(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau





(10) International Publication Number WO 2012/102449 A1

(43) International Publication Date 2 August 2012 (02.08.2012)

(51) International Patent Classification: H01L 31/18 (2006.01) **H01L 31/042** (2006.01)

(21) International Application Number:

PCT/KR2011/007394

(22) International Filing Date:

6 October 2011 (06.10.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 10-2011-0007516 25 January 2011 (25.01.2011) KR

- (71) Applicant (for all designated States except US): LG IN-NOTEK CO., LTD. [KR/KR]; Seoul Square, 541, Namdaemunno 5-ga, Jung-gu, Seoul 100-714 (KR).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): LIM, Chin Woo [KR/KR]; Seoul Square, 541, Namdaemunno 5-ga, Junggu, Seoul 100-714 (KR).
- (74) Agent: SEO, Kyo Jun; 9th Fl. Hyun Juk Bldg., 832-41, Yeoksam-dong, Gangnam-gu, Seoul 135-080 (KR).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

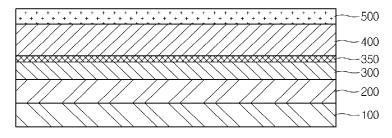
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: SOLAR CELL AND METHOD FOR MANUFACTURING THE SAME

[Fig. 1]



(57) Abstract: Disclosed are a solar cell and a method for manufacturing the same. The solar cell includes a substrate, a back electrode layer on the substrate, a light absorbing layer on the back electrode layer, a buffer layer on the light absorbing layer, and a window layer on the buffer layer. The buffer layer is formed through a chemical equation of $(A_x Zn_{1-x})O(0 \le x \le 1)$, in which the A represents a metallic element.





Description

Title of Invention: SOLAR CELL AND METHOD FOR MANU-FACTURING THE SAME

Technical Field

[1] The embodiment relates to a solar cell and a method for manufacturing the same.

Background Art

- [2] Recently, as energy consumption is increased, the development on a solar cell to convert solar energy into electrical energy has been performed.
- [3] In particular, a CIGS-based solar cell has been extensively used, in which the CIGS-based solar cell is a PN hetero junction device having a substrate structure including a glass substrate, a metallic back electrode layer, a P type CIGS-based light absorbing layer, a high resistance buffer layer, and an N type electrode layer.
- [4] In addition, studies have been performed to improve electrical characteristics such as low resistance and high transmittance in a solar cell.

Disclosure of Invention

Technical Problem

[5] The embodiment provides a solar cell representing high productivity with improved efficiency.

Solution to Problem

- [6] According to the embodiment, a solar cell includes a substrate, a back electrode layer on the substrate, a light absorbing layer on the back electrode layer, a buffer layer on the light absorbing layer, and a window layer on the buffer layer. The buffer layer is formed through a chemical equation of $(A_x Zn_{1-x})O(0 \le x \le 1)$, in which the A represents a metallic element.
- [7] According to the embodiment, a method for manufacturing a solar cell includes forming a back electrode layer on a substrate, forming a light absorbing layer on the back electrode layer, forming a buffer layer having a chemical formula of $(A_xZn_{1-x})O(0 \le x \le 1)$ on the light absorbing layer, in which the A represents a metallic element, and forming a window layer on the buffer layer.

Advantageous Effects of Invention

- [8] As described above, the embodiment can provide a solar cell capable of solving the problems related to environmental pollution due to the buffer layer without cadmium.
- [9] The embodiment can provide a solar cell capable of improving productivity by consecutively performing the manufacturing process because the buffer and window layers are formed through the same PVD process.

[10] The embodiment can provide a solar cell capable of increasing short circuit current density by increasing the transmittance due to the buffer layer including zinc, so that the photoelectric conversion efficiency can be improved.

Brief Description of Drawings

- [11] FIG. 1 is a sectional view showing a solar cell according to the embodiment; and
- [12] FIGS. 2 to 5 are sectional views showing a method for manufacturing a solar cell panel according to the embodiment.

Mode for the Invention

- [13] In the description of the embodiments, it will be understood that, when a layer (or film), a region, a pattern, or a structure is referred to as being "on" or "under" another substrate, another layer (or film), another region, another pad, or another pattern, it can be "directly" or "indirectly" over the other substrate, layer (or film), region, pad, or pattern, or one or more intervening layers may also be present. Such a position of the layer has been described with reference to the drawings. The thickness and size of each layer shown in the drawings may be exaggerated, omitted or schematically drawn for the purpose of convenience or clarity. In addition, the size of elements does not utterly reflect an actual size.
- [14] FIG. 1 is a sectional view showing a solar cell according to the embodiment. Referring to FIG. 1, a solar cell panel includes a support substrate 100, a back electrode layer 200, a light absorbing layer 300, a buffer layer 400, and a window layer 500.
- [15] The support substrate 100 has a plate shape and supports the back electrode layer 200, the light absorbing layer 300, the buffer layer 400, and the window layer 500.
- [16] The support substrate 100 may include an insulator. The support substrate 100 may include glass, polymer, or metal. In more detail, the support substrate 100 may include a soda lime glass substrate.
- [17] If the support substrate 100 includes soda lime glass, sodium (Na) contained in the soda lime glass may be diffused into the light absorbing layer 300 including CIGS when manufacturing the solar cell. Accordingly, the concentration of charges of the light absorbing layer 300 may be increased.
- [18] Therefore, the photoelectric conversion efficiency of the solar cell may be increased.
- [19] In addition, the support substrate 100 may include a ceramic substrate including alumina, stainless steel, or polymer having flexibility. Therefore, the support substrate 100 may be transparent, rigid, or flexible.
- [20] The back electrode layer 200 is provided on the support substrate 100. The back electrode layer 200 is a conductive layer. The back electrode layer 200 moves charges generated from the light absorbing layer 300 of the solar cell so that current can flow to

the outside of the solar cell. The back electrode layer 200 must represent high electrical conductivity or low resistivity to perform the functions.

- [21] In addition, since the back electrode layer 200 makes contact with a CIGS compound constituting the light absorbing layer 300, the back electrode layer 200 must make ohmic contact with the light absorbing layer 300, so that low contact resistance can be made.
- The back electrode layer 200 must maintain stability under the high-temperature condition when the heat treatment process is performed under sulfur (S) or selenium (Se) atmosphere as the CIGS compound is formed. In addition, the back electrode layer 200 must represent a superior adhesive property with respect to the support substrate 100 such that the back electrode layer 200 is not delaminated from the support substrate 100 due to the difference in the thermal expansion coefficient between the back electrode layer 200 and the support substrate 100.
- [23] The back electrode layer 200 may include one selected from the group consisting of molybdenum (Mo), gold (Au), aluminum (Al), chrome (Cr), tungsten (W), and copper (Cu). Among them, the Mo represents the low thermal expansion coefficient difference with respect to the support substrate 100 as compared with other elements. Accordingly, the Mo represents a superior adhesive property with respect to the support substrate 100 to prevent the back electrode layer 200 from being delaminated the support substrate 100. In addition, the Mo satisfies the characteristics required with respect to the back electrode layer 200.
- [24] The back electrode layer 200 may include at least two layers. In this case, the layers include the same metal, or different metals.
- The light absorbing layer 300 may be formed on the back electrode layer 200. The light absorbing layer 300 includes a P type semiconductor compound. In more detail, the light absorbing layer 300 includes group I-III-V compounds. For example, the light absorbing layer 300 may have a Cu-In-Ga-Se-based crystal structure (Cu(In,Ga)Se2;CIGS), a Cu-In-Se-based crystal structure, or a Cu-Ga-Se based crystal structure.
- [26] The energy band gap of the light absorbing layer 300 may be in the range of about 1.1eV to about 1.2eV.
- The buffer layer 400 is provided on the light absorbing layer 300. In a solar cell including a CIGS compound constituting the light absorbing layer 300, a PN junction is formed between a CIGS compound thin film including a P type semiconductor and the window layer 500 including an N type semiconductor. However, since two above materials represent great difference in a lattice constant and band gap energy, a buffer layer having the intermediate band gap between the band gaps of the two materials is required in order to form a superior junction.

[28] The buffer layer 400 includes CdS or ZnS, and the CdS represents superior generating efficiency of the solar cell. However, a buffer layer including cadmium (Cd) causes environmental pollution. To this regard, according to the embodiment, the buffer layer 400 includes an organic metallic compound including zinc (Zn) instead of the CdS buffer layer.

- [29] According to the embodiment, the buffer layer 400 may include $(A_xZn_{1-x})O(0 \le x \le 1)$ materials, in which the A represents a group II element. According to the embodiment, although the buffer layer 400 includes MgZnO, the buffer layer 400 may include a compound containing Zn, and an element such as Ca or Sr may be used instead of Mg.
- [30] In the chemical formula of the buffer layer 400, the x has a value in the range of about 0.1 to about 0.5. The buffer layer 400 may have energy band gap in the range of about 3.3eV to about 3.6eV, and have a thickness in the range of about 10nm to about 100nm.
- [31] A zinc diffusion layer 350 may be formed at the contact region between the light absorbing layer 300 and the buffer layer 400. The zinc diffusion layer 350 is formed by the diffusion of Zn, which is contained in the buffer layer 400 when the buffer layer 400 is formed, into the light absorbing layer 300. For example, the zinc diffusion layer 350 may represent as a chemical formula of CIGS:Zn.
- [32] The zinc diffusion layer 350 may have a thickness of about 10nm to about 100nm. Since the zinc diffusion layer 350 includes an N type semiconductor. Since the buffer layer 400 including the N type semiconductor and the zinc diffusion layer 350 form homo-junction, the recombination of carriers can be reduced at the boundary surface between the light absorbing layer 300 and the buffer layer 400, so that the electrical characteristic of the solar cell can be improved.
- [33] The energy band gap of the zinc diffusion layer 350 may be in the range of about 2.4eV to about 2.8eV.
- [34] The window layer 500 is formed on the buffer layer 400. The window layer 500 is a transparent conductive layer. In addition, the resistance of the window layer 500 is higher than that of the back electrode layer 200.
- [35] The window layer 500 includes an oxide. For example, the window layer 500 may include zinc oxide, indium tin oxide (ITO), or indium zinc oxide (IZO).
- [36] For example, according to the embodiment, the window layer 500 may include Ga doped zinc oxide (ZnO:Ga). The mass ratio of Ga in the ZnO:Ga may be in the range of about 0.1% to about 3%. The mass ratio having the range is required to form the window layer 500 having energy band gap higher than that of the buffer layer 400, and the energy band gap of the window layer 500 may be in the range of about 3.6eV to about 3.8eV.
- [37] In addition, the oxide may include conductive impurities such as aluminum (Al),

- alumina (Al₂O₃), magnesium (Mg), or gallium (Ga). In more detail, the window layer 500 may include Al doped zinc oxide (AZO) or Ga doped zinc oxide (GZO).
- [38] According to the solar cell of the embodiment, the buffer layer 400 without Cd is formed, so that the problems related to the environmental pollution can be solved. In addition, since the buffer layer 400 includes Zn, transmittance can be increased, so that short circuit current density J_{sc} can be increased.
- [39] In addition, since the buffer layer 400 and the window layer 500 are formed through the same PVD (Physical Vapor Deposition) process, the manufacturing process can be consecutively performed, so that productivity can be improved.
- [40] FIGS. 2 to 5 are sectional views showing the method for manufacturing the solar cell according to the embodiment. The description about the method for manufacturing the solar cell will be made based on the above description about the solar cell. The description about the solar cell may be basically linked with the description about the method for manufacturing the solar cell.
- [41] Referring to FIG. 2, after forming the back electrode layer 200 on the support substrate 100, the back electrode layer 200 may be deposited by using Mo. The back electrode layer 200 may be formed through the PVD scheme or a plating scheme.
- [42] In addition, an additional layer such as an anti-diffusion layer may be interposed between the support substrate 100 and the back electrode layer 200.
- [43] Referring to FIG. 3, the light absorbing layer 300 is formed on the back electrode layer 200.
- [44] For example, the light absorbing layer 300 may be formed through various schemes such as a scheme of forming a Cu(In,Ga)Se2 (CIGS) based-light absorbing layer 300 by simultaneously or separately evaporating Cu, In, Ga, and Se and a scheme of performing a selenization process after a metallic precursor film has been formed.
- [45] Regarding the details of the selenization process after the formation of the metallic precursor layer, the metallic precursor layer is formed on the back contact electrode 200 through a sputtering process employing a Cu target, an In target, or a Ga target.
- [46] Thereafter, the metallic precursor layer is subject to the selenization process so that the Cu(In,Ga)Se2 (CIGS) based-light absorbing layer 300 is formed.
- [47] Different from the above, the sputtering process employing the Cu target, the In target, and the Ga target and the selenization process may be simultaneously performed.
- [48] In addition, a CIS or a CIG light absorbing layer 300 may be formed through a sputtering process employing only Cu and In targets or only Cu and Ga targets and the selenization process.
- [49] Referring to FIG. 4, the buffer layer 400 is formed on the light absorbing layer 300. The buffer layer 400 may include Zn. Although the buffer layer 400 includes MgZnO,

which is an organic metallic compound including Mg or O according to the present embodiment, the buffer layer 400 may include a group II element such as Ca or Sr other than Mg. The buffer layer 400 may be formed through the PVD scheme, and may have a thickness of about 10nm to about 100nm.

- [50] The zinc diffusion layer 350 may be formed by the diffusion of Zn, which is contained in the buffer layer 400, into the light absorbing layer 300. The zinc diffusion layer 350 may have an intermediate band gap between band gaps of the light absorbing layer 300 and the buffer layer 400. For example, the zinc diffusion layer 350 may have a band gap in the range of about 2.2eV to about 2.8eV.
- [51] Referring to FIG. 5, the window layer 500 is formed on the buffer layer 400. The window layer 500 is formed by depositing a transparent conductive material on the buffer layer 400.
- [52] As described above, the embodiment can provide a solar cell capable of solving problems related to environmental pollution by employing a buffer layer without cadmium.
- [53] The embodiment can provide a solar cell capable of improving productivity by consecutively performing the manufacturing process because the buffer and window layers are formed through the same vacuum process.
- [54] In addition, the embodiment can provide a solar cell capable of increasing short circuit current density by increasing the transmittance due to the buffer layer including Zn, so that the photoelectric conversion efficiency can be improved.
- [55] Any reference in this specification to 'one embodiment', 'an embodiment', 'example embodiment', etc., means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the invention. The appearances of such phrases in various places in the specification are not necessarily all referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with any embodiment, it is submitted that it is within the purview of one skilled in the art to effect such feature, structure, or characteristic in connection with other ones of the embodiments.
- [56] Although embodiments have been described with reference to a number of illustrative embodiments thereof, it should be understood that numerous other modifications and embodiments can be devised by those skilled in the art that will fall within the spirit and scope of the principles of this disclosure. More particularly, various variations and modifications are possible in the component parts and/or arrangements of the subject combination arrangement within the scope of the disclosure, the drawings and the appended claims. In addition to variations and modifications in the component parts and/or arrangements, alternative uses will also be apparent to those skilled in the art.

Claims

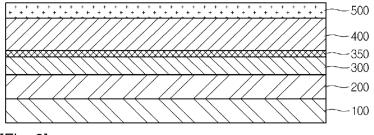
[Claim 1]	A solar cell comprising: a substrate;
	a back electrode layer on the substrate;
	a light absorbing layer on the back electrode layer;
	a buffer layer on the light absorbing layer; and
	a window layer on the buffer layer,
	wherein the buffer layer is formed through a chemical equation of (A _x
	Zn_{1-x})O(0 \le x \le 1), in which the A represents a metallic element.
[Claim 2]	The solar cell of claim 1, wherein the A of the buffer layer represents a group II element.
[Claim 3]	The solar cell of claim 1, wherein the A of the buffer layer represents
	magnesium (Mg).
[Claim 4]	The solar cell of claim 1, wherein the x has a value in a range of about
	0.1 to about 0.5.
[Claim 5]	The solar cell of claim 1, wherein the buffer layer has band gap in a
	range of about 3.3eV to about 3.6eV.
[Claim 6]	The solar cell of claim 1, wherein the buffer layer has a thickness in a
	range of about 10nm to about 100nm.
[Claim 7]	The solar cell of claim 1, further comprising a zinc diffusion layer
	formed in the light absorbing layer making contact with the buffer
	layer.
[Claim 8]	The solar cell of claim 7, wherein the zinc diffusion layer has band gap
	in a range of about 2.2eV to about 2.8eV.
[Claim 9]	The solar cell of claim 7, wherein the zinc diffusion layer has a
	thickness in a range of about 10nm to about 100nm.
[Claim 10]	The solar cell of claim 1, wherein the substrate includes at least one of
	glass and polymer metal.
[Claim 11]	A method for manufacturing a solar cell, the method comprising:
	forming a back electrode layer on a substrate;
	forming a light absorbing layer on the back electrode layer;
	forming a buffer layer having a chemical formula of $(A_x Zn_{1-x})$
	$O(0 \le x \le 1)$ on the light absorbing layer, in which the A represents a
	metallic element; and
F.C.1	forming a window layer on the buffer layer.
[Claim 12]	The method of claim 11, wherein the buffer layer is formed through a
	physical vapor deposition process.

PCT/KR2011/007394

WO 2012/102449

[Claim 13]	The method of claim 11, wherein the x has a value in a range of about
	0.1 to about 0.5.
[Claim 14]	The method of claim 11, wherein the window layer is formed through a
	physical vapor deposition process.

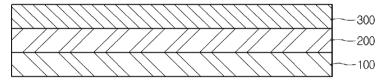




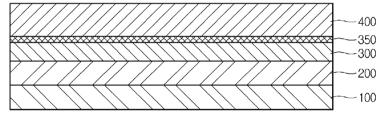
[Fig. 2]



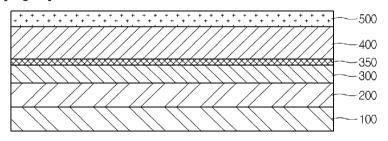
[Fig. 3]



[Fig. 4]



[Fig. 5]



International application No. PCT/KR2011/007394

A. CLASSIFICATION OF SUBJECT MATTER

H01L 31/042(2006.01)i, H01L 31/18(2006.01)i

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 31/042; H01L 31/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS(KIPO internal) & Keywords: Buffer, ZnO, MgO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2008-0009346 A (LG CHEM. LTD.) 29 January 2008 See paragraphs [0021]-[0039] and claims 1-5.	1-14
A	KR 10-2010-0066975 A (LG INNOTEK CO., LTD.) 18 June 2010 See abstract and claims 1-3.	1-14
А	WO 2010-058640 A1 (MITSUBISHI HEAVY INDUSTRIES, LTD. et al.) 27 May 2010 See abstract and claims 1-4.	1-14

		Further	documents	are	listed	in	the	conti	nuatior	ιof	`Box	C.
--	--	---------	-----------	-----	--------	----	-----	-------	---------	-----	------	----

 \boxtimes

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
- 'E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of 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
21 JUNE 2012 (21.06.2012)

Date of mailing of the international search report

22 JUNE 2012 (22.06.2012)

Name and mailing address of the ISA/KR



Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

KIM Min Soo

Telephone No. 82-42-481-8249



INTERNATIONAL SEARCH REPORT

International application No.

Information on patent family members

Information on patent family members			PCT/KR2011/007394		
Patent document cited in search report	Publication date	Patent family member(s)	Publication date		
KR 10-2008-0009346 A	29.01.2008	None			
KR 10-2010-0066975 A	18.06.2010	None			
WO 2010-058640 A1	27.05.2010	CN 102113127 A EP 2348541 A1 JP 2010-123737 A KR 10-2011-0018951 A US 2011-0120521 A1	29.06.2011 27.07.2011 03.06.2010 24.02.2011 26.05.2011		