(54) Title: METHOD FOR ELECTRICALLY ISOLATING LARGE AREA ELECTRODE BODIES

(57) Abstract

Method for electrically isolating large area electrode bodies to facilitate cascade interconnection of semiconductor bodies which may be deposited afterwards includes applying a maskant in a preselected pattern onto a substrate, depositing a conformal layer of an electrically conductive electrode material atop the patterned maskant and removing the maskant and the electrode material deposited thereon by dissolving in a solvent which is substantially chemically inert with respect to subsequently deposited materials to expose at least portions of the substrate and electrically isolate the remaining portions of the electrode material so that selective electrical interconnections may be made between electrically isolated electrode portions. This method substantially eliminates the need for laser or mechanical scribing of semiconductor bodies on a large area substrate.
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DESCRIPTION

METHOD FOR ELECTRICALLY ISOLATING

LARGE AREA ELECTRODE BODIES

5 TECHNICAL FIELD

The subject invention pertains to a method for electrically isolating large area electrode bodies for further fabrication to produce semiconductor devices, especially solar cells.

10 BACKGROUND ART

Electronic device production involves many intricate steps and precise handling. It is often necessary to separate the underlying constituents of devices to facilitate interconnection for the production of series-connected devices. In the manufacture of such devices, the process of electrically isolating can be difficult and intricate.

To electrically isolate various layers of adjoining cells or units in a device, it is well-known in the art to utilize a laser beam which is moved across a substrate surface to separate semiconductor bodies. Mechanical separation is currently achieved by abrading apparatus and abrasive trimmers having nozzles for directing an abrasive stream at a microelectronic device. Removing portions of a material layer between the semiconductor bodies reduces the cross-sectional area disposed between the bodies until the electrical resistance of the element is adjusted
upwardly to a desired value.

In conventional practice, the deposition of a patterned material layer was accomplished by the use of holding a mechanical mask against the substrate during the deposition process. Unfortunately, mechanical masking has the effect of blocking significant areas of the substrate because the areas under the mask that are required to achieve suitable separation are too great for the production of a semiconductor device. In addition, problems arise due to difficulties associated with mask misalignment.

U.S. Patent No. 3,691,695 issued September 19, 1972 to Green et al. discloses an abrasive trimmer for microelectronic devices including a nozzle for directing abrasive materials at a microelectronic device to be trimmed. The nozzle is pivot-mounted and spring-biased into a first, normally operative position. A circuit senses the electrical characteristics of the microelectronic device being trimmed and generates a signal when predetermined characteristics are sensed.

U.S. Patent 4,443,651 issued on April 17, 1984 to Swartz discloses series-connected amorphous silicon solar cells formed on a single substrate. Methods of inexpensively forming such series-connected amorphous silicon solar cells include a "paint and peel" method utilizing a series of paint strips sprayed onto the surface through a stripped mask. The paint is then peeled
off to urge the metal strips to form spikes which extend through to overlying electrodes.

U.S. Patent 4,590,093 issued May 20, 1986 to Woerlee et al. discloses a method of providing narrow conductor tracks of metal silicide. According to the disclosure, patterned polycrystalline silicon is covered by a protective layer and converted along the edges into a metallic silicide by covering the edges with a metal. The remaining silicon is selectively removed, and the tracks obtained can serve as conductor masks.

Accordingly, it is an object of the invention to facilitate the electrical isolation of large area electrode bodies for the fabrication of semiconductor devices. Another object of the invention is to achieve separation of electrode bodies in semiconductor devices such as solar cells without requiring the use of costly laser abrasion, or contaminating mechanical scribing, which uses valuable substrate area for electrical isolation.

DISCLOSURE OF THE INVENTION

The present invention provides an improved method for electrically isolating large area electrode bodies. More specifically, the present invention provides a chemical method for the precise separation of thin film electrode bodies in the production of semiconductor devices. A maskant is applied in a preselected pattern onto a substrate surface. A desirable maskant is readily
removable by a solvent which is substantially chemically inert with respect to subsequently deposited materials such as a solvent selected from the group consisting of organic solvents and aqueous solutions. Examples of organic solvents are alcohols, actone, etc., and aqueous solutions include acidic solutions.

Conformally deposited electrically conductive electrode material is then deposited atop the patterned maskant and, by dissolving in the solvent, the maskant is removed along with the electrode material deposited thereon. After removal, at least portions of the substrate are exposed and electrically isolated so that selective electrical interconnections may be made between electrically isolated electrode portions.

Maskants are selected from the group consisting of polymeric materials, carbonaceous materials, sulphates, nitrates, photoresist, oxides, carbides, and carbonates. Preferably, the maskant is barium carbonate, calcium carbonate, or silicon carbide. Application of the maskant is accomplished by screen-printing or photolithographic processes.

Another preferred maskant, especially suitable for screen-printing, is a pasty ink which is a mixture of a masking powder, a vehicle, and other materials.

The masking powder is preferably calcium carbonate, barium carbonate, or silicon carbide, for these substances are stable even at a high temperature around 400°C.
650°C, which is the usual chemical vapor deposition temperature of the conformal layer over the maskant. Also they are substantially chemically inert with the substrate and the conformal layer deposited over the maskant. In addition, as for calcium carbonate, it is easy to get the uniformity of the particle size, which contributes to the uniform dispersion in the vehicle and therefore the uniform masking effect. Moreover, calcium carbonate is very easily removable by an acidic solution.

Preferably, the average particle size of the masking powder is smaller than 0.5 μm. More preferably the maximum particle size is smaller than 0.5 μm. As the particle size gets smaller, the maskant provides better masking effect. Also the smaller the particle size gets, the more finely the maskant can be screen-printed, that is, in smaller thickness and in smaller width. This is very important, especially in case of a photovoltaic cell, for, if the maskant is screen-printed too thick, it may cause a very high projection on the peripheral edge in each portion of the conformal layer, which is a fatal problem, because the projection may contact the back electrode of the photovoltaic cell and cause short circuit. And, if the maskant is screen-printed widely, it decreases the surface area of active photovoltaic material exposed to the sun, which decreases the conversion efficiency.

However, if the particle size of the masking powder is
too small, it has a difficulty in dispersing in the vehicle uniformly. Besides, it is hard to prepare very fine particles. For these reasons the average particle size of the masking powder is preferably less than 0.5 μm and greater than 0.05 μm.

The vehicle contained in the maskant requires to have good qualities suitable for screen-printing, such as a suitable viscosity for screen-printing in a good accuracy, and to be readily removable. Regarding these properties, it is preferable that the vehicle contains ethyl cellulose, nitro cellulose or acrylic resin. In order to adjust the viscosity, a solvent compatible with the above substance may be added. If necessary, high boiling solvent or oxidant may also be added to the vehicle.

The maskant preferably contains 40 to 60 wt% masking powder, and 60 to 40 wt% vehicle.

The preselected pattern disclosed in the present invention is adapted for cascade interconnection of semiconductor device components, and includes rectangular-shaped conductive tracks extending from one side of the substrate to the other. The tracks are deposited to achieve a minimum space between each track, from about 0.1 millimeters to about 1.0 millimeters. It should be realized that any possible shape can be made in accordance with the present invention.

 Depositing a conformal layer of an electrically conductive electrode material may be accomplished by
depositing a layer of transparent conductive oxide, including indium tin oxide, a tin oxide doped with fluorine or tin oxide doped with antimony. This layer will have a thickness of from about 300 angstroms to about 20,000 angstroms.

To remove the maskant and the electrode material deposited thereon, the substrate is ultrasonically agitated and/or chemically washed to expose portions of the substrate and to electrically isolate the remaining portions of the electrode material left on the substrate after the removal. This forms discrete bodies so that selective electrical interconnection may be made between electrically isolated electrode portions. These electrically isolated electrode portions exhibit an increased electrical resistance which produces an electrical separation greater than 1,000 ohms.

The advantage of the present invention is the inexpensive, precise removal of electrode material without the use of lasers or mechanical abrading apparatus. Other advantages and features of the present invention will be appreciated from the following description.

BRIEF DESCRIPTION OF THE DRAWING

Figures 1a through 1c are schematic views of the progressive fabrication of a semiconductor device such as a solar cell using the method of the present invention.

Figure 2 is a top view of an example of a patterned substrate according to the present invention.
BEST MODE FOR CARRYING OUT THE INVENTION

Referring now to Figure 1, the methodology of the present invention is shown through illustration of the progressive fabrication of a semiconductor device. Figure 1a is a device, generally denoted by numeral 10, having a substrate 14 and a maskant 12 applied in a preselected pattern. Substrate 14 is typically of glass, but may be another material, such as plastic, metallic foils, silicon wafers, gallium arsenide wafers and other conventional substrates. Substrate 14 may be a non-conductive, insulating substrate, such as glass. In case of an alkali-containing glass substrate, substrate 14 may include an alkali diffusion-preventing layer such as SiO₂, Al₂O₃, or ZrO₂, formed over the alkali-containing glass substrate. The substrates may be of any size, including square foot solar panels.

The material comprising maskant 12 may be selected from the group consisting of polymeric materials, carbonaceous materials, sulphates, nitrates, photoresist, oxides, carbides, and carbonates. The preferred maskant is barium carbonate, calcium carbonate, or silicon carbide. Another preferred maskant is a mixture of a masking powder, a vehicle, and other materials. Preselected patterning of maskant 12 may be achieved by screen-printing or photolithographic processes. The material composition of maskant 12 is selected due to its ability to be readily removable by a solvent selected from
the group consisting of organic solvents and aqueous solutions. Various maskant applications will, of course, require the use of different solvents.

In case of a maskant comprising a masking powder and a vehicle, it is necessary to dry or pre-bake the maskant before a conformal layer is deposited.

As described in Figure 2, maskant 12 is applied to achieve a pattern of rectangular-shaped tracks 20 extending from one side of the substrate 14 to the other in a spaced-apart relation. Deposition in tracks achieves minimum spacing 21 between each track. This especially useful in the field of photovoltaics where it is more advantageous to have a maximum surface area of active photovoltaic material exposed to the sun. The minimum space 21 between each track 20 in the preferred embodiment is from about 0.1 millimeters to about 1.0 millimeters.

Referring now to Figure 1b, a conformal layer 16 of an electrically conductive electrode material, such as a transparent conductive oxide, including indium tin oxide and fluorine or antimony doped tin oxide, is deposited atop the pattern maskant 12. The conformal layer 16 is deposited to a thickness of between 300 angstroms and 20,000 angstroms, and preferably 3,000 angstroms and 20,000 angstroms. Device 10 is then contacted with the solvent to remove maskant 12. Removing maskant 12 may be accomplished by ultrasonic agitation and/or chemical washing, such as a spray bath, a tank bath or any other
conventional washing technique in an organic solvent or aqueous solution.

Looking now to Figure 1c, the maskant material 12 has been removed, leaving a patterned electrode material layer 16 atop substrate 14. Removing maskant 12 yields an electrical separation greater than 1,000 ohms. The result is the structure shown in Figure 1c where the electrode material 16 has been divided into separate conductive elements. These elements are now capable of cascade interconnection during further production steps of a monolithic photovoltaic device.

The projection 17 on the peripheral edge can be reduced if the maskant is screen-printed in a very thin layer, which can be realized by using the masking powder whose particle size is small, preferably less than 0.5 μm.

The invention may be more fully appreciated by the following illustrative examples.

EXAMPLE 1

Barium carbonate was screen-printed onto a glass substrate measuring one foot by one foot in a preselected pattern of rectangular-shaped tracks extending from one side of the substrate to the other as described in Figure 2, each track having a measurement of approximately one centimeter in width, spaced apart at a distance of about one-half millimeter. The screen-printing process automatically applied the desired pattern of maskant. Thereafter, a transparent conductive oxide layer was
...-11-

deposited conformally on top of the patterned barium carbonate. The barium carbonate was dissolved in alcohol by chemical washing. Portions of the glass substrate were exposed and the remaining portions of the transparent conductive oxide were electrically isolated to greater than 5,000 ohms.

EXAMPLE 2

A maskant in the form of paste was prepared by mixing 100 g of calcium carbonate powder whose average particle size was about 0.3 μm, 90 g of vehicle consisting of 6 wt% ethyl cellulose and 94 wt% tri-methyl pentanediol monoisobutylate, and additional 25 g of tri-methyl pentanediol monoisobutylate to have a viscosity of about 50,000 cps at 25°C.

This maskant was screen-printed onto an alkali diffusion-preventing layer of SiO₂ formed over a soda lime silica glass substrate measuring one foot by one foot in a preselected pattern of rectangular-shaped tracks extending from one side of the substrate to the other, each track having a measurement of approximately one centimeter in width, spaced apart at a distance of about 0.4 millimeters. The screen-printing process automatically applied the desired pattern of maskant. The thickness of the maskant was about 10 μm.

The glass substrate with the pattern of maskant was dried at 150°C for 10 minutes, then carried into a CVD apparatus, and heated up to 500°C. Nitrogen gas
containing tetramethyl tin \((\text{Sn(CH}_3)_4\)) \((1.1 \times 10^{-4} \text{ mol/min})\), oxygen \((0.5 \text{ liter/min})\), and bromo-trifluoromethane \((\text{CF}_3\text{Br}, 2 \text{ liter/min})\) was applied onto the glass substrate at the flow of 2 liter/min to form a conformal layer of 1.0 wt% fluorine doped tin oxide of 5,000 angstroms thick.

Next, the maskant was dissolved in an aqueous solution by ultrasonic agitation. Portions of the glass substrate were exposed and the remaining portions of the fluorine doped tin oxide were electrically isolated to greater than 4,000 ohms. Each portion of the fluorine doped tin oxide had a projection of about 0.2 \(\mu\)m high on the peripheral edge.

Thereafter amorphous silicon layer of 4,000 angstroms thick was deposited by plasma CVD method on the glass substrate with the patterned tin oxide, and then silver layer was formed on the amorphous silicon layer to make a solar cell.

After investigating the electrical property of each portion, it was found that short circuit never occurred in any of the portions.

While the foregoing examples and illustrative descriptions describe the use of transparent conductive oxides and various maskants, other applications will become obvious to those skilled in the art. Furthermore, while the foregoing descriptions and examples are directed towards fabrication of an electrode body material, the invention's utility is not so limited. The following claims will define the scope of the invention.
CLAIMS:

1. A method for electrically isolating large area electrode bodies to facilitate cascade interconnection of semiconductor bodies deposited thereafter, comprising:
   - applying a maskant in a preselected pattern onto a substrate having a surface to support said maskant;
   - depositing a conformal layer of a transparent conductive oxide electrode material selected from the group consisting of indium tin oxide, fluorine doped tin oxide, and antimony doped tin oxide, said layer deposited atop the patterned maskant; and
   - removing the maskant and the electrode material deposited thereon by dissolving in a solvent, whereby at least portions of the substrate are exposed and the remaining portions of said electrode material are electrically isolated so that selected electrical interconnections may be made between electrically isolated electrode portions.

2. A method for electrically isolating large area electrode bodies to facilitate cascade interconnection of semiconductor bodies deposited thereafter, comprising:
   - applying a maskant in a preselected pattern onto a substrate having a surface to support said maskant, said maskant being readily removable by a solvent which is substantially chemically inert with respect to subsequently deposited materials;
   - depositing a conformal layer of an electrically
conductive electrode material atop the patterned maskant; and
removing the maskant and the electrode material deposited thereon by dissolving in said solvent, whereby
at least portions of the substrate are exposed and the remaining portions of said electrode material are electrically isolated so that selected electrical interconnection may be made between electrically isolated electrode portions.

3. A method as in Claim 1 or 2, wherein said applying a maskant is accomplished by applying a maskant selected from the group consisting of polymeric materials, carbonaceous materials, sulphates, nitrates, photoresist, oxides, carbides, and carbonates.

4. A method as in Claim 3, wherein said maskant is selected from the group consisting of barium carbonate, calcium carbonate, and silicon carbide.

5. A method as in Claim 1 or 2, wherein said applying a maskant is accomplished by applying a maskant which comprises a masking powder and a vehicle.

6. A method as in Claim 5, wherein said masking powder is selected from the group consisting of barium carbonate, calcium carbonate, and silicon carbide.

7. A method as in Claim 5, wherein said masking powder has a particle size of less than 0.5 μm.

8. A method as in Claim 5, wherein said vehicle comprises at least one selected from the group consisting of ethyl
cellulose, nitro cellulose, and acrylic resin.

9. A method as in Claim 1 or 2, wherein said applying a maskant is accomplished by applying a pattern adapted for cascade interconnection including rectangular-shaped tracks extending from one side of the substrate to another in a spaced-apart relation.

10. A method as in Claim 9, wherein said tracks are deposited to achieve a minimum space between each track.

11. A method as in Claim 10, wherein said minimum space between each track is from about 0.1 millimeters to about 1.0 millimeters.

12. A method as in Claim 1 or 2, wherein said applying a maskant onto a substrate is performed by applying the maskant onto a non-conductive, insulating substrate.

13. A method as in Claim 1 or 2, wherein said applying a maskant is performed by applying a maskant which is readily removable by a solvent selected from the group consisting of organic solvents aqueous solutions.

14. A method as in Claim 13, wherein said organic solvent is alcohol.

15. A method as in Claim 13, wherein said aqueous solution is acidic solution.

16. A method as in Claim 2, wherein said depositing a conformal layer of an electrically conductive electrode material is accomplished by depositing transparent conductive oxide material.

17. A method as in Claim 2, wherein said depositing a
conformal layer of an electrically conductive electrode material is accomplished by depositing indium tin oxide material.

18. A method as in Claim 2, wherein said depositing a conformal layer of an electrically conductive electrode material is accomplished by depositing fluorine or antimony doped tin oxide material.

19. A method as in Claim 1 or 2, wherein said depositing a conformal layer of an electrically conductive electrode material is accomplished by depositing said material to a thickness of from 3,000 angstroms to 20,000 angstroms.

20. A method as in Claim 1 or 2, wherein said removing the maskant is accomplished by ultrasonic agitation.

21. A method as in Claim 1 or 2, wherein said removing the maskant is accomplished by chemical washing.

22. A method as in Claim 1 or 2, wherein said step of applying a maskant is accomplished by screen-printing.

23. A method as in Claim 1 or 2, wherein said step of applying a maskant is accomplished by photolithographic processes.

24. A method as in Claim 1 or 2, wherein said removing the maskant yields an electrical separation greater than 1,000 ohms.

25. A method for electrically isolating large area electrode bodies to facilitate cascade interconnection of semiconductor bodies deposited thereafter, comprising:

applying barium carbonate onto a glass substrate
having a surface, said barium carbonate being deposited in a preselected pattern of rectangular-shaped tracks extending from one side of the substrate to the other, spaced apart at a distance from about 0.1 millimeters to about 1.0 millimeters;

depositing a conformal layer of transparent conductive oxide atop the patterned barium carbonate; and

removing the barium carbonate and the electrode material deposited thereon by dissolving in alcohol to expose at least portions of the glass substrate and electrically isolate the remaining portions of the transparent conductive oxide so that selective electrical interconnections may be made between electrically isolated transparent conductive oxide portions.

26. A method for electrically isolating large area electrode bodies to facilitate cascade interconnection of semiconductor bodies deposited thereafter, comprising:

applying a maskant comprising a powder of at least one selected from the group consisting of calcium carbonate, barium carbonate, and silicon carbide, and a vehicle, onto a glass substrate having a surface by screen-printing, said maskant being deposited in a preselected pattern of rectangular-shaped tracks extending from one side of the substrate to the other, spaced apart at a distance from about 0.1 millimeters to about 1.0 millimeters;

depositing a conformal layer of transparent conductive oxide atop the patterned maskant; and
removing the maskant and the electrode material deposited thereon by dissolving in aqueous solution to expose at least portions of the glass substrate and electrically isolate the remaining portions of the transparent conductive oxide so that selective electrical interconnections may be made between electrically isolated transparent conductive oxide portions:

27. A method as in Claim 26, wherein the maskant is removed in aqueous solution with ultrasonic agitation.
**INTERNATIONAL SEARCH REPORT**

**I. CLASSIFICATION OF SUBJECT MATTER** (if several classification symbols apply, indicate all)  
According to International Patent Classification (IPC) or to both National Classification and IPC  
**IPC**: H 01 L 21/48; H 01 L 27/14; H 01 L 31/02

**II. FIELDS SEARCHED**

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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

**III. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>EP. A, 0082515 (IBM CORP.) 29 June 1983, see pages 1,2,6,7; page 10, line 13 - page 14, line 20; claims; figures</td>
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<td>X</td>
<td>Chemical Abstracts, vol. 97, no. 18, 1 November 1982 (Columbus, Ohio, US), see page 642, abstract no. 153973x, &amp; JP, A, 8245992 (CITIZEN WATCH CO., LTD) 16 March 1982</td>
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**IV. CERTIFICATION**

Date of the Actual Completion of the International Search  
14th June 1988

Date of Mailing of this International Search Report  
0 8 JUL 1988

International Searching Authority  
EUROPEAN PATENT OFFICE

Signature of Authorized Officer  
P.C.G. VAN DER PITTEN

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<td>US, A, 4443651 (G.A. SWARTZ) 17 April 1984, see the whole document cited in the application</td>
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<td>A</td>
<td>US, A, 4339305 (A.B. JONES) 13 July 1982, see column 3, line 44 - column 5, line 35; figures 1-6</td>
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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. JP 8800211
SA 20885

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