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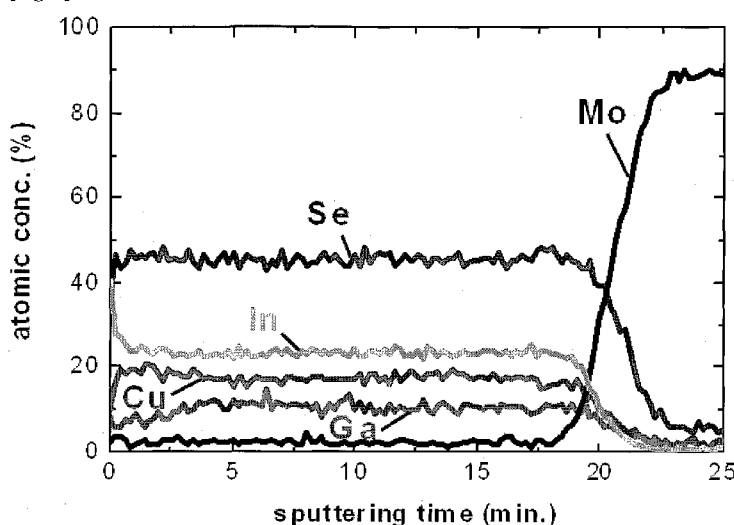
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[Continued on next page]

(54) Title: METHOD OF MANUFACTURING CIGS THIN FILM WITH UNIFORM Ga DISTRIBUTION

[Fig. 5]



(57) Abstract: A method of manufacturing a CIGS thin film with a uniform Ga distribution and a method of manufacturing a solar cell using the method are provided. The method of manufacturing a CIGS thin film with a uniform Ga distribution includes: (a) forming a Cu-In-Ga-Se precursor thin film comprising a seleni de-based compound having a covalently-bonded structure on a substrate; and (b) selenizing the precursor thin film formed in step (a). Accordingly, it is possible to uniformize the Ga distribution in a CIGS thin film and thus to enhance the efficiency of a solar cell having the CIGS thin film, by changing the sputtering precursor to a seleni de-based compound instead of pure metal or alloy to suppress the segregation of Ga in the thermal process in the Se atmosphere.



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【DESCRIPTION】**【Invention Title】**

METHOD OF MANUFACTURING CIGS THIN FILM WITH UNIFORM Ga DISTRIBUTION

【Technical Field】

<1> The present invention relates to a method of manufacturing a CIGS thin film, and more particularly, to a method of manufacturing a CIGS thin film with a uniform Ga distribution by changing the structure of a precursor thin film to a covalently-bonded structure to reduce a segregation phenomenon of Ga in the CIGS thin film.

【Background Art】

<2> Recently, development of next-generation clean energy has been increasingly important with exhaustion of fossil energy. A solar cell is a device that directly converts solar energy into electric energy, and is expected as an energy source capable of solving energy problems in the future because it causes little pollution, uses infinite resources, and is semi-permanently used.

<3> The solar cell is classified into various types depending on materials used as a light-absorbing layer. A silicon solar cell using silicon is presently used most widely. However, the cost of silicon rapidly increases with a short supply of silicon and thus attention is increasingly attracted to a thin-film solar cell. Since the thin-film solar cell is manufactured with a small thickness, the amount of material consumed is small and the weight is small, whereby the thin-film solar cell can be utilized in wide fields. Amorphous silicon, CdTe, CIS, and CIGS have been actively studied as the material of the thin-film solar cell.

<4> CIS or CIGS is one of I-III-VI compound semiconductors and exhibits the highest conversion efficiency out of thin-film solar cells experimentally manufactured. Particularly, since the CIS or CIGS thin film can be manufactured with a thickness of 10 micrometer or less and can be stably used for a long time, the CIS or CIGS thin film is expected as a material for a low-cost high-efficiency solar cell which can substitute silicon.

<5> Particularly, the CIS thin film is direct transition semiconductor and

is a material which can be formed with a small thickness, which has a band gap of 1.04 eV suitable for photoelectric conversion, and which has a high optical absorption coefficient. The CIGS thin film is a material obtained by substituting a part of In with Ga or substituting Se with S so as to improve the low open voltage of the CIS thin film.

<6> The method of manufacturing the CIGS film can be roughly classified into a vacuum vapor deposition method and a non-vacuum coating method. Specific examples of the vacuum vapor deposition method include a co-evaporation process, an in-line evaporation process, and a two-step process (precursor-reaction). Among these, the co-evaporation process is typically used to manufacture a high-efficiency CIGS thin film solar cell, but the process is complicated and it is difficult to increase the area, thereby making commercialization difficult. A two-step process of vapor deposition and selenization which can facilitate mass production has been developed as a method for solving this problem.

<7> However, an uneven composition may be caused due to a difference between the reaction rate of In and Se and the reaction rate of Ga and Se when performing heat treatment in the Se atmosphere of H_2Se gas or Se vapor after sputtering metal or alloy of Cu, In, and Ga. In other words, since In is segregated to the surface of the CIGS thin film and Ga is segregated to the interface of CIGS and Mo, the increase in band gap due to the addition of Ga and the improvement in open voltage cannot be achieved and there is a problem in that the efficiency of the solar cell decreases as the amount of Ga added increases.

【Disclosure】

【Technical Problem】

<8> The inventors made the invention by noting that the migration speed of Ga in selenide having a covalently-bonded structure is much lower than the migration speed of Ga in metal or alloy having a metal-bond structure. An object of the invention is to uniformize the Ga distribution in a CIGS thin film and thus to enhance the efficiency of a solar cell having the CIGS thin film, by changing the sputtering precursor to a selenide-based compound

instead of pure metal or alloy to suppress the segregation of Ga.

【Technical Solution】

<9> According to an aspect of the invention, there is provided a method of manufacturing a CIGS thin film with a uniform Ga distribution, comprising: (a) forming a Cu-In-Ga-Se precursor thin film comprising a selenide-based compound having a covalently-bonded structure on a substrate; and (b) selenizing the precursor thin film formed in step (a).

<10> In the method according to the aspect of the invention, the precursor thin film may be formed by deposition using a sputtering method.

<11> The sputtering method may be performed using one or more target combinations including selenium. Cu, In, Ga, and Se may be appropriately combined to sufficiently supply selenium in the precursor as one of 1) a combination of metal (Cu, In, Ga, and alloys thereof) and plural selenide compounds, 2) a combination of metal (Cu, In, Ga, and alloys thereof) and Se, and 3) a combination of selenide metal compounds. The targets may be combined such as a combination of Cu, InSe, and GaSe, a combination of CuGa, InSe, and CuSe, a combination of In, CuSe, and GaSe, a combination of Cu, In, CuGa, and Se, a combination of CuIn, CuGa, and Se, a combination of CuInGa and Se, a combination of CuSe, InSe, and GaSe, a combination of CuSe and InGaSe. Preferably, the target combination may be any one of a target combination of Cu-Se, In-Se, and Ga-Se, a target combination of Cu-Se, In-Se, and Cu-Ga, a target combination of Cu, In-Se, and Ga-Se, a target combination of Cu-Se, In, and Cu-Ga, and a target combination of Cu-In-Se and Cu-Ga. More preferably, a target combination of CuSe, In, and CuGa or a target combination of CuSe, In_2Se_3 , and CuGa can be used.

<12> The term "element-element" described in this specification is defined to include all compounds which can be formed by the respective elements. For example, "Cu-Se" is defined to include all compounds such as CuSe, Cu_2Se_3 , Cu_2Se , Cu_3Se_2 , and Cu_{2-x}Se ($x=0$ to 1) which can be stoichiometrically formed by Cu and Se.

<13> The sputtering method may be performed by co-sputtering or sequentially

at time intervals using the target combination. Known methods can be employed as the sputtering method and specific conditions thereof is not particularly limited but can be appropriately selected depending on the types of targets.

<14> The atomic ratio of Se ($\text{Se}/(\text{Cu}+\text{In}+\text{Ga})$) in the precursor thin film is preferably in the range of 0.3 to 1.0 and more preferably in the range of 0.8 to 1.0. Within this range, the amount of Se is sufficient to form the CIGS precursor thin film, the segregation of Ga is reduced, and most Ga in the precursor forms Ga-Se covalent bond to markedly lower the migration speed of Ga. Accordingly, it is possible to achieve a uniform distribution of Ga.

<15> The selenizing may be performed in a Se atmosphere of Se vapor or H_2Se gas. The selenizing is preferably performed in a state where the temperature of the substrate is in the range of 400° C to 530° C. The selenizing is preferably performed for 10 minutes to 60 minutes. The temperature range and the time range are generally optimized for selenization.

【Advantageous Effects】

<17> According to the invention, it is possible to uniformize the Ga distribution in a CIGS thin film and thus to enhance the efficiency of a solar cell having the CIGS thin film, by changing the sputtering precursor in the two-step process of vapor deposition and selenization to a selenide-based compound instead of pure metal or alloy to markedly lower the migration speed of Ga during the thermal process in the Se atmosphere and to suppress the segregation of Ga.

【Description of Drawings】

<18> Fig. 1 is a SEM image showing a cross-sectional structure of a CIGS thin film according to Example 1 of the invention.

<19> Fig. 2 is a graph illustrating the AES depth profile of the CIGS thin film according to Example 1 of the invention.

<20> Fig. 3 is a graph illustrating the output characteristic of a solar cell having the CIGS thin film according to Example 1 of the invention.

<21> Fig. 4 is a SEM image showing a cross-sectional structure of a CIGS thin film according to Example 2 of the invention.

<22> Fig. 5 is a graph illustrating the AES depth profile of the CIGS thin film according to Example 2 of the invention.

<23> Fig. 6 is a graph illustrating the output characteristic of a solar cell having the CIGS thin film according to Example 2 of the invention.

<24> Fig. 7 is a SEM image showing a cross-sectional structure of a CIGS thin film according to a comparative example of the invention.

<25> Fig. 8 is a graph illustrating the AES depth profile of the CIGS thin film according to the comparative example of the invention.

<26> Fig. 9 is a graph illustrating the output characteristic of a solar cell having the CIGS thin film according to the comparative example of the invention.

【Mode for Invention】

<27> Hereinafter, exemplary embodiments of the invention will be described in detail with reference to the accompanying drawings. The embodiments can be modified in various forms and the scope of the invention is not limited to

the embodiments. The embodiments are intended to provide complete description for those skilled in the art.

<28> A method of manufacturing a CIGS thin film with a uniform Ga distribution and a solar cell manufacturing method using the method will be first described, and manufacturing methods according to examples of the invention will be then described and will be compared with a comparative example with a non-uniform Ga distribution.

<29> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to the invention basically includes a two-step process of formation of a precursor thin film and selenization.

<30> The first step is a step of forming a selenide-based precursor thin film having a covalently-bonded structure comprising selenium (Se).

<31> The step of forming a precursor thin film comprising selenium can be performed using a sputtering method. Various target combinations of the sputtering method can be used within the technical scope of the invention.

<32> The second step is a step of selenizing the precursor thin film formed in the first step.

<33> Exemplary examples of the invention will be described below in detail.

<34>

<35> Example 1

<36> A molybdenum (Mo) rear electrode was deposited on a soda lime glass substrate with a thickness of about 1 μm through the use of a DC sputtering method.

<37> Thereafter, three targets of CuSe, In, and CuGa were prepared and were simultaneously used to sputter a precursor thin film on the substrate. At this time, the sputtering power was adjusted so as to satisfy $\text{Cu}/(\text{In}+\text{Ga})=0.75$ to 0.9 and $\text{Ga}/(\text{In}+\text{Ga})=0.3$ to 0.4.

<38> The atomic ratio of Se in the precursor thin film, that is, the value of $\text{Se}/(\text{Cu}+\text{In}+\text{Ga})$, was set to 0.3.

<39> Selenization using Se vapor was performed at a substrate temperature of 530°C for 45 minutes.

<40> The thin film formed according to Example 1 and the characteristics of

the solar cell having the thin film are shown in Figs. 1 to 3.

<41> Fig. 1 is a SEM image showing a cross-sectional structure of the CIGS thin film formed according to Example 1 of the invention. Fig. 2 is a graph illustrating the AES depth profile of the CIGS thin film formed according to Example 1 of the invention. Fig. 3 is a graph illustrating the output characteristic of a solar cell having the CIGS thin film formed according to Example 1 of the invention. Here, Voc represents an open voltage, Isc represents a short-circuit current, FF represents a fill factor, and Eff represents the efficiency of the solar cell.

<42> Referring to Figs. 1 to 3, the thickness of the Mo rear electrode in the CIGS thin film formed according to Example 1 of the invention was 1.22 μm and the thickness of the CIGS thin film was 1.42 μm .

<43> The distributions of elements with the depth from the surface of the CIGS thin film are the same as shown in the graph of Fig. 2. The output characteristics of the solar cell having the CIGS thin film formed according to Example 1 of the invention are the same as shown in Fig. 3 and, particularly, the efficiency of the solar cell was 8.36%.

<44> The characteristics of the CIGS thin film according to Example 1 and the output characteristics of the solar cell having the CIGS thin film will be compared later with those of a CIGS thin film according to a comparative example in which a precursor thin film is formed of pure metal or alloy instead of the selenide-based materials.

<45>

<46> Example 2

<47> A molybdenum (Mo) rear electrode was deposited on a soda lime glass substrate with a thickness of about 1 μm through the use of a DC sputtering method.

<48> Thereafter, three targets of CuSe, In_2Se_3 , and CuGa were prepared and were simultaneously used to sputter a precursor thin film on the substrate. At this time, the sputtering power was adjusted so as to satisfy $\text{Cu}/(\text{In}+\text{Ga})=0.75$ to 0.9 and $\text{Ga}/(\text{In}+\text{Ga})=0.3$ to 0.4.

<49> The atomic ratio of Se in the precursor thin film, that is, the value

of Se/(Cu+In+Ga), was set to 0.8.

<50> Selenization using Se vapor was performed at a substrate temperature of 530°C for 45 minutes.

<51> The thin film formed according to Example 2 and the characteristics of the solar cell having the thin film are shown in Figs. 4 to 6.

<52> Fig. 4 is a SEM image showing a cross-sectional structure of the CIGS thin film formed according to Example 2 of the invention. Fig. 5 is a graph illustrating the AES depth profile of the CIGS thin film formed according to Example 2 of the invention. Fig. 6 is a graph illustrating the output characteristic of a solar cell having the CIGS thin film formed according to Example 2 of the invention.

<53> Referring to Figs. 4 to 6, the thickness of the Mo rear electrode in the CIGS thin film formed according to Example 2 of the invention was 1.15 μm and the thickness of the CIGS thin film was 670 nm.

<54> The distributions of elements with the depth from the surface of the CIGS thin film are the same as shown in the graph of Fig. 5. The output characteristics of the solar cell having the CIGS thin film formed according to Example 2 of the invention are the same as shown in Fig. 6 and, particularly, the efficiency of the solar cell was 13%.

<55> The characteristics of the CIGS thin film according to Example 2 and the output characteristics of the solar cell having the CIGS thin film will be compared later with those of a CIGS thin film according to a comparative example in which a precursor thin film is formed of pure metal or alloy instead of the selenide-based materials and will be described along with those of Example 1.

<56>

<57> Comparative Example

<58> A molybdenum (Mo) rear electrode was deposited on a soda lime glass substrate with a thickness of about 1 μm through the use of a DC sputtering method.

<59> Thereafter, three targets comprising CuGa, CuIn, and Cu but not comprising Se were prepared and were simultaneously used to sputter a

precursor thin film on the substrate. At this time, the sputtering power was adjusted so as to satisfy $\text{Cu}/(\text{In}+\text{Ga})=0.75$ to 0.9 and $\text{Ga}/(\text{In}+\text{Ga})=0.3$ to 0.4 .

<60> Selenization using Se vapor was performed at a substrate temperature of 530°C for 45 minutes.

<61> The thin film formed according to the comparative example and the characteristics of the solar cell having the thin film are shown in Figs. 7 to 9.

<62> Fig. 7 is a SEM image showing a cross-sectional structure of the CIGS thin film formed according to the comparative example of the invention. Fig. 8 is a graph illustrating the AES depth profile of the CIGS thin film formed according to the comparative example of the invention. Fig. 9 is a graph illustrating the output characteristic of a solar cell having the CIGS thin film formed according to the comparative example of the invention.

<63> Referring to Figs. 7 to 9, the thickness of the Mo rear electrode in the CIGS thin film formed according to the comparative example of the invention was $1.24\ \mu\text{m}$ and the thickness of the CIGS thin film was $2.22\ \mu\text{m}$.

<64> The distributions of elements with the depth from the surface of the CIGS thin film are the same as shown in the graph of Fig. 8. The output characteristics of the solar cell having the CIGS thin film formed according to the comparative example of the invention are the same as shown in Fig. 9 and, particularly, the efficiency of the solar cell was 4.46%.

<65>

<66> Comparison of Element Distribution Characteristics with Depth from Surface of CIGS Thin Film

<67> Referring to Figs. 2, 5, and 8, as it gets closer to the interface of the Mo rear electrode, it can be seen that the Ga ratio in the comparative example shown in Fig. 8 becomes markedly higher than that in Example 1 shown in Fig. 2 or Example 2 shown in Fig. 5 and the segregation phenomenon is more prominent.

<68> On the contrary, it can be seen that the segregation of Ga to the interface of the Mo rear electrode in Example 1 is slightly reduced in comparison with the comparative example and the segregation of Ga in Example

2 almost disappears and Ga is uniformly distributed regardless of the depth of the CIGS thin film.

<69> In addition, it can be seen that the segregation of In to the surface in the comparative example is prominent as well as the Ga distribution, but the segregation in Example 1 is reduced and In is uniformly distributed in the overall CIGS thin film in Example 2.

<70> When the precursor thin film is formed of pure alloy having a metal-bonded structure, Ga easily migrates in the selenization. However, when the precursor thin film is formed of a selenide-based material having a covalently-bonded structure as in Examples 1 and 2 of the invention, it can be considered that the migration speed of Ga is relatively lowered or Ga hardly migrates.

<71> In Example 2, the segregation of Ga is better suppressed, that is, the uniformization is more effectively achieved, than in Example 1. From this result, it is thought that the segregation of Ga becomes more uniform as the ratio of Se in the precursor thin film becomes higher.

<72>

<73> Comparison of Output Characteristics of Solar Cells having CIGS Thin Film

<74> Referring to Figs. 3, 6, and 9, it can be seen that the solar cells having the CIGS thin films manufactured according to Examples 1 and 2 have a higher output and thus have a higher energy conversion efficiency than in the solar cell having the CIGS thin film manufactured according to the comparative example.

<75> This result reports that as Ga is more uniformly distributed without the segregation depending on the depth in the CIGS thin film, the energy conversion efficiency of a solar cell becomes higher.

<76> The energy efficiency, which is 13%, in Example 2 is much higher than that in Example 1. This proves that as the ratio of Se in the precursor thin film before completing the CIGS thin film through the selenization becomes higher to raise the ratio of the covalent bonds, the migration of Ga is further suppressed and Ga is thus distributed more uniform, whereby it is

possible to raise the energy efficiency of the solar cell having the CIGS thin film.

<77> While the invention has been described in detail with reference to the exemplary examples, the invention is not limited to the examples, but can be modified in various forms by those skilled in the art without departing from the technical concept of the invention.

【CLAIMS】**【Claim 1】**

<79> A method of manufacturing a CIGS thin film with a uniform Ga distribution, comprising:

<80> (a) forming a Cu-In-Ga-Se precursor thin film comprising a selenide-based compound having a covalently-bonded structure on a substrate; and

<81> (b) selenizing the precursor thin film formed in step (a).

【Claim 2】

<82> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 1, wherein the precursor thin film is formed by deposition using a sputtering method.

【Claim 3】

<83> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 2, wherein the sputtering method may be performed using one or more target combinations including selenium.

【Claim 4】

<84> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 3, wherein the target combination is any one of a target combination of Cu-Se, In-Se, and Ga-Se, a target combination of Cu-Se, In-Se, and Cu-Ga, a target combination of Cu, In-Se, and Ga-Se, a target combination of Cu-Se, In, and Cu-Ga, and a target combination of Cu-In-Se and Cu-Ga.

【Claim 5】

<85> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 3, wherein the sputtering method is performed by co-sputtering or sequentially at time intervals using the target combination.

【Claim 6】

<86> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 1, wherein the selenizing is performed in a Se atmosphere of Se vapor or H₂Se gas.

【Claim 7】

<87> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 6, wherein the selenizing is performed in a state where the temperature of the substrate is in the range of 400°C to 530 °C.

【Claim 8】

<88> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 6, wherein the selenizing is performed for 10 minutes to 60 minutes.

【Claim 9】

<89> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 1, wherein the atomic ratio of Se (Se/(Cu+In+Ga)) in the precursor thin film is in the range of 0.3 to 1.0.

【Claim 10】

<90> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 1, wherein the atomic ratio of Se (Se/(Cu+In+Ga)) in the precursor thin film is in the range of 0.8 to 1.0.

【Claim 11】

<91> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 3, wherein targets of CuSe, In, and CuGa are used as the target combination.

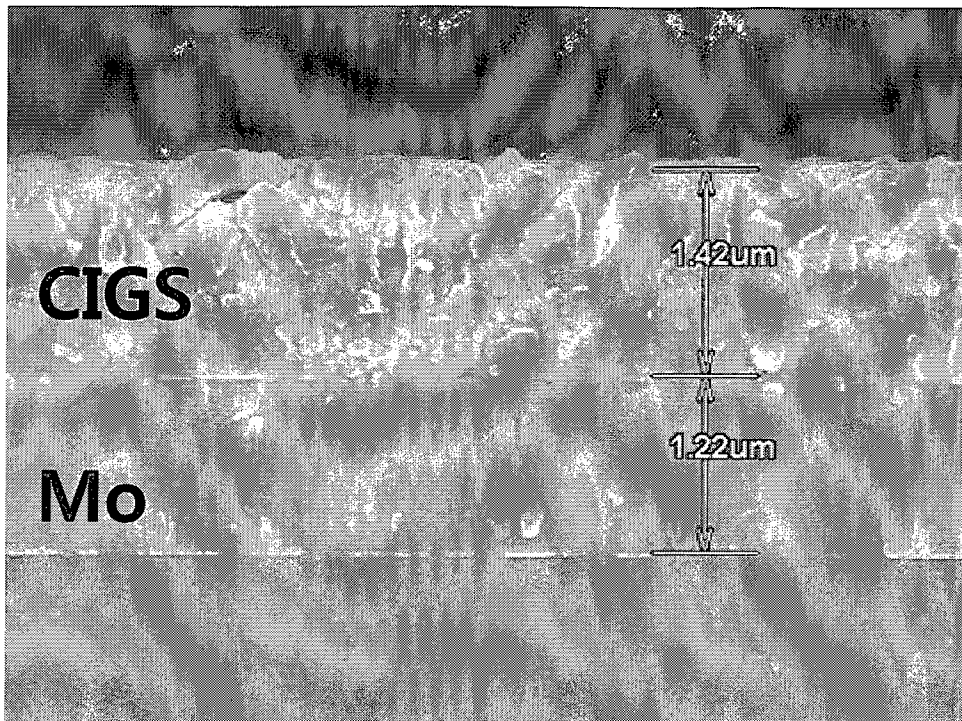
【Claim 12】

<92> The method of manufacturing a CIGS thin film with a uniform Ga distribution according to claim 3, wherein targets of CuSe, In₂Se₃, and CuGa are used as the target combination.

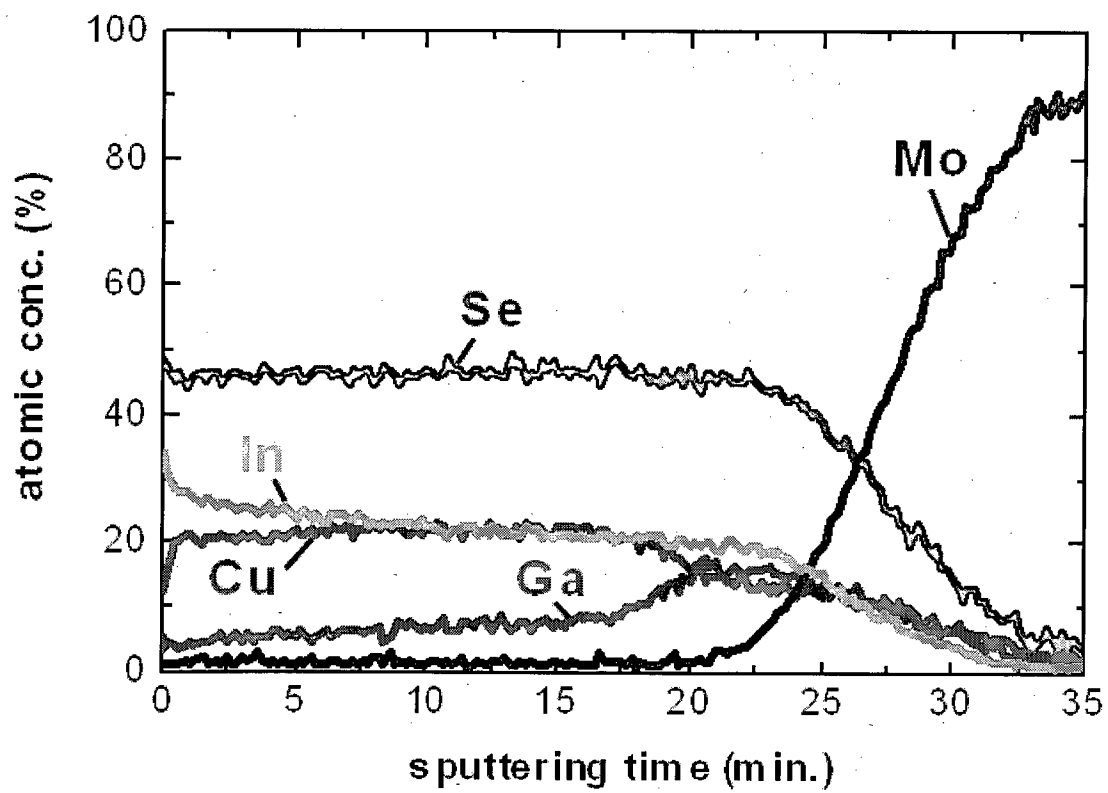
【Claim 13】

<93> A CIGS thin film with a uniform Ga distribution which is manufactured using the method according to any one of claims 1 to 12.

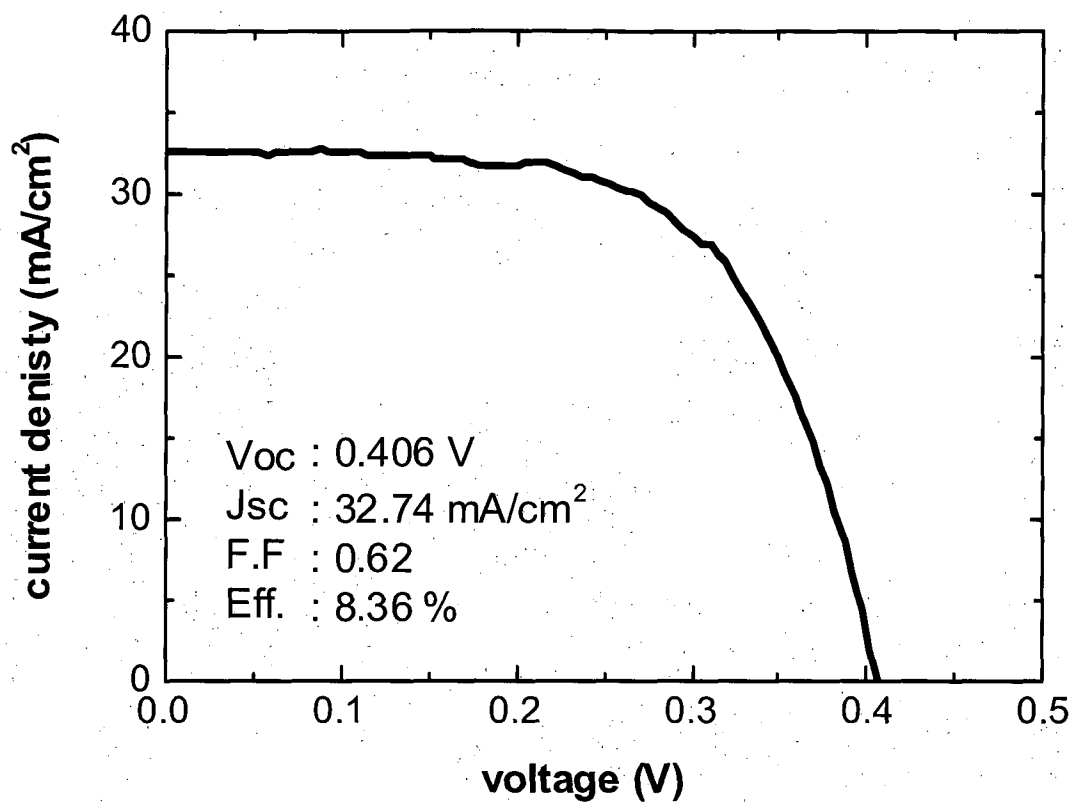
[Fig. 1]



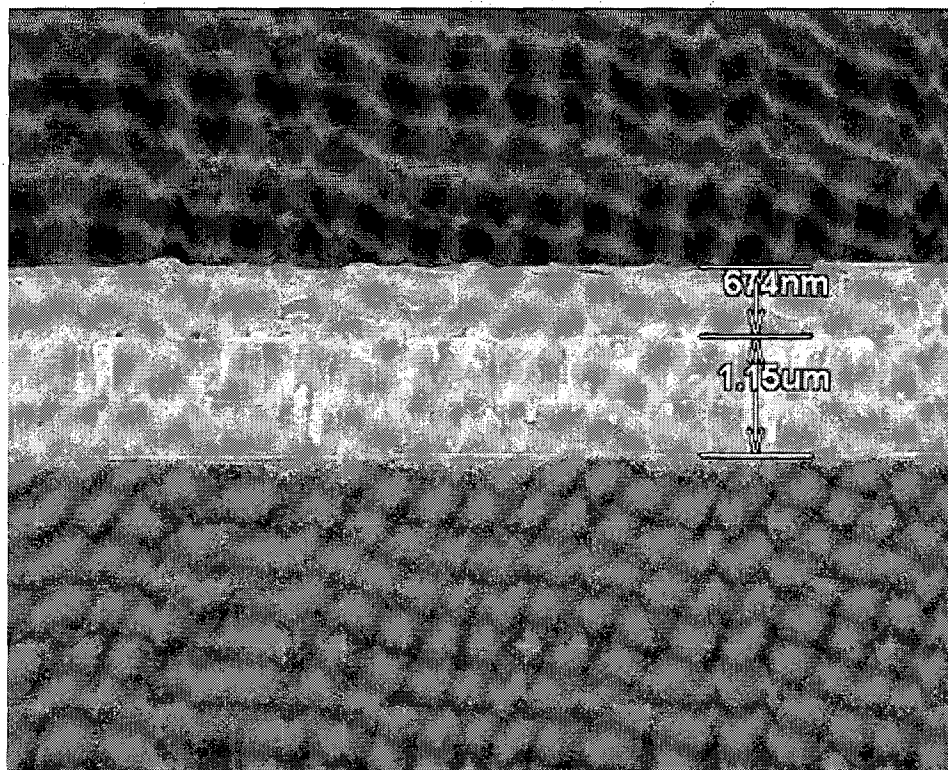
[Fig. 2]



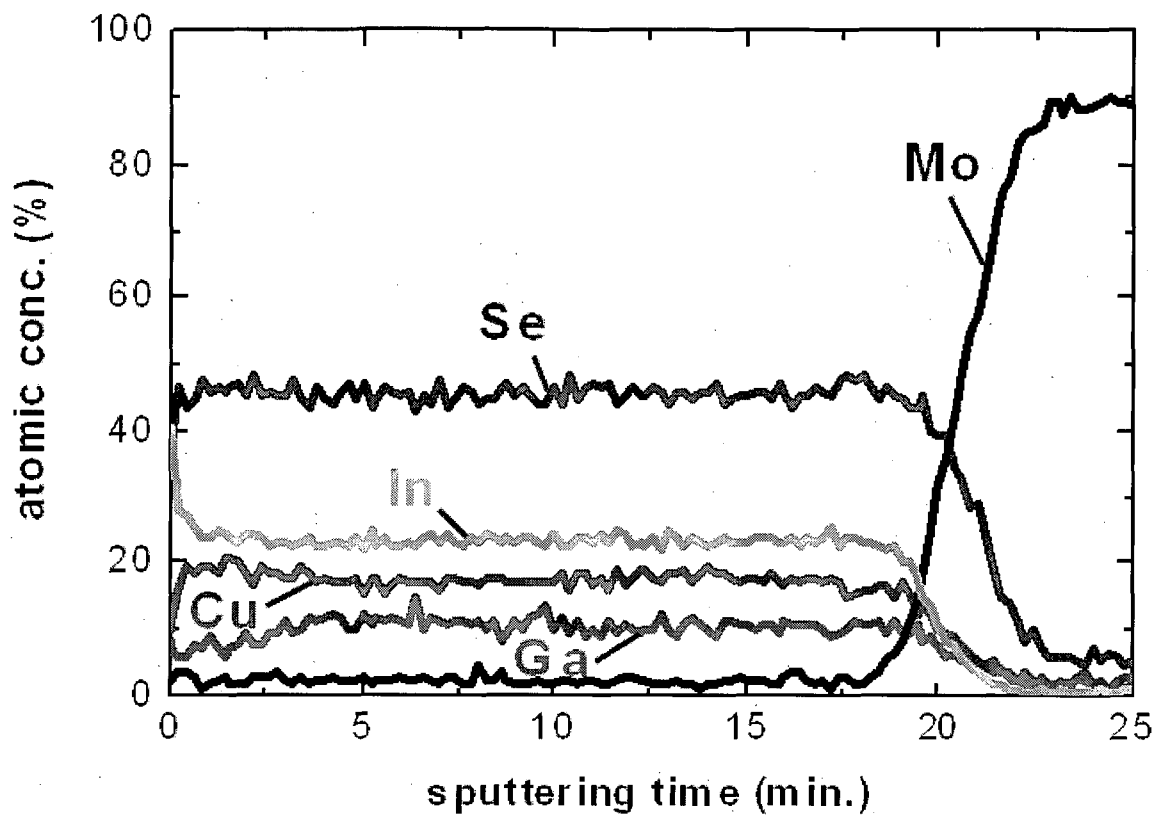
[Fig. 3]



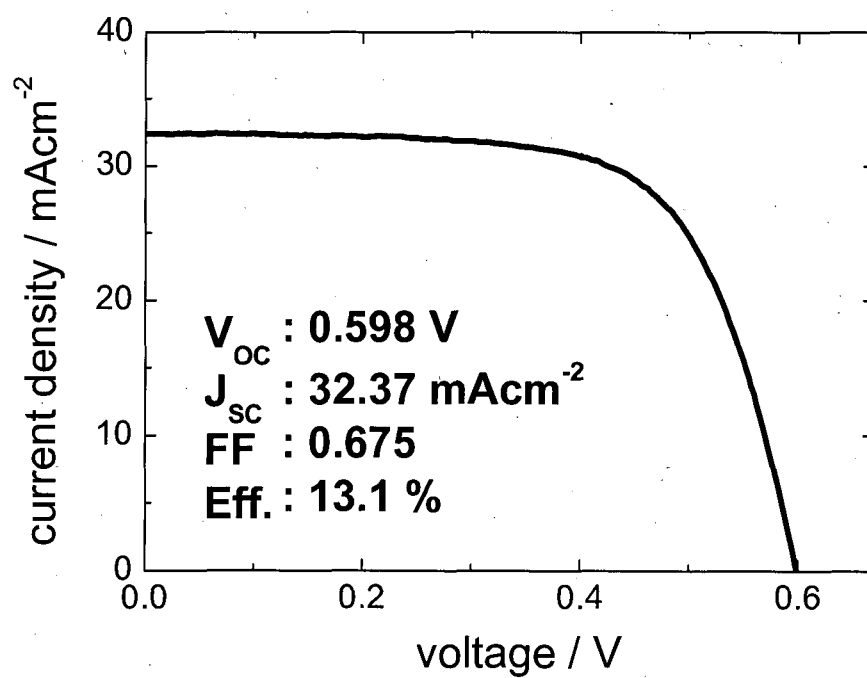
[Fig. 4]



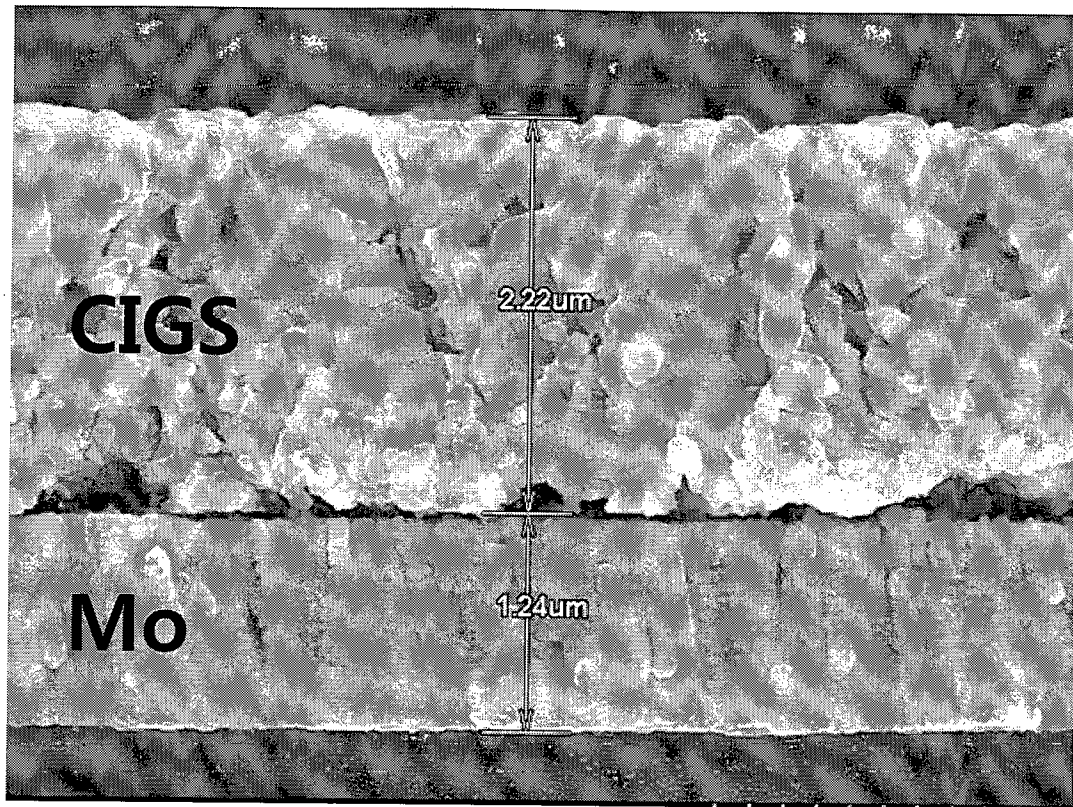
[Fig. 5]



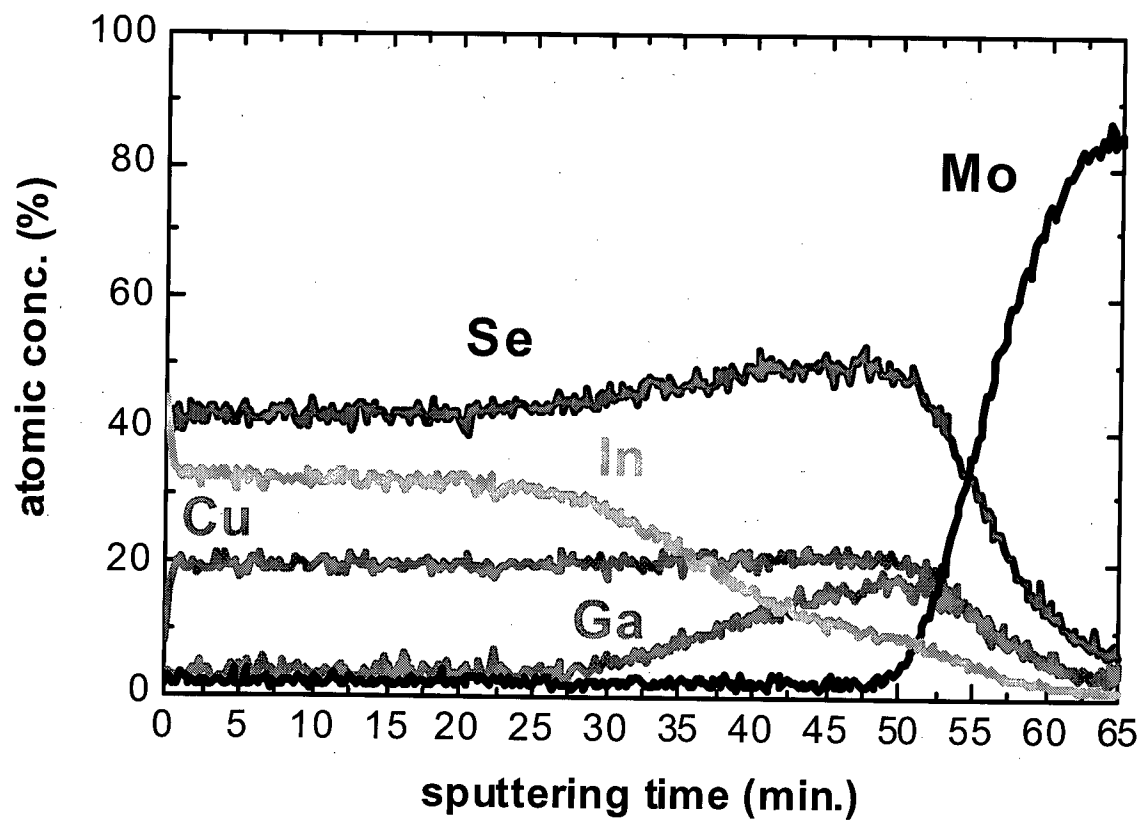
[Fig. 6]



[Fig. 7]



[Fig. 8]



[Fig. 9]

