Description

This invention relates to the etching of silicon, and, more particularly, to the improved anisotropic etching of single crystal silicon.

The anisotropic etching of single crystal silicon has been carried out for many years in the production of microelectronic devices. An essential feature is that the etching solutions etch the (100) crystallographic plane at an appreciably greater rate than the (110) and (111) planes, producing v-shaped sidewalls at 54.74° from the (100) surface. Exemplificative of the solutions which are known in the art are the following: IBM Tech. Discl. Bull., Vol. 19, No. 9 (Feb. 1977), p. 3623 discloses a solution for anisotropically etching single crystal silicon, containing ethylene diamine, pyrocatechol and water; and IBM Tech. Discl. Bull., Vol. 19, No. 10 (Mar. 1977), p. 3953 also describes such a solution, containing the three ingredients described in the preceding article, but further including hydrogen peroxide.

See also, U.S.-A-4,417,946, issued to Bohlen et al on Nov. 29, 1983, and 4,342,817, issued to Bohlen et al on Aug. 3, 1982, both of which disclose a method of making a mask, employing an etching solution consisting of ethylene diamine, pyrocatechol, water, and, optionally, hydrogen peroxide; and U.S.-A-4,293,373, issued to Greenwood on Oct. 6, 1981, and 4,229,979, issued to Greenwood on Oct. 28, 1980, both of which disclose a method of making a silicon transducer which involves etching a boron doped silicon wafer, with a solution containing ethylene diamine, pyrocatechol and water.

Note also, U.S.-A-3,650,957, issued to Shipley, Jr. et al on Mar. 21, 1972, which discloses a solution for etching copper, which includes a source of cupric ions, a complexing agent for cupric ions, such as a hydroxy-carboxylic acid or an alkanolamine, a source of chloride or bromide ions and a solution containing a soluble molybdenum, tungsten or vanadium compound.

U.S.-A-3,873,203, issued to Stevenson on Mar. 25, 1975, discloses a mixture for etching silicon, containing hydrazine and pyrocatechol.

Further, U.S.-A-3,160,539, issued to Hall et al on Dec. 8, 1964, relates to an etching solution for silicon, which includes piperidine.

IBM Tech. Discl. Bull., Vol. 15, No. 1 (June 1972), p. 173 discloses an etchant for aluminum, consisting of a solution of a secondary organic amine, such as piperidine or pyrrolidine, in water.

In addition, a particularly effective solution for etching single crystal silicon is disclosed in U.S. Pat. Appln., Ser. No. 875,833, filed by Beechko on Jun. 18, 1986. That solution comprises ethanolamine, pyrocatechol, water, hydrogen peroxide and piperidine. It has been found that the solution etches (100) silicon at a rate of about 40 µm/hr.

Now, an improved method of etching silicon has been developed which involves contacting the silicon with an etching solution which comprises gallic acid, an amine and water. The present invention is also directed to the etching solution per se.

In accordance with the invention, an etch rate for (100) silicon of about 125-140 µm/hr. has been achieved. This rate is, for example, more than three times greater than that normally obtained by employing the etching solution of the above-noted Beechko application. Moreover, the inventive etching solution is relatively safe in manufacturing and use and is environmentally compatible with current disposal techniques.

In the practice of the invention, silicon wafers to be etched are preferably immersed in the etching solution. Preferably, this is carried out at a temperature of about 100-125°C, more preferably of about 115-125°C. The actual temperature and time may vary, however, depending upon a number of factors, such as the desired etch rate, the geometry being etched, the exact formulation employed, and so forth, as will be apparent to those skilled in the art. In addition, the pH of the solution preferably ranges from about 11 - 12 in most situations.

As noted above, the etching solution employed according to the present invention includes gallic acid.

Any suitable amine compound with a relatively high polarity may be employed in the etching solution of the invention. Suitable amines include, for example, the following:

a. The primary aliphatic amines including mono-, di-, and triamines. These amines usually contain 2-8, and preferably 2-6, carbon atoms such as ethylamine, n-propylamine, n-butylamine, n-amylamine, n-hexylamine, ethylene diamine, diaminopropane, diaminobutane, pentamethylene diamine, m-xylylenediamine and diethylene triamine. Particularly preferred amines in this group are the diamines having 2-4 carbon atoms such as ethylene diamine and diaminopropane.

b. The alkanolamines, i.e., the aliphatic hydroxy amines. Usually each alkanol group in these amines contains from 2 to 5 carbon atoms. Illustrative are monoethanolamine, diethanolamine, triethanolamine, the mono-, di-, and tripropanolamines, ethanolpropanolamine, diethanolpropanolamine, and the mono-, di-, and tributanolamines. Particularly preferred alkanolamines are those in which each alkanol group contains 2-3 carbon atoms such as the ethanolamines, the propanolamines and the ethanolpropanolamines.

In a particularly preferred embodiment of the invention, monoethanolamine is employed.

Although the proportions of the ingredients may vary over wide ranges, the etching solution preferably contains about 3-6 mole percent of gallic acid 32-56 mole percent of the amine and about 65-38 mole percent of water. More preferably, the etching solution contains about 4-6 mole percent of gallic acid, about 39-56 mole percent of the amine and about 57-38 mole percent of water.

Various other ingredients may be added to the etching solution. For example, a small amount, such as about 0.2-0.3 mole percent, of pyrazine or piperidine or of hydrogen peroxide (e.g., 0.5 - 3 ml/1000 ml of amine compound) may be added in order to further enhance the etch rate of the solution. In addition, a small amount of a surfactant (e.g., 0.5 - 3 ml/1000 ml of amine compound), such as "FC-129", commercially available from Minnesota Mining & Manufacturing Company, or other fluorinated hydrocarbon surfactants, may be added. The presence of surfactant is desirable because it provides an increase in uniformity of etching, apparently by inhibiting adhesion of evolving hydrogen bubbles at the etching surface.

The etching solution of the invention provides a quality etch, i.e. with minimal pits, hillocks and faceting, and at a significantly faster rate. As such, it is desirable for use in a number of applications. For example, the etching solution can also be used to etch P-doped silicon wafers in the manner described in U.S.-A-4,342,817.

In one preferred application, the etching solution can be used to etch (100) silicon at a high rate (about 125-140 µm/hr.), while stopping at highly doped boron interfaces, allowing production of large, thin boron-rich windows on the surface of thick silicon wafers. These silicon products are useful in the manufacture of x-ray and e-beam masks.

Besides etching single crystal silicon, the etching solution of the invention is also effective in etching other silicon, such as polycrystalline silicon or epitaxial silicon.

The following examples are provided to illustrate the invention.

EXAMPLE 1

A pyrex reaction vessel (250mm x 200mm) was charged with 3 liters of monoethanolamine and 600 ml of deionized water. 900 Grams of gallic acid was added through a powder funnel, and the funnel rinsed with an additional 300 ml of deionized water. 20 Grams of pyrazine, 4.5 ml of surfactant ("FC-129") and 7.5 ml of 30% hydrogen peroxide were added, and the amber solution was brought to reflux under a water condenser.

Silicon wafers having a (100) crystallographic orientation were etched by immersing the wafers in the etching solution at a temperature of about 118-120°C for about 4 to 4.5 hrs. The etching solution etched (100) silicon at a rate of about 94 µm/hr. See Table I below.

EXAMPLE 2

A pyrex reaction vessel (250mm x 200mm) was charged with 1400 ml of deionized water, 1150 grams of gallic acid, 25 grams of pyrazine, 3800 ml of monoethanolamine and 7 ml of surfactant ("FC-129") The solution was heated to reflux under a water condenser.

Silicon wafers having a (100) crystallographic orientation were etched by immersing the wafers in the etching solution at a temperature of about 119°C for about 5.5 hrs. The etching solution etched (100) silicon at a rate of about 125 µm/hr. See Table I below.

EXAMPLE 3

A 500 ml pyrex reaction kettle was charged with 335 ml of monoethanolamine and 75 ml of deionized water. 100.4 Grams of gallic acid was added through a powder funnel. 25 ml of piperidine, 1 ml of surfactant ("FC-129") and 3 ml of 30% hydrogen peroxide were added, and the amber solution was brought to reflux under a water condenser.

Silicon wafers having a (100) crystallographic orientation were etched by immersing the wafers in the etching solution at a temperature of about 125°C for about 10 hrs. The etching solution etched (100) silicon at a rate of about 60-70 µm/hr. See Table I below.

COMPARATIVE EXAMPLES A-G

For purposes of comparison, the procedure of Example 3 was repeated using the formulations as shown in Table I. In each Comparative Example, an aromatic compound, other than as defined in the description above was used in the formulation in place of gallic acid. In each case, the etch rate results for (100) silicon were found to be unacceptable. The formulations and the corresponding results are summarized in Table I below.

TABLE I

	Example			Comparative Example						
	1	2	3	A	B	C	D	E	F	G
Formulation										
Monoethanolamine	X	X	X	X	X	X	X	X	X	X
Piperidine			X	X	X	X	X	X	X	X
Pyrazine	X	X								
Water	X	X	X	X	X	X	X	X	X	X
Surfactant (FC-129)	X	X	X	X	X	X			X	X
Hydrogen Peroxide	X		X	X	X	X			X	X
Gallic Acid	X	X	X							
Quinhydrone					X					
1,2-Naphthoquinone-4-Sulfonic Acid						X				
Alizarin							X			
Quinalizarin								X		
2,3-Dihydroxypyridine									X	
3,6-Dihydroxypyridazine				X						
1,2-Naphthoquinone										X
Catechol					X					
Etch Results*										
Etch Rate (μm/hr)	94	125	60-70	S	N	N	N	N	NS	VS

*The following abbreviations have been used:
S: Slow
N: None
VS: Very Slow
NS: Non-Selective

EXAMPLES 4-8

The procedure of Example 1 was followed by using the same ingredients in the same relative proportions, except that the amount of water in the solution was varied. The results are summarized in Table II below.

TABLE II

Example	Amount of Water (Mole Percent)	Etch Rate (μm/hr)
4	41	113
5	46	133
6	51	140
7	53	140
8	57	137

Claims

1. A method of selectively etching single crystal silicon with a (100) crystallographic orientation, comprising contacting said silicon with an etching solution which comprises gallic acid, an amine and water.

2. The method of claim 1, wherein said amine is selected from the group consisting of a diamine having 2-4 carbon atoms and an alkanolamine in which each alkanol group contains 2-3 carbon atoms, preferably monoethanolamine.

3. The method of claim 1 or 2, wherein said etching solution further comprises pyrazine or piperidine.

4. The method of any one of the preceding claims, wherein hydrogen peroxide is added to said etching solution.

5. The method of any one of the preceding claims, wherein a surfactant is added to said etching solution.

6. The method of any one of the preceding claims, wherein said etching solution comprises about 4-6 mole percent of gallic acid, about 39-56 mole percent of said amine and about 57-38 mole percent of water.

7. The method of any one of the preceding claims, wherein said etching solution has a temperature of about 115-125°C and has a pH of about 11-12.

8. An etching solution as disclosed in any one of claims 1 to 7 suitable for selectively etching single crystal with a (100) crystallographic orientation silicon, said solution containing gallic acid, an amine and water.

Patentansprüche

1. Verfahren zum selektiven Ätzen von einkristallinem Silicium mit einer kristallographischen (100)-Orientierung, das beinhaltet, das Silicium mit einer Ätzlösung in Kontakt zu bringen, die Gallussäure, ein Amin und Wasser enthält.

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2. Verfahren nach Anspruch 1, wobei das Amin aus der Gruppe ausgewählt wird, die aus einem Diamin mit 2 bis 4 Kohlenstoffatomen und einem Alkanolamin, bei dem jede Alkanolgruppe 2 bis 3 Kohlenstoffatome enthält, vorzugsweise Monoethanolamin, besteht.

3. Verfahren nach Anspruch 1 oder 2, wobei die Ätzlösung des weiteren Pyrazin oder Piperidin umfaßt.

4. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei Wasserstoffperoxid zu der Atzlösung hinzugefügt wird.

5. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei ein Tensid zu der Ätzlösung hinzugefügt wird.

6. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei die Ätzlösung etwa 4 Molprozent bis 6 Molprozent Gallussäure, etwa 39 Molprozent bis 56 Molprozent des Amins und etwa 57 Molprozent bis 38 Molprozent Wasser beinhaltet.

7. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei die Ätzlösung eine Temperatur von etwa 115 °C bis 125 °C und einen pH-Wert von etwa 11 bis 12 aufweist.

8. Ätzlösung wie in irgendeinem der Ansprüche 1 bis 7 offenbart, die zum selektiven Ätzen von einkristallinem Silicium mit einer kristallographischen (100)-Orientierung geeignet ist, wobei die Lösung Gallussäure, ein Amin und Wasser enthält.

Revendications

1. Procédé pour attaquer chimiquement sélectivement du silicium monocristallin avec une orientation crystallographique (100), consistant à placer ledit silicium en contact avec une solution d'attaque chimique à base d'acide gallique, d'une amine et d'eau.

2. Procédé selon la revendication 1, dans lequel ladite amine est sélectionnée parmi un groupe comprenant une diamine ayant 2 à 4 atomes de carbone et une alcanolamine dans laquelle chaque groupe alcanol contient 2 à 3 atomes de carbone, une monoéthanolamine de préférence.

3. Procédé selon la revendication 1 ou 2, dans lequel ladite solution d'attaque chimique comprend, de plus, de la pyrazine ou de la pipéridine.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel du peroxyde d'hydrogène est ajoutée à ladite solution d'attaque chimique.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel un surfacteur est ajouté à ladite solution d'attaque chimique.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite solution d'attaque chimique comprend environ 4 à 6 moles pour cent d'acide gallique, environ 39 à 56 moles pour cent de ladite amine et environ 57 à 38 moles pour cent d'eau.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite solution d'attaque chimique a une température d'environ 115 à 125°C et un pH d'environ 11 à 12.

8. Solution d'attaque chimique adaptée pour attaquer sélectivement du silicium monocristallin avec une orientation crystallographique (100) selon l'une quelconque des revendications 1 à 7.

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