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(54) METHOD FOR SELECTIVE ETCHING OF TITANIUM DIOXIDE

(71) We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED of Abacus House, 33 Gutter Lane, London, EC2V 8AH a British Company, do hereby declare

the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a method of selectively etching a layer of titanium oxide used as a mask for the localisation of the anodic oxidation of an oxidizable metal layer. It is already known to use the anodic oxidation of a metal layer, in particular aluminium, to effect the passivation of a semiconductor surface or the realization of localized contacts on said surface.

In order to obtain said anodic oxidation which thus is generally localised, a screen or mask is used which, for example, does not cover the parts to be oxidozed and which protects the parts which must not be treated.

An electrically insulating material, either a layer of impervious alumina, or a photosensitive lacquer or a layer of silicon dioxide is generally used as a mask. All the various methods using these masks present drawbacks: defects in the localisation are found in the case of alumina, bubbles may be present in the mask or the mask does not adhere adequately in the case of photosensitive lacquers, and protruberances may be present in silicon dioxide masks, the deposition of the latter necessitating temperatures which are unacceptably high.

Taking into account these numerous difficulties, it is more convenient to form the mask starting from a layer of titanium dioxide. Titanium dioxide can be deposited at a low temperature and in a thin layer which is free from bubbles. Moreover, titanium dioxide has the property of resisting corrosion and avoiding the formation of bubbles in the underlying layers.

It is for this latter reason that the etching and/or the removal of the titanium dioxide layer are very difficult. It has been found that titanium dioxide can withstand a great number of cold dilute acid solutions currently used in photoetching. It has meanwhile been found that titanium dioxide is sensitive to a hydrofluoric acid and ammonium fluoride solution but this solution also etches the metals generally disposed below the titanium dioxide layer and in particular aluminium, so that it becomes useless in these conditions for the photoetching or anodic oxidation treatments. In order to mitigate this drawback, it has been suggested to interpose an alumina layer between the titanium dioxide layer and the underlying metal layer, the alumina presenting the property of being more resistant to the action of the $HF-NH_4F$ the above etching solution than aluminium.

In these conditions, however, said alumina layer must then be removed by means of an etching solution usually comprising acetic acid and ammonium fluoride. Consequently, by this supplementary operation, the risks of deterioration of active elements adjacent to the said aluminium layer are increased either as a result of the actual chemical treatment, or due to the manipulations necessitated by said treatment, and the costs of the resulting device are also augmented. Moreover, it may be found that the result obtained is not always that which was anticipated.

It is the object of the present invention to mitigate said drawbacks and to make it possible to selectively etch a titanium dioxide layer without damaging adjacent materials and to simplify an etching method or an anodic oxidation method using a titanium dioxide mask.

The present invention provides a method of selectively etching a titanium dioxide layer used as a mask for the localisation of the anodic oxidation of an oxidisable metal layer, using an etchant consisting of a solution comprising hydrogen peroxide and ammonia.

This solution may be used for etching the titanium dioxide layer so as to give it the configuration of a mask, as well as for removing the remainder of the said layer after it has been used as a mask, and it uses commerically available materials, notably 30% by weight of H_2O_2 in water and an aqueous solution of ammonia having a specific gravity of 0·90.

Moreover, this solution also presents the

advantage of not attacking the materials generally present below the titanium dioxide layer, and in particular the said solution attacks neither aluminium nor alumina.

Advantageously, the ratio of the volume of ammonia with respect to the volume of hydrogen peroxide to form the solution according to the invention is equivalent to that obtained by adding between 0·10 and 0·50 unit volumes of an aqueous solution of ammonia having a specific gravity of 0·90 to one unit volume of 30% by weight hydrogen peroxide in water.

In this range of proportions, the etching rate of titanium dioxide by the solution is practically constant and it is rapid. For comparison it has been the etching rate of titanium dioxide decreases progressively when an etchant found that containing more than 0·50 unit volumes of the ammonia solution per unit volume of 30% by weight hydrogen peroxide is used.

The present invention also relates to the manufacture of a semi-conductor device of which the apertures in a metallic layer which are necessary for making contacts have been provided by the method according to the invention, which manufacture is characterized in that a titanium dioxide film is deposited on a metallic layer (notably of aluminium) present on the surface of a semiconductor crystal, and in that a portion of the said titanium dioxide film is selectively etched by a method according to the invention.

An embodiment of the invention will now be described with reference to the accompanying drawing in which Figures 1 to 3 are schematic cross-sections of part of a semiconductor device at different stages in the performance of a method according to the invention.

It is to noted that the dimensions in the Figures are considerably exaggerated and are not drawn to scale for the sake of clarity.

Referring now to Figures 1 to 3, on the surface of a semiconductor material 1 in which active and/or passive islands (not shown) have been formed, an aluminium layer 2 has been deposited which can be oxidised anodically and in which it is desired, for example, to form porous oxide islands. The layer 2 could, for example consist of an aluminium-based alloy (Al–Si, Al–Cu, or Al–Si–Cu). The masking is destined for the localisation of islands to be formed generally consisting of porous alumina.

A layer 3 of titanium dioxide is deposited on said layer 2 by known means, said deposit having the advantageous particularity that it can be effected at low temperature (150°C).

The next operation consists of photoetching said titanium dioxide layer 3: in order to do this a known method is used by depositing a photosensitive lacquer layer 4, locally irradiating and polymerising the lacquer layer 4 so that after development aperture 5 is formed in the lacquer layer 4 opposite to an area of the aluminium layer 2 which must be maintained conductive (Figure 1).

With the aid of the mask formed by the lacquer layer 4, an aperture 6 (Figure 2) is then etched in the titanium dioxide layer 3, said aperture being disposed opposite to the aperture 5 provided in the lacquer layer 4. The aperture 6 was etched using a solution consisting of 50 cm^3 of a solution of 30% by weight of H_2O_2 in water and 10 cm^3 of an aqueous solution of ammonia having a specific gravity of 0·90.

Said aperture 6 exposes an area 7 of the surface of the underlying aluminium layer 2.

Said exposed area 7 is then transformed into an impervious aluminium oxide film, for example by a known anodic oxidation method. The structure shown in Figure 2 is then obtained.

By means of the same solution of hydrogen peroxide and ammonia used to etch the aperture 6, the remainder of the titanium dioxide layer 3 is removed and the portion 2*a* of the aluminium layer 3 which is not protected by the aluminium oxide film 7 can then easily be transformed into oxide which is generally porous. The aluminium portion 2*b* protected by the film 7 preserves its original nature and consequently remains conductive (Figure 3) and may be used for various applications, notably as a contact.

WHAT WE CLAIM IS:—

1. A method of selectively etching a titanium dioxide film used as a mask for the localisation of the anodic oxidation of an oxidisable metallic layer, using an etchant consisting of a solution comprising hydrogen peroxide and ammonia.

2. A method as claimed in Claim 1, characterized in that the quantities of ammonia and hydrogen peroxide in the said solution are equivalent to those obtained by adding between 0·10 and 0·50 unit volumes of an aqueous solution of ammonia having a specific gravity of 0·90 to one unit volume of 30% by weight of hydrogen peroxide in water.

3. A method of selectively etching a titanium dioxide film, substantially as herein described with reference to the accompanying drawings.

4. A method of manufacturing a semiconductor device, characterized in that during

the formation of contacts an oxidisable metallic layer is deposited on the surface of the device a titanium dioxide film is formed on said metallic layer, and in that a part of the said titanium dioxide film is removed by the method as claimed in any of Claims 1 to 3.

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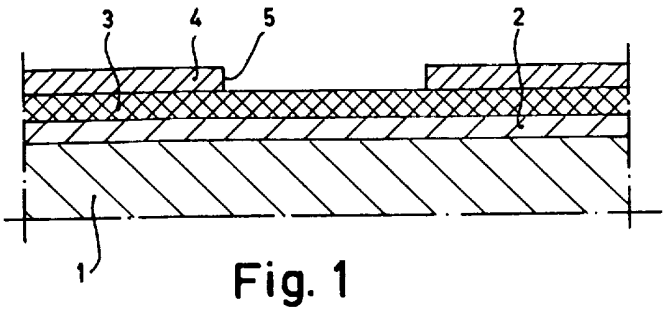

Fig. 1

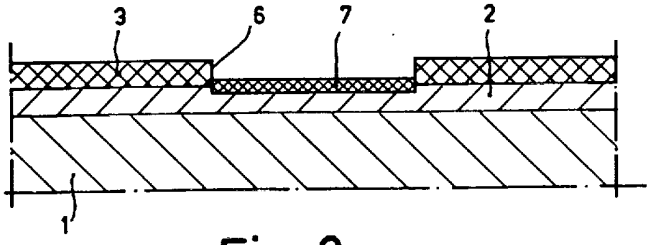

Fig. 2

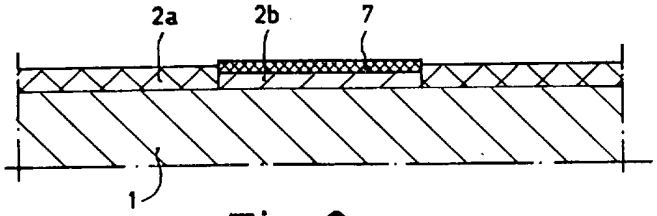

Fig. 3