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SEMICONDUCTOR ETCH AND OXIDATION PROCESS

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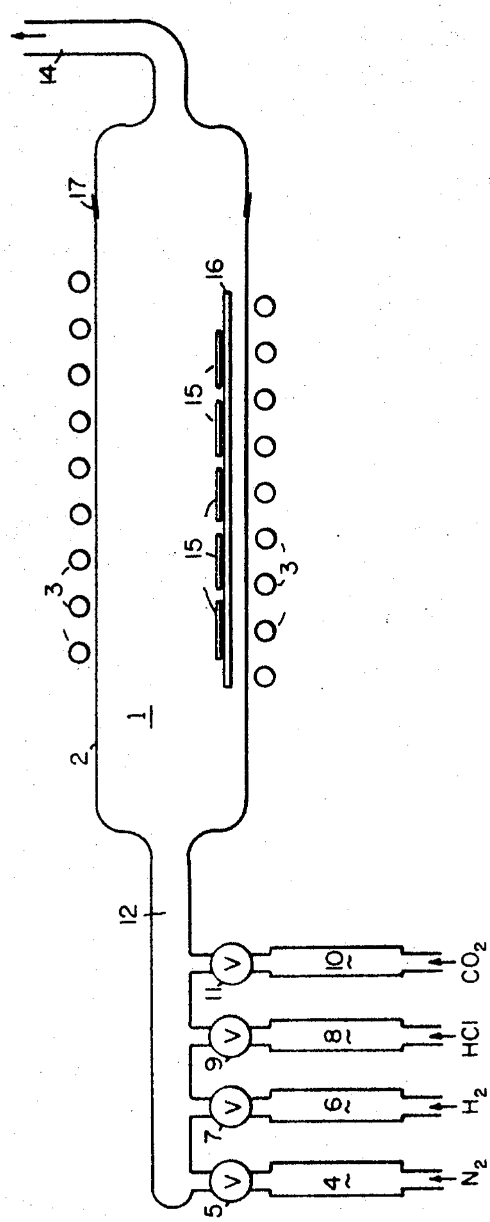

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SEMICONDUCTOR ETCH AND OXIDATION PROCESS

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My invention relates to the accomplishment of plural processes within a given enclosure and particularly to the processing of a semiconductor as to etching and oxidizing within a single enclosure.

It is known that contamination is a significant factor in the processes involved in the manufacture of semiconductor devices for electrical use, such as the well-known transistor. The purity of the initial semiconductor material far exceeds that in general chemical practice and purposely introduced impurities must in themselves be equally pure. Consequently, even careful handling between one processing department and another in a plant manufacturing semiconductor devices is not sufficient to eliminate incidental and unpredictable contamination by unwanted substances.

Contamination invariably experienced in handling between the etching and the oxidation processes is known to have unwanted effects upon the electrical characteristics of the completed devices. Although the art has long sought processing steps which would allow these two processes to take place within a given enclosure, a hydrogen furnace for example, this has not been possible.

Single crystal slices of semiconductor material are normally strongly etched as a first step in transistor manufacturing in an acid mixture such as the known CP4 or CP6 mixtures. These mixtures contain various proportions of hydrofluoric acid, HF, nitric acid, HNO_3, and acetic acid, HCO_2CH_3. This etching is performed prior to the thermal oxidation step, which is the start of the manufacturing process of a planar transistor, for example. Between the etching and the oxidizing steps the slices must be rinsed and dried, which handling gives rise to the possible contamination.

A more recently developed etching procedure employs hydrogen chloride, HCl, gas, usually diluted with hydrogen, H_2, flowing over the heated semiconductor slices at a temperature within the range of from 900° C. to 1300° C. for silicon, and several hundred degrees lower for germanium, such as within the range of from 500° C. to 800° C. This procedure gave rise to the hope that when the vapor etching was completed, the gas flow could be changed and oxidation effected without removing or in any way disturbing the freshly etched, and therefore clean, wafer slice.

However, oxidation is normally accomplished by employing water vapor, H_2O, or oxygen, O_2 at elevated temperatures; or the two combined at an elevated temperature.

Oxygen is undesirable in a hydrogen furnace for obvious reasons of safety.

Water vapor combines safely with hydrogen and grows an excellent oxide if hydrogen chloride is not present. It has been found, however, that if even only a trace of hydrogen chloride is present when the water vapor is introduced the semiconductor surface becomes clouded and unusable. The reverse situation is also true; namely, that if there is residual water vapor present the hydrogen chloride etching will not be satisfactorily accomplished.

Hydrogen chloride and water vapor are thus not compatible within a single system as required for semiconductor processing. Furthermore, water vapor contaminates the system and no amount of purging the same by means of inert gases or the equivalent accomplishes compatible operation. Such contamination on the "upstream," or inlet side, of such a gas flow furnace is serious. Contamination on the "downstream," or outlet side, of such a furnace is not serious, since such contamination cannot reach the work in process.

After repeated attempts to accomplish etching and oxidizing successively in the same system, I discovered that if the water vapor is not chemically formed until the components thereof are at the semiconductor material being processed, all contamination problems are eliminated

I accomplish this requirement by employing a form of the "water gas reaction" in reverse equilibrium. Instead of steam being one of the components, as it is in producing hydrogen at the known artificial gas works, steam is formed by combining hydrogen and carbon dioxide gases at the surface of the semiconductor, which surface is maintained at a high temperature in the furnace.

An object of my invention is to accomplish two heretofore incompatible processing steps within one enclosure in semiconductor manufacturing.

Another object is to sequentially accomplish etching and oxidation of semiconductor material within one given enclosure.

Another object is to repeatedly sequentially accomplish etching and oxidation of semiconductor material within one given enclosure upon successive batches of such material.

Another object is to accomplish etching by hydrogen chloride and subsequent oxidation by water vapor within a single furnace in semiconductor processing.

The single figure illustrates a typical furnace and the auxiliaries employed to accomplish the process.

In the manufacture of single or multiple semiconductor devices of the nature of transistors, diodes and integrated circuits employing these devices it is necessary to initially form an oxide on the surface of the semiconductor material in order that this can be subsequently etched away in the configuration required to fabricate the device. For the semiconductor silicon, Si, the oxide, SiO_2, is an example.

By the processing detailed below it is possible to etch a semiconductor surface clean and to subsequently form silicon oxide without the need for tedious and impractical precautions, by accomplishing both of these processes within a furnace enclosure. The oxide coating produced is free of pinholes and is of excellent quality for subsequently completing the manufacture of transistor devices.

The etching process is accomplished within an enclosed gas flow furnace **1**, of which a glass tube **2** having a diameter of the order of two inches and located within the radio frequency coil **3** of an induction heater is an example. Provision is made by known glass-working techniques for introducing selected gases and for allowing the exhaust of the same from the working volume. This is accomplished in the figure for nitrogen gas, N_2, through flowmeter **4** and valve (stopcock) **5**; for hydrogen gas, H_2, through flowmeter **6** and valve **7**; for hydrogen chloride gas, HCl, through flowmeter **8** and valve **9**; and for carbon dioxide gas, CO_2, through flowmeter **10** and valve **11**. A selected sequential gas flow is accomplished by suitable manipulation of the valves, as will be described below. The selected gas or combination of gases flows through inlet manifold **12**, through furnace **1** and out through exhaust **14** to the roof or other safe dissipation area. The semiconductor wafers **15** to be processed preferably lie on a silicon carbide coated carbon support **16**. A ground glass joint **17**, or equivalent means, is provided in tube **2** to allow the wafers **15** to be placed into and removed from furnace **1**.

A gas flow of hydrogen of a few liters per minute is established prior to heating the furnace and this flow is continued until the previously given operating temperatures for the semiconductor material being processed is reached. At such time a flow of a few hundred milliliters is started of hydrogen chloride (milliliters per minute) in addition and this is continued for approximately thirty minutes in order to etch a preferred amount away for semiconductor processing.

At the end of this period the furnace is purged by continuing the hydrogen flow only for a period of five minutes. This five minute period may be reduced somewhat if rapidity in processing is important.

Thereafter, a flow of carbon dioxide, CO_2, is started, of the order of a few liters per minute. Preferably, this is equal in amount to the flow of hydrogen. The equation for this oxidation agent formation is:

$$CO_2+H_2 \rightleftarrows CO+H_2O$$

It is seen that the molal quantities of these reactants are all unity. Although I prefer to introduce approximately equal amounts of carbon dioxide and hydrogen, the proportions may be drastically varied, in which case the oxidation proceeds properly, but more slowly.

During this oxidation processing the semiconductor material is maintained at a temperature within the range of from 900° C. to 1350° C., for silicon. The processing is continued until a desired thickness of oxide is formed upon the silicon surface. The rate of formation is approximately 1000 angstrom units of oxide thickness for 20 minutes of processing.

In the above equation the equilibrium point shifts from left to right as the temperature is increased. The high temperatures previously set forth are required for the formation of any water. Thus, there is present only the gases CO_2 and H_2 in the upstream, or inlet, side of my apparatus and only when the hot semiconductor is reached by this combined gas flow does water vapor form. This, of course, is immediately active in forming the oxide coating desired.

While a radio frequency furnace has been specified, this type is not essential. The diffusion furnace known to this art may be employed. For larger furnace sizes for processing more semiconductor material at one time the gas flows specified are increased proportionately and vice versa.

This invention has been disclosed by exemplary embodiments thereof. It will be understood that various modifications may be made in these specific embodiments without departing from the scope and spirit of the invention, as is set forth in the following claims.

Having thus fully described my invention and the manner in which it is to be practiced, I claim:

1. In a method of manufacturing semiconductor devices wherein plural processes are successively accomplished in a single furnace the steps of

(a) raising silicon semiconductor material to an elevated temperature within the range of from 900° C. to 1,300° C. in an atmosphere of hydrogen gas,

(b) etching said semiconductor material by introducing hydrogen chloride gas into said furnace,

(c) flushing said hydrogen chloride gas out of said furnace with hydrogen gas,

(d) introducing a mixture of carbon dioxide and hydrogen gases into said furnace,

(e) maintaining the temperature of said semiconductor material within the range of from 1,000° C. to 1,250° C. to accomplish the reaction of said carbon dioxide and hydrogen gases to carbon monoxide gas and water vapor at the surface of said semiconductor,

(f) continuing the conditions of (e) above until said water vapor oxidizes said semiconductor to a selected depth determined by the temperature and the time interval of processing according to step (e).

2. The method of claim 1 in which the concentration of the hydrogen chloride gas in step (b) is in the range of from 3% to 10%.

3. The method of claim 1 in which the gaseous mixture in step (d) is approximately half carbon dioxide and half hydrogen.

4. The method of claim 1 in which the duration of the etching step (b) is of the order of thirty minutes.

5. The method of claim 1 in which the time interval of step (f) to produce an oxide coating on silicon to a depth of 1,000 angstrom units is approximately twenty minutes.

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