

June 11, 1963

J. J. LANDER ETAL

3,093,507

PROCESS FOR COATING WITH SILICON DIOXIDE

Filed Oct. 6, 1961

2 Sheets-Sheet 1

FIG. 1

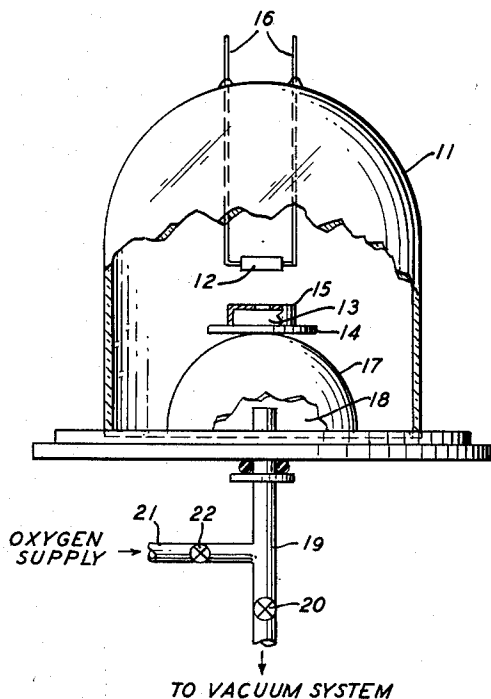
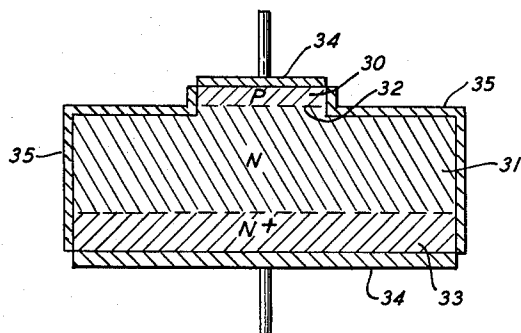


FIG. 3



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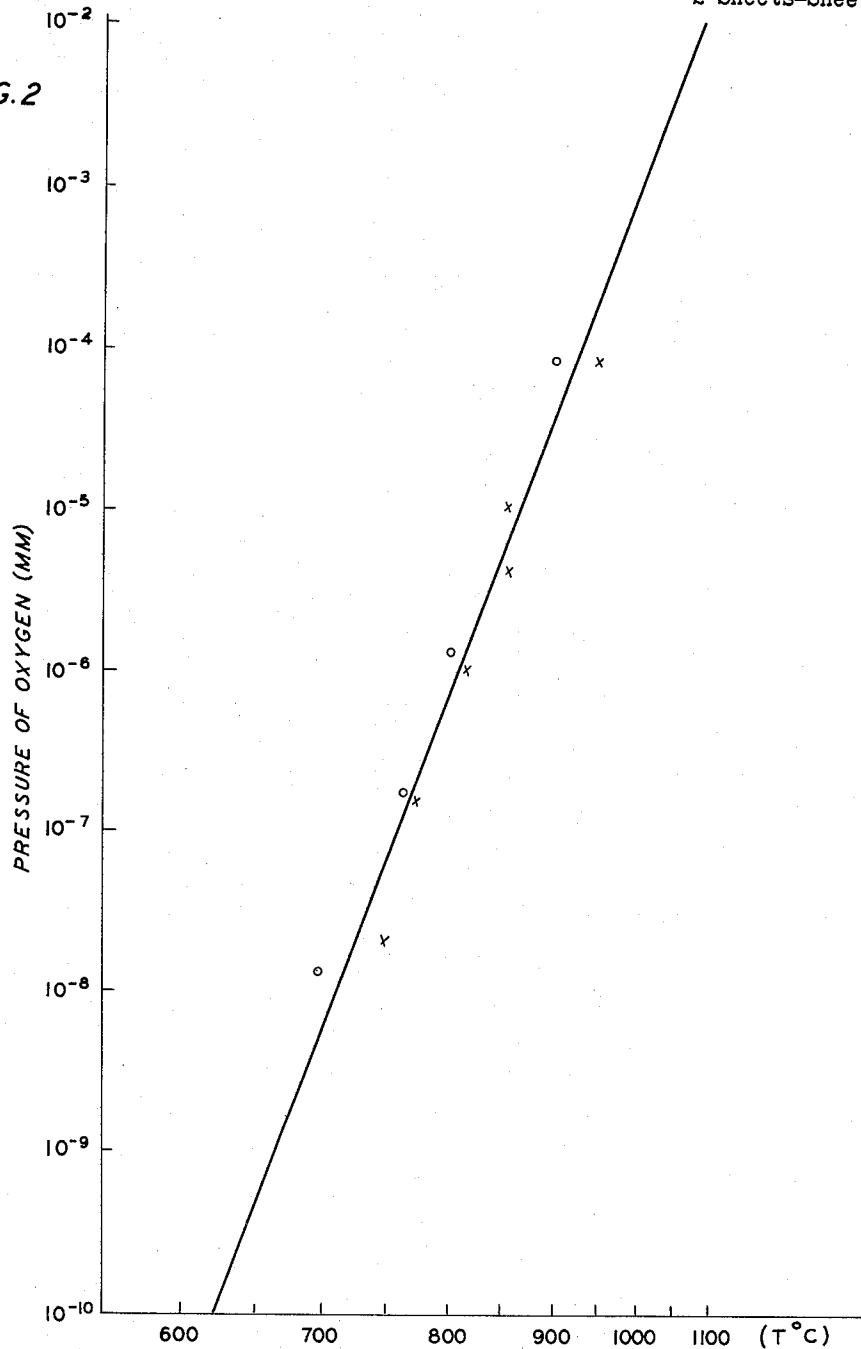
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2 Sheets-Sheet 2

FIG. 2



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PROCESS FOR COATING WITH SILICON DIOXIDE
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5 Claims. (Cl. 117—201)

This invention relates to a process for coating semiconductor surfaces with silicon dioxide.

From the outset of the semiconductor art, the significance of the device surface has been a subject of extensive study. There has been some appreciation of the desirability of providing protective coatings on particular surfaces of semiconductor devices. For example, United States Patent 2,816,850, granted to H. E. Haring on December 17, 1957, discloses the application of a particular protective coating over the intermediate conductivity type region of junction type transistors. United States Patent 2,899,344 issued to M. M. Atalla et al. on August 11, 1959, discloses a method for producing a semiconductor surface of prescribed physical and electrical characteristics immediately prior to the application of a thermally grown oxide coating.

With the advancement of semiconductor technology more and more interest has been devoted to providing protective coatings for semiconductor surfaces. Recently, a vacuum evaporation technique was developed wherein a mixture of silicon and silicon dioxide is heated in vacuo at temperatures of the order of 1200° C. thereby resulting in a condensed coating which analyzes as silicon monoxide. However, it has been determined that protective coatings of silicon dioxide are considered advantageous in certain uses from a standpoint of maintaining the stability of electrical characteristics of the surface being coated.

In accordance with this invention a process is described for coating the surfaces of semiconductor devices with a thin film of silicon dioxide. These protective coatings are formed by heating a body of silicon of high purity in the presence of oxygen at elevated temperatures and subatmospheric pressures whereby silicon oxide is evolved from the surface of the source silicon and deposited by condensation on the device surfaces.

The invention will be more readily understood from the following detailed description, taken in conjunction with the accompanying drawing in which:

FIG. 1 is a front elevational view, partly in section, of an apparatus suitable for use in producing protective coatings of silicon dioxide on semiconductor surfaces in accordance with the present invention,

FIG. 2 is a graphical representation on coordinates of oxygen pressure in millimeters of mercury against temperature in degrees centigrade defining the operative temperature and pressure ranges of the present inventive technique, and

FIG. 3 is a front elevational view, in section, of a semiconductive device comprising a single crystal body of silicon having thereon a protective coating of silicon dioxide produced in accordance with the present invention.

With reference now more particularly to the drawing, FIG. 1 depicts apparatus suitable for depositing a silicon dioxide film by vacuum evaporation. Shown in FIG. 1 is a vacuum chamber 11 in which are disposed silicon source 12 and a semiconductor device, for example, a silicon diode, hereinafter designated as receiver 13. Platform 14 is employed as a positioning support for receiver 13, upon which the silicon dioxide film is to be deposited. Platform 14 may suitably be fabricated from any metal; however, it is convenient to utilize aluminum for this

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purpose. Mask 15 is placed on receiver 13 to restrict the deposition of the film to the desired area.

The spacing between silicon source 12 and receiver 13 is not critical. However, for the best efficiency during the coating process, receiver 13 should be positioned at a distance (from source 12) equal to the length of the source 12. In order to assure efficient condensation of the vapors of silicon oxide on the surface of the receiver, it is necessary that the temperature of the receiver be less than that of the source. The permissible temperature range will depend upon the properties of the specific receiver employed; thus, a high vapor pressure material such as zinc must be maintained at approximately room temperature. Silicon receivers are preferably maintained at temperatures approximately 50–100° C. lower than the source silicon in order to avoid evaporation of the deposited silicon dioxide. In general, it may be stated that the receiver is maintained at temperatures approximately 50° C. below the melting point for most efficient operation.

Silicon source 12 comprises a thin wafer of silicon, the surface area of which is a function of the rate of evolution of silicon monoxide. The ends of silicon source 12 are shown connected to electrical leads 16 which permit heating of the source silicon by means of an electrical power supply, not shown.

Platform 14 is suitably positioned atop aluminum hemisphere 17 which serves to permit uniform dispersion of oxygen during the coating process through aperture 18. Reaction chamber 11 is preferably composed of glass, although other materials, such as stainless steel, may be employed.

Provision is made for evacuating chamber 11 via conduit 19 controlled by valve 20. Oxygen enters the chamber via conduits 19 and 21, which are controlled by valve 22, during the coating process.

In the operation of the process, vacuum chamber 11 is evacuated by means of any pumping procedure well known in the art, such as oil diffusion, ion or mercury pumps, to a pressure within the range of 10⁻³ to 10⁻¹⁰ millimeters of mercury dependent on considerations of temperature as discussed below. During the evacuation of the chamber, the pump is attached to conduit 19 while maintaining valve 20 in the open position and valve 22 in the closed position.

Following the evacuation, oxygen is admitted to the system via conduit 21 while maintaining valves 22 and 20 in the open position. In this manner the pressure is regulated within the desired range while the system is pumped continuously.

Next, silicon source 12 is heated by means of an electrical voltage to temperatures within the range of 700 to 1000° C. dependent on the pressure employed, as discussed below. The rate of evaporation of silicon from the surface of source 12 may be determined by calculation from the formula

$$k=7 \times 10^{18} \times P$$

where k is equal to the rate of evaporation in atoms/cm.² second and P is equal to the oxygen pressure in millimeters of mercury.

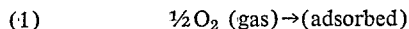
Receiver 13 may be any semiconductor device requiring a protective coating or it may be any other material which can be usefully coated, such as a reflecting or transmitting optical lens or an electron tunneling device requiring a thin coating of silica.

Silicon source 12 may be any high grade silicon in common use, such as silicon having a purity of approximately 99.9%. It will be appreciated by those skilled in the art that the coating requirements will vary depending upon the particular surface being coated and it may be stated generally that impurities may be tolerated in moderation.

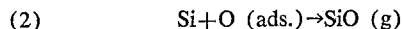
At a given temperature and pressure, reaction and

evaporation of the source silicon is continued until a silicon dioxide coating of desired thickness is obtained. Films as thin as 100 Angstroms have been found useful in stabilizing surface properties but thicker films are generally preferred. There is no upper limit on the thickness of the films obtained, but for practical reasons films of 10,000 Angstroms are suitable for most purposes.

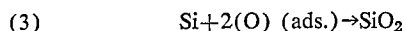
A consideration of the chemical reactions involved in the process described herein results in the following explanation of the reaction mechanism (for an open system):



in which oxygen is adsorbed chemically on the source silicon,



in which oxygen is removed by evaporation of silicon monoxide, which apparently does not form associated molecules; and



which is favored by increasing oxygen pressure, so inhibiting the evolution of silicon monoxide gas.

A further distinction between Reactions 2 and 3 resides in the fact that Reaction 3 requires the cooperation of a group of Si—O units to nucleate a stable silica film, which proceeds in energetically significant steps. Accordingly, high surface coverage favors Reaction 3 over Reaction 2. The above equations predict the following sequence of reactions:

(a) A steady state region of low coverage at low oxygen pressures and high temperatures, of the order of 800° C., in which the surface is relatively clean and in which the rates of oxygen adsorption and silicon monoxide evaporation are equal.

(b) A transition region of steady states in which oxygen coverage approaches that required to nucleate a silica film and in which the rates of adsorption and evaporation are still equal.

(c) A region in which growth of the film takes place and evolution of silicon monoxide is inhibited.

The evaporated silicon monoxide which coats the receiver is further oxidized by the ambient oxygen to silicon dioxide, thereby forming a coating of silicon dioxide on the receiver.

Referring now to FIG. 2, there is shown a graphical representation on coordinates of pressure in millimeters of mercury against temperature in degrees centigrade which indicates the relationship between temperature and pressure in the described process. The transition region (b) found between clean and oxidized source silicon is indicated by the solid line in the figure. The various points (O for oxidized surface and X for clean surface) were obtained by observing rates of silicon monoxide evolution. In the region to the left of the solid line, evolution is inhibited by the growth of an oxide film on the source. In order to obtain the desired rates discussed above it is essential to operate the process at temperatures and pressures represented by the region to the right of the solid line.

Upon analysis of FIG. 2 it is determined that the range of interest, that is, where receiver 13 is coated with a thin film of silicon dioxide, is defined by oxygen pressures defined by the straight line joining the approximate points of 10^{-10} millimeters of mercury at 625° C. and oxygen pressures of the order of 10^{-3} millimeters of mercury at 1000° C. on semilog coordinates as indicated.

FIG. 3 is an enlarged sectional view of a silicon diode device coated with a protective layer of silicon dioxide in accordance with the present inventive technique. The device comprises a single crystal body of silicon having p-type region 30, n-type region 31, p-n junction 32 between them, and strongly n-type or n⁺ type region 33. 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. Phosphorous, 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, as shown in FIG. 3.

Metallic layers 34, 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 herein. Thin protective oxide film 35 is thereby formed on the silicon surfaces.

The following example is given by way of illustration and is not to be construed as limiting the invention, many variations of which are possible within the scope and spirit thereof.

Example

A silicon diode device like that shown in FIG. 3 was 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 phosphorous 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 wafer 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 wafer was then re-etched for five seconds in the 6:1 HNO₃-HF mixture, quenched in NHO₃, and rinsed in deionized water. It was next soaked for 15 minutes in HNO₃ at 100° C., rinsed in deionized water for 15 minutes and air dried. The wafer was then inserted in the apparatus of FIG. 1 and a silicon dioxide coating produced thereon by heating a pure silicon wafer (source silicon) at 900° C. at an oxygen pressure of 10^{-6} millimeters of mercury. The diode had a silicon dioxide coating, approximately 1000 Angstroms thick after 45 minutes.

What is claimed is:

1. A method of coating a surface with a protective coating of silicon dioxide which comprises heating a silicon source having a purity of at least 99.9% to a temperature within the range of 625 to 1000° C. in the presence of oxygen maintained at a pressure within the range of 10^{-10} to 10^{-3} millimeters of mercury, the lower temperature corresponding with the lower pressure, thereby vaporizing silicon monoxide from the surface of said silicon source, and condensing said silicon monoxide on said surface which is maintained at a temperature approximately 50° C. below that of the source silicon, thereby resulting in a coating of silicon dioxide.

2. The method of claim 1 wherein said coating has a thickness of at least 100 Angstroms.

3. The method of claim 1 wherein said coating has a thickness within the range of 100 to 10,000 Angstroms.

4. The method of coating the surface of a diffused junction silicon diode with a protective coating of silicon dioxide which comprises heating a silicon source having a purity of at least 99.9% to a temperature within the range of 625 to 1000° C. in the presence of oxygen maintained at a pressure within the range of 10^{-10} to 10^{-3} millimeters of mercury, the lower temperature corresponding with the lower pressure, thereby vaporizing sil-

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icon monoxide from the surface of said silicon source, and condensing said silicon monoxide on the surface of said diffused junction silicon diode which is maintained at a temperature approximately 50° C. below that of the source silicon, thereby resulting in a coating of silicon dioxide.

5. The method of claim 4 wherein said source silicon is heated to a temperature of 900° C. in the presence of oxygen maintained at a pressure of 10⁻⁶ millimeters of mercury.

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