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LEE et al.(10) **Pub. No.: US 2012/0006687 A1**(43) **Pub. Date: Jan. 12, 2012**(54) **METHOD OF FORMING CIGS THIN FILM****Publication Classification**(76) Inventors: **Chi-Woo LEE**, Seoul (KR);
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(KR); **Ik-Ho CHOI**, Daejeon (KR)(51) **Int. Cl.**
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(57) **ABSTRACT**

Disclosed herein is a method of forming a CIGS thin film, comprising the steps of: immersing a substrate comprising an electrode into an electrolyte solution comprising Na₂SO₄, a water-soluble copper (Cu) precursor, a water-soluble indium (In) precursor, a water-soluble gallium (Ga) precursor, and a water-soluble selenium (Se) precursor; performing electrodeposition in such a way as to apply a direct current (DC) voltage of -0.95V~-0.85V to the electrolyte solution at room temperature and normal pressure for 10~120 minutes to form a preliminary CIGS thin film; and heat-treating the preliminary CIGS thin film at 230~270° C. to form a CIGS thin film.

FIG. 1

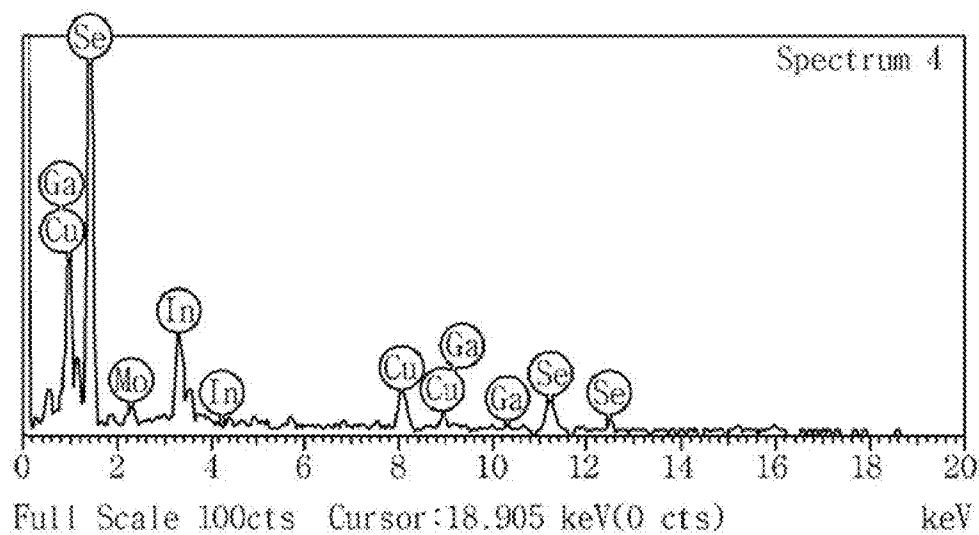
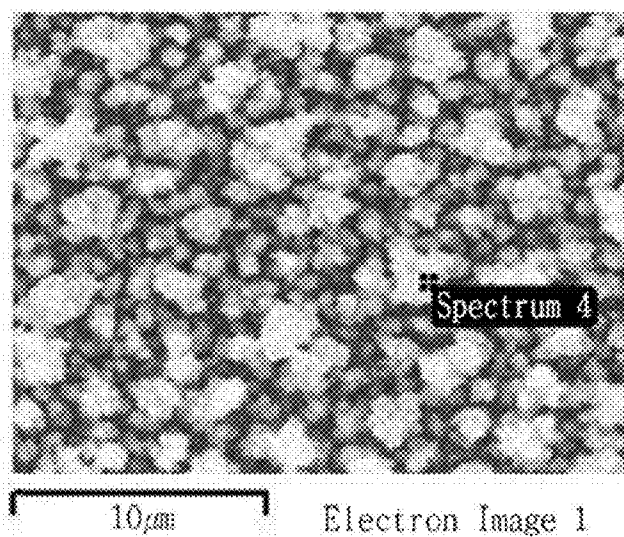


FIG. 2

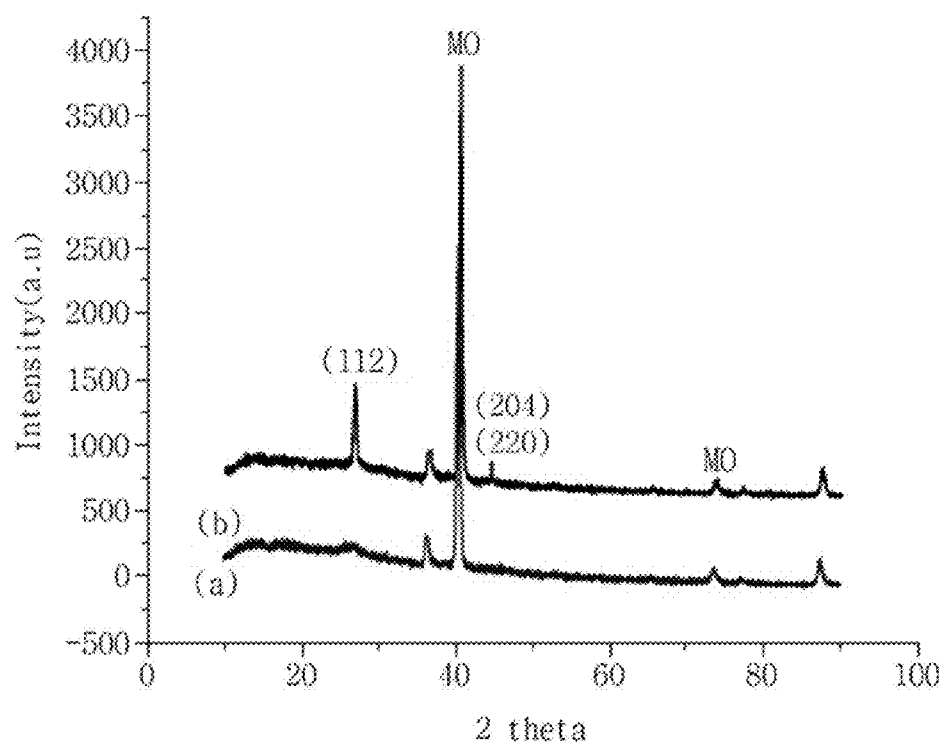


FIG. 3

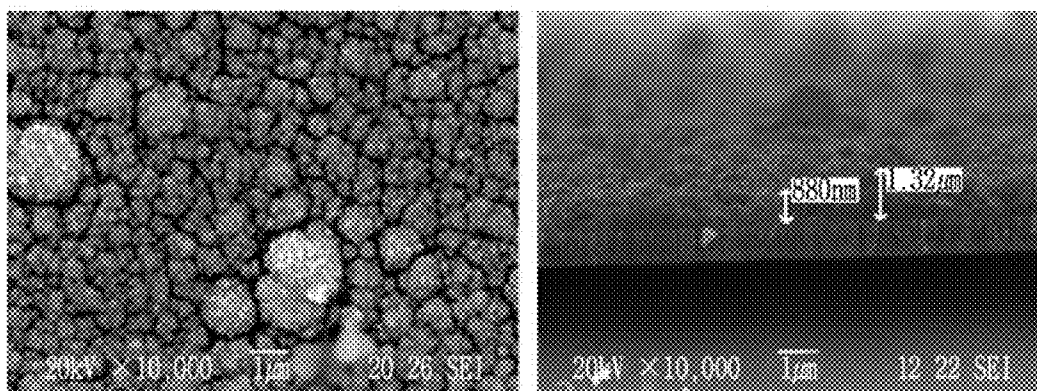


FIG. 4

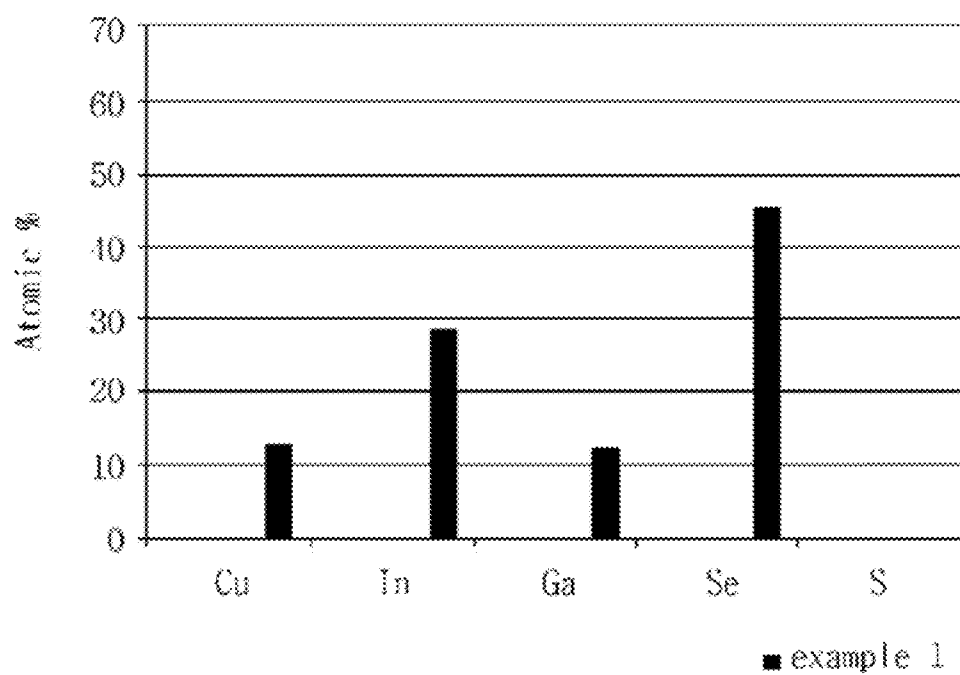


FIG. 5

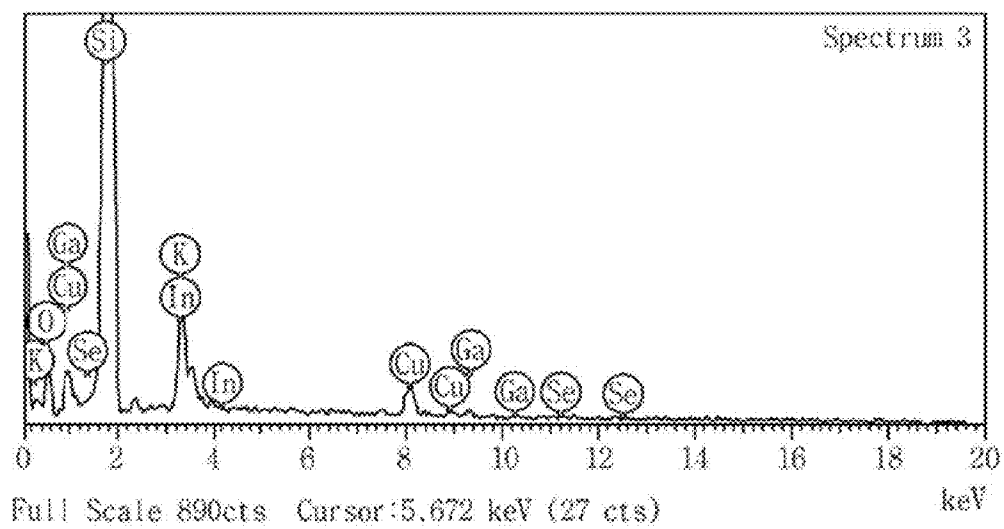
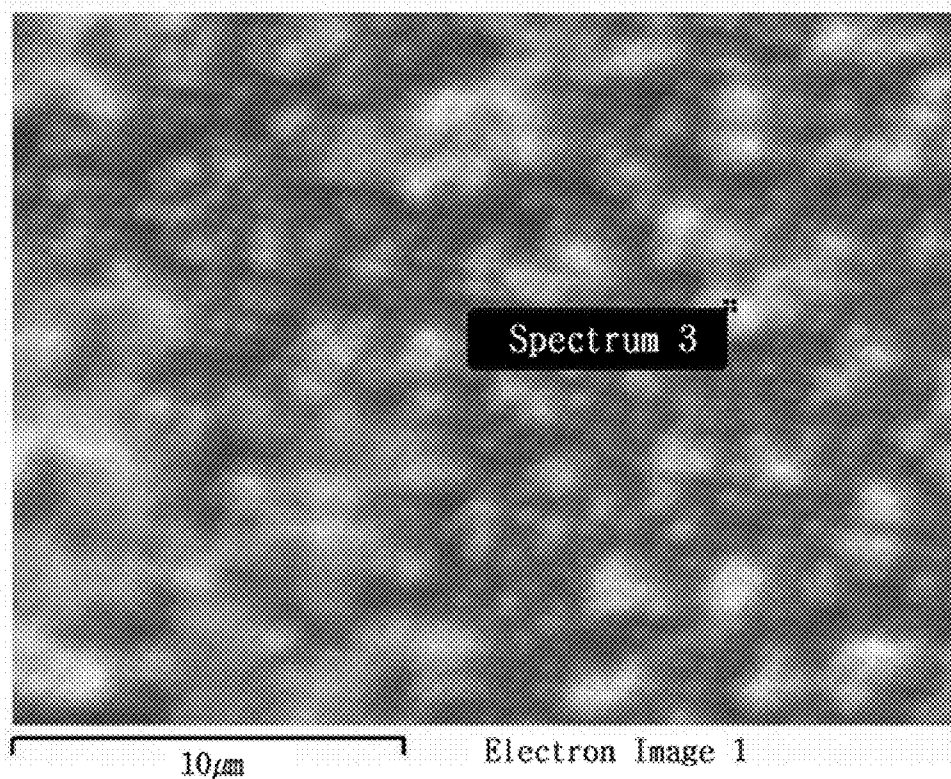
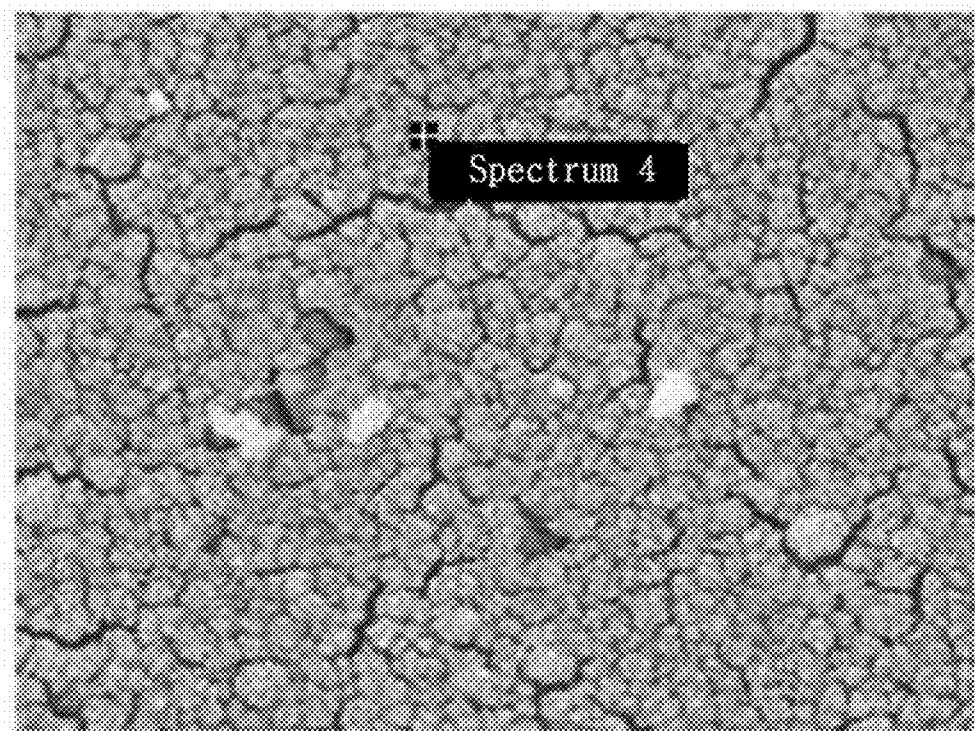


FIG. 6



10 μ m

Electron Image 1

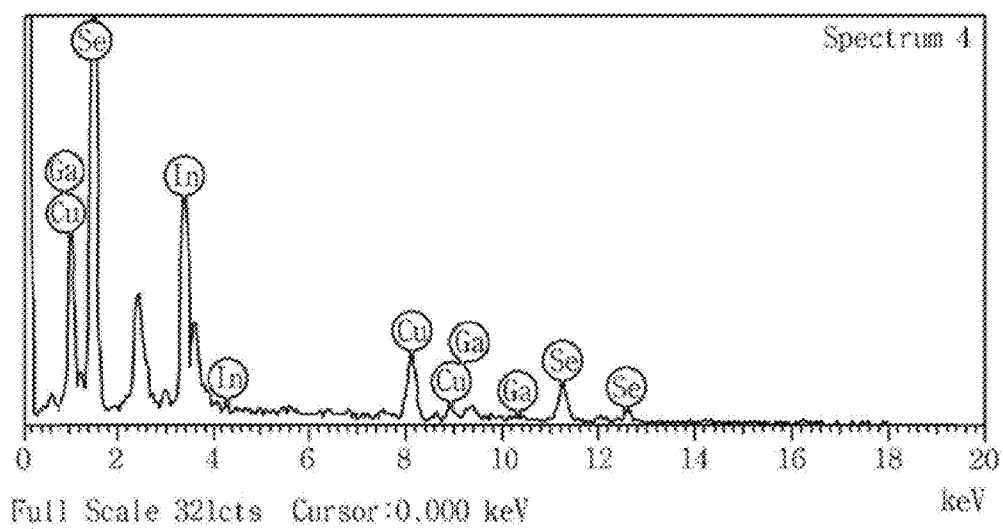


FIG. 7

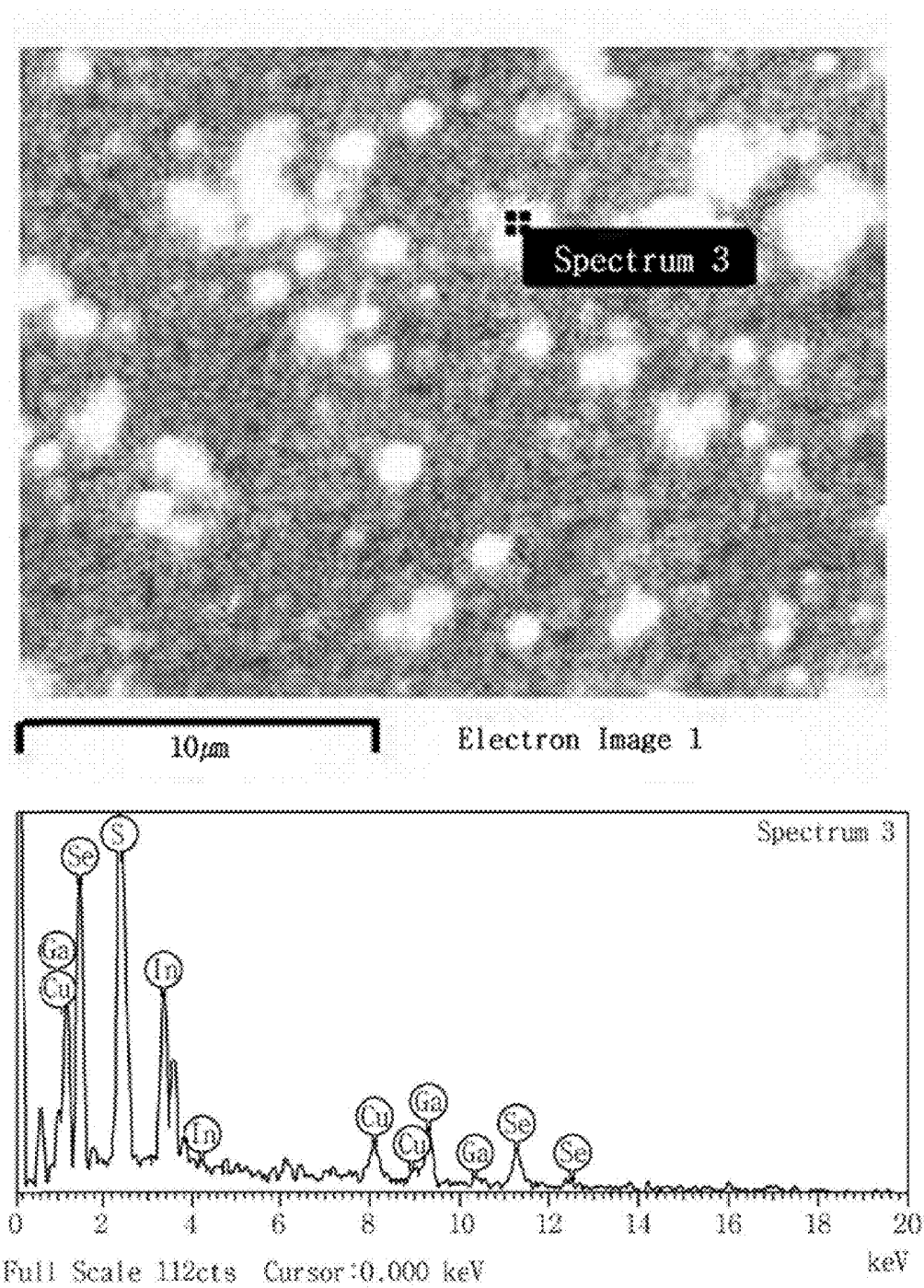


FIG. 8

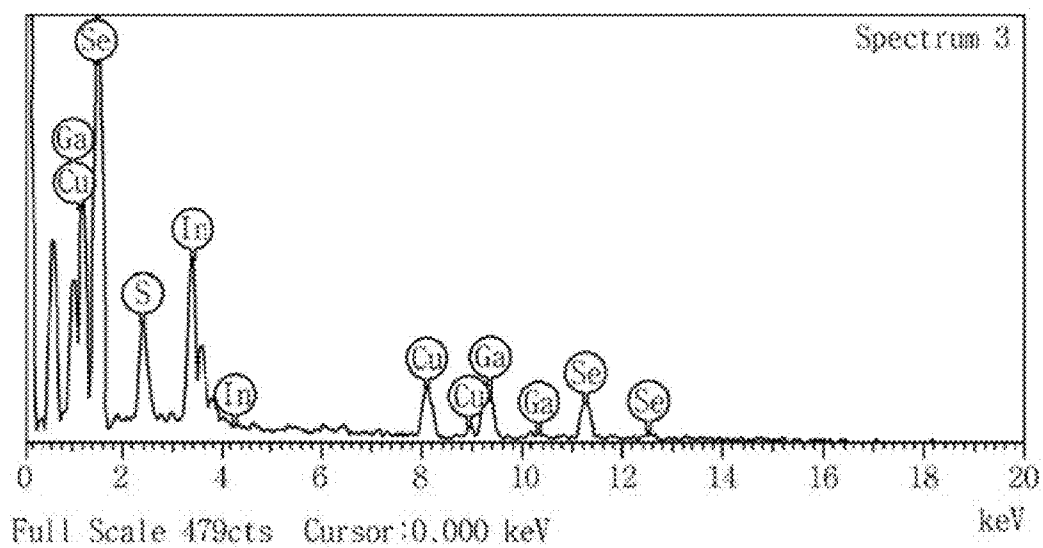
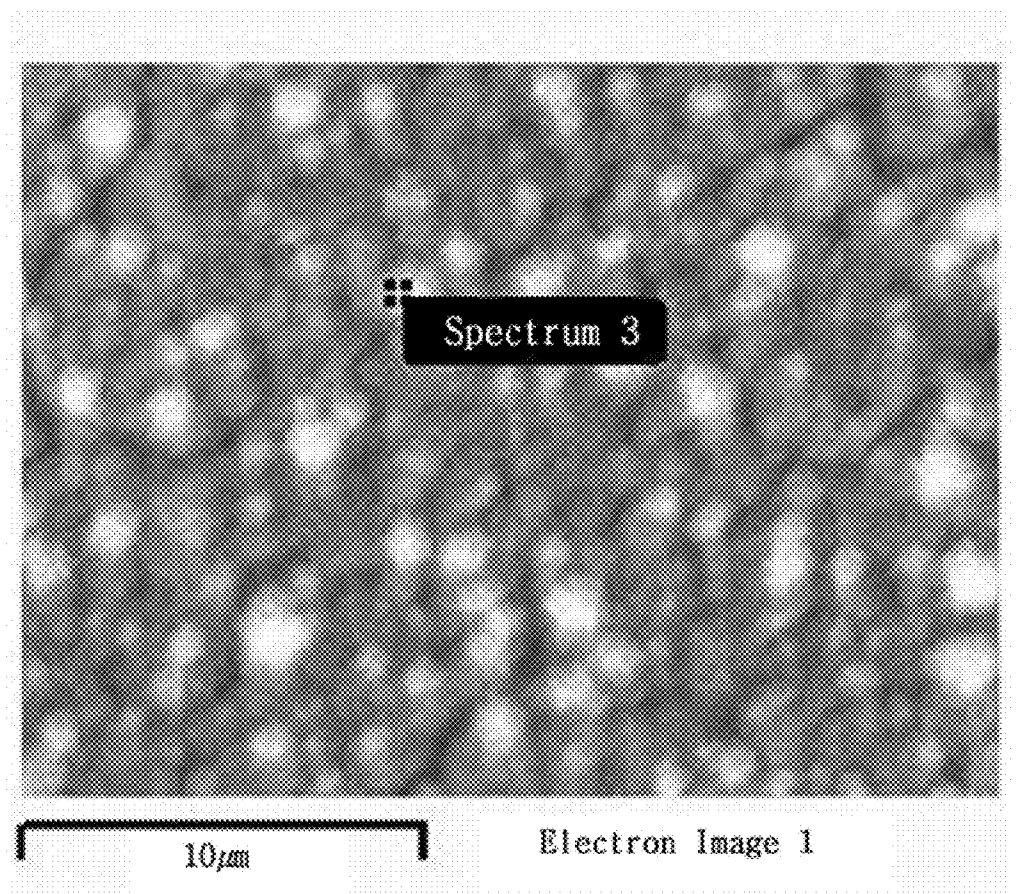


FIG. 9

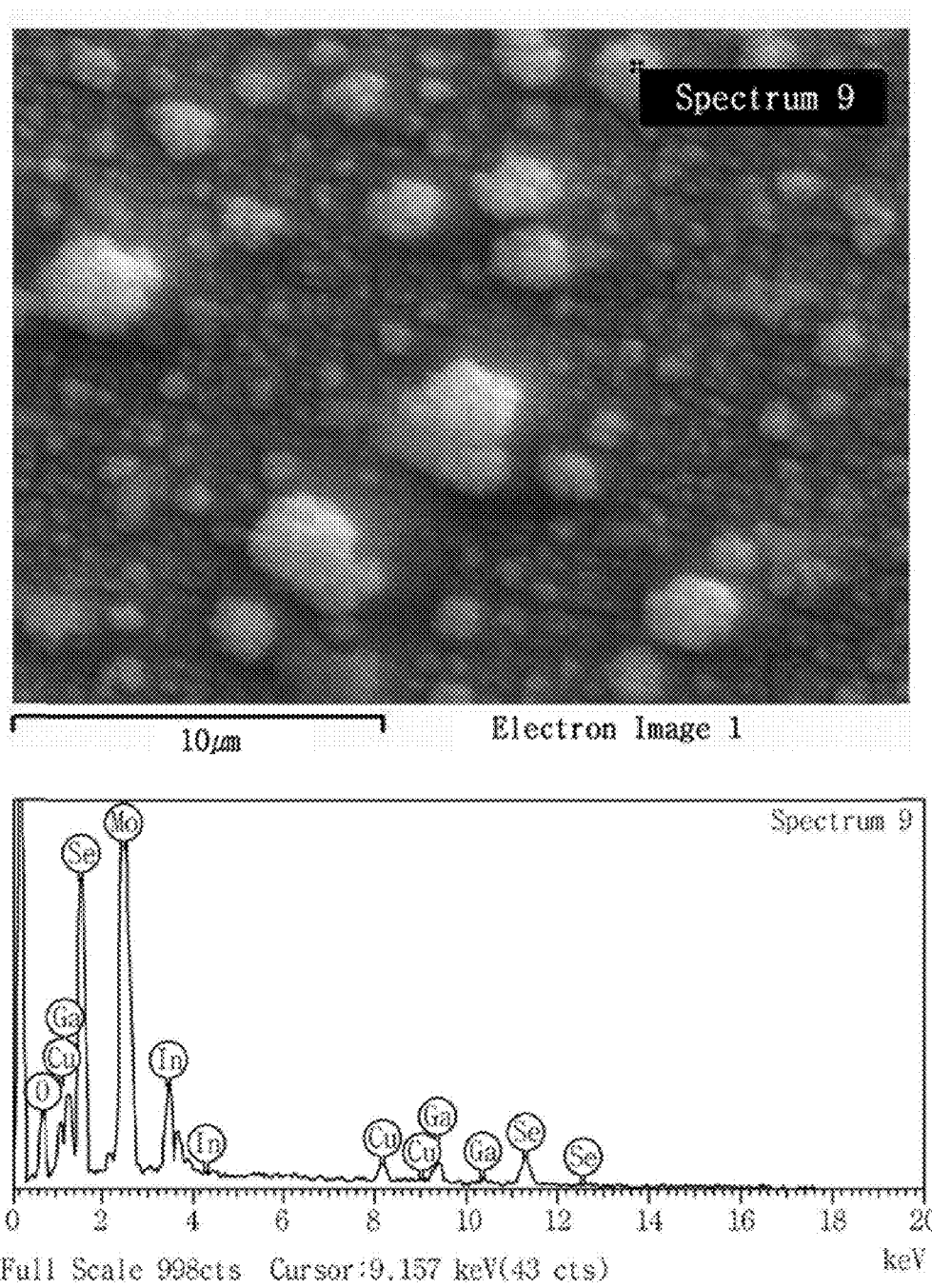


FIG. 10

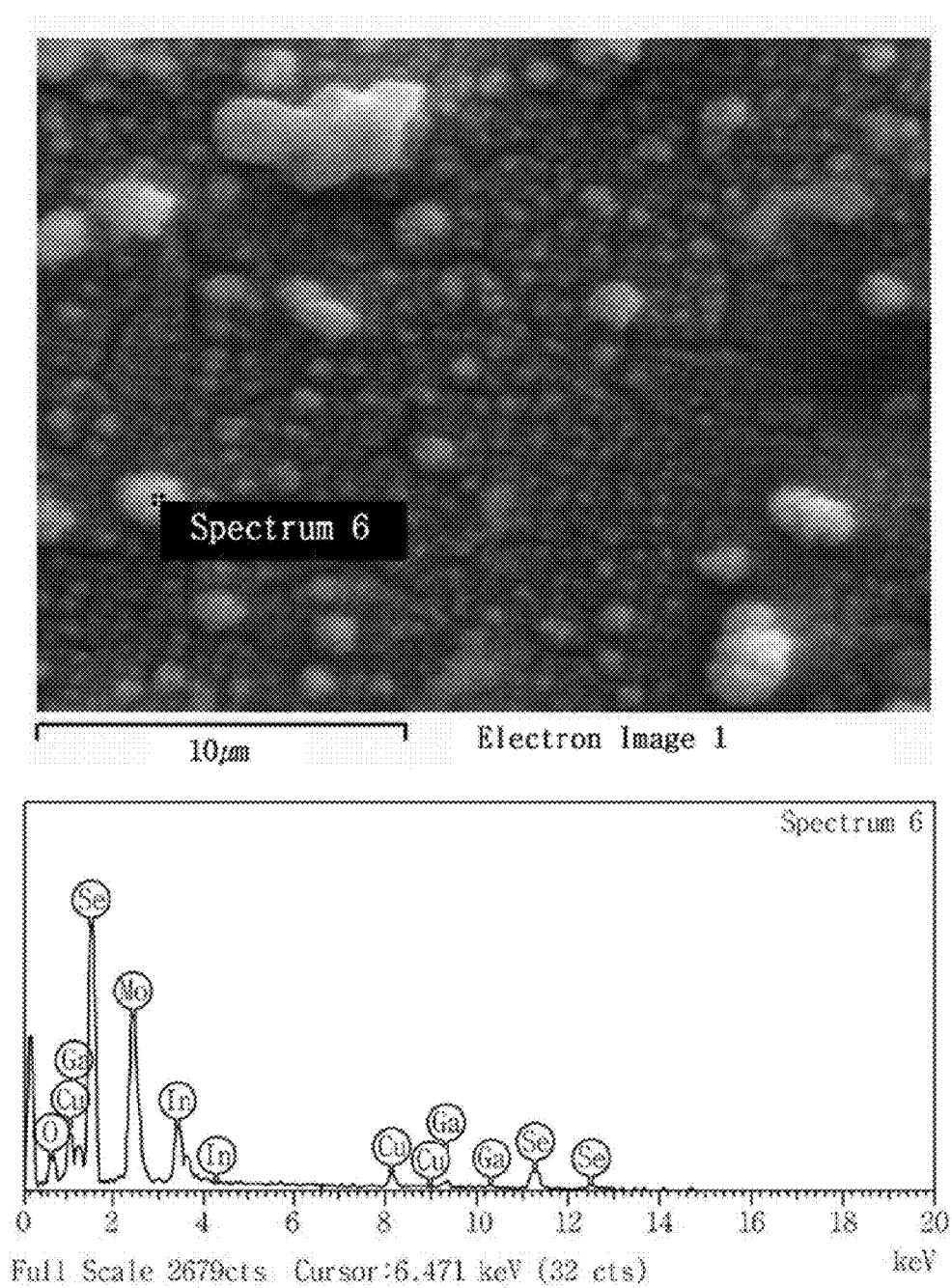
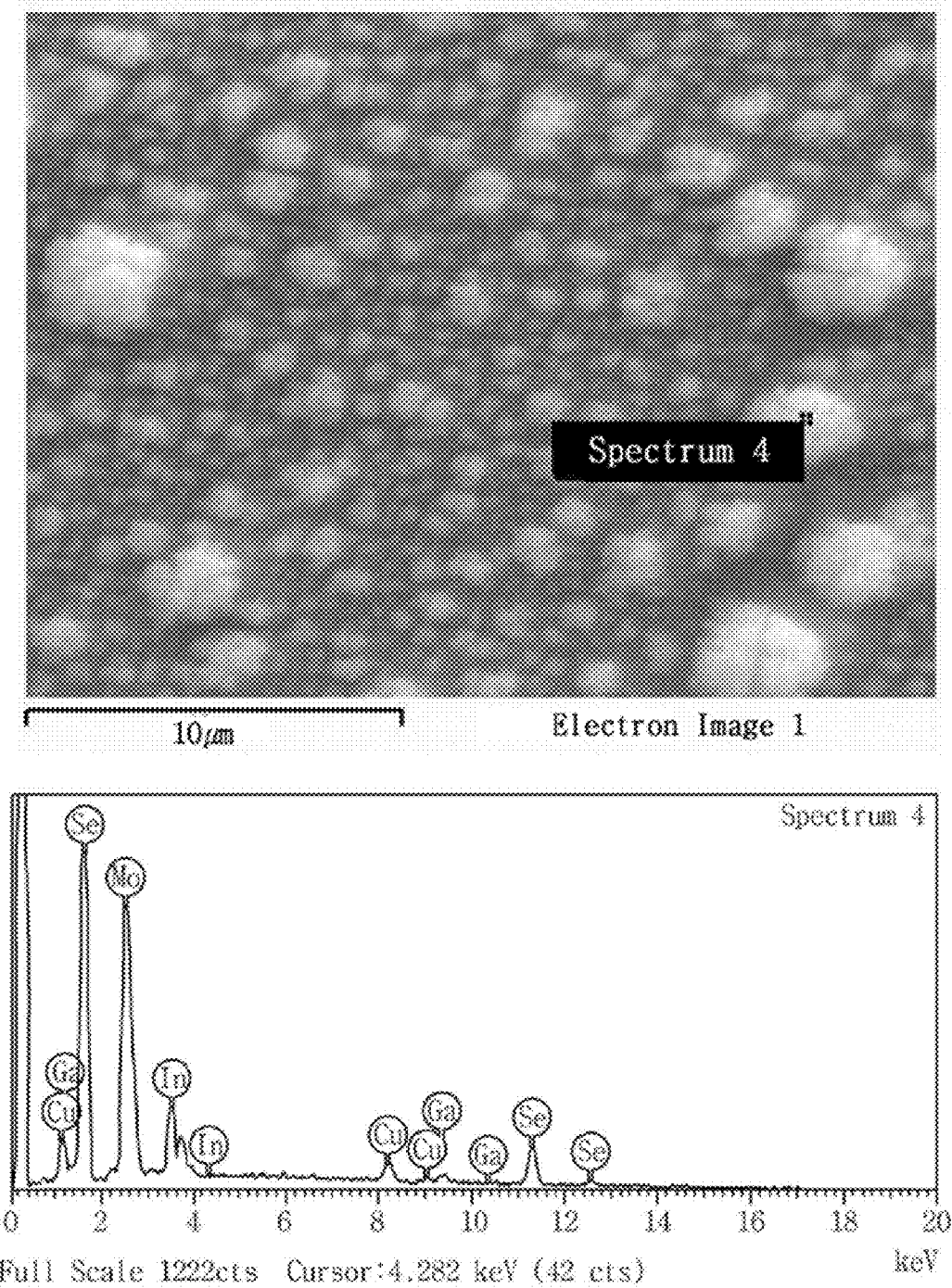


FIG. 11



METHOD OF FORMING CIGS THIN FILM

BACKGROUND OF THE INVENTION

[0001] 1. Technical Field

[0002] The present invention relates to a method of forming a CIGS thin film.

[0003] 2. Description of the Related Art

[0004] In the last several years, a I-III-VI group semiconductor compound represented by CuInSe_2 has been highlighted as a raw material of a novel high-efficiency solar cell which can replace a currently-used crystal silicon solar cell. Here, a thin-film solar cell containing the semiconductor compound CuInSe_2 is referred to as a CuInSe_2 thin-film solar cell. CuInSe_2 has a chalcopyrite structure.

[0005] Meanwhile, the CuInSe_2 thin-film solar cell has a bandgap of 1.04 eV, which is smaller than the bandgap of 1.4 eV at which solar light is ideally absorbed. In order to enlarge the bandgap of the CuInSe_2 thin-film solar cell, a part of the indium (In) in the CuInSe_2 is replaced by gallium (Ga), and a part of the selenium (Se) in the CuInSe_2 may be replaced by sulfur (S). As such, a five-component compound whose component has been replaced by a different component is represented by $\text{CIGSS} \{ \text{Cu}(\text{In}_x\text{Ga}_{1-x})(\text{Se}_y\text{S}_{1-y})_2 \}$, and is generally referred to as a CIGS material together with the quaternary compound $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$.

[0006] CIGS material has a very high absorption coefficient of $1 \times 10^5 \text{ cm}^{-1}$ in a semiconductor because it has a direct transition type of energy bandgap. The fact that the absorbance of a light-absorbing layer of a solar cell is high means that it is possible to manufacture a high-efficiency solar cell using a thin film having a thickness of 1–2 μm . When CIGS material is used to manufacture a thin-film solar cell, there are economical advantages.

[0007] According to the documents reported to date, a CIGS thin-film solar cell has a higher efficiency than do thin-film solar cells made of other materials in a module as well as a laboratory unit. Further, the CIGS thin-film solar cell compares favorably with a crystal silicon solar cell. In the case of a laboratory unit, the National Renewable Energy Laboratory (NREL) of U.S.A. reported that a CIGS thin-film solar cell has an efficiency of 19.9%. The efficiency of the CIGS thin-film solar cell is higher than those of other commercial thin-film solar cells such as thin-film solar cells made of amorphous silicon or CdTe, and approximates to 20.3% which is the maximum efficiency of conventional polycrystalline silicon solar cells.

[0008] A process of forming a CIGS thin film is very complicated because CIGS is a multi-component compound. Physical thin film forming methods include co-evaporation, sputtering, and the like. Electrochemical thin film forming methods include electrodeposition and the like. Among these methods, co-evaporation and sputtering are already being used commercially. Co-evaporation is a technology used to form a CIGS thin film by putting components into a vacuum chamber, resistance-heating the components and then vacuum-depositing the heated components on a substrate. Co-evaporation has been widely used in laboratories for a long time because the structure of the apparatus used in co-evaporation is simple. However, co-evaporation is problematic in that it is difficult to form a thin film having a large area, and in that it is not easy to form a high-quality thin film because the inner part of a vacuum apparatus becomes seriously contaminated. Currently, in the case of the CIGS thin-film solar cell having an energy conversion efficiency of

19.9% reported by the NREL, since a light-absorbing layer was formed by co-evaporation, it is determined that CIGS-based solar cells can be technically advanced in terms of efficiency. Meanwhile, sputtering has also been widely used to form a CIGS thin film for the purpose of research and production because metals or insulating materials can be easily deposited by a relatively simple apparatus. In particular, sputtering is effectively used to form an oxide thin film or a nitride thin film because compounds accompanying reactions can be deposited using inert gas such as argon gas and the like. Further, sputtering is considered to be a technology suitable for commercializing a CIGS thin-film solar cell because it can form a large-area thin film. Sputtering is advantageous in that a large-area thin film can be easily formed. However, sputtering is problematic in that it is difficult to form a high-quality thin film, so that the maximum energy conversion efficiency of the thin film obtained by sputtering does not reach that of the thin film obtained by co-evaporation.

[0009] Therefore, a method of forming a CIGS thin film, employing the advantages of both co-evaporation and sputtering, is required.

SUMMARY OF THE INVENTION

[0010] Accordingly, the present invention has been devised to solve the above-mentioned problems, and an object of the present invention is to provide a method of forming a CIGS thin film, which can form a large-area thin film at room temperature and normal pressure without using a vacuum chamber.

[0011] Another object of the present invention is to provide a method of forming a CIGS thin film, which can form a simple and cheap CIGS thin film having high light efficiency.

[0012] Still another object of the present invention is to provide a method of forming a CIGS thin film, which can improve the crystallinity of a CIGS thin film.

[0013] In order to accomplish the above objects, an aspect of the present invention provides a method of forming a CIGS thin film, comprising the steps of immersing a substrate comprising an electrode into an electrolyte solution comprising Na_2SO_4 , a water-soluble copper (Cu) precursor, a water-soluble indium (In) precursor, a water-soluble gallium (Ga) precursor, and a water-soluble selenium (Se) precursor; performing electrodeposition in such a way as to apply a direct current (DC) voltage of $-0.95\text{V} \sim -0.85\text{V}$ to the electrolyte solution at room temperature and normal pressure for 10–120 minutes to form a preliminary CIGS thin film; and heat-treating the preliminary CIGS thin film at $230 \sim 270^\circ \text{C}$. to form a CIGS thin film.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The above and other objects, features and advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

[0015] FIG. 1 shows the SEM of the surface of a preliminary CIGS thin film of Example 1 and EDS data of the preliminary CMS thin film of Example 1;

[0016] FIG. 2 is a graph showing XRD analysis data of a preliminary CIGS thin film (a) and a CIGS thin film (b) of Example 1;

[0017] FIG. 3 shows the SEM data of a CIGS thin film of Example 1;

[0018] FIG. 4 is a graph showing the EDS data of a CIGS thin film of Example 1;

[0019] FIG. 5 shows the SEM of the surface of a CIGS thin film of Comparative Example 1 and EDS data of the CIGS thin film of Comparative Example 1;

[0020] FIG. 6 shows the SEM of the surface of a CIGS thin film of Comparative Example 2 and EDS data of the CIGS thin film of Comparative Example 2;

[0021] FIG. 7 shows the SEM of the surface of a CIGS thin film of Comparative Example 5 and EDS data of the CIGS thin film of Comparative Example 5;

[0022] FIG. 8 shows the SEM of the surface of a CIGS thin film of Comparative Example 6 and EDS data of the CIGS thin film of Comparative Example 6;

[0023] FIG. 9 shows the SEM of the surface of a CIGS thin film of Comparative Example 7 and EDS data of the CIGS thin film of Comparative Example 7;

[0024] FIG. 10 shows the SEM of the surface of a CIGS thin film of Comparative Example 8 soluble indium (In) precursor, a water-soluble gallium (Ga) precursor, and a water-soluble selenium (Se) precursor each in a concentration of 0.1~10 mM. When each of the precursors is comprised of a concentration of 0.1~10 mM, there is an advantage in that it is easy to electrodeposit a preliminary CIGS thin film for forming a CIGS thin film having a targeted composition.

[0025] The electrolyte solution does not additionally comprise an additive and a buffer solution. Therefore, the electrodeposition of the present invention can be conducted more simply and efficiently than a conventional electrodeposition.

[0026] The water-soluble copper (Cu) precursor may be selected from the group consisting of $\text{Cu}(\text{NO}_3)_2$, CuSO_4 , and hydrates thereof. The water-soluble indium (In) precursor may be selected from the group consisting of $\text{In}(\text{NO}_3)_3$, $\text{In}_2(\text{SO}_4)_3$, and hydrates thereof. The water-soluble gallium (Ga) precursor may be selected from the group consisting of $\text{Ga}(\text{NO}_3)_3$, $\text{Ga}_2(\text{SO}_4)_3$, and hydrates thereof. The water-soluble selenium (Se) precursor may be selected from the group consisting of SeO_2 , H_2SeO_3 , and hydrates thereof. The water-soluble precursors of the present invention are environment-friendly because they do not include chloride (Cl^-).

[0027] The atom ratio of copper, indium, gallium and selenium in the formed preliminary CIGS thin film may be changed depending on pH of an electrolyte solution, the status of the surface of an electrode, temperature, the concentration of each element, the existence and nonexistence of an additive, the kind of additive, the electrodeposition potential, the electrodeposition time and the like. The atom ratio of copper, indium, gallium, and selenium in the electrolyte solution used in the present invention may be 0.8~1.2:0.8~1.2:1.8~2.2:2.8~3.2, preferably, 1:1:2:3. When the atom ratio thereof falls within the above range, the bandgap of a CIGS thin film is increased, thus forming a high-quality CIGS thin film.

[0028] Further, the pH of the electrolyte solution may be 2~3. Only when the pH thereof falls in this range, it is easy to form a CIGS thin film.

[0029] The method of forming a CIGS thin film according to the present invention is comprised of the step of performing electrodeposition in such a way as to apply a direct current (DC) voltage of $-0.95\text{V} \sim -0.85\text{V}$ to the electrolyte solution at room temperature and normal pressure for 10~120 minutes to form a preliminary CIGS thin film.

[0030] When the voltage is applied to the electrolyte solution under the above condition, the simultaneous growth of

four kinds of metal particles of the CIGS thin film can be explained by the reduction reactions attributable to the movement of electrons from the back electrode toward to the metal ions of the precursors in the electrolyte solution. A standard reduction potential of each oldie metal ions is as follows (vs. NHE <Normal Hydrogen Electrode>, an aqueous acidic to solution in the case of Se).

$\text{Cu}^{2+} + 2\text{e}^- \leftrightarrow \text{Cu}$	$E^0 = +0.34 \text{ V}$
$\text{In}^{3+} + 3\text{e}^- \leftrightarrow \text{In}$	$E^0 = -0.34 \text{ V}$
$\text{Ga}^{3+} + 3\text{e}^- \leftrightarrow \text{Ga}$	$E^0 = -0.56 \text{ V}$
$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow \text{Se} + 3\text{H}_2\text{O}$	$E^0 = +0.74 \text{ V}$

[0031] Meanwhile, when CIGS is used as a raw material of a solar cell, it is known that it is greatly effective to increase the efficiency of a solar cell when a CuInSe_2 phase having a bandgap of 1.04 eV and a CuGaSe_2 phase having a bandgap of 1.7 eV are mixed with each other to maximize the solar light absorption of a light-absorbing layer or the solar cell. In this case, the atom ratio of the two phases, $\text{Ga}/(\text{In}+\text{Ga})$, may be 0.2~0.4, more preferably, 0.3. When the atomic ratio thereof falls within the above range, the bandgap increases, so that the bandgap approximates an ideal bandgap, thereby increasing the solar light absorption of the light-absorbing layer of the solar cell. The present inventors examined the optimal electrodeposition potential for setting the correlation ratio of In and Ga, and, as a result, they found that the direct current (DC) voltage of $-0.95\text{V} \sim -0.85\text{V}$ is the most suitable for the optimal electroposition potential. Further, the electrodeposition of the CIGS thin film depends on various experimental variables, such as the surface resistance of the molybdenum electrode deposited on glass, etc., and the characteristics of the layer that is electrodeposited depending on the above experimental variables is not strictly defined.

[0032] The method of forming a CIGS thin film according to the present invention is comprised of the step of heat-treating the preliminary CIGS thin film at $230 \sim 270^\circ \text{C}$. to form a CIGS thin film.

[0033] When heat treatment is performed within the above range, the crystallinity of the CIGS thin film becomes high, and the consumption of energy is not high because the heat treatment temperature is relatively low, so that the method of forming a CIGS thin film according to the present invention is economical. Further, when the treatment is performed within the above range, the phenomenon in which selenium of the CIGS thin film volatilizes and thus disappears does not occur. Therefore, an additional process for replenishing selenium is not required. The melting points of the elements included in the preliminary CIGS thin film are 1083°C . (Cu), 156°C . (In), 29.78°C . (Ga), and 217°C . (Se), respectively. However, the elements included in the preliminary CIGS thin film formed by electrodeposition exist in the form of compounds rather than independently. For this reason, the preliminary CIGS thin film is comparatively stable during the low-temperature heat treatment thereof. Due to the heat treatment of the preliminary CIGS thin film, various phases of compounds including two kinds of elements, three kinds of elements and four kinds of elements can be produced. The present invention is to provide a method and condition of forming a CIGS thin film having a suitable composition by heat-treating the electrodeposited preliminary CIGS thin film in an atmosphere at low temperature.

[0034] The method of forming CIGS thin film according to the present invention is advantageous in that a large-area thin film can be formed at room temperature and normal pressure without using a vacuum chamber. Further, the method of forming CIGS thin film according to the present invention is advantageous in that a simple and cheap CIGS thin film having high light efficiency can be formed. Furthermore, the method of forming a CIGS thin film according to the present invention is advantageous in that the crystallinity of a CIGS thin film can be improved upon.

[0035] Hereinafter, the present invention will be described in more detail with reference to the following Examples. These Examples are set forth only to illustrate the present invention, and it is considered obvious by those skilled in the art that the scope of the present invention is not limited to these Examples.

Example 1, Comparative Examples 1 to 7

Formation of a CIGS Thin Film

[0036] A substrate, in which molybdenum (Mo) was deposited on soda-lime glass to a thickness of about 1 μm in the form of a two-layer structure by sputtering, was provided. Molybdenum had a specific resistance of about 15 $\mu\Omega\cdot\text{cm}$. The surface of the formed molybdenum layer was a uniform mirror surface.

[0037] Meanwhile, water-soluble precursors, a buffer solution and an additive were mixed with a 0.5M Na_2SO_4 electrolyte aqueous solution (here, distilled water Milli-Q was used as a solvent) as shown in Table 1 below to prepare an electrolyte solution. In this case, the pH of the electrolyte solution was adjusted using 2 mM of hydrochloric acid, and the pH thereof was about 2.7. Here, the contents of each of the water-soluble precursors, the buffer solution and the additive mean the contents thereof in the electrolyte solution.

TABLE 1

	CuSO_4 (mM)	$\text{In}_2(\text{SO}_4)_3$ (mM)	$\text{Ga}_2(\text{SO}_4)_3$ (mM)	H_2SeO_3 (mM)	buffer solution (ppm)	additive (mM)
Ex. 1	1	1	2	3	—	—
Co Ex. 1	1	2	2	5	A-1	B-1
Co Ex. 2	1	1	2	3	A-1	B-1
Co Ex. 3	1	1	2	3	A-1	B-1
Co Ex. 4	1	1	2	3	A-1	B-1
Co Ex. 5	1	2	2	5	A-1	B-1
Co Ex. 6	1	2	2	5	—	—
Co Ex. 7	1	2	2	5	A-1	B-1
Co Ex. 8	1	2	2	5	A-1	—
Co Ex. 9	1	2	2	5	—	B-1

CuSO_4 (manufacturing company: Aldrich, purity: 99.999%)

$\text{In}_2(\text{SO}_4)_3$ (manufacturing company: Aldrich, purity: 99.99%)

$\text{Ga}_2(\text{SO}_4)_3$ (manufacturing company: Aldrich, purity: 99.995%)

H_2SeO_3 (manufacturing company: Aldrich, purity: 98%)

A-1: Hydron pH 3 buffer

B-1: SDS (Sodium Dodecyl Sulfate)

[0038] Subsequently, the substrate was immersed into the electrolyte solution. Then, an electric potential was applied between the electrodes in the electrolyte solution at room temperature and normal pressure during the time that electrolytic deposition was carried out as given in Table 2 below to form a preliminary CIGS thin film. Here, a potentiostat/galvanostat (model M 270, manufactured by EG&G Corp.) was

used as a potentiostat, Ag/AgCl was used as a reference electrode, and a platinum (Pt) wire was used as a counter electrode.

[0039] Subsequently, the preliminary CIGS thin film was heat-treated at the temperature of heat treatment and for the duration of the heat treatment as given in Table 2 below to complete a CIGS thin film.

TABLE 2

	applied potential (V)	electrolytic deposition time (min)	heat treat- ment tem- perature ($^{\circ}\text{C}$.)	heat treat- ment time (min)
Ex. 1	-0.92	60	250	60
Co Ex. 1	-0.90	60	550	30
Co Ex. 2	-0.91	60	300	60
Co Ex. 3	-0.91	60	200	60
Co Ex. 4	-0.91	60	100	60
Co Ex. 5	-0.91	60	—	—
Co Ex. 6	-0.91	60	—	—
Co Ex. 7	-0.90	30	—	—
Co Ex. 8	-0.90	30	—	—
Co Ex. 9	-0.90	30	—	—

Experimental Example

Evaluation of Characteristic of CIGS Thin Film

[0040] FIG. 1 shows the SEM (scanning electron microscope) image of the surface of the preliminary CIGS thin film of Example 1 and EDS (energy dispersive spectrometer) data of the preliminary CIGS thin film of Example 1. Further, in Table 3 below, the EDS data of the preliminary CIGS thin film was expressed numerically. Here, "preliminary CIGS thin film" means a CIGS thin film which was electrodeposited but not heat-treated yet.

TABLE 3

	Approximate Concentration	Intensity correlation	Weight %	Weight % Sigma	Atomic %
Se	0.55	0.5118	47.10	0.05	48.75
Cu	0.37	1.0589	14.90	0.04	19.16
In	0.42	1.8662	21.02	0.04	14.97
Ga	0.21	1.0730	8.30	0.06	9.73
Mo	0.12	0.5956	8.68	0.03	7.40
Totals			100.00		

[0041] Referring to FIG. 1 and Table 3, it can be seen that four components, Cu, In, Ga, and Se, exist together. Examining the quantitative analysis of the atom ratio of each of the components given in Table 3, it is determined that the composition ratio of the preliminary CIGS thin film approximates the optimal value under the experimental condition that the atom ratio thereof is $\text{Cu}:\text{In}:\text{Ga}:\text{Se}=1.00:0.78:0.50:2.54$. Here, molybdenum (Mo) constituting an electrode was measured with Cu, In, Ga, and Se. The fact that the atomic percentage of Molybdenum (Mo), as a matrix material, is 7.40% verifies that the preliminary CIGS thin film is not uniform, is generally thin or is a non-uniform and thin film because this preliminary CIGS thin film is a thin film synthesized to such a degree that X-ray beams penetrate this preliminary CIGS thin film.

[0042] FIG. 2 is a graph showing the XRD analysis data of a preliminary CIGS thin film (a) and a CIGS thin film (b) of

Example 1. Here, the preliminary CIGS thin film (a) means a CIGS and EDS data of the CIGS thin film of Comparative Example 8; and

[0043] FIG. 11 shows the SEM of the surface of a CIGS thin film of Comparative Example 9 and EDS data of the CIGS thin film of Comparative Example 9.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0044] Hereinafter, the present invention will be described in detail with reference to the attached drawings.

[0045] The method of forming a CIGS thin film according to the present invention is comprised of the step of immersing a substrate comprising an electrode into an electrolyte solution comprising Na_2SO_4 , a water-soluble copper (Cu) precursor, a water-soluble indium (In) precursor, a water-soluble gallium (Ga) precursor and a water-soluble selenium (Se) precursor.

[0046] The substrate is not particularly limited as long as it is a substrate for a solar cell. However, a substrate comprising a molybdenum electrode or a substrate comprising a silicon electrode may be used as the substrate. Preferably, a substrate comprising a molybdenum electrode may be used as the substrate. The reason why the substrate comprising a molybdenum electrode is preferably used is because molybdenum has high electroconductivity and because the ohmic contact between molybdenum and a CIGS layer is excellent. Molybdenum is stable in a high-temperature selenium atmosphere. Even when a CIGS solar cell comprising a back electrode made of molybdenum is being operated for a long time, its energy conversion efficiency does not fall. Further, since molybdenum is relatively cheap, it is economical for the mass production of solar cells.

[0047] Here, the substrate comprising a silicon electrode may be a silicon wafer used in a semiconductor process.

[0048] The electrolyte solution may comprise a water-soluble copper (Cu) precursor, a water-thin film which was electrodeposited but not heat-treated yet. The CIGS thin film (b) means a CIGS thin film which was electrodeposited and heat-treated.

[0049] Referring to FIG. 2, when the 2θ values of the preliminary CIGS thin film of Example 1 were 40.1, 72.3 and 88.6 degrees, Mo (110), (211) and (220) peaks were observed, respectively, and simultaneously a wide and weak (112) peak of CIS was observed at a 2θ value of 28 degrees. Therefore, it is determined that line CIS crystals having a particle size of several nanometers are formed even by electrodeposition.

[0050] In the CIGS thin film of Example 1, (112) and (220) diffraction peaks of CIS chalcopyrite were observed, and traces of CIGS were observed in the vicinity of a 2θ value of 45 degrees. In the case of CIS (112), it was observed that its XRD pattern was very sharp and its intensity was increased. Therefore, it is determined that CIS chalcopyrite is considerably crystallized by heat treatment at 250° C.

[0051] That is, according to the present invention, since a CIGS thin film of line particles is formed only by electrodeposition at room temperature and normal pressure, it is predicted that the CIGS thin film formed by the electrodeposition can be crystallized at a lower temperature than the heat treatment temperature of 500° C. or more which is required by sputtering.

[0052] FIG. 3 shows the SEM of the CIGS thin film of Example 1. The EDS data of the CIGS thin film of Example

1 are given in Table 4. FIG. 4 is a graph showing the EDS data of the CIGS thin film of Example 1.

TABLE 4

Atomic %	
Se	46.37
In	28.36
Cu	13.0
Ga	12.27
Totals	100

[0053] FIG. 4 and Table 4 show that the atom ratio of Ga/(In+Ga) reached 0.3. Therefore, it can be determined from FIG. 4 and Table 4 that a CIGS thin film having high crystallinity and a proper composition ratio was formed.

[0054] FIG. 5 shows the SEM of the surface of a CIGS thin film of Comparative Example 1 and EDS data of the CIGS thin film of Comparative Example 1. Here, in Comparative Example 1, a silicon wafer was used as a substrate. The atomic weights of the components in the CIGS thin film of Comparative Example 1 before and after heat treatment are given in Table 5 below.

TABLE 5

	atomic weight (at %) before heat treatment	atomic weight (at %) after heat treatment
Si	47.062	66.112
Se	32.038	0
Cu	7.872	1.526
O	6.782	29.362
In	5.858	1.942
Ga	0.282	0.572
S	0.136	0.402

[0055] Referring to Table 5, it is observed that selenium (Se) does not remain in the CIGS thin film after heat treatment. Therefore, it is determined that Comparative Example 1, unlike the present invention, needs an additional process of replenishing selenium (Se).

[0056] FIG. 6 shows the SEM of the surface of a CIGS thin film of Comparative Example 2 and EDS data of the CIGS thin film of Comparative Example 2. The numerical values of the EDS data of "spectrum 4" which is one site of the CIGS thin film of Comparative Example 2 are given in Table 6 below. Further, the numerical values of the average EDS data of the CIGS thin film of Comparative Example 2 are given in Table 7 below.

TABLE 6

	Approximate Concentration	Intensity Correlation	Weight %	Weight % Sigma	Atomic %
Se	1.35	0.5028	48.03	0.08	50.80
In	1.63	0.9190	31.65	0.07	23.02
Cu	0.93	1.0496	15.82	0.07	20.79
Ga	0.27	1.0730	4.50	0.09	5.38
Totals			100.00		

[0057] Table 7 shows that the atom ratio of Ga/(In+Ga) is 0.27. However, the CIGS thin film of Comparative Example 2

is relatively non-economical compared to the CIGS thin film of Example 1 because it includes a buffer and SDS.

[0058] Further, Table 7 shows the change of the compositions of CIGS thin films of Comparative Examples 2, 3 and 4 before and after heat treatment. In Table 7, the unit of each atom is atomic percent (at %).

TABLE 7

	Comp. Exp 2		Comp Exp 3		Comp. Exp 4	
	before heat treat- ment	after heat treat- ment	before heat treat- ment	after heat treat- ment	before heat treat- ment	after heat treat- ment
Se	59	48	59	52	58	58
In	21	24	23	24	21	21
Cu	13	19	12	16	14	15
Ga	7	9	6	8	7	6
total	100	100	100	100	100	100

[0059] FIG. 7 shows the SEM of the surface of a CIGS thin film of Comparative Example 5 and EDS data of the CIGS thin film of Comparative Example 5. The numerical values of the EDS data of "spectrum 3" which is one site of the CIGS thin film of Comparative Example 5 are given in Table 8 below.

TABLE 8

	Approximate Concentration	Intensity Correlation	Weight %	Weight % Sigma	Atomic %
S	0.14	0.7190	0.19	0.01	30.87
Se	0.20	0.4653	0.43	0.02	28.13
Ga	0.23	1.0410	0.22	0.04	16.71
In	0.30	0.8684	0.35	0.03	15.60
Cu	0.11	1.0382	0.11	0.03	8.69
Totals			1.29		

[0060] FIG. 7 and Table 8 show that, although the CIGS thin film of Comparative Example 5 was formed using an electrolyte solution to which a buffer and SDS were added, when the composition ratio of Cu:In:Ga:Se in the electrolyte solution was 1:2:2:5, a CIGS thin film having an atom ratio of Ga/(Ga+In)=0.5 was formed. Therefore, it can be seen that the composition ratio of ions in the electrolyte solution is more important than the addition of a buffer and SDS in the formation of a CIGS thin film having a proper atom ratio using electrodeposition. The CIGS thin film of Comparative Example 5 is not suitable for being used as a light-absorbing layer of a solar cell because it does not have an excellent bandgap.

[0061] FIG. 8 shows the SEM of the surface of a CIGS thin film of Comparative Example 6 and EDS data of the CIGS thin film of Comparative Example 6. The numerical values of the EDS data of the CIGS thin film of Comparative Example 6 are given in Table 9 below.

TABLE 9

	Approximate Concentration	Intensity Correlation	Weight %	Weight % Sigma	Atomic %
Se	0.98	0.4755	2.07	0.04	43.00
In	0.98	0.8881	1.10	0.05	15.77

TABLE 9-continued

	Approximate Concentration	Intensity Correlation	Weight %	Weight % Sigma	Atomic %
Ga	0.70	1.0615	0.66	0.08	15.52
Cu	0.58	1.0577	0.55	0.04	14.22
S	0.15	0.6746	0.22	0.02	11.50
Totals			4.61		

[0062] FIG. 8 and Table 9 show that the CIGS thin film of Comparative Example 6 was formed using an electrolyte solution to which a buffer and SDS were not added, and the composition ratio of Cu:In:Ga:Se in the electrolyte solution was 1:2:2:5. Table 9 show that a CIGS thin film having an atom ratio of Ga/(Ga+In)=0.5 was formed, which is similar to that of Comparative Example 5. Comparing Table 9 with Table 8, it can be seen that the CIGS thin film shown in Table 8 includes a larger amount of sulfur (S) than that shown in Table 9, that is, when SDS is added to the electrolyte solution, a preliminary CIGS thin film containing a large amount of sulfur (S) is formed. Therefore, it is not preferred that an additive be added to the electrolyte solution in the present experimental conditions.

[0063] Further, comparing Table 9 with Table 3, it is shown that the ratio of the gallium (Ga) in the CIGS thin film is sensitive to changes depending on the composition ratio of Cu:In:Ga:Se in the electrolyte. The ratio of (Ga) in the electrolyte solution of Comparative Example 6 is relatively small compared to that of gallium (Ga) in the electrolyte solution of Example 1, whereas the ratio of gallium (Ga) in the CIGS thin film of Comparative Example 6 is relatively large compared to that of gallium (Ga) in the preliminary CIGS thin film of Example 1. It is determined that these results are attributable to electrode reaction kinetic characteristics occurring in a multi-component system, like CIGS.

[0064] The composition of the CIGS thin film of Comparative Example 5 and that of the CIGS thin film of Comparative Example 6 are compared in Table 10 below.

TABLE 10

	Cu	In	Ga	Se	S
Comp. Exp. 5	10.86	14.31	11.79	26.16	36.88
Comp. Exp. 6	15.2	15.88	14.92	44.36	9.64

[0065] FIG. 9 shows the SEM of the surface of a CIGS thin film of Comparative Example 7 and EDS data of the CIGS thin film of Comparative Example 7. The numerical values of the EDS data of the CIGS thin film of Comparative Example 7 are given in Table 11 below.

TABLE 11

	Approximate Concentration	Intensity Correlation	Weight %	Weight % Sigma	Atomic %
O	3.72	0.3947	20.63	0.28	58.96
Mo	12.71	0.7445	37.32	0.33	17.79
Se	5.37	0.5464	21.46	0.22	12.43
In	3.95	0.7671	11.26	0.24	4.48
Ga	2.66	1.0082	5.77	0.38	3.78
Cu	1.60	0.9816	3.55	0.22	2.56
Totals			100.00		

[0066] Referring to Table 11, a large amount of oxygen is discovered. Comparing the compositions of the CIGS thin films in Table 8 and Table 11, which were produced by using the electrolyte solution of the same composition of the four elements with the different potentials applied, a considerable amount of sulfur (S) is discovered in Table 8, whereas a large amount of oxygen (O) is discovered in Table 11. It is determined that these results are due to the fact that the voltages applied between the electrodes to the electrolyte solutions of Comparative Example 5 and Comparative Example 7 are -0.91 and -0.90 V, respectively. Further, it is determined that the applied voltage, compared to the composition of the electrolyte solution, is an experimental factor greatly influencing the composition of the preliminary CIGS thin film formed on the surface of a molybdenum (Mo) electrode. The fact that Sulfur (S) was not discovered at all in the CIGS thin film of Comparative Example 7, unlike Comparative Example 5, also shows that the composition of a CIGS thin film can be changed by controlling the applied voltage regardless of the existence of SDS in the electrolyte solution.

[0067] FIG. 10 shows the SEM of the surface of a CIGS thin film of Comparative Example 8 and EDS data of the CIGS thin film of Comparative Example 8. The numerical values of the EDS data of the CIGS thin film of Comparative Example 8 are given in Table 12 below.

TABLE 12

	Approximate Concentration	Intensity correlation	Weight %	Weight % Sigma	Atomic %
O	4.06	0.4039	15.23	0.34	49.31
Se	12.85	0.5746	33.84	0.33	22.19
Mo	12.82	0.6862	28.28	0.37	15.26
In	7.04	0.7924	13.45	0.30	6.06
Cu	3.10	0.9992	4.69	0.27	3.82
Ga	3.06	1.0287	4.51	0.40	3.35
Totals			100.00		

[0068] Referring to Table 12, a large amount of oxygen (O) was discovered as in Table 11 above. It is analyzed that these results are due to the fact that the voltages applied to the electrolyte solutions of Comparative Example 7 and Comparative Example 8 are equal to each other. It is determined that oxygen (O) serves to produce oxides of Cu, In, Ga or Se by reducing oxygen molecules or hydroxide ions at the time of forming a preliminary CIGS thin film. Therefore, it is not preferred that large amount of oxygen (O) be discovered.

[0069] FIG. 11 shows the SEM of the surface of a CIGS thin film of Comparative Example 9 and EDS data of the CIGS thin film of Comparative Example 9. The numerical values of the EDS data of the CIGS thin film of Comparative Example 9 are given in Table 13 below.

TABLE 13

	Approximate Concentration	Intensity correlation	Weight %	Weight % Sigma	Atomic %
Se	7.29	0.5912	35.95	0.26	39.88
Mo	9.54	0.6989	39.82	0.30	36.35
In	3.90	0.7638	14.89	0.25	11.36
Cu	1.98	1.0503	5.49	0.24	7.57
Ga	1.44	1.0903	3.85	0.35	4.84
Totals			100.00		

[0070] Table 13 shows that oxygen (O) or sulfur (S) was not discovered. Comparative Example 9 is greatly different from other Comparative Examples in that a large amount of molyb-

denum (Mo) was discovered. This result verifies that an additive does not greatly influence the formation of a CIGS thin film. In Comparative Example 9, unlike Comparative Example 7, oxygen (O) was not discovered although the same voltage of -0.90 V was applied. This result verifies that buffer influences an electrode reaction rate in addition to adjusting the pH of an electrolyte solution.

[0071] As described above, the method of forming a CIGS thin film according to the present invention is advantageous in that a large-area thin film can be formed at room temperature and normal pressure without using a vacuum chamber. Further, the method of trimming a CIGS thin film according to the present invention is advantageous in that a simple and cheap CIGS thin film having high light efficiency can be formed. Furthermore, the method of forming a CIGS thin film according to the present invention is advantageous in that the crystallinity of a CIGS thin film can be improved.

[0072] 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.

What is claimed is:

1. A method of forming a CIGS thin film, comprising the steps of:

immersing a substrate comprising an electrode into an electrolyte solution comprising Na_2SO_4 , a water-soluble copper (Cu) precursor, a water-soluble indium (In) precursor, a gallium (Ga) water-soluble precursor, and a water-soluble selenium (Se) precursor;

performing electrodeposition in such a way as to apply a direct current (DC) voltage of -0.95V ~ -0.85V to the electrolyte solution at room temperature and normal pressure for 10~120 minutes to form a preliminary CIGS thin film; and

heat-treating the preliminary CIGS thin film at 230 ~ 270°C . to form a CIGS thin film.

2. The method according to claim 1, wherein the substrate comprising an electrode is a substrate comprising a molybdenum electrode or a silicon electrode.

3. The method according to claim 1, wherein the electrolyte solution comprises a water-soluble copper (Cu) precursor, a water-soluble indium (In) precursor, a water-soluble gallium (Ga) precursor, and a water-soluble selenium (Se) precursor, each of which is of a concentration of 0.1 ~ 10 mM.

4. The method according to claim 1, wherein the water-soluble copper (Cu) precursor is selected from the group consisting of $\text{Cu}(\text{NO}_3)_2$, CuSO_4 , and hydrates thereof.

5. The method according to claim 1, wherein the water-soluble indium (In) precursor is selected from the group consisting of $\text{In}(\text{NO}_3)_3$, $\text{In}_2(\text{SO}_4)_3$, and hydrates thereof.

6. The method according to claim 1, wherein the water-soluble gallium (Ga) precursor is selected from the group consisting of $\text{Ga}(\text{NO}_3)_3$, $\text{Ga}_2(\text{SO}_4)_3$, and hydrates thereof.

7. The method according to claim 1, wherein the water-soluble selenium (Se) precursor is selected from the group consisting of SeO_2 , H_2SeO_3 , and hydrates thereof.

8. The method according to claim 1, wherein the electrolyte solution has a pH of 2 ~ 3 .

9. The method according to claim 1, wherein an atom ratio of copper, indium, gallium, and selenium in the electrolyte solution is 0.8 ~ 1.2 : 0.8 ~ 1.2 : 1.8 ~ 2.2 : 2.8 ~ 3.2 .

10. The method according to claim 9, wherein the atom ratio of copper, indium, gallium, and selenium in the electrolyte solution is 1 : 1 : 2 : 3 .

11. The method according to claim 1, wherein the CIGS thin film has an atom ratio of $\text{Ga}/(\text{In}+\text{Ga})$ of 0.2 ~ 0.4 .