



(43) International Publication Date
29 November 2012 (29.11.2012)

- (51) International Patent Classification:
H01L 31/0749 (2012.01) *H01L 31/18* (2006.01)
H01L 31/042 (2006.01)
- (21) International Application Number:
PCT/KR2012/000813
- (22) International Filing Date:
2 February 2012 (02.02.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
10-2011-0049768 25 May 2011 (25.05.2011) KR
- (71) Applicant (for all designated States except US): **KOREA INSTITUTE OF ENERGY RESEARCH** [KR/KR]; 102 Gajeong-ro, Yuseong-gu, Daejeon 305-343 (KR).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **AHN, SeJin** [KR/KR]; 1101-1206, Yeolmae Maeul 11 Danji, Noeun-dong, Yuseong-gu, Daejeon 305-768 (KR). **YOON, Kyung-Hoon** [KR/KR]; 101 -202, Hyundai Apt., Doryong-dong, Yuseong-gu, Daejeon 305-340 (KR). **YUN, Jae-Ho** [KR/KR]; 210-704, Beodeunae Apt., Taepyeong-dong, Jung-gu, Daejeon 301-150 (KR). **GWAK, Ji-hye** [KR/KR]; 710, Taesan Sigmavil, 936 Dunsan-dong,

Seo-gu, Daejeon 302-120 (KR). **CHO, Ara** [KR/KR]; 110-802, Gwanak Dreamtown Apt., Bongcheon 5-dong, Gwanak-gu, Seoul 151-050 (KR). **SHIN, Kee-Shik** [KR/KR]; 505-801, Expo Apt., Jeonmin-dong, Yuseong-gu, Daejeon 305-762 (KR). **AHN, SeungKyu** [KR/KR]; 202, 113-11 Eoeun-dong, Yuseong-gu, Daejeon 305-807 (KR).

(74) Agent: **DAWOOL PATENT AND LAW FIRM**; 5th Floor, Hyejeon Bldg., 224 Bongeunsa-ro, Gangnam-gu, Seoul 135-913 (KR).

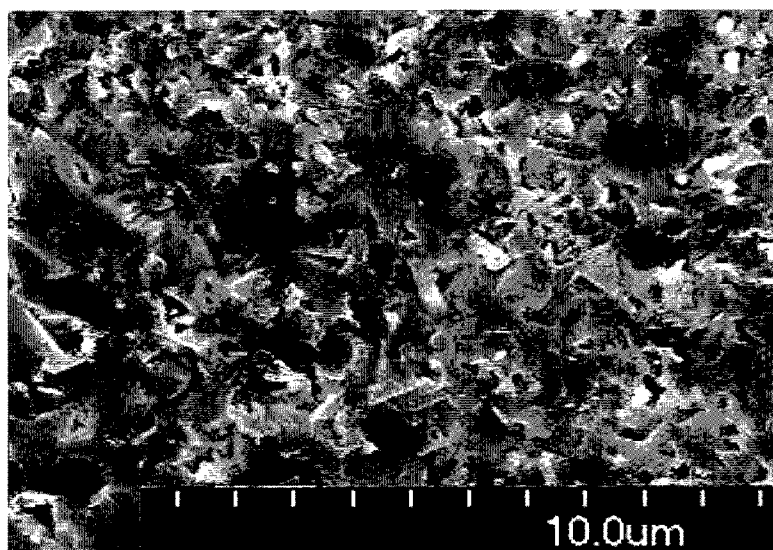
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, 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,

[Continued on next page]

(54) Title: METHOD OF MANUFACTURING CIS-BASED THIN FILM HAVING HIGH DENSITY

[Fig. 1]



(57) Abstract: Disclosed is a method of manufacturing a high-density CIS-based compound thin film for a solar cell, which includes (1) preparing CIS-based compound nanopart icles, (2) mixing the CIS-based compound nanoparticles, a chelating agent and a solvent, thus preparing a CIS-based compound slurry, (3) applying the CIS-based compound slurry, thus forming a CIS-based compound thin film, and (4) thermally treating the CIS-based compound thin film, whereby the structure of the CIS-based thin film suitable for use as a light absorption layer of a thin-film solar cell can become dense.



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))*

【DESCRIPTION】**【Invention Title】**

METHOD OF MANUFACTURING CIS-BASED THIN FILM HAVING HIGH DENSITY

【Technical Field】

<1> The present invention relates to a method of manufacturing a high-density CIS-based compound thin film for a solar cell, and more particularly to a method of manufacturing a CIS-based compound thin film having high density, wherein, upon application of CIS compound nanoparticles, CIGS compound nanoparticles or CZTS compound nanoparticles using a non-vacuum coating process, the surface of the precursor particles is modified, so that the density of the thin film is increased during thermal post-treatment, and to a method of manufacturing a thin-film solar cell using the CIS-based compound thin film.

【Background Art】

<2> Recently, the need to develop next-generation clean energy is gaining in importance in light of severe environmental contamination and the exhaustion of fossil energy. In particular, solar cells, which are used to directly convert solar energy into electric energy, are expected to become an energy source able to solve the energy problems of the future because they generate less pollution and use an unlimited resource and have a semi-permanent lifetime.

<3> Solar cells are classified into a variety of types depending on the material used for the light absorption layer. The mainly available type is the Si solar cell. However, as the price of Si has drastically increased attributable to a shortage of the Si supply in recent years, thin-film solar cells are receiving attention. Thin-film solar cells are manufactured to be thin so that smaller amounts of materials are consumed, and also are lightweight and thus the application field thereof is wide. Thorough research is ongoing into using amorphous Si and CdTe, CIS or CIGS as materials in such thin-film solar cells.

<4> The CIS thin film or the CIGS thin film corresponds to a Group I-III-VI compound semiconductor, and achieves the greatest conversion efficiency

(20.3%) among thin-film solar cells which have been experimentally produced. Furthermore, this film may be manufactured to a thickness of 10 μm or less and is stable even upon extended use, so that an inexpensive high-efficiency solar cell capable of replacing Si that uses this film is expected.

<5> In particular, the CIS thin film is a direct transition type semiconductor and may thus be provided in the form of a thin film, and has a band gap of 1.04 eV and is thus comparatively adapted for light conversion, and the coefficient of light absorption thereof is the greatest amongst the materials used in solar cells.

<6> The CIGS thin film is a material developed by replacing part of In with Ga or replacing Se with S to improve the low open-circuit voltage of a CIS thin film.

<7> The CIGS-based solar cell is manufactured in the form of a thin film having a thickness of ones of μm , and the manufacturing method thereof includes for example a vapor deposition process in a vacuum, and a process comprising applying a precursor material in a non-vacuum and thermally treating it. Although the vapor deposition process is advantageous because a high-efficiency absorption layer may be formed, uniformity may decrease upon forming a large-area absorption layer and an expensive apparatus should be used, and the manufacturing cost may become high due to the material loss of 20 ~ 50%. Whereas, the process comprising applying the precursor material and thermally treating it at high temperature may decrease the process cost and allows the large area to be uniformly formed, but the efficiency of the absorption layer is undesirably low.

<8> The CIGS thin film formed by applying a precursor material in a non-vacuum has many pores and is not dense, and thus needs thermal treatment for selenization. However, conventional thermal treatment for selenization is disadvantageous because the use of hydrogen selenide (H_2Se) which is a toxic gas causes problems related to stability, and thus safety equipment must be mounted which caused the installation cost to be very high, and also because thermal treatment should be carried out for a long period of time, undesirably increasing the price of the CIGS thin film.

<9> Moreover, because the melting point of the CIGS thin film is 1000°C or more and is very high, even when CIGS compound nanoparticles having a size of tens of nm are used, it is not easy to grow particles and achieve densification with thermal post-treatment.

【Disclosure】

【Technical Problem】

<10> Accordingly, the present invention has been made keeping in mind the above problems occurring in the related art, and an object of the present invention is to provide a method of manufacturing a CIS-based compound thin film, wherein a non-vacuum coating process that has a comparatively low process cost is introduced, thus enabling the structure of the thin film to be densified during the process, resulting in decreased manufacturing cost, and also enabling a high-efficiency thin-film solar cell to be provided that uses the high-density thin film.

【Technical Solution】

<11> In order to accomplish the above object, the present invention provides a method of manufacturing a CIS-based compound thin film having high density, comprising (1) preparing CIS-based compound nanoparticles; (2) mixing the CIS-based compound nanoparticles, a chelating agent and a solvent, thus preparing a CIS-based compound slurry; (3) applying the CIS-based compound slurry, thus forming a CIS-based compound thin film; and (4) thermally treating the CIS-based compound thin film.

<12> In a preferred embodiment of the present invention, the CIS-based compound nanoparticles may be CIS compound nanoparticles, CIGS compound nanoparticles or CZTS compound nanoparticles.

<13> The chelating agent may be any one selected from among MEA (monoethanolamine), DEA (diethanolamine), TEA (triethanolamine), ethylenediamine, EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), HEDTA (hydroxyethylenediaminetetraacetic acid), GEDTA (glycoletherdiaminetetraacetic acid), TTHA (triethylenetetraminehexacetic acid), HIDA (hydroxyethyliminodiacetic acid), and DHEG (dihydroxyethylglycine).

- <14> The solvent may be an alcoholic solvent.
- <15> The alcoholic solvent may include any one selected from among ethanol, methanol, pentanol, propanol and butanol.
- <16> The slurry may be prepared by means of dispersion using ultrasound.
- <17> The CIS-based compound thin film may be formed using a non-vacuum coating process.
- <18> The non-vacuum coating process may be any one selected from among spraying, ultrasonic spraying, spin coating, doctor blading, screen printing and ink-jet printing.
- <19> In (3), drying may be additionally performed after applying the CIS-based compound thin film.
- <20> In (3), applying and drying the CIS-based thin film may be sequentially repeated a plurality of times.
- <21> Also, (4) may be performed by carrying out thermal treatment while supplying Se vapor.
- <22> The thermal treatment may be performed at a temperature of a substrate having the CIS-based compound thin film of 400 ~ 530°C.
- <23> In addition, the present invention provides a CIS-based compound thin film having high density, suitable for use as a light absorption layer of a solar cell, wherein the CIS-based compound thin film has a structure in which CIS-based compound nanoparticles are uniformly grown upon thermal treatment for selenization by means of a chelating agent.
- <24> In a preferred embodiment of the present invention, the CIS-based compound nanoparticles may be CIS compound nanoparticles, CIGS compound nanoparticles or CZTS compound nanoparticles.
- <25> The chelating agent may be any one selected from among MEA, DEA, TEA, ethylenediamine, EDTA, NTA, HEDTA, GEDTA, TTHA, HIDA, and DHEG.
- <26> In addition, the present invention provides a solar cell comprising the CIS-based compound thin film having high density as above.

【Advantageous Effects】

<28> According to the present invention, precursor nanoparticles are mixed with a chelating agent to form a precursor thin film which is then thermally treated, thus completing a CIS-based compound thin film. As such, the chelate compound formed on the surface of the nanoparticles can delay the crystallization of the particles upon thermal treatment for selenization and enables the efficient viscous flow of the material, thereby densifying the structure of the thin film. Also, the CIS-based compound thin film according to the present invention can be used as the light absorption layer of a thin-film solar cell thus achieving a high-efficiency thin-film solar cell.

【Description of Drawings】

<29> FIG. 1 is a scanning electron microscope (SEM) image showing the surface of a CIS thin film manufactured in an example according to the present invention;

<30> FIG. 2 is a graph showing output properties of a solar cell using the CIS thin film manufactured in the example according to the present invention;

<31> FIG. 3 is a SEM image showing the surface of a CIS compound thin film manufactured in a comparative example; and

<32> FIG. 4 is a dark current-voltage curve of a solar cell using the CIS compound thin film manufactured in the comparative example.

【Mode for Invention】

<33> Hereinafter, a detailed description will be given of preferred embodiments of the present invention with reference to the appended drawings. The following embodiments may be variously modified and are not construed as limiting the scope of the present invention. The embodiments of the present invention are merely intended to provide a complete description to a person having ordinary knowledge in the art.

<34> According to the present invention, a method of manufacturing a CIS-based compound thin film is specifically described below.

<35> The method of forming the CIS-based compound thin film according to the present invention may include mixing a slurry of CIS-based compound nanoparticles with a chelating agent thus preparing a mixed slurry which is

then applied and thermally treated, thus obtaining a dense CIS-based compound thin film. This method is stepwisely described below.

<36> First, CIS-based compound nanoparticles are prepared (step 1).

<37> As used herein, the term "CIS-based compound" means a ternary compound including not only Cu-In-Se but also Cu-In-S, Cu-Ga-S, Cu-Ga-Se and so on, as Group IB-IIIA-VIA compound semiconductors, a quaternary compound such as Cu-In-Ga-Se and so on, and a quinary or senary compound such as Cu-In-Ga-Se-(S,Se), Cu-In-Al-Ga-(S,Se), Cu-In-Al-Ga-Se-S, etc. More widely, the CIS-based compound is defined as including a CZTS-based compound which includes Cu-Zn-Sn-(Se,S) wherein all of Group IIIA elements of the CIS-based compound, such as In, Ga, Al, etc., are replaced with Group IIB element (e.g. Zn) + Group IVA element (e.g. Sn), and also which includes Cu-In-Ga-Zn-Sn-(Se,S) wherein part of Group IIIA elements thereof are replaced.

<38> Using the CIS-based compound as mentioned above, the CIS-based nanoparticles may be prepared. As such, a process known in the art, for example, a low-temperature colloidal process, a solvent heat synthesis process, a microwave process, an ultrasonic synthesis process, etc., may be applied.

<39> Next, a CIS-based compound slurry including a chelating agent is prepared (step 2).

<40> This slurry is prepared by mixing the CIS-based compound nanoparticles obtained in step 1 with a solvent and a chelating agent.

<41> The solvent may be an alcoholic solvent such as methanol, ethanol, pentanol, propanol, butanol, etc.

<42> The chelating agent is inherently viscous and may thus be used as a binder, thus obviating the need to use an additional binder.

<43> Examples of the chelating agent may include MEA (monoethanolamine), DEA (diethanolamine), TEA (triethanolamine), ethylenediamine, EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), HEDTA (hydroxyethylenediaminetetraacetic acid), GEDTA (glycoletherdiaminetetraacetic acid), TTHA (triethylenetetraminehexacetic acid), HIDA (hydroxyethyliminodiacetic acid), DHEG (dihydroxyethylglycine),

etc., but are not limited thereto.

<44> Any chelating agent may be used within the scope of the present invention so long as it is a ligand able to form a chelate compound on the surface of the CIS-based nanoparticles.

<45> As such, the proportion of the CIS-based compound nanoparticles may be adjusted to control the concentration of the slurry, and the proportion of the chelating agent may be adjusted to control the degree of chelating.

<46> The CIS-based compound nanoparticles and the chelating agent are mixed with the solvent, and then well dissolved using ultrasonic treatment, thus preparing the CIS-based compound slurry including the chelating agent.

<47> Next, the CIS-based compound slurry including the chelating agent is applied, thus forming a CIS-based compound thin film (step 3).

<48> In the present invention, the CIS-based compound thin film is formed using a non-vacuum coating process. The non-vacuum coating process may include for example spraying, ultrasonic spraying, spin coating, doctor blading, screen printing, ink-jet printing, etc., and any other non-vacuum coating process may be applied so long as it is well known in the art. The use of such a non-vacuum coating process may decrease the manufacturing cost.

<49> After applying the CIS-based slurry including the chelating agent under non-vacuum conditions, drying may be additionally done in order to remove the alcoholic solvent. The coating and drying procedures are repeated so as to form a CIS-based compound thin film including the chelating agent at a desired thickness. The number of repeating these procedures may vary depending on the needs but is preferably set to 3 ~ 5.

<50> The unshared electron pairs of the chelating agent are bound with Cu, In, Ga on the surface of the nanoparticles thus forming a metal ion-chelating agent complex. The chelate compound formed on the surface of the particles may decrease the reactivity of the particles upon selenization at high temperature, and thus may increase the crystallization temperature of the particles.

<51> Next, the CIS-based compound thin film including the chelating agent formed in step 3 is thermally treated for selenization using Se vapor (step

4).

<52> Thermal treatment using Se vapor may be performed by increasing the temperature of the substrate having the thin film while supplying Se vapor formed by evaporating Se solid using heat. The chelate compound formed on the surface of the particles decreases the reactivity of the particles, and thus the crystallization of the particles may become slow and simultaneously the viscous flow of the material may increase, thereby more effectively filling the spaces between the particles, resulting in a CIS-based compound thin film having high density.

<53> Thereby, the precursor thin film after step 3 is selenized, so that the structure of the thin film is finally densified, thus completing the CIS-based compound thin film having high density according to the present invention.

<54> A better understanding of the present invention may be conducted via the following example.

<55> Example

<56> In a glove box, 0.343 g of CuI and 0.991 g of InI₃ were mixed with 30 ml of a distilled pyridine solvent, after which the resultant mixture was stirred for about 10 min on a hot plate at 50°C. After stirring for about 10 min, the opaque solution was made transparent. The Cu/In mixture was mixed with 0.5 g of Na₂Se in 20 ml of distilled methanol, so as to correspond to the atomic ratio of Cu : In : Se = 0.9 : 1 : 2. Subsequently, the mixture of methanol and pyridine was mechanically stirred in an ice bath at 0°C and reacted for 1 min thus synthesizing CIS nanoparticles. The synthesized CIS colloid was centrifuged at 4000 rpm for about 30 min, treated with ultrasound for 5 min and washed with distilled methanol, and such procedures were repeated, thus completely removing by-products and pyridine from the product, resulting in synthesized high-purity CIS compound nanoparticles.

<57> 0.3 g of the CIS compound nanoparticles thus synthesized and 0.3 g of a chelating agent were mixed with 1.2 g of a methanol solvent, and then treated with ultrasound for 30 min so that they were efficiency dispersed, thus preparing a CIS compound slurry including the chelating agent.

<58> Thereafter, the CIS compound slurry including the chelating agent was applied using spin coating (1000 rpm, 20 sec) on a soda-lime glass substrate having a Mo thin film deposited thereon, and then subjected to two-stage drying on a hot plate to remove the alcoholic solvent, including primary drying at 100°C for 3 min and secondary drying at 300°C for 5 min.

<59> Such coating and drying procedures were repeated five times, thus forming a CIS compound slurry including the chelating agent at a predetermined thickness, namely, a precursor thin film.

<60> Finally, while Se vapor was supplied at a substrate temperature of 530 °C, selenization was conducted for 30 min, thus completing a CIS compound thin film having high density.

<61> The SEM image of the surface of the CIS thin film thus manufactured is shown in FIG. 1, and the output properties of a solar cell using such a CIS thin film are graphed in FIG. 2.

<62> As shown in FIG. 2, the energy conversion efficiency of the solar cell using the CIS thin film obtained in the example according to the present invention is 4.41%.

<63> Comparative Example

<64> CIS compound nanoparticles were prepared in the same manner as in the above example, after which 0.3 g of the CIS compound nanoparticles and 0.3 g of propyleneglycol were dissolved in 1.2 g of methanol, followed by performing ultrasonic treatment for 30 min, thus obtaining a CIS compound slurry.

<65> Subsequently, the CIS compound slurry was applied using spin coating (1000 rpm, 20 sec) on a soda-lime glass substrate having a Mo thin film deposited thereon, and dried on a hot plate at 60°C for 5 min and further dried at 180°C for 2 min to remove the alcoholic solvent and the binder.

<66> Such coating and drying procedures were repeated five times, thus forming a CIS compound thin film on the substrate.

<67> Finally, while Se vapor was supplied at a substrate temperature of 530 °C, selenization was performed.

<68> The SEM image of the surface of the CIS compound thin film obtained in

this comparative example is shown in FIG. 3.

<69> The solar cell using the CIS thin film of this example did not exhibit photoelectric conversion properties. This is because there occurs contact between the conductive Al:ZnO film and the lower Mo thin film via the pores of the CIS thin film as shown in FIG. 3. The contact between the upper and lower conductive thin films and the short circuit thereby can be seen from the dark current-voltage curve of FIG. 4.

<70> With reference to FIGS. 1 and 3, the inner structure of the CIS thin film according to the example of the present invention was comparatively denser than that of the CIS thin film of the comparative example. Specifically, the inner structure of the CIS thin film of the example had a decreased pore size and a remarkably lowered number of pores thanks to the growth of the particles.

<71> Accordingly, it is recognized that the chelating agent is added to the slurry that forms the thin film in the example, and thus the chelate compound is formed on the surface of the particles so that the reactivity of the particles may decrease, thereby delaying the crystallization of the particles upon selenization and increasing the viscous flow of the material, resulting in increased density.

<72> When the surface of the precursor nanoparticles is modified using the chelating agent in this way, the density of the CIS-based thin film may be remarkably increased upon selenization compared to the conventional case. That is, even when thermal treatment is performed at a temperature comparatively lower than that of the conventional case, a CIS-based thin film having a density similar thereto may be finally obtained. Therefore, the method of manufacturing a high-density CIS-based thin film according to the present invention can effectively reduce the process cost.

<73> Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

【CLAIMS】**【Claim 1】**

<75> A method of manufacturing a CIS-based compound thin film having high density, comprising:

<76> (1) preparing CIS-based compound nanoparticles;

<77> (2) mixing the CIS-based compound nanoparticles, a chelating agent and a solvent, thus preparing a CIS-based compound slurry;

<78> (3) applying the CIS-based compound slurry, thus forming a CIS-based compound thin film; and

<79> (4) thermally treating the CIS-based compound thin film.

【Claim 2】

<80> The method of claim 1, wherein the CIS-based compound nanoparticles are CIS compound nanoparticles, CIGS compound nanoparticles or CZTS compound nanoparticles.

【Claim 3】

<82> The method of claim 1, wherein the chelating agent is any one selected from among MEA (monoethanolamine), DEA (diethanolamine), TEA (triethanolamine), ethylenediamine, EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), HEDTA (hydroxyethylenediaminetetraacetic acid), GEDTA (glycoletherdiaminetetraacetic acid), TTHA (triethylenetetraminehexacetic acid), HIDA (hydroxyethyliminodiacetic acid) and DHEG (dihydroxyethylglycine).

【Claim 4】

<84> The method of claim 1, wherein the solvent is an alcoholic solvent.

【Claim 5】

<86> The method of claim 4, wherein the alcoholic solvent includes any one selected from among ethanol, methanol, pentanol, propanol and butanol.

【Claim 6】

<88> The method of claim 1, wherein the slurry is prepared by means of dispersion using ultrasound.

【Claim 7】

<90> The method of claim 1, wherein the CIS-based compound thin film is

formed using a non-vacuum coating process.

<91> **【Claim 8】**

<92> The method of claim 7, wherein the non-vacuum coating process is any one selected from among spraying, ultrasonic spraying, spin coating, doctor blading, screen printing and ink-jet printing.

<93> **【Claim 9】**

<94> The method of claim 1, wherein in (3) drying is additionally performed after applying the CIS-based compound thin film.

<95> **【Claim 10】**

<96> The method of claim 9, wherein in (3) applying and drying the CIS-based thin film are sequentially repeated a plurality of times.

<97> **【Claim 11】**

<98> The method of claim 1, wherein (4) is performed by carrying out thermal treatment while supplying Se vapor.

<99> **【Claim 12】**

<100> The method of claim 11, wherein the thermal treatment is performed at a temperature of a substrate having the CIS-based compound thin film of 400 ~ 530°C.

<101> **【Claim 13】**

<102> A CIS-based compound thin film having high density, suitable for use as a light absorption layer of a solar cell, wherein the CIS-based compound thin film has a dense structure as a result of growing CIS-based compound nanoparticles using a chelating agent.

<103> **【Claim 14】**

<104> The CIS-based compound thin film of claim 13, wherein the CIS-based compound nanoparticles are CIS compound nanoparticles, CIGS compound nanoparticles or CZTS compound nanoparticles.

<105> **【Claim 15】**

<106> The CIS-based compound thin film of claim 13, wherein the chelating agent is any one selected from among MEA (monoethanolamine), DEA (diethanolamine), TEA (triethanolamine), ethylenediamine, EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), HEDTA

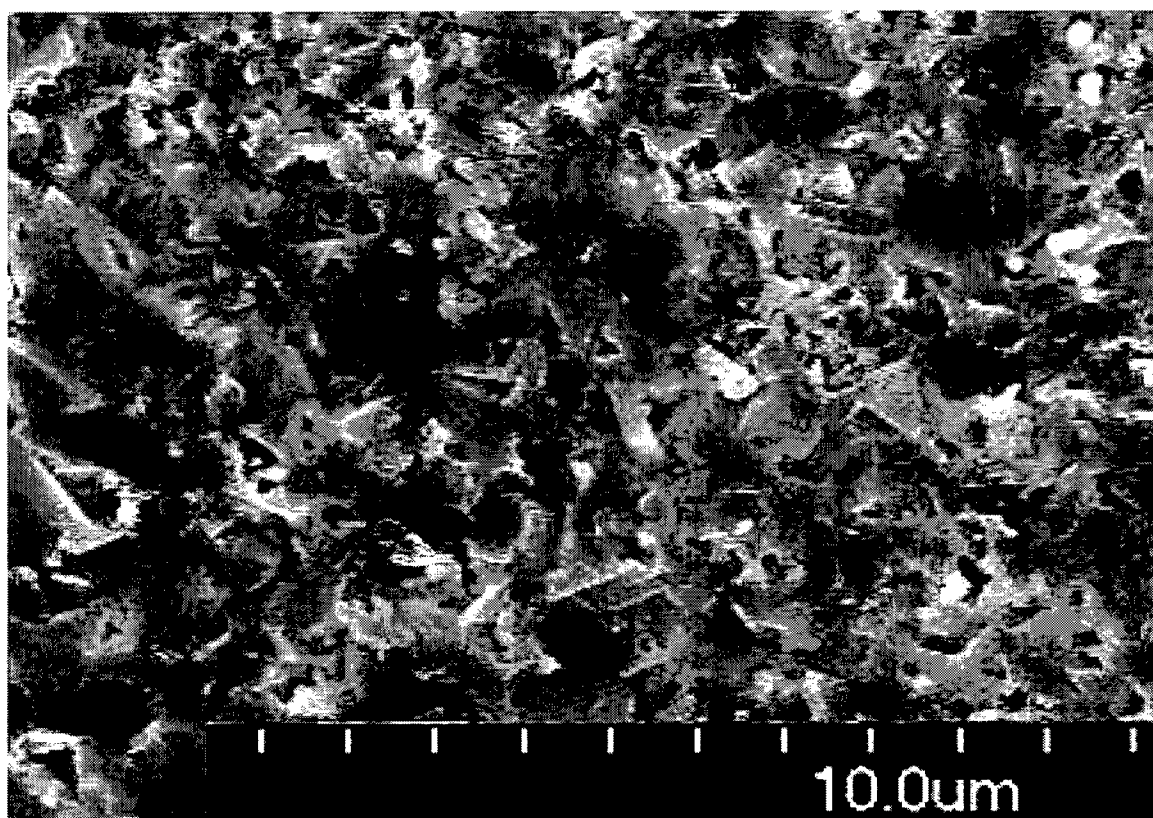
(hydroxyethylenediaminetetraacetic acid), GEDTA (glycoletherdiaminetetraacetic acid), TTHA (triethylenetetraminehexacetic acid), HIDA (hydroxyethyliminodiacetic acid) and DHEG (dihydroxyethylglycine).

<107> **【Claim 16】**

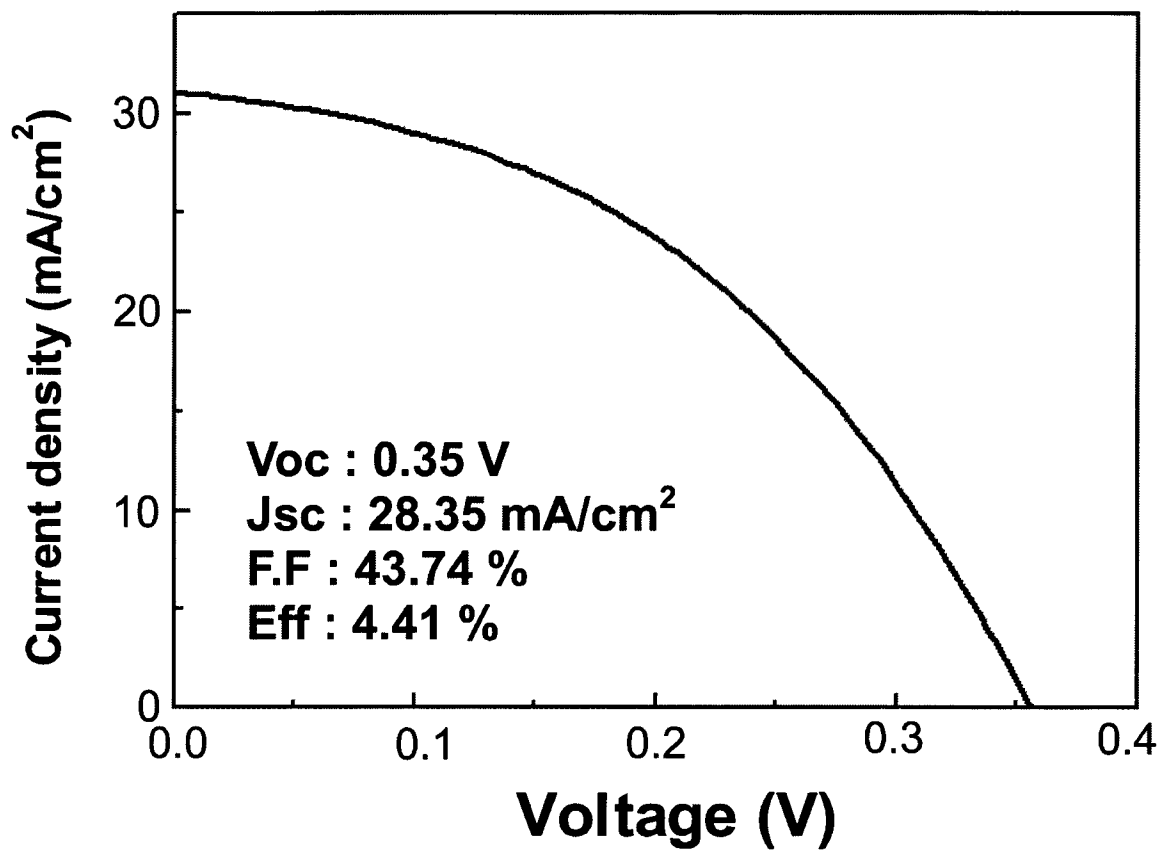
<108> A solar cell comprising the CIS-based compound thin film of any one of claims 13 to 15.

[Drawings]

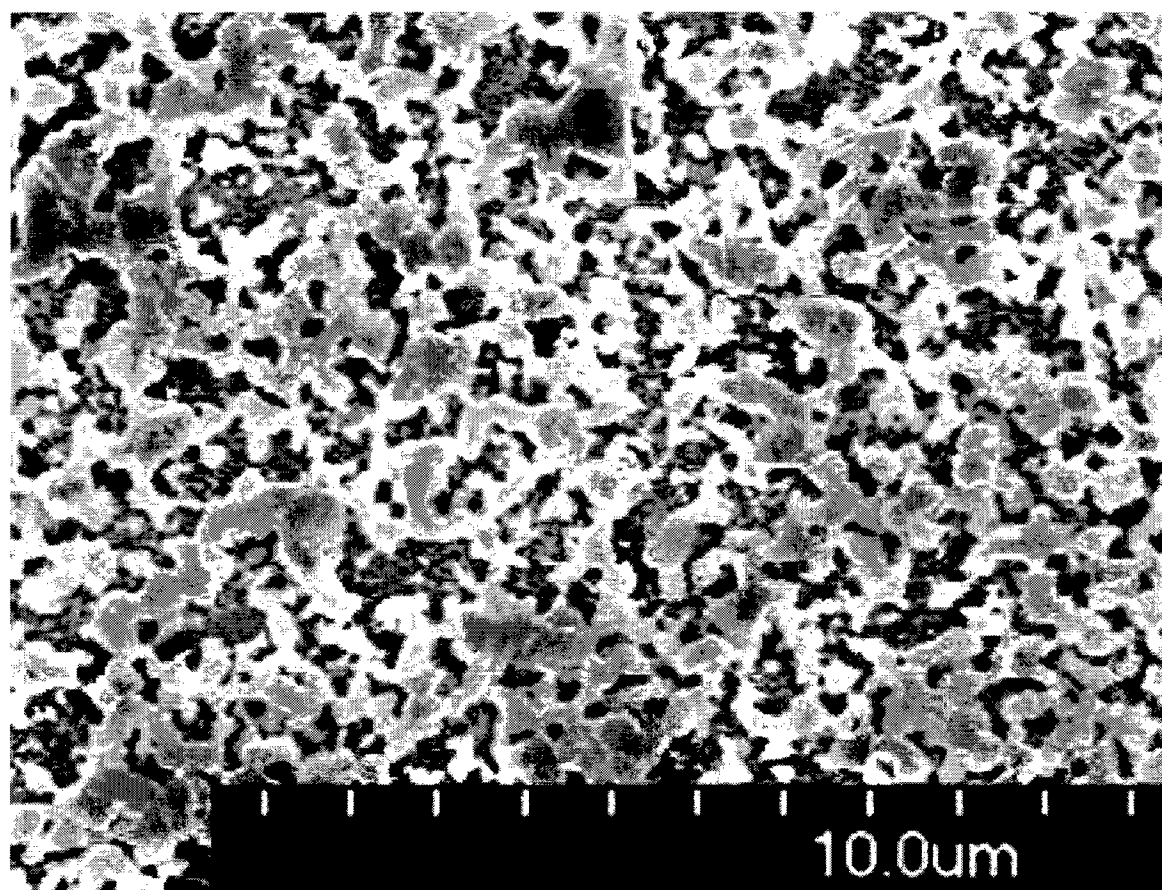
[Fig. 1]



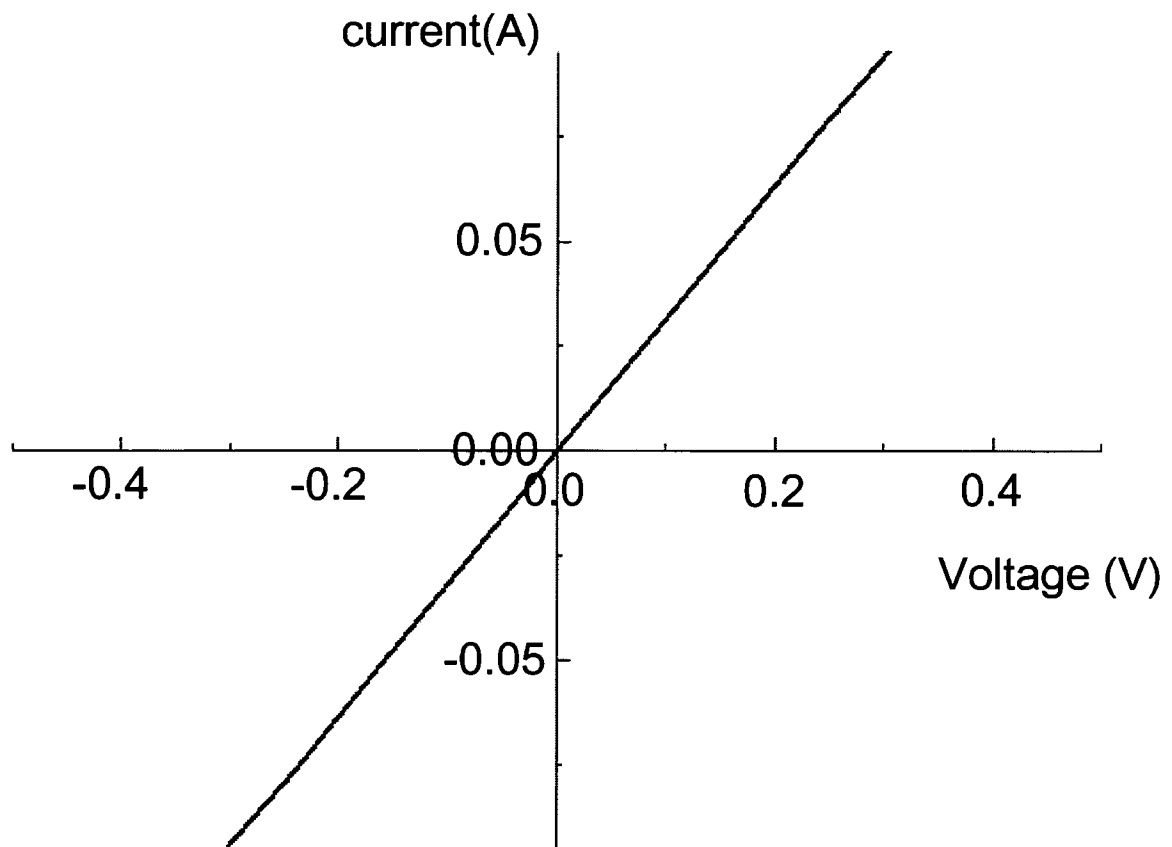
[Fig. 2]



[Fig. 3]



[Fig. 4]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2012/000813**A. CLASSIFICATION OF SUBJECT MATTER****H01L 31/0749(2012.01)i, 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 31/0749; H01L 21/36; C09D 11/02; C01B 19/00; H01L 31/0272

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:chelating agent. nanoparticle

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2011/0023750 A1 (CHI-JANE WANG) 3 February 2011 See paragraphs [35]-[39] and claims 1-8.	13-16 1-12
Y	US 2010/0120192 A1 (DUK-YOUNG JUNG et al.) 13 May 2010 See paragraphs [64]-[68] and claims 1-5.	1-12
Y A	US 2009/0242033 A1 (SEOK-JYUN YOON et al.) 1 October 2009 See paragraph [55].	9-10 1-8, 11-16

☐ 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

"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

19 SEPTEMBER 2012 (19.09.2012)

Date of mailing of the international search report

21 SEPTEMBER 2012 (21.09.2012)

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, Tae Yeon

Telephone No. 82-42-481-8547



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2012/000813

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0023750 A1	03.02.2011	None	
US 2010-0120192 A1	13.05.2010	EP 2134644 A1 JP 2010-526007 A KR 10-1030780 B1 KR 10-2011-0028609 A US 7955586 B2 WO 2009-064056 A1	23.12.2009 29.07.2010 27.04.2011 21.03.2011 07.06.2011 22.05.2009
US 2009-0242033 A1	01.10.2009	CN 101496180 B KR 10-0909179 B1 KR 10-2008-0009345A TW 200815631 A WO 2008-013383 A1	03.11.2010 22.07.2009 29.01.2008 01.04.2008 31.01.2008