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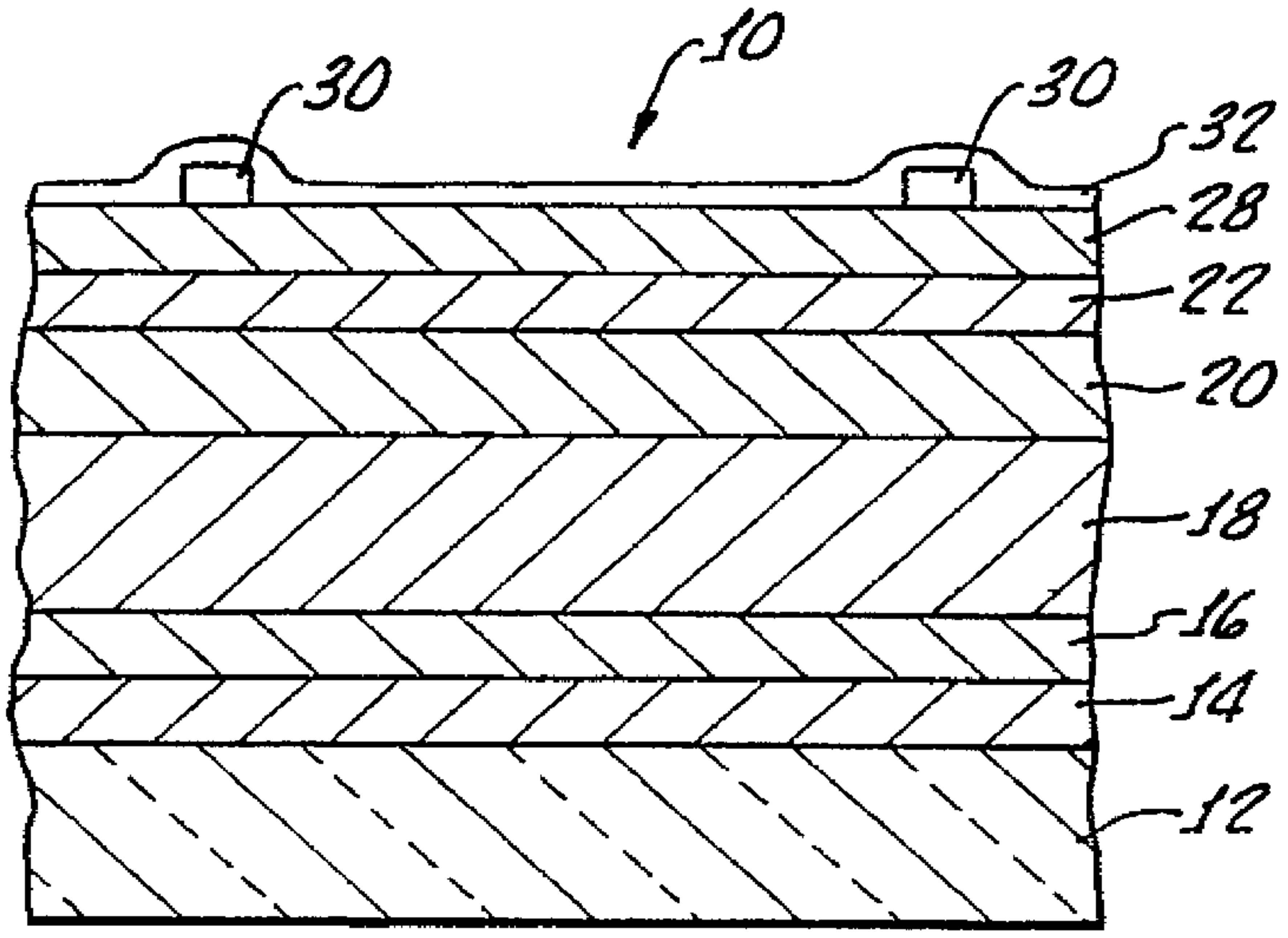
(54) Titre : ELABORATION DE PELLICULE-PRECURSEURS EN $Cu_xIn_yGa_zSe_n$ (X=0-2, Y=0-2, Z=0-2, N=0-3) PAR GALVANOSPLASTIE POUR LA FABRICATION DE CELLULES SOLAIRES A HAUT RENDEMENT

(54) Title: PREPARATION OF $Cu_xIn_yGa_zSe_n$ (X=0-2, Y=0-2, Z=0-2, N=0-3) PRECURSOR FILMS BY ELECTRODEPOSITION FOR FABRICATING HIGH EFFICIENCY SOLAR CELLS



(57) Abrégé/Abstract:

High quality thin films of copper-indium-gallium-diselenide useful in the production of solar cells are prepared by electrodepositing at least one of the constituent metals (18) onto a glass/Mo substrate (12, 14), followed by physical vapor deposition (20) of copper and selenium or indium and selenium to adjust the final stoichiometry of the thin film to approximately $Cu(In,Ga)Se_2$. Using an AC voltage of 1-100 KHz in combination with a DC voltage for electrodeposition improves the morphology and growth rate of the deposited thin film. An electrodeposition solution comprising at least in part an organic solvent may be used in conjunction with an increased cathodic potential to increase the gallium content of the electrodeposited thin film.

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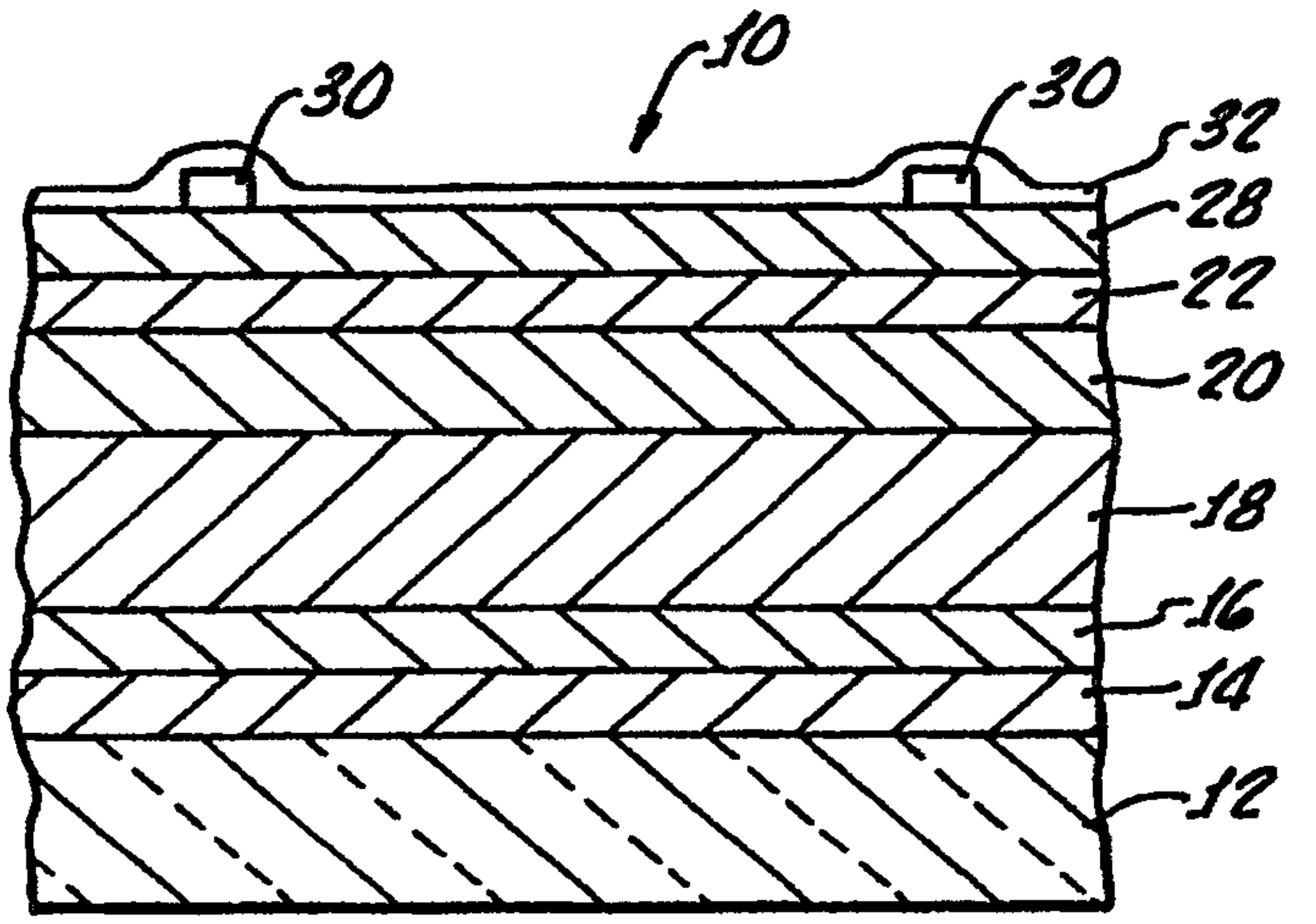
(57) Abstract

High quality thin films of copper-indium-gallium-diselenide useful in the production of solar cells are prepared by electrodepositing at least one of the constituent metals (18) onto a glass/Mo substrate (12, 14), followed by physical vapor deposition (20) of copper and selenium or indium and selenium to adjust the final stoichiometry of the thin film to approximately $Cu(In,Ga)Se_2$. Using an AC voltage of 1-100 KHz in combination with a DC voltage for electrodeposition improves the morphology and growth rate of the deposited thin film. An electrodeposition solution comprising at least in part an organic solvent may be used in conjunction with an increased cathodic potential to increase the gallium content of the electrodeposited thin film.



PREPARATION OF $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3) PRECURSOR FILMS BY ELECTRODEPOSITION FOR FABRICATING HIGH EFFICIENCY SOLAR CELLS

The government has rights in this invention pursuant to National Renewable Energy Laboratory (NREL) contract No. 1326.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The field of the present invention relates to the preparation of thin film semiconductor devices. More particularly, the present invention relates to electrodeposition of copper-indium-gallium-selenide films for solar cells.

2. Description of the Related Art

Chalcopyrite ternary thin films of copper-indium-diselenide ($CuInSe_2$) and copper-indium-gallium-diselenide ($CuIn_{1-x}Ga_xSe_2$), both of which are generically referred to as $Cu(In,Ga)Se_2$, CIGS, or simply CIS, have become the subject of considerable interest and study for semiconductor devices in recent years. Sulphur can also be, and sometimes is, substituted for selenium, so the compound is sometimes also referred to even more generically as $Cu(In,Ga)(Se,S)_2$ so as to encompass all of these possible combinations. These devices are also referred to as I-III-VI_2 devices according to their constituent elemental groups.

These devices are of particular interest for photovoltaic device or solar cell absorber applications. For photovoltaic applications, the p-type CIGS layer is combined with an n-type CdS layer to form a p-n heterojunction CdS/CIGS device. The direct energy gap of CIGS results in a large optical absorption coefficient, which in turn permits the use of thin layers on the order of 1-2 μm. An additional advantage of CIGS devices is their long-term stability.

Various methods have been reported for fabricating CIGS thin films. Some of the earliest techniques involved heating copper and indium on a substrate in the presence of a selenium-containing gas, including H_2Se. The heating of copper and indium films in the presence of a selenium-containing gas is known as selenization. One drawback to selenizing with H_2Se is that H_2Se gas is highly toxic, thus presenting serious hazards to humans in large scale production environments.

In U.S. Patent No. 5,045,409, Eberspacher et al. disclose depositing copper and indium films by magnetron sputtering, and depositing a selenium film by thermal evaporation, followed by heating in the presence of various gases. Other methods for producing CIS films have included Molecular Beam Epitaxy, electrodeposition either in single or multiple steps, and vapor deposition of single crystal and polycrystalline films.

Although vapor deposition techniques have been used to yield solar cells with efficiencies as high as seventeen percent (17%), vapor deposition is costly. Accordingly, solar cells made by vapor deposition have generally been limited to devices for laboratory experimentation, and are not suitable for large scale production. On the other hand, thin film solar cells made by electrodeposition techniques are generally much less expensive. However, solar cells produced by electrodeposition generally suffer from low efficiencies. For example, in *Solar Cells with Improved Efficiency Based on Electrodeposited Copper Indium Diselenide Thin Films*, ADVANCED MATERIALS, Vol. 6 No. 5 (1994), Guillemoles et al. report solar cells prepared by electrodeposition with efficiencies on the order of 5.6%.

SUMMARY OF THE INVENTION

Accordingly, it is a general object of this invention to provide an improved process for fabricating high quality thin film $Cu(In,Ga)Se_2$ solar cells.

It is also an object of this invention to provide low cost, high quality thin film solar cells having high conversion efficiencies.

It is a further object of this invention to provide a process for producing Cu-In, Cu-Se, Cu-In-Se, and Cu-In-Ga-Se metallic thin films that have applications in solar and non-solar cells.

It is a still further object of this invention to provide a process for electrodepositing a gallium-containing metallic thin-film solar cell precursor.

To achieve the forgoing and other objects and advantages in accordance with the purpose of the present invention, as embodied and broadly described herein, the process of this invention includes electrodepositing a layer of $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3), preferably using direct current in combination with alternating current, followed by vapor depositing additional copper and selenium or indium and selenium to adjust the final composition very close to stoichiometric $Cu(In,Ga)Se_2$. This unique two-step film deposition process allows precursor metal films to be deposited by inexpensive electrodeposition, and then adjusted using the more expensive but more precise technique of physical vapor deposition to bring the final film into the desire stoichiometric range. Solar cells may then be completed as for example by chemical bath deposition (CBD) of CdS followed by sputtering of ZnO, and addition of bi-layer metal contacts as well as optional anti-reflective coating. A solar cell made according to the present process has exhibited a device efficiency of 9.44%.

In accordance with one aspect of the invention there is provided a process for preparing a metal-containing thin film, the process including the step of electrodepositing a layer of $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3) on a substrate, the electrodeposition proceeding at a DC voltage of approximately 1-10 V and an AC voltage of approximately 0.2-5.0 V at 1-100 KHz superimposed upon the DC voltage. The process also includes the step of depositing a sufficient amount of either In+Se or Cu+Se on the layer of $Cu_xIn_yGa_zSe_n$ by vapor deposition to produce a thin film of $Cu(In,Ga)Se_2$ on the substrate wherein the thin film has stoichiometric ratios of approximately Cu= 1-1.2 (In,Ga) = 1-1.2: Se = 2-2.5.

In accordance with another aspect of the invention there is provided a solar cell including: a metal-containing thin film prepared according to the process of claim 1, the solar cell producing an electrical potential when exposed to light and an electrical circuit utilizing the electric potential of the solar cell.

In accordance with another aspect of the invention there is provided a process for electrodepositing a solar cell precursor thin film, the process including the steps of: electrodepositing a thin film containing copper, indium, gallium, and selenium onto a substrate, the electrodeposition proceeding in an electrodeposition solution including copper, indium, gallium, and selenium ions.

In accordance with another aspect of the invention there is provided a process for preparing a solar cell precursor thin film, the process including the steps of: electrodepositing a metallic precursor thin film onto a substrate using a DC voltage in combination with an AC voltage of approximately 0.1-5.0 V.

In accordance with another aspect of the invention there is provided a process for preparing a solar cell precursor thin film, the process including the steps of: providing an electrodeposition solution containing copper, indium, gallium, and selenium ions; immersing a substrate into the electrodeposition solution; and electroplating the copper, indium, gallium, and selenium ions simultaneously onto the substrate by applying a cathodic potential thereto of 1-10 VDC voltage and 0.2-5.0 VAC at 1-100 KHz superimposed thereon.

Additional objects, advantages, and novel features of the present invention will be set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the following description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of a CIGS photovoltaic device prepared according to the present invention.

FIG. 2 is a cross sectional view of the conducting zinc oxide layer 28 shown in FIG. 1.

FIG. 3 is the current vs. voltage performance plot of a $CdS/CuInSe_2$ solar cell prepared according to Example 3 of the present invention.

FIG. 4 is a plot of relative quantum efficiency verses wavelength for the $CdS/CuInSe_2$ solar cell of Example 3.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention includes an essentially two-step process for fabricating high quality, low cost thin film CIGS semiconductor devices that exhibit photovoltaic characteristics and are especially adaptable for solar cell applications. In the first step, a precursor film of $Cu_xIn_yGa_zSe_n$ ($x=0\text{-}2$, $y=0\text{-}2$, $z=0\text{-}2$, $n=0\text{-}3$) is electrodeposited on a substrate such as glass coated with molybdenum. This first step may include a unique process and electrodeposition bath for electrodepositing gallium concurrently with other elements, as well as the unique use of an alternating current in conjunction with a direct current.

The second step is physical vapor deposition of either Cu+Se or In+Se, either alone or in combination with Ga. In this second step the composition of the overall film is carefully controlled so that the resulting thin film is very close to stoichiometric $Cu(In,Ga)Se_2$. Both of these steps may be performed on substrates having large surface areas. Accordingly, the process of the present invention allows large area, high efficiency solar cells to be economically produced.

Referring now to FIG. 1, CdS/CIGS photovoltaic device 10 includes a substrate 12 which may be, for example, soda-lime silica glass or amorphous 7059 glass. Substrate 12 further includes a back contact layer 14 of molybdenum, about 1-2 μm thick. The molybdenum may be deposited using DC sputtering from a rotating cylindrical magnetron target (CMAG). To improve adhesion between the Mo layer 14 and the precursor film to be deposited, an additional adhesion layer 16 of copper may also be deposited as by electrodeposition. After Mo layer 14 and optional copper adhesion layer 16 have been deposited, the substrate should be degreased as for example with propanol and dried in flowing nitrogen gas.

A metallic precursor film 18 is then deposited by electrodeposition. The precursor film contains one or more of the elements copper, indium, gallium, and selenium. Electrodeposition is generally a less expensive method of depositing these metals than vapor deposition. However, it is not possible to control the ratios of metals deposited during electrodeposition as precisely as desired. Consequently, prior CIGS layers deposited entirely by electrodeposition produced low conversion efficiencies. In the present invention, the electrodeposition step is integrated with the vapor deposition step that follows. This allows precursor metal to be deposited in bulk using an economical electrodeposition step, followed by a vapor deposition step to carefully control the final metal ratios. This results in economical production yet high efficiencies of the resulting cell. The composition of metal precursor film 18 is generally denoted as $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3). The metal precursor film 18 should be deposited to about 1-3 μm thick, with thickness being controlled by coulometric measurements.

It has been found that electrodepositing the films using an AC voltage in addition to a DC voltage produces improved results. An AC voltage improves the morphology of the film. It is also believed that the AC voltage improves nucleation (growth) of the thin film by allowing additional nucleation centers to be created. For an entirely aqueous plating solution, the applicable DC voltage range is approximately 1-5 VDC, with a preferred voltage of approximately 2 VDC. Improved results may be obtained by superimposing an AC voltage of 0.2-5.0 VAC at 1-100 Khz, with preferred values of approximately 0.3-1.0 VAC at 10-30 KHz. A value of approximately 0.45 VAC at approximately 18.1 KHz was found to yield good results. The plating solution is adjusted to have a pH of approximately 1.0 to 4.0, and more preferably to about 1.4 to 2.4. The plating solution should preferably be at about 10 °C to 80 °C, and more preferably at about 24 °C. Adding a supporting electrolyte to the plating bath can additionally increase the conductivity of the plating solution, allowing for a further increase in the electrodeposition rate. Salts such as NaCl, LiCl, or Na_2SO_4 have been found to be suitable supporting electrolytes for use with certain embodiments of the present invention.

In completely aqueous solutions, electrolysis of water molecules begins to occur to an undesirable extent at approximately 2-3 volts. The resulting O^{2-} and OH^- ions combine with deposition metal ions or deposited metal to form unwanted metal oxides and hydroxides on the precursor film 18. To overcome this disadvantage, the water in the plating solution may be either partially or completely replaced by one or more organic solvents such as dimethyl sulfoxide (DMSO). Increasing the organic solvent content of the electrodeposition solution allows the cathodic potential to be increased without unacceptable increases in metal oxide and hydroxide formation rates. The increased cathodic potential increases the deposition rate of the precursor films. An additional advantage is that increasing the cathodic potential increases the deposition rate of gallium relative to the deposition rates of other deposited metals. Therefore, using a solution containing one or more organic solvents allows the cathodic potential to be selected from a wider range so as to achieve a more desired stoichiometry of the as-deposited precursor film 18. When an organic solvent is used, the preferred cathodic potential is approximately 3-10 VDC and 0.2-5.0 VAC at approximately 1-100 KHz. Value of approximately 5 VDC and 0.45 VAC at approximately 18.1 KHz were found to yield good results.

If desired, a second electroplating solution may be employed to adjust the stoichiometry of the electrodeposited film prior to the vapor deposition phase. For example, a first electrodeposition step may produce a CIGS precursor film with less gallium than optimally desired. Although the gallium content can be increased during the vapor deposition phase, it may be less expensive to deposit a certain amount of gallium using a second electrodeposition solution to make a coarse stoichiometric adjustment prior to proceeding to fine stoichiometric adjustment at the vapor deposition step. Another potential motivation for using a second electrodeposition solution is to achieve a composition gradient in the deposited film, as suggested by U.S. Patent No. 4,335,266 issued to Michelsen et al. ,for its teachings of composition-graded CIGS thin films for solar cell and other applications. Yet another way of achieving composition grading during electrodeposition is to vary process parameters such as cathodic potential, ionic concentrations, pH, or temperature, as electrodeposition proceeds.

Several examples of electrodeposited metal precursor films fabricated according to the present invention are given. These examples include In-Se, Cu-Se, and Cu-In-Se precursor films. For these precursor films, Ga should be added to raise the energy gap. The Ga may be added by a separate electrodeposition step, though is preferably added at the vapor deposition step by vaporizing elemental gallium. An example is also given of a novel solution and process that allows Ga to be electrodeposited along with other precursor metals, to produce a Cu-In-Ga-Se precursor film electrodeposited in a single step. The solution includes ions of each of the elements of copper, indium, gallium, and selenium. These ions may be supplied in the form of dissolved metal salts.

After the precursor film 18 has been electrodeposited it should be cleaned. A suitable method is to rinse precursor film 18 with deionized water and dry it in flowing nitrogen gas. After precursor film 18 has been cleaned, an additional layer 20 of In+Se or Cu+Se, either alone or in combination with gallium, is deposited by physical vapor deposition to adjust the final film composition to the ratios of approximately Cu= 1-1.2: (In,Ga)= 1-1.2: Se= 2-2.5, and most preferably to approximately 1:1:2. By controlling the ratio of In/Ga the energy gap between the CdS and the CIGS layers can be adjusted to the optimal or nearly optimal value. An energy gap of approximately 1.45 eV is considered optimal for terrestrial solar energy conversion, and is achieved by an In/Ga ratio of approximately 3:1. The substrate (precursor film) temperature should be 300 °C to 600 °C during PVD, and preferably about 550 °C.

After PVD, the films should then be annealed. Annealing improves the homogeneity and quality of the films. A high quality CIGS film is one that does not exhibit an excessive amount of copper nodules, voids, or vacancies in the film which would reduce conversion efficiencies. Annealing the films at 250 °C to 500 °C in a vacuum, followed by slow cooling at a rate of approximately 3 °C/min to avoid thermal shock was found to yield good results. Because selenium has a much higher vapor pressure than either copper, indium, or gallium, selenium may be lost from the film during the high temperature steps of vapor deposition and annealing. To compensate, the atmosphere during these steps may contain a moderate overpressure of selenium. In the preferred embodiment, the film is selenized at a rate of 5-100 Å/s during cool-down from PVD temperature to annealing temperature.

Once the CIGS layers 18 and 20 collectively are deposited and annealed, a thin layer 22 of n-type semiconductor comprising cadmium sulfide is deposited next. CdS layer 22 is preferably deposited by chemical bath deposition (CBD) to a thickness of approximately 200-1000 Å. The CBD bath may be prepared from 0.08 gm $CdSO_4$, 2.5 gm thiourea, and 27.5 gm NH_4OH dissolved in 200 ml water. The deposition temperature should be approximately 40-80° C.

A layer 28 of conducting wide bandgap n-type semiconductor materials is deposited next. In the preferred embodiment, layer 28 comprises two zinc oxide layers 24 and 26 as shown in FIG. 2. First zinc oxide layer 24 is deposited with RF sputtering at approximately 0.62 watts/cm^2 in an argon plasma at 10 millitorrs pressure. Second zinc oxide layer 26, comprising approximately 1-5% Al_2O_3-doped zinc oxide, is also prepared using RF sputtering at approximately 1.45 watts/cm^2 in an argon plasma at 10 millitorrs pressure. In an exemplary embodiment the resistivity of the first layer was 50-200 ohm/cm^2, and resistivity of the second layer was 15-20 ohm/cm^2. The transmissivity of the overall ZnO layer was 80-85%.

Bi-layer metal contacts 30 may then be prepared with an e-beam system or other techniques. In an exemplary embodiment a first metal contact layer was 500-1000 Å thick Ni and the second metal contact layer was 1-3 μm thick Al. Metal contacts 30 will generally be laid out in fine grid lines across the collecting surface of the device and connected to a suitable current collecting electrode (not shown). The efficiency of the resulting device can be further increased by adding an antireflection coating 32, such as a 600-1000 Å layer of MgF_2 by electron beam. A device prepared according to Example 3 below exhibited a conversion efficiency of 9.44%.

Example 1

A metallic precursor film of $In_{1-2}Se_{1-3}$ was electrodeposited on glass substrates coated with a Mo or Mo/Cu layer approximately 500 Å thick. The precursor film was deposited using an electroplating solution containing 2.25 gm $InCl_3$ and 0.41 gm H_2SeO_3 dissolved in 200 ml of water. The pH of the solution was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2-5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. The films were 1-3 μm thick and adhered to the substrate.

Example 2

A metallic precursor film of $Cu_{1-2}Se_{1-3}$ was electrodeposited on a substrate using an electroplating solution containing 6.21 gm $Cu(NO_3)_2 \cdot 6H_2O$ and 1.16 gm

H_2SeO_3 dissolved in 300 ml water. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2-5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1-3 μm thick and adhered to the substrate.

Example 3

A metallic precursor film of $Cu_{1-2}In_{1-2}Se_{1-3}$ was electrodeposited on a substrate using an electroplating solution containing 4.47 gm $CuCl_2$, 5.67 gm $InCl_3$ and 3.39 gm H_2SeSO_3 dissolved in 1050 ml water. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2-5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1-3 μm thick and adhered to the substrate. The electrodeposited film was slightly indium poor. Indium was then added by vapor deposition to adjust the final content to approximately $CuInSe_2$. CdS and ZnO were then added to complete the solar cell. The resulting solar cell was exposed to ASTM E892-87 Global (1000 Wm^{-2}) standard irradiance spectrum at 25 °C. Performance parameters for the finished solar cell, having an area of 0.4285 cm^2, were measured as:

V_{oc} = 0.4138 V $\quad$ V_{Pmax} = 0.3121 V
I_{sc} = 15.40 mA $\quad$ I_{Pmax} = 12.96 mA
J_{sc} = 35.94 mA cm^{-2} $\quad$ P_{max} = 4.045 mW
Fill Factor = 63.47% $\quad$ Efficiency = 9.44%

FIG. 3 is an I-V plot for the device. FIG. 4 is a plot of the relative quantum efficiency of the device. The device contained only Cu-In-Se, without any gallium. The device exhibited an efficiency of 8.76% without antireflective coating, and 9.44% after an antireflective coating was added. It is believed that by adding gallium the efficiency of the resulting cell could be improved to around fourteen percent (14%).

Example 4

A metallic precursor film of $Cu_{1-2}In_{1-2}Ga_{0.01-1}Se_{1-3}$ was electrodeposited using a solution containing 1.12 gm $Cu(NO_3)_2 \cdot 6H_2O$, 12.0 gm $InCl_3$, 4.60 gm $Ga(NO_3)_3 \cdot xH_2O$ and 1.80 gm H_2SeO_3 dissolved in 450 ml of water. This is equivalent to approximately 2.49 gm/l $Cu(NO_3)_2 \cdot 6H_2O$, 26.7 gm/l $InCl_3$, 10.2 gm/l $Ga(NO_3)_3 \cdot xH_2O$ and 4.0 gm/l H_2SeO_3, and approximately 0.0084, 0.12, 0.28, and 0.31 molal of copper, indium, gallium, and selenium ions, respectively. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2-5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1-3 μm thick and adhered to the substrate.

Example 5

A metallic precursor film of $Cu_{1-2}In_{1-2}Ga_{0.01-1}Se_{1-3}$ was electrodeposited using a solution containing 1.496 gm $Cu(No_3) \cdot 5H_2O$, 14.929 gm $InCl_3$, 1.523 gm H_2SeO_3, and 7.192 gm $Ga(NO_3)_3$ dissolved in 450 ml of DMSO. The films were deposited at 25 °C and also at 50 °C at an applied voltage of 5 VDC.

Example 6

A metallic precursor film of $Cu_{1-2}In_{1-2}Ga_{0.01-1}Se_{1-3}$ was electrodeposited using a solution containing 1.496 gm $Cu(No_3) \cdot 5H_2O$, 14.929 gm $InCl_3$, 1.523 gm H_2SeO_3, and 7.192 gm $Ga(NO_3)_3$ dissolved in a mixture of 400 ml DMSO and 50 ml water. The films were deposited at 25 °C and also at 50 °C at an applied voltage of 5 VDC.

Example 7

A metallic precursor film of $Cu_{1-2}In_{1-2}Ga_{0.01-1}Se_{1-3}$ was electrodeposited using a solution containing 1.496 gm $Cu(No_3) \cdot 5H_2O$, 14.929 gm $InCl_3$, 1.523 gm H_2SeO_3, 7.192 gm $Ga(NO_3)_3$, and 10 gm Na_2SO_4, and 20 gm LiCl dissolved in a mixture of 400 ml DMSO and 50 ml water. The films were deposited at 25 °C and also at 50 °C at an applied voltage of 5 VDC.

The present invention as described above may be incorporated in a variety of applications, as for example the conversion of solar energy to electric energy for baseline power generation. Other applications include appliances such as solar-powered calculators, battery charges such as those used with freeway emergency call boxes, photoelectric eyes, night security light activators, light meters for photographic and other purposes, and the like.

Although the present invention has thus been described in detail with regard to the preferred embodiments and drawings and examples thereof, it should be apparent to those skilled in the art that various adaptations and modifications of the present invention may be accomplished without departing from the spirit and the scope of the invention. Accordingly, it is to be understood that the detailed description and the accompanying drawings as set forth hereinabove are not intended to limit the breadth of the present invention, which should be inferred only from the following claims and their appropriately construed legal equivalents.

WHAT IS CLAIMED IS:

1. A process for preparing a metal-containing thin film, the process comprising the steps of:

electrodepositing a layer of $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3) on a substrate, the electrodeposition proceeding at a DC voltage of approximately 1-10 V and an AC voltage of approximately 0.2-5.0 V at 1-100 KHz superimposed upon said DC voltage; and

depositing a sufficient amount of either In+Se or Cu+Se on said layer of $Cu_xIn_yGa_zSe_n$ by vapor deposition to produce a thin film of $Cu(In,Ga)Se_2$ on the substrate wherein said thin film has stoichiometric ratios of approximately Cu=1-1.2:(In,Ga)=1-1.2:Se=2-2.5.

2. The process of claim 1 wherein said layer of $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3) comprises $In_{1-2}Se_{1-3}$.

3. The process of claim 1 wherein said layer of $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3) comprises $Cu_{1-2}Se_{1-3}$.

4. The process of claim 1 wherein said layer of $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3) comprises $Cu_{1-2}In_{1-2}Se_{1-3}$.

5. The process of claim 1 wherein said layer of $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3) comprises $Cu_{1-2}In_{1-2}Ga_{0.01-1}Se_{1-3}$ (x=1-2, y=1-2, z=0.01-1, n=1-3).

6. The process of claim 1 wherein the vapor deposition comprises physical vapor deposition.

7. The process of claim 6 wherein the physical vapor deposition proceeds at a temperature of approximately 550°C.

8. The process of claim 1, wherein the electrodeposition proceeds at a DC voltage of approximately 1-10 V.

9. The process of Claim 8, where the electrodeposition proceeds at an AC voltage of approximately 0.2-5.0 V. at 1-100 KHz.

10. The process of claim 1 wherein the electrodeposition proceeds in an aqueous electrodeposition solution, said DC voltage is approximately 1-5 volts, and said AC voltage is approximately 0.3-1.0 volts at approximately 10-30 KHz.

11. The process of claim 10 wherein said DC voltage is approximately 2 volts and said AC voltage is approximately 0.45 volts at approximately 18.1 KHz.

12. The process of claim 1 wherein said DC voltage is approximately 3-10 volts, and the electrodeposition proceeds in an electrodeposition solution comprising at least one organic solvent, and the electrodeposition further proceeds at an AC voltage of approximately 0.2-5.0 volts at approximately 1-100 KHz superimposed upon said DC voltage.

13. The process of claim 12 wherein said AC voltage is approximately 0.45 volts at approximately 18.1 KHz.

14. The process of claim 1 wherein the electrodeposition step proceeds in an electrodeposition solution comprising at least one supporting electrolyte for raising the conductivity of the electrodeposition solution and increasing the deposition rate of the $Cu_xIn_yGa_zSe_n$ layer.

15. The process of claim 14 wherein said supporting electrolyte comprises at least one compound selected from the group consisting of NaCl, LiCl, and Na_2SO_4.

16. The process of claim 1 further comprising the steps of:

depositing a CdS layer on the $Cu_xIn_yGa_zSe_n$ film by chemical bath deposition; and

depositing a ZnO layer on the CdS layer by RF sputtering.

17. A process for electrodepositing a solar cell precursor thin film, the process comprising the steps of:

electrodepositing a thin film containing copper, indium, gallium, and selenium onto a substrate, the electrodeposition proceeding in an electrodeposition solution comprising copper, indium, gallium, and selenium ions.

18. The process of claim 17, wherein said electrodeposition solution comprises copper, indium, gallium, and selenium ions at concentrations of approximately 0.0084, 0.12, 0.28, and 0.31 molal, respectively.

19. The process of claim 18, wherein said electrodeposition solution comprises approximately 2.49 gm/l $Cu(NO_3)_2 \bullet 6H_2O$, 26.7 gm/l $InCl_3$, 10.2 gm/l $Ga(NO_3)_3$, and 4.0 gm/l H_2SeO_3.

20. The process of claim 17 wherein the electrodeposition solution has a pH of approximately 1.0-4.0.

21. The process of claim 17 wherein the electrodeposition proceeds at a DC voltage of 1-10 V.

22. The process of claim 21 wherein the electrodeposition proceeds at an AC voltage of approximately 0.2-5.0 V at a frequency of approximately 1-100 KHz.

23. The process of claim 22 wherein said AC voltage is approximately 0.45 VAC at a frequency of approximately 18.1 KHz.

24. The process of claim 17 wherein the electrodeposition solution further comprises at least one organic solvent, and the electrodeposition proceeds at a DC voltage of approximately 3-10 volts.

25. A process for preparing a solar cell precursor thin film, the process comprising the steps of:

electrodepositing a metallic precursor thin film having the composition $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3) onto a substrate using a DC voltage in combination with an AC voltage of approximately 0.2-5.0 V.

26. The process of claim 25 wherein said AC voltage is approximately 0.3-1.0 V at approximately 10-30 KHz.

27. The process of claim 26 wherein said AC voltage is approximately 0.45 V at approximately 18.1 KHz.

28. A process for preparing a solar cell precursor thin film, the process comprising the steps of:

(a) providing an electrodeposition solution containing copper, indium, gallium, and selenium ions;

(b) immersing a substrate into said electrodeposition solution; and

(c) electroplating said copper, indium, gallium, and selenium ions simultaneously onto said substrate by applying a cathodic potential thereto of 1-10 VDC voltage and 0.2-5.0 VAC at 1-100 KHz superimposed thereon.

29. The process according to claim 28, wherein said electrodeposition solution includes at least one organic solvent.

30. The process according to claim 28, wherein said cathodic potential is approximately 1-5 VDC and 0.3-1.0 VAC at 10-30 KHz superimposed thereon.

31. The process according to claim 30, wherein said cathodic potential is approximately 2 VDC and approximately 0.45 VAC at 10-30 KHz superimposed thereon.

32. The process according to claim 30, wherein said electrodeposition solution comprises approximately 2.49 gm/l $Cu(NO_3)_2{\bullet}6H_2O$, 26.7 gm/l $InCl_3$, 10.2 gm/l $Ga(NO_3)_3$, and 4.0 gm/l H_2SeO_3.

33. The process according to claim 32, wherein said electrodeposition solution includes at least one organic solvent.

34. The process of any one of claims 1 to 16, wherein said layer is deposited to a thickness of 1-3 μm.

35. The process according to any one of claims 1 to 7, wherein said electrodeposition solution includes at least one organic solvent.

36. The process according to claim 35 wherein said cathodic potential of 3-10 VCD is employed with has 0.2-5.0 VAC at 1-100 KHz superimposed thereon.

37. The process according to claim 35, wherein a cathodic potential of approximately 5 VDC is employed which has approximately 0.45 VAC at 18.1 KHz superimposed thereon.

38. The process according to any one of claims 35 to 37, wherein said electrodeposition solution comprises approximately 2.49 gm/l $Cu(NO_3)_2{\bullet}6H_2O$, 26.7 gm/l $InCl_3$, 10.2 gm/l $Ga(NO_3)_3$, and 4.0 gm/l H_2SeO_3.

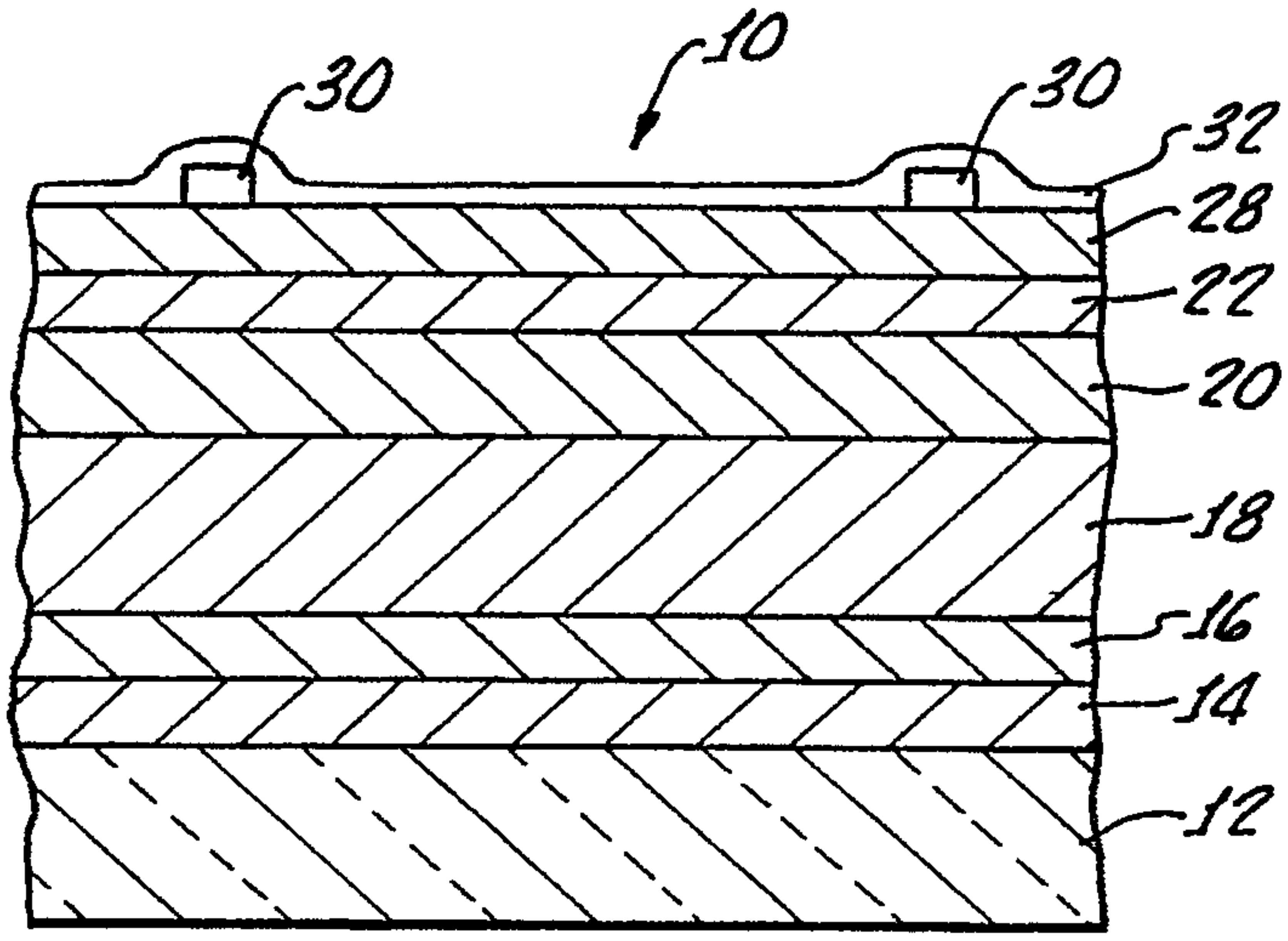


FIG. 1.

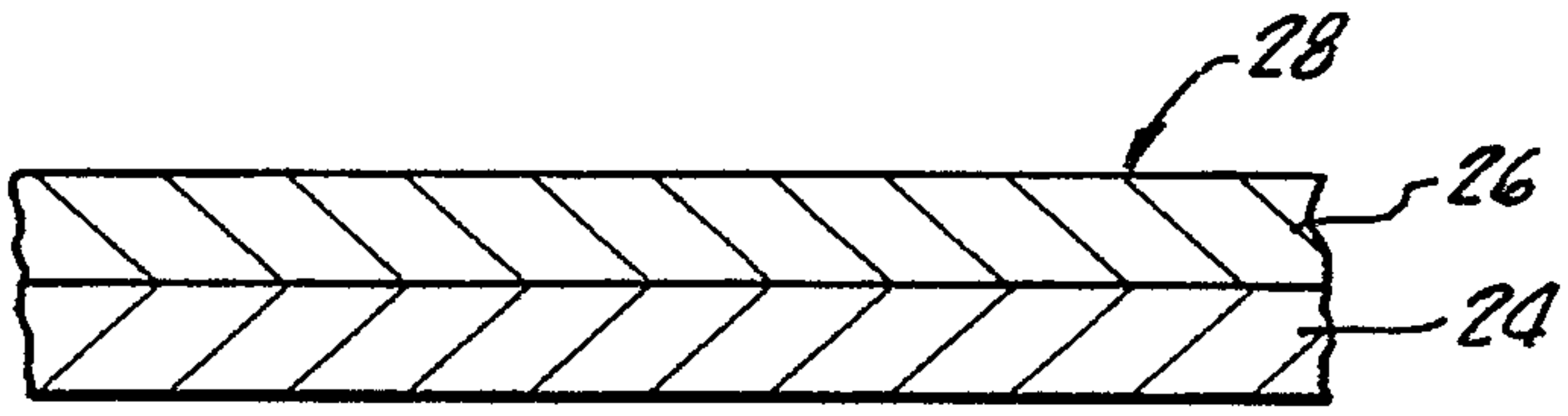
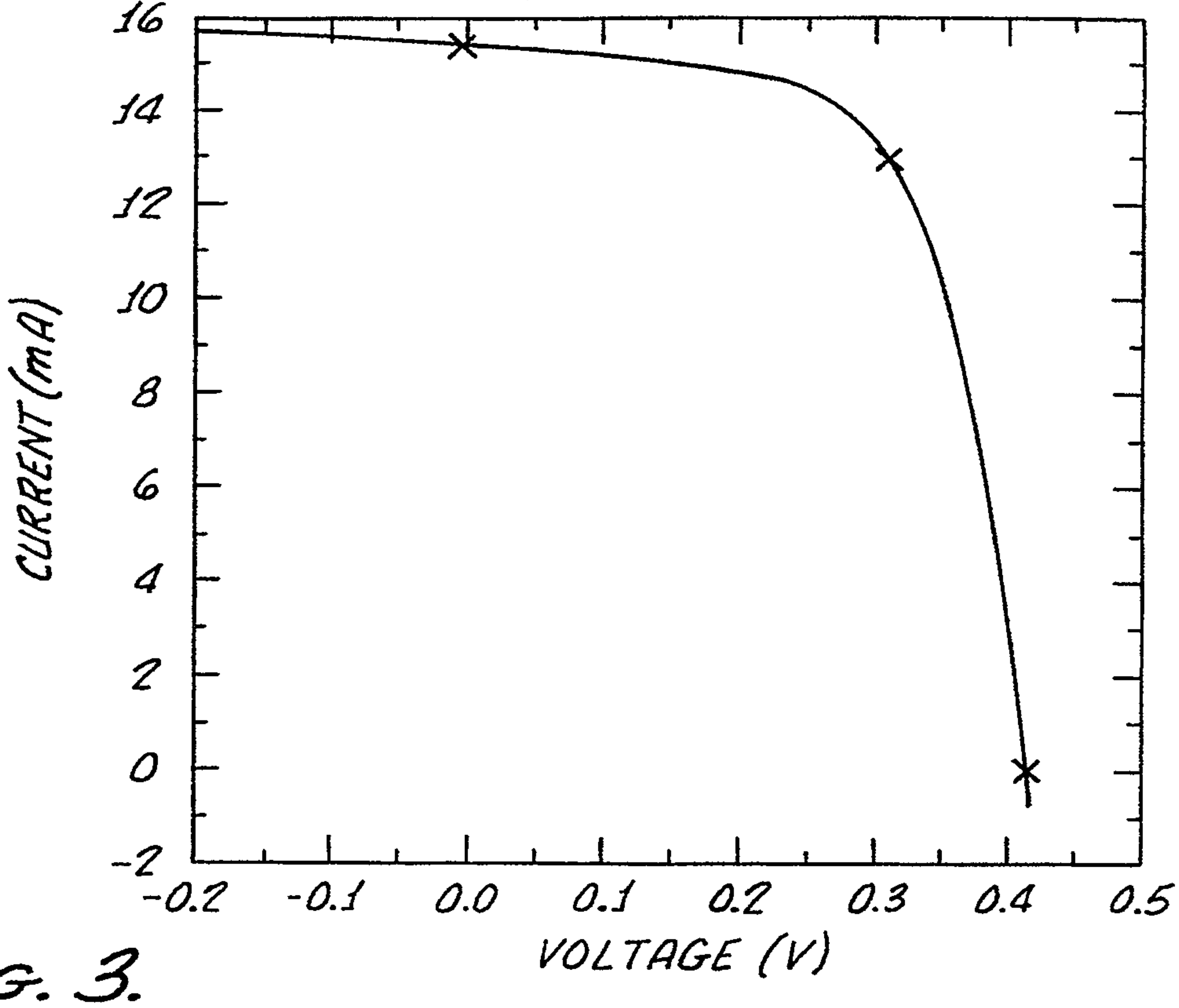


FIG. 2.


16
14
12
10
8
6
4
2
0
-2
CURRENT (mA)
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-0.1
0.0
0.1
0.2
0.3
0.4
0.5
VOLTAGE (V)

FIG. 3.

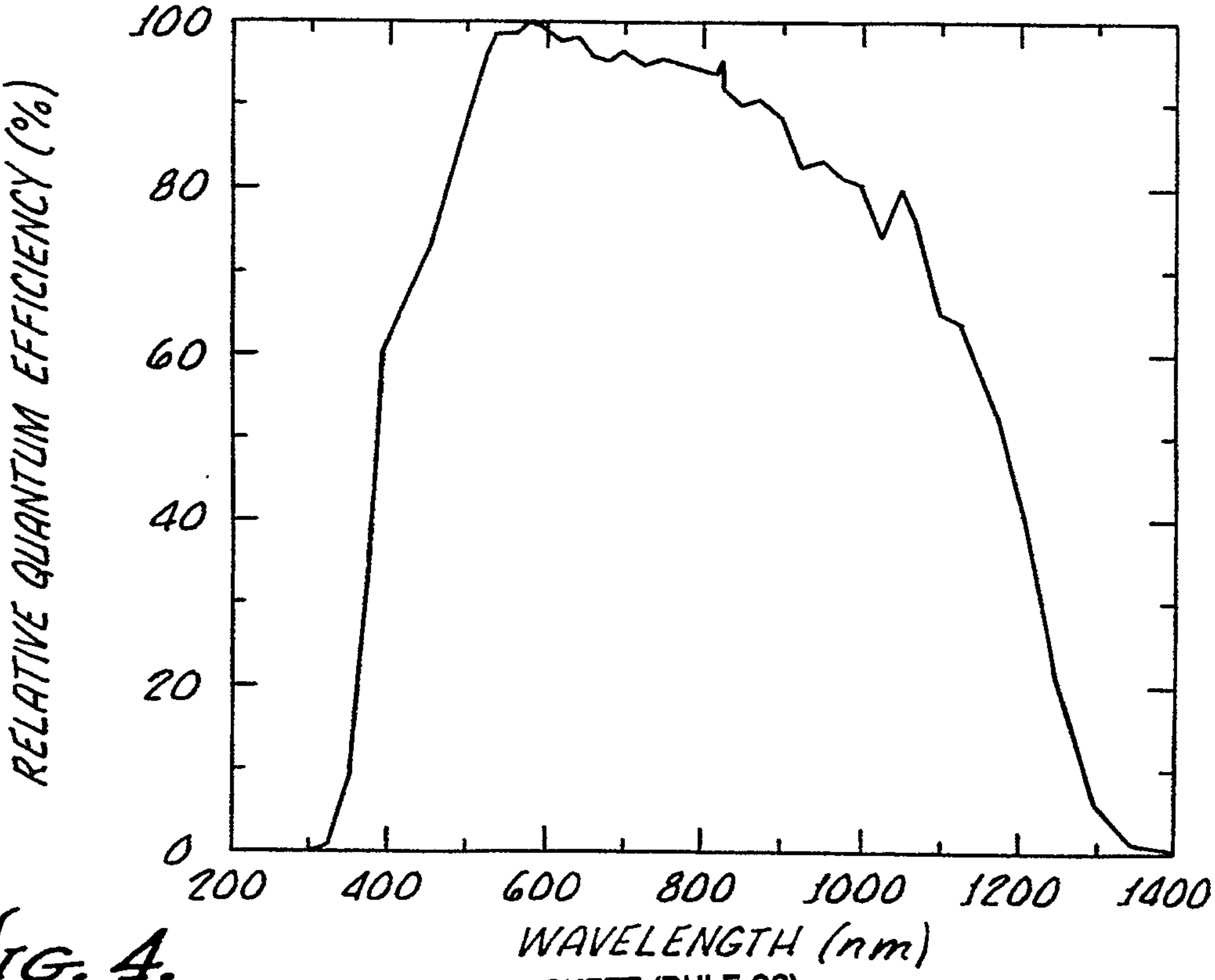
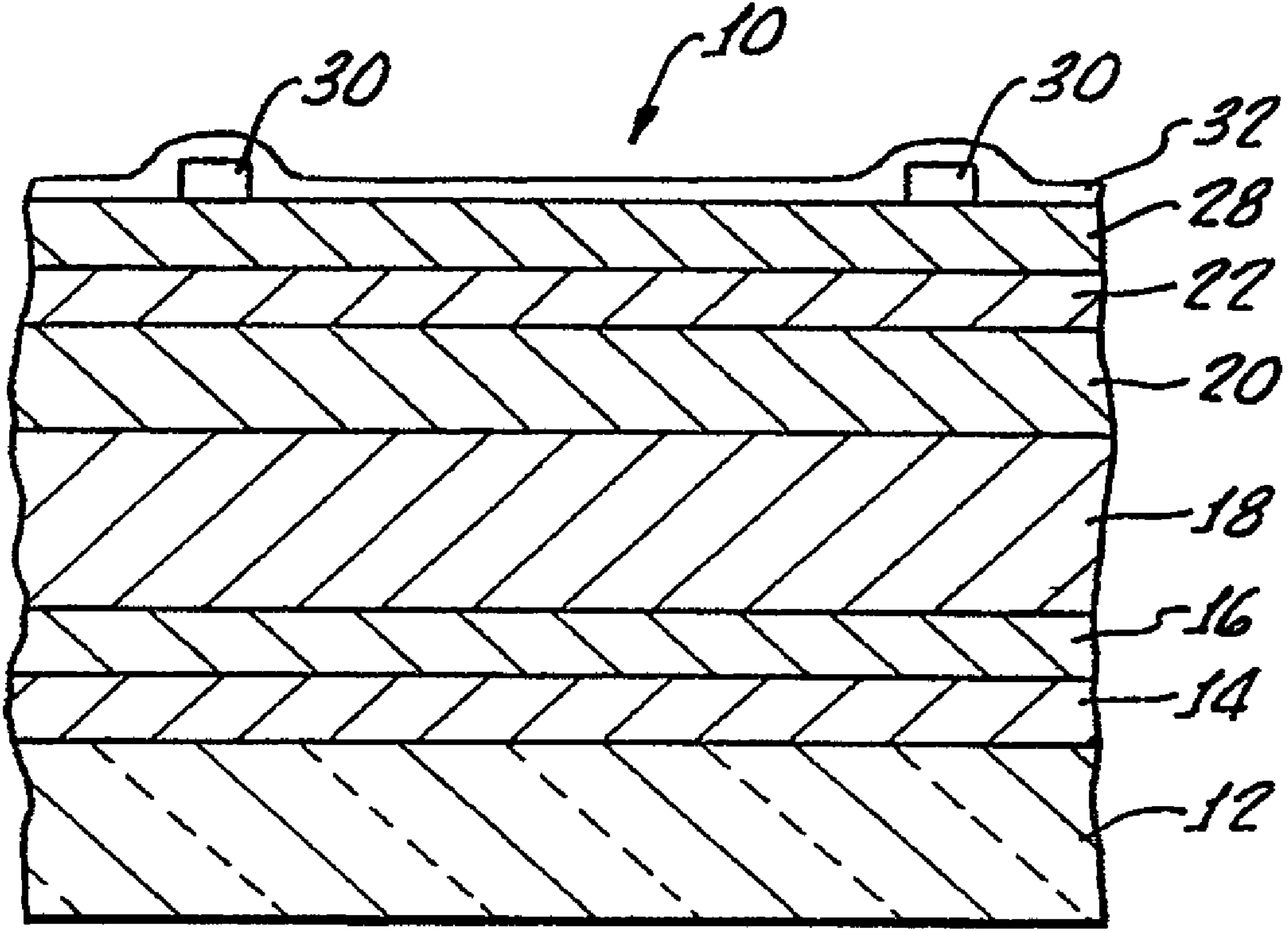

100
80
60
40
20
0
RELATIVE QUANTUM EFFICIENCY (%)
200
400
600
800
1000
1200
1400
WAVELENGTH (nm)

FIG. 4.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