

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) METHOD OF TREATING SEMICONDUCTOR DEVICES TO IMPROVE LIFETIME

(71) We, RCA CORPORATION (formerly RADIO CORPORATION OF AMERICA), a corporation organised under the laws of the State of Delaware, United States of America, of 30 Rockefeller Plaza, City and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for treating semi-conductor devices so as to improve the carrier lifetime thereof.

Many semiconductor devices include at least one region of semiconductor material covered by an overlying layer of insulating material. In particular, metal-oxide-semiconductor field devices, as well as planar devices (in which a protective insulating layer overlies the semiconductor surface at points where one or more P-N junction regions within the semiconductor material extend to the surface), employ this construction.

In many semiconductor devices of this type, it is important that instabilities due to surface states at the semiconductor-insulator interface and to trapped charges in the insulating layer be substantially eliminated. This requirement is especially severe in field effect devices employing the insulating layer as a biased dielectric.

In other applications, such as the recently introduced silicon vidicon structure it is important that the semiconductor material exhibit a relatively long carrier lifetime.

According to the invention we provide a process for manufacturing a semiconductor device, comprising the steps of: providing a substrate having a number of operating semiconductor regions forming at least one passive semiconductor element, at least one of said regions being contiguous with a given surface of said substrate; forming a layer of insulating material on said given surface overlying at least a part of said at least one

region; exposing said layer to an atmosphere comprising a hydrogen halide of a kind which does not remove the insulating layer; and heating said substrate to a given temperature sufficient to convert any deleterious metal present to the metal halide and to volatilize the halide at the exposed surface of said insulating layer, said atmosphere being maintained substantially free of water vapour.

The accompanying drawing shows a silicon vidicon target structure manufactured according to the invention.

In order to provide a substantial increase in the carrier lifetime of a semiconductor material, it is necessary to remove from the material any contaminants which degrade lifetime. Such contaminants are usually present in the form of heavy metals such as gold, copper and iron which act as trapping or recombination sites.

We have found that heat treatment of the semiconductor material in an atmosphere comprising hydrogen chloride and substantially free of water vapor produces a considerable improvement in lifetime.

A process for manufacturing a semiconductor device will now be described by way of example.

A monocrystalline silicon wafer is cleaned by conventional methods. The wafer is then gas etched at 1100°C in an atmosphere comprising hydrogen and including a volumetric concentration of hydrogen chloride of about 1%. This etching treatment is carried out for a sufficient time to remove approximately 4 microns of silicon from the exposed surface of the wafer.

The wafer is then allowed to cool, and the hydrogen/hydrogen chloride atmosphere is replaced by dry oxygen. The silicon wafer is exposed to the dry oxygen for approximately 3 minutes at a temperature of about 1200°C in order to form a thin protective thermally grown silicon dioxide layer on the semiconductor surface. The purpose of this thin

initial layer is to preclude undesirable etching of the silicon surface when hydrogen chloride gas is subsequently introduced into the oxygen atmosphere.

5 After the initial 3 minute oxidation, a 1% volumetric concentration of hydrogen chloride is introduced into the dry oxygen atmosphere, and the semiconductor wafer is treated in this atmosphere at the 1200°C
10 temperature for approximately 4 hours. During this time, the thickness of the oxide layer increases, and the hydrogen chloride acts to remove deleterious lifetime killing contaminants from the semiconductor-insulator structure.

15 After the 4 hour treatment, the atmosphere is changed to helium in order to remove any residual hydrogen chloride from the treated wafer.

20 The wafer is allowed to cool and then annealed in a hydrogen atmosphere at a temperature of about 500°C for a time of 15 minutes or more.

25 The annealing process improves performance of devices by reducing or eliminating surface states at the semiconductor-insulator interface.

30 A capacitance-voltage curve obtained from a wafer processed according to the method described above showed no measurable oxide charge, surface states or polarization.

35 The carrier lifetime of a wafer processed as described above was measured by applying an evaporated aluminum electrode to the exposed surface of the silicon dioxide layer, and subjecting the resultant structure to a large voltage pulse, applied between the aluminum electrode and the semiconductor material, in a polarity so as to establish a
40 large depletion region at the semiconductor surface adjacent the electrode. The carrier lifetime was determined by measuring the time constant associated with relaxation of the depletion region to its equilibrium condition. This measuring technique is described in detail in a paper by F. P. Heiman
45 entitled "On the Determination of Minority Carrier Lifetime from the Transient Response of an MOS Capacitor", published in the IEEE Transactions on Electron Devices, November 1967, p. 781.

50 This measurement technique indicated a carrier lifetime of from 10 to 300 microseconds, whereas the same measurement, when taken on a wafer processed as described
55 above but without the addition of hydrogen chloride to the oxygen atmosphere, yielded a lifetime of 0.2 to 1.0 microseconds.

60 While the preferred embodiment of our process is directed to the use of hydrogen chloride, any hydrogen halide which does not remove the silicon dioxide insulating layer may be employed. In particular, hydrogen bromide and hydrogen iodide may be
65 substituted for the hydrogen chloride.

While we prefer to carry out the heat treatment step in the hydrogen chloride/oxygen atmosphere at a temperature in the range of 1000° to 1200°C, this treatment may be satisfactorily accomplished at temperatures in the range of 800° to 1350°C. While our heat treatment step is carried out at an oxygen flow rate of about 1000 to 3000 c.c. per minute, and at atmospheric pressure, other pressures and flow rates may be employed. While the preferred volumetric concentration of hydrogen chloride is about 1%, good results are obtained with a volumetric concentration of 0.5% and other concentrations in the range of 0.1 to 2.0% may be employed. On the other hand, a volumetric concentration of 10% results in reaction of the hydrogen chloride with the oxygen to produce water vapor; devices treated in the 10% hydrogen chloride atmosphere show negligible improvement in carrier lifetime, and pitting of the silicon surface.

The process of our invention may, e.g., be carried out in either a resistance heated or a cold wall (induction heated) furnace. Based upon the aforementioned and other data which we have obtained, heat treatment in an atmosphere comprising dry oxygen and hydrogen chloride, the atmosphere being substantially free of water vapor, results in an increase of carrier lifetime by the factor of 10 to 1000 or more. The absence of water vapor during our heat treatment process was confirmed by monitoring the oxidation rate of the silicon semiconductor material, it being well known that silicon oxidizes much more rapidly in water vapor than in a dry oxygen atmosphere.

Our process is particularly applicable to the manufacture of a light sensitive image pickup tube (hereinafter referred to as a Silicon Vidicon) which employs an electron beam addressed silicon diode array of the type shown in Figure 1. Such a structure requires relatively high (about 10 microseconds or more) carrier lifetimes in the semiconductor material; such lifetimes may be reproducibly attained by the process of our invention.

In a silicon vidicon tube, a target 1 is scanned by a low velocity electron beam 2 emanating from a cathode 3. The electron beam 2 is formed, collimated, focussed, deflected and accelerated by a suitable electron gun structure (not shown). Typically the electron beam 2 may have a circular cross-section with a diameter of about 1 mil.

The target 1 comprises a substrate 4 of monocrystalline semiconductor material, preferably silicon, of one conductivity type into which a large number of small regions 5 of opposite conductivity type are diffused. Preferably, the substrate 4 is of N type conductivity and the diffused regions 5 are

of P type conductivity. The diffused P type regions 5 are of a diameter substantially smaller than the diameter of the electron beam 2, so that the beam 2 subtends a number of the regions 5, thus making it unnecessary to register the beam 2 with the individual regions.

Each of the diffused P type regions 5 has a small P-N junction 6 to form a diode in conjunction with the substrate 4. The exposed surface of the substrate 4 adjacent the P type regions is provided with a thin silicon dioxide coating 7 which overlies and protects the P-N junctions 6 where they extend to the semiconductor surface.

A thin surface layer 8 of relatively high electrical conductivity is disposed adjacent the opposite surface of the substrate 4, i.e. the surface which may be illuminated by a light image to be scanned. The conductive layer 8 may comprise a layer of N⁺ conductivity type formed by diffusion of a suitable donor impurity into the substrate 4. The conductive layer 8 and the substrate 4 are sufficiently thin so that carriers generated by the light incident upon the exposed surface of the layer 8 may penetrate the substrate 4 to reach the P-N junctions 6.

The substrate 4 is supported by a ring 9 of relatively thick semiconductor material, which may be secured to the inside envelope of the silicon vidicon tube.

Each of the P-N junctions 6 is reverse biased by means of (i) a voltage source 10, which may typically have a value of about 10 volts, and (ii) a load resistor 11, which may typically have a value of several hundred thousand ohms. When the electron beam 2 is not scanning a particular P type region 5, the P-N junction 6 associated with that region is discharged by incident photons from the light image, the amount of discharge being dependent upon the photon flux. When the scanning electron beam 2 returns to this particular P-N junction, electrons flow to the P type region to provide a current which recharges the associated diode. This recharging current is directly related to the photon flux (light intensity) from the light image incident upon the P-N junction 6, and a corresponding voltage signal is developed across the load resistor 11. This signal is coupled to suitable amplifier circuitry by means of a capacitor 12.

The incident light discharges the individual diodes by generating electron-hole pairs in the vicinity of the associated P-N junctions. These generated electrons and holes diffuse into the P-N junction region and are swept across the junction by the associated space charge field therein, thus serving to discharge the associated diodes. A number of the carriers created by the incident photons recombine and are lost, so that they do not contribute to discharge of the associated

diodes. This recombination reduces the collection efficiency of the target 1, and directly degrades the sensitivity of the silicon vidicon.

The collection efficiency may be improved by increasing the bulk carrier lifetime and reducing the surface recombination velocity of the semiconductor material comprising the target 1. Specifically, long carrier lifetimes and low recombination velocities provide high collection efficiency and therefore improve optical sensitivity.

The target 1 may be manufactured by providing a silicon substrate 4 of N type conductivity, having a N⁺ surface layer 8 diffused therein. To form the P type regions 5, the corresponding surface of the substrate 4 is coated with a thermally grown silicon dioxide layer 7, which may typically have a thickness of from 0.5 to 1 micron. The silicon dioxide layer 7 is grown in an atmosphere comprising dry oxygen and a volumetric concentration of hydrogen chloride of about 1%, in the manner previously described.

After the silicon dioxide layer has been grown, holes are etched therein exposing small regions of the substrate 4. A thin glassy layer containing a suitable acceptor impurity material is deposited on the semiconductor surface, and subsequently heated to form the diffused P type regions 5. Preferably, borosilicate glass may be employed as the impurity source. During or after the diffusion process, the borosilicate glass is exposed to an atmosphere comprising hydrogen chloride, the atmosphere being substantially free of water vapor, in order to further improve the carrier lifetime of the semiconductor material in the manner previously described.

Thereafter, the portion of the borosilicate glass layer overlying the active P type regions 5 may be removed by photoetching.

WHAT WE CLAIM IS:—

1. A process for manufacturing a semiconductor device, comprising the steps of: providing a substrate having a number of operating semiconductor regions forming at least one passive semiconductor element, at least one of said regions being contiguous with a given surface of said substrate; forming a layer of insulating material on said given surface overlying at least a part of said at least one region; exposing said layer to an atmosphere comprising a hydrogen halide of a kind which does not remove the insulating layer; and heating said substrate to a given temperature sufficient to convert any deleterious metal present to the metal halide and to volatilize the halide at the exposed surface of said insulating layer, said atmosphere being maintained substantially free of water vapour.

2. A process as claimed in claim 1,

of P type conductivity. The diffused P type regions 5 are of a diameter substantially smaller than the diameter of the electron beam 2, so that the beam 2 subtends a number of the regions 5, thus making it unnecessary to register the beam 2 with the individual regions.

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diodes. This recombination reduces the collection efficiency of the target 1, and directly degrades the sensitivity of the silicon vidicon.

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WHAT WE CLAIM IS:—

1. A process for manufacturing a semiconductor device, comprising the steps of: providing a substrate having a number of operating semiconductor regions forming at least one passive semiconductor element, at least one of said regions being contiguous with a given surface of said substrate; forming a layer of insulating material on said given surface overlying at least a part of said at least one region; exposing said layer to an atmosphere comprising a hydrogen halide of a kind which does not remove the insulating layer; and heating said substrate to a given temperature sufficient to convert any deleterious metal present to the metal halide and to volatilize the halide at the exposed surface of said insulating layer, said atmosphere being maintained substantially free of water vapour.

2. A process as claimed in claim 1,



wherein said atmosphere comprises (i) substantially dry oxygen and (ii) hydrogen chloride, hydrogen bromide or hydrogen iodide.

5 3. A process as claimed in claim 1, wherein said semiconductor material comprises silicon and said insulating layer comprises silicon dioxide, at least a part of said silicon dioxide layer being thermally
10 grown in said atmosphere comprising a hydrogen halide.

15 4. A process as claimed in claim 3, wherein said atmosphere includes dry oxygen and the volumetric concentration of said halide is less than 10%.

20 5. A process as claimed in claim 4, wherein said halide comprises hydrogen chloride at a volumetric concentration in the range of 0.1 to 2%.

25 6. A process as claimed in claim 4, wherein said halide comprises hydrogen chloride at a volumetric concentration of about 1%, said atmosphere being maintained at normal atmospheric pressure.

7. A process as claimed in claim 3, wherein said atmosphere comprises dry oxygen and hydrogen chloride, and said thermally grown silicon dioxide is grown at a

temperature in the range of 800° to 1350°C, said given temperature also being in the range of 800° to 1350°C.

8. A process as claimed in claim 7, wherein said temperatures are in the range of about 1000° to 1200°C.

9. A process as claimed in any one of claims 1 to 8, comprising the additional step of, after said insulating layer forming and exposing steps, annealing said device by heating said substrate in an atmosphere comprising hydrogen gas.

10. A process as claimed in claim 9, wherein said atmosphere comprises hydrogen and said annealing step is carried out at a temperature of about 500°C for a time of at least 15 minutes.

11. A process for manufacturing a semiconductor device substantially as described in the example disclosed herein.

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