

[54]	METHOD OF POLISHING SEMICONDUCTOR SURFACES	2,375,823	5/1945	Saunders et al.	51/308
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[75]	Inventors: Helmut Deckert; Herbert Jacob, both of Burghausen-Obb, Germany	2,955,030	10/1960	Baldwin et al.	51/308
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[57] **ABSTRACT**

Method of polishing semiconductor surfaces with mechanical polishing agents, in which said polishing agents are precipitated silicates and/or silicofluorides.

1 Claim, No Drawings

METHOD OF POLISHING SEMICONDUCTOR SURFACES

This is a continuation of application Ser. No. 810,353, filed Mar. 25, 1969, and now abandoned.

BACKGROUND OF THE INVENTION

Disks made of semiconductor materials, which are in particular demand as substrata for the epitaxial growing process (a process that is becoming more and more important in the manufacture of semiconductors) have been produced by a mechanical polishing process, using abrasives like corundum powders, zirconium dioxide, cerium oxide, diamonds, or silicon carbide. Since mechanical polishing has always caused a more or less severe destruction of the surface layer, which disturbs the subsequent epitaxial growing process, the disks must undergo a chemical cauterization or etching before they can be further processed. And this, of course, impairs the oft required smoothness of the surfaces.

Since it is almost impossible to manufacture the above-mentioned polishing powders in a uniform grain size, difficulties arise due to scraping points coming into play in the course of the polishing operation on the disk surfaces. Even if it were possible to separate the coarse material during the manufacture of polishing powders, after passing same through sieves, air separators, and sedimentation processes, into fractions of a certain range of grain sizes, it would still be impossible to eliminate completely the small portions of relatively coarse grains in the powder which cause the scraping in the polishing process.

Attempts have been made to overcome these drawbacks by using silicic acid brine and silicic acid gels as polishing substances. These can be produced, for example, by acidifying a silicate solution or stirring in water the silicic acid formed by the burning of silicon tetrachloride. Unlike the above-mentioned crystalline polishing powders, the silicic acid brine and gels are amorphous, i.e. they show no crystalline reflex, under X-ray examination. Their polishing effect, too, is very slight.

SUMMARY OF THE INVENTION

We have now discovered a method of polishing semiconductor surfaces by means of efficient mechanical polishing agents. Our method is characterized by the use of precipitated silicates and/or silicofluorides as polishing means. With this method it is possible to obtain uniform particle sizes of the maximum possible hardness.

The performance of this method has proved the advisability of using silicates that are difficultly soluble, having been precipitated by adding silicate-forming metallic salts or metallic salt solutions to silicic acid solutions, their salts or derivatives.

Salts of metals of the second and third Group and Subgroup of the Periodic System, as well as silicate-forming salts of heavy metals, for instance, zirconium, iron, lead, nickel, cobalt, are suitable as silicate-forming metallic salts. Besides, soluble salts of magnesium, calcium, strontium, barium, zinc or aluminum may also be used with good results.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In general, when we refer to silicic acid solutions and their salts we mean solutions having anions that are made up of one or more silicon atoms, that are coordinately surrounded by oxygen atoms, and that the oxygen atoms may have attached thereto hydrogen or organic groups; for instance SiO_3^{-2} , $\text{H}_2\text{SiO}_4^{-2}$, HSiO_3^{-1} , $\text{H}_3\text{SiO}_4^{-1}$, $\text{Si}_2\text{O}_6^{-4}$, $\text{HSi}_2\text{O}_6^{-3}$, $\text{H}_2\text{Si}_2\text{O}_6^{-2}$, $\text{H}_3\text{Si}_2\text{O}_6^{-1}$. Precipitation of alkali silicate solutions, for instance sodium silicate solutions, have turned out here to be of particular value.

When we refer to solutions of silicic acids, their salts or derivatives, we refer, in general, to aqueous solutions. Other solvents, like organic solvents, i.e. alcohols, ketones, esters, should also be considered.

Silicic acid esters, for example, may be used as derivatives of silicic acid, after they have been partly or completely hydrolyzed — for instance, partly hydrolyzed silicic acid tetra-n-butyl ester.

Silicon fluorides which are difficultly soluble are used as silicon fluorides, after they have been precipitated by the addition of silicon fluoride-forming metallic compounds or their solutions into solutions of fluosilicic acid, their salts or derivatives. Salts, oxides or hydroxides of the metals of the first, second, third Groups of the Periodic System, particularly sodium, potassium, magnesium, calcium, barium, aluminum or zinc, are suitable here as silicon fluoride-forming metallic compounds. Solutions of the metal salts can be added individually as well as in mixtures.

As compared with the pure silicic acid suspensions, the polishing suspensions produced in accordance with the invention are characterized by a considerably higher rate of erosion without causing, however, any marked destruction of the crystalline structure on the burnished surfaces of the semiconductor disks. Furthermore, the polishing suspension applied in the polishing process may be used as either a neutral or an alkaline solution.

Roentgenographic and analytical examinations show that the polished bodies accrue in a crystalline form. After all, they are metallic salts of silicates or silicofluorides and not just silicic acids. By varying the precipitation conditions, for instance by inducing precipitation at elevated temperatures, it is a simple matter to change the size of the particles and adapt them to the properties of the semiconductor material which is being polished.

In contrast to the crystalline polishing powders, polishing suspensions produced in accordance with the invention contain no oversize grains to cause scraping.

In view of the fact that polishing suspensions are manufactured by the simple process of pouring together solutions of raw materials previously filtered or decanted, any impurities caused by foreign bodies are easily eliminated.

EXAMPLE 1

The polishing suspension is manufactured in the following manner:

120 ml of water glass solution (33% SiO_2) are diluted by the addition of 1800 ml of deionized water. Then a solution of 25 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 ml of water is added slowly. The precipitate obtained is very finely divided; the grain size ranges about 20 μ .

Round silicon disks of 32 mm diameter and 300 μ thick, obtained by sawing of a monocrystalline silicon rod, are fine-polished with corundum powder (grain size of 5 μ) abrading or wearing each side by 50 μ. Every 12 disks are cemented on with bee's wax to a circular refined steel alloy supporting plate of 180 mm diameter, then applied to a rotary plate or dish (450 mm diameter) of a polishing machine covered with a polishing cloth, and finally loaded with 1.5 kg. The rotary dish is made to revolve at a speed of 90 rpm. The polishing suspension drips out onto the rotary dish at the rate of 1 to 2 drops per minute.

After a polishing period of 20 minutes the surface of the silicon disk is polished smooth and free of scratches and ready for epitaxial coating.

EXAMPLES 2

Silicon disks, previously pretreated as described in Example 1, are polished with a polishing suspension which has been manufactured in the following manner:

120 ml of sodium silicate solution (33% SiO₂) are diluted with 1800 ml of deionized water and heated to 80°C. While stirring a solution of 150 g CaCl₂·6H₂O in 200 ml of water is added slowly. A white crystalline precipitate having a grain size of about 60 m μ precipitates. The composition of the precipitate corresponds to about the formula CaO, 2 SiO₂. The polishing suspension can be used immediately after it has cooled. After a polishing period of 15 minutes the silicon disks are so well polished that they are ready for the epitaxial charging.

EXAMPLE 3

Disks of a thickness of about 300 microns are sawed off a monocrystalline rod of gallium arsenide and fine-polished with corundum powder of a grain size of about

2 to 3 microns. In this way about 30 microns were worn off each side. The polishing is performed as in Example 1, and an aqueous suspension of barium hexafluosilicate, manufactured as indicated below, is used as the polishing means:

5 560 ml of an aqueous hydrofluoric acid (48% HF) are diluted with 500 ml of deionized water and mixed with 120 g of SiO₂. The dissolution of the silicon dioxide results in hexafluosilicic acid. As a solution of 75 g of BaCl₂·2H₂O in the form of a saturated aqueous solution is slowly added, an X-ray crystalline precipitation of BaSiF₆ precipitates. Next, the strongly acid polishing suspension is neutralized. After a polishing period of 15 minutes, the gallium arsenide disks display a completely undisturbed, smooth and shining surface.

The invention claimed is:

1. Process of finish polishing the surface of a semiconductor which comprises applying to said surface a polishing agent consisting essentially of a finely divided, freshly precipitated, difficultly soluble member of the group consisting of a metal silicate and a metal fluosilicate having a particle size range from about 20 to about 60 mμ, said metal silicate being precipitated from an aqueous solution of an alkali silicate by addition of a water soluble compound of a metal of the group consisting of zirconium, iron, lead, nickel, cobalt, magnesium, calcium, strontium, barium, zinc and aluminum, and said metal fluosilicate being precipitated from an aqueous solution of fluosilicic acid or an alkali fluosilicate by addition of a water soluble compound of a metal of the group consisting of sodium, potassium, calcium, barium and aluminum, said freshly precipitated difficultly soluble metal silicate or fluosilicate being in suspension in the aqueous reaction medium in which it is formed by precipitation.

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