⑲ **Europäisches Patentamt**
European Patent Office
Office européen des brevets

⑪ Publication number: **0 121 707**
A2

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **84101834.4**

㉒ Date of filing: **22.02.84**

(51) Int. Cl.³: **B 24 B 37/04**

㉚ Priority: **10.03.83 US 474120**

㊸ Date of publication of application: **17.10.84**
Bulletin 84/42

(84) Designated Contracting States: **DE FR GB**

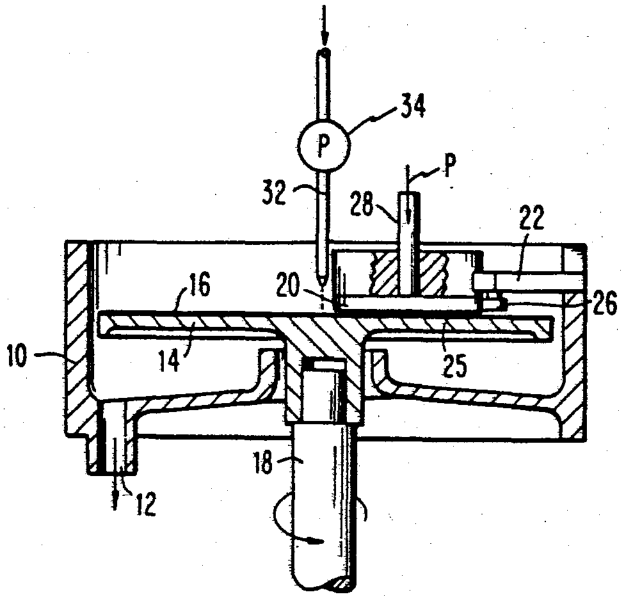
(71) Applicant: **International Business Machines Corporation,**
Old Orchard Road, Armonk, N.Y. 10504 (US)

(72) Inventor: **Basi, Jagtar Singh, 97 Nantucket Drive, Fishkill**
New York 12524 (US)
Inventor: **Mendel, Eric, 3 High Point Drive, Poughkeepsie**
New York 12603 (US)

(74) Representative: **Oechssler, Dietrich Dr. rer. nat.,**
Schönaicher Strasse 220, D-7030 Böblingen (DE)

(54) Method for polishing amorphous aluminum oxide.

(57) The method comprises the chemical-mechanical polishing of amorphous aluminum oxide surfaces to a high degree of perfection. The aluminum oxide surfaces are continuously wetted with a water-citric acid slurry containing a soft abrasive material. The continuously wiping of the aluminum oxide surface is accomplished with a firm surface (16) using pressure while maintaining a relative movement between the aluminum oxide surface and the firm surface (16) to remove the water reacted aluminum oxide product from the high points of the aluminum oxide surface. This method is continued until a high degree of perfection of the surface is accomplished. The slurry is typically composed of colloidal silicon dioxide dispersed in water containing citric acid.



EP 0 121 707 A2

ACTORUM AG

METHOD FOR POLISHING AMORPHOUS ALUMINUM OXIDE

This invention relates to a method of chemical-mechanical polishing of an amorphous aluminum oxide surface.

Various mechanical parts, particularly those which are moving in relation to other parts, require a polished surface having a high degree of perfection. It has been proposed to form mechanical parts of high temperature pressed parts composed of titanium carbide powders alone or in combination with particles of aluminum oxide or similar material. On the surface of these parts a layer of amorphous aluminum oxide is formed. The resulting parts have desired properties of resistance to breakage, improved machining and good wearability. It is also desirable to have such mechanical parts highly polished to a substantial degree of perfection.

Aluminum oxide is a chemically non-reactive, relatively hard material. Polishing of such films which have been deposited upon surfaces of mechanical parts have not been accomplished up to the present.

There has been substantial work done in the polishing of very hard materials in the semiconductor parts. Particularly, silicon and sapphire wafers have been polished to a high degree of perfection by various workers in the field. Examples of this work are H.W. Gutsche, U.S. Patent 4 011 099, March 8, 1977; J.S. Basi, U.S. Patent 4 057 939, November 15, 1977; "The Preparation of Sapphire Surfaces for Silicon Epitaxy" by T.A. Zeveke et al. published in Soviet Physics-Crystallography, Vol. 13, No. 3, November-December 1968, p. 493 through p. 495; "Removal of the

Microscopic Polishing Damage From Sapphire and Spinel" by M. Berkenblit et al., IBM Technical Disclosure Bulletin, Vol. 13, No. 12, May 1971, pp. 3781 and 3782; "The Chemical Polishing and Etch Pitting of Sapphire" by R.G. Vardiman, published in J. Elec. Chem. Soc., Vol. 118, No. 11, pp. 1804 through 1809, November 1971; and "Polishing of Sapphire and Colloidal Silica" by H.W. Gutsche et al., J. Elec. Soc. Solid State Science and Technology, Vol. 125, No. 1, pp. 136 through 138, January 1978. The chemical and mechanical polishing of other materials have also been accomplished, for example, zinc selenide in J.S. Basi, U.S. Patent 3 869 323, March 4, 1975 and cadmium telluride by J.S. Basi, U.S. Patent 3 869 324, March 4, 1975.

It is the object of the invention to provide a simple method for polishing an amorphous aluminum oxide surface to a high degree of perfection.

This object is achieved by a method as defined at the beginning of this specification having the features of the characterizing part of claim 1.

With the inventive method a resulting surface flatness of less than about 5.08 nm after said polishing can be obtained.

The inventive method can be summarized as follows:

The method comprises the chemical-mechanical polishing of amorphous aluminum oxide surfaces to a high degree of perfection. The aluminum oxide surfaces are continuously wetted with a water-citric acid slurry containing a soft abrasive material. The continuously wiping of the aluminum oxide surface is accomplished with a firm surface using pressure while maintaining a relative movement between the aluminum oxide surface and the firm surface to remove the water-citric acid reacted aluminum oxide product from the high points of the aluminum oxide surface. This method is continued until a high degree of perfection of the surface is accomplished. The slurry is typically composed of colloidal silicon dioxide dispersed in water containing citric acid.

Advantageous embodiments of the invention are disclosed in the subclaims.

The invention will become more apparent from the following detailed description taken in conjunction with the accompanying drawings.

The drawings show the following:

FIGURE 1	illustrates the layered structure of the present invention.
FIGURE 2	shows a side view of an apparatus, partially in section which is useful in practicing the polishing process of the invention.
FIGURE 3	shows a plan view of the Fig. 2 apparatus.

Fig. 1 illustrates a cross-sectional view of the mechanical part 25 to be polished by the polishing process of the present description. The [illegible] 25 includes a substrate 8 and an amorphous aluminum oxide layer 9 of about 5 to 8 micrometers in thickness formed upon the substrate. It is preferred to utilize as the substrate 8 a combination of aluminum oxide and titanium carbide in a fine grain mixture that has been pressed and sintered or hot pressed. However, titanium carbide particles alone may be compressed into desired parts in a similar fashion. The mixture is characterized by an average particle size of less than about 5 microns and preferably the particles are 1 to 2 microns in length. The preferred mixture is in the range of about 60 to 80 % aluminum oxide and 40 to 20 % titanium carbide by weight. The high density mixture has low porosity and exhibits improvement in Young's and Shear moduli of elasticity and modulus of rupture.

To produce a material for the substrate 8 having the desired properties the materials are ground into powders of the desired particle sizes and mixed in the desired composition of about 80 to 60 % aluminum oxide to 20 to 40 % titanium carbide to a homogeneous mixture. The dry powder is measured and poured to fill a graphite pressing mold. The powder charge is then precompacted with an applied load of approximately 68.95 to 206.85 bar. The precompacted mold is loaded into a hot press and heated to a temperature in the range of 1400°C to 1650°C. The pressed part is hot pressed, when the desired temperature is reached at a pressure of between 275.8 and 413.7 bar. The pressed part is cooled to room temperature for a desired time to maintain a stress-free condition. The cooled part is removed from the mold, deburred and sand blasted to remove any excess graphite. The part is now machined to the desired shape and dimensions using conventional diamond machining and mechanical lapping methods.

Amorphous aluminum oxide films can be deposited using chemical vapor deposition or rf sputtering methods. In general, the rf sputtering method entails the use of a dielectric target of high purity. When depositing aluminum oxide films one would use an aluminum oxide disc of high purity. The target is metallized on one side and bonded to a flat water cooled aluminum disc using a silver epoxy bonding agent or other suitable conducting bonding agents. The water cooled aluminum disc forms part of the vacuum chamber wall through a system of vacuum seals and an insulating ring. A protective metal shield surrounds the exposed areas of the water cooled aluminum disc at an appropriate spacing of 0.5 cm in order to prevent sputtering from this region. The source of power is an rf generator. In a typical system one would monitor and control the power delivered to the discharge because the power density affects the rate of deposition, the density, the dielectric constant, the conductivity, and the surface characteristics. "RF Sputtered Aluminum Oxide Films on Silicon" by C.A.T. Salama published in J. Electrochemical Soc., July 1970, Vol. 117, pp. 913-917, may be referred to for further more detailed information concerning rf sputtering.

The polishing process for aluminum oxide or the like may be understood with reference to Figs. 2 and 3. The polishing machine includes a bowl 10 having a slurry outlet 12 and a driven plate 14. Mounted on the plate 14 by any suitable means (not shown) is a soft, firm surface or pad 16 composed of a poromeric material. The pad materials used are true poromeric comprised of a top coat and substrate layer. The thickness of top coat is critical. Top coat thickness is 381-508 µm, substrate is 508-635 µm. Total package is 1022 ± 50.8 µm thick. The top coat is designed and made by a coagulation process to obtain a macro and micro pore random structure. The macro pores are irregularly shaped and randomly dispersed without any preferred orientation in the top coat layer. The micro pore comprise the rest of top layer. For further information concerning this material reference can be made to "Pad Materials for Chemical-Mechanical Polishing" by Eric Mendel et al., in Vol. 79-1, Extended Abstracts of Elec. Chem. Soc. Spring Meeting, Boston, Mass. May 6-11, 1979, Abs. No. 186, pp. 488-490. Pads of this type which are commercially available include: Rodel 210 made by Rodel Inc. of Newark, Delaware USA, POLTEX made by the GEOS Corp., Stanford, CT. and NEWMAN polishing pads made by the G. Newman & Co., Santa Clara, California. The plate 14 is rotated by means of suitable driving means (not shown) coupled through shaft 18. Mechanical parts 25 to be polished, are mounted on the plate 20 by means of suitable adhesive or other suitable method. This plate 20 with its mounted parts thereon is maintained against the surface 16 by arm 22 having bearing surfaces 26 and a substantial pressure P applied through shaft 28 to urge the wafers strongly against the surface 16. The preferred pressure is between about 1.5×10^4 to 5.25×10^4 Pa (about 150 to 425 gm/cm^2). The arm 22 is suspended from the polishing bowl edge and positioned on the side of the plate 20 in the path of its normal rotation which is caused by the rotation of plate 14. The rotation of plate 14 produces a rotation of the plate 20. The surface of the parts 25 is continuously wetted with excess quantity of polishing slurry by flowing it through the pipe 32 with its restricted opening onto the surface 16 of rotating plate 14. A parastolic pump 34 moves the slurry through the pipe 32. Excess slurry is splashed from the end of the rotating plate 14 and flows out of the excess slurry opening 12.

The citric acid-aqueous dispersion of silicon dioxide can be conveniently employed in the form of silica sols and silica gels having silicon dioxide particle sizes in the range of 1 to 500 nm (millimicrons), in concentrations of 6 to 16 weight percent silica. Convenient sources of the aqueous dispersion of the silicon dioxide, is the trademarked silica sol composition LUDOX colloidal silica made by E.I. Dupont Co., Wilmington, Del., NALCOAG 1034A colloidal silica made by Nalco Chem. Co., Chicago, Ill., QUSO silicas made by Philadelphia Quartz Co. of Philadelphia, Pa., SYLOID 701 wafer polishing material made by Davison Chem. Div. of W.R. Grace and Co., Baltimore, Md. and "Syton HT-50" made by Monsanto Company, St. Louis, Mo., USA.

The citric acid-aqueous dispersion of silicon dioxide or silicon dioxide slurry is required to have a pH in the range of about 7 to 9. It is preferable that the slurry have a pH slightly basic and of the order of 8. The basic pH may be obtained by adding small quantities of citric acid solution of 80 grams/liter water to the dilute silicon dioxide slurry to produce the desired pH. The slurry with the citric acid is stable for 48 hours without any gelling or precipitation. Slurries with other acids such as hydrochloric acid are stable for only short periods of time. At higher pH than 9 the surface will roughen, giving an orange-peel like effect. Lower pH polishing produces undesirably slow polishing rates. The polishing time is also dependent upon the pre-polishing surface roughness condition. It is preferred to have the roughness of the pre-polishing surface about 101.6 nm (peak to valley height). The roughness of the pre-polishing surface depends upon the roughness of the substrate upon which the alumina is deposited, and upon the deposition method. That is the reason there is needed a highly perfect, polished substrate. The film is too thin for lapping, that is it cannot be abrasively polished for the same reason plus damage.

A chemical mechanical polishing process for polishing aluminum oxide operates very effectively to produce surface finishes of less than the order of 5.08 nm (0.2 micro inches) (peak to valley height). This measurement is actually the lower limit of the equipment so the surface finish is even better than that 5.08 nm. The surface finish is measured by the conventional stylus method.

The chemical reaction is not fully understood but it appears that the citric acid water slurry has a reaction between the aluminum oxide and the water in the slurry to form an aluminum oxide-citric acid complex on the specimen surface which is in turn removed by the silicon dioxide slurry and polishing pad. The apparent chemical reaction is:

$$Al_2O_3 + \text{citric acid} \rightarrow Al_2O_3 \cdot \text{citric acid complex}$$

The resulting polishing produces under these conditions no relief between the aluminum oxide grain boundaries and a highly perfect surface.

The following example is included merely to aid in the understanding of the invention, and variations may be made by one skilled in the art without departing from the spirit and scope of the invention.

Example 1

An amorphous aluminum oxide layer having a thickness of 5-8 µm was formed onto aluminum oxide-titanium carbide mechanical parts made by the high temperature pressure molding technique described above in the specification. The aluminum oxide layer was formed thereon by the sputtering process as described above. These parts were placed in the polishing apparatus illustrated by Fig. 2 and 3. A mixture of 1 part silica sol with 4 parts of deionized water was prepared. The silica sol has a silica content of about 50 weight percent with maximum partical size of 40 to 45 nm. This slurry has a solids content of 10 weight percent silica. A citric acid solution comprising 80 grams citric acid in one liter of deionized water was added to the silica sol slurry while monitoring the pH of the solution. The solution was adjusted to a pH of 8 in this manner. The polishing pressure used was 2.225 x 10^4 Pa. The removal rate was 1.5 µm/hour. The polished surface is rinsed in deionized water. The polished surface finish (peak to valley) was 5.08 nm as determined by the conventional stylus method described in "Report on the Measurement of Surface Finish by Stylus Methods" by R.E. Reason, et al., published by the Rank Taylor Hobson Division Leicester, England 1944.

The resulting surfaces were flat to less than 1 µm over the part surface and void of polishing induced defects. The polished area when measured with in interferometer set at one µm per fringe sensitivity, typically shows but one fringe indicating a flatness of one µm for these surfaces tested. These samples give similar results to the state of the art of surface flatness in the silicon technology.

Example 2

Amorphous aluminum oxide layers were prepared as in the Example 1. They were polished as described in Example 1 using pH of 9.5 and 11. the surfaces were visually unacceptable, due to pits and orange-peel. No removal rate data taken.

Example 3

The pH was adjusted with citric acid additions. At pH of 6 polishing was very slow and impossible to measure accurately. At pH of 7 to 9 as best as could be determined the removal rate was 2-3 µm per hour at a pressure of 3.75×10^4 Pa.

CLAIMS

1. A method of chemical-mechanical polishing of an amorphous aluminum oxide surface

providing a substrate (8) having a surface layer (9) of said aluminum oxide of a thickness in the order of µm's;

maintaining said aluminum oxide surface continuously wetted with an excess quantity of an aqueous dispersion containing citric acid and a soft abrasive material;

continuously wiping the aluminum oxide surface with a firm surface (16) using pressure while maintaining relative movement between the aluminum oxide surface and the firm surface (16) to remove the citric acid reacted aluminum oxide product from the high points of the aluminum oxide surface.

2. The method of claim 1 wherein the pH of said aqueous dispersion is between about 7 to 9.

3. The method of claim 1 or 2 wherein the said aluminum oxide surface layer is a sputtering layer of 5 to 8 µm in thickness.

4. The method of any one of claims 1 to 3 wherein after polishing the aluminum oxide surface is rinsed with deionized water.

5. The method of any one of claims 1 to 4 wherein said aluminum oxide surface layer is located on

the surface of a body comprised of a fine grain mixture of aluminum oxide and titanium carbide.

6. The method of any one of claims 1 to 5 wherein said soft abrasive material is colloidal silicon dioxide.

7. The method of claim 6 wherein the silicon dioxide portion of the dispersion is between about 60 to 16 weight percent.

8. The method of any one of claims 1 to 7 wherein the removal rate is between about 1.5 to 3 μm per hour at a pressure of less than 4.25×10^4 Pa (about 425 gm/cm^2).

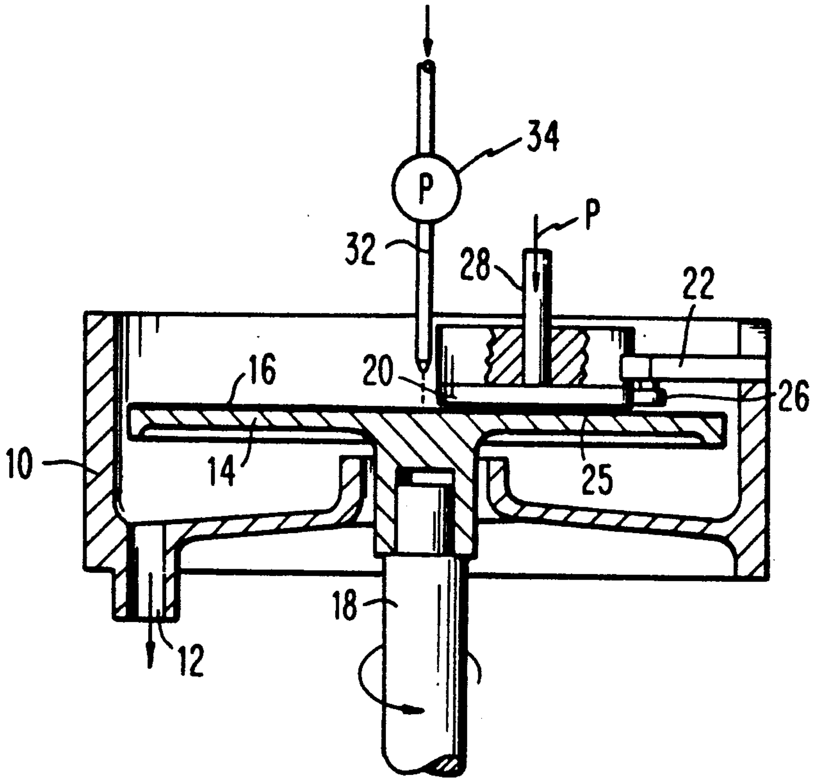


FIG. 2

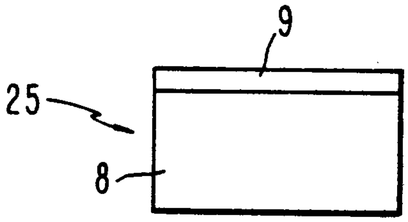


FIG. 1

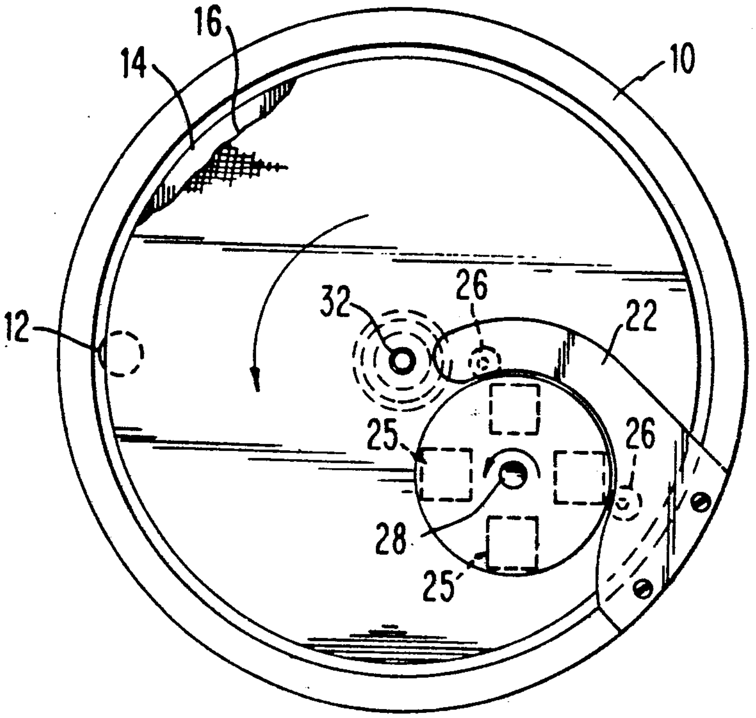


FIG. 3