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[54] **METHOD FOR THE PREPARATION OF A ZINC
OXIDE FILM**
6 Claims, 3 Drawing Figs.

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215, 211, 93.3, 106 R, 217

[56]

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ABSTRACT: This invention relates to a method for the preparation of a zinc oxide by oxidizing a zinc selenide film. In detail, this invention relates to a method for the preparation of a zinc oxide film by vapordepositing zinc selenide as an evaporating source in place of zinc oxide to produce a zinc selenide film and then oxidizing said zinc selenide film.

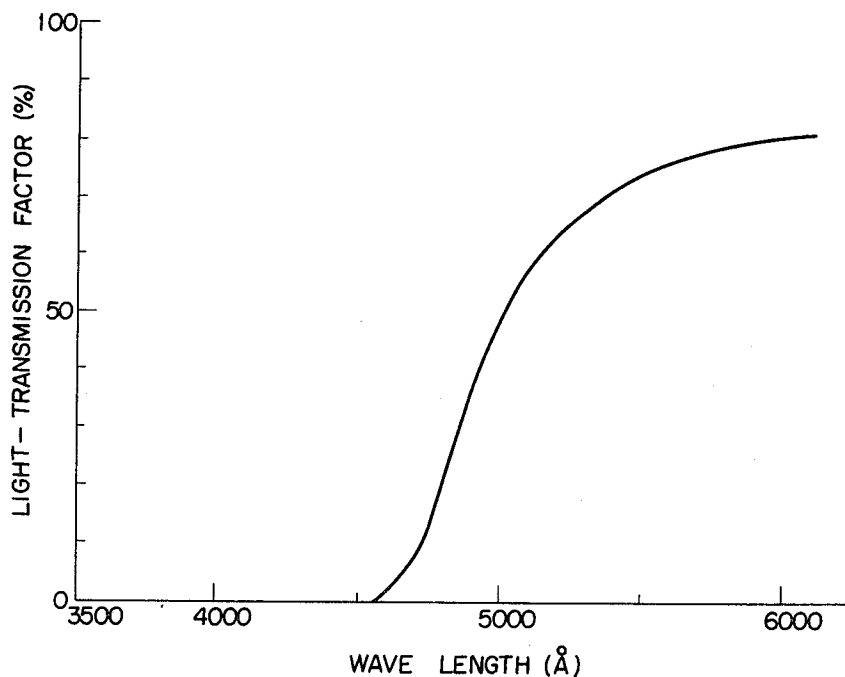


FIG. 1

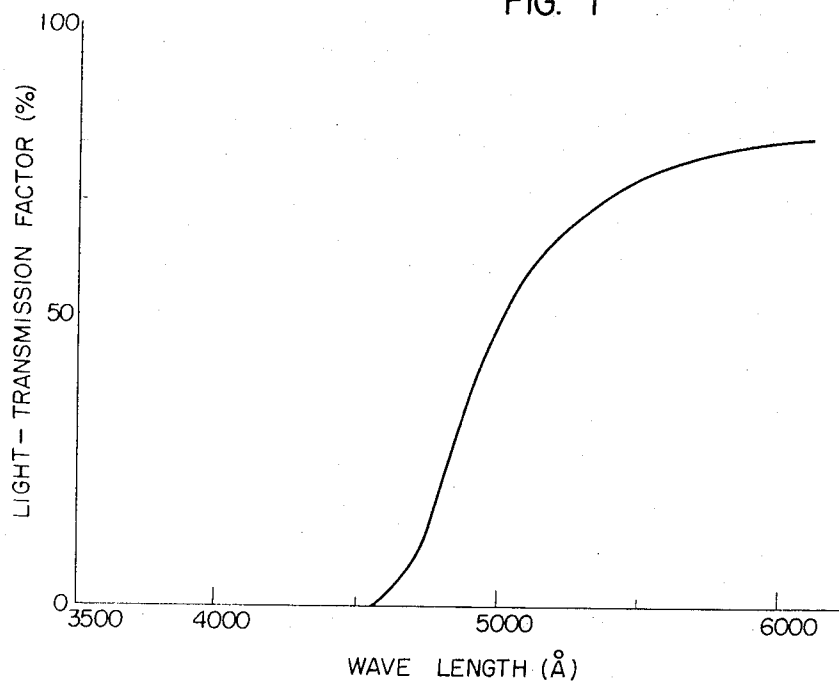


FIG. 2

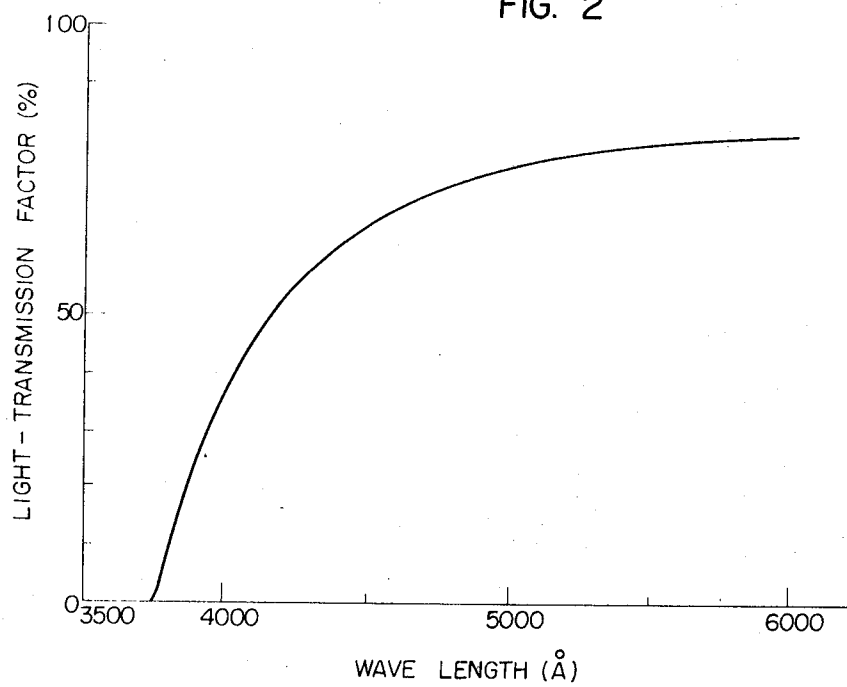
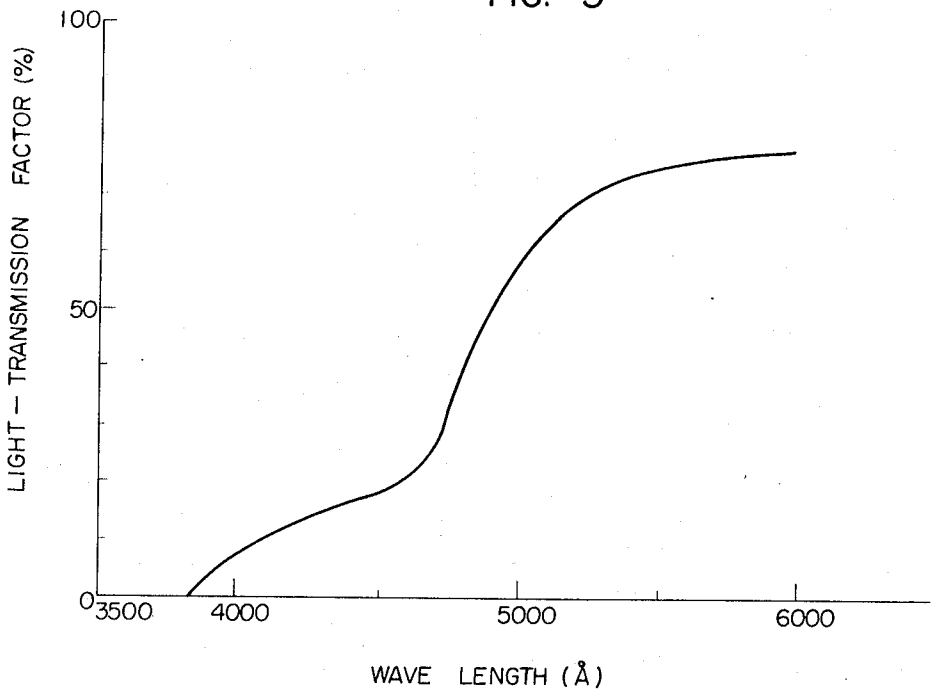


FIG. 3



METHOD FOR THE PREPARATION OF A ZINC OXIDE FILM

PRIOR TECHNIQUES AND A BACKGROUND OF INVENTION

Heretofore, a zinc oxide film was regarded as a material for use as an electric oscillation-electroacoustic transducer as the zinc oxide film has a high piezoelectric constant. However, a zinc oxide has a high sublimation temperature of above 1,800° C. and therefore the zinc oxide can hardly be formed into the zinc oxide film by using the conventional resistance heating system and the vacuum evaporation technique. Such a defect of the prior technique is due to the fact that the zinc oxide having the high sublimation temperature is used as the evaporating source. Accordingly, there is usually practiced by the sputtering a powder of zinc oxide in a reduced atmosphere for forming the zinc oxide film. Such a sputtering technique, however, has the defect that the zinc oxide film can hardly be formed into a thick film and has little utility in practice. Further, there are few reports that a zinc oxide film has been made by the sputtering technique and there was not found a suitable method using an impure additive. Still further, it is difficult to produce a zinc oxide film by using such an impure additive in carrying out the technique in which the zinc oxide itself having the high sublimation temperature is used as the evaporating source. This invention has been developed under the above mentioned environment for producing the zinc oxide film and it is based on the principles that the defects adherent to the conventional vacuum evaporation technique can be removed if the zinc oxide film will be produced by using a zinc compound, which is different from the zinc oxide and has a lower sublimation temperature than that of the zinc oxide, as an evaporating source to produce a vacuum evaporation film and then oxidizing said film. In accordance with this invention, zinc selenide (ZnSe) is used as the evaporating source in place of zinc oxide for producing the zinc oxide film.

OBJECTS OF INVENTION

An object of this invention is to provide an excellent zinc oxide film by removing the difficulties encountered in the preparation of the zinc oxide film by the conventional technique.

Another object of this invention is to provide a method for the preparation of a zinc oxide film by forming a zinc selenide film which can be easily oxidized into a zinc oxide film at a relatively low temperature.

A further object of this invention is to provide a method for the preparation of a zinc oxide film by effectively adding a desirable impure additive to the zinc oxide film by removing the difficulties encountered in the preparation of the zinc oxide film by the conventional technique.

A still further object of this invention is to provide a method for the preparation of a zinc oxide film 1) effectively adding a desirable impure additive in a simple manner 2) the zinc oxide film

EXPLANATION OF DRAWINGS

In the accompanying drawings,

FIG. 1 shows a curve illustrating the spectrotransmission factor of a zinc selenide film which is produced by the vacuum evaporation technique.

FIG. 2 shows a curve illustrating the spectrotransmission factor of a zinc oxide film which is produced in accordance with this invention.

FIG. 3 shows a curve illustrating the spectrotransmission factor of a film which consists of zinc selenide and zinc oxide, and is produced in accordance with this invention.

DETAILED EXPLANATION OF INVENTION

This invention is illustrated hereinafter by referring to an example in which zinc selenide is used.

In an embodiment of this invention, at the first step a zinc selenide film is formed by depositing a vapor of zinc selenide by using the vacuum evaporation technique and the like. Then, the zinc selenide film is oxidized into a zinc oxide film by subjecting said zinc selenide film to thermal treatment in the presence of an atmosphere such as oxygen, air or a mixed gas containing an inert gas and oxygen or the like which contains oxygen in an amount sufficient for producing a zinc oxide film by oxidizing a zinc selenide film. The temperature used for heating the zinc selenide film and oxidizing said film is a temperature at which a selenium oxide is sublimated but a zinc oxide is not sublimated. The selen dioxide (SeO₂) has a sublimation temperature of 315° C. to 317° C. (refer to the book entitled as "Handbook of Chemistry and Physics," 39th edition, 1957-1958, published from the Chemical Rubber Publisher) and therefore it is necessary to heat the zinc selenide at a temperature of above 315° C. for oxidizing it. When the thermal treating of the zinc selenide film is conducted at a temperature within the temperature range in which the selenium oxide is sublimated but the zinc oxide is not sublimated, a selenium component contained in the zinc selenide film is sublimated and only the zinc oxide is retained in the resulting film.

A preferable embodiment of this invention is illustrated by the following example. In the example, zinc selenide was vapor deposited to form a film having a thickness of 3 microns onto a glass plate which was kept at 300° C. in a vacuum vessel under the reduced pressure of about 1×10^{-7} mm Hg. In this case, a powder of the zinc selenide having a purity of above 99.999 percent was used as the evaporating source and it was vaporized for 20 minutes for depositing a zinc selenide film by using the resistance-heating technique. FIG. 1 shows a curve illustrating the spectrotransmission factor of the zinc selenide film thus produced as measured at room temperature. As shown by the curve, the basic absorption occurred on 4,700 Å. as in the single crystal of the zinc selenide. It should be understood that the curve as shown in FIG. 1 is modified by depending upon the conditions for carrying out the vapor-depositing technique and the thermal treating after the zinc selenide film was produced. Then, the zinc selenide film thus produced was heated at 550° C. for 2 hours in the air and the heated film was tested for its spectrotransmission factor as shown by the curve in FIG. 2. It was observed that the basic absorption occurred on 3,850 Å. as shown in the curve which corresponds to the basic absorption of the zinc oxide. Also, the heated film was tested for its X-ray diffraction and found that the diffraction peak corresponds to that of the zinc oxide. This proves the fact that the heated film was a zinc oxide film which was produced by oxidizing the zinc selenide film.

Now, it is well known that the optical and electrical properties of the zinc selenide film are varied depending on the vapor-depositing conditions such as the depositing speed, the temperature of the base plate and the pressure of the residual gas, and also the thermal treatment which is conducted in vacuum and in the presence of the inert gases after the zinc selenide film was deposited. Also it is well known that the speed of the oxidation reaction is varied depending on the properties of the zinc selenide film when it was subjected to thermal treatment in the presence of an atmosphere containing oxygen. In general, the film is easily oxidized when it has incomplete structure. Although the zinc selenide film was illustrated to be produced by using the vacuum evaporation technique and the resistance-heating technique, it is also produced by using various techniques such as the electron beam technique and the sputtering technique. Therefore, it should be understood that any zinc selenide film is within the scope of this invention as far as the zinc selenide film is oxidized to the zinc oxide film regardless of the conditions and techniques for the preparation of the zinc selenide film.

When the zinc selenide film is subjected to thermal treatment, it is possible to produce a film containing the zinc oxide and the zinc selenide in a suitable proportion by selecting oxidation conditions so that the zinc selenide film is not

completely oxidized by shortening a period of time for thermal treatment or reducing the temperature for thermal treatment. For example, the zinc selenide film can be heated at 500° C. for 20 minutes in the air to produce a film containing the zinc oxide and the zinc selenide. FIG. 3 shows the curve indicating the spectrotransmission factor of such a film in which the basic absorptions occurred at the points corresponding to those of the zinc selenide and the zinc oxide respectively.

Also, it is considered that the atmosphere for oxidizing the zinc selenide film may be widely varied. For example, it is possible to use a water vapor in addition to an inert gas and oxygen for accelerating or delaying the oxidation speed. Also, it should be noted that the oxidation is affected by changing the pressure of the atmosphere and it is possible to use the atmospheric pressure, reduced pressure and increased pressure. Therefore, it should be understood that any gaseous atmospheres and any pressures may be used in accordance with this invention as far as the atmospheres and the pressures of such atmospheres can be used for the preparation of the zinc oxide film by oxidizing the zinc selenide film.

Another preferable embodiment of this invention is illustrated by the following example. In the example, a zinc selenide film was formed on a refractory and electric insulating baseplate such as glass, ceramics, ruby, mica or the like by heating a zinc selenide at a temperature of 800° C. to 1,200° C. by using the vacuum evaporation technique in which the resistance-heating or the electron beam-heating is used, or the sputtering technique under a reduced pressure of the atmosphere or the vapor-depositing technique in the presence of the stream of zinc selenide or the thermal decomposing technique in which a chemical reaction is used. Therefore, it should be understood that any zinc selenide film may be used in accordance with this invention regardless of the techniques for the preparation of the zinc selenide film. Now, the example is illustrated by the case when the zinc selenide film was prepared by using the resistance-heating technique. The baseplate was kept at a temperature of 200° C. to 400° C. for improving the crystals of the zinc selenide or strengthening the adhesive strength of the zinc selenide film. It is, of course, possible to produce the zinc selenide film on a baseplate without heating. The thickness of the zinc selenide film can be controlled as desired. If desired, the crystallinity of the zinc selenide can be improved by heating it at a temperature of 400° C. to 700° C. for 30 minutes to 300 minutes under vacuum or in the presence of an inert gas before the zinc selenide film was oxidized. The zinc selenide film was placed in an atmosphere containing oxygen under a reduced pressure and the electric field of direct current or alternative current was applied to the atmosphere to produce the ionized oxygen ions which accelerate its migration and the zinc selenide film was impacted with the ionized oxygen ions and easily oxidized to the zinc oxide film. In order to accelerate the oxidation of the zinc selenide film by impacting the ionized oxygen ions, it is effective to concentrate or deflect the ionic beam by the action of the electric field or the electromagnetic field. When the baseplate is not heated, it is observed that the zinc selenide film is oxidized by placing it in the oxygen atmosphere or the oxygen-containing atmosphere which is ionized by the action of the alternative electric field and maintained at a reduced pressure of 10^{-7} to 10^{-1} mm. Hg. When the zinc selenide film is oxidized at room temperature, a selenium oxide is retained in the zinc selenide film as a selen dioxide (SeO_2) is sublimated at a temperature of 315° C. to 317° C. at the atmospheric pressure. The zinc selenide film, however, is completely oxidized to the zinc oxide film having the high sublimation temperature when the zinc selenide film is heated at a temperature of 320° C. to 400° C. and oxidized by the impact of the ionized oxygen ions while the selenium oxide is sublimated. In such a case, it is possible to oxidize the zinc selenide film at a relatively low temperature but the thermal diffusion of the zinc oxide is not highly effected and so the zinc selenide film is oxidized only at the upper layer to produce a film having the junction of the zinc oxide and the zinc sele-

nide. It is, of course, possible to oxidize homogeneously the zinc selenide film by increasing the temperature of the baseplate. It should be understood that the zinc selenide film can be oxidized by heating it in the presence of an atmosphere containing oxygen which is not ionized.

Next, this invention is illustrated by an example in which a desirable impure additive is previously added to the zinc selenide and then the resulting zinc selenide is oxidized to the zinc oxide film.

In carrying out the method of the example, at first, a powder of the zinc selenide having a purity of 99.999 percent was prepared. It is noted that the low grade and cheap zinc selenide may be used and also that the single crystalline or agglutinative massive zinc selenide may be used with a gaseous product to be released from the powdered zinc selenide should be avoided. When indium was used as an impure additive, indium chloride, InCl_3 or indium nitrate, $\text{In}(\text{NO}_3)_3$ was dissolved in a solvent such as methyl alcohol or distilled water to form a solution and then the solution was mixed with the powder of the zinc selenide in a suitable amount under agitation and then the resulting powder was dried under reduced pressure in a drier to remove the solvent or water. The dried powder was calcined in the presence of an inert gas or a hydrogen gas or a mixed gas of the inert gas and the hydrogen gas. Such a procedure is effective for producing the calcined powder containing the impure additive in a larger amount and adding the impure additive to the zinc selenide in a large amount when the calcined powder is used as the vaporizing source.

The calcined powder was vaporized and deposited onto the baseplate to form a zinc selenide film. The concentration of indium contained in the zinc selenide film thus produced was reduced to $1/n$ to $0.1/n$ (n is an integer) time amount of indium contained in the calcined powder but the indium can be homogeneously distributed in the zinc selenide film. Such a phenomenon is usually observed in the vacuum evaporation technique and it is considered that such a phenomenon is based on the difference in the vapor pressure between the impure additive and the base matrix. It is well known in the art that such a phenomenon can be removed by using the flash-vacuum evaporation technique.

The zinc selenide film containing indium as the impure additive was subjected to thermal treatment in the presence of oxygen or the air or an inert gas and oxygen. When the zinc selenide film was formed on the baseplate such as a glass plate or a glass plate on which a transparent and electric conductive layer was formed, it is preferable to heat such as baseplate at a temperature of 400° C. to 650° C. for 1 hour to 8 hours in the air for oxidizing the zinc selenide film to the zinc oxide film. When the zinc selenide film was heated at a temperature of 300° C. to 1,800° C., the selenium oxide was sublimated but the zinc oxide and the indium were retained in the zinc selenide film. The indium which was added into the zinc selenide film is a three valency element and so the indium can be replaced with the two valency zinc at a lattice point to produce an indium atom having one positive valency and such a positive valency indium atom acts as a donative impurity which is a source for transmitting an electron. It is considered that the donative impurity can easily be excited at room temperature and therefore the zinc oxide film becomes to have a low specific resistance by adding the indium as the impure additive to the zinc oxide film. Also, it is possible to control the specific resistance in a wide range by varying the concentration of the indium contained in the zinc oxide film. In the same manner, aluminum, gallium and other elements having three valencies can be used as the impure additive.

On the contrary to the donative impurity, it is considered that Au, Ag, Cu, or Li, Na and K which have one valency can be used as the impure additives for increasing the specific resistance of the zinc oxide film. It should be understood that this invention covers the use of any impure additives regardless of their functions and effects for achieving the decreasing and increasing of the specific resistance of emitting

the luminescent radiation or improving the crystallinity of the zinc oxide film.

Still further, some embodiments of this invention are illustrated hereinafter and it should be noted that this invention consists of the three essential steps as listed below. *a.*

- a. The zinc selenide film containing the impure additive is produced. *b.*
- b. The zinc selenide film containing the impure additive is oxidized. *c.*
- c. The zinc oxide film containing the impure additive is produced.

The step (a) is carried out by using the vacuum evaporation technique, in which the resistance-heating technique is used, the electron beam evaporation technique, the flash evaporation technique or other technique, in which zinc and selenium are vaporized respectively by using an individual vaporizing source, for producing the zinc selenide film. The impure additive can be added into the zinc selenide film by using various techniques which are classified into the three types in terms of the time when the impure additive is added.

1. The zinc selenide is mixed with the impure additive before the zinc selenide is deposited on the baseplate as the zinc selenide film.

2. The impure additive is mixed with the zinc selenide film after the zinc selenide is deposited on the baseplate as the zinc selenide film. Such a procedure is exemplified as follows:

I. The zinc selenide is heated in the presence of a gaseous atmosphere containing an impure additive.

II. The zinc selenide is immersed into a solution containing the impure additive and then impregnated zinc selenide is subjected to thermal treatment.

III. The impure additive is mixed with the powder of the zinc selenide and then the base plate is inserted into the mixture under heating.

IV. The thin layer of the impure additive is formed on the zinc selenide or such a thin layer is formed under the layer of zinc selenide and then the resulting zinc selenide is subjected to thermal treatment.

V. The impure additive is ionized in the presence of the electric field to accelerate the speed of the ionized additive ions and the ions are entered into the zinc selenide film.

3. The zinc selenide is vaporized and simultaneously the impure additive, which is placed in the outside of the system, is vaporized to produce the zinc selenide film.

It is apparent to those skilled in the art that there are various modifications of the step (a) and so this invention covers the use of any zinc selenide film containing the impure additive which can be retained in the zinc oxide film after the zinc selenide film is oxidized regardless of the techniques for the preparation of the additive-containing zinc selenide film.

The step (b) can be carried out by using oxygen, air or a mixture of an inert gas and oxygen as the oxidizing atmosphere under the atmospheric pressure or increased pressure or reduced pressure. Also it is preferable to use the oxidizing atmosphere containing the impure additive for oxidizing the zinc selenide film and adding the additive into the zinc oxide film. Also it is possible to produce a film containing the zinc oxide and the zinc selenide by oxidizing the zinc selenide film in which it is partially oxidized. It should be understood therefore that this invention covers the use of any atmosphere so far as the atmosphere acts to oxidize the zinc selenide film to form the zinc oxide film.

This invention can be applied to the manufacture of a photoconductive element, an electroacoustic transducer and a switching element or an element using the light transmissibility of the zinc oxide film having the good transparency.

In accordance with this invention, the zinc oxide film can easily be manufactured at a relatively low temperature and also the impure additive can easily be added into the zinc oxide film. The additive-containing zinc selenide or zinc sulfide can be tested for the concentration of the additive. Also the zinc selenide film can be oxidized in the presence of the

oxidizing atmosphere containing the impure additive. The metals such as aluminum indium, thallium and gallium can be used for decreasing the specific resistance of the zinc oxide film and on the contrary, the metals such as gold, silver, copper, alkali metals, iron and its family, and rare earth metals can be used for increasing the specific resistance of the zinc oxide film. The techniques for incorporating the impure additive in the zinc selenide film are as mentioned above. The oxidizing atmospheres used in this invention are as mentioned above. The examples of the baseplates are not only limited to glass, ceramics and mica but also can be applied to an electroconductive metal plate, a crystalline plate and a transparent insulating plate on which a transparent conductive film such as a tin oxide film or a metal film of semitransparency is formed.

From the foregoing, it is obvious that this invention has the advantageous merits as listed below.

1. The zinc oxide film can be produced at relatively low temperatures.
2. The zinc selenide film can be oxidized on the upper layer to produce their junction.
3. The zinc oxide film can be produced in the homogeneous state.
4. The impure additive can easily be added into the zinc selenide film.

This invention can be applied to the manufacture of various devices or elements such as an optical element, an electric element, a resistant element, a photoconductive element, and an electric oscillation-electroacoustic transducer. The application of this invention is varied depending on the nature and structure of the baseplate on which the zinc selenide film is formed. Although this invention was illustrated in the case when the glass plate is used as the baseplate, it should be noted that any materials, which are maintained in the solid state under the conditions for evaporating the zinc selenide can be used as the baseplate. Examples of such materials are ceramics, glass, plastics, mica, crystals of various alkali halides, a plate quartz and a rod quartz, foils of metals such as aluminum molybdenum, gold, tantalum and tungsten, compounds of metals selected from II Group to V Group of the periodic Table and semiconductors. In order to obtain an electric signal, a metallic layer is formed on an insulating baseplate and then the zinc selenide film is disposed on the metallic layer. In order to produce a light transmission plate, an electroconductive layer is formed on an electric insulating baseplate such as glass and then the zinc selenide film is disposed on the electroconductive layer. In a special case, the zinc selenide film, which was disposed on the baseplate, is removed from the baseplate and then the zinc selenide film is oxidized and also the zinc selenide film is formed on the baseplate and the zinc selenide film is oxidized as it is and then removed from the baseplate.

As mentioned above, this invention can produce a zinc oxide film with ease and at relatively low temperatures without the sublimation of zinc oxide itself. Also the zinc oxide film has the uniformity and the smooth surface and therefore such a zinc oxide film can be used for the manufacture of a sandwich type electrode element or used as a light transmission element.

What we claim is:

1. A method for the preparation of a zinc oxide film, comprising the steps of (1) growing a zinc selenide film on a baseplate and (2) oxidizing the zinc selenide film over the whole or part thereof in the presence of an atmosphere containing oxygen in an amount sufficient to cause an oxidation reaction to produce the zinc oxide film.
2. A method for the preparation of a zinc oxide film, by comprising the steps of growing (1) a zinc selenide film on a solid base plate and (2) impacting the zinc selenide film with ionized oxygen ions in the presence of an atmosphere containing oxygen under a reduced pressure to oxidize the zinc selenide film.

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3. A method for the preparation of a zinc oxide film containing an impure additive, comprising the steps of (1) growing a zinc selenide film on a baseplate, (2) adding the impure additive to the zinc selenide film and (3) oxidizing the zinc selenide film over the whole or part of the baseplate in the presence of an atmosphere containing oxygen in an amount sufficient to cause an oxidation reaction to produce the zinc oxide film.

4. A method for the preparation of a zinc oxide film containing an impure additive, comprising the steps of (1) growing a zinc selenide film on a baseplate, (2) adding the impure additive to the zinc selenide film and simultaneously (3) oxidizing the zinc selenide film in the presence of an atmosphere containing the impure additive and oxygen in an amount sufficient to cause an oxidation reaction to produce the zinc oxide film.

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5. A method for the preparation of a zinc oxide film containing an impure additive, comprising the steps of (1) growing a zinc selenide film on a solid baseplate, (2) adding the impure additive to the zinc selenide film and (3) impacting the zinc selenide film or the zinc sulfide film with ionized oxygen ions in the presence of an atmosphere containing oxygen under a reduced pressure to oxidize the zinc selenide film.

6. A method for the preparation of a zinc oxide film, comprising the steps of growing a zinc selenide film on a solid baseplate and (2) impacting the zinc selenide film with ionized oxygen ions in the presence of an atmosphere containing oxygen under a reduced pressure to oxidize surface parts of the zinc selenide film to form a junction between a zinc oxide film and a zinc selenide film all over the surface or in part of the surface of the said zinc oxide film.

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