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3,764,491

ELECTROLYTIC OXIDATION OF SILICON

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FIG. 1

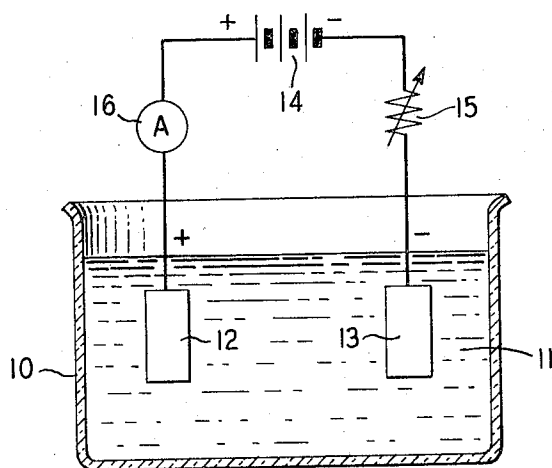
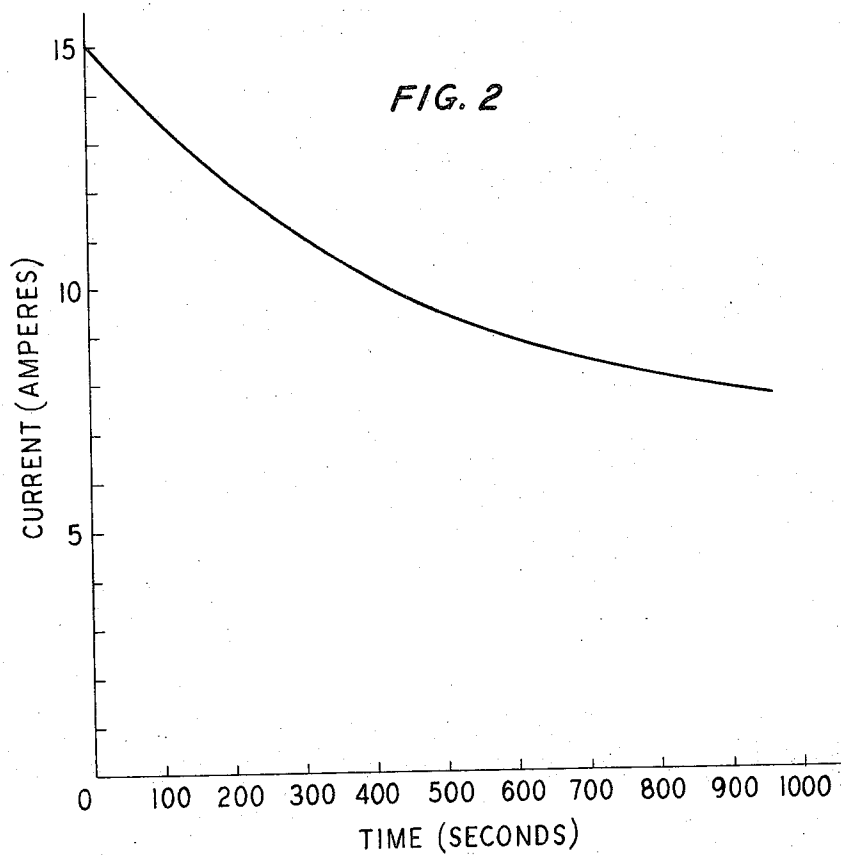


FIG. 2



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ELECTROLYTIC OXIDATION OF SILICON

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6 Claims

ABSTRACT OF THE DISCLOSURE

An electrolytic oxidation system is described for growing an oxide on the surface of silicon semiconductors. The electrolyte is an aqueous solution of hydrogen peroxide. Thick oxides may be grown in relatively short periods of time at room temperature, thus avoiding thermal damage to the junction characteristics of the semiconductor. The system is devoid of any metallic ionic component which can affect the properties of the oxide and semiconductor.

BACKGROUND OF THE INVENTION

This invention relates to the electrolytic oxidation of silicon semiconductors.

The oxidation of silicon is a significant step in the production of discrete semiconductor devices and integrated circuits. Various means have been proposed to grow the oxide, with varying degrees of success. Most processes require raising the temperature of the silicon for long periods of time. These thermal oxidations often affect the junction characteristics of the semiconductor. To avoid this problem, various electrolytic oxidation processes have been proposed which can be performed at room temperature. Typically, the electrolyte in these systems comprises some oxidizing agent, such as KNO_3 in a nonaqueous solvent, such as *n*-methyl acetamide. A problem arising from these prior art systems is that the metallic ionic component of the electrolyte (e.g., alkali metal ions) gets trapped in the oxide and ultimately penetrates the oxide to contaminate the semiconductor.

It is therefore desirable to devise an electrolytic system for silicon capable of producing oxides at room temperature which are free of any contaminating ions.

SUMMARY OF THE INVENTION

These and other objects are achieved in accordance with the invention which describes an electrolytic system utilizing an aqueous solution of H_2O_2 as the electrolyte. In one example of the use of the system, an oxide approximately 1200 angstroms thick was grown in approximately 1000 seconds.

BRIEF DESCRIPTION OF THE DRAWING

These and other features of the invention will be delineated in detail in the description to follow. In the drawing:

FIG. 1 is a schematic representation of an electrolytic oxidation system in accordance with one embodiment of the invention; and

FIG. 2 is a graph of current through the system as a function of time for a particular applied potential.

DETAILED DESCRIPTION

The discussion of the electrolytic oxidation system of the present invention is made with reference to FIG. 1 which illustrates the system schematically. Within a container 10 is placed the liquid electrolyte 11. In accordance with the invention, the electrolyte is an aqueous solution of H_2O_2 . Preferably, the solution is 30% by weight of H_2O_2 since this is readily available commercially. However, a range of 3–90% by weight would be effective. The silicon semiconductor 12 is immersed in the solution along with a material 13 comprising one of the noble metals. Electrically coupled to these materials are a D.C. potential

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source, 14, and a variable resistance, 15, which together comprise a constant voltage source. Connection is made so that the silicon is the anode of the cell and the noble metal is the cathode. An ammeter, 16, is included in the system for measuring the current.

In a particular embodiment, a sample of B-doped p-type silicon with a resistivity of .001 ohm-cm. was made the anode of the cell. It should be noted that n-type silicon may also be oxidized in accordance with the invention. The cathode was platinum. The electrolyte was a 30% aqueous solution of H_2O_2 . The solution was kept at room temperature while a constant potential of 80 volts was applied to the cell. After 1000 seconds, the power was turned off and the sample was rinsed and dried. Drying was effected by heating the sample at 200° C. for 3 hours in a nitrogen ambient. It was determined that an oxide had grown on the surface of the silicon. The interference color of the film was in the blue range indicating an oxide thickness of approximately 1200 angstroms.

The current through the cell during oxidation was also measured and the results are shown in the graph of FIG. 2. The current decreases with time since the growing oxide provides an increasing electrical resistance in the system. This suggests that once the resistivity of the film is measured, it is possible to calculate the time required to achieve any predetermined thickness based on the resistance exhibited. It will also be noted in FIG. 2 that the current decreases asymptotically. This suggests that the growth process can be made self-limiting by allowing the current to reach its asymptotic limit, at which time the growth of the oxide will essentially cease.

Of course, other values of applied potential may be chosen depending upon particular needs. A useful range of potential is 5–150 volts. If a potential of greater than 150 volts is applied it was observed that cracks appeared in the resulting oxide. This effect may be avoided by using a pulsed D.C. potential, for example, pulsed on $\frac{1}{3}$ of a cycle and off $\frac{2}{3}$ of a cycle, so that oxide growth is not fast enough to cause depletion of the reagent at the semiconductor interface. Another possibility is to raise the temperature of the electrolyte to near its boiling point so that the resulting motion of the liquid prevents depletion. This temperature (approximately 100° C.) is still significantly less than that required for thermal oxidation processes and is not expected to adversely affect the electrical characteristics of the semiconductor.

While the system has been described in terms of a constant potential applied to the cell, it should be obvious that a constant current may be supplied instead. A predetermined thickness is achieved when the potential reaches a predetermined value based on the increasing resistivity of the oxide.

A useful range for drying the oxide appears to be 150–250° C. for $\frac{1}{2}$ hour to 5 hours in a nitrogen ambient.

Various additional modifications and extensions of this invention will become apparent to those skilled in the art. All such variations and deviations which basically relay on the teachings through which this invention has advanced the art are properly considered within the scope and spirit of this invention.

What is claimed is:

1. A method of growing a film consisting essentially of an oxide of silicon on the surface of a silicon semiconductor comprising making the semiconductor the anode in an electrolytic cell wherein the electrolyte consists essentially of an aqueous solution of H_2O_2 , passing a current through said electrolytic cell, and drying said film by heating to a temperature of approximately 150°–250° C. for approximately $\frac{1}{2}$ hour to 5 hours.

2. The method according to claim 1 wherein a constant potential is applied to said cell until the current flow

through the cell decreases to some predetermined value due to the electrical resistance of the resulting oxide film.

3. The method according to claim 1 wherein a constant current is supplied to said cell until the voltage across the cell increases to some predetermined value due to the electrical resistance of the resulting oxide film.

4. The method according to claim 1 wherein the applied potential is a pulsed D.C. potential.

5. The method according to claim 1 wherein the temperature of the electrolyte is held near the boiling point of said solution.

6. The method according to claim 1 wherein the applied potential lies within the range of 5-150 volts.

References Cited

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