TO: KSI/Scientific & Technical Information Division
   Attn: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code KSI, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No.: 3,796,592

Government or Corporate Employee: U.S. Government

Supplementary Corporate Source (if applicable):

NASA Patent Case No.: ERC-101073-1

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

YES ☑ NO ☒

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of the first page of the Specification, following the words "...with respect to an invention of ..."

Bonnie L. Woerner
Enclosure
METHOD AND APPARATUS FOR STABLE SILICON DIOXIDE LAYERS ON SILICON GROWN IN SILICON NITRIDE AMBIENT
Filed Sept. 9, 1969

Fig. 1.

Fig. 2.

Fig. 3.

INVENTORS
RONALD A. COHEN &
ROY K. WHEELER

BY

ATTORNEYS
METHOD AND APPARATUS FOR STABLE SILICON DIOXIDE LAYERS ON SILICON GROWN IN SILICON NITRIDE AMBIENT

Ronald A. Cohen, South Acton, and Roy K. Wheeler, Littleton, Mass., assignors to the United States of America as represented by the Administrator of the National Aeronautics and Space Administration

Filed Sept. 9, 1969, Ser. No. 856,253

Int. Cl. B05b 13/00; C23c 11/00

U.S. Cl. 117—95 2 Claims

ABSTRACT OF THE DISCLOSURE

A method and apparatus for thermally growing stable silicon dioxide layers on silicon is disclosed. A previously etched and baked silicon nitride tube placed in a furnace is used to grow the silicon dioxide. First, pure oxygen is allowed to flow through the tube to initially coat the inside surface of the tube with a thin layer of silicon dioxide. After the tube is coated with the thin silicon dioxide, the silicon is oxidized thermally in a normal fashion. If the tube becomes contaminated, the silicon dioxide is etched off thereby exposing clean silicon nitride and then the inside of the tube is recoated with silicon dioxide. As disclosed, the silicon nitride tube can be also used as the ambient for the pyrolytic decomposition of silane and ammonia to form thin layers of clean silicon nitride.

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

This invention relates to the growing of silicon dioxide layers on silicon, and more specifically, to the growing of stable silicon dioxide layers on silicon in a silicon nitride ambient and also relates to the pyrolytic decomposition of silane and ammonia in a silicon nitride ambient to grow clean layers of silicon nitride.

Silicon dioxide layers and silicon nitride layers have widespread use as passivation and dielectric layers for semiconductor devices such as integrated circuits, insulated gate field effect transistors, etc.

Stable layers are needed because unstable layers may cause circuit failure or system malfunction due to the fact that unstable layers produce poor parameters such as high leakage current, low Beta and high threshold voltages. In addition, unstable layers result in a poor yield caused by high failure rate with subsequent increase in cost and most important, to space applications poor reliability.

Prior art methods of thermally growing stable silicon dioxide on silicon generally require ultraclean conditions.

It is therefore an object of this invention to provide a method for forming thin layers of silicon nitride.

A still further object of this invention is to provide a method for forming thin layers of silicon nitride.

BRIEF DESCRIPTION OF THE DRAWINGS

The above objects and others will become apparent from the following detailed description of the invention when read in conjunction with the annexed drawings in which:

FIG. 1 is a pictorial view of the apparatus for growing stable silicon dioxide layers on silicon in accordance with the invention;

FIG. 2 is a pictorial view of the apparatus for forming thin layers of silicon nitride in accordance with the invention and;

FIG. 3 is a pictorial view of the tube sectioned showing the silicon dioxide layer and the silicon slice.

DESCRIPTION OF THE INVENTION

Referring now to FIG. 1, a silicon nitride tube 1 passing through a furnace or a heat chamber 2 is shown. The furnace 2 is shown in cross-section to more clearly show the silicon nitride tube 1. A flexible tube 5 is attached to one end of the tube 1. The tube 5 can be made of any suitable material such as Teflon. The other end of the tube 5 is connected to a needle valve 6 which may be an oxygen singlestage regulator valve such as is made by Airco. A tank of liquid oxygen (gas withdrawal) 7 is connected to the valve 6 by means of a second section of tubing 10. A wafer or a slice of silicon 3 is housed on a platform 4 inside the silicon nitride tube 1. The platform 4 can be made of any suitable material that will not contaminate the silicon slice 3 or the silicon nitride tube 1; for example, Si,N, platform, SiC, or ultrapure quartz. Of course, the silicon slice 3 could be placed directly inside the tube 1 without any platform if the ambient temperature is on the order of 1000°C. Prior to the first usage, the silicon nitride tube is cleaned by etching with 24% hydrofluoric acid, rinsed in distilled, deionized water, and baked dry (at 1000°C). Silicon dioxide is thermally grown on the silicon wafer 3 in the following manner: The valve 6 is opened permitting pure gaseous oxygen from the tank to flow through the silicon nitride tube in the furnace 2 at a temperature of 1000°C to 1200°C. Under these conditions a thin coating of silicon dioxide is formed on the inside of
the silicon nitride tube 1. Silicon dioxide is then thermal-
ly grown on the silicon wafer 3 in a normal fashion. The
silicon wafer 3 having been placed inside the tube 1
prior to the initial step of forming a coating of silicon di-
oxide on the inside of the silicon nitride tube 1. The state-
ment that silicon dioxide is grown on the cleaned silicon
wafer 3 in a normal manner means that the silicon dioxide
is grown on the silicon wafer 3 by any suitable well kown
prior art method such as described in the review article
titled "The Si—SiO\textsubscript{2} Solid-Solid Interface System," A.

FIG. 2 shows the apparatus of the invention for form-
ing thin layers of silicon nitride. The apparatus of FIG.
2 is identical to the apparatus of FIG. 1 except that the
liquid oxygen tank 7 of FIG. 1 has been replaced by a
first tank 9 containing ammonia and a second tank 9
containing silane has also been connected to the valve
6 by means of a section of tubing 11. Also, a nitrogen
tank 12 has been added for flushing purpose and a hydra-
gen chloride and/or hydrogen tank can be added for
optional in situ cleaning of the silicon wafer. In addition,
the wafer or slice 3 can be made of any suitable material
including silicon, germanium, gallium arsenide, etc. Wafer
3 serves as a substrate upon which the silicon nitride is
formed.

In the apparatus of FIG. 2, the inside of the silicon ni-
tride tube 1 is initially coated with a thin layer of silicon
dioxide. In order to form the silicon nitride layer, the
valve 6 is turned on permitting the silane and ammonia
to flow through the tube 1 with the furnace 2 at a tem-
perature of 800° C. to 1200° C. A layer of silicon nitride
is formed on the substrate 3 by the pyrolytic decomposi-
tion of the ammonia and silane.

The relative positions of the elements inside the silicon
nitride tube 1 are clearly shown in FIG. 3. As shown, the
inside of the silicon nitride tube 1 is coated with a layer
of silicon dioxide 13. The platform or boat 4 is generally
centrally located inside the tube 1 and the substrate 3
which is shown as being a silicon slice in this figure is
seated on the boat 4.

While the invention has been described with reference
to specific embodiments, it will be obvious to those skilled
in the art that various changes and modifications can be
made. For example, the silicon nitride container can be
used as a noncontaminating environment for other chemi-
cal reactions, such as deposited alumina, Al\textsubscript{2}O\textsubscript{3} and as a
tube for sintering aluminum contacts to silicon integrated
circuits.

What is claimed is:
1. A method for growing stable silicon dioxide layers
on a silicon substrate comprising the steps of:
placing said substrate in a silicon nitride tube;
heating said tube to a temperature in the range of
1000° C. to 1200° C.;
flowing pure oxygen through said tube when heated to
said temperature range to thereby provide a coating
of silicon dioxide on the inside surface of said silicon
nitride tube; and
thermally growing a layer of silicon dioxide on the
silicon wafer inside said tube by thermal oxidation.

2. A method for growing thin films of silicon nitride
on a substrate comprising the steps of:
placing the substrate in a silicon nitride tube;
heating said tube to a temperature in the range of
1000° C. to 1200° C.;
flowing pure oxygen through said tube when in said
temperature range to thereby provide a coating of
silicon dioxide on the inside surface of said tube;
flowing a mixture of silane and ammonia through said
tube when maintained in a temperature range of
800° C. to 1200° C. to thereby form a layer of sili-
con nitride on said substrate by the pyrolytic de-
composition of the ammonia and silane.

References Cited
UNITED STATES PATENTS
FOREIGN PATENTS
1,190,308 10/1959 France 117—Nitride
OTHER REFERENCES
Sage and Histed: Application of Silicon Nitride,
Powder Metallurgy, 1961, No. 8, pp. 210-211.
B. E. Deal: “Electrochemical Society, Extended
Translation of French Pat. 1,190,308.

ALFRED L. LEAVITT, Primary Examiner
M. F. ESPOSITO, Assistant Examiner
U.S. Cl. X.R.
117—106 R, 106 A, 201, Digest 12