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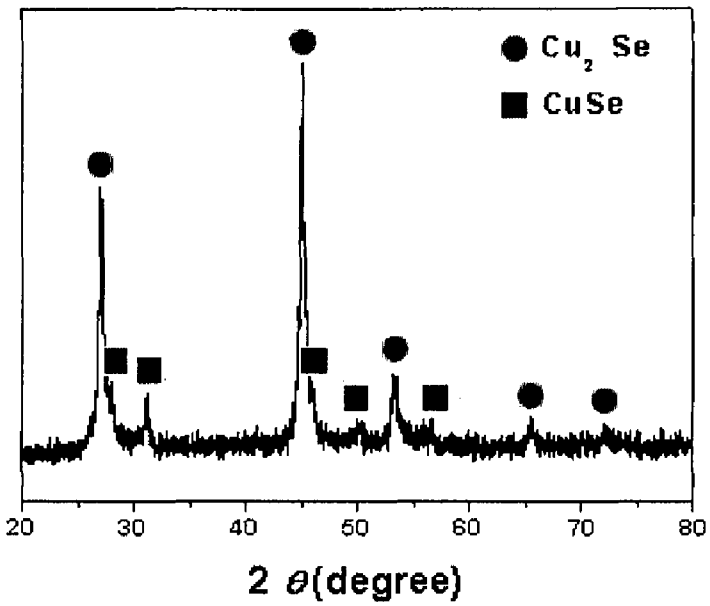
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(54) Title: FABRICATION METHOD OF PHOTO ACTIVE LAYER FOR SOLAR CELL



(57) Abstract: Provided is a fabrication method of a photo active layer for a solar cell, the fabrication method including: a) coating ink containing composite particles in which a first chalcogenide of Group 1 1 metals and a second chalcogenide of Group 11 metals having a melting point lower than that of the first chalcogenide are mixed in a single particle and a precursor of at least one element selected from Groups 12 to 14 elements onto a substrate to form a coating film; and b) heat treating the coating film to prepare a multinary chalcogenide.

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Description

Title of Invention: FABRICATION METHOD OF PHOTO ACTIVE LAYER FOR SOLAR CELL

Technical Field

[1] The present invention relates to a fabrication method of a photo active layer for a solar cell, and more particularly, to a fabrication method of a compound semiconductor based photo active layer for a solar cell.

Background Art

[2] In a manufacturing process of a compound semiconductor (CIG(S, Se), CZT(S, Se)) photo active layer based on an existing vapor deposition method, there is a limitation in that process cost is expensive in spite of excellent characteristics. Therefore, in order to commercialize a solar cell using the compound semiconductor, a fabrication method of a CIG(S, Se) or CZT(S, Se) photo active layer using a solution process is considered as an essential technology.

[3] As disclosed in US Patent Nos. 6127202 and 6268014, a fabrication method of a photo active layer using a particle based solution process of coating a mixture of metal oxide nanoparticles or a mixture of a metal oxide and particles that are not metal oxides on a substrate and performing a reaction under a reducing atmosphere and Se gas atmosphere to prepared a CI(G)S film has been attempted.

[4] However, in the case of fabricating the photo active layer using the metal oxide based solution process, a parenthetical reduction process should be necessarily performed, and a defect may be generated in a film at the time of the reduction process, which may cause non-uniformity of the reaction at the time of heat-treatment process under Se gas atmosphere.

[5] Therefore, research into a new economical method for fabricating a dense single phase CIG(S, Se) or CZT(S, Se) film by heat-treatment at about 550°C, which is a process allowable temperature, has been demanded.

[6]

Disclosure of Invention

Technical Problem

[7] An object of the present invention is to provide ink capable of fabricating a dense compound semiconductor based photo active layer composed of a single phase through heat treatment at a low temperature of 550°C or less, which is a process allowable temperature.

[8] Another object of the present invention is to provide a fabrication method of a dense compound semiconductor based photo active layer composed of a single phase through

heat treatment at a low temperature of 550°C or less, which is a process allowable temperature, and a photo active layer fabricated therefrom.

Solution to Problem

[9] In one general aspect, there is provided an ink including: composite particles in which a first chalcogenide of Group 11 metals and a second chalcogenide of Group 11 metals having a melting point lower than that of the first chalcogenide are mixed in a single particle; and a precursor of at least one element selected from Groups 12 to 14 elements.

[10] The precursor of at least one element selected from Groups 12 to 14 elements may be chloride, nitrate, sulfate, acetate, phosphate, silicate, or hydrochloride of one or at least two elements selected from the Groups 12 to 14 elements, or a mixture thereof.

[11] The precursor of at least one element selected from Groups 12 to 14 elements may be a third chalcogenide of one or at least two elements selected from Groups 12 to 14 elements.

[12] In another general aspect, there is provided a fabrication method of a photo active layer for a solar cell, the fabrication method including: a) coating ink containing composite particles in which a first chalcogenide of Group 11 metals (hereinafter, referred to as a high melting point first chalcogenide) and a second chalcogenide of Group 11 metals (hereinafter, referred to as a low melting point second chalcogenide) having a melting point lower than that of the first chalcogenide are mixed in a single particle and a precursor of at least one element selected from Groups 12 to 14 elements onto a substrate to form a coating film; and b) heat treating the coating film to prepare a multinary chalcogenide.

[13] The low melting point second chalcogenide may have a melting point of 220 to 550°C.

[14] The composite particle may contain 10 to 900 parts by weight of the high melting point first chalcogenide based on 100 parts by weight of the low melting point second chalcogenide.

[15] A molar ratio of at least one element selected from Groups 12 to 14 elements and contained in the ink to the Group 11 metal contained in the first and second chalcogenides may be 1:0.7 to 1.2.

[16] The high melting point first chalcogenide may include Cu_2Se, and the low melting point second chalcogenide may include CuSe, $CuSe_2$, or a mixture thereof.

[17] The composite particle including the first and second chalcogenides may be prepared by preparing a first solution containing a precursor of a Group 11 metal and a second solution containing a surfactant, which is trioctylphosphine, trioctylphosphineoxide, acid, or a mixture thereof, and a chalcogenide precursor and then injecting the first

solution into the second solution having a temperature of 160 to 240°C.

[18] The heat treatment may be performed at 400 to 550°C.

[19] The heat treatment may be performed under chalcogen atmosphere.

[20] The precursor of at least one element selected from Groups 12 to 14 elements may be chloride, nitrate, sulfate, acetate, phosphate, silicate, or hydrochloride of one or at least two elements selected from the Groups 12 to 14 elements, or a mixture thereof.

[21] The precursor of at least one element selected from Groups 12 to 14 elements may be a third chalcogenide of one or at least two elements selected from Groups 12 to 14 elements.

[22] The third chalcogenide may include one or at least two particles selected from $(In_xGa_{1-x})_4(S_ySe_{1-y})_3$ particles, $(In_xGa_{1-x})(S_ySe_{1-y})$ particles, $(In_xGa_{1-x})_6(S_ySe_{1-y})_7$ particles, $(In_xGa_{1-x})_9(S_ySe_{1-y})_{11}$ particles, $(In_xGa_{1-x})_2(S_ySe_{1-y})_3$ particles, and $(In_xGa_{1-x})_5(S_ySe_{1-y})_7$ particles (x and y are real numbers satisfying the following Equations, respectively: $0\leq x\leq 1$ and $0\leq y\leq 1$); or include one or at least two particles selected from $Sn(S_ySe_{1-y})$ particles, $Sn_2(S_ySe_{1-y})_3$ particles, and $Sn(S_ySe_{1-y})_2$ particles (y is a real number satisfying the following Equation: $0\leq y\leq 1$) and $Zn(S_ySe_{1-y})$ particles (y is a real number satisfying the following Equation: $0\leq y\leq 1$).

[23] A single phase multinary chalcogenide may be formed by the heat treatment.

[24] In another general aspect, there is provided an ink including: copper nanoparticles; and chalcogenide particles of one or at least two elements selected from Groups 12 to 14 elements. In this case, the ink may be ink for a photo active layer of a solar cell.

[25] In another general aspect, there is provided a fabrication method of a photo active layer for a solar cell, the fabrication method including: a) coating ink containing copper nanoparticles; and chalcogenide particles of one or at least two elements selected from Groups 12 to 14 elements onto a substrate to form a coating film; and b) heat treating the coating film to prepare a multinary chalcogenide film of copper and one or at least two elements selected from Groups 12 to 14 elements.

[26] The Group 12 element may include zinc (Zn), the Group 13 element may be at least one selected from indium and gallium, the Group 14 element may include Sn, and a chalcogen element may be at least one selected from sulfur and selenium.

[27] The chalcogenide particles may include chalcogen (S and/or Se) compound particles of at least one selected from In and Ga. For example, the chalcogenide particles may include one or at least two particles selected from $(In_xGa_{1-x})_4(S_ySe_{1-y})_3$ particles, $(In_xGa_{1-x})(S_ySe_{1-y})$ particles, $(In_xGa_{1-x})_6(S_ySe_{1-y})_7$ particles, $(In_xGa_{1-x})_9(S_ySe_{1-y})_{11}$ particles, $(In_xGa_{1-x})_2(S_ySe_{1-y})_3$ particles, and $(In_xGa_{1-x})_5(S_ySe_{1-y})_7$ particles. In these chalcogenide particles, x and y may be real numbers satisfying the following Equations, respectively: $0\leq x\leq 1$ and $0\leq y\leq 1$.

[28] The chalcogenide particles may include chalcogen (S and/or Se) compound particles

of at least one selected from Sn and Zn. For example, the chalcogenide particles may include a mixture of one or at least two particles selected from $Sn(S_ySe_{1-y})$ particles, $Sn_2(S_ySe_{1-y})_3$ particles, and $Sn(S_ySe_{1-y})_2$ particles and $Zn(S_ySe_{1-y})$ particles. In these chalcogenide particles, each y may be a real number satisfying the following Equation: $0 \leq y \leq 1$.

[29] A molar ratio of one or at least two elements selected from Groups 12 to 14 elements and contained in the ink to copper may be 1:0.7 to 1.2.

[30] The heat treatment may be performed at 400 to 550°C.

[31] The heat treatment may be performed under chalcogen atmosphere.

[32] A single phase multinary chalcogenide may be formed by the heat treatment.

[33] The copper nanoparticles may be copper nanoparticles prepared by heating and stirring a copper precursor solution containing a copper precursor, acid, and amine and then injecting a reducing agent thereinto to thereby be capped with acid and amine.

[34] In another general aspect, there is provided a photo active layer for a solar cell fabricated by the fabrication method as described above.

[35] In another general aspect, there is provided a solar cell provided with a photo active layer for a solar cell fabricated by the fabrication method as described above.

[36]

Advantageous Effects of Invention

[37] With a fabrication method of a photo active layer according to the present invention, a high quality multinary chalcogenide (photo active layer) may be prepared, a photo active layer made of a single phase multinary chalcogenide may be fabricated at a temperature within a process allowable temperature of 550°C or less, and a photo active layer having compositional stability, excellent uniformity, and a dense micro structure and composed of coarse grains may be fabricated, by a significantly simple, safe, and easy process of coating ink containing composite particles in which a high melting point first chalcogenide of Group 11 metals and a low melting point second chalcogenide of Group 11 metals are mixed in a single particle and a precursor of at least one element selected from Groups 12 to 14 elements and heat treating a coating film at a low temperature.

[38] With a fabrication method of a photo active layer according to the present invention, a high quality multinary chalcogenide (photo active layer) may be prepared, a photo active layer made of a single phase multinary chalcogenide may be fabricated at a temperature within a process allowable temperature of 550°C or less, and a photo active layer having excellent uniformity and a dense micro structure and composed of coarse grains having a micrometer-order size may be fabricated, by a significantly simple, safe, and easy process of coating ink containing copper nanoparticles and chalcogenide

particles and heat treating a coating film at a low temperature.

Brief Description of Drawings

[39] The above and other objects, features and advantages of the present invention will become apparent from the following description of preferred embodiments given in conjunction with the accompanying drawings, in which:

[40] FIG. 1 is a view showing a result obtained by X-ray diffraction (XRD) analysis of copper chalcogenide particles prepared in Preparation Example 1;

[41] FIG. 2 is a scanning electron microscope (SEM) photograph of the copper chalcogenide particles prepared in Preparation Example 1;

[42] FIG. 3 is scanning electron microscope (SEM) photographs of a cross section of a photo active layer fabricated in Preparation Example 1;

[43] FIG. 4 is a view showing a result obtained by X-ray diffraction analysis of the photo active layer fabricated in Preparation Example 1;

[44] FIG. 5 is a view showing a result obtained by X-ray diffraction analysis of copper chalcogenide particles prepared in Comparative Example 1;

[45] FIG. 6 is a scanning electron microscope (SEM) photograph of the copper chalcogenide particles prepared in Comparative Example 1;

[46] FIG. 7 is a scanning electron microscope (SEM) photograph of a cross section of a photo active layer fabricated in Comparative Example 1;

[47] FIG. 8 is scanning electron microscope (SEM) photographs of a surface of a photo active layer fabricated in Comparative Example 4;

[48] FIG. 9 is scanning electron microscope (SEM) photographs of a surface of a photo active layer fabricated in Comparative Example 5;

[49] FIG. 10 is a view showing a result obtained by X-ray diffraction analysis of copper chalcogenide particles prepared in Preparation Example 4;

[50] FIG. 11 is a scanning electron microscope (SEM) photograph of the copper chalcogenide particles prepared in Preparation Example 4;

[51] FIG. 12 is a scanning electron microscope (SEM) photograph of In_2Se_3 synthesized in Preparation Example 5;

[52] FIG. 13 is a scanning electron microscope (SEM) photograph of a photo active layer fabricated in Preparation Example 5

[53] FIG. 14 is a view showing a result obtained by X-ray diffraction analysis of the photo active layer fabricated in Preparation Example 5;

[54] FIG. 15 is a view showing a result obtained by X-ray diffraction analysis of copper chalcogenide particles prepared in Comparative Example 9;

[55] FIG. 16 is a scanning electron microscope (SEM) photograph of the copper chalcogenide particles prepared in Comparative Example 9;

[56] FIG. 17 is a scanning electron microscope (SEM) photograph of a photo active layer fabricated in Comparative Example 9;

[57] FIG. 18 is a scanning electron microscope (SEM) photograph of a surface of a photo active layer fabricated in Comparative Example 10;

[58] FIG. 19 is a scanning electron microscope (SEM) photograph of a surface of a photo active layer fabricated in Comparative Example 11;

[59] FIG. 20 is a view showing an X-ray diffraction pattern of Cu nanoparticles synthesized in Preparation Example 9;

[60] FIG. 21 is a scanning electron microscope (SEM) photograph of the Cu nanoparticles synthesized in Preparation Example 9;

[61] FIG. 22 is a scanning electron microscope (SEM) photograph of In_2Se_3 synthesized in Preparation Example 9;

[62] FIG. 23 is a scanning electron microscope (SEM) photograph of the photo active layer fabricated in Preparation Example 9

[63] FIG. 24 a view showing an X-ray diffraction pattern of a photo active layer fabricated in Preparation Example 9;

[64] FIG. 25 is a view showing an X-ray diffraction pattern of $CuInSe_2$ particles prepared in Comparative Example 12;

[65] FIG. 26 is a scanning electron microscope (SEM) photograph of the $CuInSe_2$ particles prepared in Comparative Example 12; and

[66] FIG. 27 is a scanning electron microscope (SEM) photograph of a cross section of a photo active layer fabricated in Comparative Example 12.

Mode for the Invention

[67] Hereinafter, ink and a fabrication method of a photo active layer according to the present invention will be described in detail with reference to accompanying drawings. The drawings to be provided below are provided by way of example so that the idea of the present invention can be sufficiently transferred to those skilled in the art to which the present invention pertains. Therefore, the present invention is not limited to the drawings to be provided below, but may be modified in many different forms. In addition, the drawings to be provided below may be exaggerated in order to clarify the scope of the present invention. Technical terms and scientific terms used in the present specification have the general meaning understood by those skilled in the art to which the present invention pertains unless otherwise defined, and a description for the known function and configuration obscuring the present invention will be omitted in the following description and the accompanying drawings.

[68] The present applicant conducted further studies on a photo active layer of a compound semiconductor based solar cell and found that in the case of using a

composite particle in which a high melting point first chalcogenide of a Group 11 metal maintaining a solid phase in a heat treatment temperature and a low melting point second chalcogenide of a Group 11 metal maintaining a liquid phase in the heat treatment temperature are mixed with each other in a single particle as a raw material, a high quality photo active layer may be fabricated by heat treatment at a low temperature of 550°C or less, which is a process allowable temperature, and a photo active layer made of a single phase multinary chalcogenide, a dense and uniform photo active layer, and a photo active layer composed of coarse grains may be fabricated.

[69] In addition, the present applicant conducted further studies on a photo active layer of a compound semiconductor based solar cell and found that a high quality photo active layer may be fabricated by heat treatment at a low temperature of 550°C or less, which is a process allowable temperature, and a photo active layer made of a single phase multinary chalcogenide, a dense photo active layer, and a photo active layer composed of coarse grains may be fabricated by performing a process of mixing and heat treating chalcogenide particles between copper nanoparticles and elements configuring a photo active layer to be fabricated except for copper.

[70] Hereinafter, ink containing composite particles and a fabrication method of a photo active layer using the composite particles will be described in detail.

[71] The ink according to the present invention contains composite particles in which a first chalcogenide of the Group 11 metal (hereinafter, referred to as the high melting point first chalcogenide) and a second chalcogenide of the Group 11 metal having a melting point lower than that of the high melting point first chalcogenide (hereinafter, referred to as the low melting point second chalcogenide) are mixed in the single particle; and a precursor of at least one element selected from Groups 12 to 14 elements. In this case, the ink according to the present invention may be ink for a photo active layer of a solar cell.

[72] In detail, the ink contains the chalcogenide of the Group 11 metals; and a precursor of an element configuring of the photo active layer to be fabricated except for the Group 11 metals and a chalcogen element, wherein the chalcogenide of the Group 11 metal contains the first chalcogenide of the group 11 metal and the second chalcogenide of the Group 11 metal that have different melting points from each other.

[73] In the ink according to an exemplary embodiment of the present invention, the high melting point first chalcogenide may maintain the solid phase, and the low melting point second chalcogenide may form a molten phase (liquid phase) at the heat treatment temperature for fabricating the photo active layer for the solar cell.

[74] In detail, the heat treatment temperature for fabricating the photo active layer for the solar cell may be 400 to 550°C. Here, the high melting point first chalcogenide may maintain the solid phase at 400 to 550°C, and the low melting point second

chalcogenide may form the molten phase at 400 to 550°C.

[75] In the ink according to the exemplary embodiment of the present invention, in order to fabricate a single phase multinary chalcogenide film to be desired by reacting the precursor contained in the ink with the chalcogenide of the Group 11 metal through the heat treatment at the low temperature of 550°C or less and fabricate a uniform and dense film, the low melting point second chalcogenide may have a melting point of 220 to 550°C. As the high melting point first chalcogenide, any chalcogenide of the Group 11 metal maintaining a solid phase at a heat treatment temperature, that is, a temperature more than 550°C may be used. For example, the first chalcogenide may have a melting point of 600 to 1200°C.

[76] In the ink according to the exemplary embodiment of the present invention, the high melting point first chalcogenide and the low melting point second chalcogenide may be mixed with each other in the single particle and may be homogeneously aggregated with each other in a synthetic step to have a particle shape.

[77] That is, the ink according to the exemplary embodiment of the present invention may contain the composite particle in which the high melting point first chalcogenide forming the solid phase at the time of heat treatment for fabricating the photo active layer and the low melting point second chalcogenide forming the liquid phase at the time of the heat treatment are homogeneously distributed in the single particle.

[78] The ink according to the exemplary embodiment of the present invention contains the low melting point second chalcogenide molten at the heat treatment temperature for fabricating the photo active layer and the high melting point first chalcogenide maintaining the solid phase at the heat treatment temperature and may include the composite particle in which the high melting point first chalcogenide and the low melting point second chalcogenide are highly homogeneously distributed in the single particle in the synthetic step. Therefore, the single phase multinary chalcogenide may be rapidly and homogeneously formed by the second chalcogenide formed in the molten phase and the first chalcogenide maintaining the solid phase, and a loss of the chalcogen element is prevented, such that compositional stability may be obtained. In the case in which the high melting point chalcogenide and low melting point chalcogenide are independently synthesized and then physically mixed with each other in a specific solvent to thereby prepare the ink, distribution of the molten phase in a heat treatment process may be determined according to the distribution of the low melting point chalcogenide after coating the ink, such that a non-uniform micro structure of the finally fabricated photo active layer may be formed. Further, in the case in which the ink is prepared based on only the low melting point chalcogenide without using the high melting point chalcogenide, evaporation of crystalline phases having low melting points may be generated due to excessive formation of the molten

phase during the heat treatment after coating the ink, such that it may be difficult to control a composition of the finally fabricated photo active layer.

[79] In the ink according to the exemplary embodiment of the present invention, the composite particle in which the high melting point first chalcogenide and the low melting point second chalcogenide are homogeneously mixed may be a nanoparticle and have an average particle size of 5 to 500nm.

[80] In the ink according to the exemplary embodiment of the present invention, the Group 11 metal may include copper, and the chalcogenide of the Group 11 metal may be a copper chalcogenide. In addition, the first chalcogenide may be a first copper chalcogenide, and the second chalcogenide may be a second copper chalcogenide having a melting point lower than that of the first copper chalcogenide. The first and second copper chalcogenides may be crystalline phases, respectively, have different crystalline phases from each other, and have different melting points from each other by the different crystalline phases.

[81] In the ink according to the exemplary embodiment of the present invention, the first chalcogenide may include Cu_2Se, and the second chalcogenide may include CuSe, $CuSe_2$, or a mixture thereof.

[82] In the ink according to the exemplary embodiment of the present invention, composite particle may contain 10 to 900 parts by weight of the first chalcogenide based on 100 parts by weight of the second chalcogenide. In the case in which a weight ratio of the second chalcogenide to the first chalcogenide is out of the above-mentioned range, low temperature reactivity and film quality may be deteriorated by the low melting point of the second chalcogenide, and a loss of the chalcogen element may be generated. In the ink according to the exemplary embodiment of the present invention, composite particle may contain 10 to 900 parts by weight of the first chalcogenide, preferably 100 to 900 parts by weight of the first chalcogenide, and more preferably 200 to 600 parts by weight of the first chalcogenide, based on 100 parts by weight of the second chalcogenide.

[83] In the ink according to the exemplary embodiment of the present invention, the chalcogenide (chalcogenide of the Group 11 metal) including the first and second chalcogenides that are contained in the ink may be a chalcogenide prepared by preparing a first solution containing a precursor of the Group 11 metals and a second solution containing the surfactant, which is trioctylphosphine, trioctylphosphine oxide, acid, or a mixture thereof, and a chalcogen precursor and then injecting the first solution into the second solution having a temperature of 160 to 240°C.

[84] The chalcogenide of the Group 11 metals may be prepared in a composite particle shape in which the first and second chalcogenides are homogeneously aggregated with each other by the fabrication method of the chalcogenide as described above, and

chalcogenide nanoparticles reacting with the precursor of at least one element selected from Groups 12 to 14 elements to have a stable composition and including a dense film of the single phase multinary chalcogenide formed thereon may be prepared by the heat treatment at a low temperature of 550°C or less.

[85] In the fabrication method of the chalcogenide as described above, a relative ratio of the first and second chalcogenides in the synthesized chalcogenide may be controlled by the temperature of the second solution into which the first solution is injected simultaneously with using trioctylphosphine, trioctylphosphine oxide, acid, or the mixture thereof as the surfactant. Chalcogenide particles (composite particles) in which the weight ratio of the first chalcogenide to the second chalcogenide is 10 to 900(first chalcogenide):100(second chalcogenide), preferably 100 to 900(first chalcogenide):100(second chalcogenide), more preferably 200 to 600(first chalcogenide):100(second chalcogenide) may be prepared by controlling the temperature of the second solution to 160~240°C. A molar ratio of the surfactant may be preferably 0.1 to 30 based on the precursor of the Group 11 metal.

[86] In the fabrication method of the chalcogenide as described above, the precursor of the Group 11 metal may include a copper precursor, wherein the copper precursor may be any one or at least two selected from copper chloride, copper nitrate, copper sulfate, copper acetate, copper phosphate, copper silicate, and copper hydrochloride.

[87] In the fabrication method of the chalcogenide as described above, the acid used as the surfactant may be a saturated or unsaturated acid and have one or at least two shapes selected from a linear shape, a branched shape, or a circular shape in which 6 to 30 carbon atoms are contained. Substantial examples of the acid may include one or at least two acids selected from oleic acid, ricinoleic acid, stearic acid, hydroxy stearic acid, linoleic acid, aminodecanoic acid, hydroxy decanoic acid, lauric acid, decanoic acid, undecanoic acid, hexyldecanoic acid, hydroxy palmitic acid, hydroxy myristic acid, palmitoleic acid, and myristoleic acid.

[88] In the fabrication method of the chalcogenide as described above, a solvent of the first solution may be an amine based solvent, wherein the amine based solvent may be a saturated or unsaturated amine and have one or at least two shapes selected from a linear shape, a branched shape, or a circular shape in which 6 to 30 carbon atoms are contained. As a substantial example, the amine based solvent may include one or at least two solvents selected from diethyl amine, triethylamine, 1,3-propane diamine, 1,4-butane diamine, 1,5-pentane diamine, 1,6-hexane diamine, 1,7-heptane diamine, 1,8-octane diamine, diethylene diamine, diethylene triamine, toluene diamine, m-phenylenediamine, diphenyl methane diamine, hexamethylene diamine, triethylene tetramine, tetraethylenepentamine, hexamethylene tetramine, ethanolamine, diethanolamine, triethanolamine, and oleylamine.

[89] In the fabrication method of the chalcogenide as described above, a molar concentration of the precursor of the Group 11 metal contained in the first solution may be 0.01 to 10M, and the first solution injected into the second solution may be in a state in which it is heated to 100~200°C at the time of injection.

[90] In the fabrication method of the chalcogenide as described above, the chalcogen precursor may include a precursor of sulfur (S) and/or selenium (Se) and include sulfur (S) and/or selenium (Se) powder.

[91] In the fabrication method of the chalcogenide as described above, a solvent of the second solution may be an amine based solvent, independently from the solvent of the first solution, wherein the amine based solvent may be a saturated or unsaturated amine and have one or at least two shapes selected from a linear shape, a branched shape, or a circular shape in which 6 to 30 carbon atoms are contained. As a substantial example, the amine based solvent may include one or at least two solvents selected from diethyl amine, triethylamine, 1,3-propane diamine, 1,4-butane diamine, 1,5-pentane diamine, 1,6-hexane diamine, 1,7-heptane diamine, 1,8-octane diamine, diethylene diamine, diethylene triamine, toluene diamine, m-phenylenediamine, diphenyl methane diamine, hexamethylene diamine, triethylene tetramine, tetraethylenepentamine, hexamethylene tetramine, ethanolamine, diethanolamine, triethanolamine, and oleylamine.

[92] In the fabrication method of the chalcogenide as described above, a molar concentration of the chalcogen precursor contained in the second solution may be 0.01 to 10M, and the molar ratio of chalcogen precursor(in the second solution) based on the precursor of the group 11 metal(in the first solution) is 0.8 to 1.2, preferably 0.9 to 1.1 at mixing of the first solution and the second solution.

[93] In the fabrication method of the chalcogenide as described above, the surfactant, which is trioctylphosphine, trioctylphosphine oxide, acid, or a mixture thereof, may be contained in the second solution together with the chalcogen precursor, and the surfactant contained in the second solution may be added at a molar ratio of 0.1 to 30 based on the precursor of the group 11 metal.

[94] In the fabrication method of the chalcogenide as described above, the chalcogenide may be prepared by heating the second solution containing the chalcogen precursor to 160~240°C together with the surfactant, which is trioctylphosphine, trioctylphosphine oxide, acid, or a mixture thereof, and instantaneously injecting the first solution heated to 100~200°C into the second solution in a state in which the second solution is heated to 160~240°C, followed by maintaining the temperature (160~240°C) of the second solution for 30 minutes to 2 hours.

[95] In the ink according to the exemplary embodiment of the present invention, a precursor of one or at least two elements selected from Groups 12 to 14 elements (hereinafter, referred to as a Groups 12 to 14 element precursor) is contained therein

together with the composite particles of the first and second chalcogenides.

[96] In the ink according to the exemplary embodiment of the present invention, a Group 12 element may include zinc (Zn), a Group 14 element may include tin (Sn), and a Group 13 element may include one or at least two elements selected from indium (In) and gallium (Ga). More specifically, the precursor of one or at least two elements selected from Groups 12 to 14 elements may include a precursor of one or at least two elements selected from Group 13 elements and/or a precursor of one or at least two elements selected from each of the Groups 12 and 14 elements.

[97] In the ink according to the exemplary embodiment of the present invention, the Groups 12 to 14 element precursors may be a precursor dissolved in a solvent forming a liquid medium of the ink. For example, the precursor may be chloride, nitrate, sulfate, acetate, phosphate, silicate, or hydrochloride of one or at least two elements selected from Groups 12 to 14 elements, or a mixture thereof.

[98] As a specific example, in the case in which the photo active layer to be fabricated is made of CI(S,Se) (Cu-In-(S,Se)), the Groups 12 to 14 element precursors may be chloride, nitrate, sulfate, acetate, phosphate, silicate, and hydrochloride of In, or a mixture thereof.

[99] As a specific example, in the case in which the photo active layer to be fabricated is made of CIG(S,Se) (Cu-In-Ga-(S,Se)), the Groups 12 to 14 element precursors may include one or at least two indium precursors selected from chloride, nitrate, sulfate, acetate, phosphate, silicate, and hydrochloride of In and one or at least two gallium precursors selected from chloride, nitrate, sulfate, acetate, phosphate, silicate, and hydrochloride of Ga.

[100] As a specific example, in the case in which the photo active layer to be fabricated is made of CZT(S,Se) (Cu-Zn-Sn-(S,Se)), the Groups 12 to 14 element precursors may include one or at least two zinc precursors selected from chloride, nitrate, sulfate, acetate, phosphate, silicate, and hydrochloride of Zn and one or at least two tin precursors selected from chloride, nitrate, sulfate, acetate, phosphate, silicate, and hydrochloride of Sn.

[101] In the ink according to the exemplary embodiment of the present invention, the Groups 12 to 14 element precursor may be a third chalcogenide, which is a chalcogenide of one or at least two elements selected from Groups 12 to 14 elements. That is, the ink according to the exemplary embodiment of the present invention may contain the composite particle in which the first chalcogenide of the Group 11 metal (hereinafter, referred to as the high melting point first chalcogenide) and the second chalcogenide of the Group 11 metal having a melting point lower than that of the high melting point first chalcogenide (hereinafter, referred to as the low melting point second chalcogenide) are mixed in the single particle; and the third chalcogenide of

one or at least two elements selected from Groups 12 to 14 elements.

[102] More specifically, the third chalcogenide may include a chalcogenide of one or at least two elements selected from Group 13 elements and/or a chalcogenide of one or at least two elements selected from each of the Groups 12 and 14 elements.

[103] The Group 12 element may include zinc (Zn), the Group 14 element may include tin (Sn), and the Group 13 element may include one or at least two elements selected from indium (In) and gallium (Ga).

[104] In detail, the third chalcogenide contained in the ink may be a chalcogenide particle containing all of the elements configuring the photo active layer to be fabricated except for copper.

[105] As an example, in the case in which the photo active layer to be fabricated is made of CI(S,Se) (Cu-In-(S,Se)), the third chalcogenide may be a chalcogenide particle containing In. As a substantial example, the chalcogenide particle containing In may be an In-Se compound particle, an In-S compound particle, or an In-Se-S compound particle.

[106] As an example, in the case in which the photo active layer to be fabricated is made of CIG(S,Se) (Cu-In-Ga-(S,Se)), the third chalcogenide may be a chalcogenide particle containing In-Ga. As a substantial example, the chalcogenide particle containing In-Ga may be an In-Ga-Se compound particle, an In-Ga-S compound particle, or an In-Ga-Se-S compound particle.

[107] As an example, in the case in which the photo active layer to be fabricated is made of CZT(S,Se) (Cu-Zn-Sn-(S,Se)), the third chalcogenide may be a chalcogenide particle containing Zn and Sn As a substantial example, the chalcogenide particles containing Zn and Sn may be a mixed particle of at least one particle selected from a Sn-Se compound particle, a Sn-S compound particle, and Sn-Se-S compound particle and at least one particle selected from a Zn-Se compound particle, a Zn-S compound particle, and Zn-Se-S compound particle.

[108] A substantial example of the third chalcogenide may include one or at least two particles selected from $(In_xGa_{1-x})_4(S_ySe_{1-y})_3$ particles, $(In_xGa_{1-x})(S_ySe_{1-y})$ particles, $(In_xGa_{1-x})_6(S_ySe_{1-y})_7$ particles, $(In_xGa_{1-x})_9(S_ySe_{1-y})_{11}$ particles, $(In_xGa_{1-x})_2(S_ySe_{1-y})_3$ particles, and $(In_xGa_{1-x})_5(S_ySe_{1-y})_7$ particles. Here, in the third chalcogenide particle, x and y are real numbers satisfying the following Equations, respectively: $0\leq x\leq 1$ and $0\leq y\leq 1$. A substantial example of the third chalcogenide may include a mixture of one or at least two selected from $Sn(S_ySe_{1-y})$ particles, $Sn_2(S_ySe_{1-y})_3$ particles, and $Sn(S_ySe_{1-y})_2$ particles and $Zn(S_ySe_{1-y})$ particles. Here, in the third chalcogenide particle, y is a real number satisfying the following Equation: $0\leq y\leq 1$.

[109] As a more substantial example, the third chalcogenide may include one or at least two particles selected from an In_2Se_3 particle, a Ga_2S_3 particle, a ZnS particle, and a

SnS particle.

[110] In the ink according to the exemplary embodiment of the present invention, the third chalcogenide particles may be nanoparticles in view of low temperature reactivity with the copper nanoparticles and have an average particle size of 5 to 200nm.

[111] In the ink according to the exemplary embodiment of the present invention, the third chalcogenide particles may be amorphous chalcogenide particles. Therefore, the third chalcogenide particles react with copper nanoparticles at a low temperature within the process allowable temperature, such that the single phase multinary chalcogenide may be rapidly and uniformly prepared.

[112]

[113] In the ink according to the exemplary embodiment of the present invention, when the photo active layer to be fabricated is made of CIGS (Cu-In-Ga-Se or Cu-In-Ga-S), CIGSS (Cu-In-Ga-Se-S), CZTS (Cu-Zn-Sn-Se or Cu-Zn-Sn-S), or CZTSS (Cu-Zn-Sn-Se-S), a molar ratio of one or at least two elements selected from Groups 12 to 14 elements contained in the ink to the Group 11 metal contained in the first and second chalcogenides may be 1:0.7 to 1.2. That is, a molar ratio of Groups 12 to 14 elements contained in the Groups 12 to 14 element precursors (including the third chalcogenide) to the Group 11 metal contained in the chalcogenide (first and second chalcogenides) may be 1:0.7 to 1.2.

[114] The ink according to the exemplary embodiment of the present invention may further contain a solvent dissolving or dispersing a precursor of at least one element selected from Groups 12 to 14 elements or dispersing the composite particle.

[115] As the solvent contained in the ink, any solvent may be used as long as it contains a particle phase and is used for a general ink composition used in a coating process. For example, the solvent may contain one or at least two solvents selected from a non-polar solvent, a polyol based solvent, an amine based solvent, a phosphine based solvent, an alcohol based solvent, and a polar solvent.

[116] A substantial example of the polyol based solvent may include one or at least two solvents selected from diethylene glycol, diethylene glycol ethyl ether, diethylene glycol butyl ether, triethylene glycol, polyethylene glycol (Mw: 200~100,000), poly(ethylene glycol) diacrylate, poly(ethylene glycol) dibenzonate, dipropylene glycol, dipropylene glycol, and glycerol.

[117] A substantial example of the amine based solvent may include one or at least two solvents selected from diethyl amine, triethylamine, 1,3-propane diamine, 1,4-butane diamine, 1,5-pentane diamine, 1,6-hexane diamine, 1,7-heptane diamine, 1,8-octane diamine, diethylene diamine, diethylene triamine, toluene diamine, m-phenylenediamine, diphenyl methane diamine, hexamethylene diamine, triethylene tetramine, tetraethylenepentamine, hexamethylene tetramine, ethanolamine, di-

ethanolamine, and triethanolamine.

[118] A substantial example of the phosphine based solvent may include one or at least two solvents selected from trioctylphosphine, trioctylphosphineoxide, and acid.

[119] A substantial example of the alcohol based solvent may include one or at least two solvents selected from methyl cellosolve, ethyl cellosolve, butyl cellosolve, and alcohols having 1 to 8 carbon atoms.

[120] A substantial example of the non-polar solvent may include one or at least two solvents selected from toluene, chloroform, chlorobenzene, dichlorobenzene, anisole, xylene, and hydrocarbon based solvents having 6 to 14 carbon atoms.

[121] A substantial example of the polar solvent may include one or at least two solvents selected from formamide, diformamide, acetonitrile, tetrahydrofuran, dimethyl-sulfoxide, acetone, α-terpineol, β-terpineol, dihydro-terpineol, and water.

[122] The ink according to the exemplary embodiment of the present invention may further contain a dispersant and an organic binder.

[123] As the dispersant and the organic binder, any dispersant and organic binder may be used as long as they contain a particle phase and are used for a general ink composition used in a coating process.

[124] Examples of the dispersant may include one or at least two selected from low molecular weight anionic compounds such as fatty acid salts (soap), α-sulfofatty acid ester salts (MES), alkyl benzene sulfonate (ABS), linear alkyl benzene sulfonate (LAS), alkyl sulfonate (AS), alkyl ether sulfonate ester salts (AES), alkyl sulfonate triethanol, and the like; low molecular weight non-ionic compounds such as fatty acid ethanol amide, polyoxyethylenealkylether (AE), polyoxyethylenealkylphenylether (APE), sorbitol, sorbitan, and the like; lower molecular weight cationic compounds such as alkyltrimethyl ammonium salts, dialkyldimethyl ammonium chloride, alkylpyridinium chloride, and the like; low molecular weight ampholytic compounds such as alkylcarboxybetaine, sulfobetaine, and lecithin; high molecular weight aqueous dispersants such as a condensate of naphthalene sulfonate with formalin, polystyrene sulfonate, polyacrylate, copolymer salts of vinyl compounds and carboxylic acid based monomer, carboxymethylcellulose, and polyvinylalcohol; high molecular weight non-aqueous dispersants such as partial alkyl ester of polyacrylate and polyalkylenepolyamine; and high molecular cationic dispersants such as copolymers of polyethyleneimine and aminoalkylmethacrylate.

[125] As a non-restrictive example of the dispersant may be a commercialized product. For example, EFKA4008, EFKA4009, EFKA4010, EFKA4015, EFKA4046, EFKA4047, EFKA4060, EFKA4080, EFKA7462, EFKA4020, EFKA4050, EFKA4055, EFKA4400, EFKA4401, EFKA4402, EFKA4403, EFKA4300, EFKA4330, EFKA4340, EFKA6220, EFKA6225, EFKA6700, EFKA6780, EFKA6782, and

EFKA8503 (manufactured by EFKA ADDITIVES B. V.), TEXAPHOR-UV21 and TEXAPHOR-UV61 (manufactured by Cognis Japan Ltd.), DisperBYK101, DisperBYK102, DisperBYK106, DisperBYK108, DisperBYK111, DisperBYK116, DisperBYK130, DisperBYK140, DisperBYK142, DisperBYK145, DisperBYK161, DisperBYK162, DisperBYK163, DisperBYK164, DisperBYK166, DisperBYK167, DisperBYK168, DisperBYK170, DisperBYK171, DisperBYK174, DisperBYK180, DisperBYK182, DisperBYK192, DisperBYK193, DisperBYK2000, DisperBYK2001, DisperBYK2020, DisperBYK2025, DisperBYK2050, DisperBYK2070, DisperBYK2155, DisperBYK2164, BYK220S, BYK300, BYK306, BYK320, BYK322, BYK325, BYK330, BYK340, BYK350, BYK377, BYK378, BYK380N, BYK410, BYK425, and BYK430 (manufactured by Bigchemi Japan Co., Ltd.), FTX-207S, FTX-212P, FTX-220P, FTX-220S, FTX-228P, FTX-710LL, FTX-750LL, Ftergent212P, Ftergent220P, Ftergent222F, Ftergent228P, Ftergent245F, Ftergent245P, Ftergent250, Ftergent251, Ftergent710FM, Ftergent730FM, Ftergent730LL, Ftergent730LS, Ftergent750DM, and Ftergent750FM (manufactured by Neos Co., Ltd), MEGAFACE F-477, MEGAFACE 480SF, or MEGAFACE F-482 (manufactured by DIC Corp.) may be used.

[126] An example of the organic binder may include one or at least two selected from polyvinyl alcohol (PVA), polyvinyl butyral (PVB), polyvinyl pyrrolidone (PVP), polyvinylidene difluoride (PVDF), a self-cross linking acrylic resin emulsion, hydroxy ethyl cellulose (HEC), carboxy methyl cellulose (CMC), styrene butadiene rubber (SBR), a copolymer of C1-10 alkyl(meth)acrylate and unsaturated carboxylic acid, nitrocellulose, gelatine, thixoton, starch, polyether-polyol, amine terminated polystyrene ($PS\text{-}NH_2$), hydroxycellulose, methylcellulose, ethylcellulose, ethylhydroxyethyl-cellulose, polyethyleneoxide, polyurethane, a resin including a carboxyl group, a phenolic resin, a mixture of ethylcellulose and a phenolic resin, an ether polymer, a methacrylate polymer, a copolymer having an ethylenically unsaturated group, ethyl-cellulose based materials, acrylate based material, and epoxy resin based materials.

[127] The ink according to the exemplary embodiment of the present invention may contain 200 to 900 parts by weight of the solvent based on 100 parts by weight of the particle phase including the first and second chalcogenides.

[128] In the case in which the ink according to the exemplary embodiment of the present invention further contains the dispersant and the organic binder, the ink may contain 0.5 to 10 parts by weight of the dispersant and 0.5 to 10 parts by weight of the organic binder, based on 100 parts by weight of the particle phase including the first and second chalcogenides.

[129] The content of the solvent, and selectively, contents of the dispersant and the organic binder based on the particle phase including the first and second chalcogenides may be

contents at which the coating process may be smoothly performed, and deterioration of mechanical strength for maintaining a shape of a film, deterioration of adhesive force with a substrate onto which the ink is coated, deterioration of quality of the film by organic materials dissolved and removed at the time of drying and heat-treatment may be prevented.

[130] Hereinafter, a fabrication method of a photo active layer for a solar cell using the above-mentioned ink will be described in detail.

[131] The fabrication method of a photo active layer for a solar cell according to another exemplary embodiment of the present invention includes: a) coating the above-mentioned ink containing the composite particle in which the first chalcogenide of the Group 11 metal and the second chalcogenide of the Group 11 metal having a melting point lower than that of the first chalcogenide are mixed in the single particle and the precursor of at least one element selected from Groups 12 to 14 elements onto a substrate to form a coating film; and b) heat-treating the coating film to fabricate a multinary chalcogenide film of the Group 11 metal, a chalcogen element, and one or at least two elements selected from the Groups 12 to 14 elements.

[132] As described above, in the case in which the precursor of at least one element selected from the Groups 12 to 14 elements is a third chalcogenide of one or at least two element selected from the Groups 12 to 14 elements, the fabrication method of a photo active layer for a solar cell according to another exemplary embodiment of the present invention may include: a) coating the above-mentioned ink containing the composite particle in which the first chalcogenide of the Group 11 metal and the second chalcogenide of the Group 11 metal having a melting point lower than that of the high melting point first chalcogenide are mixed in the single particle and the third chalcogenide of one or at least two element selected from Groups 12 to 14 elements onto a substrate to form a coating film; and b) heat-treating the coating film to fabricate a multinary chalcogenide film of the Group 11 metal and one or at least two elements selected from the Groups 12 to 14 elements.

[133] Since a general compound semiconductor (CIG(S,Se)) or CZT(S,Se)) based photo active layer is made of a multinary compound, a fabrication process thereof is significantly complicated. As a physical fabrication method of a thin film, there are an evaporation method and a sputtering-selenization method, and as a chemical fabrication method thereof, there is an electro-deposition method. In each method, various fabrication methods are used according to the kind of raw materials.

[134] However, in the fabrication method according to the present invention, gas-phase organic metal compounds of which cost is expensive and handling is difficult or an expensive vacuum equipment are not used, and a highly complicated process such as multilayer deposition is not needed. That is, in the fabrication method according to the

present invention, a high quality multinary chalcogenide (photo active layer) may be prepared by a significantly simple, safe, and easy process of coating the ink containing the composite particle of chalcogenides (first and second chalcogenides) of the Group 11 metals that have different melting points from each other and the precursor material configuring the photo active layer to be fabricated and heat treating the coating film at a low temperature.

[135] In addition, in the fabrication method according to the present invention, the photo active layer is fabricated using the above-mentioned ink, such that a photo active layer made of a single phase multinary chalcogenide may be fabricated at a temperature lower than the process allowable temperature of 550°C or less, and a photo active layer having excellent uniformity and a dense micro structure may be fabricated.

[136] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, the substrate onto which the ink is coated may include a laminated substrate in which a back contact generally used in a solar cell field is laminated on an insulating substrate generally used in the solar cell field. As an example of the insulating substrate, there is a glass substrate, a sodalime glass substrate, a ceramic substrate, or a semiconductor substrate. As an example of the back contact formed on the insulating substrate, there is a molybdenum (Mo) layer.

[137] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, the coating of the ink may be performed by one or at least two methods selected from a spin coating method, a bar coating method, a dip coating method, a drop casting method, an ink-jet printing method, a micro-contact printing method, an imprinting method, a gravure printing method, a gravure-offset printing method, a flexography printing method, and a screen printing method.

[138] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, after step a) and before step b), drying the coating film may be further performed. The drying is to evaporate and remove a liquid phase contained in the coating film, and any drying method may be used as long as the method may be generally used in a field in which a film is formed by coating ink. As a non-restrictive example, the drying of the coating film may be performed at 60 to 90°C in the air.

[139] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, the heat treatment of the coating film formed by coating ink onto the substrate may be performed at 400 to 550°C, preferably 500 to 530°C.

[140] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, densification of the film, crystal

growth, phase transition into the single phase multinary chalcogenide may be performed by heat treatment of the coating film. That is, the coating film is heat treated, such that the phase transition into the single phase of the desired multinary chalcogenide may be performed by reaction between the copper and elements configuring the photo active layer to be fabricated except for copper.

[141] As described above, the pure single phase multinary chalcogenide is formed by phase transition, such that a multinary chalcogenide film having significantly dense, stable, and homogeneous composition may be fabricated at a low heat treatment temperature within the process allowable temperature of 550°C or less at which mechanical strength of the glass substrate generally used as the insulating substrate for a solar cell is maintained.

[142] In the fabrication method according to the present invention, the heat treatment of the coating film may be performed under chalcogen atmosphere. The chalcogen atmosphere includes an atmosphere in which sulfur (S), selenium (Se), or a mixed gas thereof are present.

[143] In detail, the coating film may be heat treated while supplying chalcogen containing gas or heat treated together with chalcogen powder to use the chalcogen powder as a source of chalcogen gas.

[144] In more detail, the coating film may be heat treated under chalcogen atmosphere containing sulfur (S), selenium (Se), or a mixed gas thereof. In this case, the chalcogen gas atmosphere may be formed by supplying gas containing a chalcogen element (S, Se) such as H_2S or H_2Se, evaporating the chalcogen element (S, Se) and then supplying the evaporated chalcogen element, or heat treating the chalcogen powder, which is a powder phase of the chalcogen element, together with the coating film to use the chalcogen powder as the source of the chalcogen gas.

[145] As a substantial example, in the case of supplying the chalcogen gas, chalcogen containing gas including H_2S or H_2Se, chalcogen element (S, Se) vapor, or a mixed gas thereof may be supplied at a flow of 5 to 300 sccm.

[146] As a substantial example, in the case of evaporating chalcogen powder itself containing S powder, Se powder, or a mixed powder thereof to form the chalcogen atmosphere in a chamber in which the heat treatment of the coating film is performed, a temperature at which the chalcogen powder is heated may be the same as or different from that of the coating film on which heat treatment is performed.

[147] More specifically, in the case in which the chalcogen powder is used as the source of the chalcogen gas, the chalcogen powder may be heated to 80~250°C.

[148] In the case in which the chalcogen powder is used as the source of the chalcogen gas, the chalcogen powder in a heat treatment apparatus may be positioned on a region different from a region on which the coating film is positioned. In this case, the heat

treatment may be performed using an apparatus provided with a heater and a controller so that at least two uniform zones may be each independently formed in a single heat treatment space in which fluid may flow, and a heating temperature of the chalcogen powder may be adjusted by adjusting a position on which the chalcogen powder is positioned in a general heat treatment apparatus forming a single uniform zone.

[149] The heat treatment of the coating film may be performed under any pressure, but as a non-restrictive example, the heat treatment may be performed under vacuum or atmospheric pressure.

[150] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, the multinary chalcogenide may include $CuIn_xGa_{1-x}Se_yS_{1-y}$(x and y are real numbers satisfying the following Equations, respectively: $0\leq x\leq 1$ and $0\leq y\leq 1$) and $Cu_2Zn_zSn_{2-z}(Se_yS_{1-y})_4$ (z and y are real numbers satisfying the following Equations, respectively: $0\leq z\leq 2$ and $0\leq y\leq 1$).

[151] As an example, a single phase multinary chalcogenide represented by $CuIn_xGa_{1-x}Se_2$ (x is a real number satisfying the following Equation: $0\leq x\leq 1$) may be prepared using ink containing composite particles in which a first chalcogenide (Cu_2Se) and a second chalcogenide (CuSe) are mixed in a single particle and a precursor of In and/or Ga. In this case, as described above, a molar ratio of In and/or Ga (In and/or Ga of the precursor) to Cu (Cu contained in the composite particle of the first and second chalcogenides) that are contained in the ink may be 1:0.7 to 1.2.

[152] As an example, a single phase multinary chalcogenide represented by $Cu_2Zn_zSn_{2-z}Se_4$ (z is a real number satisfying the following Equation: $0\leq z\leq 2$) may be prepared using ink containing composite particles in which the first chalcogenide (Cu_2Se) and the second chalcogenide (CuSe) are mixed in a single particle and the precursor of Zn and/or Sn. In this case, as described above, a molar ratio of Zn and/or Sn (Zn and/or Sn of the precursor) to Cu (Cu contained in the composite particle of the first and second chalcogenides) that are contained in the ink may be 1:0.7 to 1.2, wherein a molar ratio of Zn to Sn may satisfy the composition of the desired photo active layer (for example, Zn: Sn=z: 2-z, where z is a real number satisfying the following Equation: $0\leq z\leq 2$).

[153] As an example, a single phase multinary chalcogenide ($CuInSe_2$) may be prepared using ink containing composite particles in which the first chalcogenide (Cu_2Se) and the second chalcogenide (CuSe) are mixed in a single particle and chalcogenide (In_2Se_3) particles.

[154] As an example, a single phase multinary chalcogenide represented by $CuIn_xGa_{1-x}Se_yS_{1-y}$ (x and y are real numbers satisfying the following Equations, respectively: $0\leq x\leq 1$ and $0\leq y\leq 1$) may be prepared using ink containing composite particles in which the first chalcogenide (Cu_2Se) and the second chalcogenide (CuSe) are mixed in a single particle and third chalcogenide particles, which are mixed particles of chalcogenides

represented by In_2Se_3 and Ga_2S_3. In this case, a molar ratio of In and Ga (In and Ga of the chalcogenide particle) to Cu (Cu of the copper particle) that are contained in the ink may be 1:0.7 to 1.2, wherein a molar ratio of In to Ga may depend on a molar ratio (x:1-x) of In to Ga of the multinary chalcogenide to be prepared.

[155] As an example, a single phase multinary chalcogenide represented by $Cu_2Zn_mSn_{2-m}(Se_nS_{1-n})_4$ (m and n are real numbers satisfying the following Equations, respectively: $0\leq m\leq 2$ and $0\leq n\leq 1$) may be prepared using ink containing composite particles in which the first chalcogenide (Cu_2Se) and the second chalcogenide (CuSe) are mixed in a single particle; and third chalcogenide particles, which are mixed particles of chalcogenides represented by ZnS_ySe_{1-y} (y is a real number satisfying the following Equation: $0\leq y\leq 1$) and SnS_ySe_{1-y} (y is a real number satisfying the following Equation: $0\leq y\leq 1$). In this case, a molar ratio of Zn and Sn (Zn and Sn of the chalcogenide particle) to Cu (Cu of the copper particle) that are contained in the ink may be 1:0.7 to 1.2, wherein a molar ratio of Zn to Sn may depend on a molar ratio (m:2-m) of Zn to Sn of the multinary chalcogenide to be prepared.

[156] Hereinafter, ink containing copper nanoparticles and a fabrication method of a photo active layer using the copper nanoparticles will be described in detail.

[157] The ink according to the present invention contains copper nanoparticles; and chalcogenide particles of one or at least two elements selected from Groups 12 to 14 elements. In this case, the ink according to the present invention may be ink for a photo active layer of a solar cell.

[158] In detail, the copper particle contained in the ink is a nanoparticle having a nano size in order to obtain driving force for sintering and low temperature reactivity with the chalcogenide particle. As a substantial example, the copper nanoparticles may have an average particle size of 5 to 200nm and have uni-modal, bi-modal, or multi-modal distribution. Here, in the case in which the copper nanoparticles have the bimodal or multi-modal distribution, central points of the peaks may be each independently 5 to 200nm.

[159] In detail, the chalcogenide particles contained in the ink is chalcogenide particles containing all of the elements configuring the photo active layer to be fabricated except for copper.

[160] As an example, in the case in which the photo active layer to be fabricated is made of CI(S,Se) (Cu-In-(S,Se)), the chalcogenide particle may be a chalcogenide particle containing In. As a substantial example, the chalcogenide particle containing In may be an In-Se compound particle, an In-S compound particle, or an In-Se-S compound particle.

[161] As an example, in the case in which the photo active layer to be fabricated is made of CIG(S,Se) (Cu-In-Ga-(S,Se)), the chalcogenide particle may be a chalcogenide

containing In-Ga. As a substantial example, the chalcogenide particle containing In-Ga may be an In-Ga-Se compound particle, an In-Ga-S compound particle, or an In-Ga-Se-S compound particles.

[162] As an example, in the case in which the photo active layer to be fabricated is made of CZT(S,Se) (Cu-Zn-Sn-(S,Se)), the chalcogenide particle may be a chalcogenide particle containing Zn and Sn. As a substantial example, the chalcogenide particle containing Zn and Sn may be a mixed particle of at least one particle selected from a Sn-Se compound particle, a Sn-S compound particle, and Sn-Se-S compound particle and at least one particle selected from a Zn-Se compound particle, a Zn-S compound particle, and Zn-Se-S compound particle.

[163] A substantial example of the chalcogenide particle may include one or at least two particles selected from $(In_xGa_{1-x})_4(S_ySe_{1-y})_3$ particles, $(In_xGa_{1-x})(S_ySe_{1-y})$ particles, $(In_xGa_{1-x})_6(S_ySe_{1-y})_7$ particles, $(In_xGa_{1-x})_9(S_ySe_{1-y})_{11}$ particles, $(In_xGa_{1-x})_2(S_ySe_{1-y})_3$ particles, and $(In_xGa_{1-x})_5(S_ySe_{1-y})_7$ particles$_7$. Here, in the chalcogenide particle, x and y are real numbers satisfying the following Equations, respectively: $0\leq x\leq 1$ and $0\leq y\leq 1$. A substantial example of the chalcogenide particle may include a mixture of one or at least two selected from $Sn(S_ySe_{1-y})$ particles, $Sn_2(S_ySe_{1-y})_3$ particles, and $Sn(S_ySe_{1-y})_2$ particles and $Zn(S_ySe_{1-y})$ particles. Here, in the chalcogenide particle, y is a real number satisfying the following Equation: $0\leq y\leq 1$.

[164] A more substantial example of the chalcogenide particle may include one or at least two particles selected from an In_2Se_3 particle, a Ga_2S_3 particle, a ZnS particle, and a SnS particle.

[165] In the ink according to the exemplary embodiment of the present invention, the chalcogenide particles may be nanoparticles in view of low temperature reactivity with the copper nanoparticles and have an average particle size of 5 to 200nm. In this case, the chalcogenide particle may have uni-modal, bi-modal, or multi-modal distribution.

[166] In the ink according to the exemplary embodiment of the present invention, in order to prepare the single phase multinary chalcogenide by reacting the copper nanoparticles with the chalcogenide particles at a low heat treatment temperature of 550°C or less, which is the process allowable temperature, and prepare the multinary chalcogenide composed of coarse grains, the average particle size of the chalcogenide particle may be smaller than that of the copper nanoparticles.

[167] As a substantial example, in order to prepare a single phase multinary chalcogenide having an average grain size of micrometer-order at a low heat treatment temperature, the average particle size of the chalcogenide particle may be preferably 1/100 or 1/10 of the average particle size of the copper nanoparticles.

[168] As a more substantial example, the average particle size of the chalcogenide particles may be 1 to 20nm, and the average particle size of the copper nanoparticles may be 10

to 200nm.

[169] In the ink according to the exemplary embodiment of the present invention, the chalcogenide particles may be amorphous chalcogenide particles. Therefore, the chalcogenide particles react with copper nano particles at a low temperature within the process allowable temperature, such that the single phase multinary chalcogenide may be rapidly and uniformly prepared.

[170] In the ink according to the exemplary embodiment of the present invention, the copper nanoparticles contained in the ink may be copper nanoparticles prepared by heating and stirring a copper precursor solution containing a copper precursor, acid, and amine and then injecting a reducing agent thereinto to thereby be capped with acid and amine.

[171] The copper nanoparticles prepared by heating the copper precursor solution simultaneously containing the copper precursor, acid, and amine and then injecting the reducing agent thereinto are capped with acid and amine, such that formation of a surface oxide film on the particles may be prevented at the time of forming the copper nanoparticles. In addition, formation of a surface oxide film on the particles may be prevented regardless of a storage state and storage time of the ink, thereby making it possible to significantly prevent reactivity from being deteriorated by the surface oxide film of the copper nanoparticles.

[172] At the time of preparing the copper nanoparticles, the copper precursor may be one or at least two selected from inorganic salts consisting of copper nitrate, copper sulfate, copper acetate, copper phosphate, copper silicate, and copper hydrochloride.

[173] At the time of preparing the copper nanoparticles, the acid contained in the copper precursor solution may be a saturated or unsaturated acid and have one or at least two shapes selected from a linear shape, a branched shape, or a circular shape in which 6 to 30 carbon atoms are contained. Substantial examples of the acid contained in the copper precursor solution may include one or at least two acids selected from oleic acid, ricinoleic acid, stearic acid, hydroxy stearic acid, linoleic acid, aminodecanoic acid, hydroxy decanoic acid, lauric acid, decanoic acid, undecanoic acid, hexyldecanoic acid, hydroxy palmitic acid, hydroxy myristic acid, palmitoleic acid, and myristoleic acid.

[174] In this case, in the copper precursor solution, a molar ratio between the copper precursor and the acid may be 1 (copper precursor):0.2 to 4 (acid). The molar ratio of acid to the copper precursor is a ratio at which the copper nanoparticles may be prepared in a shape in which the particles are capped with acid and amine while preventing formation of the surface oxide film and perfectly performing the capping. That is, when the molar ratio of the acid to the precursor is less than 0.2, the capping may not be perfectly performed, such that cupper that is not partially capped may be

oxidized, and when the molar ratio is more than 4, all of the capping agents may not be reacted but coagulated with each other, such that it is impossible to obtain the capped particles.

[175] At the time of preparing the copper nanoparticles, amine contained in the copper precursor solution may serve as a solvent as well as the capping agent together with acid. The amine as the capping agent and the solvent may be a saturated or unsaturated amine and have one or at least two shapes selected from a linear shape, a branched shape, or a circular shape in which 6 to 30 carbon atoms are contained. A substantial example of the amine contained in the copper precursor solution may include one or at least two amines selected from hexyl amine, heptyl amine, octyl amine, dodecyl amine, 2-ethylhexyl amine, 1,3-dimethyl-n-butyl amine, and 1-aminotridecane.

[176] In this case, in the copper precursor solution, a molar ratio between the copper precursor and the amine may be 1 (copper precursor):5 to 15 (amine). The molar ratio of the amine to the precursor is a ratio at which the amine may serve as the solvent and the capping agent and form a capping film together with the acid so that formation of the surface oxide film is prevented.

[177] At the time of preparing the copper nanoparticles, the reducing agent may include one or at least two materials selected from hydrazine, phenylhydrazine, tetrabutyl ammonium borohydride, tetramethyl ammonium borohydride, tetraethyl ammonium borohydride, sodium phosphate, sodium borohydride, and ascorbic acid.

[178] At the time of preparing the copper nanoparticles, the copper precursor solution may be heated and stirred to 100~240°C, preferably 140~240°C, and the reducing agent may be injected thereto in a state in which the copper precursor solution is heated (100~240°C).

[179] At the time of preparing the copper nanoparticles, 80 to 200 parts by weight of the reducing agent may be injected based on 100 parts by weight of the copper precursor solution heated to a temperature of 100~240°C.

[180] The reducing agent is injected after heating the copper precursor solution simultaneously containing the copper precursor, the amine, and the acid to the temperature of 100~240°C, such that the copper particles capped with acid and amine may be prepared at a nano size, and copper nanoparticles (capped copper nanoparticles) having a uniform spherical shape may be prepared. Further, the reaction is carried out by injecting amine and the acid are injected at a time, such that the process may be simplified, and an oxide film that may be formed when the copper nanoparticles are capped with only amine may be perfectly prevented, thereby making it possible to prepare copper nanoparticle on which the surface oxide film is not at all present.

[181] The ink according to the exemplary embodiment of the present invention may further contain a solvent forming a dispersion medium of the copper nanoparticles and the

chalcogenide particles.

[182] As the solvent forming the dispersion medium, any solvent may be used as long as it contains a particle phase and is used for a general ink composition used in a coating process one or at least two solvents selected from a non-polar solvent, a polyol based solvent, an amine based solvent, a phosphine based solvent, an alcohol based solvent, and a polar solvent.

[183] A substantial example of the polyol based solvent may include one or at least two solvents selected from diethylene glycol, diethylene glycol ethyl ether, diethylene glycol butyl ether, triethylene glycol, polyethylene glycol (Mw: 200~100,000), poly(ethylene glycol) diacrylate, poly(ethylene glycol) dibenzonate, dipropylene glycol, dipropylene glycol, and glycerol.

[184] A substantial example of the amine based solvent may include one or at least two solvents selected from diethyl amine, triethylamine, 1,3-propane diamine, 1,4-butane diamine, 1,5-pentane diamine, 1,6-hexane diamine, 1,7-heptane diamine, 1,8-octane diamine, diethylene diamine, diethylene triamine, toluene diamine, m-phenylenediamine, diphenyl methane diamine, hexamethylene diamine, triethylene tetramine, tetraethylenepentamine, hexamethylene tetramine, ethanolamine, di-ethanolamine, and triethanolamine.

[185] A substantial example of the phosphine based solvent may include one or at least two solvents selected from trioctylphosphine and trioctylphosphineoxide.

[186] A substantial example of the alcohol based solvent may include one or at least two solvents selected from methyl cellosolve, ethyl cellosolve, butyl cellosolve, and alcohol having 1 to 8 carbon atoms.

[187] A substantial example of the non-polar solvent may include one or at least two solvent selected from toluene, chloroform, chlorobenzene, dichlorobenzene, anisole, xylene, and hydrocarbon based solvents having 6 to 14 carbon atoms.

[188] A substantial example of the polar solvent may include one or at least two solvents selected from formamide, diformamide, acetonitrile, tetrahydrofuran, dimethyl-sulfoxide, acetone, α-terpineol, β-terpineol, dihydro-terpineol, and water.

[189] The ink according to the exemplary embodiment of the present invention may further contain a dispersant and an organic binder.

[190] As the dispersant and the organic binder, any dispersant and organic binder may be used as long as they contain a particle phase and are used for a general ink composition used in a coating process.

[191] Examples of the dispersant may include one or at least two selected from low molecular weight anionic compounds such as fatty acid salts (soap), α-sulfofatty acid ester salts (MES), alkyl benzene sulfonate (ABS), linear alkyl benzene sulfonate (LAS), alkyl sulfonate (AS), alkyl ether sulfonate ester salts (AES), alkyl sulfonate

triethanol, and the like; low molecular weight non-ionic compounds such as fatty acid ethanol amide, polyoxyethylenealkylether (AE), polyoxyethylenealkylphenylether (APE), sorbitol, sorbitan, and the like; lower molecular weight cationic compounds such as alkyltrimethyl ammonium salts, dialkyldimethylammonium chloride, alkylpyridinium chloride, and the like; low molecular weight ampholytic compounds such as alkylcarboxybetaine, sulfobetaine, and lecithin; high molecular weight aqueous dispersants such as a condensate of naphthalene sulfonate with formalin, polystyrene sulfonate, polyacrylate, copolymer salts of vinyl compounds and carboxylic acid based monomer, carboxymethylcellulose, and polyvinylalcohol; high molecular weight non-aqueous dispersants such as partial alkyl ester of polyacrylate and polyalkylenepolyamine; and high molecular cationic dispersants such as copolymers of polyethyleneimine and aminoalkylmethacrylate.

[192] As a non-restrictive example of the dispersant may be a commercialized product. For example, EFKA4008, EFKA4009, EFKA4010, EFKA4015, EFKA4046, EFKA4047, EFKA4060, EFKA4080, EFKA7462, EFKA4020, EFKA4050, EFKA4055, EFKA4400, EFKA4401, EFKA4402, EFKA4403, EFKA4300, EFKA4330, EFKA4340, EFKA6220, EFKA6225, EFKA6700, EFKA6780, EFKA6782, and EFKA8503 (manufactured by EFKA ADDITIVES B. V.), TEXAPHOR-UV21 and TEXAPHOR-UV61 (manufactured by Cognis Japan Ltd.), DisperBYK101, DisperBYK102, DisperBYK106, DisperBYK108, DisperBYK111, DisperBYK116, DisperBYK130, DisperBYK140, DisperBYK142, DisperBYK145, DisperBYK161, DisperBYK162, DisperBYK163, DisperBYK164, DisperBYK166, DisperBYK167, DisperBYK168, DisperBYK170, DisperBYK171, DisperBYK174, DisperBYK180, DisperBYK182, DisperBYK192, DisperBYK193, DisperBYK2000, DisperBYK2001, DisperBYK2020, DisperBYK2025, DisperBYK2050, DisperBYK2070, DisperBYK2155, DisperBYK2164, BYK220S, BYK300, BYK306, BYK320, BYK322, BYK325, BYK330, BYK340, BYK350, BYK377, BYK378, BYK380N, BYK410, BYK425, and BYK430 (manufactured by Bigchemi Japan Co., Ltd.), FTX-207S, FTX-212P, FTX-220P, FTX-220S, FTX-228P, FTX-710LL, FTX-750LL, Ftergent212P, Ftergent220P, Ftergent222F, Ftergent228P, Ftergent245F, Ftergent245P, Ftergent250, Ftergent251, Ftergent710FM, Ftergent730FM, Ftergent730LL, Ftergent730LS, Ftergent750DM, and Ftergent750FM (manufactured by Neos Co., Ltd), MEGAFACE F-477, MEGAFACE 480SF, or MEGAFACE F-482 (manufactured by DIC Corp.) may be used.

[193] An example of the organic binder may include one or at least two selected from polyvinyl alcohol (PVA), polyvinyl butyral (PVB), polyvinyl pyrrolidone (PVP), polyvinylidene difluoride (PVDF), a self-cross linking acrylic resin emulsion, hydroxy ethyl cellulose (HEC), carboxy methyl cellulose (CMC), styrene butadiene rubber

(SBR), a copolymer of C1-10 alkyl(meth)acrylate and unsaturated carboxylic acid, nitrocellulose, gelatine, thixoton, starch, polyether-polyol, amine terminated polystyrene ($PS-NH_2$), hydroxycellulose, methylcellulose, ethylcellulose, ethylhydroxyethylcellulose, polyethyleneoxide, polyurethane, a resin including a carboxyl group, a phenolic resin, a mixture of ethylcellulose and a phenolic resin, an ether polymer, a methacrylate polymer, a copolymer having an ethylenically unsaturated group, ethylcellulose based materials, acrylate based material, and epoxy resin based materials.

[194] In the ink according to the exemplary embodiment of the present invention, when the photo active layer to be fabricated is made of CIGS (Cu-In-Ga-Se or Cu-In-Ga-S), CIGSS (Cu-In-Ga-Se-S), CZTS (Cu-Zn-Sn-Se or Cu-Zn-Sn-S), or CZTSS (Cu-Zn-Sn-Se-S), the copper nanoparticles and the chalcogenide particles are contained so that a molar ratio of one or at least two elements selected from Groups 12 to 14 elements (Groups 12 to 14 elements contained in the chalcogenide) to copper may be 1:0.7 to 1.2.

[195] The ink according to the exemplary embodiment of the present invention may contain 200 to 900 parts by weight of the solvent based on 100 parts by weight of the particle phase including the copper nanoparticles and the chalcogenide particles.

[196] In the case in which the ink according to the exemplary embodiment of the present invention further contains the dispersant and the organic binder, the ink may contain 0.5 to 10 parts by weight of the dispersant and 0.5 to 10 parts by weight of the organic binder, based on 100 parts by weight of the particle phase including the copper nanoparticles and the chalcogenide particles.

[197] The content of the solvent, and selectively, contents of the dispersant and the organic binder based on the particle phase including the copper nanoparticles and the chalcogenide particles may be contents at which a coating process may be smoothly performed, and deterioration of mechanical strength for maintaining a shape of a film, deterioration of adhesive force with a substrate onto which the ink is applied, and deterioration of quality of the film by organic materials dissolved and removed at the time of drying and heat-treatment may be prevented.

[198] Hereinafter, a fabrication method of a photo active layer for a solar cell using ink containing the copper nanoparticles as described above will be described in detail.

[199] The fabrication method of a photo active layer for a solar cell according to the present invention includes: a) coating the above-mentioned ink containing the copper nano-particles and the chalcogenide particles of one or at least two elements selected from Groups 12 to 14 elements onto a substrate to form a coating film; and b) heat treating the coating film to fabricate a multinary chalcogenide film of copper and one or at least two elements selected from the Groups 12 to 14 elements.

[200] Since a general compound semiconductor (CIG(S,Se)) or CZT(S,Se)) based photo

active layer is made of a multinary compound, a fabrication process thereof is significantly complicated. As a physical fabrication method of a thin film, there are an evaporation method and a sputtering-selenization method, and as a chemical fabrication method thereof, there is an electro-deposition method. In each method, various fabrication methods are used according to the kind of raw materials.

[201] However, in the fabrication method according to the present invention, gas-phase organic metal compounds of which cost is expensive and handling is difficult or an expensive vacuum equipment are not used, and a highly complicated process such as multilayer deposition is not needed. That is, in the fabrication method according to the present invention, a high quality multinary chalcogenide (photo active layer) may be prepared by a significantly simple, safe, and easy process of coating the ink containing the copper nanoparticles and the chalcogenide particles and heat treating the coating film.

[202] Further, in the fabrication method according to the present invention, the photo active layer is fabricated using the above-mentioned ink, such that the photo active layer made of the single phase multinary chalcogenide may be fabricated at a temperature within the process allowable temperature of 550°C or less at which mechanical strength of an organic substrate generally used as an insulating substrate of a solar cell is maintained, and the photo active layer having excellent uniformity and a dense micro structure and composed of coarse grains having a micrometer-order size may be fabricated.

[203] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, the substrate onto which the ink is coated may include a laminated substrate in which a back contact generally used in a solar cell field is laminated on an insulating substrate generally used in the solar cell field. As an example of the insulating substrate, there is a glass substrate, a sodalime glass substrate, a ceramic substrate, or a semiconductor substrate. As an example of the back contact formed on the insulating substrate, there is a molybdenum (Mo) layer.

[204] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, the coating of the ink may be performed by one or at least two methods selected from a spin coating method, a bar coating method, a dip coating method, a drop casting method, an ink-jet printing method, a micro-contact printing method, an imprinting method, a gravure printing method, a gravure-offset printing method, a flexography printing method, and a screen printing method.

[205] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, after step a) and before step b), drying the coating film may be further performed. The drying is to evaporate and remove a

liquid phase contained in the coating film, and any drying method may be used as long as the method may be generally used in a field in which a film is formed by coating ink. As a non-restrictive example, the drying of the coating film may be performed at 60 to 90°C in the air.

[206] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, the heat-treating of the coating film formed by coating the ink on the substrate ink may be performed at 400 to 550°C, preferably 500 to 530°C.

[207] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, densification of the film, crystal growth, phase transition to the single phase multinary chalcogenide may be performed by heat treating the coating film. That is, the coating film is heat treated, such that the phase transition into the single phase of the desired multinary chalcogenide may be performed by reaction between copper and the chalcogenides containing elements configuring the photo active layer to be fabricated except for copper.

[208] As described above, as the pure single phase multinary chalcogenide is formed by the phase transition, the multinary chalcogenide having an average grain size of micrometer-order, substantially 1 to 5㎛ may be formed at a heat treatment temperature of 550°C or less.

[209] In the fabrication method according to the present invention, the heat treating of the coating film may be performed under chalcogen atmosphere. The chalcogen atmosphere includes an atmosphere in which sulfur (S), selenium (Se), or a mixed gas thereof are present.

[210] In detail, the coating film may be heat treated while supplying chalcogen containing gas or heat treated together with chalcogen powder used as a source of chalcogen gas.

[211] In more detail, the coating film may be heat treated under chalcogen atmosphere containing sulfur (S), selenium (Se), or a mixed gas thereof. In this case, the chalcogen gas atmosphere may be formed by supplying gas containing a chalcogen element (S, Se) such as H_2S or H_2Se, evaporating the chalcogen element (S, Se) and then supplying the evaporated chalcogen element, or heat treating the chalcogen powder, which is a powder phase of the chalcogen element, together with the coating film to use the chalcogen powder as the source of the chalcogen gas.

[212] As a substantial example, in the case of supplying the chalcogen gas, chalcogen containing gas including H_2S or H_2Se, chalcogen element (S, Se) vapor, or a mixed gas thereof may be supplied at a flow of 5 to 300 sccm.

[213] As a substantial example, in the case of evaporating chalcogen powder itself containing S powder, Se powder, or a mixed powder thereof to form the chalcogen atmosphere in a chamber in which the heat treatment of the coating film is performed, a

temperature at which the chalcogen powder is heated may be the same as or different from that of the coating film on which heat treatment is performed.

[214] More specifically, in the case in which the chalcogen powder is used as the source of the chalcogen gas, the chalcogen powder may be heated to 80~250°C.

[215] In the case in which the chalcogen powder is used as the source of the chalcogen gas, the chalcogen powder in a heat treatment apparatus may be positioned on a region different from a region on which the coating film is positioned. In this case, the heat treatment may be performed using an apparatus provided with a heater and a controller so that at least two uniform zones may be each independently formed in a single heat treatment space in which fluid may flow, and a heating temperature of the chalcogen powder may be adjusted by adjusting a position on which the chalcogen powder is positioned in a general heat treatment apparatus forming a single uniform zone.

[216] The heat treatment of the coating film may be performed under any pressure, but as a non-restrictive example, the heat treatment may be performed under vacuum or atmospheric pressure.

[217] In the fabrication method of a photo active layer for a solar cell according to the exemplary embodiment of the present invention, examples of the multinary chalcogenide may include $CuIn_kGa_{1-k}Se_lS_{1-l}$ (k and l are real numbers satisfying the following Equations, respectively: $0\leq k\leq 1$ and $0\leq l\leq 1$) and $Cu_2Zn_mSn_{2-m}(Se_nS_{1-n})_4$ (m and n are real numbers satisfying the following Equations, respectively: $0\leq m\leq 2$ and $0\leq n\leq 1$).

[218] As an example, a single phase multinary chalcogenide represented by $CuIn_kGa_{1-k}Se_lS_{1-l}$ (k and l are real numbers satisfying the following Equations, respectively: $0\leq k\leq 1$ and $0\leq l\leq 1$) may be prepared using ink containing Cu nanoparticles; and chalcogenide particles represented by $(In_xGa_{1-x})_2(Se_yS_{1-y})_3$ (x and y are real numbers satisfying the following Equations, respectively: $0\leq x\leq 1$ and $0\leq y\leq 1$). In this case, as described above, a molar ratio of In and Ga (In and Ga of the chalcogenide particles) to Cu (Cu of the copper particles) that are contained in the ink may be 1:0.7 to 1.2.

[219] As an example, a single phase multinary chalcogenide ($CuInSe_2$) may be prepared using ink containing Cu nanoparticles and chalcogenide (In_2Se_3) particles.

[220] As an example, a single phase multinary chalcogenide represented by $CuIn_kGa_{1-k}Se_lS_{1-l}$ (k and l are real numbers satisfying the following Equations, respectively: $0\leq k\leq 1$ and $0\leq l\leq 1$) may be prepared using ink containing Cu nanoparticles; and chalcogenides (In_2Se_3 and Ga_2S_3) particles. In this case, a molar ratio of In and Ga (In and Ga of the chalcogenide particles) to Cu (Cu of the copper particles) that are contained in the ink may be 1:0.7 to 1.2, wherein a molar ratio of In to Ga may depend on a molar ratio (k:1-k) of In to Ga of the multinary chalcogenide to be prepared.

[221] As an example, a single phase multinary chalcogenide represented by $Cu_2Zn_mSn_{2-m}$

$(Se_nS_{1-n})_4$ (m and n are real numbers satisfying the following Equations, respectively: $0\leq m\leq 2$ and $0\leq n\leq 1$) may be prepared using ink containing Cu nanoparticles; and chalcogenides particles represented by ZnS_ySe_{1-y} (y is a real number satisfying the following Equation: $0\leq y\leq 1$) and SnS_ySe_{1-y} (y is a real number satisfying the following Equation: $0\leq y\leq 1$). In this case, a molar ratio of Zn and Sn (Zn and Sn of the chalcogenide particles) to Cu (Cu of the copper particles) that are contained in the ink may be 1:0.7 to 1.2, wherein a molar ratio of Zn to Sn may depend on a molar ratio (m:2-m) of Zn to Sn of the multinary chalcogenide to be prepared.

[222] The present invention includes a photo active layer fabricated by the above-mentioned fabrication method.

[223] The present invention includes a solar cell provided with a photo active layer fabricated by the above-mentioned fabrication method.

[224] The solar cell according to another exemplary embodiment of the present invention may include the above-mentioned photo active layer formed on a substrate (substrate formed with a lower electrode); a buffer layer formed on the photo active layer; a window layer formed on the buffer layer; and a grid electrode formed on the window layer.

[225] As the buffer layer, any buffer layer may be used as long as the buffer layer is used in a general compound semiconductor based solar cell in order to alleviate differences in a lattice constant and band gap energy between two layers at the time of p-n junction between the photo active layer, which is a first conductive semiconductor (as an example, in the case of CIGS, p-type), and the window layer, which is a second conductive semiconductor (as an example, in the case of a ZnO thin film, n-type). For example, the buffer layer may be a CdS thin film.

[226] The window layer is a layer having semiconductor characteristics complementary to those of the photo active layer, and any window layer may be used as long as it may form the p-n junction with the photo active layer and be used in the general compound semiconductor based solar cell. For example, the window layer may be a ZnO thin film.

[227] The grid electrode, which is to collect current from a surface of the solar cell, may include a finger electrode and a bus bar electrode, and a front electrode structure and a material used in the general compound semiconductor based solar cell may be used. For example, the grid electrode may have a fish bone structure and be made of Al or Ni/Al.

[228] The solar cell according to the exemplary embodiment of the present invention may further include an anti-reflection film formed on the grid electrode, wherein as the anti-reflection film, any anti-reflection film may be used as long as it is used in the general compound semiconductor based solar cell. For example, the anti-reflection film may

be a silicon oxide film.

[229] Hereinafter, although the present invention is described based on Preparation Examples, they are provided only for assisting in the entire understanding of the present invention. Therefore, the present invention is not limited to the following Preparation Examples, and various modifications and changes may be made by those skilled in the art to which the present invention pertains from this description.

[230] (Preparation Example 1)

[231] 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, Cu_2Se nanoparticles containing a CuSe second phase were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[232] In order to prepare ink, the Cu_2Se nanoparticles containing the CuSe second phase were added to tetrahydrofuran, such that a dispersion solution containing 20 weight% of copper chalcogenide particles (nanoparticles in which CuSe and Cu_2Se are mixed with each other) was prepared. $InCl_3$ was added to the prepared dispersion solution so that a molar ratio of Cu in the copper chalcogenide particles (CuSe and Cu_2Se nanoparticles) to In is 1:1, thereby preparing ink. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[233] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[234]

[235] (Preparation Example 2)

[236] 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, Cu_2Se nanoparticles containing a CuSe second phase were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[237] In order to prepare ink, the Cu_2Se nanoparticles containing the CuSe second phase

were added to tetrahydrofuran, such that a dispersion solution containing 20 weight% of copper chalcogenide particles (nanoparticles in which CuSe and Cu_2Se are mixed with each other) was prepared. $InCl_3$ and $Ga(NO_3)_3$ were added to the prepared dispersion solution so that a molar ratio of Cu in the copper chalcogenide particles (CuSe and Cu_2Se nanoparticles) to (In+Ga) was 1:1, thereby preparing ink. A molar ratio of In to Ga was 7:3. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[238] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuIn_{0.7}Ga_{0.3}Se_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[239]

[240] (Preparation Example 3)

[241] 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, Cu_2Se nanoparticles containing a CuSe second phase were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[242] In order to prepare ink, the Cu_2Se nanoparticles containing the CuSe second phase were added to tetrahydrofuran, such that a dispersion solution containing 20 weight% of copper chalcogenide particles (nanoparticles in which CuSe and Cu_2Se are mixed with each other) was prepared. $Cu(C_2O_2H_3)_2$, $Zn(C_2O_2H_3)_2$, and $SnCl_2$ were added to the prepared dispersion solution so that a molar ratio of Cu in the copper chalcogenide particles (CuSe and Cu_2Se nanoparticles):Zn:Sn was 2:1:1, thereby preparing ink. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[243] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $Cu_2ZnSnSe_4$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[244]

[245] (Comparative Example 1)

[246] 50ml of oleylamine was put into two flasks, respectively, and a temperature was

fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and Se powder (10mmol) was added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, pure Cu_2Se nanoparticles in which a CuSe second phase was not present were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[247] In order to prepare ink, the synthesized Cu_2Se nanoparticles were added to tetrahydrofuran, such that a dispersion solution containing 20 weight% of Cu_2Se particles was prepared. $InCl_3$ was added to the prepared dispersion solution so that a molar ratio of Cu in the Cu_2Se nanoparticles to In is 1:1, thereby preparing ink. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[248] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[249]

[250] (Comparative Example 2)

[251] 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 250°C, copper chalcogenide nanoparticles were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 250°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[252]

[253] (Comparative Example 3)

[254] 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 150°C, a solution in the first flask was instantaneously injected into the second flask, and then the temperature was maintained at 150°C for 1 hour.

[255]

[256] (Comparative Example 4)

[257] In order to synthesize Cu_2Se nanoparticles, 50ml of oleylamine was put into two

flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and Se powder (10mmol) was added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, pure Cu_2Se nanoparticles in which a second phase was not present were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[258] In order to synthesize $CuSe_2$ nanoparticles, 3.75g of copper nitrate and 5.16g of H_2SeO_3 were mixed in a flask charged with 200ml of polyethylene glycol solvent. After the inside of the flask was saturated with Ar, the mixture was reacted at 160°C for 4 hours. Thereafter, washing and separation were performed by precipitation and centrifugation.

[259] In order to prepare ink, the synthesized Cu_2Se nanoparticles and $CuSe_2$ nanoparticles were added to tetrahydrofuran, such that a dispersion solution containing 20 weight% of the Cu_2Se nanoparticles and $CuSe_2$ nanoparticles was prepared. In this case, a molar ratio of Cu_2Se to $CuSe_2$ was 1:1. $InCl_3$ was added to the prepared dispersion solution so that a molar ratio of Cu in the Cu_2Se nanoparticles and the $CuSe_2$ nanoparticles to In is 1:1, thereby preparing ink. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[260] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[261]

[262] (Comparative Example 5)

[263] In order to synthesize $CuSe_2$ nanoparticles, 3.75g of copper nitrate and 5.16g of H_2SeO_3 were mixed in a flask charged with 200ml of polyethylene glycol solvent. After the inside of the flask was saturated with Ar, the mixture was reacted at 160°C for 4 hours. Thereafter, washing and separation were performed by precipitation and centrifugation.

[264] In order to prepare ink, the synthesized $CuSe_2$ nanoparticles were added to tetrahydrofuran, such that a dispersion solution containing 20 weight% of $CuSe_2$ nanoparticles was prepared. $InCl_3$ was added to the prepared dispersion solution so that a molar ratio of Cu in the $CuSe_2$ nanoparticles to In is 1:1, thereby preparing ink. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[265] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat

treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[266] The copper chalcogenide particles synthesized in Preparation Example 1 and Comparative Examples 1 to 3 were analyzed using X-ray diffraction, and results obtained by measuring presence or absence of the second phase and a kind thereof were shown in Table 1.

[267] (Table 1)

[268]

	Synthetic temperature (°C)	Surfactant	Crystalline phase
Preparation Example 1	200	TOPO	CuSe and Cu_2Se
Comparative Example 1	200	X	Cu_2Se
Comparative Example 2	250	TOPO	Cu_2Se
Comparative Example 3	150	TOPO	Particles were not synthesized

[269] As shown in Table 1, it may be appreciated that in the case of Preparation Example 1, the nanoparticles including crystalline CuSe and Cu_2Se were synthesized by preparing a first solution containing a Group 11 metal precursor and a second solution containing a surfactant, which is trioctylphosphine, trioctylphosphineoxide, or a mixture thereof, and a chalcogen precursor and then injecting the first solution to the second solution having a temperature of 160 to 240°C.

[270] In the case of Comparative Examples 1 and 2, only pure single phase Cu_2Se was prepared, and in the case of Comparative Example 3, particles were not synthesized.

[271] FIG. 1 shows a result obtained by X-ray diffraction (XRD) analysis of the copper chalcogenide particles prepared in Preparation Example 1. As shown in FIG. 1, it may be appreciated that the nanoparticles in which high melting point crystalline Cu_2Se and low melting point crystalline CuSe were mixed were formed in a synthetic step and a weight ratio of CuSe to Cu_2Se in the nanoparticles was 100(CuSe):400(Cu_2Se). As a result of composition analysis using a transmission electron microscope (TEM) equipment, a change in composition was not present in each nanoparticle. Therefore, it may be appreciated that crystalline Cu_2Se and CuSe were mixed with each other in a single nanoparticle.

[272] FIG. 2 is a scanning electron microscope (SEM) photograph of the copper

chalcogenide particles prepared in Preparation Example 1. As shown in FIG. 2, it may be appreciated that the copper chalcogenide particles (composite particles) having an average particle size of 40nm were prepared.

[273] FIG. 3 is scanning electron microscope (SEM) photographs of a cross section of the photo active layer fabricated in Preparation Example 1. As shown in FIG. 3, it may be confirmed that a dense thin film of which a micro structure was significantly improved was fabricated.

[274] FIG. 4 is a view showing a result obtained by X-ray diffraction analysis of the photo active layer fabricated in Preparation Example 1. As shown in FIG. 4, it may be confirmed that the photo active layer made of single phase $CuInSe_2$ was fabricated.

[275] FIG. 5 is a view showing a result obtained by X-ray diffraction analysis of the copper chalcogenide particles prepared in Comparative Example 1, and it may be appreciated that only pure Cu_2Se particles were synthesized.

[276] FIG. 6 is a scanning electron microscope (SEM) photograph of the copper chalcogenide particles prepared in Comparative Example 1, and FIG. 7 is a scanning electron microscope (SEM) photograph of a cross section of the photo active layer fabricated in Comparative Example 1. As shown in FIGS. 6 and 7, it may be appreciated that shapes and sizes of the nanoparticles in Comparative Example 1 were similar to those of the particles synthesized in Preparation Examples, but a porous thin film in which the shape of the nanoparticle was present as it is was fabricated in Comparative Example 1 as shown in the photograph of the cross section of the photo active layer.

[277] FIG. 8 is a scanning electron microscope (SEM) photograph of a surface of the photo active layer fabricated in Comparative Example 4. Unlike the case of using the composite particles in which high melting point and low melting point crystalline phases were mixed with each other in Preparation Examples, it may be confirmed that in the case of the photo active layer fabricated from the ink obtained by independently synthesizing the high melting point chalcogenide and low melting point chalcogenide and physically mixed them, since a chemical reaction between the different crystalline phases did not effectively occur during the heat treatment process, the photo active layer had a non-uniform micro structure.

[278] FIG. 9 is a scanning electron microscope (SEM) photograph of a surface of a photo active layer fabricated in Comparative Example 5. Unlike the case of using the composite particles in which high melting point and low melting point crystalline phases were mixed with each other in Preparation Examples, in the case of the photo active layer fabricated from the ink composed of only the low melting point chalcogenide, specific crystalline phases were evaporated due to excessive formation of a liquid phase during the heat treatment process. This may cause a non-uniform

micro structure and make it difficult to control the composition of the finally obtained photo active layer.

[279] Whether or not a dense structure was formed in the photo active layers fabricated in Preparation Examples 1 to 3 and Comparative Examples 1, 4, and 5 were shown in Table 2.

[280] (Table 2)

[281]

	Ink composition	Photo active layer
Preparation Example 1	$CuSe/Cu_2Se$ crystalline phase mixed nanoparticles $InCl_3$	Uniform and dense structure
Preparation Example 2	$CuSe/Cu_2Se$ crystalline phase mixed nanoparticles $InCl_3$, $Ga(NO_3)_3$	Uniform and dense structure
Preparation Example 3	$CuSe/Cu_2Se$ crystalline phase mixed nanoparticles $Cu(C_2O_2H_3)_2$, $Zn(C_2O_2H_3)_2$, $SnCl_2$	Uniform and dense structure
Comparative Example 1	Cu_2Se nanoparticles $InCl_3$	Uniform and dense structure
Comparative Example 4	Cu_2Se nanoparticles $CuSe_2$ nanoparticles $InCl_3$	Non-uniform and dense structure
Comparative Example 5	$CuSe_2$ nanoparticles $InCl_3$	Non-uniform and dense structure

[282] As shown in Table 2, it may be appreciated that in Preparation Examples 2 and 3, a uniform and dense structure was formed similarly to that in Preparation Example 1. On the other hand, it may be appreciated that photo active layer fabricated in Comparative Example 1 had a porous structure instead of a dense structure, and the photo active layers fabricated in Comparative Examples 4 and 5 had a dense structure but uniformity thereof was significantly deteriorated.

[283]

[284] (Preparation Example 4)

[285] In order to synthesize a chalcogenide (composite particle) of a Group 11 metal, 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to

200°C, Cu_2Se nanoparticles containing a CuSe second phase were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[286]

[287] (Preparation Example 5)

[288] In order to synthesize a chalcogenide (composite particle) of a Group 11 metal, 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, Cu_2Se nanoparticles containing a CuSe second phase were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[289] In order to synthesize a third chalcogenide, 80ml of oleylamine was put into a flask and a temperature of the flask was fixed to 60°C. Then, $In(acac)_3$ (acac=acetylacetonate, pentane-2,4-dione, 8mmol) and Se powder (12mmol) were added to the flask and heated to 290°C, and then the temperature was maintained at 290°C for 1 hour, thereby synthesizing In_2Se_3 nanoparticles. Thereafter, the synthesized chalcogenide particles were separated using a centrifugation method and then washed with toluene.

[290] In order to prepare ink, Cu_2Se nanoparticles (composite particles) containing the CuSe second phase and the In_2Se_3 nanoparticles were added to toluene, thereby preparing ink containing 20 weight% of particle phase (CuSe nanoparticle, Cu_2Se nanoparticles, In_2Se_3 nanoparticles). In the prepared ink, a molar ratio of Cu in the composite particles, which were copper chalcogenide particles, to In of In_2Se_3 nanoparticles was 1:1. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[291] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[292]

[293] (Preparation Example 6)

[294] In order to synthesize a chalcogenide (composite particle) of a Group 11 metal, 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to

60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, Cu_2Se nanoparticles containing a CuSe second phase were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[295] In order to synthesize a third chalcogenide, 80ml of oleylamine was put into a flask and a temperature of the flask was fixed to 60°C. Then, $In(acac)_3$ (acac=acetylacetonate, pentane-2,4-dione, 8mmol) and Se powder (12mmol) were added to the flask and heated to 290°C, and then the temperature was maintained at 290°C for 1 hour, thereby synthesizing In_2Se_3 nanoparticles. Thereafter, the synthesized chalcogenide particles were separated using a centrifugation method and then washed with toluene.

[296] In order to prepare ink, the Cu_2Se nanoparticles (composite particles) containing the CuSe second phase, the In_2Se_3 nanoparticles, and Ga_2S_3 (Aldrich) were mixed together with toluene. These materials were added to toluene so that a molar ratio of Cu to (In+Ga) was 1:1 and a molar ratio of In to Ga was 7:3. In this case, a content of toluene was 400 parts by weight based on 100 parts by weight of the particle phase. After the particle phase was injected into toluene, for homogeneous mixing, ball milling was performed at 20Hz for 60 minutes.

[297] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $Cu(In_{0.7}Ga_{0.3})(S,Se)_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[298]

[299] (Preparation Example 7)

[300] In order to synthesize a chalcogenide (composite particle) of a Group 11 metal, 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, Cu_2Se nanoparticles containing a CuSe second phase were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[301] In order to prepare ink, the Cu_2Se nanoparticles (composite particles) containing the

CuSe second phase, ZnS (Aldrich), and SnS (Aldrich) were mixed together with toluene. These materials were added to toluene so that a molar ratio of Cu: Zn: Sn was 2:1:1. In this case, a content of toluene was 400 parts by weight based on 100 parts by weight of the particle phase. After the particle phase was injected into toluene, for homogeneous mixing, ball milling was performed at 20Hz for 60 minutes.

[302] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while supplying H_2S gas at a flow rate of 100sccm, thereby fabricating a photo active layer, which was a Cu_2ZnSnS_4 thin film.

[303]

[304] (Preparation Example 8)

[305] In order to synthesize a chalcogenide (composite particle) of a Group 11 metal, 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, Cu_2Se nanoparticles containing a CuSe second phase were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[306] In order to prepare ink, the Cu_2Se nanoparticles (composite particles) containing the CuSe second phase, ZnS (Aldrich), and SnS (Aldrich) were mixed together with toluene. These materials were added to toluene so that a molar ratio of Cu: Zn: Sn was 2:1:1. In this case, a content of toluene was 400 parts by weight based on 100 parts by weight of the particle phase. After the particle phase was injected into toluene, for homogeneous mixing, ball milling was performed at 20Hz for 60 minutes.

[307] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $Cu2ZnSn(S,Se)_4$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[308]

[309] (Comparative Example 6)

[310] 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and Se powder (10mmol) was added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, pure Cu_2Se nanoparticles in which a second phase was not present were synthesized by instantaneously injecting a solution in the

first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[311]

[312] (Comparative Example 7)

[313] 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 250°C, copper chalcogenide nanoparticles were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 250°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[314]

[315] (Comparative Example 8)

[316] 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and 3g of trioctylphosphineoxide (TOPO, 77mmol) and Se powder (10mmol) were added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 150°C, a solution in the first flask was instantaneously injected into the second flask, and then the temperature was maintained at 150°C for 1 hour.

[317]

[318] (Comparative Example 9)

[319] In order to synthesize Cu_2Se nanoparticles, 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and Se powder (10mmol) was added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, pure Cu_2Se nanoparticles in which a CuSe second phase was not present were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[320] In order to synthesize chalcogenide (In_2Se_3) particles, 80ml of octylamine was put into a flask and a temperature of the flask was fixed to 60°C. Then, $In(acac)_3$ (acac=acetylacetonate, pentane-2,4-dione, 8mmol) and Se powder (12mmol) were added to the flask and heated to 290°C, and then the temperature was maintained at 290°C for 1 hour, thereby synthesizing In_2Se_3 particles. Thereafter, the synthesized chalcogenide particles were separated using a centrifugation method and then washed with toluene.

[321] In order to prepare ink, the synthesized Cu_2Se nanoparticles and In_2Se_3 nanoparticles were added to toluene, thereby preparing a dispersion solution containing 20 weight% of particle phase. Here, a molar ratio of Cu to In was 1:1. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[322] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[323]

[324] (Comparative Example 10)

[325] In order to synthesize Cu_2Se nanoparticles, 50ml of oleylamine was put into two flasks, respectively, and a temperature was fixed to 60°C. Then, $CuCl_2$ (10mmol) was added to a first flask, and Se powder (10mmol) was added to a second flask. Next, after the first flask was heated to 130°C and the second flask was heated to 200°C, pure Cu_2Se nanoparticles in which a CuSe second phase was not present were synthesized by instantaneously injecting a solution in the first flask into the second flask and maintaining the temperature to 200°C for 1 hour. Thereafter, the synthesized particles were separated using a centrifugation method and then washed with toluene.

[326] In order to synthesize $CuSe_2$ nanoparticles, 3.75g of copper nitrate and 5.16g of H_2SeO_3 were mixed in a flask charged with 200ml of polyethylene glycol solvent. After the inside of the flask was saturated with Ar, the mixture was reacted at 160°C for 4 hours. Thereafter, washing and separation were performed by precipitation and centrifugation.

[327] In order to synthesize chalcogenide (In_2Se_3) particles, 80ml of octylamine was put into a flask and a temperature of the flask was fixed to 60°C. Then, $In(acac)_3$ (acac=acetylacetonate, pentane-2,4-dione, 8mmol) and Se powder (12mmol) were added to the flask and heated to 290°C, and then the temperature was maintained at 290°C for 1 hour, thereby synthesizing In_2Se_3 particles. Thereafter, the synthesized chalcogenide particles were separated using a centrifugation method and then washed with toluene.

[328] In order to prepare ink, the synthesized Cu_2Se nanoparticles, $CuSe_2$ nanoparticles, and In_2Se_3 nanoparticles were added to toluene, thereby preparing a dispersion solution containing 20 weight% of particle phase. Here, a molar ratio of Cu_2Se to $CuSe_2$ was 1:1, and a molar ratio of Cu to In was 1:1. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[329] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat

treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[330]

[331] (Comparative Example 11)

[332] In order to synthesize $CuSe_2$ nanoparticles, 3.75g of copper nitrate and 5.16g of H_2SeO_3 were mixed in a flask charged with 200ml of polyethylene glycol solvent. After the inside of the flask was saturated with Ar, the mixture was reacted at 160°C for 4 hours. Thereafter, washing and separation were performed by precipitation and centrifugation.

[333] In order to synthesize chalcogenide (In_2Se_3) particles, 80ml of octylamine was put into a flask and a temperature of the flask was fixed to 60°C. Then, $In(acac)_3$ (acac=acetylacetonate, pentane-2,4-dione, 8mmol) and Se powder (12mmol) were added to the flask and heated to 290°C, and then the temperature was maintained at 290°C for 1 hour, thereby synthesizing In_2Se_3 particles. Thereafter, the synthesized chalcogenide particles were separated using a centrifugation method and then washed with toluene.

[334] In order to prepare ink, the synthesized $CuSe_2$ nanoparticles and In_2Se_3 nanoparticles were added to toluene, thereby preparing a dispersion solution containing 20 weight% of particle phase. In this case, a molar ratio of Cu to In was 1:1. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes.

[335] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[336]

[337] The copper chalcogenide particles synthesized in Preparation Example 4 and Comparative Examples 6 to 8 were analyzed using X-ray diffraction, and results obtained by measuring presence or absence of the second phase and a kind thereof were shown in Table 3.

[338] (Table 3)

[339]

	Synthetic temperature (°C)	Surfactant	Crystalline phase
Preparation Example 4	200	TOPO	CuSe and Cu_2Se
Comparative Example 6	200	X	Cu_2Se
Comparative Example 7	250	TOPO	Cu_2Se
Comparative Example 8	150	TOPO	Particles were not synthesized

[340] As shown in Table 3, it may be appreciated that the nanoparticles in which CuSe and Cu_2Se crystal phases were homogeneously agglomerated and distributed were synthesized in Preparation Example 4 by preparing a first solution containing a Group 11 metal precursor and a second solution containing a surfactant, which is trioctylphosphine, trioctylphosphineoxide, acid, or a mixture thereof, and a chalcogen precursor and then injecting the first solution to the second solution having a temperature of 160 to 240°C.

[341] In the case of Comparative Examples 6 and 7, only pure single phase Cu_2Se was prepared, and in the case of Comparative Example 8, particles were not synthesized.

[342] FIG. 10 shows a result obtained by X-ray diffraction (XRD) analysis of the copper chalcogenide particles prepared in Preparation Example 4. As shown in FIG. 10, it may be appreciated that the nanoparticles in which high melting point crystalline Cu_2Se and low melting point crystalline CuSe were mixed were formed in a synthetic step and a weight ratio of CuSe to Cu_2Se in the nanoparticles was 100:400. As a result of composition analysis using a transmission electron microscope (TEM) equipment, a change in composition was not present in each nanoparticle. Therefore, it may be appreciated that crystalline Cu_2Se and CuSe were mixed with each other in a single nanoparticle.

[343] FIG. 11 is a scanning electron microscope (SEM) photograph of the copper chalcogen particles prepared in Preparation Example 4. As shown in FIG. 11, it may be appreciated that the copper chalcogenide particles (composite particles) having an average particle size of 40nm were prepared.

[344] FIG. 12 is a scanning electron microscope (SEM) photograph of In_2Se_3 synthesized in Preparation Example 5. As shown in FIG. 12, it may be appreciated that the chalcogenide (In_2Se_3) particles having an average particle size of 13nm were synthesized. As a result of XRD analysis of the synthesized In2Se3 particles, it was confirmed that amorphous particles were prepared, and as a result of inductively

coupled plasma (ICP) composition analysis, it was confirmed that particles having an In_2Se_3 composition were prepared.

[345] FIG. 13 is a scanning electron microscope (SEM) of a cross section of the photo active layer fabricated in Preparation Example 5. As shown in FIG. 13, it may be confirmed that a dense thin film of which a micro structure was significantly improved was fabricated.

[346] FIG. 14 is a view showing a result obtained by X-ray diffraction analysis of the photo active layer fabricated in Preparation Example 5. As shown in FIG. 14, it may be confirmed that the photo active layer made of single phase $CuInSe_2$ was fabricated.

[347] FIG. 15 is a view showing a result obtained by X-ray diffraction analysis of the copper chalcogenide particles prepared in Comparative Example 9, and it may be appreciated that only pure Cu_2Se particles were synthesized.

[348] FIG. 16 is a scanning electron microscope (SEM) photograph of the copper chalcogenide particles prepared in Comparative Example 9, and FIG. 17 is a scanning electron microscope (SEM) photograph of a cross section of the photo active layer fabricated in Comparative Example 9. As shown in FIGS. 16 and 17, it may be appreciated that shapes and sizes of the nanoparticles in Comparative Example 9 were similar to those of the particles synthesized in Preparation Examples, but a porous thin film in which the shape of the nanoparticle was present as it is was fabricated in Comparative Example 9 as shown in the photograph of the cross section of the photo active layer.

[349] FIG. 18 is a scanning electron microscope (SEM) photograph of a surface of the photo active layer fabricated in Comparative Example 10. It may be confirmed that unlike the case of using the composite particles in which high melting point and low melting point crystalline phases were mixed with each other in the Preparation Examples, in the case of the photo active layer fabricated from the ink obtained by independently synthesizing the high melting point chalcogenide and low melting point chalcogenide and physically mixed them, since a chemical reaction between the different crystalline phases did not effectively occur during the heat treatment process, the photo active layer had a non-uniform micro structure.

[350] FIG. 19 is a scanning electron microscope (SEM) photograph of a surface of the photo active layer fabricated in Comparative Example 11. Unlike the case of using the composite particles in which high melting point and low melting point crystalline phases were mixed with each other in the Preparation Examples, in the case of the photo active layer fabricated from the ink composed of only the low melting point chalcogenide, specific crystalline phases were evaporated due to excessive formation of a liquid phase during the heat treatment process. This may cause a non-uniform micro structure and make it difficult to control the composition of the finally obtained

photo active layer.

[351] Whether or not a dense structure was formed in the photo active layers fabricated in Preparation Examples 5 to 8 and Comparative Examples 9 to 11 were shown in Table 4.

[352] (Table 4)

[353]

	Ink composition	Heat treatment atmosphere	Micro structure
Preparation Example 5	CuSe/Cu_2Se crystalline phase composite particles In_2Se_3	Se atmosphere	Uniform and dense
Preparation Example 6	CuSe/Cu_2Se crystalline phase composite particles In_2Se_3, Ga_2S_3	Se atmosphere	Uniform and dense
Preparation Example 7	CuSe/Cu_2Se crystalline phase composite particles ZnS, SnS	S atmosphere	Uniform and dense
Preparation Example 8	CuSe/Cu_2Se crystalline phase composite particles ZnS, SnS	Se atmosphere	Uniform and dense
Comparative Example 9	Cu_2Se nanoparticles In_2Se_3	Se atmosphere	Uniform and porous
Comparative Example 10	Cu_2Se nanoparticles $CuSe_2$ nanoparticles In_2Se_3	Se atmosphere	Non-uniform and dens
Comparative Example 11	$CuSe_2$ nanoparticles In_2Se_3	Se atmosphere	Non-uniform and dens

[354] As shown in Table 4, it may be appreciated that in Preparation Examples 6 to 8, a uniform and dense structure was formed similarly to that in Preparation Example 5. On the other hand, it may be appreciated that photo active layer fabricated in Comparative Example 9 had a porous structure instead of a dense structure, and the photo active layers fabricated in Comparative Examples 10 and 11 had a dense structure but

uniformity thereof was significantly deteriorated.

[355]

[356] (Preparation Example 9)

[357] In order to synthesize Cu nanoparticles, after 73.63g of octylamine and 25.1g of oleic acid were mixed with each other in a flask, 10.38g of Cu acetate was added thereto, thereby preparing a copper precursor solution. After inert atmosphere was formed using nitrogen gas, the copper precursor solution was heated to 150°C, and 87.4g of phenylhydrazine was added thereto to induce a reduction reaction of copper ions, thereby synthesizing copper nanoparticles. Thereafter, the synthesized copper nanoparticles were separated using a centrifugation method and then washed with toluene.

[358] In order to synthesize chalcogenide particles, 80ml of octylamine was put into a flask and a temperature of the flask was fixed to 60°C. Then, $In(acac)_3$ (acac=acetylacetonate, pentane-2,4-dione, 8mmol) and Se powder (12mmol) were added to the flask and heated to 290°C, and then the temperature was maintained at 290°C for 1 hour, thereby synthesizing In_2Se_3 particles. Thereafter, the synthesized chalcogenide particles were separated using a centrifugation method and then washed with toluene.

[359] The prepared Cu nanoparticles and In_2Se_3 particles were added to toluene so that a molar ratio of Cu to In was 1:1. In this case, a content of toluene was 400 parts by weight based on 100 parts by weight of the particle phase including the Cu nanoparticles and In_2Se_3 particles. After the particle phase was injected into toluene, for homogeneous mixing, ball milling was performed at 20Hz for 60 minutes.

[360] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[361]

[362] (Preparation Example 10)

[363] In order to synthesize Cu nanoparticles, after 73.63g of octylamine and 25.1g of oleic acid were mixed with each other in a flask, 10.38g of Cu acetate was added thereto, thereby preparing a copper precursor solution. After inert atmosphere was formed using nitrogen gas, the copper precursor solution was heated to 150°C, and 87.4g of phenylhydrazine was added thereto to induce a reduction reaction of copper ions, thereby synthesizing copper nanoparticles. Thereafter, the synthesized copper nanoparticles were separated using a centrifugation method and then washed with toluene.

[364] In order to synthesize chalcogenide (In_2Se_3) particles, 80ml of octylamine was put into a flask and a temperature of the flask was fixed to 60°C. Then, $In(acac)_3$ (acac=acetylacetonate, pentane-2,4-dione, 8mmol) and Se powder (12mmol) were added to the flask and heated to 290°C, and then the temperature was maintained at 290°C for 1 hour, thereby synthesizing In_2Se_3 particles. Thereafter, the synthesized chalcogenide particles were separated using a centrifugation method and then washed with toluene.

[365] In order to prepare ink for a photo active layer, the synthesized copper nanoparticles, In_2Se_3 particles, and Ga_2S_3 (Aldrich) were mixed with toluene. These materials were added to toluene so that a molar ratio of Cu to (In+Ga) was 1:1 and a molar ratio of In to Ga was 7:3. In this case, a content of toluene was 400 parts by weight based on 100 parts by weight of the mixed materials. After the particle phase was injected into toluene, for homogeneous mixing, ball milling was performed at 20Hz for 60 minutes.

[366] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $Cu(In_{0.7}Ga_{0.3})(S,Se)_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[367]

[368] (Preparation Example 11)

[369] In order to synthesize Cu nanoparticles, after 73.63g of octylamine and 25.1g of oleic acid were mixed with each other in a flask, 10.38g of Cu acetate was added thereto, thereby preparing a copper precursor solution. After inert atmosphere was formed using nitrogen gas, the copper precursor solution was heated to 150°C, and 87.4g of phenylhydrazine was added thereto to induce a reduction reaction of copper ions, thereby synthesizing copper nanoparticles. Thereafter, the synthesized copper nanoparticles were separated using a centrifugation method and then washed with toluene.

[370] In order to prepare ink for a photo active layer, the synthesized copper nanoparticles, ZnS (Aldrich), and SnS (Aldrich) were mixed with toluene. These materials were added to toluene so that a molar ratio of Cu: Zn: Sn was 2:1:1. In this case, a content of toluene was 400 parts by weight based on 100 parts by weight of the mixed materials. After the particle phase was injected into toluene, for homogeneous mixing, ball milling was performed at 20Hz for 60 minutes.

[371] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while supplying H_2S gas at a flow rate of 100sccm, thereby fabricating a photo active layer, which was a Cu_2ZnSnS_4 thin film.

[372]

[373] (Preparation Example 12)

[374] In order to synthesize Cu nanoparticles, after 73.63g of octylamine and 25.1g of oleic acid were mixed with each other in a flask, 10.38g of Cu acetate was added thereto, thereby preparing a copper precursor solution. After inert atmosphere was formed using nitrogen gas, the copper precursor solution was heated to 150°C, and 87.4g of phenylhydrazine was added thereto to induce a reduction reaction of copper ions, thereby synthesizing copper nanoparticles. Thereafter, the synthesized copper nanoparticles were separated using a centrifugation method and then washed with toluene.

[375] In order to prepare ink for a photo active layer, the synthesized copper nanoparticles, ZnS (Aldrich), and SnS (Aldrich) were mixed with toluene. These materials were added to toluene so that a molar ratio of Cu: Zn: Sn was 2:1:1. In this case, a content of toluene was 400 parts by weight based on 100 parts by weight of the mixed materials. After the particle phase was injected into toluene, for homogeneous mixing, ball milling was performed at 20Hz for 60 minutes.

[376] After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $Cu_2ZnSn(S,Se)_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[377]

[378] (Comparative Example 12)

[379] 10ml of oleylamine was put into first and second flasks, respectively, and a temperature was fixed to 60°C. 0.32ml of oleic acid was put into the first flask, and $CuCl_2$ (2mmol) and $InCl_3$ (2mmol) were added thereto. After Se powder (4mmol) was added to the second flask, the first flask was heated to 130°C and the second flask was heated to 240°C, thereby dissolving these materials for 1 hour. Next, after the first flask was cooled to 100°C and the second flask was cooled to 200°C, a solution in the first flask was instantaneously injected into the second flask when the temperature of the second flask arrived at 200°C, and the second flask was heated to 240°C simultaneously with instantaneous injection, followed by maintaining the temperature for 1 hour, thereby synthesizing $CuInSe_2$ particles. Thereafter, the synthesized $CuInSe_2$ particles were separated using a centrifugation method and then washed with toluene.

[380] The synthesized $CuInSe_2$ particles were mixed with toluene, such that ink containing 20 weight% of the $CuInSe_2$ particles was prepared. At this time, for homogeneous mixing of the ink, ball milling was performed at 20Hz for 60 minutes. After the prepared ink was bar-coated onto a sodalime glass substrate on which a Mo electrode

was deposited and dried at 80°C, the ink coated glass substrate was heat treated at 530°C while heating Se powder to 230°C, thereby fabricating a photo active layer, which was a $CuInSe_2$ thin film. In this case, pressure in a heat treatment chamber was 10^{-5}torr.

[381]

[382] Results obtained by observing micro structures of the photo active layers fabricated in Preparation Examples 9 to 12 and Comparative Example 12 using a scanning electron microscope (SEM) were shown in Table 5.

[383] (Table 5)

[384]

	Ink composition	Heat treatment atmosphere	Micro structure
Preparation Example 9	Cu, In_2Se_3	Se atmosphere	Dense
Preparation Example 10	Cu, In_2Se_3, Ga_2S_3	Se atmosphere	Dense
Preparation Example 11	Cu, CuS, SnS	S atmosphere	Dense
Preparation Example 12	Cu, CuS, SnS	Se atmosphere	Dense
Comparative Example 12	$CuInSe_2$	Se atmosphere	Porous

[385] As shown in Table 5, it may be confirmed that the photo active layer fabricated from the ink composition containing the copper nanoparticles had a dense micro structure, but the photo active layer fabricated from the ink composition containing single phase $CuInSe_2$ nanoparticles had a porous structure.

[386] FIG. 20 is a view showing an X-ray diffraction pattern of the Cu nanoparticles synthesized in Preparation Example 9, and FIG. 21 is a scanning electron microscope (SEM) photograph of the copper nanoparticles synthesized in Preparation Example 9. As shown in FIGS. 20 and 21, it may be appreciated that bimodal copper nanoparticles having average particle sizes of 40nm and 100nm were synthesized in a spherical shape. In addition, as a result of X-ray photoelectron spectroscopy (XPS) analysis of the Cu nanoparticles prepared in Preparation Example 9, it was confirmed that an oxide film was not formed thereon.

[387] FIG. 22 is a scanning electron microscope (SEM) photograph of In_2Se_3 synthesized in Preparation Example 9. As shown in FIG. 22, it may be appreciated that the

chalcogenide (In_2Se_3) particles having an average particle size of 13nm were synthesized.

[388] As a result of XRD analysis of the synthesized In_2Se3 particles, It was confirmed that amorphous particles were prepared, and as a result of ICP composition analysis, it was confirmed that particles having an In_2Se_3 composition were prepared.

[389] FIG. 24 is a view showing an X-ray diffraction pattern of the photo active layer, which was the $CuInSe_2$ thin film fabricated in Preparation Example 9, and FIG. 23 is a scanning electron microscope (SEM) photograph of the photo active layer fabricated in Preparation Example 9.

[390] As shown in FIG. 23, it may be appreciated that the thin film made of $CuInSe_2$ was fabricated. In addition, as shown in FIG. 24, it may be appreciated that a significantly improved thin film having a dense micro structure was fabricated at 530°C, and a coarse-grained photo active layer having an average grain size of 1μm or more was fabricated. Further, it may be confirmed that a photo active layer thin film having only a pure single phase without a second phase was fabricated through a densification behavior and a process of the phase transition into $CuInSe_2$ single phase.

[391] FIG. 25 is a view showing an X-ray diffraction pattern of the $CuInSe_2$ particles prepared in Comparative Example 12, and FIG. 26 is a scanning electron microscope (SEM) photograph of the $CuInSe_2$ particles prepared in Comparative Example 12. As shown in FIGS. 25 and 26, it may be appreciated that crystalline $CuInSe_2$ particles having an average particle size of 15nm was prepared in Comparative Example 12.

[392] FIG. 27 is a scanning electron microscope (SEM) photograph of a cross section of the photo active layer fabricated using the ink containing the $CuInSe_2$ particles prepared in Comparative Example 12. As shown in FIG. 27, it may be appreciated that a porous photo active layer thin film having shapes of the $CuInSe_2$ nanoparticles contained in the ink as it is was fabricated, and densification and particle growth were not at all performed.

[393] Although the present invention is described based on Preparation Examples, the spirit of the present invention should not be limited to the above-described Preparation Examples, and the following claims as well as all modified equally or equivalently to the claims are intended to fall within the scopes and spirits of the invention.

Claims

[Claim 1] An ink comprising:
composite particles in which a first chalcogenide of Group 11 metals and a second chalcogenide of Group 11 metals having a melting point lower than that of the first chalcogenide are mixed in a single particle; and
a precursor of at least one element selected from Groups 12 to 14 elements.

[Claim 2] The ink of claim 1, wherein the precursor of at least one element selected from Groups 12 to 14 elements is chloride, nitrate, sulfate, acetate, phosphate, silicate, or hydrochloride of one or at least two elements selected from the Groups 12 to 14 elements, or a mixture thereof.

[Claim 3] The ink of claim 1, wherein the precursor of at least one element selected from Groups 12 to 14 elements is a third chalcogenide of one or at least two elements selected from Groups 12 to 14 elements.

[Claim 4] A fabrication method of a photo active layer for a solar cell, the fabrication method comprising:
a) coating ink containing composite particles in which a first chalcogenide of Group 11 metals and a second chalcogenide of Group 11 metals having a melting point lower than that of the first chalcogenide are mixed in a single particle and a precursor of at least one element selected from Groups 12 to 14 elements onto a substrate to form a coating film; and
b) heat treating the coating film to prepare a multinary chalcogenide.

[Claim 5] The fabrication method of claim 4, wherein the first chalcogenide maintains a solid phase at the time of the heat treatment in step b), and the second chalcogenide maintains a molten phase at the time of the heat treatment in step b).

[Claim 6] The fabrication method of claim 4, wherein the second chalcogenide has a melting point of 220 to 550°C.

[Claim 7] The fabrication method of claim 4, wherein the composite particle contains 10 to 900 parts by weight of the first chalcogenide based on 100 parts by weight of the second chalcogenide.

[Claim 8] The fabrication method of claim 4, wherein a molar ratio of at least one element selected from Groups 12 to 14 elements and contained in the ink to the Group 11 metal contained in the first and second

chalcogenides is 1:0.7 to 1.2.

[Claim 9] The fabrication method of claim 4, wherein the first chalcogenide includes Cu_2Se, and the second chalcogenide includes CuSe, $CuSe_2$, or a mixture thereof.

[Claim 10] The fabrication method of claim 4, wherein the heat treatment is performed at 400 to 550°C under chalcogen atmosphere.

[Claim 11] The fabrication method of claim 4, wherein the composite particle including the first and second chalcogenides are prepared by preparing a first solution containing a precursor of a Group 11 metal and a second solution containing a surfactant, which is trioctylphosphine, tri-octylphosphineoxide, acid, or a mixture thereof, and a chalcogenide precursor and then injecting the first solution into the second solution having a temperature of 160 to 240°C.

[Claim 12] The fabrication method of claim 4, wherein the precursor of at least one element selected from Groups 12 to 14 elements is chloride, nitrate, sulfate, acetate, phosphate, silicate, or hydrochloride of one or at least two elements selected from the Groups 12 to 14 elements, or a mixture thereof.

[Claim 13] The fabrication method of claim 4, wherein the precursor of at least one element selected from Groups 12 to 14 elements is a third chalcogenide of one or at least two elements selected from Groups 12 to 14 elements.

[Claim 14] The fabrication method of claim 13, wherein the third chalcogenide includes one or at least two particles selected from $(In_xGa_{1-x})_4(S_ySe_{1-y})_3$ particles, $(In_xGa_{1-x})(S_ySe_{1-y})$ particles, $(In_xGa_{1-x})_6(S_ySe_{1-y})_7$ particles, $(In_xGa_{1-x})_9(S_ySe_{1-y})_{11}$ particles, $(In_xGa_{1-x})_2(S_ySe_{1-y})_3$ particles, and $(In_xGa_{1-x})_5(S_ySe_{1-y})_7$ particles (x and y are real numbers satisfying the following Equations, respectively: $0\leq x\leq 1$ and $0\leq y\leq 1$); or includes one or at least two particles selected from $Sn(S_ySe_{1-y})$ particles, $Sn_2(S_ySe_{1-y})_3$ particles, and $Sn(S_ySe_{1-y})_2$ particles (y is a real number satisfying the following Equation: $0\leq y\leq 1$) and $Zn(S_ySe_{1-y})$ particles (y is a real number satisfying the following Equation: $0\leq y\leq 1$).

[Claim 15] A photo active layer for a solar cell fabricated by the fabrication method of any one of claims 4 to 14.

[Claim 16] An ink comprising:
copper nanoparticles; and
chalcogenide particles of one or at least two elements selected from Groups 12 to 14 elements.

[Claim 17] A fabrication method of a photo active layer for a solar cell, the fab-

rication method comprising:

a) coating ink containing copper nanoparticles; and chalcogenide particles of one or at least two elements selected from Groups 12 to 14 elements onto a substrate to form a coating film; and

b) heat treating the coating film to prepare a multinary chalcogenide film of copper and one or at least two elements selected from Groups 12 to 14 elements.

[Claim 18] The fabrication method of claim 17, wherein the Group 12 element includes zinc (Zn), the Group 13 element is at least one selected from Indium and gallium, the Group 14 element includes Sn, and a chalcogen element is at least one selected from sulfur and selenium.

[Claim 19] The fabrication method of claim 17, wherein the chalcogenide particles includes one or at least two particles selected from $(In_xGa_{1-x})_4(S_ySe_{1-y})_3$ particles, $(In_xGa_{1-x})(S_ySe_{1-y})$ particles, $(In_xGa_{1-x})_6(S_ySe_{1-y})_7$ particles, $(In_xGa_{1-x})_9(S_ySe_{1-y})_{11}$ particles, $(In_xGa_{1-x})_2(S_ySe_{1-y})_3$ particles, and $(In_xGa_{1-x})_5(S_ySe_{1-y})_7$ particles (x and y are real numbers satisfying the following Equations, respectively: $0\leq x\leq 1$ and $0\leq y\leq 1$); or includes one or at least two particles selected from $Sn(S_ySe_{1-y})$ particles, $Sn_2(S_ySe_{1-y})_3$ particles, and $Sn(S_ySe_{1-y})_2$ particles (y is a real number satisfying the following Equation: $0\leq y\leq 1$) and $Zn(S_ySe_{1-y})$ particles (y is a real number satisfying the following Equation: $0\leq y\leq 1$).

[Claim 20] The fabrication method of claim 17, wherein a molar ratio of one or at least two elements selected from Groups 12 to 14 elements and contained in the ink to copper is 1:0.7 to 1.2.

[Claim 21] The fabrication method of claim 17, wherein the heat treatment is performed at 400 to 550°C under chalcogen atmosphere.

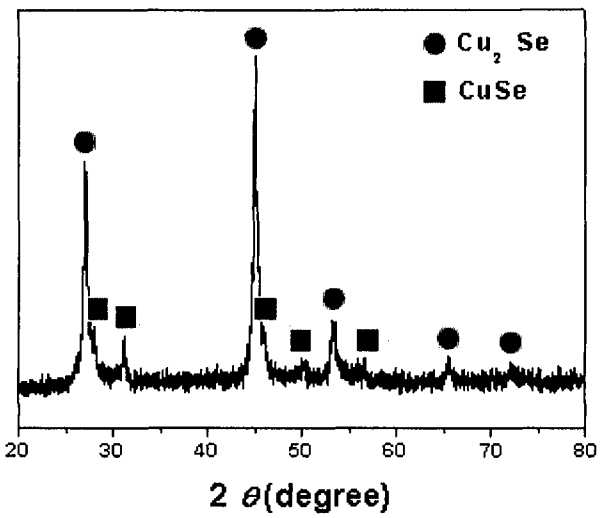
[Claim 22] The fabrication method of claim 17, wherein the copper nanoparticles is copper nanoparticles prepared by heating and stirring a copper precursor solution containing a copper precursor, acid, and amine and then injecting a reducing agent thereinto to thereby be capped with acid and amine.

[Claim 23] The fabrication method of claim 17, wherein a single phase multinary chalcogenide is formed by the heat treatment.

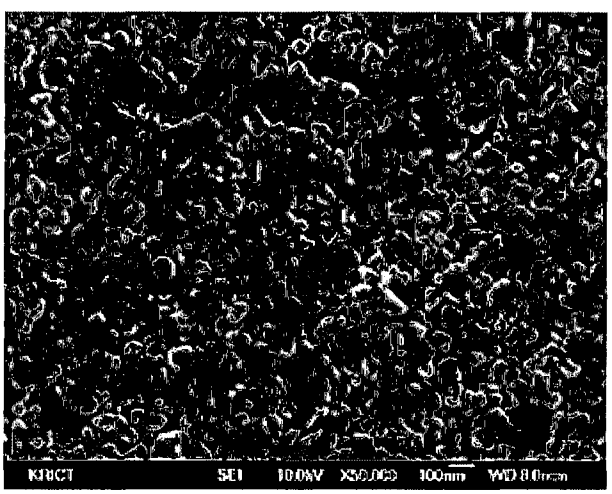
[Claim 24] A photo active layer for a solar cell fabricated by the fabrication method of any one of claims 17 to 23.

【DRAWINGS】

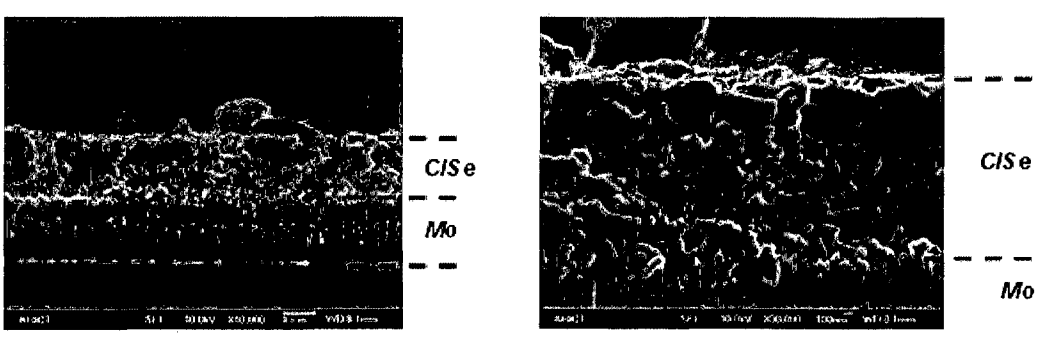
【Figure 1】



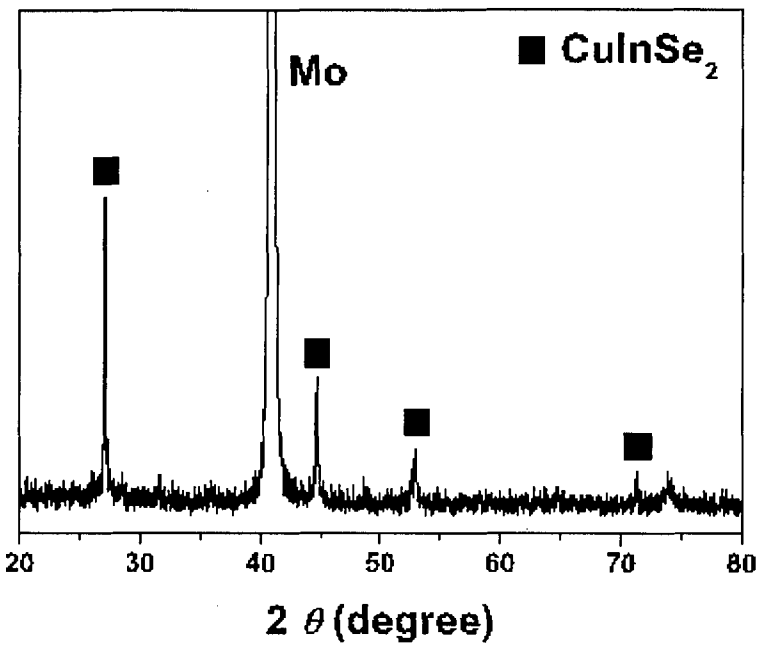
【Figure 2】



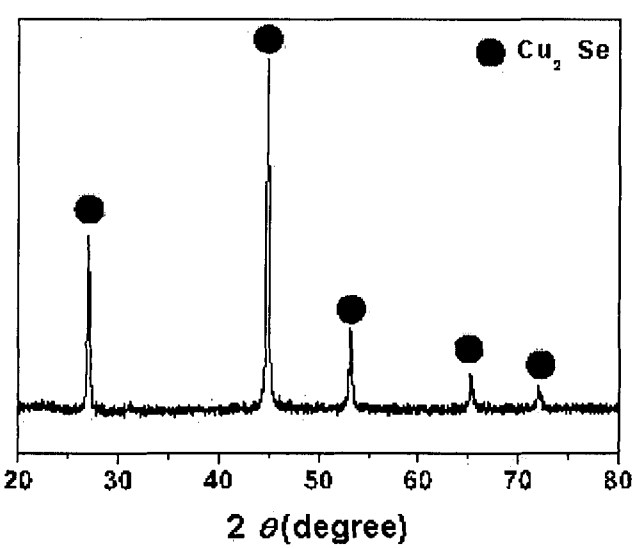
【Figure 3】



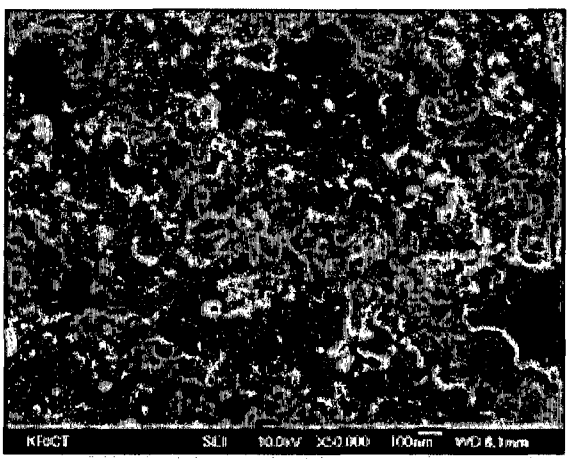
【Figure 4】



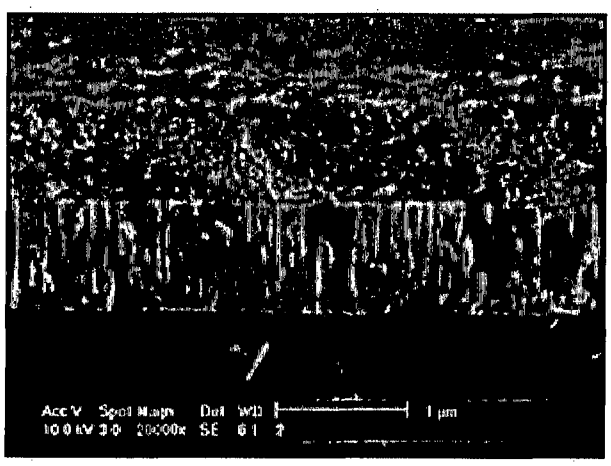
【Figure 5】



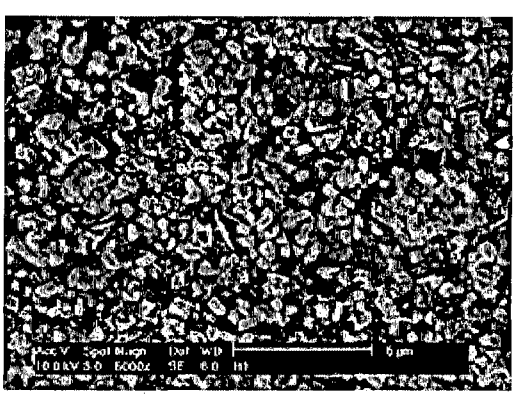
【Figure 6】



【Figure 7】

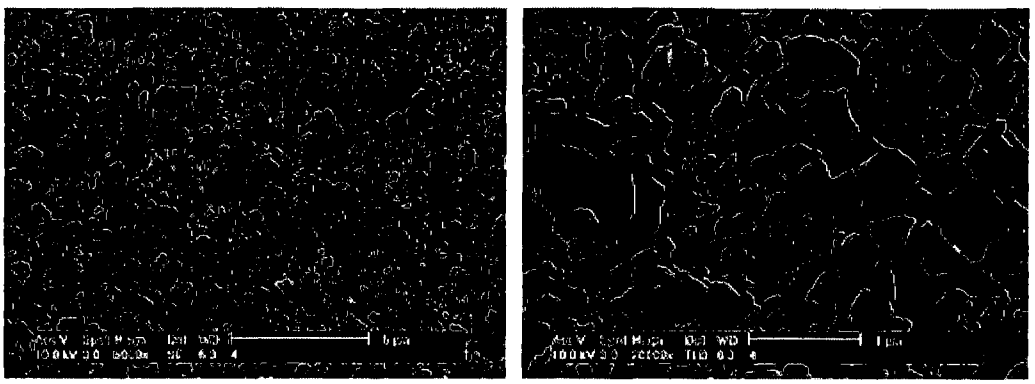


【Figure 8】

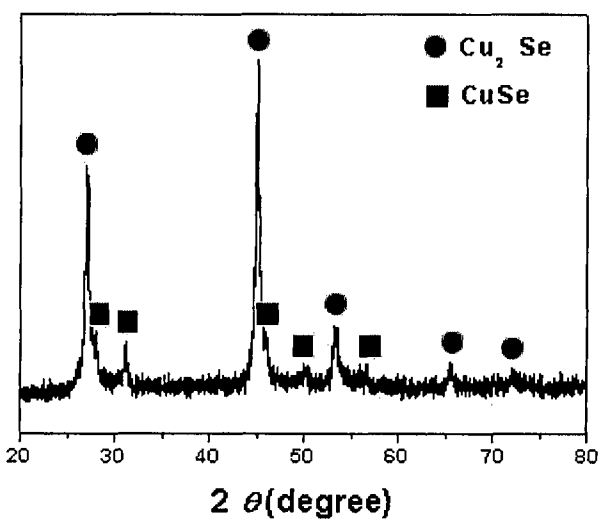




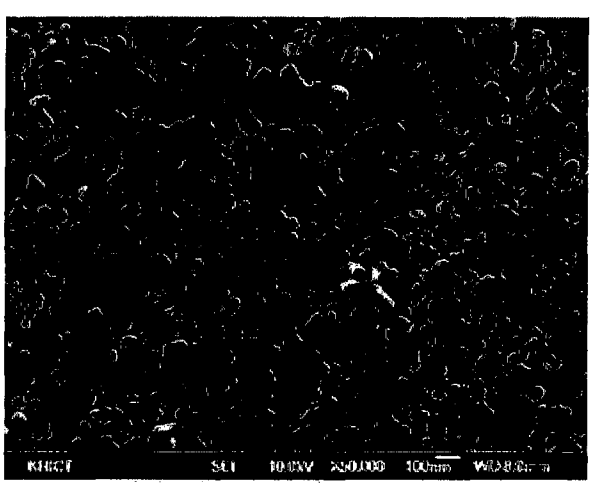
【Figure 9】



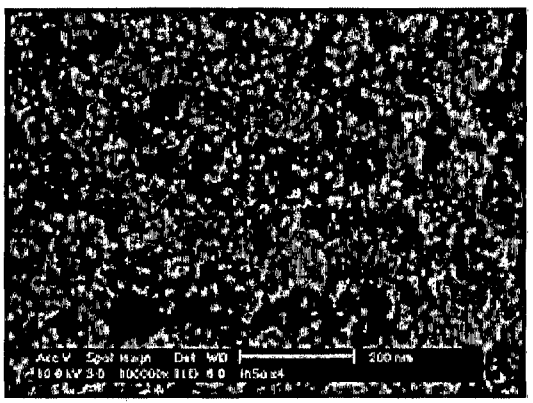
【Figure 10】



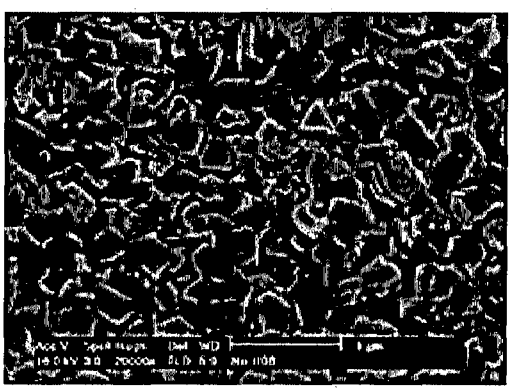
【Figure 11】



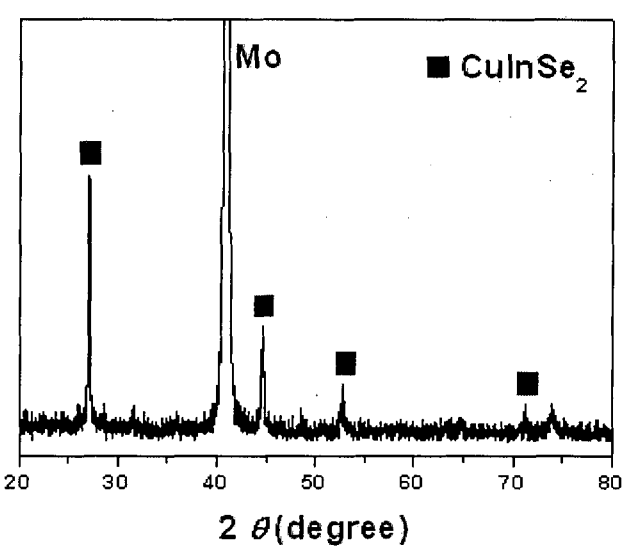
【Figure 12】



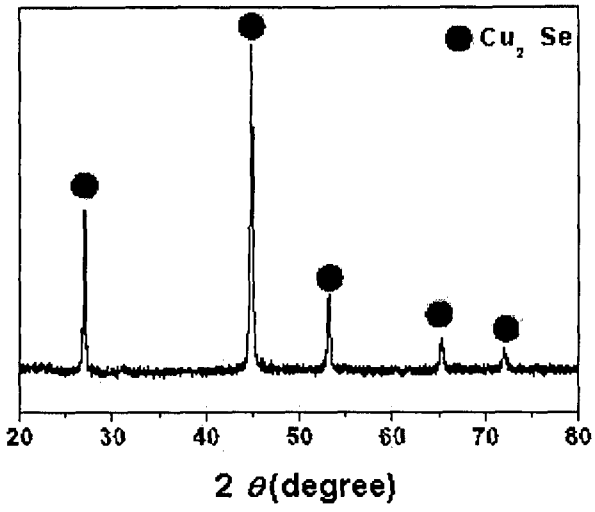
【Figure 13】



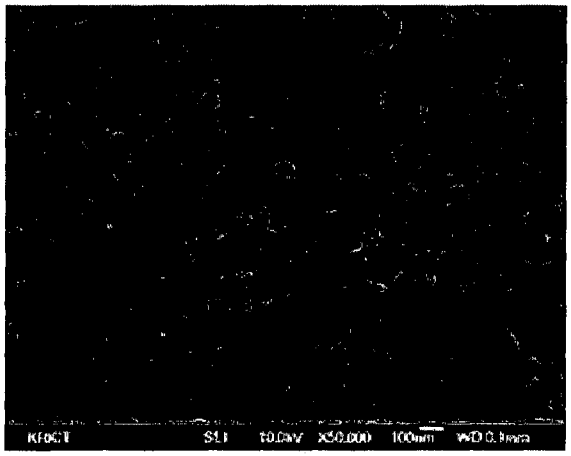
【Figure 14】



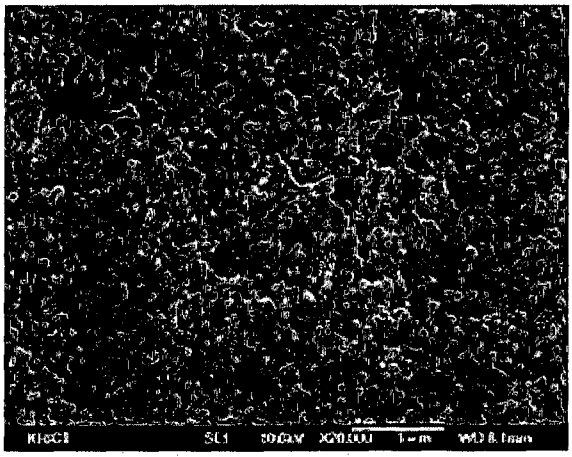
【Figure 15】



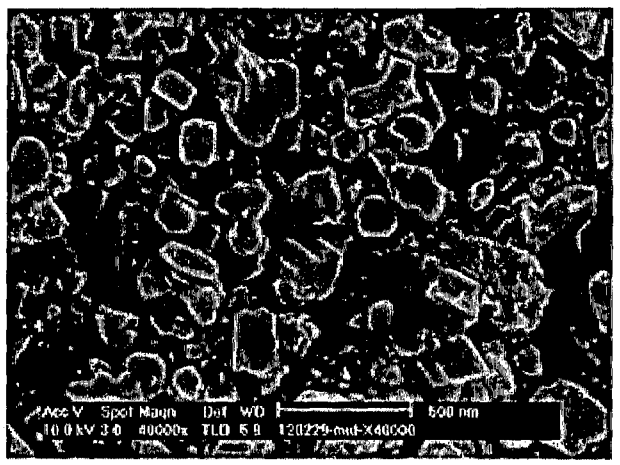
【Figure 16】



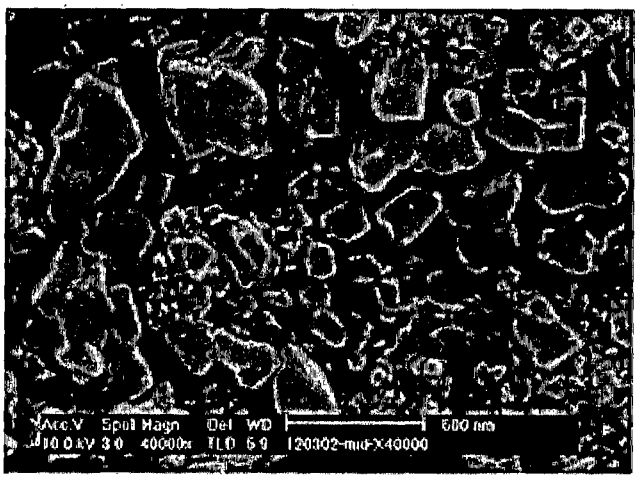
【Figure 17】



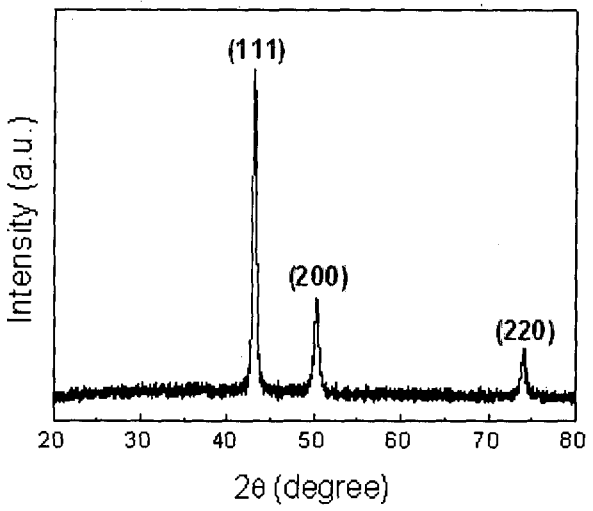
【Figure 18】



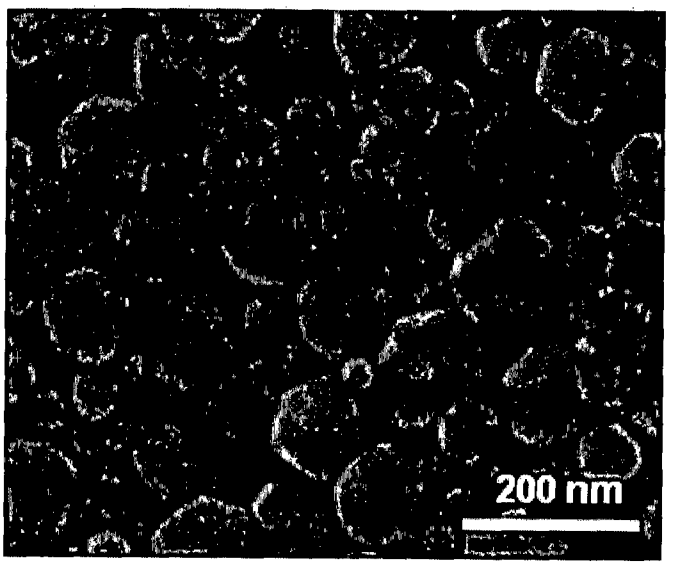
【Figure 19】



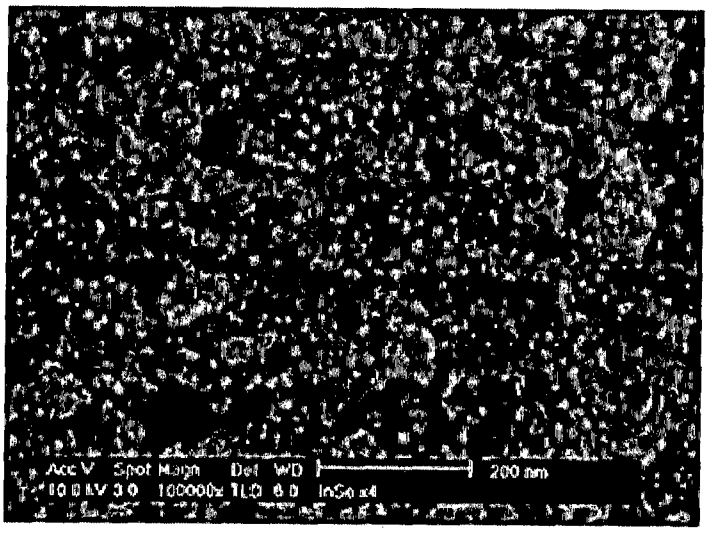
【Figure 20】



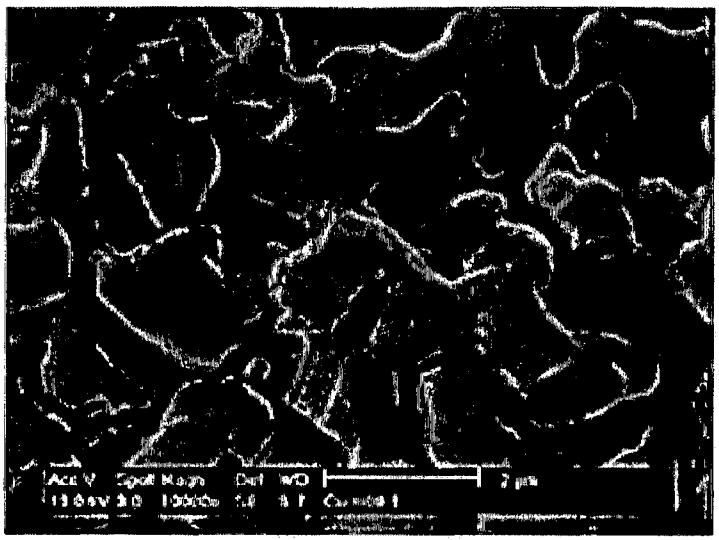
【Figure 21】



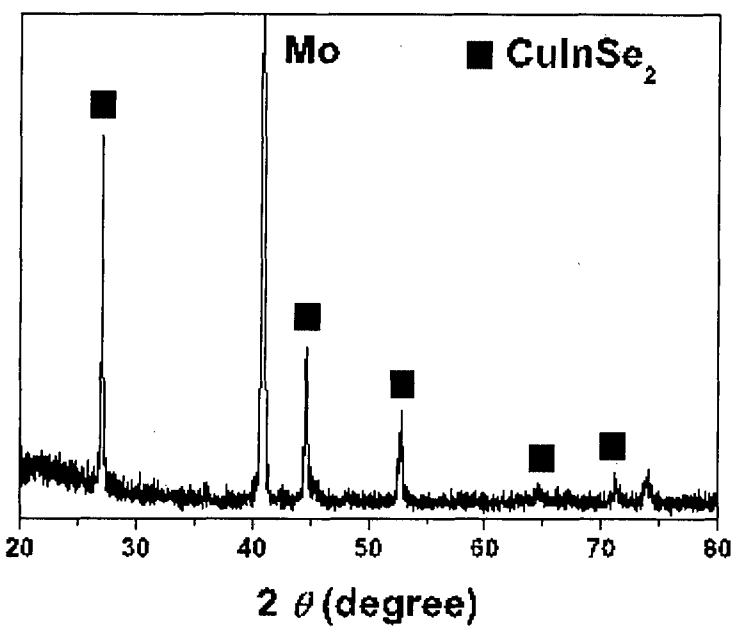
【Figure 22】



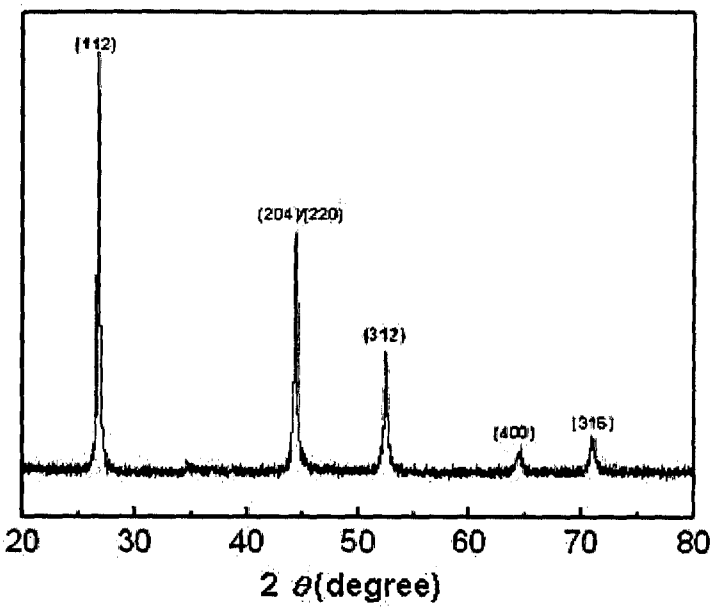
【Figure 23】



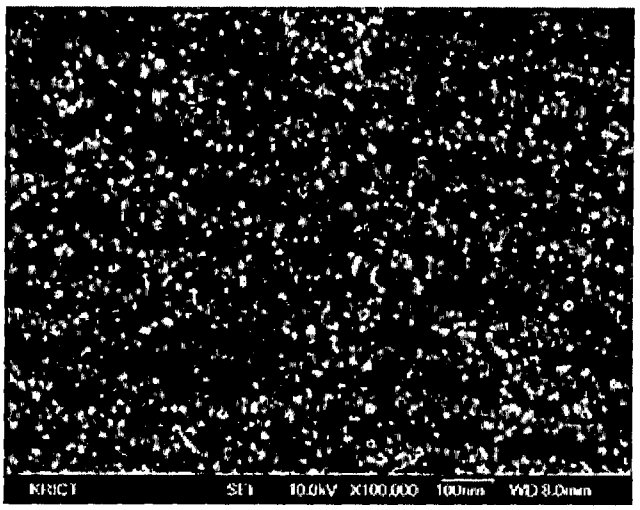
【Figure 24】



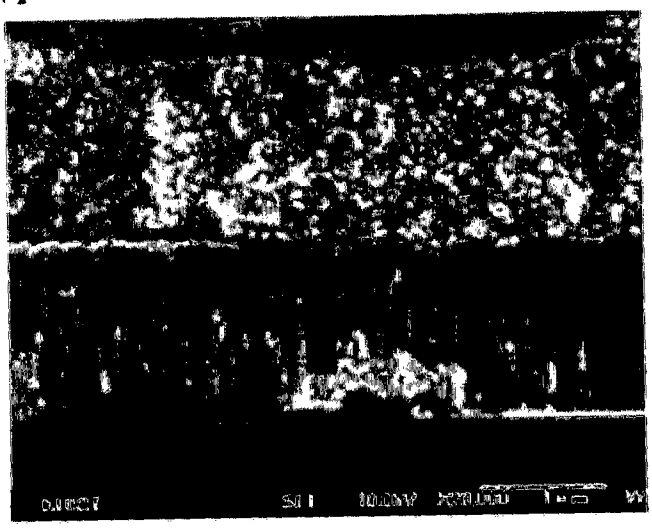
【Figure 25】



【Figure 26】



【Figure 27】



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2013/003063

A. CLASSIFICATION OF SUBJECT MATTER

C09D 11/00(2006.01)i, H01L 31/042(2006.01)i, H01B 1/22(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)
C09D 11/00; H01L 31/0272; C09D 1/00; H01L 31/042; H01B 1/22

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: ink, composite particle, metal chalcogenide, melting point, precursor, and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-1069576 B1 (KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY) 05 October 2011 See claims 1, 3, paras. 0003, 0031, and examples 1-6.	1-10,12-15
A		11,16-24
Y	KR 10-1066020 B1 (LG CHEM. LTD.) 20 September 2011 See claim 13 and example 1.	1-10,12-15
A		11,16-24
A	KR 10-2010-0034817 A (LG INNOTEK CO., LTD.) 02 April 2010 See claim 1 and paras. 0023, 0025.	1-24

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"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	Date of mailing of the international search report
31 July 2013 (31.07.2013)	**31 July 2013 (31.07.2013)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR2013/003063

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 10-1069576 B1	05/10/2011	None	
KR 10-1066020 B1	20/09/2011	None	
KR 10-2010-0034817 A	02/04/2010	None	