

PATENT SPECIFICATION

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(54) METHOD OF TREATING SEMICONDUCTOR DEVICES

(71) We, RCA CORPORATION, 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 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 semiconductor devices during manufacture so as to improve one or more performance parameters thereof.

In manufacture of semiconductor devices, it is common to employ an insulating layer comprising, e.g., silicon dioxide as a protective covering on the semiconductor surface. In the fabrication of metal-oxide-semiconductor field effect devices, a thin silicon dioxide layer is employed as a dielectric to provide capacitive coupling between a selected portion of the semiconductor surface and an overlying metal (gate) control electrode.

In such applications, it is important that the insulating layer be free of contaminants which produce instabilities in behaviour.

In particular, alkali metals such as sodium, potassium and calcium which find their way into the silicon dioxide layer cause development of a residual charge or polarization which tends to produce severe instability in the operating characteristics of metal-oxide-semiconductor devices. These alkali metals, when present in a silicon dioxide layer overlying a bipolar semiconductor device, cause the formation of thin surface "inversion" layers which increase the device leakage characteristics and adversely affect other operating parameters.

Heavy metal impurities, such as gold, copper and iron, act as trapping or recombination sites which seriously degrade minority carrier lifetime in the semiconductor material. This degradation of lifetime results in reduced gain and increased forward current dissipation in the device affected.

Prior techniques for overcoming these contamination problems are directed to (i) methods for preventing the contaminants from initially entering the semiconductor device, and (ii) methods for removing the contaminants as close as possible to the termination of the device manufacturing process.

The former, or "clean handling", methods require careful cleaning of all materials and equipment, and manufacturing and assembly operations to be carried out in a dust-free laminar flow atmosphere. These methods are effective, but cumbersome to employ and expensive because of the requirements for constant vigilance, contamination measurements and personnel indoctrination.

Other impurity removal processes heretofore known involve heat treatment in the presence of nickel or nickel alloys. These processes are believed to improve minority carrier life-time by reducing the number of recombination centers in the semiconductor material.

According to the invention we provide a process for manufacturing a semiconductor device comprising a pyrolytically depositing an undensified insulating layer on a given surface of a substrate from the vapour phase, exposing said layer to an atmosphere comprising a hydrogen halide, which acts to convert any deleterious metal present to the metal halide, whilst simultaneously heating said substrate, and densifying said layer by heat treatment during or after hydrogen halide treatment.

In co-pending application no. 11096/69 (Serial No. 1266002) there is described a process for manufacturing a semiconductor device in which deleterious metals are out-diffused simultaneously with the growth of the insulating layer. In a particular example this is achieved by heating a silicon substrate and exposing a given surface thereof to an atmosphere containing steam and hydrogen chloride.

In the present invention, rather than thermally growing the silicon dioxide, or other insulating layer, the insulating layer is pyro-

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lytically deposited. A hydrogen halide heat treatment process is then carried out prior to or while the layer is being densified. The reason for this procedure is that the densified layer is less permeable to out-diffusion of the metallic contaminants to be removed than is an undensified layer.

A particular method of carrying out the invention is as follows:

Silicon nitride is pyrolytically deposited on a silicon substrate by vapor phase reaction of silane (SiH_4) and ammonia (NH_3) at a temperature in the range of 500° to 700°C . A hydrogen chloride heat treatment is then carried out (in this case preferably in an atmosphere free of water vapor) at a temperature of 600° to 800°C . After the hydrogen chloride treatment is completed the silicon nitride layer may be densified by heat treatment at a temperature of about 900°C .

Instead of densifying the insulating layer after the hydrogen chloride treatment, densifying may be carried out simultaneously with the hydrogen chloride operation.

It has been found that by applying hydrogen chloride in the manner described to a silicon dioxide or nitride layer, the stability and minority carrier lifetime of the resultant device is substantially improved.

The substantial improvement realized by the hydrogen chloride treatment process in accordance with the invention is due to reaction of the hydrogen chloride with deleterious metals such as sodium, potassium, calcium (which causes residual charge or polarization) and gold, copper and iron (which reduces minority carrier lifetime). The hydrogen chloride reacts with these, and possibly other, metals at the exposed surface of the silicon dioxide or nitride layer to convert them into the corresponding metal chlorides.

The resulting metal chlorides, being relatively volatile at the processing temperature, leave the silicon dioxide or nitride surface.

This process establishes a gradient for out-diffusion of the metallic contaminants from the semiconductor wafer through the silicon dioxide or nitride layer, and from the exposed surface of the silicon dioxide or nitride layer into the surrounding atmosphere.

This "out-diffusion" reaction, i.e. conversion of the metal contaminants to the corresponding metal chlorides and volatilization of the chlorides at the exposed surface of the silicon dioxide layer, may be carried out at temperatures in the range of 600° to 1200°C .

Since the other halides of the metal contaminants are also volatile, other hydrogen halides may be used instead of hydrogen chloride. In the case where silicon dioxide is

employed as the insulating material, hydrogen bromide and hydrogen iodide may be substituted for the hydrogen chloride. Hydrogen fluoride cannot be used in this case since it etches silicon dioxide.

In addition to utilizing silicon dioxide or nitride as the insulating or dielectric material disposed on the semiconductor wafer surface, other insulating materials which may be treated in accordance with the invention are Al_2O_3 , SiO , Ta_2O_5 , Nb_2O_5 , HfO_2 , ZrO_2 and combinations thereof.

The process described herein, by removing impurity centers from the insulating layer, improves the radiation resistance of the resultant device.

In addition to silicon, other semiconductor materials such as germanium, gallium arsenide, gallium phosphide and other III-V or II-VI semiconductor materials may be protected by an insulating layer and treated with a hydrogen halide in the manner described herein to improve the operating characteristics of the resultant device.

WHAT WE CLAIM IS:—

1. A process for manufacturing a semiconductor device comprising pyrolytically depositing an undensified insulating layer on a given surface of a substrate from the vapour phase, exposing said layer to an atmosphere comprising a hydrogen halide which acts to convert any deleterious metal present to the metal halide, whilst simultaneously heating said substrate, and densifying said layer by heat treatment during or after hydrogen halide treatment.

2. A process as claimed in claim 1, wherein said undensified layer is silicon nitride deposited by vapour phase reaction of silane and ammonia.

3. A process as claimed in claim 2, wherein the reaction takes place at a temperature of from 500°C to 700°C .

4. A process as claimed in claim 1 or 2 wherein said hydrogen halide is hydrogen chloride and said exposure is at a temperature of from 600°C to 800°C .

5. A process as claimed in any one of the preceding claims, wherein the insulating layer is densified at a temperature of about 900°C .

6. A process for manufacturing a semiconductor device substantially as described herein.

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