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(54) ALUMINA SINTERED BODY AND MANUFACTURING METHOD THEREFOR

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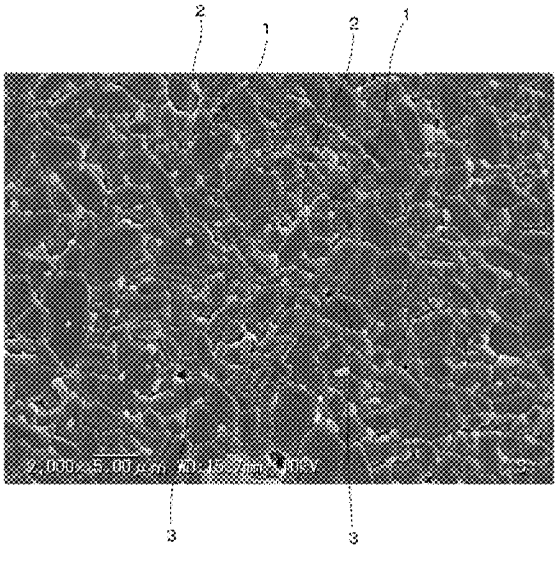
(57) ABSTRACT

The present invention relates to an alumina sintered body and a manufacturing method therefor; for example, the present invention relates to an alumina sintered body that is suitably utilized for a member or similar used in a plasma processing device, an etcher for semiconductor/liquid crystal display device manufacturing, a CVD device, or similar, or that is suitably utilized for a substrate or similar of a plasma-resistant member which is to be coated, as well as a manufacturing method for said alumina sintered body.

9 Claims, 1 Drawing Sheet



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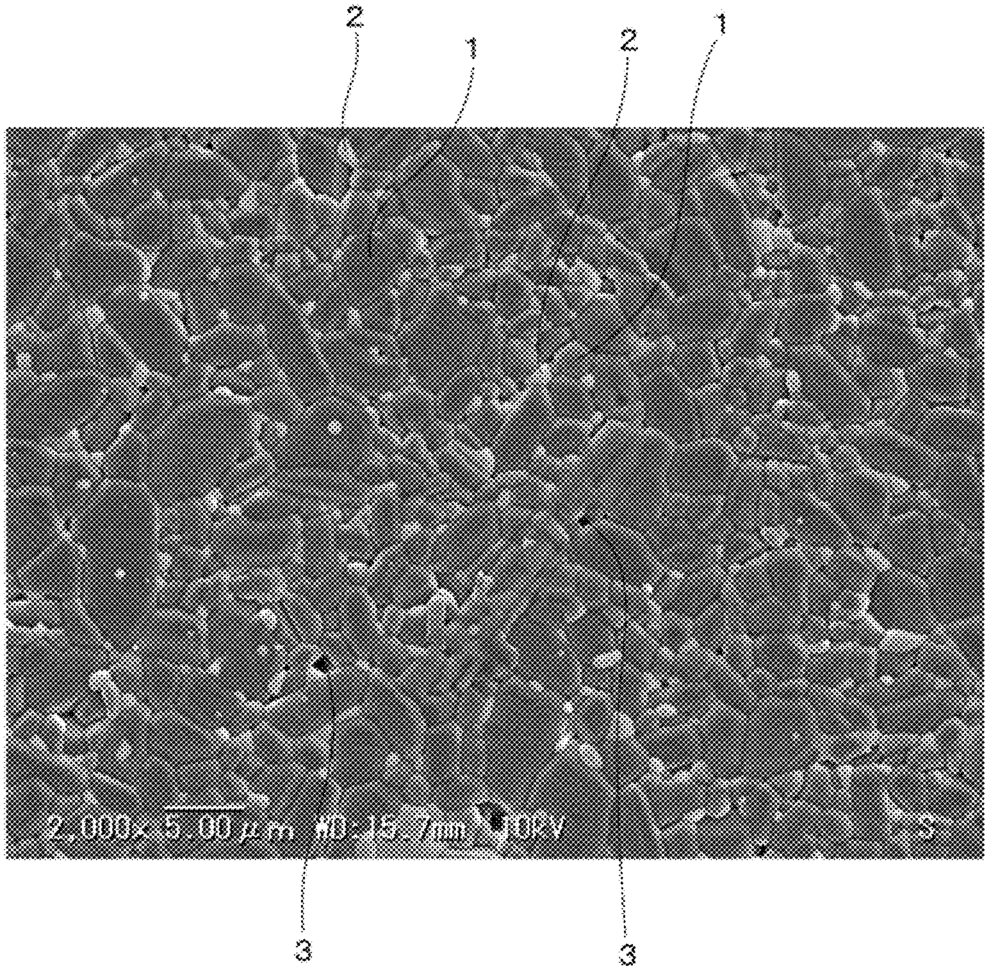
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ALUMINA SINTERED BODY AND MANUFACTURING METHOD THEREFOR

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a US. National Stage entry of PCT Application. No. PCT/JP2018/036914, filed on Oct. 2, 2018, which claims priority to JP Application No. 2018-180299, filed Sep. 26, 2018, which claims priority to JP Application No. 2018-178652, filed Sep. 25, 2018, which claims priority to JP Application No. 2017-195292, filed Oct. 5, 2017. The contents of the foregoing are incorporated by reference.

TECHNICAL FIELD

The present invention relates to an alumina-based sintered object and a process for producing the same. More particularly, the present invention relates to an alumina-based sintered object which is suitable for use as, for example, members for use in plasma treatment devices, etchers for semiconductor/liquid-crystal display device production, CVD devices, etc., or is suitable for use as, for example, the substrates of plasma-resistant members which are to be coated, and also relates to a process for producing the alumina-based sintered object.

BACKGROUND ART

Alumina-based sintered objects are excellent in terms of heat resistance, chemical resistance, and plasma resistance and have a small dielectric loss tangent (tan δ) in a high-frequency region. Alumina-based sintered objects are hence used, for example, as members for use in plasma treatment devices, etchers for semiconductor/liquid-crystal display device production, CVD devices, etc., or as the substrates of plasma-resistant members which are to be coated.

Various proposals have been made in order to improve the corrosion resistance and dielectric loss tangent (dielectric loss) of the alumina-based sintered objects.

For example, Patent Document 1 proposes an alumina-based sintered object which has an Na content, in terms of Na_2O content, of 30 ppm to 500 ppm of all the constituent components and an Al content, in terms of Al_2O_3 content, of 99.4% by mass or higher based on all the constituent components and has a value of dielectric loss tangent at 8.5 GHz which is up to 0.5 times the Na content in terms of Na_2O content, for the purpose of providing: an alumina-based sintered object having high corrosion resistance and having a small dielectric loss tangent although containing an Na oxide; a member for semiconductor production devices; and a member for liquid-crystal panel production devices.

Patent Document 2 proposes an alumina-based sintered object which has an Al_2O_3 content in the range of 99.4% to 99.8% by mass and an Si content, in terms of SiO_2 content, in the range of 0.11% to 0.38% by mass and in which the deviation of crystal grain diameter in each of a surface-layer part and an inner part is 0.06 μm or less and the deviation of the proportion of crystals with a grain diameter of 6.5 μm or larger in each of the surface-layer part and the inner part is 0.6% or less, for the purpose of providing an alumina-based sintered object capable of differing in dielectric loss tangent between different positions and a process for producing the sintered object.

Patent Document 3 proposes an alumina-based sintered object which has an Al_2O_3 purity of 99.3 wt % or higher and contains solute Ti in the Al_2O_3 crystal grains in an amount in the range of 0.08 wt % to 0.20 wt % in terms of TiO_2 amount and in which Si is contained in an amount in the range of 0.05 wt % to 0.40 wt % in terms of SiO_2 amount, for the purpose of providing an alumina-based sintered object which can stably has a reduced dielectric loss tangent while retaining improved processability and a process for producing the sintered object.

Patent Document 4 proposes a technique in which in cases when lower cost or substrate strength is required for producing a plasma-resistant member, a plasma-resistant film including Y_2O_3 or YAG is formed on a surface of an alumina ceramic substrate.

Furthermore, with respect to film formation, Patent Document 5, for example, indicates that a thermal-sprayed ceramic coating film having a thickness of 200 μm or less is formed on a surface of a base member for configuring a semiconductor production device. Patent Document 5 indicates that the thermal-sprayed film has a porosity of 5% to 10%.

CITATION LIST

Patent Document

Patent Document 1: JP-A-2015-163569
Patent Document 2: JP-A-2013-155398
Patent Document 3: JP-A-2013-180909)
Patent Document 4: JP-A-2005-225745
Patent Document 5: JP-A-2013-95973

SUMMARY OF INVENTION

Technical Problem

In the members for semiconductor production devices shown in Patent Documents 4 and 5, which have thermal-sprayed ceramic coating film, the thermal-sprayed coating film has a thickness of about 200 pun and a porosity of 5% to 10%. There has hence been a concern that in cases when these members are used in the state of being exposed to plasma, the thermal-sprayed coating film might partly peel off to generate particles.

Meanwhile, due to the nowadays diversification of film deposition techniques, the thermal-sprayed films tend to have smaller thicknesses, e.g., about several micrometers. There has hence been a problem in that in depositing a film having a reduced thickness by thermal spraying on a substrate, even film deposition is inhibited by pores present in the substrate.

Although several proposals have been made with regard to the corrosion resistance and dielectric loss tangent (dielectric loss) of alumina-based sintered objects as shown in Patent Documents 1 to 3, no proposals have been made on any alumina-based sintered object on which a dense film can be evenly deposited by thermal spraying, so far as the present applicant knows.

Under these circumstances, the present inventors diligently made investigations in order to develop an alumina-based sintered object suitable for use as a plasma-resistant-member substrate to be coated. As a result, the present inventors have conceived of an alumina-based sintered object that has both corrosion resistance and low-dielectric-loss characteristics and is suitable for use as a substrate on which a dense film can be evenly deposited. The present invention has been thus completed.

An object of the present invention is to provide: an alumina-based sintered object which has both corrosion resistance and low-dielectric-loss characteristics and on which a dense film can be evenly deposited; and a process for producing the alumina-based sintered object.

Solution to Problem

In order to accomplish the object, the present invention provides, in a first aspect thereof, an alumina-based sintered object having an Al content, in terms of Al_2O_3 content, of 70% by weight or higher, in which the alumina-based sintered object has a Zr content, in terms of ZrO_2 content, of 30% by weight or less, an Si content, in terms of SiO_2 content, of 170 ppm to 600 ppm, and an Na content, in terms of Na_2O content, of 27 ppm or less.

The alumina-based sintered object having the specific configuration according to the first aspect of the present invention has both corrosion resistance and low-dielectric-loss characteristics.

Specifically, the alumina-based sintered object has a dielectric loss tangent tan δ of 10^{-3} or less. Furthermore, the alumina-based sintered object has so small a number of pores that, when a thin film is formed on the surface thereof, the number of voids on the surface of the thin film is 100 or less in a region of about 200 μm×200 μm and an average diameter of the voids is 5 μm or less. Namely, an even and dense film can be deposited on the substrate.

In addition, the alumina-based sintered object according to the first aspect has high flexural strength. Specifically, this alumina-based sintered object has a three-point bending strength of 320 MPa or higher.

It is desirable that the Al_2O_3 crystals contained in the alumina-based sintered object have an average crystal grain diameter of 3 μm to 15 μm.

This makes it possible to deposit an even film on the surface of the alumina-based sintered object.

In order to accomplish the object shown above, the present invention provides, in a second aspect thereof, an alumina-based sintered object having an Al content, in terms of Al_2O_3 content, of 70% by weight or higher, in which the alumnina-based sintered object has a Zr content, in terms of ZrO_2 content, of 30% by weight or less, a Y content, in terms of Y_2O_3 content, of 1% to 10% by weight, an Si content, in terms of SiO_2 content, of 170 ppm to 600 ppm, and an Na content, in terms of Na_2O content, of 27 ppm or less, and the Y content, in terms of Y_2O_3 content, is not more than the Zr content, in terms of ZrO_2 content.

The alumina-based sintered object having the specific configuration according to the second aspect of the present invention has both corrosion resistance and low-dielectric-loss characteristics.

Specifically, this alumina-based sintered object has a dielectric loss tangent tan δ of 10^{-3} or less. Furthermore, the alumina-based sintered object has so small a number of pores that, when a thin film is formed on the surface thereof, the number of voids on the surface of the thin film is 100 or less in a region of about 200 μm×200 μm and an average diameter of the voids is 5 μm or less. Namely, an even and dense film can be deposited on the substrate.

In addition, this alumina-based sintered object has high flexural strength. Specifically, this alumina-based sintered object has a three-point bending strength of 320 MPa or higher.

It is desirable that the Al_2O_3 crystals contained in this alumina-based sintered object have an average crystal grain diameter of 3 μm to 15 μm.

This makes it possible to deposit an even film on the surface of the alumina-based sintered object.

Furthermore, in order to accomplish the object shown above, the present invention provides, in a third aspect thereof, an alumina-based sintered object having an Al content, in terms of Al_2O content, of 99.8 wt % or higher, in which the alumina-based sintered object has an Si content, in terms of SiO_2 content, of 170 ppm to 600 ppm and an Na content, in terms of Na_2O content, of 27 ppm or less, and the alumina-based sintered object has a density of 3.96 g/cm^3 or higher.

The alumina-based sintered object having the specific configuration according to the third aspect of the present invention has both corrosion resistance and low-dielectric-loss characteristics. Furthermore, this alumina-based sintered object has denseness, with a density of 3.96 g/cm^3 or higher. As a result, this alumina-based sintered object has so small a number of pores that an even and dense film can be deposited on a surface of the substrate.

In the third aspect of the present invention, it is desirable that the alumina-based sintered object contains Mg in an amount which, in terms of MgO content, is 1.0 to 4.0 times the Si content in terms of SiO_2 content.

It is desirable that the alumina-based sintered object contains Ca in an amount which, in terms of CaO content, is up to 3.0 times the Si content in terms of SiO_2 content.

It is also desirable that the alumina-based sintered object has an average pore diameter of 5 μm or less. It is desirable that the Al_2O_3 crystals contained in the alumina-based sintered object have an average crystal grain diameter of 3 μm to 40 μm.

Furthermore, a corrosion-resistant film or a corrosion-resistant layer may be formed on at least a part of this alumina-based sintered object.

This alumina-based sintered object according to the present invention may be produced by granulating and molding a raw-material powder to obtain a molded object and firing the molded object in a hydrogen atmosphere at 1,600° C. to 1,900° C.

Advantageous Effects of Invention

According to the present invention, it is possible to obtain an alumina-based sintered object which has both corrosion resistance and low-dielectric-loss characteristics. According to the present invention, it is also possible to obtain an alumina-based sintered object in which, when a film is formed on the surface thereof, a dense film can be evenly formed.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** shows a photograph of a cross-section obtained in Example 1A.

DESCRIPTION OF EMBODIMENTS

The alumina-based sintered object of a first embodiment according to the first aspect of the present invention is explained below.

The alumina-based sintered object according to the first embodiment is an alumina-based sintered object having an Al content, in terms of Al_2O_3 content, of 70% by weight or higher, in which the alumina-based sintered object has a Zr content, in terms of ZrO_2 content, of 30% by weight or less, an Si content, in terms of SiO_2 content, of 170 ppm to 600 ppm, and an Na content, in terms of Na_2O content, of 27 ppm or less.

This alumina-based sintered object has high flexural strength, has both corrosion resistance and low-dielectric-loss characteristics, and serves as a substrate on which an even and dense film can be deposited.

This alumina-based sintered object has an Al content, in terms of Al_2O_3 content, of 70% by weight or higher and has a Zr content, in terms of ZrO_2 content, of 30% by weight or less.

In this alumina-based sintered object, a ZrO_2 crystal phase has been formed besides the main crystals of Al_2O_3. This ZrO_2 crystal phase not only contributes to a reduction in the amount of pores but also is inhibited from undergoing abnormal grain growth and has a reduced grain diameter. The ZrO_2 crystal phase hence serves to enhance the strength.

However, in case where the Zr content in terms of ZrO_2 content exceeds 30% by weight, the Al content in terms of Al_2O_3 content is less than 70% by weight and this alumina-based sintered object does not have high resistance to corrosion by highly reactive halogen-based corrosive gases or plasmas thereof. Such Zr contents are hence undesirable.

In addition, in case where the Zr content in terms of ZrO_2 content exceeds 30% by weight, the ZrO_2 crystal phase is present in an increased amount and this results in a decrease in the strength of the alumina-based sintered object. Furthermore, the dielectric loss tangent tan δ exceeds 10^{-3}. Such Zr contents are hence undesirable.

Consequently, the Al content in terms of Al_2O_3 content is 70% by weight or higher, and the Zr content in terms of ZrO_2 content is 30% by weight or less.

Any ingredients contained in the alumina-based sintered object other than Al_2O_3 and ZrO_2 are substances which have unavoidably come into the alumina in the steps for alumina production. Examples thereof include Si, Mg, Na, and Ca.

In this alumina-based sintered object, the Si content in terms of SiO_2 content is 170 ppm to 600 ppm.

In case where the Si content in terms of SiO_2 content is less than 170 ppm, silicates which are necessary for imparting low-dielectric-loss characteristics are not evenly formed, resulting in an increase in dielectric loss and making it impossible to obtain the effect of power saving. Such Si contents are hence undesirable.

Meanwhile, in case where the Si content in terms of SiO_2 content exceeds 600 ppm, this alumina-based sintered object has a low density and is not dense. Such Si contents are hence undesirable.

In the alumina-based sintered object according to the first embodiment, the Na content in terms of Na_2O content is 27 ppm or less. In case where the Na content in terms of Na_2O content exceeds 27 ppm, this alumina-based sintered object has an increased dielectric loss and does not have the effect of power saving. Such Na contents are hence undesirable.

It is preferable that, in the alumina-based sintered object according to the first embodiment, the content of Mg, in terms of MgO content, is 1.0 to 4.0 times the Si content in terms of SiO_2 content.

In cases when the content of Mg, in terms of MgO content, is 1.0 to 4.0 times the Si content in terms of SiO_2 content, silicates can be formed at grain boundaries of the alumina-based sintered object. Hence, an alumina-based sintered object having a high density and a low dielectric loss can be obtained.

It is preferable that in the alumina-based sintered object according to the first embodiment, the content of Ca, in terms of CaO content, is up to 3.0 times the Si content in terms of SiO_2 content.

In cases when the content of Ca, in terms of CaO content, is up to 3.0 times the Si content in terms of SiO_2 content, silicates can be formed at grain boundaries. Hence, an alumina-based sintered object having a low dielectric loss can be obtained.

It is preferable that, in the alumina-based sintered object according to the first embodiment, the Al_2O_3 crystals have an average crystal grain diameter of 3 μm to 15 μm.

In cases when the Al_2O_3 crystals contained in the alumina-based sintered object have an average crystal grain diameter of 3 μm to 15 μm, this alumina-based sintered object can be made to have a smaller amount of pores. It is hence possible to obtain a sintered object having a higher density and to obtain an alumina-based sintered object having a three-point bending strength of 320 MPa or higher.

It is preferable that the alumina-based sintered object according to the first embodiment has a water absorption of 0.2% or less. The water absorption is the smaller, the porosity of the alumina-based sintered object is smaller. Thus the smaller the water absorption is, the denser the alumina-based sintered object is.

Consequently, a thin film can be evenly formed on the surface of the alumina-based sintered object having a water absorption of 0.2% or less.

It is preferable that the alumina-based sintered object according to the first embodiment has an average pore diameter of 5 μm or less. In cases when the alumina-based sintered object has an average pore diameter of 5 μm or less, a thin film can be more evenly formed on the surface of the alumina-based sintered object.

Although the alumina-based sintered object according to the first embodiment may be used as such, the alumina-based sintered object may be used after a dense film is formed on a surface thereof.

The film is obtained, for example, by depositing a film of an yttria material on the alumina-based sintered object using an aerosol deposition method or PVD. The alumina-based sintered object on which a film of an yttria material has been thus deposited has high plasma resistance, is highly inhibited from causing dusting, and is capable of attaining power saving, etc. due to the low-dielectric-loss characteristics of the substrate.

As stated above, in cases when the alumina-based sintered object has a water absorption of 0.2% or less, a thin film can be evenly formed on the surface of this alumina-based sintered object.

Especially in the case where the alumina-based sintered object has an average pore diameter of 5 μm or less, a thin film of yttria can be more evenly deposited on the surface of the alumina-based sintered object.

The film to be formed on the surface of the alumina-based sintered object is not limited to yttria materials. For example, the film may be any of: a composite oxide (YAG) including yttrium oxide and aluminum oxide; erbium oxide; oxides of other rare earth elements; and composite oxides including oxides of rare earth elements.

It is desirable that the surface of the alumina-based sintered object on which a film is to be formed has a surface roughness Ra of less than 0.1 μm. The surface of the alumina-based sintered object may be mirror-polished before film formation, thereby reducing the surface roughness to less than 0.1 pun. Namely, it is desirable that the surface of the alumina-based sintered object on which a film is to be formed has an average pore diameter of 5 μm or less and a surface roughness Ra of less than 0.1 μm.

On the alumina-based sintered object having such a surface, a thin film can be more evenly formed. This thin film is inhibited from peeling off, and particle generation can be inhibited.

The film to be formed on the alumina-based sintered object may be one to be formed on a part of the surface of the alumina-based sintered object. The thickness of the film is not particularly limited. However, the thickness thereof is preferably 1 μm to 20 μm.

The alumina-based sintered object can be produced by a process generally used for producing an alumina-based sintered object. For example, the alumina-based sintered object can be produced by the following process.

First, a ZrO_2 powder or an aqueous solution thereof is added to an Al_2O_3 powder having a predetermined median diameter. A binder or the like (e.g., PVA) is added thereto to prepare a raw-material powder. This raw-material powder is stirred and mixed by a mixer to obtain a raw-material slurry, which is then granulated.

The resultant granules are molded to thereby produce a molded object. For the molding, use can be made of various methods such as uniaxial press molding, CIP molding, wet molding, and pressure casting.

The molded object is fired at a temperature in the range of 1,600° C. to 1,900° C. for 6 hours or longer in a hydrogen atmosphere, thereby obtaining the alumina-based sintered object.

By thus firing the molded object at 1,600° C. to 1,900° C. in a hydrogen atmosphere, an alumina-based sintered object having a high density can be obtained.

Next, the alumina-based sintered object of a second embodiment according to the second aspect of the present invention is explained.

The alumina-based sintered object according to the second embodiment is an alumina-based sintered object having an Al content, in terms of Al_2O_3 content, of 70% by weight or higher, in which the alumina-based sintered object has a Zr content, in terms of ZrO_2 content, of 30% by weight or less, a Y content, in terms of Y_2O_3 content, of 1% to 10% by weight, an Si content, in terms of SiO_2 content, of 170 ppm to 600 ppm, and an Na content, in terms of Na_2O content, of 27 ppm or less, and the Y content, in terms of Y_2O_3 content, is not more than the Zr content, in terms of ZrO_2 content.

The alumina-based sintered object according to the second embodiment has high flexural strength, has both corrosion resistance and low-dielectric-loss characteristics, and serves as a substrate on which an even and dense film can be deposited.

In the alumina-based sintered object according to the second embodiment, the content of Al, in terms of Al_2O_3 content, is 70% by weight or higher. The content of Zr therein, in terms of ZrO_2 content, is 30% by weight or less, and the content of Y therein, in terms of Y_2O_3 content, is 1% to 10% by weight.

In the alumina-based sintered object according to the second embodiment, a ZrO_2 crystal phase has been formed besides the main crystals of Al_2O_3. The ZrO_2 crystal phase not only contributes to a reduction in the amount of pores but also is inhibited from undergoing abnormal grain growth and has a reduced grain diameter. The ZrO_2 crystal phase hence serves to enhance the strength.

However, in case where the Zr content in terms of ZrO_2 content exceeds 30% by weight, the Al content in terms of Al_2O_3 content is less than 70% by weight and this alumina-based sintered object does not have high resistance to corrosion by highly reactive halogen-based corrosive gases or plasmas thereof. Such Zr contents are hence undesirable.

In addition, in case where the Zr content in terms of ZrO_2 content exceeds 30% by weight, the ZrO_2 crystal phase is present in an increased amount and this results in a decrease in the strength of the alumina-based sintered object. Furthermore, the dielectric loss tangent tan δ exceeds 10^{-3}. Such Zr contents are hence undesirable.

Consequently, the Al content in terms of Al_2O_3 content is 70% by weight or higher, and the Zr content in terms of ZrO_2 content is 30% by weight or less.

Furthermore, in this embodiment, the content of Y, in terms of Y_2O_3 content, is 1% to 10% by weight.

In cases when the Zr addition amount is large, this alumina-based sintered object may crack due to the influence of phase transition. Yttrium has the effect of inhibiting the cracking due to the addition of Zr.

With respect to the addition amount of Y, in case where the content of Y, in terms of Y_2O_3 content, is less than 1% by weight, the effect of cracking inhibition is too low. In case where Y is added in an amount exceeding 10% by weight, some of the Y reacts with Al_2O_3 during the firing step to yield YAG. In case where the YAG is present in too large an amount, the alumina-based sintered object has a reduced three-point bending strength. The content of Y is hence 10% by weight or less.

In addition, in case where the content of Y, in terms of Y_2O_3 content, is more than the content of Zr, in terms of ZrO_2 content, the alumina-based sintered object has a reduced three-point bending strength, and hence it is not preferable. Therefore, it is preferable that the content of Y, in terms of Y_2O_3 content, is not more than the content of Zr, in terms of ZrO_2 content.

Any ingredients contained in the alumina-based sintered object according to the second embodiment other than Al_2O_3, ZrO_2, and Y_2O_3 are substances which have unavoidably come into the alumina in the steps for alumina production, as in the first embodiment. Examples thereof include Si, Mg, Na, and Ca.

As in the first embodiment, the content of Si, in terms of SiO_2 content, in this alumina-based sintered object is 170 ppm to 600 ppm. The content of Na therein, in terms of Na_2O content, is 27 ppm or less. It is preferable that the content of Mg, in terms of MgO content, is 1.0 to 4.0 times the Si content in terms of SiO_2 content.

Furthermore, it is preferable that the content of Ca, in terms of CaO content, is up to 3.0 times the Si content in terms of SiO_2 content.

It is preferable that the Al_2O_3 crystals contained in the alumina-based sintered object according to the second embodiment have an average crystal grain diameter of 3 μm to 15 μm, as in the first embodiment.

It is preferable that the alumina-based sintered object according to the second embodiment has a water absorption of 0.2% or less, as in the first embodiment.

It is preferable that this alumina-based sintered object has an average pore diameter of 5 μm or less.

Although the alumina-based sintered object according to the second embodiment may be used as such, the alumina-based sintered object may be used after a dense film is formed on a surface thereof, as in the first embodiment.

The film is obtained, for example, by depositing a film of an yttria material on the alumina-based sintered object using an aerosol deposition method or PVD, as in the first embodiment.

As stated above, in cases when the alumina-based sintered object has a water absorption of 0.2% or less, a thin film can be evenly formed on the surface of this alumina-based sintered object.

Especially in the case where the alumina-based sintered object has an average pore diameter of 5 μm or less, a thin film of yttria can be more evenly deposited on the surface of the alumina-based sintered object.

The film to be formed on the surface of the alumina-based sintered object is not limited to yttria materials. For example, the film may be any of: a composite oxide (YAG) including yttrium oxide and aluminum oxide; erbium oxide; oxides of other rare earth elements; and composite oxides including oxides of rare earth elements.

It is desirable that the surface of the alumina-based sintered object on which a film is to be formed has a surface roughness Ra of less than 0.1 μm, as in the first embodiment. The surface of the alumina-based sintered object may be mirror-polished before film formation, thereby reducing the surface roughness to less than 0.1 μm. Namely, it is desirable that the surface of the alumina-based sintered object on which a film is to be formed has an average pore diameter of 5 μm or less and a surface roughness Ra of less than 0.1 μm.

On the alumina-based sintered object having such a surface, a thin film can be more evenly formed. This thin film is inhibited from peeling off, and particle generation can be inhibited.

The film to be formed on the alumina-based sintered object may be one to be formed on a part of the surface of the alumina-based sintered object. The thickness of the film is not particularly limited. However, the thickness thereof is preferably 1 μm to 20 μm.

The alumina-based sintered object can be produced by a process generally used for producing an alumina-based sintered object, as stated above with regard to the first embodiment. For example, the alumina-based sintered object can be produced by the following process.

First, either a ZrO_2 powder and a Y_2O_3 powder or an aqueous solution of these is added to an Al_2O_3 powder having a predetermined median diameter. A binder or the like (e.g., PVA) is added thereto to prepare a raw-material powder. This raw-material powder is stirred and mixed by a mixer to obtain a raw-material slurry, which is then granulated.

The resultant granules are molded to thereby produce a molded object. For the molding, use can be made of various methods such as uniaxial press molding, CIP molding, wet molding, and pressure casting.

The molded object is fired at a temperature in the range of 1,600° C. to 1,900° C. for 6 hours or longer in a hydrogen atmosphere, thereby obtaining the alumina-based sintered object.

By thus firing the molded object at 1,600° C. to 1,900° C. in a hydrogen atmosphere, an alumina-based sintered object having a three-point bending strength of 320 MPa or higher, including Al_2O_3 crystals with an average crystal grain diameter of 3 μm to 15 μm, and having a water absorption of 0.2% or less is obtained. This alumina-based sintered object can be obtained as an alumina-based sintered object which has such low-dielectric-loss characteristics that the value of the dielectric loss tangent tan δ at 10 MHz to 20 MHz is 10^{-3} or less.

The alumina-based sintered object of a third embodiment according to the third aspect of the present invention is explained.

The alumina-based sintered object according to the third embodiment is an alumina-based sintered object having an Al content, in terms of Al_2O_3 content, of 99.8 wt % or higher, in which the alumina-based sintered object has an Si content, in terms of SiO_2 content, of 170 ppm to 600 ppm and an Na content, in terms of Na_2O content, of 27 ppm or less, and the alumina-based sintered object has a density of 3.96 g/cm^3 or higher.

The alumina-based sintered object according to the third embodiment has both corrosion resistance and low-dielectric-loss characteristics and serves as a substrate on which an even and dense film can be deposited.

The alumina-based sintered object according to the third embodiment has an Al content, in terms of Al_2O_3 content, of 99.8 wt % or higher. In case where the content of Al in terms of Al_2O_3 content is less than 99.8 wt %, this alumina-based sintered object does not have high resistance to corrosion by highly reactive halogen-based corrosive gases or plasmas thereof. Such Al contents are hence undesirable.

Any ingredients contained in the alumina-based sintered object according to the third embodiment other than Al_2O_3 are substances which have unavoidably come into the alumina in the steps for alumina production. Examples thereof include Si, Mg, Na, and Ca.

In the alumina-based sintered object according to the third embodiment, the Si content in terms of SiO_2 content is 170 ppm to 600 ppm.

In case where the Si content in terms of SiO_2 content is less than 170 ppm, silicates which are necessary for imparting low-dielectric-loss characteristics are not evenly formed, resulting in an increase in dielectric loss and making it impossible to obtain the effect of power saving. Such Si contents are hence undesirable.

Meanwhile, in case where the Si content in terms of SiO_2 content exceeds 600 ppm, this alumina-based sintered object has a low density and is not dense. Such Si contents are hence undesirable.

Specifically, the density of the alumina-based sintered object according to the third embodiment is 3.96 g/cm^3 or higher.

In the alumina-based sintered object according to the third embodiment, the Na content in terms of Na_2O content is 27 ppm or less. In case where the Na content in terms of Na_2O content exceeds 27 ppm, this alumina-based sintered object has an increased dielectric loss and does not have the effect of power saving. Such Na contents are hence undesirable.

It is preferable that, in the alumina-based sintered object according to the third embodiment, the content of Mg, in terms of MgO content, is 1.0 to 4.0 times the Si content in terms of SiO_2 content.

In cases when the content of Mg, in terms of MgO content, is 1.0 to 4.0 times the Si content in terms of SiO_2 content, silicates can be formed at grain boundaries of the alumina-based sintered object. Hence, an alumina-based sintered object having a high density and a low dielectric loss can be obtained.

It is preferable that, in the alumina-based sintered object according to the third embodiment, the content of Ca, in terms of CaO content, is up to 3.0 times the Si content in terms of SiO_2 content.

In cases when the content of Ca, in terms of CaO content, is up to 3.0 times the Si content in terms of SiO_2 content, silicates can be formed at grain boundaries. Hence, an alumina-based sintered object having a low dielectric loss can be obtained.

It is preferable that, in the alumina-based sintered object according to the third embodiment, the Al_2O_3 crystals have an average crystal grain diameter of 3 μm to 40 μm. The average crystal grain diameter thereof is more preferably 10 μm to 25 μm.

In cases when the Al_2O_3 crystals in the alumina-based sintered object have an average crystal grain diameter of 3 μm to 40 μm, this alumina-based sintered object can be made to have a smaller amount of pores. It is hence possible to obtain a sintered object having a higher density and to obtain an alumina-based sintered object having a three-point bending strength of 250 MPa or higher.

It is preferable that the alumina-based sintered object according to the third embodiment has an average pore diameter of 5 μm or less. In cases when the alumina-based sintered object has an average pore diameter of 5 μm or less, a thin film can be evenly formed on the surface of the alumina-based sintered object.

Although the alumina-based sintered object according to the third embodiment may be used as such, the alumina-based sintered object may be used after a dense film is formed on a surface thereof.

The film is obtained, for example, by depositing a film of an yttria material on the alumina-based sintered object using an aerosol deposition method or PVD. The alumina-based sintered object on which a film of an yttria material has been thus deposited has high plasma resistance, is highly inhibited from causing dusting, and is capable of attaining power saving, etc. due to the low-dielectric-loss characteristics of the substrate.

As stated above, in cases when the alumina-based sintered object has an average pore diameter of 5 μm or less, a thin film of yttria can be evenly deposited on the surface of the alumina-based sintered object.

The film to be formed on the surface of the alumina-based sintered object is not limited to yttria materials. For example, the film may be any of: a composite oxide (YAG) including yttrium oxide and aluminum oxide; erbium oxide; oxides of other rare earth elements; and composite oxides including oxides of rare earth elements.

It is desirable that the surface of the alumina-based sintered object on which a film is to be formed has a surface roughness Ra of less than 0.1 μm. The surface of the alumina-based sintered object may be mirror-polished before film formation, thereby reducing the surface roughness to less than 0.1 μm. Namely, it is desirable that the surface of the alumina-based sintered object on which a film is to be formed has an average pore diameter of 5 μm or less and a surface roughness Ra of less than 0.1 μm.

On the alumina-based sintered object having such a surface, a thin film can be more evenly formed. This thin film is inhibited from peeling off, and particle generation can be inhibited.

The film to be formed on the alumina-based sintered object may be one to be formed on a part of the surface of the alumina-based sintered object. The thickness of the film is not particularly limited. However, the thickness thereof is preferably 1 μm to 20 μm.

The alumina-based sintered object can be produced by a process generally used for producing an alumina-based sintered object. For example, the alumina-based sintered object can be produced by the following process.

First, a binder or the like (e.g., PVA) is added to an Al_2O_3 powder having a predetermined median diameter to prepare a raw-material powder. This raw-material powder is stirred and mixed by a mixer to obtain a raw-material slurry, which is then granulated.

The resultant granules are molded to thereby produce a molded object. For the molding, use can be made of various methods such as uniaxial press molding, CIP molding, wet molding, and pressure casting.

The molded object is fired at a temperature in the range of 1,600° C. to 1,900° C. for 6 hours or longer in a hydrogen atmosphere, thereby obtaining the alumina-based sintered object.

By thus firing the molded object at 1,600° C. to 1,900° C. in a hydrogen atmosphere, an alumina-based sintered object having a high density can be obtained.

EXAMPLES

The present invention is explained below in detail by reference to Examples, but the invention should not be construed as being limited by the following Examples.

Experiment 1A

As shown in Table 1, a ZrO_2 powder was added to an alumina powder having a median diameter of 2 μm or less using water as a medium, and PVA was added thereto to prepare a raw-material powder. This raw-material powder was stirred and mixed for 16 hours or longer to obtain a raw-material slurry. This raw-material slurry was granulated, and the granules were packed into a molding die and molded by CIP at a molding pressure of 1.5 tons.

Furthermore, the resultant molded object was subjected to a degreasing step in the air and then fired at 1,600° C. in a hydrogen atmosphere. Thus, samples of Examples 1A to 7A and Comparative Examples 1A to 6A were produced.

SiO_2 and Na_2O were added according to need so as to give sintered objects each having an Si content and an Na content within the ranges according to the present invention.

The samples of Examples 1A to 7A and Comparative Examples 1A to 6A were evaluated for water absorption, average Al_2O_3 crystal grain diameter, dielectric loss tangent tan δ, and three-point bending strength. The results thereof are shown in Table 1.

The average alumina crystal gram diameter was determined by mirror-polishing a cross-section of each sample, subjecting the polished cross-section to thermal etching, subsequently taking a photograph of the cross-section with a scanning electron microscope (SEM), and calculating the average crystal grain diameter by image analysis.

The photograph of the cross-section taken with the scanning electron microscope (SEM) in Example 1A is shown in FIG. **1**.

The three-point bending strength was measured in accordance with JIS R 1601:2008. The purity of each sintered object was determined by ICP emission analysis. The dielectric loss tangent tan δ was determined at frequencies of 10 MHz to 20 MHz using an impedance analyzer.

The water absorption was determined by obtaining dry weight W1 and weight in water W2 by the same method as that described in JIS R 1634:1998 and calculating the water absorption using the following equation.

$$\text{Water absorption } (\%)=(W2-W1)W1\times 100$$

Furthermore, a surface of each of the samples (alumina-based sintered object) of Examples 1A to 7A and Comparative Examples 1A to 6A obtained above was mirror-polished so as to result in Ra<0.1 μm, and the polished surface was coated with an yttrium oxide material in a thickness of 1 μm by the aerosol deposition method.

The deposition material was dried at 270° C. for 12 hours or longer as a pretreatment, and the deposition was then conducted by aerosol jetting under the following conditions:

Sample temperature, room temperature; powder container temperature, 150° C.; raising/conveying gas, He; powder raising rate, 3 L/min; powder conveying rate, 10 L/min; powder collision angle, 60σ; nozzle opening shape, 5×0.3 mm; sample-to-nozzle distance, 5 mm; sample traveling speed, 200 mm/min; number of passes for deposition, 10.

The thus-obtained thin-film-coated samples of Examples 1A to 7A and Comparative Examples 1A to 6A were each examined for surface state over a range of about 200 μm×200 μm using a scanning electron microscope. From the image obtained, the diameters of voids and the number of the voids were determined using an image analysis software. As shown in Table 1, each sample which satisfied the number of voids of 100 or less was regarded as having been coated with an even film and indicated by "A", and each sample which did not satisfy the requirement was regarded as having been coated with an uneven film and indicated by "B".

In Comparative Example 4A, the alumina-based sintered object had a low three-point bending strength and a tan δ exceeding 10^{-3} because of the high Si and Na contents. In addition, this alumina-based sintered object had a large average Al_2O_3 crystal grain diameter, and it was found that formation of an even film on the surface of this alumina-based sintered object was difficult.

In Comparative Example 5A, the alumina-based sintered object had a tan δ exceeding 10^{-3} because of the low Si content. It was found that formation of an even film on the surface of this alumina-based sintered object was difficult.

In Comparative Example 6A, the alumina-based sintered object had a tan δ exceeding 10^{-3} because of the high Na content. This alumina-based sintered object was found to have poor dielectric loss characteristics.

TABLE 1

	Al content (in terms of Al_2O_3) (wt %)	Zr content (in terms of ZrO_2) (wt %)	Si content (in terms of SiO_2) (ppm)	Na content (in terms of Na_2O) (ppm)	Three-point bending strength (MPa)	tanδ @10 to 20 MHz	Average crystal-grain diameter (μm)	Water absorption (%)	State of voids in thin-film surface: Number of voids ≤ 100; Average diameter ≤ 5 μm
Example 1A	90	10	300	10	350	$<10^{-3}$	5	≤0.2	A
Example 2A	90	10	300	27	350	$<10^{-3}$	5	≤0.2	A
Example 3A	90	10	300	2	350	$<10^{-3}$	5	≤0.2	A
Example 4A	90	10	170	10	340	$<10^{-3}$	4	≤0.2	A
Example 5A	90	10	600	10	340	$<10^{-3}$	6	≤0.2	A
Example 6A	70	30	300	10	320	$<10^{-3}$	3	≤0.2	A
Example 7A	99	1	300	10	325	$<10^{-3}$	12	≤0.2	A
Comparative Example 1A	50	50	300	10	250	$>10^{-3}$	3	>0.2	B
Comparative Example 2A	50	50	800	10	230	$>10^{-3}$	3	>0.2	B
Comparative Example 3A	90	10	800	10	310	$<10^{-3}$	16	>0.2	B
Comparative Example 4A	90	10	800	50	310	$>10^{-3}$	16	>0.2	B
Comparative Example 5A	90	10	5	10	330	$>10^{-3}$	5	>0.2	B
Comparative Example 6A	90	10	300	50	350	$>10^{-3}$	5	≤0.2	A

Table 1 shows that the samples of Examples 1A to 7A each had a three-point bending strength of 320 MPa or higher, a tan δ of less than 10^{-3}, an average alumina crystal grain diameter of 3 μm to 15 μm, and a water absorption of 0.2% or less. It was thus ascertained that these samples were alumina-based sintered objects which had high strength, were dense, and had low-dielectric-loss characteristics.

Furthermore, as FIG. **1** shows, it is ascertained that ZrO_2 crystal grains having a small diameter had come into the spaces between alumina crystal grains to inhibit the inclusion of pores.

Furthermore, in each of the thin films, the number of surface voids in a region of about 200 μm×200 μm was 100 or less and the average diameter thereof was 5 μm or less. It was thus ascertained that an even film was able to be formed.

In Comparative Examples 1A and 2A, the alumina-based sintered objects each had a low three-point bending strength and a tan δ exceeding 10^{-3} because of the too high Zr content. Furthermore, these alumina-based sintered objects had cracked.

In Comparative Example 3A, the alumina-based sintered object had a low three-point bending strength and a large average Al_2O_3 crystal grain diameter because of the high Si content. It was found that formation of an even film on the surface of this alumina-based sintered object was difficult.

Experiment 2A

Next, as shown in Table 2, a ZrO_2 powder and a Y_2O_3 powder were added to an alumina powder having a median diameter of 2 μm or less using water as a medium, and PVA was added thereto to prepare a raw-material powder. This raw-material powder was stirred and mixed for 16 hours or longer to obtain a raw-material slurry. This raw-material slurry was granulated, and the granules were packed into a molding die and molded by CIP at a molding pressure of 1.5 tons.

Furthermore, the resultant molded object was subjected to a degreasing step in the air and then fired at 1,600° C. in a hydrogen atmosphere. Thus, samples of Examples 8A to 12A and Comparative Examples 7A and 8A were produced.

SiO_2 and Na_2O were added according to need so as to give sintered objects having an Si content and an Na content within the ranges according to the present invention.

As in Experiment 1A, the samples of Examples 8A to 12A and Comparative Examples 7A and 8A were evaluated for water absorption, average Al_2O_3 crystal grain diameter, dielectric loss tangent tan δ, and three-point bending strength. The results thereof are shown in Table 2.

Furthermore, as in Experiment 1A, a surface of each of the samples (alumina-based sintered object) of Examples 8A to 12A and Comparative Examples 7A and 8A obtained above was mirror-polished so as to result in Ra<0.1 μm, and the polished surface was coated with an yttrium oxide material in a thickness of 1 μm by the aerosol deposition method. The deposition material was dried at 270° C. for 12 hours or longer as a pretreatment, and the deposition was then conducted by aerosol jetting under the same conditions as in Example 1A.

The thus-obtained thin-film-coated samples of Examples 8A to 12A and Comparative Examples 7A and 8A were each examined for surface state over a range of about 200 μm×200 μm using a scanning electron microscope in the same manner as in Experiment 1A. From the image obtained, the diameters of voids and the number of the voids were determined using an image analysis software. As shown in Table 2, each sample which satisfied the number of voids of 100 or less was regarded as having been coated with an even film and indicated by "A", and each sample which did not satisfy the requirement was regarded as having been coated with an uneven film and indicated by "B", as in Experiment 1A.

TABLE 2

	Al content (in terms of Al_2O_3) (wt %)	Zr content (in terms of ZrO_2) (wt %)	Y content (in terms of Y_2O_3) (wt %)	Si content (in terms of SiO_2) (ppm)	Na content (in terms of Na_2O) (ppm)	Three-point bending strength (MPa)	tanδ @10 to 20 MHz	Average crystal-grain diameter (μm)	Water absorption (%)	State of voids in thin-film surface: Number of voids ≤ 100; Average diameter ≤ 5 μm
Example 8A	85	10	5	300	10	350	$<10^{-3}$	7	≤0.2	A
Example 9A	90	5	5	300	10	340	$<10^{-3}$	5	≤0.2	A
Example 10A	65	30	5	300	10	360	$<10^{-3}$	4	≤0.2	A
Example 11A	89	10	1	300	10	350	$<10^{-3}$	5	≤0.2	A
Example 12A	80	10	10	300	10	320	$<10^{-3}$	10	≤0.2	A
Comparative Example 7A	70	10	20	300	10	290	$<10^{-3}$	16	≤0.2	A
Comparative Example 8A	60	10	30	300	10	250	$<10^{-3}$	18	≤0.2	A

Table 2 shows that the samples of Examples 8A to 12A each had a three-point bending strength of 320 MPa or higher, a tan δ of less than 10^{-3}, an average alumina crystal grain diameter of 4 μm to 10 μm, and a water absorption of 0.2% or less. It was thus ascertained that these samples were alumina-based sintered objects which had high strength, were dense, and had low-dielectric-loss characteristics.

Furthermore, in each of the thin films, the number of surface voids in a region of about 200 μm×200 μm was 100 or less and the average diameter thereof was 5 μm or less. It was thus ascertained that an even film was able to be formed.

In Comparative Examples 7A and 8A, the alumina-based sintered objects each had a large average Al_2O_3 crystal grain diameter because of the high Y content. In addition, these alumina-based sintered objects each had a low three-point bending strength.

Experiment 1B

As shown in Table 3, PVA was added to an alumina powder having a purity of 99.7 wt % to 99.9 wt % and a median diameter of 2 μm or less to prepare a raw-material powder. This raw-material powder was stirred and mixed for 16 hours or longer to obtain a raw-material slurry. This raw-material slurry was granulated, and the granules were packed into a molding die and molded by CIP at a molding pressure of 1.5 tons.

Furthermore, the resultant molded object was subjected to a degreasing step in the air and then fired in a hydrogen atmosphere at 1,800° C. (Examples 1B to 4B and 7B and Comparative Examples 1B to 4B), 1,700° C. (Example 5B and Comparative Example 5B), or 1,900° C. (Examples 6B and Comparative Example 6B). Thus, samples of Examples 1B to 7B and Comparative Examples 1B to 6B were produced.

SiO_2 and Na_2O were added according to need so as to give sintered objects each having an Si content and an Na content within the ranges according to the present invention. Furthermore, the median diameter of the alumina powder was changed so that the sintered objects each had a density within the range according to the present invention.

The samples of Examples 1B to 7B and Comparative Examples 1B to 6B were evaluated for density and dielectric loss tangent tan. The results thereof are shown in Table 3.

In Experiment 1B and in the following Experiments 2B to 4B, the density was determined in accordance with JIS R 1634:1998. The tan δ was determined at frequencies of 10 MHz 20 MHz using an impedance analyzer. Furthermore, the average alumina crystal grain diameter was determined by mirror-polishing a cross-section of each sample, subjecting the polished cross-section to thermal etching, subsequently taking a photograph of the cross-section with a scanning electron microscope (SEM), and calculating the average crystal grain diameter by image analysis. The three-point bending strength was measured in accordance with JIS R 1601:2008. The purity of each sintered object was determined by ICP emission analysis.

Furthermore, a surface of each of the samples (alumina-based sintered object) of Examples 1B to 7B and Comparative Examples 1B to 6B obtained above was mirror-polished so as to result in Ra<0.1 μm, and the polished surface was coated with an yttrium oxide material in a thickness of 1 μm by the aerosol deposition method.

The deposition material was dried at 270° C. for 12 hours or longer as a pretreatment, and the deposition was then conducted by aerosol jetting under the following conditions:

Sample temperature, room temperature; powder container temperature, 150° C.; raising/conveying gas, He: powder raising rate, 3 L/min; powder conveying rate, 10 L/min; powder collision angle, 60°; nozzle opening shape, 5×0.3 mm; sample-to-nozzle distance, 5 mm; sample traveling speed, 200 mm/min: number of passes for deposition, 10.

The thus-obtained thin-film-coated samples of Examples 1B to 7B and Comparative Examples 1B to 6B were each examined for surface state over a range of about 200 μm×200 μm using a scanning electron microscope. From the image obtained, the diameters of voids and the number of the voids were determined using an image analysis software. As shown in Table 3, each sample which satisfied the number of voids of 100 or less was regarded as having been coated with an even film and indicated by “A”, and each sample which did not satisfy the requirement was regarded as having been coated with an uneven film and indicated by “B”. Moreover, especially preferred samples in which the average void diameter was 5 μm or less and the number of voids was less than 80 were indicated by “AA”. Consequently, “A” indicates that the number of voids was 80 to 100. The criteria for “AA”, “A” and “B” apply also in Tables 4 to 6, which will be given later.

TABLE 3

	Purity of alumina (wt %)	Si content (in terms of SiO_2) (ppm)	Na content (in terms of Na_2O) (ppm)	Density of sintered object (g/cm^3)	tanδ @10 to 20 MHz	State of voids in thin-film surface: Number of voids ≤ 100; Average diameter ≤ 5 μm
Example 1B	99.9	385	4.3	3.99	$<10^{-3}$	AA
Example 2B	99.9	363	18.9	4.00	$<10^{-3}$	AA
Example 3B	99.9	492	27.0	4.00	$<10^{-3}$	AA
Example 4B	99.9	600	13.0	3.99	$<10^{-3}$	AA
Example 5B	99.9	471	6.8	3.98	$<10^{-3}$	AA
Example 6B	99.9	321	1.1	4.00	$<10^{-3}$	AA
Example 7B	99.9	203	3.4	3.99	$<10^{-3}$	AA
Comparative Example 1B	99.9	407	41.2	3.95	$>10^{-3}$	B
Comparative Example 2B	99.9	54	32.4	3.99	$>10^{-3}$	AA
Comparative Example 3B	99.8	1305	6.3	3.94	$<10^{-3}$	B
Comparative Example 4B	99.8	1070	8.6	3.95	$<10^{-3}$	B
Comparative Example 5B	99.7	600	17.5	3.95	$>10^{-3}$	B
Comparative Example 6B	99.7	600	27.0	3.95	$>10^{-3}$	B

Table 3 shows that the samples of Examples 1B to 7B each had a density of 3.96 g/cm^3 or higher and a tan δ of less than 10^{-3}. It was thus ascertained that these samples were alumina-based sintered objects which were dense and had low-dielectric-loss characteristics.

In Comparative Example 1B, the alumina-based sintered object had a density of less than 3.96 g/cm^3 because of the high Na content, and had a tan δ exceeding 10^{-3}. This alumina-based sintered object was thus found to be poor in denseness and dielectric loss characteristics.

In Comparative Example 2B, the alumina-based sintered object had a tan δ exceeding 10^{-3} because of the low Si content and high Na content. Namely, this alumina-based sintered object was found to have poor dielectric loss characteristics.

In Comparative Example 3B, the alumina-based sintered object had a density of less than 3.96 g/cm^3 because of the high Si content. Namely, this alumina-based sintered object was found to have poor denseness.

In Comparative Example 4B, densification had been inhibited due to the too high Si content, and the alumina-based sintered object had a density of less than 3.96 g/cm^3. Namely, this alumina-based sintered object was found to have poor denseness, making it difficult to form a dense film on the surface of the alumina-based sintered object.

In Comparative Example 5B, the purity of the alumina was low and the alumina-based sintered object had a density of less than 3.96 g/cm^3 and a tan δ exceeding 10^3. Namely, this alumina-based sintered object was found to have poor denseness.

In Comparative Example 6B, the purity of the alumina was low and the alumina-based sintered object had a density of less than 3.96 g/cm^3 and a tan δ exceeding 10^{-3}. Namely, this alumina-based sintered object was found to have poor denseness.

The thin films formed on the samples of Examples 1B to 7B and Comparative Examples 2B each had a surface state in which the average diameter of voids was 5 μm or less and the number of the voids in a region of about 200 μm×200 μm was 100 or less (less than 80). It was found that an even film was able to be formed thereon.

Experiment 2B

Next, as shown in Table 4, PVA was added to an alumina powder having a purity of 99.8 wt % to 99.9 wt % and a median diameter of 2 μm or less to prepare a raw-material powder. This raw-material powder was stirred and mixed for 16 hours or longer to obtain a raw-material slurry. This raw-material slurry was granulated, and the granules were packed into a molding die and molded by CIP at a molding pressure of 1.5 tons.

Furthermore, the resultant molded object was subjected to a degreasing step in the air and then fired in a hydrogen atmosphere at 1,800° C. Thus, samples of Examples 9B, 118B, 13B, and 15B were produced. Meanwhile, the molded object was subjected to a degreasing step in the air and then fired in a hydrogen atmosphere at 1,900° C. Thus, samples of Examples 8B, 10B, 12B, and 14B were produced.

As shown in Table 4, SiO_2 and Na_2O were added so as to give sintered objects each having an Si content and an Na content within the ranges according to the present invention, and MgO was added so that the ratio of the content of Mg, in terms of MgO, to the Si content, in terms of SiO_2, was in the range of 0.9 to 4.1. Furthermore, the median diameter of the alumina powder was changed so that the sintered objects each had a density within the range according to the present invention.

The samples of Examples 8B to 15B were evaluated for density and dielectric loss tangent tan δ. The results thereof are shown in Table 4.

As Examples 8B, 9B, 12B, and 13B in Table 4 show, it was found that sintered objects having higher densities of 3.99 g/cm^3 and 4.00 g/cm^3 were able to be obtained.

Furthermore, as in Experiment 1B, a surface of each of the samples (alumina-based sintered object) of Examples 8B to

15B was mirror-polished so as to result in Ra<0.1 μm, and the polished surface was coated with an yttrium oxide material in a thickness of 1 μm by the aerosol deposition method. The state of the surface of the thin film was examined. The results thereof are shown in Table 4.

As Table 4 shows, the thin films formed on the samples of Examples 8B to 15B each had a surface state in which the average diameter of voids was 5 μm or less and the number of the voids in a region of about 200 μm×200 μm was 100 or less (less than 80). It was found that an even film was able to be formed thereon.

TABLE 4

	Purity of alumina (wt %)	Si content (in terms of SiO_2) (ppm)	Na content (in terms of Na_2O) (ppm)	Ratio of Mg content to Si content	Density of sintered object (g/cm^3)	tanδ @10 to 20 MHz	State of voids in thin-film surface: Number of voids ≤ 100; Average diameter ≤ 5 μm
Example 8B	99.8	600	13.0	4.0	3.99	$<10^{-3}$	AA
Example 9B	99.9	600	13.0	1.0	3.99	$<10^{-3}$	AA
Example 10B	99.9	600	13.0	0.9	3.98	$<10^{-3}$	AA
Example 11B	99.8	600	13.0	4.1	3.97	$<10^{-3}$	AA
Example 12B	99.9	170	13.0	4.0	4.00	$<10^{-3}$	AA
Example 13B	99.9	170	13.0	1.0	4.00	$<10^{-3}$	AA
Example 14B	99.9	170	13.0	0.9	3.98	$<10^{-3}$	AA
Example 15B	99.9	170	13.0	4.1	3.98	$<10^{-3}$	AA

Experiment 3B

Next, as shown in Table 5, PVA was added to an alumina powder having a purity of 99.8 wt % to 99.9 wt % and a median diameter of 2 μm or less to prepare a raw-material powder. This raw-material powder was stirred and mixed for 16 hours or longer to obtain a raw-material slurry. This raw-material slurry was granulated, and the granules were packed into a molding die and molded by CIP at a molding pressure of 1.5 tons.

Furthermore, the resultant molded object was subjected to a degreasing step in the air and then fired in a hydrogen atmosphere at 1,600° C. Thus, samples of Examples 16B, 17B, 18B, and 19B were produced.

The samples of Examples 16B, 17B, 18B, and 19B were evaluated for density, average Al_2O_3 crystal grain diameter, dielectric loss tangent tan δ, and three-point bending strength. The samples of Examples 8B, 10B, 12B, and 14B described above were also evaluated for average Al_2O_3 crystal grain diameter and three-point bending strength. The results thereof are shown in Table 5.

The average alumina crystal grain diameter was determined by mirror-polishing a cross-section of each sample, subjecting the polished cross-section to thermal etching, subsequently taking a photograph of the cross-section with a scanning electron microscope (SEM), and calculating the average crystal grain diameter by image analysis. The three-point bending strength was measured in accordance with JIS R 1601:2008. The purity of each sintered object was determined by ICP emission analysis.

As a result, it was found that sintered objects each having a density of 3.97 g/cm^3 or higher and a three-point bending strength of 250 MPa or higher were obtained as shown by Examples 8B and 16B and Examples 12B and 18B in Table 5.

Furthermore, as in Experiment 1B, a surface of each of the samples (alumina-based sintered object) of Examples 16B to 19B was mirror-polished so as to result in Ra<0.1 μm, and the polished surface was coated with an yttrium oxide material in a thickness of 1 μm by the aerosol deposition method. The state of the surface of the thin film was examined. The results thereof are shown in Table 5.

As Table 5 shows, the thin films formed on the samples of Examples 16B and 18B each had a surface state in which the average diameter of voids was 5 μm or less and the number of the voids in a region of about 200 μm×200 μm was 100 or less (less than 80). It was found that an even film was able to be formed thereon. Meanwhile, the thin films formed on the samples of Examples 17B and 19B each had a surface state in which the average diameter of voids was 5 μm or less and the number of the voids in a region of about 200 μm×200 μm was 80 to 100. It was found that an even film was able to be formed thereon.

TABLE 5

	Si content (in terms of SiO_2) (ppm)	Na content (in terms of Na_2O) (ppm)	Average crystal grain diameter (μm)	Density of sintered object (g/cm^3)	tanδ @10 to 20 MHz	Three-point bending strength (MPa)	State of voids in thin-film surface: Number of voids ≤ 100; Average diameter ≤ 5 μm
Example 16B	600	13.0	3.0	3.97	$<10^{-3}$	300	AA
Example 8B	600	13.0	40.0	3.99	$<10^{-3}$	270	AA
Example 17B	600	13.0	2.0	3.96	$<10^{-3}$	310	A
Example 10B	600	13.0	45.0	3.98	$<10^{-3}$	240	AA
Example 18B	170	13.0	3.0	3.97	$<10^{-3}$	315	AA
Example 12B	170	13.0	40.0	4.00	$<10^{-3}$	270	AA
Example 19B	170	13.0	2.0	3.96	$<10^{-3}$	320	A
Example 14B	170	13.0	45.0	3.98	$<10^{-3}$	245	AA

Experiment 4B

Next, PVA was added to an alumina powder having the same alumina purity and median diameter as in Example 18B to prepare a raw-material powder. This raw-material powder was stirred and mixed for 16 hours or longer to obtain a raw-material slurry. This raw-material slurry was granulated, and the granules were packed into a molding die and molded by CIP at a molding pressure of 1.5 tons.

Furthermore, the resultant molded object was subjected to a degreasing step in the air and then fired under the conditions shown in Table 6. Thus, samples of Examples 20B to 22B and Comparative Examples 7B to 10B were produced.

The samples of Examples 20B to 22B and Comparative Examples 7B to 10B were evaluated for density and dielectric loss tangent tan. The results thereof are shown in Table 6 together with the results obtained in Example 18B.

Furthermore, as in Experiment 1B, a surface of each of the samples (alumina-based sintered object) of Examples 20B to 22B and Comparative Examples 7B to 10B was mirror-polished so as to result in $Ra<0.1$ μm, and the polished surface was coated with an yttrium oxide material in a thickness of 1 μm by the aerosol deposition method. The state of the surface of the thin film was examined. The results thereof are shown in Table 6 together with the results obtained in Example 18B.

TABLE 6

	Firing atmosphere	Firing temperature (° C.)	Density of sintered object (g/cm^3)	tanδ @10 to 20 MHz	State of voids in thin-film surface: Number of voids ≤100; Average diameter ≤5 μm
Example 18B	hydrogen	1600	3.97	$<10^{-3}$	AA
Example 20B	hydrogen	1700	3.98	$<10^{-3}$	AA
Example 21B	hydrogen	1800	3.99	$<10^{-3}$	AA
Example 22B	hydrogen	1900	4.00	$<10^{-3}$	AA
Comparative Example 7B	hydrogen	1500	3.81	$<10^{-3}$	B
Comparative Example 8B	hydrogen	2000	4.00	$>10^{-3}$	AA
Comparative Example 9B	air	1600	3.91	$>10^{-3}$	B
Comparative Example 10B	air	1800	3.95	$>10^{-3}$	B

It was found from Examples 18B and 20B to 22B that the sintered objects obtained through firing in a hydrogen atmosphere at 1,600° C. to 1.900° C. each had a density of 3.96 g/cm^3 or higher and a dielectric loss tangent tan δ of less than 10^{-3}.

Furthermore, as Table 6 shows, the thin films formed on the samples of Examples 18B and 20B to 22B each had a surface state in which the average diameter of voids was 5 μm or less and the number of the voids in a region of about 200 μm×200 μm was 100 or less (less than 80). It was found that an even film was able to be formed thereon.

This application is based on a Japanese patent application filed on Oct. 5, 2017 (Application No. 2017-195292), a Japanese patent application filed on Sep. 25, 2018 (Application No. 2018-178652), and a Japanese patent application filed on Sep. 26, 2018 (Application No. 2018-180299), the contents thereof being incorporated herein by reference.

INDUSTRIAL APPLICABILITY

The present invention is usable as constituent members for use in, for example, production devices in the field of semiconductor production and the field of liquid-crystal display device production. For example, the present invention is suitable for use as members for use in plasma treatment devices, etchers for semiconductor/liquid-crystal display device production, CVD devices, etc. The alumina-based sintered objects according to the present invention may be used as such, or may be used as plasma-resistant members after a plasma-resistant corrosion-resistant film or corrosion-resistant layer is formed on a part or all of the surfaces of the alumina-based sintered objects as substrates.

REFERENCE SIGNS LIST

1 Al_2O_3 crystal grain
2 ZrO_2 crystal grain
3 Pore

The invention claimed is:

1. An alumina-based sintered object having an Al content, in terms of Al_2O_3 content, of 99.8 wt % or higher,

wherein the alumina-based sintered object has an Si content, in terms of SiO_2 content, of 321 ppm to 600 ppm and an Na content, in terms of Na_2O content, of more than zero and 27 ppm or less, and

wherein the alumina-based sintered object has a density of 3.96 g/cm^3 or higher and an average pore diameter of 5 μm or less.

2. The alumina-based sintered object according to claim **1**, containing Mg in an amount which, in terms of MgO content, is 1.0 to 4.0 times the Si content in terms of SiO_2 content.

3. The alumina-based sintered object according to claim **1**, containing Ca in an amount which, in terms of CaO content, is up to 3.0 times the Si content in terms of SiO_2 content.

4. The alumina-based sintered object according to claim **1**, wherein Al_2O_3 crystals contained in the alumina-based sintered object have an average crystal grain diameter of 3 μm to 40 μm.

5. The alumina-based sintered object according to claim **1**, wherein a corrosion-resistant film or a corrosion-resistant layer is formed on at least a part of the alumina-based sintered object.

6. The alumina-based sintered object according to claim **1**, wherein the alumina-based sintered object has a surface roughness Ra of less than 0.1 μm.

7. The alumina-based sintered object according to claim **1**, wherein the Na content, in terms of the Na_2O content, is in a range from 2 ppm to 27 ppm.

8. The alumina-based sintered object according to claim **1**, wherein the Na content, in terms of the Na_2O content, is in a range from 10 ppm to 27 ppm.

9. A process for producing the alumina-based sintered object according to claim **4**, the process comprising: granulating and molding a raw-material powder to obtain a molded object, and firing the molded object in a hydrogen atmosphere at 1,600° C. to 1,900° C.

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