

[54] **PROCESS FOR PREPARING A LAYER OF COMPOUNDS OF GROUPS II AND VI**

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[*] Notice: The portion of the term of this patent subsequent to Feb. 19, 1991, has been disclaimed.

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 172,454, Aug. 17, 1971, Pat. No. 3,793,069.

[52] U.S. Cl. 117/201, 117/62, 117/106 A, 117/215

[51] Int. Cl. B44d 1/02

[58] **Field of Search** 117/106 A, 62, 215, 201, 117/106 R

[56] References Cited

UNITED STATES PATENTS

3,793,069 2/1974 Shimizu et al. 117/201

Primary Examiner—Mayer Weinblatt
Attorney, Agent, or Firm—Kemon, Palmer & Estabrook

[57] ABSTRACT

A process for preparing a layer of compounds of Groups II and VI characterized in that a layer of the compounds is formed on the surface of a substrate, and the formed layer is heat-treated in an atmosphere comprising an inert gas, 0.1–10% by volume of oxygen on the basis of said inert gas and vapour of at least one element selected from a group consisting of sulfur, selenium and tellurium so that uniform grain growth with a narrow range grain size distribution is effected.

7 Claims, 3 Drawing Figures

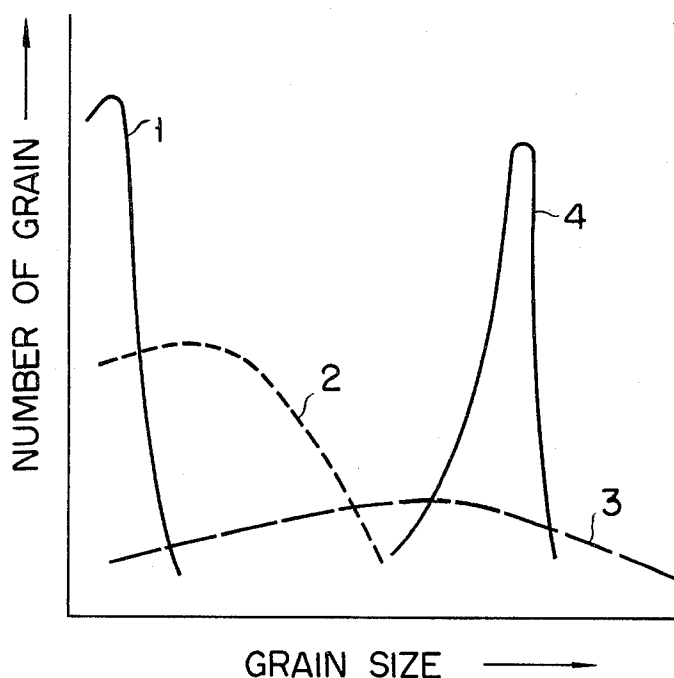
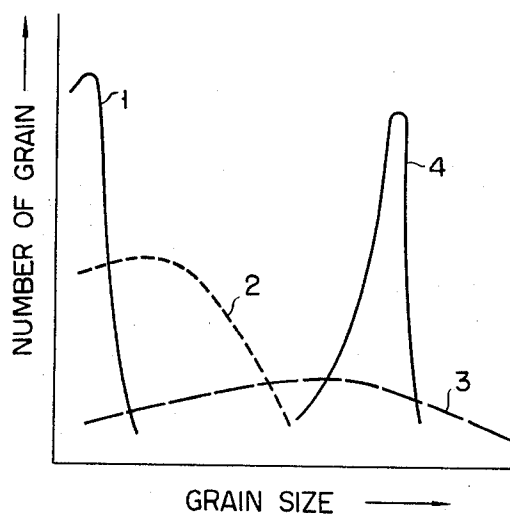


FIG. 1



SHEET 2 OF 2

FIG. 2

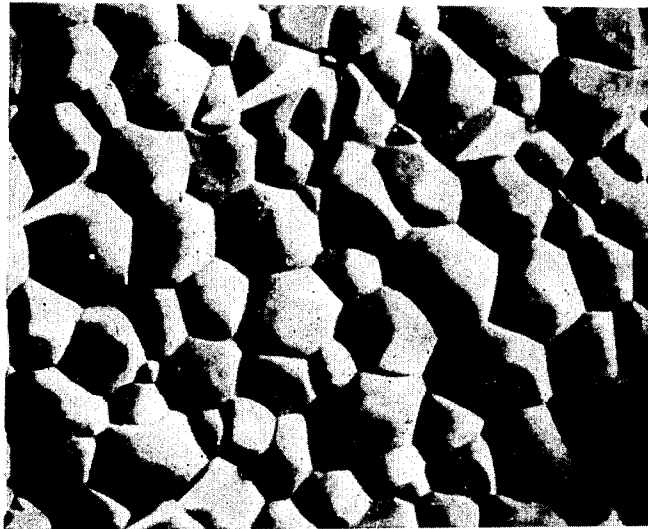


FIG. 3



PROCESS FOR PREPARING A LAYER OF COMPOUNDS OF GROUPS II AND VI

CROSS-REFERENCE TO RELATED APPLICATION

This is continuation-in-part of the U.S. patent No. application Ser. No. 172,454 filed on Aug. 17, 1971, now U.S. Pat. No. 3,793,069.

FIELD OF THE INVENTION

This invention relates to a process for preparing a layer of Groups II-VI compounds with narrow grain size distribution.

DESCRIPTION OF THE PRIOR ART

A film of a large area of a compound or a film of a compound separately distributed over a large area is useful as a light-electricity transducer in a wide range of technical fields, such as solar cells, solid state photo-sensors for image pickup application, photoconductive film for image pickup tubes, etc. Such films should be furnished not only with electrical properties satisfactory enough for desired performance, but also with uniformity in such properties over a wide area. For instance, local unbalance in photosensitivity or intensity of luminescence of a film element not only abates the commercial value thereof, but constitutes a fatal factor which restricts the life of the film element.

Usually such a film is formed by vacuum evaporation or gaseous phase reaction on the surface of a substrate plate. In order to improve the electrical properties thereof, however, heat treatment is necessary after film formation in many cases. Such heat treatment is generally accompanied by growth of grains which constitute the film. Therefore the characteristics of a film element, especially uniformity of the characteristics over a wide area is often influenced by the grain growth during the heat treatment. In order to secure desirable grain growth in the heat treatment, it is important to select a suitable temperature, but the maximum temperature may be limited because of heat resistance of the substrate material, possible decomposition of the compound constituting the film, etc. Therefore, fluxes are widely employed in such heat treatment.

A typical example of such fluxes used in the heat treatment is cadmium chloride, which is employed in the treatment of cadmium sulfide used for photoconductive elements. Cadmium chloride is effective for cadmium selenide or cadmium sulfoselenide film, too. To make the effect of the heat treatment satisfactory, consideration is paid to making the flux concentration as uniform as possible. However, when cadmium chloride is used in the heat treatment of cadmium sulfide or cadmium selenide photoconductive films, a large quantity of chlorine penetrates into the photoconductive film and in some cases the concentration thereof reaches as high as 10^{20} atoms/cm³. This chlorine builds up a shallow donor level in the cadmium sulfide or selenide. The existence of such high concentration of a shallow donor level impairs photosensitivity of the films and in some other cases retards response to light.

The advantage of the above-mentioned heat treatment in which the flux is used is that grain size is rather uniform after grain growth. In contrast, in methods in which flux is not used, but, for instance, simply temperature is raised for promotion of grain growth, the grain growth rate varies from part to part and a film with a wide range distribution of grain size results. This is the

cause of non-uniformity in film thickness and causes fatal defects such as pinhole, peeling-off of film, etc.

In order to carry out the uniform grain growth of a film which comprises amorphous or extremely fine grains, it is necessary in general to generate a suitable number of uniformly distributed nuclei on the surface of the film.

SUMMARY OF THE INVENTION

In accordance with this invention, such uniformly distributed nuclei which lead to a film of a uniform structure with narrow range grain size distribution are provided on the surface of a film of Groups II-VI compounds by carrying out the heat treatment of said film in an atmosphere comprising an inert gas and 0.1-10% by volume of oxygen on the basis of said inert gas and the vapour of at least one element selected from a group consisting of sulfur, selenium and tellurium.

BRIEF DESCRIPTION OF THE DRAWING

This invention can be more fully understood from the following detailed description when taken with reference to the accompanying drawings, in which:

FIG. 1 is a diagram showing the grain size distribution characteristic of the film obtained in accordance with this invention in comparison with those of the prior art films;

FIG. 2 is a photomicrograph (x 5,000) of a film obtained by the process of this invention; and

FIG. 3 is a photomicrograph of a film obtained by the prior art process at the same magnification.

DESCRIPTION OF PREFERRED EMBODIMENTS

Now the invention is explained in detail with respect to an embodiment pertaining to a preparation of a photoconductive element. A thin film of cadmium selenide, 5 μ thick for instance, is deposited on the surface of a substrate plate kept at 150°C in vacuo by vacuum evaporation technique. The thus obtained film is heat-treated in an inert gas such as nitrogen containing 5% by volume of oxygen at 500°C for 1 hour, wherein selenium vapour exhibiting saturation vapour pressure at 500°C co-exists. This selenium vapour can be mixed with the oxygen prior to the heat treatment or can be generated in situ by suitable means. By this heat treatment, the grain size of the originally deposited film which is about 1000Å grows to about 1.5 μ and a film having grain size which is quite uniform is obtained. This grain growth is the same as the grain growth which results from a process in which 20 mole percent of cadmium chloride is mixed with cadmium selenide when the substrate plate is treated therewith and the deposited film is heat-treated in a nitrogen atmosphere.

The effect and advantage of this invention is now given below on the basis of the above-described embodiment. The point of this invention is that limited volume of oxygen is employed in combination with selenium vapour in the heat treatment atmosphere. To heat-treat cadmium selenide in a selenium vapour has been known and practiced in the prior art. However, this is a treatment for the purpose of filling the selenium vacancies in cadmium selenide film, and is carried out so as to modify the electrical properties of a film. Also heat treatment in air is frequently employed as the treatment in an oxygen-containing atmosphere. Air is regarded as a mixture of oxygen and nitrogen. Japanese Pat. Publication No. 23456/65 refers to nitro-

gen atmosphere containing 0.2–1.7% oxygen as the atmosphere containing limited amount of oxygen. However, the invention of this reference relates to a process of heat treatment in which cadmium selenide is heat-treated together with a flux, and the atmosphere comprises oxygen, nitrogen and cadmium halide vapour, whereby grain growth is effectuated with the cadmium halide flux, and oxygen is added for filling selenium vacancies merely as an auxiliary agent.

In accordance with this invention, as illustrated in the above example, oxygen and selenium vapour must co-exist in the atmosphere during the heat treatment. That is, if the atmosphere lacks either of the two, no such film as is aimed at in this invention can be obtained. For instance, if the operation of the above-mentioned working example is carried out in an atmosphere which contains no selenium vapour, grain growth does not proceed as shown by comparison of Curve 1 in FIG. 1, which represents the grain size distribution before the heat treatment, and Curve 2, which represents the grain size distribution after the heat treatment. On the other hand, when oxygen is omitted from the atmosphere, the grain size distribution after the treatment is represented by Curve 3 in FIG. 1. In this case, the range of grain size distribution is much enlarged.

In contrast, Curve 4 represents the grain size distribution when a film is heat-treated in an atmosphere in which oxygen and selenium vapour co-exist in accordance with this invention. Comparison of FIGS. 2 and 3, which show electron photomicrographs of the film of this invention and that of the prior art, shows how superior the film of this invention is to that of the prior art in the grain size and the grain size distribution. Thus, the photoconductive film of this invention, as represented by FIG. 2, is free from unevenness in photoelectric sensitivity.

Now the reason why such effect is achieved by this invention is discussed with particular reference to the above-mentioned embodiment. In the course of the heat treatment, when the temperature of the substrate plate is raised, oxygen and selenium from the atmosphere and cadmium from the film react on the surface of the film to form an intermediate oxide, for instance, cadmium selenite (CdSeO_3), which is a salt of an oxyacid. This compound is redecomposed at higher temperatures, and therefore, transient formation and decomposition of the intermediate oxide takes place in the course of temperature raise. This gives nuclei which become sites where grain growth is initiated, and rearrangement of structure begins at the surface and it proceeds into the inner parts. Such intermediate steps promote grain growth and bring about narrow distribution of grain size.

If the atmosphere in which there is to be conducted the desired reaction should contain larger proportions of oxygen than prescribed for concomitance with vapours of selenium, for example, if the reaction is performed in the ordinary air, then oxidation will proceed in excess. This will cause to form an intermediate oxide whose growth should originally stop with the formation of a nucleus prominently to settle on the treated layer to constitute an objectionable surface deposit, with the resultant deterioration of the electric properties of said layer. This is the reason why the amount of oxygen in the heat treatment atmosphere must be limited when the synergistic effect of oxygen and selenium is expected. This limit is 10% by volume on the basis of the

volume of base or carrier gas such as argon or nitrogen. It is needless to say that too small an amount of oxygen does not work. In order to effectuate smooth creation of grain growth nucleus sites, at least 0.1% by volume of oxygen is necessary.

On the other hand it is rather difficult to determine a suitable amount of concentration of selenium vapour, since the partial pressure of selenium vapour in the heat treatment atmosphere is related to the electrical properties of finished products, but at least 1 mm Hg will suffice. A temperature of at least 450°C for the heat treatment is required since the treatment is carried out without the aid of a flux.

The invention has been explained above with respect to cadmium selenide layer in particular. However, this invention is effectively applicable to compounds of Groups II and VI in general such as cadmium sulfide, cadmium telluride, zinc sulfide, zinc selenide, zinc telluride, and a mixture (solid solution or heterogeneous mixture), and films of multi-layer structure of these compounds, too. Layers of these compounds may contain known impurities. The inert gases which constitute the main component of the heat treatment atmosphere are argon, nitrogen or a mixture thereof. In conclusion, the process of this invention is characterized in that nuclei necessary for uniform grain growth are provided on the surface of a film to be treated by causing formation and decomposition of intermediate oxide, such as salt of an oxyacid, on the surface of the film in the course of the heat treatment.

According to this invention, grain growth is effected without using any flux, the film to be treated is not contaminated with the flux, and therefore, control of impurity content is much simplified.

EXAMPLE 1

A cadmium sulfoselenide of 3μ in thickness was vapour formed in an atmosphere of argon pressure of 0.5 mm Hg onto a substrate kept at 250°C. Then, the film was heat treated for 15 minutes at 600°C in a gaseous nitrogen atmosphere including 2% of volume of oxygen and under coexistence with a selenium vapour as indicating one half of a saturated vapour pressure at 600°C. The vapour formed film had a grain size of about 2000Å. After the heat treatment, however, the grain size of the film was grown to 2μ and a film with uniform grain size distribution was obtained.

The cadmium sulfoselenide film was prepared from a composition of cadmium sulfide and cadmium selenide whose molar ratio was preliminarily adjusted to be 1:2. That is, the composition ratio was preliminarily adjusted so that a wavelength present at a peak position of the spectral sensitivity of the film is in a range between about 5000Å constituting the fundamental absorption edge of cadmium sulfide and 7000Å constituting the fundamental absorption edge of cadmium selenide. The composition ratio, however, can be varied according to the usage of the adjusted film.

EXAMPLE 2

A cadmium sulfoselenide film of about 2μ in thickness prepared from a composition of cadmium sulfide and cadmium selenide whose molar ratio was preliminarily adjusted to be, for example, 1:2 was vapour formed, in an atmosphere of an inert gas, for example, an argon pressure of 0.8 mm Hg, onto a substrate kept at 250°C. Then, the film was heat treated for 15 min-

utes at 550°C in an inert gas atmosphere of, for example, nitrogen or argon, including 1.5% by volume of oxygen and under coexistence with a sulfur vapour as indicating one half of a saturated vapour pressure at 550°C.

The vapour formed film had a grain size of about 2000 Å. After the heat treatment, however, the grain size of the film was grown to about 1 μ and a film with uniform grain size distribution was obtained.

EXAMPLE 3

A cadmium sulfoselenide film of about 2 μ in thickness prepared from cadmium sulfide and cadmium selenide whose molar ratio is preliminarily adjusted to be, for example, 1:2 was vapour formed in an atmosphere of an argon pressure of 0.8 mm Hg onto a substrate kept at 250°C. The film was heat treated for 15 minutes at 580°C in an inert gas atmosphere of nitrogen or argon including 2% by volume of oxygen and under coexistence with a selenium vapour and a sulfur vapour as both showing one half of a saturated vapour pressure. The vapour formed film had a grain size of about 2000 Å. After the heat treatment, however, the grain size of the film was grown to about 1 μ and a film with uniform grain size distribution was obtained.

EXAMPLE 4

A cadmium selenide film of 2 μ in thickness was vapour formed in an atmosphere of an argon pressure of 1 mm Hg onto a substrate kept at 250°C. The film was heat treated for 15 minutes at 550°C in an atmosphere of an inert gas, for example, nitrogen or argon, including 1% by volume of oxygen and under coexistence of a sulfur vapour as indicating one half of a saturated vapour pressure at 550°C. The vapour formed film had a grain size of about 2000 Å. After the heat treatment, however, the grain size of the film was grown to about 1 μ and a film with uniform grain size distribution was obtained.

To prevent an excess replacement of the surface of a cadmium selenide film by cadmium sulfide, the heat treatment may be made, in this case, under coexistence with both said sulfur vapour and a selenium vapour as indicating a saturated vapour pressure at the heat treating temperature.

EXAMPLE 5

A cadmium sulfide film of 2.5 μ in thickness was vapour formed in vacuum onto a substrate kept at 120°C. Then, the film was heat treated for 20 minutes at 580°C in an inert gas atmosphere of, for example, nitrogen or argon including 3% by volume of oxygen and under coexistence with a selenium vapour as indicating one half of a saturated vapour pressure at 580°C. The vapour formed film had a grain size of 1000 Å. After the heat treatment, however, the grain size of the film was grown to about 1.5 μ and a film with uniform grain size distribution was obtained.

To prevent an excess replacement of the surface of a cadmium sulfide film by cadmium selenide, the heat treatment may be effected, in this case, under coexistence of both said selenium vapour and a sulfur vapour as indicating a saturated vapour pressure.

EXAMPLE 6

A cadmium sulfide film of 1 μ in thickness was vapour formed in an atmosphere of an argon pressure of 0.8

mm Hg onto a substrate kept at 200°C. Then, a cadmium selenide film of 2.5 μ in thickness was vapour formed onto the cadmium sulfide film. The composite film was heat treated for 10 minutes at 620°C in an inert gas atmosphere of nitrogen or argon including 1.5% by volume of oxygen and under coexistence with a selenium vapour as indicating a saturated vapour pressure at the heat treating temperature. The vapour formed composite film had a grain size of about 2000 Å. After the heat treatment, however, the grain size of the composite film was grown to 1 μ and a film with uniform grain size distribution was obtained.

EXAMPLE 7

A cadmium sulfide film of 2 μ in thickness was vapour formed in an atmosphere of an argon pressure of 0.8 mm Hg onto a substrate kept at 200°C. Then, a cadmium selenide film of 2 μ in thickness was vapour formed onto the cadmium sulfide film. The composite film was heat treated for 15 minutes at 600°C in an inert gas atmosphere of, for example, nitrogen or argon including 1% by volume of oxygen and under coexistence with a sulfur vapour as indicating one half of a saturated vapour pressure at 600°C. The vapour formed composite film had a grain size of about 2000 Å. After the heat treatment, however, the grain size of the composite film was grown to about 1 μ and a film was uniform grain size distribution was obtained.

EXAMPLE 8

A cadmium sulfide film of 2 μ in thickness was vapour formed in an atmosphere of an argon pressure of 0.8 mm Hg on a substrate kept at 200°C. Then, a cadmium selenide film of 2 μ in thickness was vapour formed onto the cadmium sulfide film. The composite film was heat treated for 10 minutes at 600°C in an inert gas atmosphere of, for example, nitrogen or argon including 1.5% by volume of oxygen, and under coexistence with a selenium vapour and a sulfur vapour as both indicating a saturated vapour pressure at the heat treating temperature. The vapour formed composite film had a grain size of about 2000 Å. After the heat treatment, however, the grain size of the composite film was grown to about 1 μ and a film with uniform grain size distribution was obtained.

What we claim is:

1. A process for preparing a composite layer consisting of a CdS layer and a CdSe layer which comprises forming said composite layer on a substrate plate and heat-treating it in an atmosphere comprising an inert gas, 0.1–10% by volume of oxygen on the basis of said inert gas and vapour selected from the group consisting of selenium, sulfur and mixtures of sulfur with selenium, whereby uniform-grain growth with narrow range grain size distribution is effected.

2. A process for preparing a layer of Group II-VI compound which comprises forming a layer of cadmium selenide on a substrate plate and heat-treating it in an atmosphere comprising an inert gas, 0.1–10% by volume of oxygen on the basis of said inert gas and vapour of sulfur or mixtures of sulfur with selenium, whereby uniform grain growth with narrow range grain size distribution is effected.

3. A process for preparing a layer of a Group II-VI compound which comprises forming a layer of cadmium sulfide on a substrate plate and heat-treating it in an atmosphere comprising an inert gas, 0.1–10% by

volume of oxygen on the basis of the inert gas and vapour of selenium or mixtures of selenium with sulfur, whereby uniform grain growth with narrow grain size distribution is effected.

4. A process for preparing a layer of a Group II-VI compound which comprises forming a layer of cadmium sulfoselenide on a substrate plate and heat-treating it in an atmosphere comprising an inert gas, 0.1-10% by volume of oxygen on the basis of the inert gas and vapour selected from the group consisting of selenium, sulfur and mixtures thereof, whereby uniform grain growth with narrow grain size distribution is effected.

5. The process of claim 2 wherein said atmosphere consists essentially of an inert gas selected from the

group consisting of nitrogen and argon, 0.1-10% by volume of oxygen on the basis of the inert gas and vapour of sulfur or mixtures of sulfur with selenium.

6. The process of claim 3 wherein said atmosphere consists essentially of an inert gas selected from the group consisting of nitrogen and argon, 0.1-10% by volume of oxygen on the basis of the inert gas and vapour of selenium or mixtures of selenium with sulfur.

7. The process of claim 4 wherein said atmosphere consists essentially of an inert gas selected from the group consisting of nitrogen and argon, 0.1-10% by volume of oxygen on the basis of the inert gas and vapour selected from the group consisting of selenium, sulfur and mixtures thereof.

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