 except the thickness of the photovoltaic conversion layer was 80 nm instead of 200 nm.

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#### Comparative Example 6

The multilayer photovoltaic film of Comparative Example 6 was formed exactly as described in Comparative Example 4 except the ruthenium complex type dye material (product trade name N719, manufactured by Disol Company) was included.

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#### Comparative Example 7

The multilayer photovoltaic film of Comparative Example 7 was formed exactly as described in Comparative Example 5 except the thickness of the photovoltaic conversion layer was 80 nm instead of 200 nm.

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#### Comparative Example 8

The multilayer photovoltaic film of Comparative Example 8 was a shisuru-type thin layer silicon type photovoltaic cell manufactured by Sharp Company. This photovoltaic cell includes a battery enclosed between two pieces of bonded glass (reinforced glass).

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#### Comparative Example 9

The multilayer photovoltaic film of Comparative Example 9 was an amorphous-type photovoltaic cell manufactured by Fuji Denki Manufacturing Company.

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Each of the multilayer photovoltaic films described above were individually adhered onto commercially available window glass (front plate glass manufactured by Asahi Glass Company). The following properties were measured:

- visible light transmittance coefficients (measured according to JIS R3106 using a Hitachi Photo spectrometer U-4100);

- sun radiation (light) reflection coefficient (measured according to JIS R3106 using a Hitachi Photo spectrometer U-4100);

- sun light absorption coefficient (measured according to JIS R3106 using a Hitachi Photo spectrometer U-4100);

- temperature difference (using the body sensitive demo kit MDT5001, manufactured by 3M Company, a 150 W electric bulb was lit for a period of 30 minutes and after that the temperature of the side opposite to the electric bulb was measured at a position at a distance of 100 mm. The difference between this result and the result using normal glass is reported); the infrared light reduction coefficient (measured according to JIS R3106 using a Hitachi Photo spectrometer U-4100);

- heat break properties (a 150W electric bulb was lit for a period of 30 minutes and after that the glass was visually observed and the cases where there was no heat break visually observed, was denoted as "A" and the case where a heat break was visually observed was evaluated as "C");

- scatter prevention properties (measured according to JIS R3106; examples with especially excellent scatter prevention properties were designated "AA," examples with excellent scatter prevention properties were designated as "A," and examples with poor scatter prevention properties were designated as "C"; and

- electricity generating efficiency (the electricity generation efficiency ( $\eta$ ) relative to  $0.28 \text{ cm}^2$  was measured using the following measurement devices under conditions where the light intensity is AM 1.5, SUN: solar simulator: PEC-L11, manufactured by Peccell Technologies Company and IV curve analyzer with PECK 2400-N software, manufactured by Peccell Technologies Company and Peccell I-V curve analyzer (manufactured by Peccell Technologies Company).

The results of these tests, together with the properties of the photovoltaic films, are provided in Tables 1 and 2 below.

Table 1. Data Relating to Examples 1-5

| Example                                           | Example 1           | Example 2           | Example 3           | Example 4           | Example 5          |
|---------------------------------------------------|---------------------|---------------------|---------------------|---------------------|--------------------|
| Photovoltaic battery type                         | OPV                 | OPV                 | OPV                 | OPV                 | OPV                |
| Color                                             | Green (transparent) | Green (transparent) | Green (transparent) | Green (transparent) | Blue (transparent) |
| Organic dye coating thickness (nm)                | 100                 | 100                 | 150                 | 200                 | 200                |
| Visible light transmittance coefficient (%)       | 29.80               | 33.20               | 28.90               | 20.20               | 28.90              |
| Sun light reflectance coefficient (%)             | 20.50               | 13.00               | 17.70               | 20.90               | 20.50              |
| Sun light absorption coefficient (%)              | 64.60               | 67.50               | 65.60               | 69.20               | 67.50              |
| Temperature difference (oC)                       | -12                 | -10                 | -13                 | -15                 | -15                |
| Infra red cut coefficient                         | 95.80               | 91.02               | 91.02               | 91.02               | 91.02              |
| Heat break properties                             | A                   | A                   | A                   | A                   | A                  |
| Scatter prevention                                | AA                  | AA                  | AA                  | AA                  | AA                 |
| Electricity generation conversion coefficient (%) | 1.50                | 1.50                | 2.00                | 2.25                | 3.25               |
| Infra red light reflection layer – yes/no         | Yes                 | No                  | No                  | No                  | No                 |

Table 2. Data for Comparative Examples 1-9

| Sample Material                                   | Comp Ex 1         | Comp Ex 2          | Comp Ex 3           | Comp Ex 4                     | Comp Ex 5         | Comp Ex 6                     | Comp Ex 7          | Comp Ex 8         | Comp Ex 9             |
|---------------------------------------------------|-------------------|--------------------|---------------------|-------------------------------|-------------------|-------------------------------|--------------------|-------------------|-----------------------|
| Photovoltaic battery type                         | OPV               | -                  | OPV                 | DSSC                          | OPV               | DSSC                          | OPV                | thin film silicon | amorphous             |
| Color                                             | Red (transparent) | Blue (transparent) | Green (transparent) | Green (semi-transparent)      | Red (transparent) | Red (semi-transparent)        | Blue (transparent) | Deep blue (grid)  | Red (non-transparent) |
| Organic dye coating thickness (nm)                | 200nm             | Colored PET        | 80nm                | 5 $\mu$ m (TiO <sub>2</sub> ) | 80nm              | 5 $\mu$ m (TiO <sub>2</sub> ) | 80nm               | 400nm             | 400nm                 |
| Visible light transmittance coefficient (%)       | 11.80             | 25.90              | 35.20               | 18.00                         | 28.90             | 16.00                         | 33.90              | 8.00              | 0.00                  |
| Sun light reflectance coefficient (%)             | 18.00             | 7.70               | 10.70               | 7.70                          | 7.70              | 7.70                          | 10.70              | 7.70              | 7.70                  |
| Sun light absorption coefficient (%)              | 61.80             | 6.70               | 61.70               | 58.60                         | 56.70             | 55.80                         | 6.70               | 6.70              | 6.70                  |
| Temperature difference (oC)                       | -5                | 0                  | -4                  | -4                            | -3                | -4                            | -4                 | -3                | -15                   |
| Infra red cut coefficient                         | 91.02             | 11.02              | 81.02               | 69.70                         | 91.02             | 65.70                         | 81.02              | 81.02             | 98.02                 |
| Heat break properties                             | A                 | A                  | A                   | A                             | A                 | A                             | A                  | A                 | C                     |
| Scatter prevention                                | AA                | AA                 | AA                  | AA                            | AA                | AA                            | AA                 | C                 | A                     |
| Electricity generation conversion coefficient (%) | 3.25              | -                  | 0.40                | 3.05                          | 0.80              | 3.25                          | 0.50               | 9.25              | 4.65                  |
| Infra red light reflection layer – yes/no         | No                | No                 | No                  | No                            | No                | No                            | No                 | No                | No                    |

As used herein, the terms “a”, “an”, and “the” are used interchangeably and mean one or more; “and/or” is used to indicate one or both stated cases may occur, for example A and/or B includes, (A and B) and (A or B). As used herein, the terms "comprises," "comprising," "includes," "including," "containing," "characterized by," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus and including equivalents.

All references mentioned herein are incorporated by reference.

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the present disclosure and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached  
5 claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein. Further, any numerical range recited herein is intended to include and to specifically disclose the end points specified and also all integers and fractions within that range. For example, a range of from 1% to 50% is intended to be an abbreviation and to expressly disclose the values  
10 1% and 50% and also the values between 1% and 50%, such as, for example, 2%, 40%, 10%, 30%, 1.5 %, 3.9 % and so forth.

Various embodiments and implementation of the present disclosure are disclosed. The disclosed embodiments are presented for purposes of illustration and not limitation. The implementations described above and other implementations are within the scope of  
15 the following claims. One skilled in the art will appreciate that the present disclosure can be practiced with embodiments and implementations other than those disclosed. Those having skill in the art will appreciate that many changes may be made to the details of the above-described embodiments and implementations without departing from the underlying principles thereof. It should be understood that this disclosure is not intended to be unduly  
20 limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the disclosure intended to be limited only by the claims set forth herein as follows. Further, various modifications and alterations of the present disclosure will become apparent to those skilled in the art without departing from the spirit and scope of the present  
25 disclosure. The scope of the present application should, therefore, be determined only by the following claims.

## CLAIMS

1. A multilayer photovoltaic film, comprising:  
a first plastic film and a second plastic film;  
5 an organic photovoltaic battery positioned between the first and second plastic films, the organic photovoltaic battery including a photovoltaic conversion layer containing a fullerene material and at least one of a blue organic dye and a green organic dye, the organic photovoltaic conversation layer having a thickness of between about 100 nm and about 200 nm; and  
10 an adhesive layer positioned between the photovoltaic battery and one of the first and second plastic films.
2. The multilayer photovoltaic film of claim 1 having a visible light transmission between about 20% and about 40%.
- 15 3. The multilayer photovoltaic film of claim 1 or 2, further comprising:  
an infrared light reflecting layer positioned between one of the first or second plastic films and the adhesive layer.
- 20 4. The multilayer photovoltaic film of any of claims 1-3, in which the first and second plastic films include at least one of PET and PEN.
5. The multilayer photovoltaic film of any of claims 1-4, in which the first and second plastic films include the same materials.
- 25 6. The multilayer photovoltaic film of any of claims 1-5, in which the first and second plastic films include different materials.
7. The multilayer photovoltaic film of any of claims 1-6, in which the first and second  
30 plastic films have a thickness of between about 50 microns and about 500 microns.

8. The multilayer photovoltaic film of any of claims 1-7, in which the blue organic dye is PB30TP.

9. The multilayer photovoltaic film of any of claims 1-8, in which the green organic dye is at least one of APFO Green 1 and APFO Green 2.

10. The multilayer photovoltaic film of any of claims 1-9, including both the blue organic dye and the green organic dye.

11. The multilayer photovoltaic film of any of claims 1-10, in which the photovoltaic conversion layer includes phenyl – C61 – butyric acid methyl ester.

12. The multilayer photovoltaic film of any of claims 1-11, further comprising:  
a first electroconductive layer positioned between the photovoltaic conversion layer and the adhesive layer; and  
a second electroconductive layer positioned between the photovoltaic conversion layer and one of the first and second plastic films.

13. The multilayer photovoltaic film of claim 12, wherein at least one of the first and second electroconductive layers includes at least one of poly 3, 4 – ethylene di oxy thiophene (PEDOT) and poly 4-styrene sulfonic acid (PSS).

14. The multilayer photovoltaic film of claim 3, in which the infrared light reflecting layer is a multilayer polymer film containing a first polymer layer and a second polymer layer where the first and second polymer layers include different polymers having refractive indices that vary by about 0.05 or less.

15. The multilayer photovoltaic film of either of claims 3 or 14, in which the infrared light reflecting layer includes at least one layer of a semi-crystalline type of naphthalene dicarboxylic acid polyester.

16. The multilayer photovoltaic film of any of claims 1-15, further comprising:  
a glass substrate adjacent to the adhesive layer.
17. A multilayer photovoltaic film, comprising:  
5 a first plastic film adjacent to a first side of a photovoltaic battery;  
the photovoltaic battery comprising:  
a transparent electrode layer;  
a first electroconductive layer;  
an organic photovoltaic conversion layer containing a fullerene material and  
10 at least one of a blue organic dye and a green organic dye, the organic photovoltaic  
conversion layer having a thickness of between about 100 nm and about 200 nm;  
a second electroconductive layer; and  
a grid electrode;  
a second plastic film adjacent to a second side of the photovoltaic battery;  
15 an infrared reflecting layer adjacent to the second plastic film; and  
an adhesive layer adjacent to the infrared reflecting layer.
18. The multilayer photovoltaic film of claim 17 having a visible light transmission  
between about 20% and about 40%.  
20
19. The multilayer photovoltaic film of any of claims 17 or 18, in which the first and  
second plastic films include at least one of PET and PEN.
20. The multilayer photovoltaic film of any of claims 17-19, in which the first and  
25 second plastic films include the same materials.
21. The multilayer photovoltaic film of any of claims 17-20, in which the first and  
second plastic films include different materials.
- 30 22. The multilayer photovoltaic film of any of claims 17-21, in which the first and  
second plastic films have a thickness of between about 50 microns and about 500 microns.

23. The multilayer photovoltaic film of any of claims 17-22, in which the blue organic dye is PB30TP.

24. The multilayer photovoltaic film of any of claims 17-23, in which the green organic dye is at least one of APFO Green 1 and APFO Green 2.

25. The multilayer photovoltaic film of any of claims 17-24, including both the blue organic dye and the green organic dye.

26. The multilayer photovoltaic film of any of claims 17-25, in which the photovoltaic conversion layer includes phenyl – C61 – butyric acid methyl ester.

27. The multilayer photovoltaic film of any of claims 17-26, wherein at least one of the first and second electroconductive layers includes at least one of poly 3, 4 – ethylene di oxy thiophene (PEDOT) and poly 4-styrene sulfonic acid (PSS).

28. The multilayer photovoltaic film of any of claims 17-27, in which the infrared light reflecting layer is a multi-layer polymer film containing a first polymer layer and a second polymer layer where the first and second polymer layers include different polymers having refractive indices that vary by about 0.05 or less.

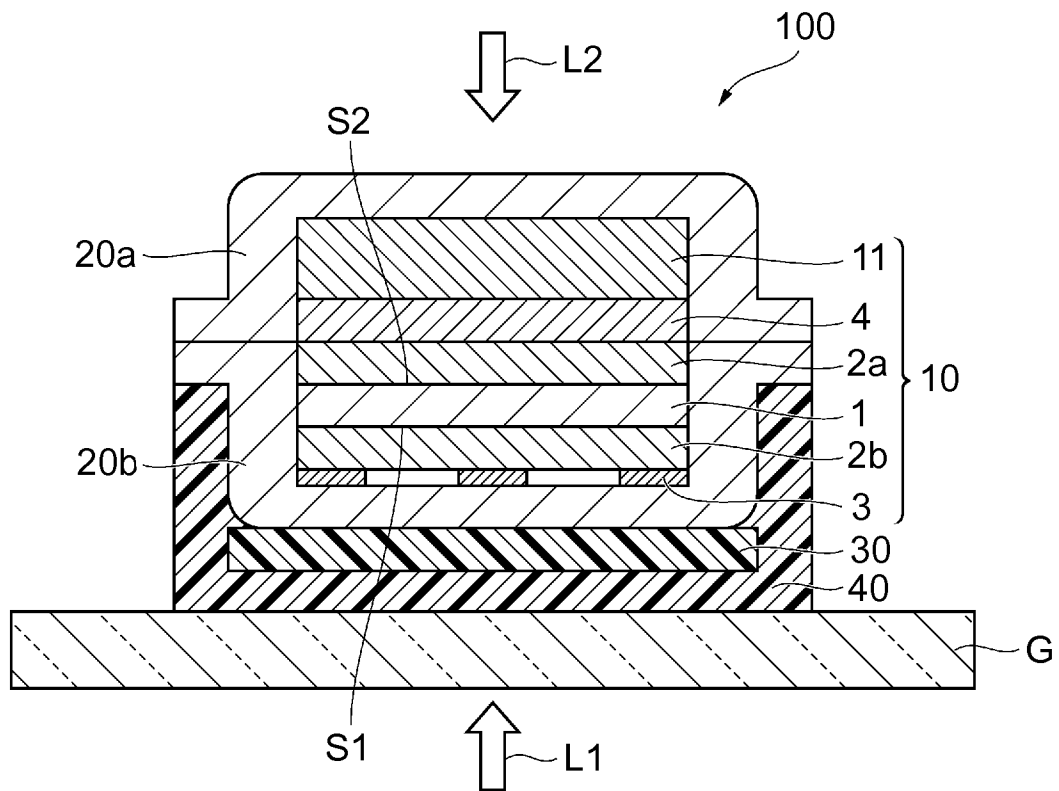
29. The multilayer photovoltaic film of any of claims 17-28, in which the infrared light reflecting layer includes at least one layer of a semi-crystalline type of naphthalene dicarboxylic acid polyester.

30. The multilayer photovoltaic film of any of claims 17-29, further comprising: a glass substrate adjacent to the adhesive layer.

31. The multilayer photovoltaic film of any of the previous claims, in which the photovoltaic conversion layer is a bulk hetero junction type photovoltaic conversion layer.

32. The multilayer photovoltaic film of any of the previous claims, in which the photovoltaic conversion layer is a photoelectric conversion layer.

1/1



**FIG. 1**

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2012/027051

## A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L51/42  
ADD. H01L51/00

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
H01L

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

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

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                    | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | DENNLER G ET AL: "A new encapsulation solution for flexible organic solar cells",<br>THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A.<br>LAUSANNE, CH,<br>vol. 511-512, 26 July 2006 (2006-07-26),<br>pages 349-353, XP025007205,<br>ISSN: 0040-6090, DOI:<br>10.1016/J.TSF.2005.12.091<br>[retrieved on 2006-07-26]<br>page 350 - page 351; figure 3<br>----- | 1-32                  |
| X         | US 2009/151776 A1 (SCHINDLER ULRICH [DE])<br>18 June 2009 (2009-06-18)<br>paragraphs [0089] - [0101]; figures 1-2<br>-----<br>-/-                                                                                                                                                                                                                     | 1-32                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

13 June 2012

Date of mailing of the international search report

25/06/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Konrádsson, Ásgeir

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/027051

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                                        |                              |
|------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                     | Relevant to claim No.        |
| A                                                    | <p>HOJUN YOON ET AL: "Application of infrared reflecting (IRR) coverglass on multijunction III-V solar cells", CONFERENCE RECORD OF THE 2006 IEEE 4TH WORLD CONFERENCE ON PHOTOVOLTAIC ENERGY CONVERSION (IEEE CAT. NO.06CH37747),, 1 May 2006 (2006-05-01), pages 1861-1864, XP031007694, ISBN: 978-1-4244-0016-4 the whole document</p> <p>-----</p> | <p>3,14,15,<br/>17,28,29</p> |

## INTERNATIONAL SEARCH REPORT

### Information on patent family members

International application No

PCT/US2012/027051

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| US 2009151776 A1                          | 18-06-2009          | DE 102007060108 A1         | 25-06-2009          |
|                                           |                     | US 2009151776 A1           | 18-06-2009          |
| -----                                     |                     |                            |                     |