March 29, 1960 J. R. LIGENZA 2,930,722

METHOD OF TREATING SILICON

Filed Feb. 3, 1959 2 Sheets-Sheet 1

FIG. 1

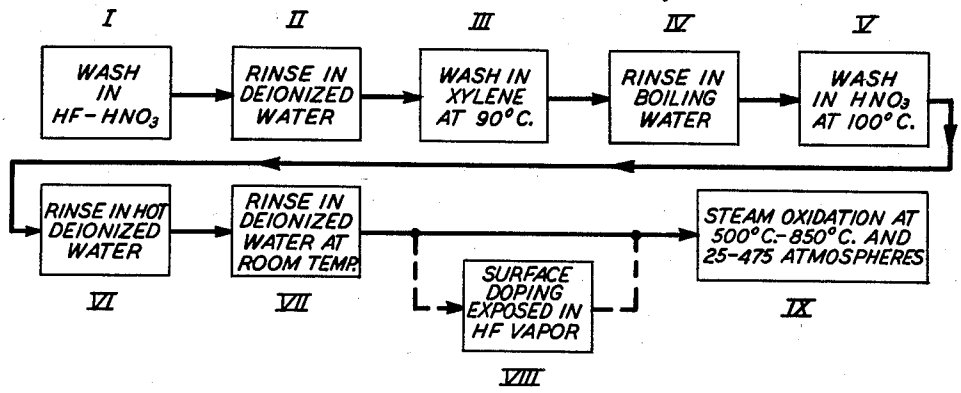

FIG. 2

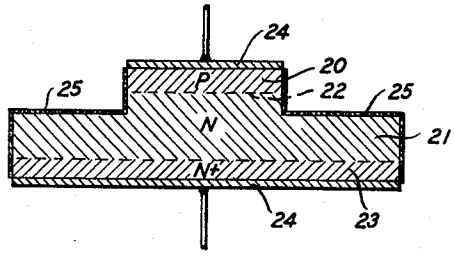

FIG. 5

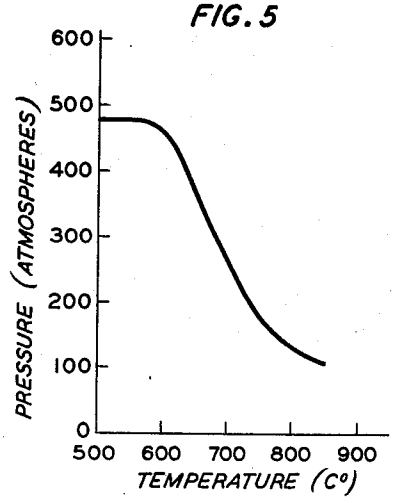

FIG. 3

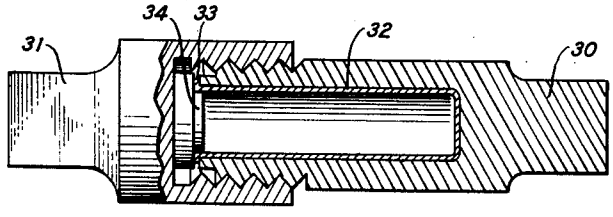

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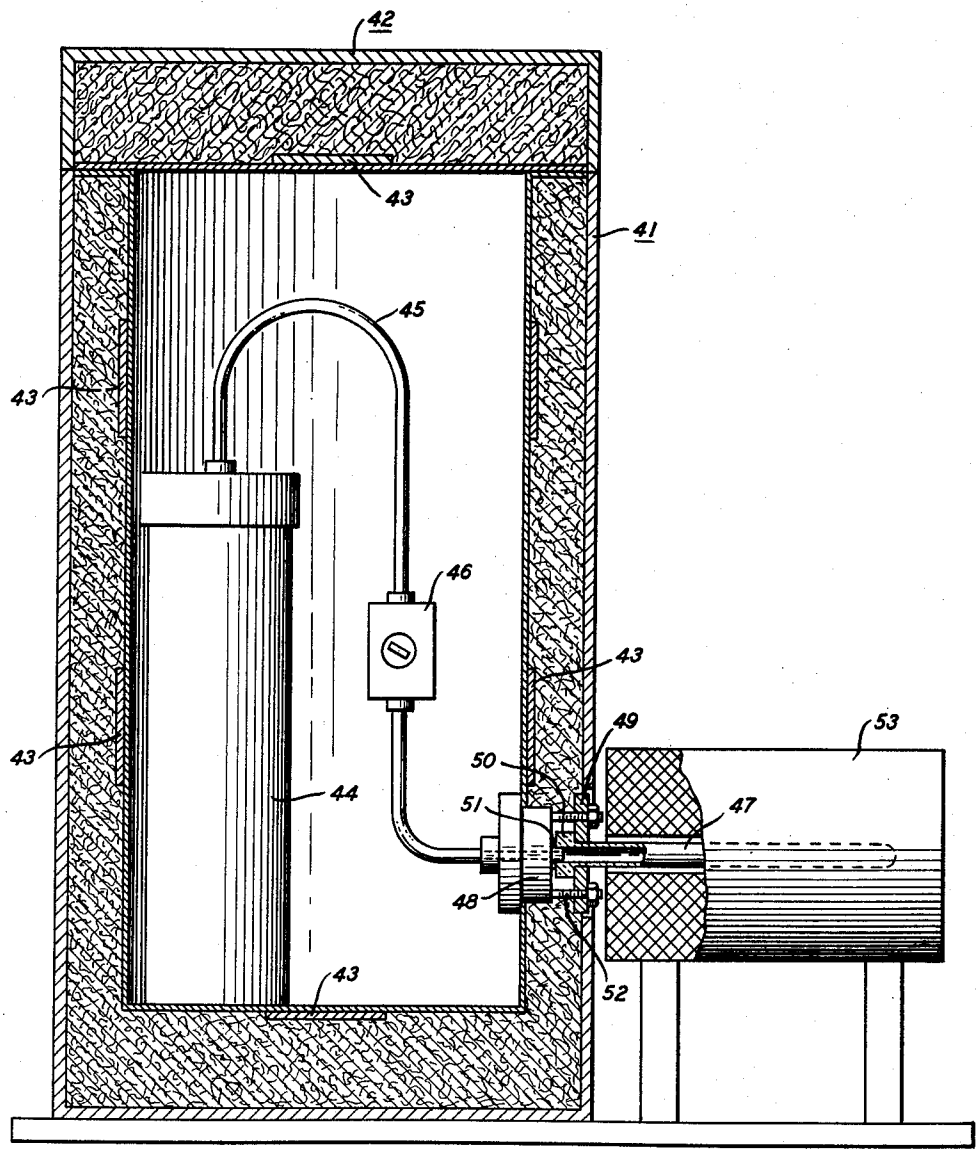
FIG. 4



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METHOD OF TREATING SILICON

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Application February 3, 1959, Serial No. 790,848

5 Claims. (Cl. 148—1.5)

This invention relates to methods of treating silicon for semiconductor devices, and relates particularly to improved methods of treating silicon to stabilize the electrical properties of silicon surfaces.

The copending patent application of M. M. Atalla, E. J. Scheibner and E. Tannenbaum, Serial No. 732,026, filed April 30, 1958, now Patent No. 2,899,344, issued August 11, 1959, teaches a method of stabilizing silicon surfaces by a preparatory technique culminating in an oxygen oxidation of the silicon at 900° centigrade to give a stable oxide film thereon. The methods of the present invention teach a preferred preparatory technique similar to that in the patent mentioned, followed by an oxidation of the clean silicon surfaces by clean steam under high pressures and at lower temperatures than those heretofore used. The modified process has several significant advantages over the process as formerly practiced.

The use of steam under pressure as an oxidizing medium results in much higher rates of film growth than are possible by oxygen oxidation. Oxidation with oxygen of a silicon surface is rate limited by the speed of thermal diffusion of silicon ions from the bulk of the material through the layers of oxide already formed on the surface. The more rapid growth rates observed when pressurized steam is employed are believed due to an attractive force exerted on silicon ions in the bulk of the body by a high concentration of oxygen ions (from the water molecule) accumulated on the silicon surface. The attractive electrostatic force of these oxygen ions is believed responsible for pulling silicon ions to the surface. Thermal diffusion is no longer rate limiting, and lower temperatures can be used to accomplish the oxidation. The high growth rates and low temperatures possible in the present method permit formation of oxide films 5000 angstroms thick, or thicker, within periods which save considerable time over oxygen oxidation.

Because lower temperatures are used for shorter periods of time in forming an oxide coating by the new process herein described, there is less danger of shifting of junctions in devices having regions of differing conductivity types. Lower temperatures and high growth rates also permit a greater variety of contacts to be made to the silicon body before treatment without danger of loosening the contacts under the influence of prolonged heating. Also lower temperatures reduce or eliminate diffusion of contact metals into the silicon substrate, which diffusion could otherwise lead to changes in electrical properties of the silicon. The avoidance of elevated temperatures made possible by steam oxidation also minimizes the danger of devitrification of the amorphous silica coatings produced. Devitrification can occur if silica films are heated to high temperatures in the presence of traces of certain inorganic materials.

It is to be understood that the steam oxidations here described have been relatively ineffective alone in producing stable surfaces on silicon without a preparatory cleaning of the surface. The surface to be oxidized

should preferably first be rendered hydrophilic, clean, and slightly oxidized. This condition is achieved by methods comprising cleaning with an organic solvent to remove waxes or other organic contaminants, rinsing in clean water, slightly oxidizing the surface with an oxidizing agent, and rinsing again. A number of variations on this skeleton process may be devised. The treatment most advantageously used comprises etching the surface of a silicon element in a mixture of hydrofluoric and nitric acids, rinsing, chemically cleaning by immersion in a hydrocarbon solvent, rinsing, treating in hot nitric acid, and rinsing the element once more before sealing into autoclaves for steam oxidation. Other aspects of the invention will become apparent from the accompanying drawings.

Fig. 1 is a flow sheet of the preferred preparatory process and steam oxidation process herein described;

Fig. 2 is a front elevation in section, greatly enlarged, of a diode device comprising a single crystal body of silicon having thereon a silicon oxide stabilizing film produced by the methods of this invention;

Fig. 3 is a front elevation, partly in section, of a simple autoclave in which a number of silicon semiconducting elements can simultaneously be oxidized with steam under high pressure;

Fig. 4 is a front elevation, partly in section of an autoclave system for the oxidation of silicon semiconducting elements in which steam is generated at a source removed from the portions of the system in which silicon oxidation occurs; and

Fig. 5 is a pressure-temperature diagram defining those conditions of temperature and pressure most satisfactory for carrying out the steam oxidations herein described.

The flow diagram of Fig. 1 shows various steps involved in the preferred process of the present invention. In step I, a single crystal body of silicon is etched at room temperature in a mixture of nitric and hydrofluoric acids, conveniently comprising six parts by volume of concentrated nitric acid to one part by volume of 48 percent hydrofluoric acid. Other acid mixtures ranging in concentration from greater than 20 to 1 to less than 1 to 1 can be used successfully, as known in the art. The etchant used is widely known and is used in the art in all proportions. This step may be followed by an optical quench in concentrated nitric acid (not shown on the flow sheet) which avoids the formation of surface stains, possibly of silicon monoxide, which may otherwise form after the etching step.

Step II is a rinsing of the etched body in deionized water, which may be characterized in having a conductivity of less than 0.05 micromho.

In step III, the washed body is treated by rinsing in a continuously flowing distillate of a hydrocarbon solvent, of which benzene and xylene are exemplary. This rinsing, continued for about fifteen minutes, aids in removing any organic residue on the surface of the semiconducting body.

Traces of the solvent used for rinsing are removed by next rinsing the washed element in boiling deionized water for about fifteen minutes, as indicated for step IV of the flow chart in Fig. 1. If further cleaning of the body is deemed necessary at this point, the body may be resubjected to etching and rinsing steps I and II before proceeding further.

In step V, the semiconductor element is next immersed for about fifteen minutes in concentrated nitric acid at a temperature of about 100° centigrade. The cleaning serves to oxidize and wash off remaining organic impurities as well as metallic impurities on the sample.

In step VI, the silicon element is rinsed in circulating deionized water at a temperature of about 90° cen-

tigrade, followed in step VII by a further rinse in a similar bath at room temperature. The steps to this stage have produced an exceptionally good silicon surface which is clean, hydrophillic, wet, slightly oxidized.

Depending on the characteristics finally desired in the silicon element, two alternative further treatments can be used. The treatment through step VII used on high purity, high resistivity, silicon produces a silicon surface which is lightly oxidized and almost perfectly hydrophilic. If induced p-type conductivity is desired in the surface regions of such high purity silicon elements, the treated elements are immediately subjected to a steam oxidation, as indicated in step IX. To inhibit possible contamination or deterioration of the cleaned and prepared surfaces, this oxidizing step should immediately follow step VII. The oxide induces a p-type conductivity in surface portions of high resistivity intrinsic silicon covered with the oxide.

However, if an n-type oxide induced conductivity region is desired in surface portions of a silicon element of high resistivity, additional step VIII may be practiced before the oxidation of step IX. As indicated in the flow chart, an n-type surface may be produced by exposing the silicon surface to vapors of hydrogen fluoride, conveniently to hydrofluoric acid vapors, for a short time (for example, one to fifteen seconds) prior to oxidation. This "surface doping" may be accomplished with various other vapors, for example chlorine, and various salt solutions.

Another technique, not shown in Fig. 1, for producing an n-type surface region comprises diffusing certain significant impurities, for example gold or iron, into the silicon body before any surface treatment is begun. During the oxidation, these impurities will be drawn from the bulk of the material into the oxide film giving an n-type conductivity surface layer.

The oxidation of low resistivity silicon bodies, such as those priorly doped for device uses, has no significant effect on the conductivity type of the underlying body. The effect of the oxide in inducing a surface conductivity type is slight, and becomes significant only for intrinsic, high resistivity, silicon substrates.

Step IX, the oxidation by steam under pressure, is discussed in greater detail later in this specification.

Fig. 2 is a greatly enlarged sectional view of a silicon diode device fabricated in part by the methods of the present invention. The element comprises a single crystal body of silicon having p-type region **20**, n-type region **21**, p-n junction **22** between them, and strongly n-type or n^+-type region **23**. The p-n junction may be produced within the body by diffusion techniques known to the art. For example, boron, which is a doping impurity for silicon, may be diffused into one side of an n-type wafer to produce a p layer and a p-n junction therebetween. Phosphorus, another significant impurity for silicon, may then be diffused into the other surface of the n-type wafer to give a three layered n^+-n-p structure like that in Fig. 2.

Metallic layers **24**, of a material such as platinum, for example, may then be affixed to both sides of the wafer by means known to the art such as in a paste, or by evaporating, sputtering, or plating, to serve as low resistance contacts for the device. Finally a central raised portion or "mesa" is formed by known cutting or etching techniques, and the device is then processed as described in Fig. 1. Thin stabilizing protective oxide film **25** is thereby formed on the silicon surfaces. Film formation is particularly desirable on the "mesa" edges in the vicinity of exposed p-n junction **22**. As mentioned earlier, formation of the oxide has no significant doping effect on the already doped silicon substrate.

Fig. 3 is a sectional view of a simple autoclave for carrying out the steam oxidations of step **9** of Fig. 1. The outer casing of the autoclave or "bomb," comprising main portion of casing **30** and threaded screw cap **31**, is of a strong metal. The alloy "Inconel X" (73 percent nickel, 15 percent chromium, 7 percent iron, 2.5 percent titanium, 1 percent columbium or niobium, balance small mounts of aluminum, silicon, manganese and carbon) has proved particularly successful as a material for the outer casing, but other strong materials are equally good. For example, an alloy of 80 percent platinum and 20 percent rhodium has been used with particularly good results. Close fitting thin inner liner **32** of an inert metal, conveniently gold, is within casing **30** to preclude possible contamination of the samples from the metals of casing **30**. Cylindrical disc **33** having a smaller disc **34** of inert metal, preferably gold, faced thereon, fits into screw cap **31**. When cap **31** is tightly joined to casing **30**, disc **34** seals inner liner **32**. Particularly if disc **34** is made of a deformable metal such as gold, a tight joint to liner **32** can be made. In use, the silicon elements are placed in the autoclaves with sufficient water to produce a desired pressure at the temperature to be used in heating the bombs. To assure that surface characteristics be uniform in any single element, it is important that thermal gradients, which favor differential growth rates of the oxide films and variation in surface properties, be avoided. For this reason, the bombs of Fig. 2 advantageously are kept small in size, the longest dimension of the casing being about two and one-half inches and that of the gold liner about one inch. The water used in the oxidation step to produce steam is high purity deionized water as is employed in the silicon cleaning process. In addition, the autoclaves are cleaned prior to use by washing in nitric acid at 100° centigrade, rinsing in hot deionized water, and then rinsing again in deionized water at room temperature.

A convenient autoclave system for oxidizing a large number of samples simultaneously is shown in Fig. 4. The system comprises double walled cabinet **41** with insulation **42**, for example glass wool, between the walls thereof. Strip heaters **43**, comprising metal clad resistance heaters, are mounted in cabinet **41** as a convenient heat source for the cabinet interior. Steam generating unit **44** is a thick walled autoclave having deionized water therein, and sealed to withstand high interior pressures. Autoclave **44** shown is a commercial item, a product of the American Instrument Company, Silver Spring, Maryland. Other similar apparatus could be used equally successfully, however. Tube **45** leads through heated valve **46**, also a commercial product, to tubular container **47**, in which the silicon elements to be oxidized are placed. Container **47** is of a chemically inert, structurally strong material. Though noble metals can be used, or a metal casing having a noble metal lining, container **47** is conveniently made of silica with a wall thickness of about ⅛ inch. A pressure-tight seal of container **47** to cabinet **41** can be made by leading tube **45** to steel ring **48** having a raised inner portion fitting into container **47**. Second steel ring **49**, fitting around container **47**, presses lip **50** of container **47** against ring **48**. Gold washer **51**, deformable under pressure, aids in forming a gas-tight seal. Bolts **52** are provided on ring **48** so that ring **50** can be clamped tightly thereto, compressing lip **50** and washer **51**. Furnace **53**, conveniently comprises a coil of resistance wire, surrounds container **47** to give uniform heating of all portions of container **47**, minimizing thermal gradients.

The advantage of the autoclave system of Fig. 4 is the generation of steam at a pressure determined by the temperature of steam generating unit **44**. Steam at this pressure is fed through tube **45** and valve **46** to container **47**, where it is used at the temperature of furnace **53**. Prior to use, all portions of the system contacting either the silicon to be oxidized or the deionized water used for the process are cleaned with hot nitric acid and rinses of deionized water as earlier described.

Oxidation of silicon surfaces under conditions of too

high temperature and pressure may result in the oxidation of silicon, not to amorphous silicon oxide, but to silicic acid. Silicon samples oxidized under conditions promoting acid formation have dull surfaces and appear to be lapped. Fig. 5 is a pressure-temperature diagram for the oxidation process, picturing the maximum recommended pressure, that is the highest pressure not leading to silicic acid reactions, at any given oxidation temperature between 500° centigrade and 850° centigrade. Some experimental points on the curve of Fig. 5 are tabulated below in Table 1.

TABLE 1

Temperature (Degrees Centigrade)	Maximum Pressures (Atmospheres)
500	475
575	475
650	375
750	175
850	105

Although oxidation of silicon by steam takes place at even very low pressures, a minimum steam pressure of 25 atmospheres, through the temperature range used, is advantageously used so that thick films can be formed in feasibly short time periods. As shown in Fig. 5, steam pressures up to 475 atmospheres can be used with good results in the lower temperature range. Temperatures between 500° centigrade and 850° centigrade are preferred for the oxidations as shown in Fig. 5. Temperatures between 600° centigrade and 700° centigrade have given particularly good oxide coatings, and a temperature of 650° centigrade has been found to yield optimum results in many instances. For the smaller temperature range mentioned above, maximum pressures, as shown in Fig. 5, range between about 465 atmospheres and 250 atmospheres. At 650° centigrade the maximum pressure is 375 atmospheres. At this temperature and pressure, the growth rate of oxide films is about 120 angstroms per minute, and a film 3000 angstroms thick can be grown in about 25 minutes. For comparison, a film of comparable thickness produced by prior art heatings in oxygen would require one hour at an elevated temperature of 1250° centigrade.

In the steam oxidation, increases in either temperature or pressure within the limits specified will increase the growth rate of oxide.

At a given temperature and pressure, oxidation is continued until an oxide coating of desired thickness is produced. Oxide films as thin as 300 angstroms have been found useful in stabilizing surface properties, but thicker films up to 10,000 angstroms, and particularly between 5000 angstroms and 10,000 angstroms, are usually preferred.

A specific example of the practice of the invention herein described follows below.

Example

Silicon diode devices like those shown in Fig. 2 were made by doping a sheet of n-type silicon by exposure to gaseous boron to form a structure having a p-n junction about 0.0015 inch below the semiconductor surface. One face of the wafer was then doped with phosphorus applied by a "paint-on" technique to produce a p-n-n+ layered structure. Both surfaces were sputtered with platinum to furnish electrical contacts to the p and n+ layers. On wafers 0.030 inch in diameter, "mesas" 0.010 inch in diameter were formed using ultrasonic cutting techniques. The wafers were then subjected to a forty second etch in a mixture containing six parts of nitric acid to one part of hydrofluoric acid to etch the exposed p-n junctions, the metal coated portions of the wafers being protected by wax. The wax was removed by solvents, and the wafers rinsed in deionized water. The wafers were then washed in xylene and rinsed again in deionized water. The wafers were then re-etched for five seconds in the 6:1 HNO_3—HF mixture, quenched in HNO_3, and rinsed in deionized water. They were next soaked for fifteen minutes in nitric acid at 100° centigrade, rinsed in deionized water for fifteen minutes, and air dried.

The samples were oxidized in small bombs like those shown in Fig. 3, made of an 80 percent platinum-20 percent rhodium alloy, with gold liners. The diodes were oxidized at 650° centigrade under a pressure of 50 atmospheres for two hours, and had an oxide coating about 3000 angstroms thick.

Table 2 presents the electrical characteristics of some of the diodes treated as described above.

TABLE 2

Breakdown voltage (volts)	Reverse current at 10 volts (in amperes)	Reverse current at breakdown voltage less two volts (in amperes)
67	$3 \ (10^{-10})$	$4 \ (10^{-9})$
65	$2.2 \ (10^{-10})$	$3 \ (10^{-9})$
57	$2.5 \ (10^{-10})$	$1.2 \ (10^{-8})$
60	$1.0 \ (10^{-9})$	$4.6 \ (10^{-8})$
57	$3.0 \ (10^{-10})$	$2.6 \ (10^{-8})$

Although specific embodiments have been shown and described, it is to be understood they are merely illustrative, and are not limiting on the scope and spirit of the invention.

What is claimed is:

1. The method of fabricating a semiconductor device, which method comprises washing a body of single crystal silicon in a mixture of nitric acid and hydrofluoric acid, rinsing said body in deionized water, washing said body in a flowing hot hydrocarbon solvent, washing said body in boiling deionized water, immersing said body in hot nitric acid, rinsing said body in hot deionzed water, rinsing said body in deionized water at room temperature, and immediately thereafter oxidizing the surface of said body with steam at a temperature between 500° centigrade and 850° centigrade and below a maximum pressure of between 475 atmospheres at 500° centigrade and 105 atmospheres at 850° centigrade for a period sufficient to produce an oxide layer having a thickness of at least 300 angstroms.

2. The method substantially as described in claim 1 which includes the step of exposing said body of silicon to vapors of hydrofluoric acid just prior to oxidizing the surface of said body with steam.

3. The method of fabricating a semiconductor device, which method comprises diffusing at least one significant impurity into a single crystal body of silicon, washing said body in a mixture of nitric acid and hydrofluoric acid, rinsing said body in deionized water, washing said body in a hot hydrocarbon solvent, washing said body in hot deionized water, immersing said body in hot nitric acid, rinsing said body in hot deionized water and then in deionized water at a lower temperature, and then oxidizing said body in steam at a temperature between 500° centigrade and 850° centigrade and below a maximum pressure of between 475 atmospheres at 500° centigrade and 105 atmospheres at 850° centigrade for a period sufficient to produce an oxide layer having a thickness of at least 300 angstroms.

4. The method of fabricating a semiconductor device, which method comprises preparing a clean hydrophilic surface on a body of single crystal silicon, and then oxidizing said body in steam at a temperature between

500° centigrade and 850° centigrade and below a maximum pressure of between 475 atmospheres at 500° centigrade and 105 atmospheres at 850° centigrade for a period sufficient to produce an oxide layer having a thickness of at least 300 angstroms.

5. The method of fabricating a semiconductor device, which method comprises washing a silicon body with an organic solvent, rinsing in water, slightly oxidizing the surface of said body, rinsing again in water, and then oxidizing said body in steam at a temperature between 500° centigrade and 850° centigrade and below a maximum pressure of between 475 atmospheres at 500° centigrade and 105 atmospheres at 850° centigrade for a period sufficient to produce an oxide layer having a thickness of at least 300 angstroms.

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