PATENT SPECIFICATION (11) 1 357 831

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(21) Application No. 43672/72 (22) Filed 21 Sept. 1972 (19)

(31) Convention Application No. 182 891 (32) Filed 25 Sept. 1971 in

(33) United States of America (US)

(44) Complete Specification published 26 June 1974

(51) International Classification C23F 1/00

(52) Index at acceptance

B6J 350 351 352 354 362 365 440 444 480 525 702 710

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(54) IMPROVEMENTS IN OR RELATING TO ETCHANTS FOR SEMICONDUCTOR COMPOUNDS

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation orga[illegible] and existing under the laws of the S[illegible] York, United States of Americ[illegible] re the invention, for wh[illegible] that a patent may be grante[illegible] the method by which it is to be [illegible], to be particularly described in and by the following statement:—

The invention relates to etchants and to a technique for preferentially etching semiconductor material. In particular, the present invention relates to a technique for anisotropically etching silicon or germanium with an alkaline etchant in the presence of an oxidizing and a passivating agent.

Semiconductor devices whether of the single element or integrated circuit type, are fabricated universally from monocrystalline material in slice form. In both the single element and integrated device fabrication, precise removal of portions of the material is an important aspect of the process. For modern integrated circuit applications, geometry control of the etch pattern has acquired paramount importance. For the air gap insulation process, in particular, it is necessary to separate the individual chips or components of the circuit from each other, and to do this in a manner which sacrifices the least amount of valuable silicon surface in order to arrive at a high density of devices per unit area.

It has been known for some time that the (111) plane of silicon etches more slowly than the (100) or (110) planes in alkaline aqueous solution, and further, that the etch rate of the (110) plane (or more properly speaking, of two adjacent (211) planes, which crystallographically are very close to the (110) plane) can be depressed by the addition of aliphatic alcohols, of which isopropyl or n-butyl alcohol are typical examples. Thus, when a (100) oriented silicon slice is etched in hot alkaline solution in the presence of an aliphatic alcohol, precise control over the geometry of the pattern to be etched is obtained.

Until now this process on (100) oriented silicon was severely hindered by a premature termination of the etching action due to the formation of innumerable (111) sided pyramids on the (100) surface undergoing etching, the etch rate of the (111) faces being extremely low.

Heretofore, reports have not appeared in the literature relative to the anisotropic etching of germanium. At the present time, silicon is generally preferred by industry because of the higher operating temperature of devices made from silicon compared to those from germanium. However, carrier mobilities in germanium are considerably higher than in silicon, and for high frequency devices, germanium substrates will always be of interest.

The invention provides an etchant comprising a mixture of an alkaline aqueous solution, an alcohol, and an oxidizing agent present in an amount of from 1 to 10 millimoles per litre of the etchant wherein the oxidizing agent and the alcohol are either (a) hydrogen peroxide and tetrahydrofurfuryl alcohol or (b) a chromate ion and either tetrahydrofurfuryl alcohol or an unsubstituted aliphatic alcohol having from 3 to 7 carbon atoms.

The invention also provides a method of etching a semiconductor material comprising contacting the semiconductor material with an etchant comprising a mixture of an alkaline aqueous solution, an oxidizing agent present in an amount of from 1 to 10 millimoles per litre of the etchant and an alcohol, the oxidizing agent and the alcohol comprising either (a) hydrogen peroxide and tetrahydrofurfuryl alcohol and (b) chromate ion and either tetrahydrofurfuryl alcohol or an unsubstituted aliphatic alcohol having from 3 to 7 carbon atoms.

[*Price 25p*]

The present invention demonstrates that addion of an oxidizing agent of a suitable redox potential eliminates the formation of (111) sided pyramids on the (100) surface of silicon during etching in alkaline aqueous solution, and that this same solution also etches germanium in precisely the same anisotropic manner as it etches silicon. In the absence of the oxidizing agent, no etching of germanium would occur, since germanium is more noble than hydrogen in the electromotive series of the elements, and is therefore not attacked by hot alkaline aqueous solutions.

The same etchant has also been found to etch germanium at a commercially practical rate, and with the same high degree of geometry control as achieved on silicon.

The etchant described herein comprises (a) a strongly alkaline aqueous solution for rapid attack upon the (100) face of silicon or germanium, (b) a passivating alcohol which depresses the undesirably rapid etch rate of the (110) planes, that is, two adjacent (211) faces as noted above, of silicon or germanium, and (c) an oxidizing agent which suppresses the formation of (111) sided pyramids on the (100) surface of silicon, and enables the etching of germanium to proceed.

The strongly alkaline aqueous solutions are typically selected from among the hydroxides of potassium and sodium. These materials have been found to be efficacious from a process standpoint and to be economically practical. However, other strongly alkaline agents such as the hydroxides of rubidium and cesium as well as quarternary ammonium hydroxides may be employed with equal efficacy.

With respect to the selection of passivating and oxidizing agents, the interrelationship therebetween must be considered. Thus, it is known that alcohols can be readily oxidized to aldehydes or ketones; however, the ease with which any specific alcohol will be oxidized is dependent upon its chemical structure, aromatic alcohols being more stable than aliphatic alcohols and long chain aliphatic alcohols being more stable than short chain aliphatic alcohols. It has been determined with respect to silicon that the redox potential must be sufficiently high to prevent the formation of (111) sided pyramids on the (100) surface but no so high as to cause the passivating alcohol to oxidize rapidly. The same considerations apply with respect to germanium with the additional requirement that the redox potential of the oxidizing agent be high enough to enable rapid attack of the (100) surface of germanium in hot alkaline solution. Since the formation of the (111) sided pyramids on the (100) surface of silicon appears to be attributed to the action of hydrogen (which results from the dissolution reaction of silicon with water) and since germanium is only slightly more noble than hydrogen, these requirements are satisfied by selecting an oxidizing agent which is strong enough to oxidize hydrogen but not strong enough to oxidize the alcohol selected at an unduly rapid rate. In light of the fact that the oxidation resistance of the various alcohols varies over a considerable range, the type and concentration of oxidizing agent selected can also vary over a wide range.

Tuning now to a consideration of specific combinations of passivating alcohol and oxidizing agent it has been found that the chromate ion in combination with aliphatic alcohols, and hydrogen peroxide in combination with tetrahydrofurfuryl alcohol are satisfactory. With respect to silicon, it has been determined that aliphatic alcohols are more suitable as passivating agents for the (110) plane than aromatic alcohols and that the [illegible]e ion fulfills the role of preventi[illegible]formation without attacking the [illegible]hol at an appreciable rate, [illegible]roxide, a stronger oxidizing [illegible] chromate ion is suitable in c[illegible]n tetrahydrofurfuryl alcohol and u[illegible]isfactory with the aliphatic alcohols because of the rapid rate of attack thereon, the same considerations obtain with respect to germanium.

The term aliphatic alcohols as employed herein includes those unsubstituted alcohols having from 3 to 7 carbon atoms in the chain. Typical materials following within the scope of this definition are n-propyl, isopropyl, n-butyl, secondary butyl, tertiary butyl, pentyl, hexyl alcohols and the like. The limitations in the number of carbon atoms in the chain are dictated by practical considerations relative to solubility at the upper limit and marginal anisotropic etching at the lower limit.

In addition to hydrogen peroxide, oxidizing agents may be selected from between potassium and sodium chromate.

The oxidizing agent is employed in an amount ranging from 1—10 millimols per litre of etchant, such range being dictated by the observed reduction in pyramid density. The alcohols are employed in a concentration sufficient to reduce the etch rate of the (110) plane. The etching procedure as described herein is conveniently conducted at a temperature within the range of 70—90°C. An etch resistant mask may, of course, be used on the surface of the material to be etched so as to delineate the region to be exposed to the etchant.

Examples of the application of the present invention are set forth below.

EXAMPLE 1

Anisotropic etching of 4 ohm-centimeter, n-type germanium bearing a micropattern of

sputtered photoresisted zirconium as an etching mask, was effected at 85°C in an etchant comprising 4.5 normal potassium hydroxide, 0.2 normal tetrahydrofurfuryl alcohol and 20 millilitres of 30% hydrogen peroxide per litre of etchant. Etching was effected to a depth of 13 microns after 20 minutes, preferentially on the (100) surface of the germanium.

EXAMPLE 2

The procedure of Example 1 was repeated utilizing 10 ohm-centimeter, n-type silicon. Etching was effected to a depth of 20 microns after 20 minutes preferentially on the (100) surface thereof. It is noted that the formation of the (111) sided pyramids, which normally tend to passivate the (100) surface prematurely, were eliminated.

For comparitive purposes, the procedure of this example was repeated in the absence of hydrogen peroxide, the oxidizing agent, it was observed that the formation of the deleterious pyramid caused passivat[illegible]e (100) surface and termination process.

EXAMPLE 3

The procedure of Examp[illegible] peated with the exception that [illegible] moles per litre of etchant of potassium chromate were substituted for the hydrogen peroxide. Etching was effected to a depth of 25 microns after 20 minutes preferentially on the (100) surface of the silicon.

EXAMPLE 4

The procedure of Example 3 was repeated wherein the tetrahydrofurfuryl alcohol was replaced first by n-propyl alcohol and subsequently by isopropyl, n-butyl, secondary butyl and tertiary butyl alcohol. Etching in each case was effected to a depth of approximately 25 microns over a 20 minute period preferentially on the (100) surface. Again, it was noted that the formation of the deleterious pyramid was obviated by means of the described etchant.

WHAT WE CLAIM IS:—

1. An etchant comprising a mixture of an alkaline aqueous solution, an alcohol, and an oxidizing agent present in an amount of from 1 to 10 millimoles per litre of the etchant wherein the oxidizing agent and the alcohol are either (a) hydrogen peroxide and tetrahydrofurfuryl alcohol or (b) a chromate ion and either tetrahydrofurfuryl alcohol or an unsubstituted aliphatic alcohol having fom 3 to 7 carbon atoms.

2. An etchant as claimed in claim 1, wherein the oxidizing agent is sodium chromate or potassium chromate.

3. An etchant as claimed in claim 1 or claim 2, wherein the alkaline solution is selected from the group consisting of potassium, sodium, cesium, quarternary ammonium and rubidium hydroxides.

4. An etchant as claimed in claim 1, wherein the aliphatic alcohol is selected from the group consisting of n-propyl, isopropyl, n-butyl, secondary butyl, tertiary butyl, pentl and hexyl alcohols.

5. An etchant as claimed in claim 1, wherein the alkaline solution is potassium hydroxide, the oxidizing agent is potassium chromate and the aliphatic alcohol is n-propyl alcohol.

6. A method of etching a semiconductor material comprising contacting the semiconductor material with an etchant comprising a mixture of an alkaline aqueous solution, an oxidizing agent present in an amount of from 1 to 10 millimoles per litre of the etchant and an alcohol, the oxidizing agent and the alcohol comprising either (a) hydrogen peroxide and tetrahydrofurfuryl alcohol or (b) a chromate ion and either tetrahydrofurfuryl alcohol or an unsubstituted aliphatic alcohol having from 3 to 7 carbon atoms.

7. A method as claimed in claim 1, wherein the semiconductor material is silicon or germanium.

8. A method as claimed in claim 6, or claim 7, wherein the alkaline solution is selected from potassium, sodium, cesium, quarternary ammonium and rubidium hydroxide.

9. A method as claimed in any one of claims 6—8, wherein the aliphatic alcohol is selected from n-propyl, isopropyl, n-butyl, secondary butyl, tertiary butyl, pentyl and hexyl alcohols.

10. A method as claimed in claim 6, wherein the alkaline solution is potassium hydroxide, the oxidizing agent is potassium chromate and the aliphatic alcohol is n-propyl alcohol.

11. A method as claimed in any one of claims 6—10, wherein the etchant is applied to the semiconductor material at a temperature of 70°C to 90°C.

12. A method as claimed in any one of claims 6—10, wherein an etch resistant mask is applied to the material before contact of the semiconductor material with the etchant.

13. A method of etching a semiconductor material substantially as hereinbefore described with reference to the accompanying examples.

14. An etchant substantially as hereinbefore described with reference to the accompanying examples.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1974.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY
from which copies may be obtained.

sputtered photoresisted zirconium as an etching mask, was effected at 85°C in an etchant comprising 4.5 normal potassium hydroxide, 0.2 normal tetrahydrofurfuryl alcohol and 20 millilitres of 30% hydrogen peroxide per litre of etchant. Etching was effected to a depth of 13 microns after 20 minutes, preferentially on the (100) surface of the germanium.

EXAMPLE 2

The procedure of Example 1 was repeated utilizing 10 ohm-centimeter, n-type silicon. Etching was effected to a depth of 20 microns after 20 minutes preferentially on the (100) surface thereof. It is noted that the formation of the (111) sided pyramids, which normally tend to passivate the (100) surface prematurely, were eliminated.

For comparitive purposes, the procedure of this example was repeated in the absence of hydrogen peroxide, the oxidizing agent, it was observed that the formation of the deleterious pyramid caused passivat[illegible] (100) surface and termination process.

EXAMPLE 3

The procedure of Exam[illegible] peated with the exception that [illegible] per litre of etchant of potassium chromate were substituted for the hydrogen peroxide. Etching was effected to a depth of 25 microns after 20 minutes preferentially on the (100) surface of the silicon.

EXAMPLE 4

The procedure of Example 3 was repeated wherein the tetrahydrofurfuryl alcohol was replaced first by n-propyl alcohol and subsequently by isopropyl, n-butyl, secondary butyl and tertiary butyl alcohol. Etching in each case was effected to a depth of approximately 25 microns over a 20 minute period preferentially on the (100) surface. Again, it was noted that the formation of the deleterious pyramid was obviated by means of the described etchant.

WHAT WE CLAIM IS:—

1. An etchant comprising a mixture of an alkaline aqueous solution, an alcohol, and an oxidizing agent present in an amount of from 1 to 10 millimoles per litre of the etchant wherein the oxidizing agent and the alcohol are either (a) hydrogen peroxide and tetrahydrofurfuryl alcohol or (b) a chromate ion and either tetrahydrofurfuryl alcohol or an unsubstituted aliphatic alcohol having fom 3 to 7 carbon atoms.

2. An etchant as claimed in claim 1, wherein the oxidizing agent is sodium chromate or potassium chromate.

3. An etchant as claimed in claim 1 or claim 2, wherein the alkaline solution is selected from the group consisting of potassium, sodium, cesium, quarternary ammonium and rubidium hydroxides.

4. An etchant as claimed in claim 1, wherein the aliphatic alcohol is selected from the group consisting of n-propyl, isopropyl, n-butyl, secondary butyl, tertiary butyl, pentl and hexyl alcohols.

5. An etchant as claimed in claim 1, wherein the alkaline solution is potassium hydroxide, the oxidizing agent is potassium chromate and the aliphatic alcohol is n-propyl alcohol.

6. A method of etching a semiconductor material comprising contacting the semiconductor material with an etchant comprising a mixture of an alkaline aqueous solution, an oxidizing agent present in an amount of from 1 to 10 millimoles per litre of the etchant and an alcohol, the oxidizing agent and the alcohol comprising either (a) hydrogen peroxide and tetrahydrofurfuryl alcohol or (b) a chromate ion and either tetrahydrofurfuryl alcohol or an unsubstituted aliphatic alcohol having from 3 to 7 carbon atoms.

7. A method as claimed in claim 1, wherein the semiconductor material is silicon or germanium.

8. A method as claimed in claim 6, or claim 7, wherein the alkaline solution is selected from potassium, sodium, cesium, quarternary ammonium and rubidium hydroxide.

9. A method as claimed in any one of claims 6—8, wherein the aliphatic alcohol is selected from n-propyl, isopropyl, n-butyl, secondary butyl, tertiary butyl, pentyl and hexyl alcohols.

10. A method as claimed in claim 6, wherein the alkaline solution is potassium hydroxide, the oxidizing agent is potassium chromate and the aliphatic alcohol is n-propyl alcohol.

11. A method as claimed in any one of claims 6—10, wherein the etchant is applied to the semiconductor material at a temperature of 70°C to 90°C.

12. A method as claimed in any one of claims 6—10, wherein an etch resistant mask is applied to the material before contact of the semiconductor material with the etchant.

13. A method of etching a semiconductor material substantially as hereinbefore described with reference to the accompanying examples.

14. An etchant substantially as hereinbefore described with reference to the accompanying examples.

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