PROCESS FOR ETCH-POLISHING SAPPHIRE AND OTHER OXIDES

Filed June 13, 1966 4 Sheets-Sheet 1

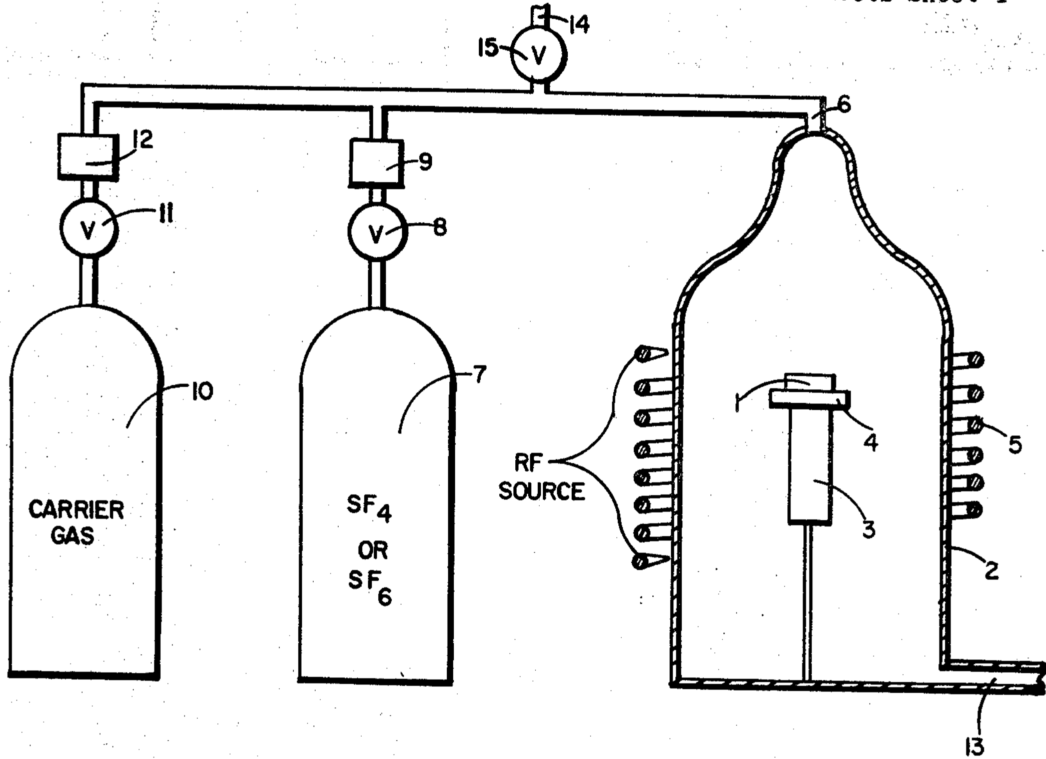

FIG. 1

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PROCESS FOR ETCH-POLISHING SAPPHIRE AND OTHER OXIDES

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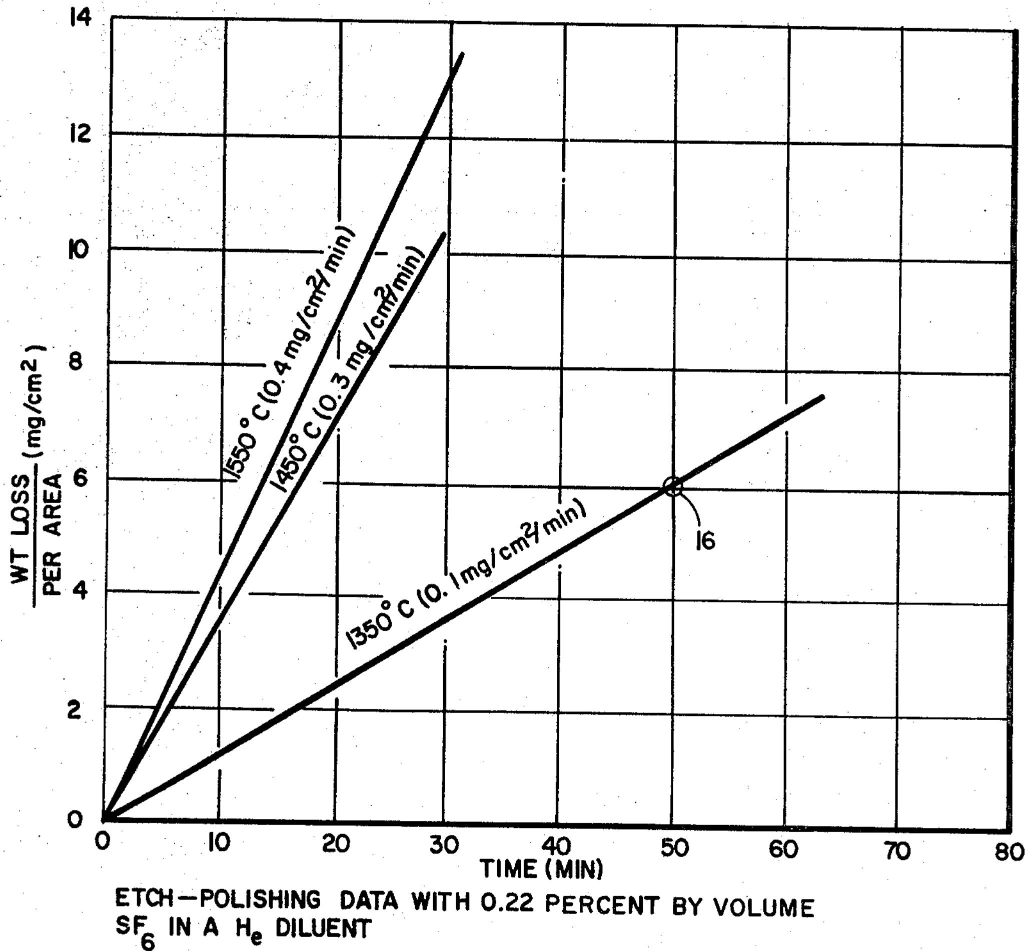

ETCH—POLISHING DATA WITH 0.22 PERCENT BY VOLUME SF_6 IN A H_e DILUENT

FIG. 2

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PROCESS FOR ETCH-POLISHING SAPPHIRE AND OTHER OXIDES

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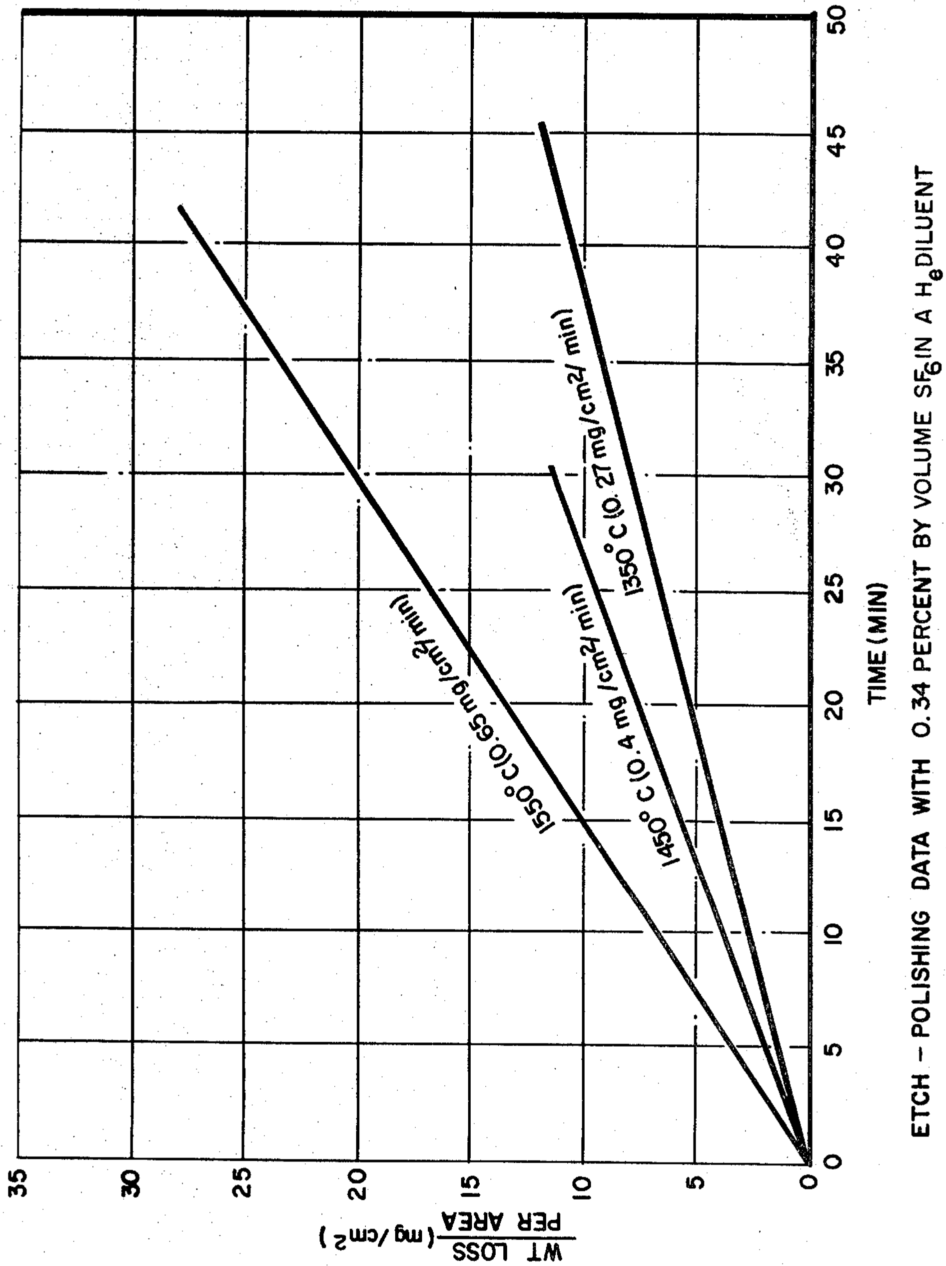

FIG. 3

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PROCESS FOR ETCH-POLISHING SAPPHIRE AND OTHER OXIDES

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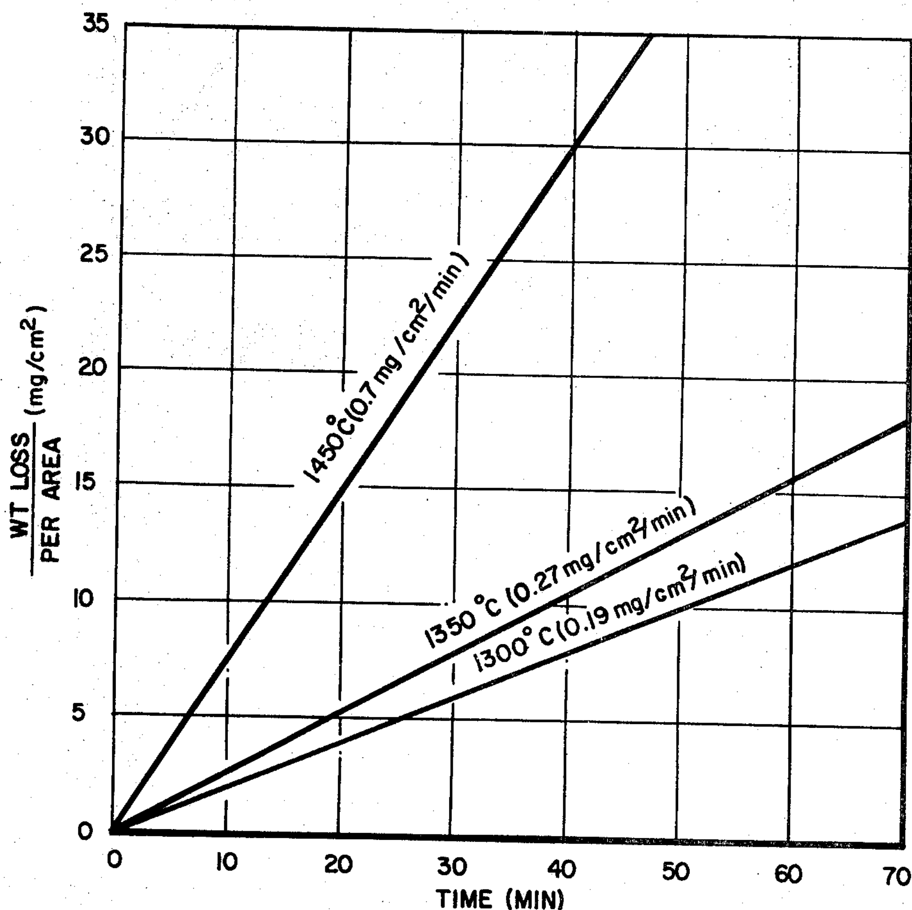

ETCH—POLISHING DATA WITH 0.60 PERCENT BY VOLUME SF_6 IN A He DILUENT

FIG. 4

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United States Patent Office

3,546,036

Patented Dec. 8, 1970

3,546,036
PROCESS FOR ETCH-POLISHING SAPPHIRE AND OTHER OXIDES

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Filed June 13, 1966, Ser. No. 556,977
Int. Cl. C09g *1/00;* C23f *3/00, 7/24*
U.S. Cl. 156—17 9 Claims

ABSTRACT OF THE DISCLOSURE

The invention is directed to a process for improving the quality of surfaces of refractory inorganic oxide materials comprising etch-polishing of the surfaces of the material by the steps of heating the material to an elevated temperature and exposing the surface of the material to a fluoride containing gas.

This invention relates to a process for etch-polishing sapphire and other oxides and more particularly to a process using a gaseous fluoride etchant for etch-polishing sapphire and other oxides.

The quality of epitaxial films grown on substrate materials such as sapphire, spinel, MgO, BeO, and chrysoberyl, is determined by the quality of the substrate surface. Previous processes for improving the surface includes the use of a diamond paste to polish the surface. However, unless great care was taken during such polishing, various size scratches, visible at high magnification (e.g. $\times 400$), remained on the surface of the sapphire after polishing. The presence of these scratches affects the nucleation mechanism, and hence, the quality of epitaxially grown silicone or other material deposited on the substrate surface.

An alumina buff process often is used to augment the diamond polishing for the purpose of removing the fine scratches. However, in this process, the deeper scratches sometimes are filled with alumina powder, rather than being removed. Optically the surface appears to have a good quality, but during subsequent hydrogen etching and/or film growth the unremoved surface defects are exposed.

Certain so called "wet" chemical processes have been only partially successful in improving the substrate. Moreover, they have the disadvantage that such liquid processes cannot easily be accomplished within the deposition chamber itself. Hence, the liquid cleaned substrate must be handled and exposed to the atmosphere and/or other contaminants prior to deposition of the epitaxial semiconductor layer.

Some gas phase etchants previously have been used partially to etch the surface so as to improve its quality. However, these prior art gaseous etchants removed the substrate material slowly and had a tendency to react with the material so as to degrade, rather than improve the substrate. For example, hydrogen gas has been used, but during time intervals which might be considered practical (perhaps up to one hour) the etch rate is very small. Etching with hydrogen chloride also requires long time periods, and should a polycrystalline spacer be used to support a monocrystalline substrate, mass transfer has been noticed to occur from the spacer to the substrate.

Ideally, it is desirable to etch-polish with a gas phase etchant at a relatively rapid rate just prior to forming the epitaxial growth layer on the substrate, and to accomplish this in the deposition chamber, so as to eliminate the need for handling the substrate between the etch-polishing and deposition steps.

It should be noted that this etch-polishing process also can be used for purposes other than the cleaning of substrate materials. For example, it can be used to etch-polish the sides and ends of ruby laser rods.

Briefly, the invention comprises etch-polishing the surface of a (single crystal) refractory inorganic oxide substrates such as sapphire, beryllium oxide, thorium oxide, zirconium oxide, spinels, chrysoberyl, etc. by exposing the material to a fluoride containing gas such as SF_4 and SF_6. During the period of exposure, the substrate is maintained at elevated temperature, most commonly between 1300° and 1600° C., although lower temperatures may be used, depending upon the material to be etch-polished. Carrier gases such as hydrogen helium argon or nitrogen as the diluent of the SF_4 or SF_6 gas, may be used to conduct the etchant to the substrate surface. Other inert gases also may be used as the diluent.

Therefore, it is an object of this invention to provide a gas-phase etch-polishing material for rapidly polishing the surface of refractory inorganic oxide materials.

It is another object of this invention to provide a process for gas-phase etch-polishing the surfaces of refractory inorganic oxide materials such as sapphire, BeO, Spinel, Chrysoberyl, thorium oxide, and the like.

It is another object of this invention to provide a process for gas-phase etch-polishing the surface of an inorganic oxide material which is to be used as a substrate for epitaxial deposition of semiconductor materials.

It is another object of this invention to provide a gas-phase process for etch-polishing the surface of a refractory inorganic oxide substrate materials in the same chamber as, and immediately prior to, epitaxial deposition of a semiconductor material onto said substrate surface.

It is another object of this invention to provide a gas-phase process for etch-polishing the surface of a refractory inorganic oxide substrate material in the same chamber as that in which epitaxial deposition onto said substrate surface is to occur, so that the substrate material need not be handled between the etch-polishing and epitaxial deposition steps.

It is another object of this invention to provide a gas-phase process for etch-polishing a refractory inorganic oxide substrate materials to obtain a no-work-damage surface to facilitate the epitaxial deposition of semiconductor layers having low dislocation counts.

Yet another object of this invention is to provide a gas-phase process for etch-polishing the sides and ends of ruby (or other refractory inorganic oxide) laser rods.

These and other objects of this invention will become apparent from the following description and drawings which are included for illustrative purposes only.

FIG. 1 is an illustration of an apparatus which may be used in practicing the process described herein.

FIGS. 2, 3 and 4 are graphs showing typical values of weight loss per unit area as a function of time for three different concentrations of SF_6 etchant.

As shown in FIG. 1, the refractory material **1** to be etch-polished is placed inside a vertical reactor **2**, on a pedestal **3** and separated therefrom by spacer **4**. Pedestal **3** may be composed of a high density carbon, although silicon, molybdenum, or other materials which can be heated inductively and which will not introduce undesired impurities into the system could be substituted. The spacer **4** optimally is composed of a form of the material to be etch-polished; this minimizes interaction between the spacer and the material to be etch-polished. Thus, e.g., if sapphire were being etch-polished, use of a spacer of alumina (Al_2O_3) would be appropriate.

Pedestal **3** is suspended in an area surrounded by coil **5** which coil is activated by an RF source (not shown) to cause inductive heating of pedestal **3**. The system includes channel **6** opening into the chamber of reactor **2**, which

channel interconnects a source **7** of gas-phase etchant SF_4 or SF_6. The rate of flow of the etchant is controlled by valve **8** and monitored by flow-meter **9**. Channel **6** also connects a source **10** of carrier gas, which could be hydrogen, helium, argon or nitrogen or an inert gas. When SF_6 is used, an inert gas such as He is the preferred carrier. Valve **11** is used to control the flow of carrier gas, and the rate of flow is monitored on flow meter **12** gases from the reaction chamber **2** exit via exhaust channel **13** which is connected to exhaust means (not shown). Channel **14** and associated valve **15** are provided to allow introduction of semiconductor deposition materials into chamber **2** subsequent to the etch-polishing process.

It should be obvious that the invention is not limited to the particular apparatus shown and described but may include various reactor channel arrangements well known in the art for exposing substrates to gaseous environments. However, it is desirable that the pedestal be located downstream from the material to be etch-polished to prevent reaction products of the pedestal material and the gaseous etchant from contaminating the material being etch-polished.

When sapphire is the material to be etch-polished, it has been determined that small amounts of sulfur tetrafluoride (SF_4) (possibly less than 1% by volume) in a hydrogen or helium carrier gas result in satisfactory etch-polishing of the sapphire surface. Temperatures of 1300° C. or above are recommended; since at about 1150° C., indications of the beginning of epitaxial growth, presumably of AlF_3 on sapphire, were observed. At about 1300° C., the vapor pressure of the material is apparently high enough that it does not interfere with the etching process.

Using SF_4 with a concentration of about 0.5–1.0 percent by volume in a carrier gas, sapphire etch rates of about 2 microns per minute at a pedestal temperature of 1450° C. can be obtained. Good quality single crystal sapphire etch-polished in this manner exhibited a very highly polished scratch-free surface well suited for the deposition of epitaxial layers. Some accentuation of the sapphire grain boundaries was noticed subsequent to the etch-polishing.

Use of sulfur hexafluoride (SF_6) in a helium diluent also was found to result in considerable etch polishing of sapphire. SF_6 is even more desirable gas phase etch-polishing material than SF_4, since the hexafluoride can be obtained in greater purity and is less expensive than SF_4; and, being unreactive with Pyrex, O_2, H_2O, etc., it is less hazardous at room temperatures. However, when a hydrogen diluent is used with SF_6, very little etch-polishing of sapphire can be obtained under the same conditions which yield excellent etch-polishing by SF_6 in a helium diluent.

When SF_6 in an He diluent was used to etch-polish sapphire, optimum etch-polishing was achieved with pedestal temperatures between 1300° C. and 1600° C. FIGS. 2, 3 and 4 contain graphs showing the typical valves of sapphire weight loss per unit area as a function of time for three concentrations (0.22, 0.34, and 0.60 percent by volume, respectively) of SF_6 in helium diluent, for pedestal temperatures of 1350° C., 1450° C. and 1550° C. in each case, arbitrary flow rates of 2.5 liters per minute were used, with a reactor chamber **2** having a diameter of 60 mm. a 1.5 inch diameter high density carbon pedestal **3**, and a polycrystalline alumina spacer **4**.

Referring to FIG. 2, it can be seen, for example, that when sapphire was etch-polished with a 0.22 percent by volume concentration of SF_6 in helium for a period of 50 minutes, at a pedestal temperature of 1350° C., the sapphire exhibited a weight loss of 6 milligrams per square centimeter. This point is indicated by point **16** in FIG. 2. Note also that this corresponds to an etch-polishing rate of 0.1 mg./cm.^{2}/min.

The above processes also can be used effectively to etch-polish fine-ground sapphire surfaces (about a 30 microinch finish) rather than diamond polished substrate materials. This has the dual advantages of minimizing work damage due to polishing and of reducing substrate costs considerably. Experience has indicated that exposure times in the order of five times that required for etch-polishing diamond polished surfaces are needed to accomplish such etch-polishing of fine-ground sapphire.

Analysis of results obtained with SF_6 show that it is selective in the etch-polishing capability for different orientations of sapphire. Under identical conditions, at relatively high SF_6 concentrations, $(1\bar{1}02)$ sapphire will usually exhibit a somewhat rough surface while $(11\bar{2}3)$ sapphire will exhibit a very smooth surface. But at low concentrations of SF_6, reasonably polished $(1\bar{1}02)$ surfaces have been obtained on good quality sapphire at removal rates of up to 0.4 mg./cm.^{2}/minute at 1550 C. (obs. ped. temp.). Diamond-finished surfaces oriented to the $(11\bar{2}3)$ have retained a polish at etch rates of 0.7 mg./cm.^{2}/minute at 1450 C.

Table I below is included to indicate typical values of weight loss observed when 0.3 percent by volume SF_6 in a helium diluent as used to etch-polish materials other than sapphire. As before, the data included are to be considered typical, and will vary depending on the configuration of the chamber, the type of carrier gas, flow rate, and exposure time used, the crystalline surface exposed to be etch-polished, and so forth.

TABLE I.—EFFECT OF ETCH-POLISHING REFRACTORY INORGANIC OXIDES WITH 0.3 PERCENT BY VOLUME OF SF_6 IN A HELIUM DILUENT AT 1,450° C. FOR 30 MINUTES

Material	Physical Form	Weight (mg.)			Approximate percent change in weight	Observations
		Before	After	Loss		
ThO_2	Small cube (1 mm.^{3})	13.6	13.2	0.4	3	Etch-polished.
Spinel	Oval (9.5 mm. x 12 mm.)	249.8	226.4	23.4	9.2	Do.
Chrysoberyl	Platelet (6.5 mm. x 3 mm.)	61.4	52.7	8.7	16.5	Do.
BeO	Prism (~6 mm. x 4 mm.)	87.6	81.3	6.3	7.2	Etched.

In general, the material to be etch-polished should be exposed to the gaseous etchant for a period of time sufficient to remove a layer at least equal in thickness to the maximum depth scratch observed on the material subsequent to rough-or diamond-polishing. Alternately, an etch-polishing period may be selected to remove that thickness of material containing a substantial percentage of the defects.

Although the invention has been described and illustrated in detail, it is to be understood that the same is by way of illustration and example only, and is not to be taken by way of limitation; the spirit and scope of this invention being limited only by the terms of the appended claims.

I claim:

1. A process for improving the quality of surfaces of a high temperature refractory inorganic oxide material, selected from the group consisting of beryllium oxide, thorium dioxide, spinel or chrysoberyl comprising the steps of:

heating said material to an approximate temperature ranging between 1300° C. and 1600° C.; and

exposing at least one of said surfaces to a sulfur fluoride gas for a period of time sufficient to etch-polish same.

2. The process defined in claim **1** wherein the sulfur fluoride gas is selected from the group consisting of sulfur tetrafluoride or sulfur hexafluoride.

3. The process defined in claim **1** wherein the sulfur fluoride gas is selected from the group consisting of sulfur tetrafluoride or sulfur hexafluoride, said gas being

in a diluent which is selected from the class consisting of helium, argon, nitrogen or an inert gas.

4. A process for improving the quality of the surfaces of an aluminum oxide material, comprising the steps of:
heating said material to an approximate temperature ranging between 1150° C. and 1600° C.; and
exposing at least one of the surfaces of said material to a sulfur fluoride gas for a period of time sufficient to etch-polish same.

5. The process as set forth in claim 4, wherein:
said sulfur fluoride gas is selected from the group consisting of sulfur tetrafluoride or sulfur hexafluoride.

6. The process as set forth in claim 5, wherein:
said sulfur fluoride gas is selected from the group consisting of sulfur tetrafluoride or sulfur hexafluoride, said gas being in a diluent which is selected from the group consisting of helium, argon, nitrogen or an inert gas.

7. A process for improving the quality of surfaces of a high temperature refractory material selected from the group consisting of beryllium oxide, thorium dioxide, spinel or chrysoberyl, comprising the steps of:
heating the material to an approximate temperature ranging between 1300° C. and 1600° C.; and
exposing at least one of the surfaces of said material to a gas selected from the group consisting of sulfur tetrafluoride or sulfur hexafluoride for a period of time sufficient to etch-polish same, said gas being in a diluent selected from the group consisting of helium, argon, nitrogen or an inert gas.

8. A process for improving the quality of surfaces of a high temperature refractory aluminum oxide material, comprising the steps of:
heating the material to an approximate temperature ranging between 1150° C. and 1600° C.; and

exposing at least one of the surfaces of said material to a gas selected from the group consisting of sulfur tetrafluoride or sulfur hexafluoride for a period of time sufficient to etch-polish same, said gas being in a diluent selected from the group consisting of helium, argon, nitrogen or an inert gas.

9. A process for improving the quality of surfaces of a high temperature refractory aluminum oxide material, comprising the steps of:
heating the material to an approximate temperature ranging between 1150° C. and 1600° C.; and
exposing at least one of the surfaces of said material to a gas of sulfur tetrafluoride for a period of time sufficient to etch-polish same, said gas being in a diluent selected from the group consisting of hydrogen, helium, argon, nitrogen or an inert gas.

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JACOB H. STEINBERG, Primary Examiner

U.S. Cl. X.R.

156—2; 756—20; 252—79.3; 148—1.5, 174