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T. W. O'KEEFFE

3,686,028

MASKED PHOTOCATHODE.

Original Filed April 29, 1968

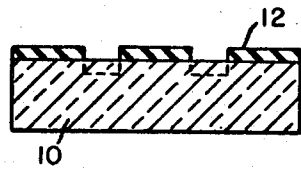


FIG. 1.

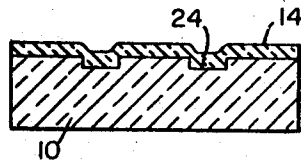


FIG. 2.

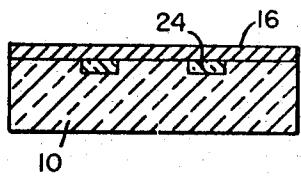


FIG. 3.

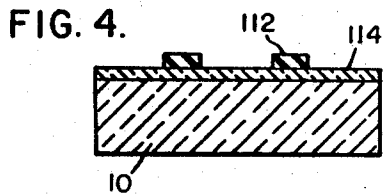


FIG. 4.

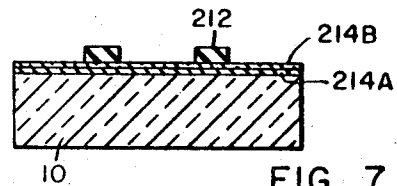


FIG. 7.

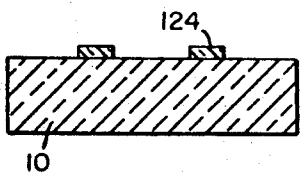


FIG. 5

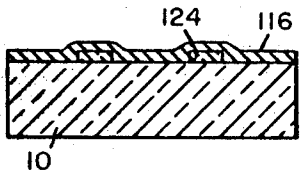


FIG. 6.

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MASKED PHOTOCATHODE

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Original application Apr. 29, 1968, Ser. No. 724,839, now Patent No. 3,588,570, dated June 28, 1971. Divided and this application Sept. 24, 1970, Ser. No. 74,992

Int. Cl. H01j 39/06

U.S. Cl. 117—212

3 Claims

ABSTRACT OF THE DISCLOSURE

A shadow mask particularly for use with ultraviolet sensitive photocathodes is provided of a material that does not transmit ultraviolet radiation and which, furthermore, does not absorb other wavelength radiation, such as visible. This permits the photocathode to be immediately adjacent the mask because when exposed by a high intensity light source appreciable heating in the mask material that would damage the photocathode does not occur. The mask may be, for example, an ultraviolet absorber, such as titanium ions in a titanium oxide.

CROSS REFERENCE TO RELATED APPLICATIONS

The application is a division of my application S.N. 724,839, filed Apr. 29, 1968, now Pat. No. 3,588,570, issued June 28, 1971, the assignee of which is the same as that of the present application.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to masked photocathodes particularly those intended for exposure to an air environment.

Description of the prior art

Numerous photocathode materials are known each having a characteristic spectral sensitivity and also a susceptibility to alteration by ambient conditions such as the chemical nature of the atmosphere to which it is subjected and the temperature.

In general a pattern is optically imaged upon the photocathode to produce a corresponding electron image. In certain applications the creation of the optical image apart from the photocathode can result in lost resolution making such a system impractical.

In copending application Ser. No. 640,164, filed May 22, 1967, now Pat. No. 3,615,935, issued Oct. 26, 1971, by the present inventor and Larkin and assigned to the assignee of this invention, there is disclosed the use of impinging electrons to alter the etching rate of insulators such as silicon dioxide. Such an effect has application to the fabrication of microminiature semiconductor devices and integrated circuits. As mentioned therein, a scanning electron beam may be used but, for a quicker effect, important over large area substrates, an electron image generated by a photocathode may be used. Reference to the above copending application should be made for further information as background to this invention. Other instances of the application of air stable photocathodes in microelectronic component fabrication exists where an electron image is desired for exposure of other electron sensitive materials such as an electron sensitive resist material.

SUMMARY OF THE INVENTION

The invention has among its purposes and objects the provision of a masked, air stable photocathode that can be readily made and employed in systems such as for the fabrication of microelectronic components utilizing elec-

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tron sensitizing effects in a layer on a workpiece in order to assist in defining a pattern therein.

The photocathode comprises a support of a material transmissive to the radiation of interest, such as fused quartz, on a surface of which is a pattern of material that does not transmit the radiation of interest, particularly ultraviolet radiation. The pattern layer also has the quality of not significantly absorbing other radiation such as in the visible or infrared portions of the spectrum so as to prevent appreciable heating of a subsequently applied photocathode layer which may be of a material such as gold or palladium selected because it is stable in air and hence permits demounting a system to change masks as necessary.

The mask layer may be one that selectively absorbs ultraviolet radiation and is transparent to other radiation. Examples of such materials are titanium ion (Ti^{+4}) containing materials such as oxides of titanium (TiO_2 and/or related oxides). The mask layer may also be one that reflects all radiation such as a layer of metallic aluminum in which case special care has to be taken to provide protection with respect to the photocathode for reasons more fully discussed hereinafter.

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1 and 7 are sectional views at different or various stages in fabrication of a masked photocathode in accordance with this invention wherein FIGS. 3, 6 and 7 are alternative embodiments of the completed structure.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the drawing, a supporting substrate 10 is chosen of a material transmissive to the radiation of interest that may be for example, fused quartz. The optical quality of the support 10 is not critical since the mask and photocathode layers are immediately adjacent each other, so that any scattering caused by imperfections in the support is harmless.

In one manner of practicing the invention as shown in FIGS. 1 to 3, there is placed on a surface of the support 10, in a pattern that is a negative of the mask pattern ultimately desired, an etch resistant mask 12 such as of a commercially available photoresistant material applied, exposed and developed by conventional techniques. The masked support is subjected to a suitable etchant such as one of a solution of hydrofluoric and nitric acids, in the case of fused quartz, for a time sufficient to etch a pattern to a depth of at least about 600 angstroms in the exposed support surface.

The photoresist 12 is then removed and, as shown in FIG. 2, a layer 14 of an ultraviolet absorber is deposited over the surface. The layer 14 can be titanium ion containing material in the form of an oxide including titanium dioxide or other materials such as Fe^{+3} containing materials. When an oxide of titanium is deposited it may be by reactively sputtering titanium in an oxidizing atmosphere or by RF sputtering of the titanium oxide itself. Following deposition of the layer 14, the surface is polished back at least to the original surface to leave the pattern of the U.V. absorber 24 embedded in a flat surface as shown in FIG. 3. Over the flat surface is then deposited a photocathode layer 16, preferably an air stable photocathode such as one of those which are well known including metallic palladium, gold, platinum, aluminum, barium, copper or cesium iodide that may be deposited by, for example, vacuum evaporation.

FIGS. 3 to 6 illustrate an alternate sequence of operations for forming a masked photocathode. A continuous layer 114 of the mask material such as titanium oxide is deposited on a flat surface of the support 10. It is masked such as by a photoresist 112 and etched to produce the

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desired pattern 124, FIG. 5, and then a suitable photocathode layer 116 is deposited over the surface as shown in FIG. 3. To be able to use a convenient etch such as sulphuric acid, it may be desirable to employ a pattern of gold as a mask.

An additional alternative process is illustrated by FIG. 7. Here there is first deposited on the support a layer 214A of metallic titanium, such as by vacuum evaporation. It is first oxidized lightly such as at about 165° C. in air for about one hour to produce a surface portion 214B of oxide in a thickness of about 50 to 100 angstroms. Then photoresist pattern 212 is formed and etching is performed with an etch such as one of about 2% concentrated hydrofluoric acid to remove any exposed TiO and Ti. Following the removal of the photoresist, the remaining titanium is completely oxidized at about 400° C. for about 4 to 5 hours in air.

This procedure produces a structure like that of FIG. 5 and is preferable to merely etching a pattern in a titanium layer followed by its oxidation. In the application of the photoresist and its baking, usually carried out at about 160° C. for about 20 to 30 minutes, a thin oxide layer will form over the exposed titanium, but not under the photoresist, and undesirable sideways etching results more readily under the photoresist through the metallic titanium.

Among the advantages of masked photocathodes in accordance with this invention is that the mask 24 or 124 is directly in contact with the photocathode to avoid loss of resolution. Also, the mask is permanent and allows easy replacement of the photocathode layer 16 or 116 or reactivation of an existing photocathode since the layer of titanium oxide is not subject to etchants such as nitric acid or aqua regia normally used for the etching of layers of gold or palladium.

Where a totally reflecting mask is provided, instead of the mask having the U.V. absorbing properties of titanium oxide, it is necessary to provide protection of the mask layer. For example, a mask of metallic aluminum of thickness about 800 Å. may be provided on the support by conventional photoresist processing and covered by a protective layer such as of sputtered quartz having a thickness of about 1500 Å. over the entire surface. Any treatment of the subsequently applied photocathode layer will therefore not affect it.

It is known that heating will affect the properties of photocathodes. When used with a high intensity light source such as a mercury vapor lamp which produces considerable radiation apart from that of wavelength less than about 2600 Å. to which the air stable photocathode mate-

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rials are particularly sensitive, absorption of this additional radiation could cause local heating and affect the photocathode performance. However, in accordance with this invention other radiation is not absorbed by the mask and in the titanium ion containing materials is harmlessly transmitted or in the case of a reflecting mask is reflected away from the structure.

Masks in accordance with this invention also are not easily damaged due to their hardness and the good adherence to the support and as discussed in connection with FIGS. 1 to 3, they can be provided in a completely smooth, flat structure.

While the present invention has been shown and described in a few forms only it will be apparent that various modifications may be made without departing from its essential teachings.

I claim as my invention:

1. A process for forming a masked photocathode comprising:

- (1) depositing a layer of titanium metal on a flat surface of a support,
- (2) oxidizing said layer to a predetermined depth,
- (3) forming a predetermined pattern in a layer of photoresist deposited over said titanium oxide,
- (4) etching away the titanium oxide and underlying titanium extraneous to the pattern,
- (5) oxidizing the remaining titanium, and
- (6) depositing a layer of a photocathode material over said titanium oxide and the surface of said support upon which the titanium oxide is disposed.

2. The process of claim 1 in which the titanium layer is oxidized to a predetermined depth by heating at about 165° C. in air for about one hour.

3. The process of claim 2 in which the remainder of the titanium is oxidized by heating at about 400° C. for about 4 to 5 hours in air.

References Cited

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RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

96-36; 117-221; 156-17