

REPLACED SHEETS SG

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TITLE OF THE INVENTION

Aluminum Nitride Sintered Body and Method of
Preparing the Same

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to an aluminum nitride sintered body having a high breakdown voltage in response to high integration of a circuit board, and a method of preparing the same.

10 Description of the Background Art

An aluminum nitride sintered body having high thermal conductivity is applied to a radiating material such as a substrate for a semiconductor device or a circuit board, for example. At present, high integration of a circuit board is developed in order to cope with high speed processing of mass data and miniaturization of information processing equipment. A material for such a highly integrated circuit board must have an excellent radiating property in order to cope with heat generated by high integration, as well as a high breakdown voltage in order to cope with narrow spaces between circuit wires.

An aluminum nitride sintered body is watched with interest as an excellent radiating substrate material, due to high thermal conductivity. A conventional aluminum nitride sintered body has a breakdown voltage of about 10



to 20 kV/mm. Thus, awaited is an aluminum nitride sintered body, which is applicable to a highly integrated circuit board with a high breakdown voltage of at least 20 kV/mm.

5 SUMMARY OF THE INVENTION

An object of the present invention is to provide an aluminum nitride sintered body having a high breakdown voltage as a substrate material which is responsive to high integration of a circuit, and a method of preparing
10 the same.

In order to solve the aforementioned problem, the inventors have found that it is possible to remarkably improve the value of a breakdown voltage of an aluminum sintered body by forming and dispersing an oxy-nitride of
15 titanium and aluminum, such as aluminate nitride of titanium, for example, in a sintered body of aluminum nitride and partially including titanium as solid solute in aluminum nitride crystal grains. The present invention has been proposed on the basis of the following
20 recognition by the inventors:

The inventors have found that there is a relation shown in Fig. 1 between a breakdown voltage of an aluminum nitride sintered body and unpaired electron concentration measured from an electron spin resonance absorption
25 spectrum. It is understood from Fig. 1 that the value of



the breakdown voltage is slightly increased with increase of the unpaired electron concentration in the aluminum nitride sintered body. However, there has been obtained no aluminum nitride sintered body having a breakdown
5 voltage exceeding 20 kV/mm as a material for a circuit board which is responsive to high integration.

The inventors have energetically made deep study, to succeed in increasing unpaired electron concentration by preparing an aluminum nitride sintered body through the
10 following steps: In a first step, aluminum nitride raw material powder is nitrified in a nitrogen atmosphere at a temperature of 800 to 1400°C, to convert a surface composition of the raw material powder from aluminum oxide (Al_2O_3) to aluminum oxy-nitride ($\text{Al}_x\text{O}_y\text{N}_z$: $0 < x < 1$, $0 < y < 1$, $0 < z < 1$). In a second step, an oxy-nitride of
15 titanium (or titanium oxide covered with aluminum salt of fatty acid such as aluminum stearate or aluminum laurate) is added to the as-nitrified aluminum nitride raw material powder with a sintering assistant such as a rare earth
20 oxide such as Y_2O_3 or an alkaline earth oxide such as CaO , and the mixture is sintered. Through such two steps, the inventors have succeeded in extremely increasing unpaired electron concentration of the aluminum nitride sintered body, improving thermal conductivity and remarkably
25 improving the value of its breakdown voltage as compared



compared with the prior art.

The aluminum nitride sintered body according to the present invention comprises aluminum nitride crystal grains, in which titanium element is included as solid solute in a weight ratio of at least 50 ppm and not more than 1000 ppm.

Further, the aluminum nitride sintered body according to the present invention contains an oxy-nitride of titanium and aluminum compound in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , with unpaired electron concentration, being obtained from an absorption spectrum of electron spin resonance, of at least $1 \times 10^{13}/\text{g}$. More preferably, the oxy-nitride of titanium and aluminum compound exists in the aluminum nitride sintered body in the form of grains, which are not more than 800 nm in diameter. The aluminum nitride sintered body has thermal conductivity of at least 150 W/mK.

On the other hand, a method of preparing an aluminum nitride sintered body according to the present invention comprises the following steps:

- a) a step of preparing aluminum nitride powder;
- b) a step of nitriding the aluminum nitride powder in an atmosphere containing nitrogen at a temperature of at least 800°C and not more than 1400°C ;



c) a step of adding a sintering assistant, and an oxy-nitride of titanium, being in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , to the as-nitrided aluminum nitride powder, thereby obtaining mixed powder;

d) a step of preparing a compact from the mixed powder; and

e) a step of firing the compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.

A method of preparing an aluminum nitride sintered body according to another aspect of the present invention comprises the following steps:

a) a step of preparing aluminum nitride powder;

b) a step of ion-implanting titanium into the aluminum nitride powder, thereby making titanium exist in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm;

c) a step of adding a sintering assistant to the aluminum nitride powder containing titanium for obtaining mixed powder;

d) a step of preparing a compact from the mixed powder; and

e) a step of firing the compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride



sintered body.

Fig. 2 illustrates absorption spectra of electron spin resonance obtained from a conventional aluminum nitride sintered body and an aluminum nitride sintered body according to the present invention. It is understood from Fig. 2 that intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is remarkably increased as compared with that of the prior art. Referring to Fig. 2, the term "marker" indicates a standard material which exhibits a peak in a certain constant magnetic field. This standard material is measured with an unknown sample, in order to prevent a measurement error caused by an apparatus.

The reason why the intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is increased, which has not yet been clarified, can be considered as follows: First, aluminum oxy-nitride which is formed on the surface of the aluminum nitride raw material powder by surface treatment (for example, Reaction Formula: I) reacts with the oxy-nitride of titanium added thereto, to form an oxy-nitride (Ti-Al-O-N) of titanium and aluminum (for example, Reaction Formula: II). Since such an oxy-nitride of titanium and aluminum is instable under a high

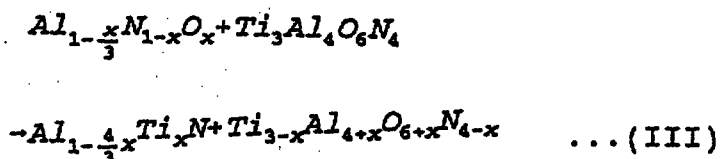
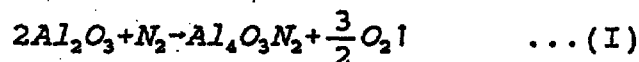


temperature exceeding 1000°C as compared with an oxide (Ti-Al-O) of titanium and aluminum, a replacement reaction takes place between oxygen (-bivalent) contained in the aluminum nitride crystal grains as an impurity and
5 nitrogen (-trivalent) in the aluminate nitride of titanium (oxy-nitride of titanium and aluminum) (for example, Reaction Formula: III). Thus, the oxy-nitride of titanium and aluminum may conceivably be stabilized due to approach to the composition of Ti-Al-O. At this time, a minus
10 valence number is increased in the aluminum nitride crystal while a plus valence number is increased in the oxy-nitride of titanium and aluminum, and hence the material enters an electrically unbalanced state. In order to compensate for such a state, however, replacement
15 takes place between aluminum (+trivalent) in the aluminum nitride crystal and titanium (+tetravalent) in the aluminate nitride of titanium, to recover electrically neutral conditions. As the result, titanium is conceivably included as solid solute in the aluminum
20 nitride crystal to increase unpaired electron concentration. Thus, the intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is remarkably increased.

25



Reaction Formula



The aluminum nitride sintered body preferably contains at least 0.1 percent by weight and not more than 5.0 percent by weight of the oxy-nitride of titanium and aluminum compound in terms of TiO_2 , including titanium which is contained as solid solute in the aluminum nitride crystal lattice. If the content of the oxy-nitride of titanium and aluminum compound is less than 0.1 percent by weight, unpaired electron concentration is not much increased and the value of the breakdown voltage of the as-obtained aluminum nitride sintered body remains substantially similar to that of the prior art. If the content of the oxy-nitride of titanium and aluminum compound exceeds 5.0 percent by weight, on the other hand, grains of this oxy-nitride of titanium and aluminum compound formed in the aluminum nitride sintered body disadvantageously exceed 800 nm in diameter, to inhibit



original high thermal conductivity of the aluminum nitride sintered body and reduce a heat radiation property of the sintered body for serving as a circuit board material.

Further, no titanium is included as solid solute in the aluminum nitride crystal grains if no surface treatment is carried out on the aluminum nitride raw material powder or a compound of titanium is not added in the form of an oxy-nitride. Thus, no increase can be expected in the breakdown voltage of the aluminum nitride sintered body.

In the inventive aluminum nitride sintered body, titanium must be included as solid solute in the aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm. If the amount of the as-dissolved titanium is less than 50 ppm, unpaired electron concentration decreases and thus breakdown voltage is not enough. If the amount of the solidly dissolved titanium exceeds 1000 ppm, on the other hand, the thermal conductivity deteriorates and thus the radiating property is not enough.

In the inventive aluminum nitride sintered body, further, the unpaired electron concentration obtained from an absorption spectrum of electron spin resonance is preferably at least $1 \times 10^{13}/g$, since it is possible to ensure a breakdown voltage of at least 20 kV/mm in this



case.

The aluminum nitride sintered body, which is obtained by forming and dispersing an oxy-nitride of titanium and aluminum compound in an aluminum nitride sintered body and partially including titanium as solid solute in aluminum crystal grains can be prepared by the following method:

Commercially available aluminum nitride raw material powder is nitrided in an atmosphere containing nitrogen within a temperature range of 800 to 1400°C. The temperature range is set at 800 to 1400°C since no nitriding reaction progresses on the surface of the aluminum nitride raw material powder if the temperature is less than 800°C, while the grain size of the powder is increased due to a solid phase reaction between aluminum nitride grains to suppress dispersion of an oxy-nitride of titanium which is added in a later step if the temperature exceeds 1400°C.

Then, 0.3 to 3.0 percent by weight of a sintering assistant such as Y_2O_3 or $CaCO_3$ in terms of CaO is added to the aluminum nitride raw material powder which is surface-treated in the aforementioned manner, with addition of 0.1 to 5.0 percent by weight of an oxy-nitride of titanium in terms of TiO_2 . At this time, the oxy-nitride of titanium as added preferably has a particle size of not more than 1 μm , more preferably not more than 0.1 μm , so that the same



is formed and dispersed in the aluminum nitride sintered body as an oxy-nitride of titanium and aluminum, and titanium is easily solidly dissolved in the aluminum nitride crystal grains. Then, about 1.0 to 3.0 percent by weight of a binder such as polyvinyl butyral is added to this aluminum nitride mixed powder, and mixed with the same in a ball mill for about 12 to 72 hours. Thereafter the powder is dried and granulated, so that the as-obtained powder is compacted under a pressure of 1.5 ton/cm², to obtain a pressed compact. At this time, the pressed compact is preferably 1.8 to 2.0 g/cm³ in density. Thereafter the pressed compact is debindered in a nitrogen atmosphere at a temperature of 600 to 800°C for about 2 to 3 hours. The as-treated pressed compact is fired in an atmosphere containing nitrogen at a temperature of 1500 to 1900°C for about 2 to 5 hours, to obtain an aluminum nitride sintered body.

In relation to the aforementioned method, it is also possible to obtain an aluminum nitride sintered body having a high breakdown voltage by ion-implanting titanium into the aluminum nitride raw material powder for making titanium exist in aluminum nitride crystal grains, and thereafter adding a sintering agent and a binder and carrying out mixing, granulation, press molding, debinding and firing under the same conditions as the



above.

The inventors have observed an aluminum nitride sintered body having unpaired electron concentration of at least $1 \times 10^{13}/\text{g}$ obtained from an absorption spectrum of electron spin resonance with an SEM (scanning electron microscope) or a TEM (transmission electron microscope). Consequently, it has been proved that crystal grains other than aluminum nitride crystal grains existed in the aluminum nitride sintered body. These grains were subjected to elementary analysis through an EDX (energy dispersive X-ray analysis) or AES (Auger electron spectroscopy) or SIMS (Secondary Ion Mass Spectroscopy), to prove that the grains formed in the aluminum nitride crystal grains included Ti, Al, N, O, Ca, Mg, Si and C, and were mainly composed of Ti, Al, O and N. Further, grains of a titanium compound formed in the aluminum nitride sintered body existed as dispersed grains of not more than $0.8 \mu\text{m}$ (800 nm) in mean grain size.

Fig. 3A typically shows TEM images of Ti-Al-O-N grain contained in the aluminum nitride crystal grain, and Fig. 3B shows results of EDX analysis of Ti in respective points A to E in Fig. 3A. As the results of the EDX analysis of the inside of the aluminum nitride crystal grain around titanium compound grain, it has been clarified that Ti was diffused from the titanium compound



grain of Ti-Al-O-N existing in AlN grains into aluminum nitride crystal grain, as shown in Fig. 3B. It has also been proved that the amount of Ti as solid solute in the aluminum nitride crystal lattice, which was varied with
5 sintering conditions, was within a range of 50 to 1000 ppm.

According to the present invention, as hereinabove described, titanium is included as solid solute in the aluminum nitride crystal lattice in a weight ratio of at
10 least 50 ppm and not more than 1000 ppm, whereby unpaired electron concentration of the aluminum nitride sintered body can be extremely increased thereby remarkably improving the breakdown voltage as compared with the prior art. Further, the inventive aluminum nitride sintered
15 body, which has unpaired electron concentration obtained from an electron spin resonance absorption spectrum of at least 1×10^{13} /g and contains at least 0.1 percent by weight and not more than 5.0 percent by weight of an oxy-nitride of titanium and aluminum in terms of TiO_2 , is
20 provided with a high breakdown voltage of at least 20 kV/mm. The inventive aluminum nitride sintered body having an excellent heat radiation property is sufficiently applicable to a circuit board material which is responsive to integration of the circuit.

25 According to the present invention, it is possible to



obtain an aluminum nitride sintered body which has a higher breakdown voltage as compared with the prior art, whereby highly integrated circuit design is enabled when the inventive sintered body is applied to a circuit board material. Thus, it is possible to contribute to high-speed processing of information following high integration of the circuit, as well as to miniaturization of information processing equipment.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a relation between unpaired electron concentration and a breakdown voltage in an aluminum nitride sintered body;

Fig. 2 is a graph showing absorption spectra of electron spin resonance obtained from a conventional aluminum nitride sintered body and an aluminum nitride sintered body according to the present invention;

Fig. 3A typically illustrates TEM images of Ti-Al-O-N grain contained in an aluminum nitride crystal grain;

Fig. 3B is a graph showing results of EDX analysis of Ti distribution in aluminum nitride crystal grain and Ti-



Al-O-N grain; and

Fig. 4 is a graph showing relations between unpaired electron concentration values and breakdown voltages in aluminum nitride sintered bodies according to comparative examples and Example of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

Aluminum nitride raw material powder shown at A in Table 1 was surface-treated in a nitrogen atmosphere at a temperature of 800°C, and thereafter 0.5 percent by weight of Y_2O_3 , serving as a sintering assistant was added to this material with addition of 0.2 percent by weight of an oxynitride of titanium ($Ti_3O_3N_2$) in terms of TiO_2 , so that the as-obtained powder was mixed in alcohol with a tumbling ball mill for 12 hours, as shown in Table 2. Thereafter 2 percent by weight of polyvinyl butyral was added as a binder to this mixed powder, which in turn was further sufficiently mixed and dried. The as-obtained powder was press-compacted under a pressure of at least 1.5 ton/cm². The as-obtained pressed compact was debindered at a temperature of 600°C for 2 hours, and then fired in a nitrogen atmosphere under a sintering temperature of 1800°C for 3 hours. The as-obtained aluminum nitride sintered body was subjected to measurement of density, a breakdown voltage, thermal conductivity, unpaired electron



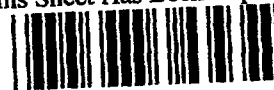
concentration, mechanical strength and an amount of titanium as solid solute in aluminum nitride crystal grains. The sintered body density was measured by an Archimedes' method, the thermal conductivity was measured by a laser flash method, the unpaired electron concentration was measured with an electron spin resonator, the mechanical strength was measured through JIS three-point bending strength, and the amount of titanium as solid solute was measured with EDX of TEM or AES, SIMS. Table 3 shows the results.

Examples 2 to 16

The aluminum nitride raw powder materials shown in Table 1 were treated at surface treatment temperatures shown in Table 2, and thereafter subjected to mixing with sintering assistants and press compacting, similarly to Example 1. The as-obtained pressed compacts were fired under sintering conditions shown in Table 2 by a method similar to that in Example 1, to prepare 15 types of aluminum nitride sintered bodies. Table 3 shows measurement values obtained as to these samples.

Example 17

Ti ions were implanted into the aluminum nitride raw material powder shown at A in Table 1, with energy of 4 MeV at about 10^{18} ions/cm². 0.5 percent by weight of Y₂O₃ was added to this powder and mixed in alcohol with a



tumbling ball mill for 12 hours. Thereafter an aluminum nitride sintered body was obtained in a similar manner to Example 1. Table 3 also shows measurement values obtained as to this sample.

5

Table 1

Raw Material Powder	A	B	C
Total Oxygen Content (wt.%)	1.3	0.9	1.2
Carbon Content in Raw Material Powder (ppm)	300	230	500
Fe Content in Raw Material Powder (ppm)	<10	<10	<10
Si Content in Raw Material Powder (ppm)	9	50	82
Specific Surface Area of Raw Material Powder (m ² /g)	3.5	2.8	2.7
Mean Particle Size of Raw Material Powder (μm)	1.3	1.1	1.0



Table 2

Example	Employed Raw Material Powder	Surface Treatment Temperature (°C)	Sintering Assistant (wt.%)	Ti Compound (wt.%, in terms of TiO_2)	Sintering Temperature (°C)	Sintering Time (hr.)
1	A	800	Y_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.2	1800	3
2	A	1000	Yb_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.5	1800	5
3	A	1200	CaO : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.5	1800	5
4	B	1200	Nd_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.5	1800	5
5	B	1300	Sm_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.5	1800	5
6	B	1000	Y_2O_3 : 0.5 CaO : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	3
7	B	1000	Yb_2O_3 : 0.5 CaO : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	5
8	C	1000	Y_2O_3 : 0.5 Nd_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	5
9	C	800	Yb_2O_3 : 0.5 Nd_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	5
10	C	1200	Nd_2O_3 : 0.5 CaO : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	3
11	C	1200	Y_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.5	1800	5
12	C	1400	Yb_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.5	1800	5
13	A	1300	Y_2O_3 : 1.5 Yb_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.5	1800	5
14	A	1200	Y_2O_3 : 1.5 Nd_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 2.0	1800	3
15	B	1200	Yb_2O_3 : 1.5 CaO : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 5.0	1500	5
16	B	1200	Yb_2O_3 : 1.5 Nd_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 3.0	1800	5
17	A		Y_2O_3 : 0.5	Ti Ion Implantation (10^{18} ions/cm ²)	1800	3

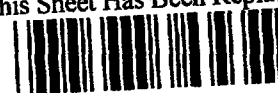


Table 3

Example	Content of Ti as Solid Solute (ppm)	Break Down Voltage (kV/mm)	Density (g/cm ³)	Mechanical Strength (kg/mm ²)	Unpaired Electron Concentration (/g)	Thermal Conductivity (W/m-K)
1	60	31	3.27	48	2.7×10^{13}	170
2	100	41	3.27	45	6.0×10^{13}	169
3	780	47	3.26	48	1.5×10^{14}	160
4	480	46	3.27	42	1.0×10^{14}	152
5	220	41	3.27	47	9.0×10^{13}	150
6	440	40	3.27	41	7.9×10^{13}	190
7	650	52	3.28	43	1.6×10^{14}	170
8	170	35	3.28	45	5.5×10^{13}	165
9	440	44	3.27	42	1.1×10^{14}	155
10	920	50	3.28	45	1.6×10^{14}	155
11	320	44	3.27	48	7.8×10^{13}	230
12	110	39	3.27	43	4.9×10^{13}	200
13	800	52	3.28	41	1.1×10^{14}	234
14	650	48	3.28	46	1.0×10^{14}	178
15	50	35	3.12	40	3.2×10^{13}	150
16	80	39	3.28	45	3.5×10^{13}	217
17	80	32	3.27	40	2.1×10^{13}	165

It is clearly understood from Table 3 that unpaired electron concentration obtained from an electron spin resonance absorption spectrum exceeds $1 \times 10^{13}/g$ when the amount of Ti as solid solute is at least 50 ppm and not more than 1000 ppm in a weight ratio, and the aluminum nitride sintered body exhibits a high breakdown voltage. It is also understood that an aluminum nitride sintered body which has unpaired electron concentration of at least $1 \times 10^{13}/g$ and contains a compound of titanium within a



range of 0.1 to 5.0 percent by weight in terms of TiO_2 has a high breakdown voltage.

As to the aluminum nitride sintered bodies obtained according to Examples 1, 2, 4 and 5, titanium compounds contained in the aluminum nitride crystal particles were examined through XRD (X-ray diffraction) or EDX. As the result, it was proved that the titanium compounds contained in the aluminum nitride sintered bodies were composed of Ti, Al, O and N, or Ti, Al, N, O, Ca, Mg and Si.

Comparative Example 1

Powder which was obtained by adding 1.0 percent by weight of Y_2O_3 , being in the form of fine particles for serving as a sintering assistant, to the aluminum nitride raw material powder shown at A in Table 1 was mixed in alcohol with a tumbling ball mill for 12 hours. Thereafter 2 percent by weight of polyvinyl butyral was added as a binder to this mixed powder, which in turn was further sufficiently mixed and dried. The as-obtained powder was press-compacted under a pressure of at least 1.5 ton/cm^2 . Thereafter the as-obtained pressed compact was debindered at a temperature of 600°C for 2 hours, and fired in a nitrogen atmosphere under a sintering temperature of 1800°C for 5 hours. The as-obtained aluminum nitride sintered body was subjected to



measurement of density, a breakdown voltage, thermal conductivity, unpaired electron concentration, mechanical strength, and an amount of titanium as solid solute in aluminum nitride crystal grains. The sintered body
5 density was measured by an Archimedes' method, the thermal conductivity was measured by a laser flash method, the unpaired electron concentration was measured with an electron spin resonator, the mechanical strength was measured through JIS three-point bending strength, and the
10 amount of titanium was measured with EDX of TEM or AES, SIMS. Table 5 shows the results.

Comparative Examples 2 to 11

The aluminum nitride raw powder materials shown in Table 1 were surface-treated under conditions shown in
15 Table 4, thereafter subjected to mixing, compacting and debinding in a method similar to that in comparative example 1, and then sintered under sintering conditions shown in Table 4. Table 5 shows measurement values obtained as to these samples of the aluminum nitride
20 sintered bodies.



Table 4

Comparative Example	Employed Raw Material Powder	Surface Treatment Temperature (°C)	Sintering Assistant (wt.%)	Ti Compound (wt.%, in terms of TiO_2)	Sintering Temperature (°C)	Sintering Time (hr.)
1	A	—	Y_2O_3 : 1.0	—	1800	5
2	A	1200	Y_2O_3 : 1.0	—	1800	5
3	A	1200	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 0.05	1800	5
4	A	1200	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 5.5	1800	5
5	A	1200	Y_2O_3 : 1.0	TiO_2 : 1.0	1800	5
6	A	—	Y_2O_3 : 1.0	TiO_2 : 1.0	1800	5
7	A	1200	Y_2O_3 : 1.0	TiN : 1.0	1800	5
8	A	—	Y_2O_3 : 1.0	TiN : 1.0	1800	5
9	A	—	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 1.0	1800	5
10	A	700	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 1.0	1800	5
11	A	1500	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 1.0	1800	5

Table 5

Comparative Example	Content of Ti as Solid Solute (ppm)	Break Down Voltage (kV/mm)	Density (g/cm^3)	Mechanical Strength (kg/mm^2)	Unpaired Electron Concentration (/g)	Thermal Conductivity (W/m·K)
1	< 10	15	3.27	32	4.0×10^{12}	137
2	< 10	18	3.26	35	9.1×10^{12}	140
3	< 10	15	3.27	30	9.6×10^{12}	149
4	< 30	17	3.28	36	6.0×10^{12}	139
5	< 30	18	3.28	34	7.5×10^{12}	142
6	< 30	14	3.28	38	9.5×10^{12}	138
7	< 30	15	3.27	33	8.1×10^{12}	141
8	< 30	18	3.27	31	7.6×10^{12}	142
9	< 30	15	3.27	34	6.5×10^{12}	140
10	< 30	12	3.27	31	5.9×10^{12}	137
11	< 30	14	3.27	36	4.1×10^{12}	139

From the results of Examples and comparative



examples, it is understood that an aluminum nitride sintered body which has an amount of Ti as solid solute within a range of 50 to 1000 ppm in a weight ratio or unpaired electron concentration of at least $1 \times 10^{13}/g$ and contains an oxy-nitride of titanium and aluminum within a range of 0.1 to 5.0 percent by weight in terms of TiO_2 has a breakdown voltage of at least 20 kV/mm.

Fig. 4 is a graph showing relations between breakdown voltages and unpaired electron concentration values obtained from the aforementioned results of Examples and comparative examples, in addition to the general relation between the breakdown voltage and the unpaired electron concentration shown in Fig. 1. It is understood from this figure that the values of the unpaired electron concentrations and the breakdown voltages of the inventive aluminum nitride sintered bodies are remarkably improved as compared with the conventional aluminum nitride sintered bodies. When the relations between the unpaired electron concentration values and the breakdown voltages are shown on a straight line to measure inclination of this straight line, it is understood that the prior art exhibits inclination of 1.0×10^{-14} while the inventive sintered body exhibits inclination of 1.3×10^{-13} , i.e., 13 times as compared with the prior art. In other words, it is possible to increase the unpaired electron



concentration by one digit as well as to increase the breakdown voltage to twice at the maximum according to the present invention.

5 From the linear relations between the unpaired electron concentration values and the breakdown voltages, it is also recognized possible to confirm the breakdown voltage of the sintered body by a nondestructive test through measurement of unpaired electron concentration.

10 Although the present invention has been described and illustrated in detail, it is clearly 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 the present invention being limited only by the terms of the appended claims.





WHAT IS CLAIMED IS:

1. An aluminum nitride sintered body comprising aluminum nitride crystal grains, titanium being included as solid solute in said aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than
5 1000 ppm.
2. An aluminum nitride sintered body in accordance with claim 1, containing an oxy-nitride of titanium and aluminum therein in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 ,
5 unpaired electron concentration in said sintered body obtained from an absorption spectrum of electron spin resonance being at least $1 \times 10^{13}/g$.
3. An aluminum nitride sintered body in accordance with claim 2, wherein said oxy-nitride exists in said aluminum nitride sintered body in the form of grains, said grains being not more than 800 nm in diameter.
4. An aluminum nitride sintered body in accordance with claim 3, having thermal conductivity of at least 150 W/mK.





5. A method of preparing an aluminum nitride sintered body, comprising:

a step of preparing aluminum nitride powder;

a step of nitriding said aluminum nitride powder in
5 an atmosphere containing nitrogen at a temperature of at
least 800°C and not more than 1400°C;

a step of adding a sintering assistant, and an oxy-
nitride of titanium, being in a weight ratio of at least
0.1 % and not more than 5.0 % in terms of TiO_2 , to said
10 nitrided aluminum nitride powder, thereby obtaining mixed
powder;

a step of preparing a compact from said mixed powder;
and

a step of firing said compact in an atmosphere
15 containing nitrogen, thereby preparing an aluminum nitride
sintered body.

6. A method of preparing an aluminum nitride sintered body, comprising:

a step of preparing aluminum nitride powder;

a step of ion-implanting titanium into said aluminum
5 nitride powder for making titanium exist in aluminum
nitride crystal lattice in a weight ratio of at least 50
ppm and not more than 1000 ppm;

a step of adding a sintering assistant to said





aluminum nitride powder containing titanium for obtaining
10 mixed powder;
a step of preparing a compact from said mixed powder;
and
a step of firing said compact in an atmosphere
containing nitrogen, thereby preparing an aluminum nitride
15 sintered body.



* C L H S *

ABSTRACT OF THE DISCLOSURE

Disclosed herein are an aluminum nitride sintered body having a high breakdown voltage for serving as a substrate material which is responsive to high integration of a circuit, and a method of preparing the same. The aluminum nitride sintered body contains titanium, which is included as solid solute in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm. Unpaired electron concentration in the sintered body obtained from an absorption spectrum of electron spin resonance is at least $1 \times 10^{13}/\text{g}$. At least 0.1 percent by weight and not more than 5.0 percent by weight of an oxy-nitride of titanium and aluminum exists in the aluminum nitride sintered body in terms of TiO_2 . The aluminum nitride sintered body has a breakdown voltage of 20 kV/mm. This aluminum nitride sintered body is obtained by nitriding aluminum nitride raw material powder in a nitrogen atmosphere at a temperature of 800 to 1400°C, adding an oxy-nitride of titanium thereto with a sintering assistant, and sintering the mixture.

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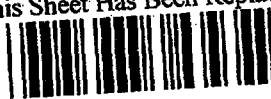
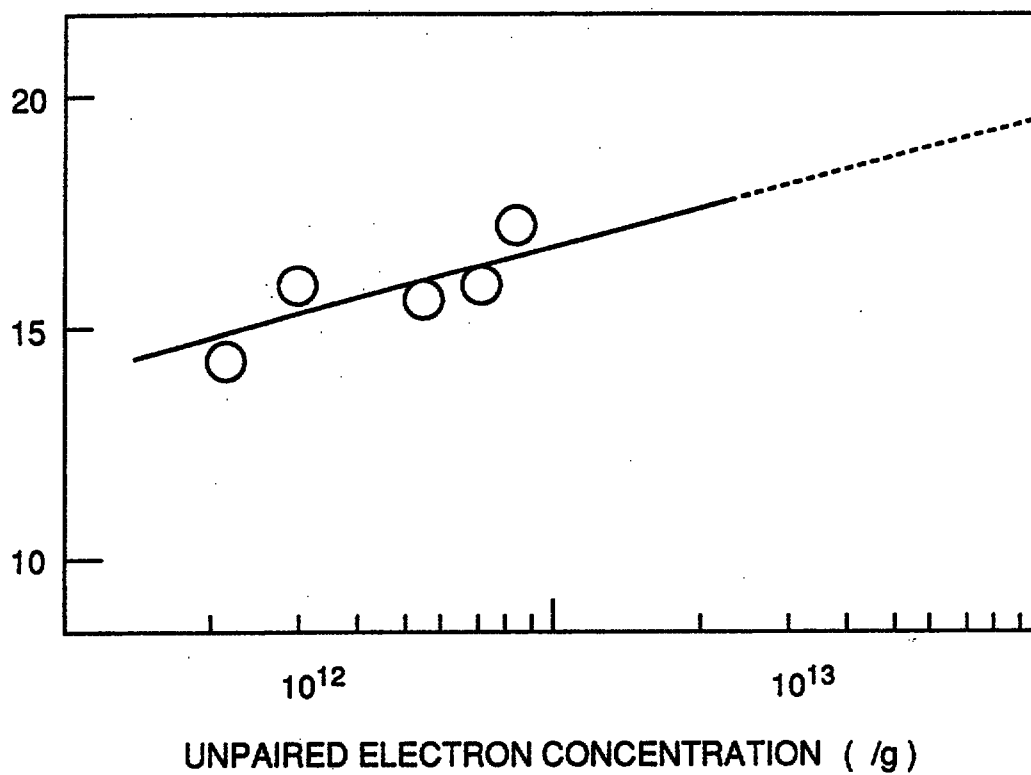


FIG. 1

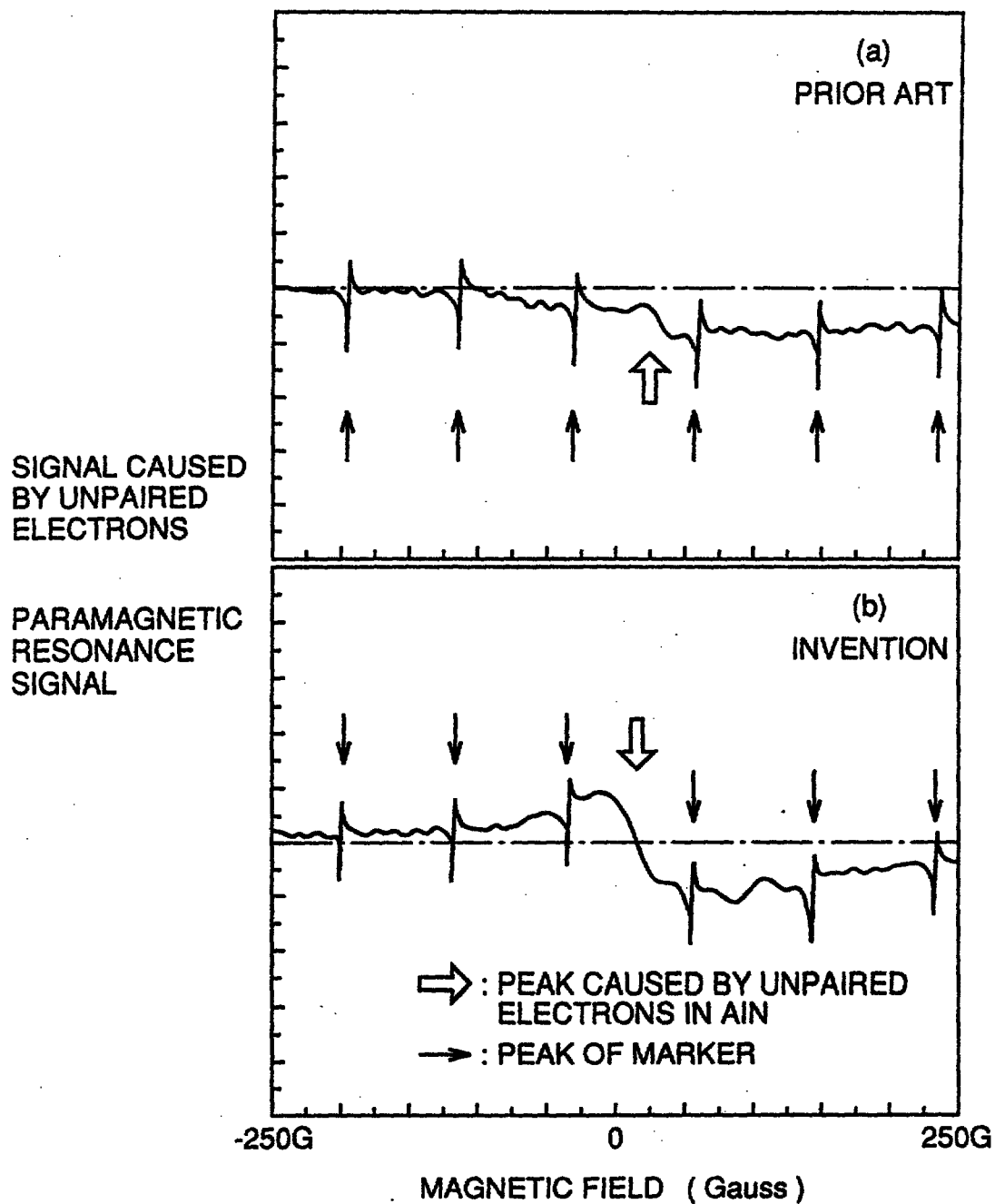
BREAKDOWN VOLTAGE
(KV/mm)



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FIG.2



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FIG.3A

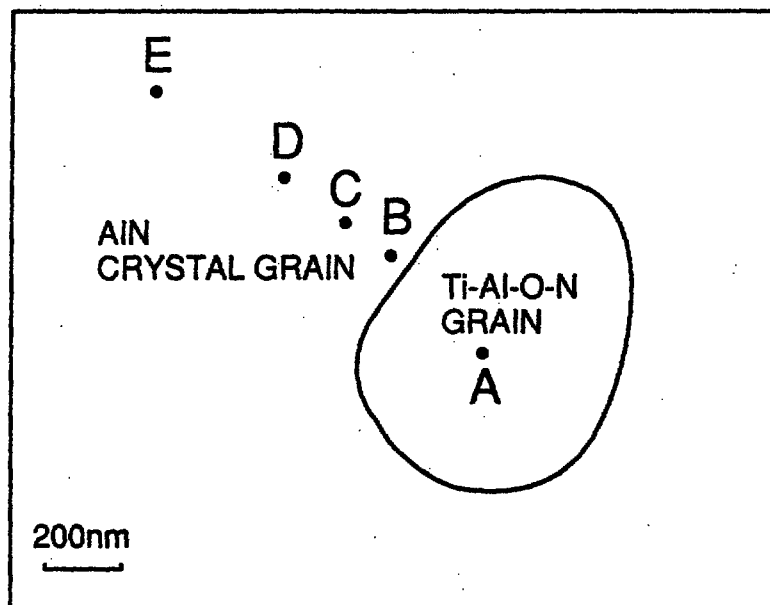
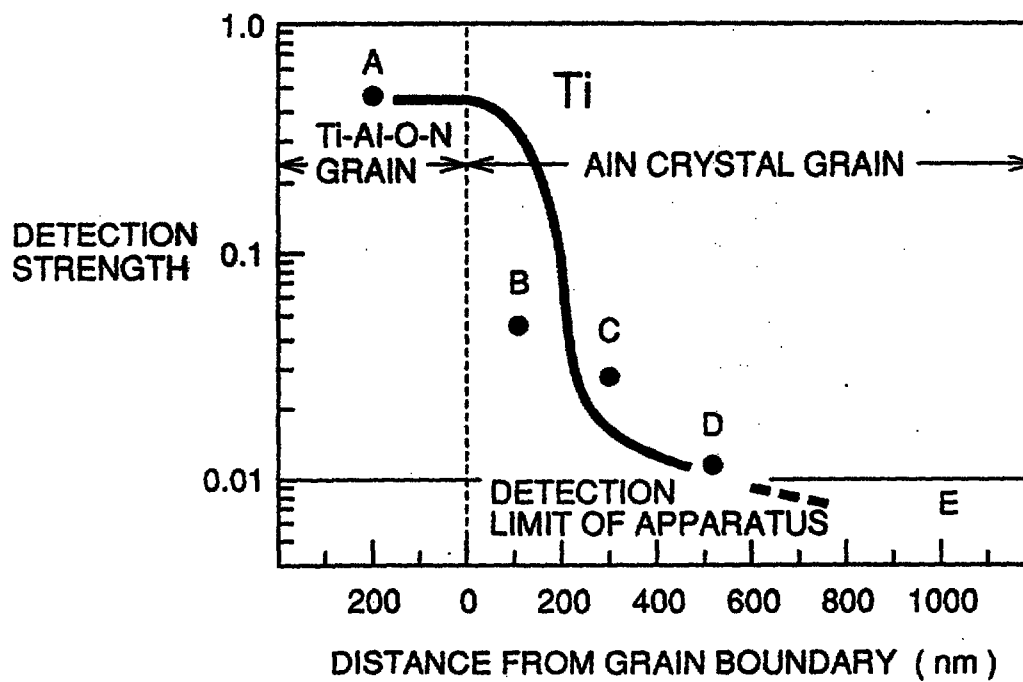


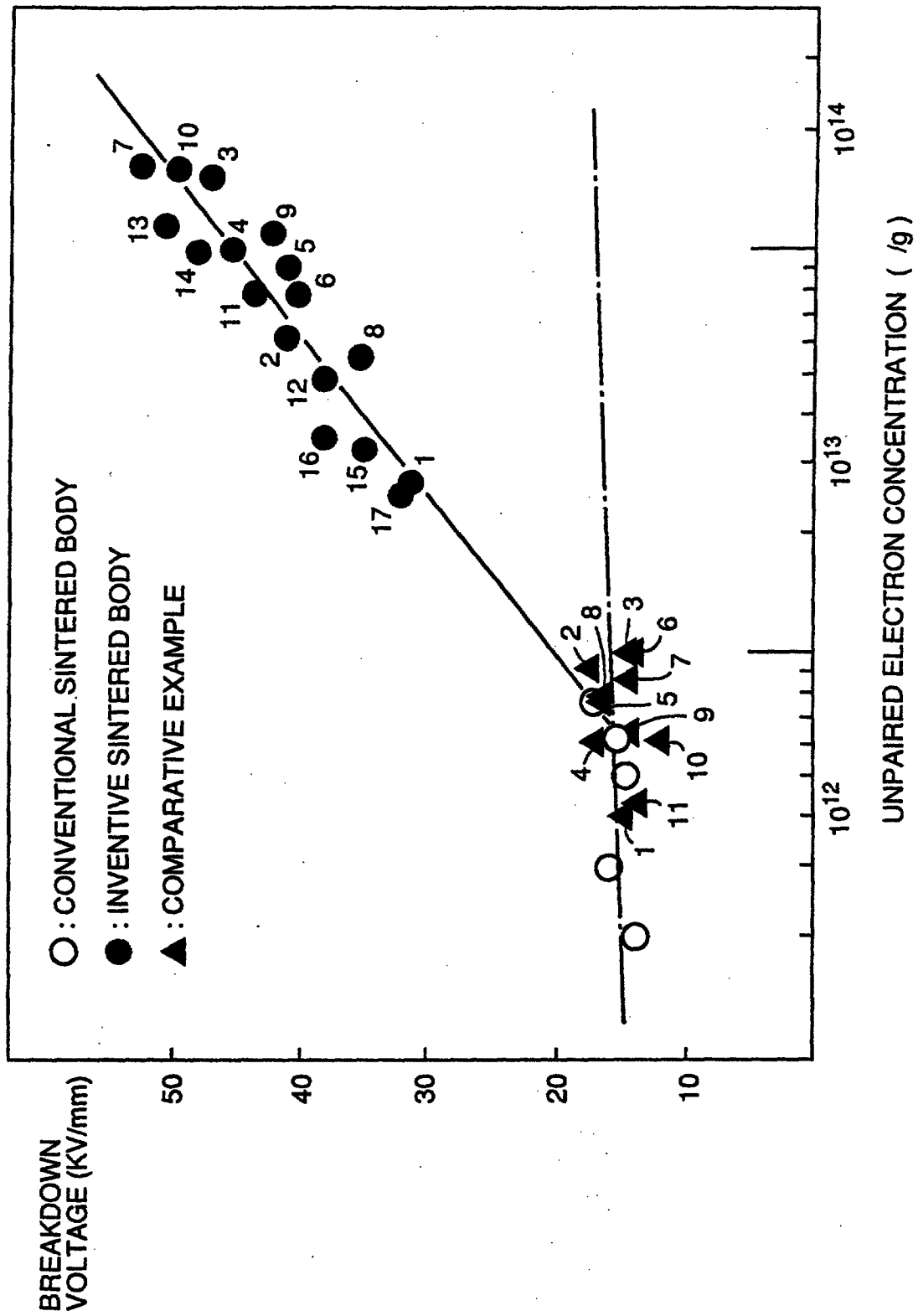
FIG.3B



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FIG.4



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TITLE OF THE INVENTION

Aluminum Nitride Sintered Body and Method of
Preparing the Same

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an aluminum nitride sintered body having a high breakdown voltage in response to high integration of a circuit board, and a method of preparing the same.

Description of the Background Art

An aluminum nitride sintered body having high thermal conductivity is applied to a radiating material such as a substrate for a semiconductor device or a circuit board, for example. At present, high integration of a circuit board is developed in order to cope with high speed processing of mass data and miniaturization of information processing equipment. A material for such a highly integrated circuit board must have an excellent radiating property in order to cope with heat generated by high integration, as well as a high breakdown voltage in order to cope with narrow spaces between circuit wires.

An aluminum nitride sintered body is watched with interest as an excellent radiating substrate material, due to high thermal conductivity. A conventional aluminum nitride sintered body has a breakdown voltage of about 10

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to 20 kV/mm. Thus, awaited is an aluminum nitride sintered body, which is applicable to a highly integrated circuit board with a high breakdown voltage of at least 20 kV/mm.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an aluminum nitride sintered body having a high breakdown voltage as a substrate material which is responsive to high integration of a circuit, and a method of preparing the same.

In order to solve the aforementioned problem, the inventors have found that it is possible to remarkably improve the value of a breakdown voltage of an aluminum sintered body by forming and dispersing an oxy-nitride of titanium and aluminum, such as aluminate nitride of titanium, for example, in a sintered body of aluminum nitride and partially including titanium as solid solute in aluminum nitride crystal grains. The present invention has been proposed on the basis of the following recognition by the inventors:

The inventors have found that there is a relation shown in Fig. 1 between a breakdown voltage of an aluminum nitride sintered body and unpaired electron concentration measured from an electron spin resonance absorption spectrum. It is understood from Fig. 1 that the value of

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the breakdown voltage is slightly increased with increase of the unpaired electron concentration in the aluminum nitride sintered body. However, there has been obtained no aluminum nitride sintered body having a breakdown voltage exceeding 20 kV/mm as a material for a circuit board which is responsive to high integration.

The inventors have energetically made deep study, to succeed in increasing unpaired electron concentration by preparing an aluminum nitride sintered body through the following steps: In a first step, aluminum nitride raw material powder is nitrided in a nitrogen atmosphere at a temperature of 800 to 1400°C, to convert a surface composition of the raw material powder from aluminum oxide (Al_2O_3) to aluminum oxy-nitride ($\text{Al}_x\text{O}_y\text{N}_z$: $0 < X < 1$, $0 < Y < 1$, $0 < Z < 1$). In a second step, an oxy-nitride of titanium (or titanium oxide covered with aluminum salt of fatty acid such as aluminum stearate or aluminum laurate) is added to the as-nitrided aluminum nitride raw material powder with a sintering assistant such as a rare earth oxide such as Y_2O_3 or an alkaline earth oxide such as CaO , and the mixture is sintered. Through such two steps, the inventors have succeeded in extremely increasing unpaired electron concentration of the aluminum nitride sintered body, improving thermal conductivity and remarkably improving the value of its breakdown voltage as compared

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compared with the prior art.

The aluminum nitride sintered body according to the present invention comprises aluminum nitride crystal grains, in which titanium element is included as solid solute in a weight ratio of at least 50 ppm and not more than 1000 ppm.

Further, the aluminum nitride sintered body according to the present invention contains an oxy-nitride of titanium and aluminum compound in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , with unpaired electron concentration, being obtained from an absorption spectrum of electron spin resonance, of at least $1 \times 10^{13}/\text{g}$. More preferably, the oxy-nitride of titanium and aluminum compound exists in the aluminum nitride sintered body in the form of grains, which are not more than 800 nm in diameter. The aluminum nitride sintered body has thermal conductivity of at least 150 W/mK.

On the other hand, a method of preparing an aluminum nitride sintered body according to the present invention comprises the following steps:

- a) a step of preparing aluminum nitride powder;
- b) a step of nitriding the aluminum nitride powder in an atmosphere containing nitrogen at a temperature of at least 800°C and not more than 1400°C;

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c) a step of adding a sintering assistant, and an oxy-nitride of titanium, being in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , to the as-nitrided aluminum nitride powder, thereby obtaining mixed powder;

d) a step of preparing a compact from the mixed powder; and

e) a step of firing the compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.

A method of preparing an aluminum nitride sintered body according to another aspect of the present invention comprises the following steps:

a) a step of preparing aluminum nitride powder;

b) a step of ion-implanting titanium into the aluminum nitride powder, thereby making titanium exist in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm;

c) a step of adding a sintering assistant to the aluminum nitride powder containing titanium for obtaining mixed powder;

d) a step of preparing a compact from the mixed powder; and

e) a step of firing the compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride

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sintered body.

Fig. 2 illustrates absorption spectra of electron spin resonance obtained from a conventional aluminum nitride sintered body and an aluminum nitride sintered body according to the present invention. It is understood from Fig. 2 that intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is remarkably increased as compared with that of the prior art. Referring to Fig. 2, the term "marker" indicates a standard material which exhibits a peak in a certain constant magnetic field. This standard material is measured with an unknown sample, in order to prevent a measurement error caused by an apparatus.

The reason why the intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is increased, which has not yet been clarified, can be considered as follows: First, aluminum oxy-nitride which is formed on the surface of the aluminum nitride raw material powder by surface treatment (for example, Reaction Formula: I) reacts with the oxy-nitride of titanium added thereto, to form an oxy-nitride (Ti-Al-O-N) of titanium and aluminum (for example, Reaction Formula: II). Since such an oxy-nitride of titanium and aluminum is instable under a high

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temperature exceeding 1000°C as compared with an oxide (Ti-Al-O) of titanium and aluminum, a replacement reaction takes place between oxygen (-bivalent) contained in the aluminum nitride crystal grains as an impurity and nitrogen (-trivalent) in the aluminate nitride of titanium (oxy-nitride of titanium and aluminum) (for example, Reaction Formula: III). Thus, the oxy-nitride of titanium and aluminum may conceivably be stabilized due to approach to the composition of Ti-Al-O. At this time, a minus valence number is increased in the aluminum nitride crystal while a plus valence number is increased in the oxy-nitride of titanium and aluminum, and hence the material enters an electrically unbalanced state. In order to compensate for such a state, however, replacement takes place between aluminum (+trivalent) in the aluminum nitride crystal and titanium (+tetravalent) in the aluminate nitride of titanium, to recover electrically neutral conditions. As the result, titanium is conceivably included as solid solute in the aluminum nitride crystal to increase unpaired electron concentration. Thus, the intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is remarkably increased.

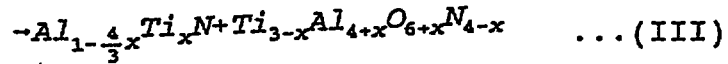
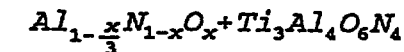
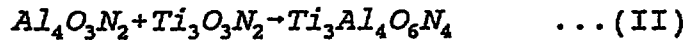
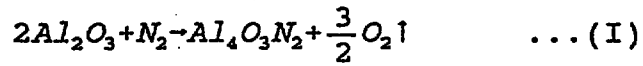
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Reaction Formula



The aluminum nitride sintered body preferably contains at least 0.1 percent by weight and not more than 5.0 percent by weight of the oxy-nitride of titanium and aluminum compound in terms of TiO_2 , including titanium which is contained as solid solute in the aluminum nitride crystal lattice. If the content of the oxy-nitride of titanium and aluminum compound is less than 0.1 percent by weight, unpaired electron concentration is not much increased and the value of the breakdown voltage of the as-obtained aluminum nitride sintered body remains substantially similar to that of the prior art. If the content of the oxy-nitride of titanium and aluminum compound exceeds 5.0 percent by weight, on the other hand, grains of this oxy-nitride of titanium and aluminum compound formed in the aluminum nitride sintered body disadvantageously exceed 800 nm in diameter, to inhibit

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original high thermal conductivity of the aluminum nitride sintered body and reduce a heat radiation property of the sintered body for serving as a circuit board material.

Further, no titanium is included as solid solute in the aluminum nitride crystal grains if no surface treatment is carried out on the aluminum nitride raw material powder or a compound of titanium is not added in the form of an oxy-nitride. Thus, no increase can be expected in the breakdown voltage of the aluminum nitride sintered body.

In the inventive aluminum nitride sintered body, titanium must be included as solid solute in the aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm. If the amount of the as-dissolved titanium is less than 50 ppm, unpaired electron concentration decreases and thus breakdown voltage is not enough. If the amount of the solidly dissolved titanium exceeds 1000 ppm, on the other hand, the thermal conductivity deteriorates and thus the radiating property is not enough.

In the inventive aluminum nitride sintered body, further, the unpaired electron concentration obtained from an absorption spectrum of electron spin resonance is preferably at least $1 \times 10^{13}/g$, since it is possible to ensure a breakdown voltage of at least 20 kV/mm in this

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case.

The aluminum nitride sintered body, which is obtained by forming and dispersing an oxy-nitride of titanium and aluminum compound in an aluminum nitride sintered body and partially including titanium as solid solute in aluminum crystal grains can be prepared by the following method:

Commercially available aluminum nitride raw material powder is nitrided in an atmosphere containing nitrogen within a temperature range of 800 to 1400°C. The temperature range is set at 800 to 1400°C since no nitriding reaction progresses on the surface of the aluminum nitride raw material powder if the temperature is less than 800°C, while the grain size of the powder is increased due to a solid phase reaction between aluminum nitride grains to suppress dispersion of an oxy-nitride of titanium which is added in a later step if the temperature exceeds 1400°C.

Then, 0.3 to 3.0 percent by weight of a sintering assistant such as Y_2O_3 or $CaCO_3$ in terms of CaO is added to the aluminum nitride raw material powder which is surface-treated in the aforementioned manner, with addition of 0.1 to 5.0 percent by weight of an oxy-nitride of titanium in terms of TiO_2 . At this time, the oxy-nitride of titanium as added preferably has a particle size of not more than 1 μm , more preferably not more than 0.1 μm , so that the same

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is formed and dispersed in the aluminum nitride sintered body as an oxy-nitride of titanium and aluminum, and titanium is easily solidly dissolved in the aluminum nitride crystal grains. Then, about 1.0 to 3.0 percent by weight of a binder such as polyvinyl butyral is added to this aluminum nitride mixed powder, and mixed with the same in a ball mill for about 12 to 72 hours. Thereafter the powder is dried and granulated, so that the as-obtained powder is compacted under a pressure of 1.5 ton/cm², to obtain a pressed compact. At this time, the pressed compact is preferably 1.8 to 2.0 g/cm³ in density. Thereafter the pressed compact is debindered in a nitrogen atmosphere at a temperature of 600 to 800°C for about 2 to 3 hours. The as-treated pressed compact is fired in an atmosphere containing nitrogen at a temperature of 1500 to 1900°C for about 2 to 5 hours, to obtain an aluminum nitride sintered body.

In relation to the aforementioned method, it is also possible to obtain an aluminum nitride sintered body having a high breakdown voltage by ion-implanting titanium into the aluminum nitride raw material powder for making titanium exist in aluminum nitride crystal grains, and thereafter adding a sintering agent and a binder and carrying out mixing, granulation, press molding, debinding and firing under the same conditions as the

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above.

The inventors have observed an aluminum nitride sintered body having unpaired electron concentration of at least $1 \times 10^{13}/\text{g}$ obtained from an absorption spectrum of electron spin resonance with an SEM (scanning electron microscope) or a TEM (transmission electron microscope). Consequently, it has been proved that crystal grains other than aluminum nitride crystal grains existed in the aluminum nitride sintered body. These grains were subjected to elementary analysis through an EDX (energy dispersive X-ray analysis) or AES (Auger electron spectroscopy) or SIMS (Secondary Ion Mass Spectroscopy), to prove that the grains formed in the aluminum nitride crystal grains included Ti, Al, N, O, Ca, Mg, Si and C, and were mainly composed of Ti, Al, O and N. Further, grains of a titanium compound formed in the aluminum nitride sintered body existed as dispersed grains of not more than $0.8 \mu\text{m}$ (800 nm) in mean grain size.

Fig. 3A typically shows TEM images of Ti-Al-O-N grain contained in the aluminum nitride crystal grain, and Fig. 3B shows results of EDX analysis of Ti in respective points A to E in Fig. 3A. As the results of the EDX analysis of the inside of the aluminum nitride crystal grain around titanium compound grain, it has been clarified that Ti was diffused from the titanium compound

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grain of Ti-Al-O-N existing in AlN grains into aluminum nitride crystal grain, as shown in Fig. 3B. It has also been proved that the amount of Ti as solid solute in the aluminum nitride crystal lattice, which was varied with sintering conditions, was within a range of 50 to 1000 ppm.

According to the present invention, as hereinabove described, titanium is included as solid solute in the aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm, whereby unpaired electron concentration of the aluminum nitride sintered body can be extremely increased thereby remarkably improving the breakdown voltage as compared with the prior art. Further, the inventive aluminum nitride sintered body, which has unpaired electron concentration obtained from an electron spin resonance absorption spectrum of at least $1 \times 10^{13}/g$ and contains at least 0.1 percent by weight and not more than 5.0 percent by weight of an oxynitride of titanium and aluminum in terms of TiO_2 , is provided with a high breakdown voltage of at least 20 kV/mm. The inventive aluminum nitride sintered body having an excellent heat radiation property is sufficiently applicable to a circuit board material which is responsive to integration of the circuit.

According to the present invention, it is possible to

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obtain an aluminum nitride sintered body which has a higher breakdown voltage as compared with the prior art, whereby highly integrated circuit design is enabled when the inventive sintered body is applied to a circuit board material. Thus, it is possible to contribute to high-speed processing of information following high integration of the circuit, as well as to miniaturization of information processing equipment.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a relation between unpaired electron concentration and a breakdown voltage in an aluminum nitride sintered body;

Fig. 2 is a graph showing absorption spectra of electron spin resonance obtained from a conventional aluminum nitride sintered body and an aluminum nitride sintered body according to the present invention;

Fig. 3A typically illustrates TEM images of Ti-Al-O-N grain contained in an aluminum nitride crystal grain;

Fig. 3B is a graph showing results of EDX analysis of Ti distribution in aluminum nitride crystal grain and Ti-

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Al-O-N grain; and

Fig. 4 is a graph showing relations between unpaired electron concentration values and breakdown voltages in aluminum nitride sintered bodies according to comparative examples and Example of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

Aluminum nitride raw material powder shown at A in Table 1 was surface-treated in a nitrogen atmosphere at a temperature of 800°C, and thereafter 0.5 percent by weight of Y_2O_3 serving as a sintering assistant was added to this material with addition of 0.2 percent by weight of an oxynitride of titanium ($Ti_3O_3N_2$) in terms of TiO_2 , so that the as-obtained powder was mixed in alcohol with a tumbling ball mill for 12 hours, as shown in Table 2. Thereafter 2 percent by weight of polyvinyl butyral was added as a binder to this mixed powder, which in turn was further sufficiently mixed and dried. The as-obtained powder was press-compacted under a pressure of at least 1.5 ton/cm². The as-obtained pressed compact was debindered at a temperature of 600°C for 2 hours, and then fired in a nitrogen atmosphere under a sintering temperature of 1800°C for 3 hours. The as-obtained aluminum nitride sintered body was subjected to measurement of density, a breakdown voltage, thermal conductivity, unpaired electron

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concentration, mechanical strength and an amount of titanium as solid solute in aluminum nitride crystal grains. The sintered body density was measured by an Archimedes' method, the thermal conductivity was measured by a laser flash method, the unpaired electron concentration was measured with an electron spin resonator, the mechanical strength was measured through JIS three-point bending strength, and the amount of titanium as solid solute was measured with EDX of TEM or AES, SIMS. Table 3 shows the results.

Examples 2 to 16

The aluminum nitride raw powder materials shown in Table 1 were treated at surface treatment temperatures shown in Table 2, and thereafter subjected to mixing with sintering assistants and press compacting, similarly to Example 1. The as-obtained pressed compacts were fired under sintering conditions shown in Table 2 by a method similar to that in Example 1, to prepare 15 types of aluminum nitride sintered bodies. Table 3 shows measurement values obtained as to these samples.

Example 17

Ti ions were implanted into the aluminum nitride raw material powder shown at A in Table 1, with energy of 4 MeV at about 10^{18} ions/cm². 0.5 percent by weight of Y₂O₃ was added to this powder and mixed in alcohol with a

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tumbling ball mill for 12 hours. Thereafter an aluminum nitride sintered body was obtained in a similar manner to Example 1. Table 3 also shows measurement values obtained as to this sample.

Table 1

Raw Material Powder	A	B	C
Total Oxygen Content (wt.%)	1.3	0.9	1.2
Carbon Content in Raw Material Powder (ppm)	300	230	500
Fe Content in Raw Material Powder (ppm)	<10	<10	<10
Si Content in Raw Material Powder (ppm)	9	50	82
Specific Surface Area of Raw Material Powder (m ² /g)	3.5	2.8	2.7
Mean Particle Size of Raw Material Powder (μm)	1.3	1.1	1.0

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Table 2

Example	Employed Raw Material Powder	Surface Treatment Temperature (°C)	Sintering Assistant (wt.%)	Ti Compound (wt.%, in terms of TiO ₂)	Sintering Temperature (°C)	Sintering Time (hr.)
1	A	800	Y ₂ O ₃ : 0.5	Ti ₃ O ₃ N ₂ : 0.2	1800	3
2	A	1000	Yb ₂ O ₃ : 0.5	Ti ₃ O ₃ N ₂ : 0.5	1800	5
3	A	1200	CaO: 0.5	Ti ₃ O ₃ N ₂ : 0.5	1800	5
4	B	1200	Nd ₂ O ₃ : 0.5	Ti ₃ O ₃ N ₂ : 0.5	1800	5
5	B	1300	Sm ₂ O ₃ : 0.5	Ti ₃ O ₃ N ₂ : 0.5	1800	5
6	B	1000	Y ₂ O ₃ : 0.5 CaO: 0.5	Ti ₃ O ₃ N ₂ : 1.0	1650	3
7	B	1000	Yb ₂ O ₃ : 0.5 CaO: 0.5	Ti ₃ O ₃ N ₂ : 1.0	1650	5
8	C	1000	Y ₂ O ₃ : 0.5 Nd ₂ O ₃ : 0.5	Ti ₃ O ₃ N ₂ : 1.0	1650	5
9	C	800	Yb ₂ O ₃ : 0.5 Nd ₂ O ₃ : 0.5	Ti ₃ O ₃ N ₂ : 1.0	1650	5
10	C	1200	Nd ₂ O ₃ : 0.5 CaO: 0.5	Ti ₃ O ₃ N ₂ : 1.0	1650	3
11	C	1200	Y ₂ O ₃ : 1.5	Ti ₃ O ₃ N ₂ : 1.5	1800	5
12	C	1400	Yb ₂ O ₃ : 1.5	Ti ₃ O ₃ N ₂ : 1.5	1800	5
13	A	1300	Y ₂ O ₃ : 1.5 Yb ₂ O ₃ : 1.5	Ti ₃ O ₃ N ₂ : 1.5	1800	5
14	A	1200	Y ₂ O ₃ : 1.5 Nd ₂ O ₃ : 1.5	Ti ₃ O ₃ N ₂ : 2.0	1800	3
15	B	1200	Yb ₂ O ₃ : 1.5 CaO: 1.5	Ti ₃ O ₃ N ₂ : 5.0	1500	5
16	B	1200	Yb ₂ O ₃ : 1.5 Nd ₂ O ₃ : 1.5	Ti ₃ O ₃ N ₂ : 3.0	1800	5
17	A		Y ₂ O ₃ : 0.5	Ti Ion Implantation (10 ¹⁸ ions/cm ²)	1800	3

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Table 3

Example	Content of Ti as Solid Solute (ppm)	Break Down Voltage (kV/mm)	Density (g/cm ³)	Mechanical Strength (kg/mm ²)	Unpaired Electron Concentration (/g)	Thermal Conductivity (W/m·K)
1	60	31	3.27	48	2.7×10^{13}	170
2	100	41	3.27	45	6.0×10^{13}	169
3	780	47	3.26	48	1.5×10^{14}	160
4	480	46	3.27	42	1.0×10^{14}	152
5	220	41	3.27	47	9.0×10^{13}	150
6	440	40	3.27	41	7.9×10^{13}	190
7	650	52	3.28	43	1.6×10^{14}	170
8	170	35	3.28	45	5.5×10^{13}	165
9	440	44	3.27	42	1.1×10^{14}	155
10	920	50	3.28	45	1.6×10^{14}	155
11	320	44	3.27	48	7.8×10^{13}	230
12	110	39	3.27	43	4.9×10^{13}	200
13	800	52	3.28	41	1.1×10^{14}	234
14	650	48	3.28	46	1.0×10^{14}	178
15	50	35	3.12	40	3.2×10^{13}	150
16	80	39	3.28	45	3.5×10^{13}	217
17	80	32	3.27	40	2.1×10^{13}	165

It is clearly understood from Table 3 that unpaired electron concentration obtained from an electron spin resonance absorption spectrum exceeds $1 \times 10^{13}/g$ when the amount of Ti as solid solute is at least 50 ppm and not more than 1000 ppm in a weight ratio, and the aluminum nitride sintered body exhibits a high breakdown voltage. It is also understood that an aluminum nitride sintered body which has unpaired electron concentration of at least $1 \times 10^{13}/g$ and contains a compound of titanium within a

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range of 0.1 to 5.0 percent by weight in terms of TiO_2 , has a high breakdown voltage.

As to the aluminum nitride sintered bodies obtained according to Examples 1, 2, 4 and 5, titanium compounds contained in the aluminum nitride crystal particles were examined through XRD (X-ray diffraction) or EDX. As the result, it was proved that the titanium compounds contained in the aluminum nitride sintered bodies were composed of Ti, Al, O and N, or Ti, Al, N, O, Ca, Mg and Si.

Comparative Example 1

Powder which was obtained by adding 1.0 percent by weight of Y_2O_3 , being in the form of fine particles for serving as a sintering assistant, to the aluminum nitride raw material powder shown at A in Table 1 was mixed in alcohol with a tumbling ball mill for 12 hours. Thereafter 2 percent by weight of polyvinyl butyral was added as a binder to this mixed powder, which in turn was further sufficiently mixed and dried. The as-obtained powder was press-compacted under a pressure of at least 1.5 ton/cm^2 . Thereafter the as-obtained pressed compact was debindered at a temperature of 600°C for 2 hours, and fired in a nitrogen atmosphere under a sintering temperature of 1800°C for 5 hours. The as-obtained aluminum nitride sintered body was subjected to

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measurement of density, a breakdown voltage, thermal conductivity, unpaired electron concentration, mechanical strength, and an amount of titanium as solid solute in aluminum nitride crystal grains. The sintered body density was measured by an Archimedes' method, the thermal conductivity was measured by a laser flash method, the unpaired electron concentration was measured with an electron spin resonator, the mechanical strength was measured through JIS three-point bending strength, and the amount of titanium was measured with EDX of TEM or AES, SIMS. Table 5 shows the results.

Comparative Examples 2 to 11

The aluminum nitride raw powder materials shown in Table 1 were surface-treated under conditions shown in Table 4, thereafter subjected to mixing, compacting and debinding in a method similar to that in comparative example 1, and then sintered under sintering conditions shown in Table 4. Table 5 shows measurement values obtained as to these samples of the aluminum nitride sintered bodies.

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Table 4

Comparative Example	Employed Raw Material Powder	Surface Treatment Temperature (°C)	Sintering Assistant (wt.%)	Ti Compound (wt.%, in terms of TiO ₂)	Sintering Temperature (°C)	Sintering Time (hr.)
1	A	—	Y ₂ O ₃ : 1.0	—	1800	5
2	A	1200	Y ₂ O ₃ : 1.0	—	1800	5
3	A	1200	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 0.05	1800	5
4	A	1200	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 5.5	1800	5
5	A	1200	Y ₂ O ₃ : 1.0	TiO ₂ : 1.0	1800	5
6	A	—	Y ₂ O ₃ : 1.0	TiO ₂ : 1.0	1800	5
7	A	1200	Y ₂ O ₃ : 1.0	TiN: 1.0	1800	5
8	A	—	Y ₂ O ₃ : 1.0	TiN: 1.0	1800	5
9	A	—	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 1.0	1800	5
10	A	700	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 1.0	1800	5
11	A	1500	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 1.0	1800	5

Table 5

Comparative Example	Content of Ti as Solid Solute (ppm)	Break Down Voltage (kV/mm)	Density (g/cm ³)	Mechanical Strength (kg/mm ²)	Unpaired Electron Concentration (/g)	Thermal Conductivity (W/m·K)
1	< 10	15	3.27	32	4.0 × 10 ¹²	137
2	< 10	18	3.26	35	9.1 × 10 ¹²	140
3	< 10	15	3.27	30	9.6 × 10 ¹²	149
4	< 30	17	3.28	36	6.0 × 10 ¹²	139
5	< 30	18	3.28	34	7.5 × 10 ¹²	142
6	< 30	14	3.28	38	9.5 × 10 ¹²	138
7	< 30	15	3.27	33	8.1 × 10 ¹²	141
8	< 30	18	3.27	31	7.6 × 10 ¹²	142
9	< 30	15	3.27	34	6.5 × 10 ¹²	140
10	< 30	12	3.27	31	5.9 × 10 ¹²	137
11	< 30	14	3.27	36	4.1 × 10 ¹²	139

From the results of Examples and comparative

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examples, it is understood that an aluminum nitride sintered body which has an amount of Ti as solid solute within a range of 50 to 1000 ppm in a weight ratio or unpaired electron concentration of at least $1 \times 10^{13}/\text{g}$ and contains an oxy-nitride of titanium and aluminum within a range of 0.1 to 5.0 percent by weight in terms of TiO_2 has a breakdown voltage of at least 20 kV/mm.

Fig. 4 is a graph showing relations between breakdown voltages and unpaired electron concentration values obtained from the aforementioned results of Examples and comparative examples, in addition to the general relation between the breakdown voltage and the unpaired electron concentration shown in Fig. 1. It is understood from this figure that the values of the unpaired electron concentrations and the breakdown voltages of the inventive aluminum nitride sintered bodies are remarkably improved as compared with the conventional aluminum nitride sintered bodies. When the relations between the unpaired electron concentration values and the breakdown voltages are shown on a straight line to measure inclination of this straight line, it is understood that the prior art exhibits inclination of 1.0×10^{-14} while the inventive sintered body exhibits inclination of 1.3×10^{-13} , i.e., 13 times as compared with the prior art. In other words, it is possible to increase the unpaired electron

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concentration by one digit as well as to increase the breakdown voltage to twice at the maximum according to the present invention.

From the linear relations between the unpaired electron concentration values and the breakdown voltages, it is also recognized possible to confirm the breakdown voltage of the sintered body by a nondestructive test through measurement of unpaired electron concentration.

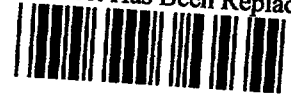
Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

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WHAT IS CLAIMED IS:

1. An aluminum nitride sintered body comprising aluminum nitride crystal grains, titanium being included as solid solute in said aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm.

2. An aluminum nitride sintered body in accordance with claim 1, containing an oxy-nitride of titanium and aluminum therein in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 ,

unpaired electron concentration in said sintered body obtained from an absorption spectrum of electron spin resonance being at least $1 \times 10^{13}/g$.

3. An aluminum nitride sintered body in accordance with claim 2, wherein said oxy-nitride exists in said aluminum nitride sintered body in the form of grains, said grains being not more than 800 nm in diameter.

4. An aluminum nitride sintered body in accordance with claim 3, having thermal conductivity of at least 150 W/mK.



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5. A method of preparing an aluminum nitride sintered body, comprising:

a step of preparing aluminum nitride powder;

a step of nitriding said aluminum nitride powder in an atmosphere containing nitrogen at a temperature of at least 800°C and not more than 1400°C;

a step of adding a sintering assistant, and an oxy-nitride of titanium, being in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , to said nitrified aluminum nitride powder, thereby obtaining mixed powder;

a step of preparing a compact from said mixed powder; and

a step of firing said compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.

6. A method of preparing an aluminum nitride sintered body, comprising:

a step of preparing aluminum nitride powder;

a step of ion-implanting titanium into said aluminum nitride powder for making titanium exist in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm;

a step of adding a sintering assistant to said

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aluminum nitride powder containing titanium for obtaining mixed powder;

a step of preparing a compact from said mixed powder;
and

a step of firing said compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.

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ALUMINUM NITRIDE SINTERED BODY AND METHOD
OF PREPARING THE SAME

ABSTRACT OF THE DISCLOSURE

Disclosed herein are an aluminum nitride sintered body having a high breakdown voltage for serving as a substrate material which is responsive to high integration of a circuit, and a method of preparing the same. The aluminum nitride sintered body contains titanium, which is included as solid solute in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm. Unpaired electron concentration in the sintered body obtained from an absorption spectrum of electron spin resonance is at least $1 \times 10^{13}/\text{g}$. At least 0.1 percent by weight and not more than 5.0 percent by weight of an oxy-nitride of titanium and aluminum exists in the aluminum nitride sintered body in terms of TiO_2 . The aluminum nitride sintered body has a breakdown voltage of 20 kV/mm. This aluminum nitride sintered body is obtained by nitriding aluminum nitride raw material powder in a nitrogen atmosphere at a temperature of 800 to 1400°C , adding an oxy-nitride of titanium thereto with a sintering assistant, and sintering the mixture.

FIGURE 3A.

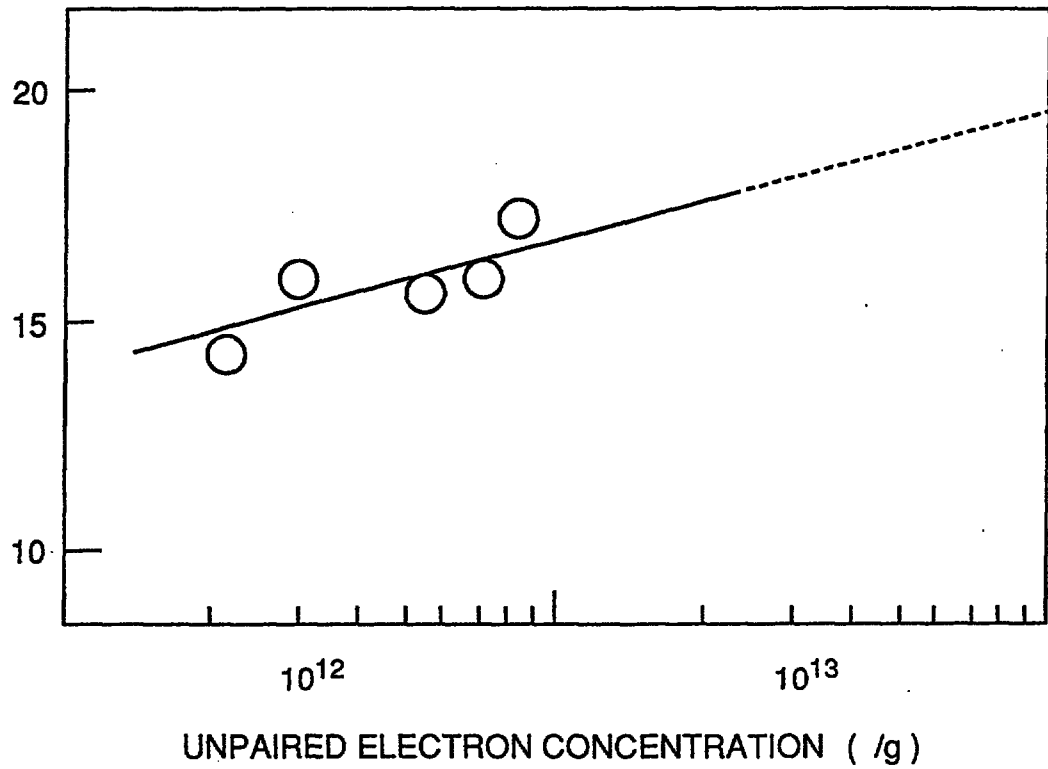
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FIG.1

BREAKDOWN VOLTAGE
(KV/mm)



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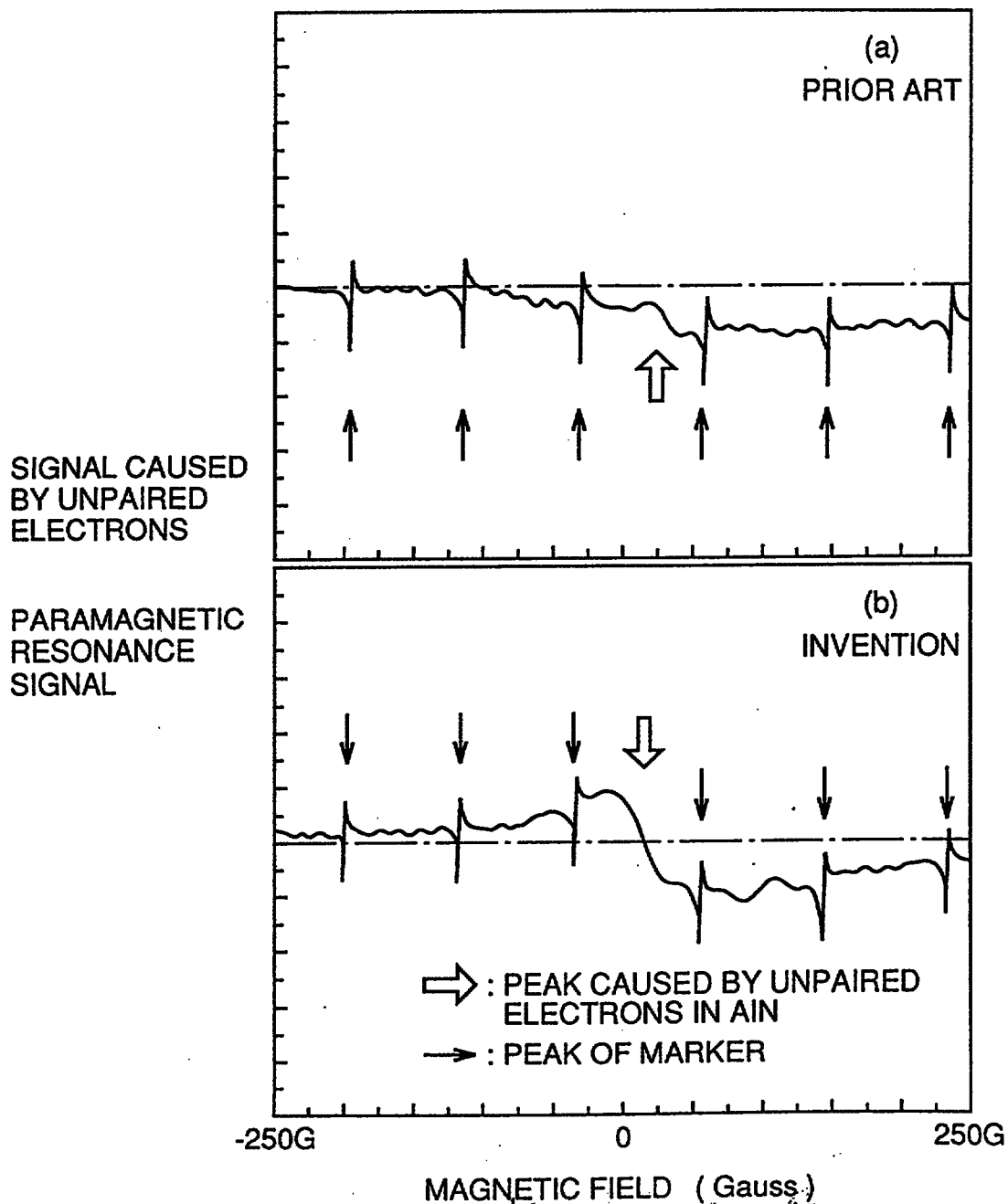


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FIG.2



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FIG.3A

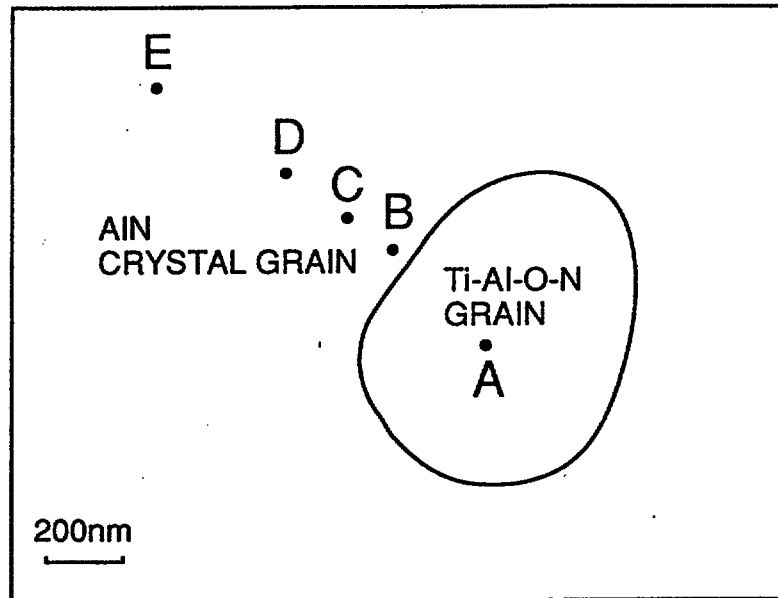
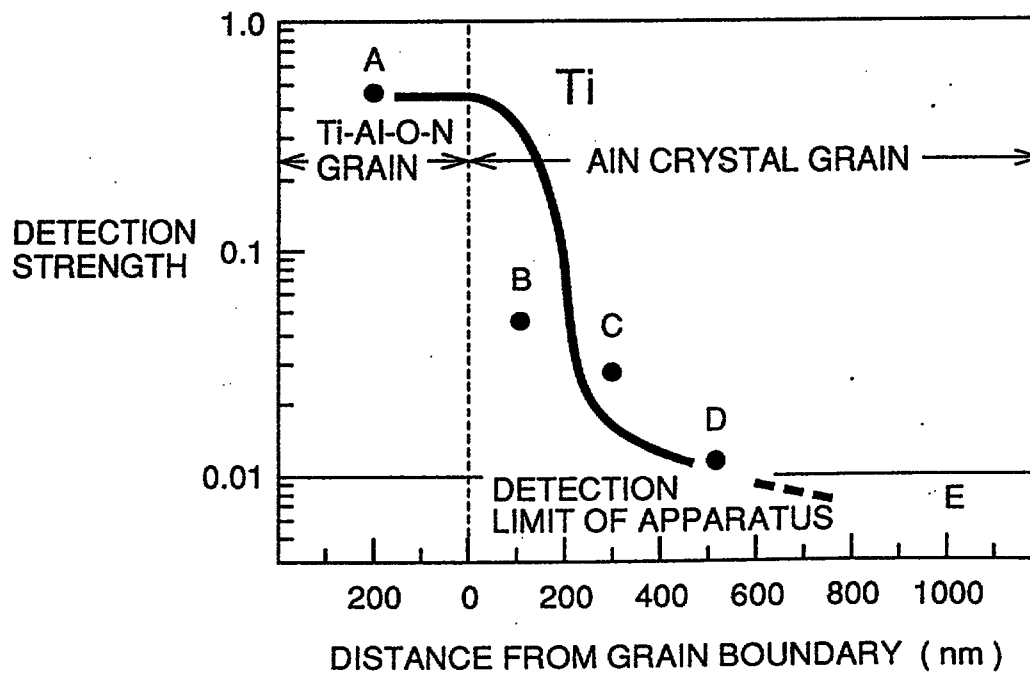


FIG.3B



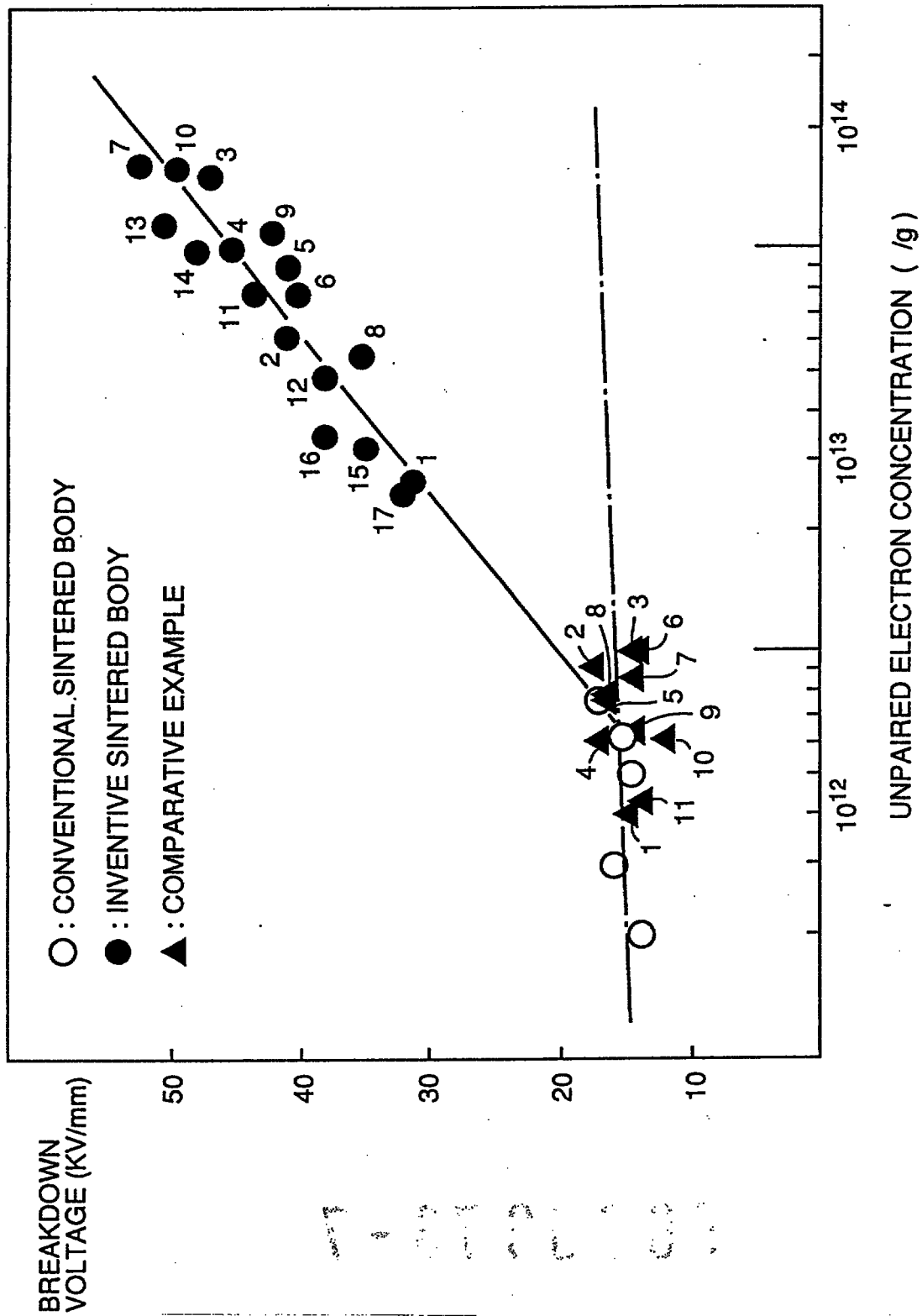
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FIG.4



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☒ Claim(s) : paged 9 to paged 1
☒ Drawing(s) : paged 1 to paged 4
☐ Abstract : paged 1 to paged 1

☒ Description : paged 1 to paged 8
☒ Claim(s) : paged 9 to paged 1
☒ Drawing(s) : paged 1 to paged 4
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Aluminum nitride sintered body and method of preparing the same

Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an aluminum nitride sintered body having a high breakdown voltage in response to high integration of a circuit board, and a method of preparing the same.

Description of the Background Art

An aluminum nitride sintered body having high thermal conductivity is applied to a radiating material such as a substrate for a semiconductor device or a circuit board, for example. At present, high integration of a circuit board is developed in order to cope with high speed processing of mass data and miniaturization of information processing equipment. A material for such a highly integrated circuit board must have an excellent radiating property in order to cope with heat generated by high integration, as well as a high breakdown voltage in order to cope with narrow spaces between circuit wires.

An aluminum nitride sintered body is watched with interest as an excellent radiating substrate material, due to high thermal conductivity. A conventional aluminum nitride sintered body has a breakdown voltage of about 10 to 20 kV/mm. Thus, awaited is an aluminum nitride sintered body, which is applicable to a highly integrated circuit board with a high breakdown voltage of at least 20 kV/mm. EP-A-507 961 discloses an aluminum sintered body containing a titanium compound.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an aluminum nitride sintered body having a high breakdown voltage as a substrate material which is responsive to high integration of a circuit, and a method of preparing the same.

In order to solve the aforementioned problem, the inventors have found that it is possible to remarkably improve the value of a breakdown voltage of an aluminum sintered body by forming and dispersing an oxy-nitride of titanium and aluminum, such as aluminate nitride of titanium, for example, in a sintered body of aluminum nitride and partially including titanium as solid solute in aluminum nitride crystal grains. The present invention has been proposed on the basis of the following recognition by the inventors:

The inventors have found that there is a relation shown in Fig. 1 between a breakdown voltage of an aluminum nitride sintered body and unpaired electron concentration measured from an electron spin resonance absorption spectrum. It is understood from Fig. 1 that the value of the breakdown voltage is slightly increased with increase of the unpaired electron concentration in the aluminum nitride sintered body. However, there has been obtained no aluminum nitride sintered body having a breakdown voltage exceeding 20 kV/mm as a material for a circuit board which is responsive to high integration.

The inventors have energetically made deep study, to succeed in increasing unpaired electron concentration by preparing an aluminum nitride sintered body through the following steps: In a first step, aluminum nitride raw material powder is nitrided in a nitrogen atmosphere at a temperature of 800 to 1400°C, to convert a surface composition of the raw material powder from aluminum oxide (Al_2O_3) to aluminum oxy-nitride ($Al_xO_yN_z$; $0 < X < 1$, $0 < Y < 1$, $0 < Z < 1$). In a second step, an oxy-nitride of titanium (or titanium oxide covered with aluminum salt of fatty acid such as aluminum stearate or aluminum laurate) is added to the as-nitrided aluminum nitride raw material powder with a sintering assistant such as a rare earth oxide such as Y_2O_3 or an alkaline earth oxide such as CaO, and the mixture is sintered. Through such two steps, the inventors have succeeded in extremely increasing unpaired electron concentration of the aluminum nitride sintered body, improving thermal conductivity and remarkably improving the value of its breakdown voltage as compared with the prior art.

The aluminum nitride sintered body according to the present invention comprises aluminum nitride crystal grains, in which titanium element is included as solid solute in a weight ratio of at least 50 ppm and not more than 1000 ppm.

Further, the aluminum nitride sintered body according to the present invention contains an oxy-nitride of titanium and aluminum compound in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , with unpaired electron concentration, being obtained from an absorption spectrum of electron spin resonance, of at least $1 \times 10^{13}/g$. More preferably, the oxy-nitride of titanium and aluminum compound exists in the aluminum nitride sintered body in the form of grains, which are not more than 800 nm in diameter. The aluminum nitride sintered body has thermal conductivity of at least 150 W/mK.

On the other hand, a method of preparing an aluminum nitride sintered body according to the present invention comprises the following steps:

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- a) a step of preparing aluminum nitride powder;
- b) a step of nitriding the aluminum nitride powder in an atmosphere containing nitrogen at a temperature of at least 800°C and not more than 1400°C;
- c) a step of adding a sintering assistant, and an oxy-nitride of titanium, being in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , to the as-nitrided aluminum nitride powder, thereby obtaining mixed powder;
- d) a step of preparing a compact from the mixed powder; and
- e) a step of firing the compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.

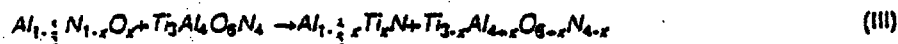
A method of preparing an aluminum nitride sintered body according to another aspect of the present invention comprises the following steps:

- a) a step of preparing aluminum nitride powder;
- b) a step of ion-implanting titanium into the aluminum nitride powder, thereby making titanium exist in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm;
- c) a step of adding a sintering assistant to the aluminum nitride powder containing titanium for obtaining mixed powder;
- d) a step of preparing a compact from the mixed powder; and
- e) a step of firing the compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.

Fig. 2 illustrates absorption spectra of electron spin resonance obtained from a conventional aluminum nitride sintered body and an aluminum nitride sintered body according to the present invention. It is understood from Fig. 2 that intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is remarkably increased as compared with that of the prior art. Referring to Fig. 2, the term "marker" indicates a standard material which exhibits a peak in a certain constant magnetic field. This standard material is measured with an unknown sample, in order to prevent a measurement error caused by an apparatus.

The reason why the intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is increased, which has not yet been clarified, can be considered as follows: First, aluminum oxy-nitride which is formed on the surface of the aluminum nitride raw material powder by surface treatment (for example, Reaction Formula: I) reacts with the oxy-nitride of titanium added thereto, to form an oxy-nitride (Ti-Al-O-N) of titanium and aluminum (for example, Reaction Formula: II). Since such an oxy-nitride of titanium and aluminum is instable under a high temperature exceeding 1000°C as compared with an oxide (Ti-Al-O) of titanium and aluminum, a replacement reaction takes place between oxygen (-bivalent) contained in the aluminum nitride crystal grains as an impurity and nitrogen (-trivalent) in the aluminate nitride of titanium (oxy-nitride of titanium and aluminum) (for example, Reaction Formula: III). Thus, the oxy-nitride of titanium and aluminum may conceivably be stabilized due to approach to the composition of Ti-Al-O. At this time, a minus valence number is increased in the aluminum nitride crystal while a plus valence number is increased in the oxy-nitride of titanium and aluminum, and hence the material enters an electrically unbalanced state. In order to compensate for such a state, however, replacement takes place between aluminum (+trivalent) in the aluminum nitride crystal and titanium (+tetravalent) in the aluminate nitride of titanium, to recover electrically neutral conditions. As the result, titanium is conceivably included as solid solute in the aluminum nitride crystal to increase unpaired electron concentration. Thus, the intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is remarkably increased.

Reaction Formula



The aluminum nitride sintered body preferably contains at least 0.1 percent by weight and not more than 5.0 percent by weight of the oxy-nitride of titanium and aluminum compound in terms of TiO_2 , including titanium which is contained as solid solute in the aluminum nitride crystal lattice. If the content of the oxy-nitride of titanium and aluminum compound is less than 0.1 percent by weight, unpaired electron concentration is not much increased and the value of the breakdown voltage of the as-obtained aluminum nitride sintered body remains substantially similar to that of the prior

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art. If the content of the oxy-nitride of titanium and aluminum compound exceeds 5.0 percent by weight, on the other hand, grains of this oxy-nitride of titanium and aluminum compound formed in the aluminum nitride sintered body disadvantageously exceed 800 nm in diameter, to inhibit original high thermal conductivity of the aluminum nitride sintered body and reduce a heat radiation property of the sintered body for serving as a circuit board material.

Further, no titanium is included as solid solute in the aluminum nitride crystal grains if no surface treatment is carried out on the aluminum nitride raw material powder or a compound of titanium is not added in the form of an oxy-nitride. Thus, no increase can be expected in the breakdown voltage of the aluminum nitride sintered body.

In the inventive aluminum nitride sintered body, titanium must be included as solid solute in the aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm. If the amount of the as-dissolved titanium is less than 50 ppm, unpaired electron concentration decreases and thus breakdown voltage is not enough. If the amount of the solidly dissolved titanium exceeds 1000 ppm, on the other hand, the thermal conductivity deteriorates and thus the radiating property is not enough.

In the inventive aluminum nitride sintered body, further, the unpaired electron concentration obtained from an absorption spectrum of electron spin resonance is preferably at least $1 \times 10^{13}/\text{g}$, since it is possible to ensure a breakdown voltage of at least 20 kV/mm in this case.

The aluminum nitride sintered body, which is obtained by forming and dispersing an oxy-nitride of titanium and aluminum compound in an aluminum nitride sintered body and partially including titanium as solid solute in aluminum crystal grains can be prepared by the following method:

Commercially available aluminum nitride raw material powder is nitrided in an atmosphere containing nitrogen within a temperature range of 800 to 1400°C. The temperature range is set at 800 to 1400°C since no nitriding reaction progresses on the surface of the aluminum nitride raw material powder if the temperature is less than 800°C, while the grain size of the powder is increased due to a solid phase reaction between aluminum nitride grains to suppress dispersion of an oxy-nitride of titanium which is added in a later step if the temperature exceeds 1400°C.

Then, 0.3 to 3.0 percent by weight of a sintering assistant such as Y_2O_3 or CaCO_3 in terms of CaO is added to the aluminum nitride raw material powder which is surface-treated in the aforementioned manner, with addition of 0.1 to 5.0 percent by weight of an oxy-nitride of titanium in terms of TiO_2 . At this time, the oxy-nitride of titanium as added preferably has a particle size of not more than 1 μm , more preferably not more than 0.1 μm , so that the same is formed and dispersed in the aluminum nitride sintered body as an oxy-nitride of titanium and aluminum, and titanium is easily solidly dissolved in the aluminum nitride crystal grains. Then, about 1.0 to 3.0 percent by weight of a binder such as polyvinyl butyral is added to this aluminum nitride mixed powder, and mixed with the same in a ball mill for about 12 to 72 hours. Thereafter the powder is dried and granulated, so that the as-obtained powder is compacted under a pressure of 1.5 ton/cm², to obtain a pressed compact. At this time, the pressed compact is preferably 1.8 to 2.0 g/cm³ in density. Thereafter the pressed compact is debindered in a nitrogen atmosphere at a temperature of 600 to 800°C for about 2 to 3 hours. The as-treated pressed compact is fired in an atmosphere containing nitrogen at a temperature of 1500 to 1900°C for about 2 to 5 hours, to obtain an aluminum nitride sintered body.

In relation to the aforementioned method, it is also possible to obtain an aluminum nitride sintered body having a high breakdown voltage by ion-implanting titanium into the aluminum nitride raw material powder for making titanium exist in aluminum nitride crystal grains, and thereafter adding a sintering agent and a binder and carrying out mixing, granulation, press molding, debinding and firing under the same conditions as the above.

The inventors have observed an aluminum nitride sintered body having unpaired electron concentration of at least $1 \times 10^{13}/\text{g}$ obtained from an absorption spectrum of electron spin resonance with an SEM (scanning electron microscope) or a TEM (transmission electron microscope). Consequently, it has been proved that crystal grains other than aluminum nitride crystal grains existed in the aluminum nitride sintered body. These grains were subjected to elementary analysis through an EDX (energy dispersive X-ray analysis) or AES (Auger electron spectroscopy) or SIMS (Secondary Ion Mass Spectroscopy), to prove that the grains formed in the aluminum nitride crystal grains included Ti, Al, N, O, Ca, Mg, Si and C, and were mainly composed of Ti, Al, O and N. Further, grains of a titanium compound formed in the aluminum nitride sintered body existed as dispersed grains of not more than 0.8 μm (800 nm) in mean grain size.

Fig. 3A typically shows TEM images of Ti-Al-O-N grain contained in the aluminum nitride crystal grain, and Fig. 3B shows results of EDX analysis of Ti in respective points A to E in Fig. 3A. As the results of the EDX analysis of the inside of the aluminum nitride crystal grain around titanium compound grain, it has been clarified that Ti was diffused from the titanium compound grain of Ti-Al-O-N existing in AlN grains into aluminum nitride crystal grain, as shown in Fig. 3B. It has also been proved that the amount of Ti as solid solute in the aluminum nitride crystal lattice, which was varied with sintering conditions, was within a range of 50 to 1000 ppm.

According to the present invention, as hereinabove described, titanium is included as solid solute in the aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm, whereby unpaired electron concentration of the aluminum nitride sintered body can be extremely increased thereby remarkably improving the breakdown voltage as compared with the prior art. Further, the inventive aluminum nitride sintered body, which has unpaired electron concentration obtained from an electron spin resonance absorption spectrum of at least $1 \times 10^{13}/\text{g}$ and contains at least 0.1 percent by weight and not more than 5.0 percent by weight of an oxy-nitride of titanium and aluminum in

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terms of TiO_2 , is provided with a high breakdown voltage of at least 20 kV/mm. The inventive aluminum nitride sintered body having an excellent heat radiation property is sufficiently applicable to a circuit board material which is responsive to integration of the circuit.

According to the present invention, it is possible to obtain an aluminum nitride sintered body which has a higher breakdown voltage as compared with the prior art, whereby highly integrated circuit design is enabled when the inventive sintered body is applied to a circuit board material. Thus, it is possible to contribute to high-speed processing of information following high integration of the circuit, as well as to miniaturization of information processing equipment.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a relation between unpaired electron concentration and a breakdown voltage in an aluminum nitride sintered body;

Fig. 2 is a graph showing absorption spectra of electron spin resonance obtained from a conventional aluminum nitride sintered body and an aluminum nitride sintered body according to the present invention;

Fig. 3A typically illustrates TEM images of Ti-Al-O-N grain contained in an aluminum nitride crystal grain;

Fig. 3B is a graph showing results of EDX analysis of Ti distribution in aluminum nitride crystal grain and Ti-Al-O-N grain; and

Fig. 4 is a graph showing relations between unpaired electron concentration values and breakdown voltages in aluminum nitride sintered bodies according to comparative examples and Example of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

Aluminum nitride raw material powder shown at A in Table 1 was surface-treated in a nitrogen atmosphere at a temperature of 800°C, and thereafter 0.5 percent by weight of Y_2O_3 serving as a sintering assistant was added to this material with addition of 0.2 percent by weight of an oxy-nitride of titanium ($\text{Ti}_3\text{O}_3\text{N}_2$) in terms of TiO_2 , so that the as-obtained powder was mixed in alcohol with a tumbling ball mill for 12 hours, as shown in Table 2. Thereafter 2 percent by weight of polyvinyl butyral was added as a binder to this mixed powder, which in turn was further sufficiently mixed and dried. The as-obtained powder was press-compacted under a pressure of at least 1.5 ton/cm². The as-obtained pressed compact was debindered at a temperature of 600°C for 2 hours, and then fired in a nitrogen atmosphere under a sintering temperature of 1800°C for 3 hours. The as-obtained aluminum nitride sintered body was subjected to measurement of density, a breakdown voltage, thermal conductivity, unpaired electron concentration, mechanical strength and an amount of titanium as solid solute in aluminum nitride crystal grains. The sintered body density was measured by an Archimedes' method, the thermal conductivity was measured by a laser flash method, the unpaired electron concentration was measured with an electron spin resonator, the mechanical strength was measured through JIS three-point bending strength, and the amount of titanium as solid solute was measured with EDX of TEM or AES, SIMS. Table 3 shows the results.

Examples 2 to 16

The aluminum nitride raw powder materials shown in Table 1 were treated at surface treatment temperatures shown in Table 2, and thereafter subjected to mixing with sintering assistants and press compacting, similarly to Example 1. The as-obtained pressed compacts were fired under sintering conditions shown in Table 2 by a method similar to that in Example 1, to prepare 15 types of aluminum nitride sintered bodies. Table 3 shows measurement values obtained as to these samples.

Example 17

Ti ions were implanted into the aluminum nitride raw material powder shown at A in Table 1, with energy of 4 MeV at about 10^{18} ions/cm². 0.5 percent by weight of Y_2O_3 was added to this powder and mixed in alcohol with a tumbling ball mill for 12 hours. Thereafter an aluminum nitride sintered body was obtained in a similar manner to Example 1. Table 3 also shows measurement values obtained as to this sample.

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Table 1

Raw Material Powder	A	B	C
Total Oxygen Content (wt.%)	1.3	0.9	1.2
Carbon Content in Raw Material Powder (ppm)	300	230	500
Fe Content in Raw Material Powder (ppm)	<10	<10	<10
Si Content in Raw Material Powder (ppm)	9	50	82
Specific Surface Area of Raw Material Powder (m ² /g)	3.5	2.8	2.7
Mean Particle Size of Raw Material Powder (μm)	1.3	1.1	1.0

Table 2

Example	Employed Raw Material Powder	Surface Treatment Temperature (°C)	Sintering Assistant (wt.%)	Ti Compound (wt.%, in terms of TiO ₂)	Sintering Temperature (°C)	Sintering Time (hr.)
1	A	800	Y ₂ O ₃ : 0.5	Ti ₃ O ₅ N ₂ : 0.2	1800	3
2	A	1000	Yb ₂ O ₃ : 0.5	Ti ₃ O ₅ N ₂ : 0.5	1800	5
3	A	1200	CaO: 0.5	Ti ₃ O ₅ N ₂ : 0.5	1800	5
4	B	1200	Nd ₂ O ₃ : 0.5	Ti ₃ O ₅ N ₂ : 0.5	1800	5
5	B	1300	Sm ₂ O ₃ : 0.5	Ti ₃ O ₅ N ₂ : 0.5	1800	5
6	B	1000	Y ₂ O ₃ : 0.5 CaO: 0.5	Ti ₃ O ₅ N ₂ : 1.0	1650	3
7	B	1000	Yb ₂ O ₃ : 0.5 CaO: 0.5	Ti ₃ O ₅ N ₂ : 1.0	1650	5
8	C	1000	Y ₂ O ₃ : 0.5 Nd ₂ O ₃ : 0.5	Ti ₃ O ₅ N ₂ : 1.0	1650	5
9	C	800	Yb ₂ O ₃ : 0.5 Nd ₂ O ₃ : 0.5	Ti ₃ O ₅ N ₂ : 1.0	1650	5
10	C	1200	Nd ₂ O ₃ : 0.5 CaO: 0.5	Ti ₃ O ₅ N ₂ : 1.0	1650	3
11	C	1200	Y ₂ O ₃ : 1.5	Ti ₃ O ₅ N ₂ : 1.5	1800	5
12	C	1400	Yb ₂ O ₃ : 1.5	Ti ₃ O ₅ N ₂ : 1.5	1800	5
13	A	1300	Y ₂ O ₃ : 1.5 Yb ₂ O ₃ : 1.5	Ti ₃ O ₅ N ₂ : 1.5	1800	5
14	A	1200	Y ₂ O ₃ : 1.5 Nd ₂ O ₃ : 1.5	Ti ₃ O ₅ N ₂ : 2.0	1800	3
15	B	1200	Yb ₂ O ₃ : 1.5 CaO: 1.5	Ti ₃ O ₅ N ₂ : 5.0	1500	5
16	B	1200	Yb ₂ O ₃ : 1.5 Nd ₂ O ₃ : 1.5	Ti ₃ O ₅ N ₂ : 3.0	1800	5
17	A		Y ₂ O ₃ : 0.5	Ti Ion Implantation (10 ¹⁶ ions/cm ²)	1800	3

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Table 3

Example	Content of Ti as Solid Solute (ppm)	Break Down Voltage (kV/mm)	Density (g/cm ³)	Mechanical Strength (kg/mm ²)	Unpaired Electron Concentration (/g)	Thermal Conductivity (W/m·K)
1	50	31	3.27	48	2.7×10^{13}	170
2	100	41	3.27	45	6.0×10^{13}	169
3	780	47	3.26	48	1.5×10^{14}	160
4	480	46	3.27	42	1.0×10^{14}	152
5	220	41	3.27	47	9.0×10^{13}	150
6	440	40	3.27	41	7.9×10^{13}	190
7	650	52	3.28	43	1.6×10^{14}	170
8	170	35	3.28	45	5.5×10^{13}	165
9	440	44	3.27	42	1.1×10^{14}	155
10	920	50	3.28	45	1.6×10^{14}	155
11	320	44	3.27	48	7.8×10^{13}	230
12	110	39	3.27	43	4.9×10^{13}	200
13	800	52	3.28	41	1.1×10^{14}	234
14	650	48	3.28	46	1.0×10^{14}	178
15	50	35	3.12	40	3.2×10^{13}	150
16	80	39	3.28	45	3.5×10^{13}	217
17	80	32	3.27	40	2.1×10^{13}	165

It is clearly understood from Table 3 that unpaired electron concentration obtained from an electron spin resonance absorption spectrum exceeds $1 \times 10^{13}/g$ when the amount of Ti as solid solute is at least 50 ppm and not more than 1000 ppm in a weight ratio, and the aluminum nitride sintered body exhibits a high breakdown voltage. It is also understood that an aluminum nitride sintered body which has unpaired electron concentration of at least $1 \times 10^{13}/g$ and contains a compound of titanium within a range of 0.1 to 5.0 percent by weight in terms of TiO_2 has a high breakdown voltage.

As to the aluminum nitride sintered bodies obtained according to Examples 1, 2, 4 and 5, titanium compounds contained in the aluminum nitride crystal particles were examined through XRD (X-ray diffraction) or EDX. As the result, it was proved that the titanium compounds contained in the aluminum nitride sintered bodies were composed of Ti, Al, O and N, or Ti, Al, N, O, Ca, Mg and Si.

Comparative Example 1

Powder which was obtained by adding 1.0 percent by weight of Y_2O_3 , being in the form of fine particles for serving as a sintering assistant, to the aluminum nitride raw material powder shown at A in Table 1 was mixed in alcohol with a tumbling ball mill for 12 hours. Thereafter 2 percent by weight of polyvinyl butyral was added as a binder to this mixed powder, which in turn was further sufficiently mixed and dried. The as-obtained powder was press-compacted under a pressure of at least 1.5 ton/cm². Thereafter the as-obtained pressed compact was debindered at a temperature of 600°C for 2 hours, and fired in a nitrogen atmosphere under a sintering temperature of 1800°C for 5 hours. The as-obtained aluminum nitride sintered body was subjected to measurement of density, a breakdown voltage, thermal conductivity, unpaired electron concentration, mechanical strength, and an amount of titanium as solid solute in aluminum nitride crystal grains. The sintered body density was measured by an Archimedes' method, the thermal conductivity was measured by a laser flash method, the unpaired electron concentration was measured with an electron spin resonator, the mechanical strength was measured through JIS three-point bending strength, and the amount of titanium was measured with EDX of TEM or AES, SIMS. Table 5 shows the results.

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Comparative Examples 2 to 11

The aluminum nitride raw powder materials shown in Table 1 were surface-treated under conditions shown in Table 4, thereafter subjected to mixing, compacting and debinding in a method similar to that in comparative example 1, and then sintered under sintering conditions shown in Table 4. Table 5 shows measurement values obtained as to these samples of the aluminum nitride sintered bodies.

Table 4

Comparative Example	Employed Raw Material Powder	Surface Treatment Temperature (°C)	Sintering Assistant (wt.%)	Ti Compound (wt.%, in terms of TiO ₂)	Sintering Temperature (°C)	Sintering Time (hr.)
1	A	---	Y ₂ O ₃ : 1.0	----	1800	5
2	A	1200	Y ₂ O ₃ : 1.0	----	1800	5
3	A	1200	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 0.05	1800	5
4	A	1200	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 5.5	1800	5
5	A	1200	Y ₂ O ₃ : 1.0	TiO ₂ : 1.0	1800	5
6	A	---	Y ₂ O ₃ : 1.0	TiO ₂ : 1.0	1800	5
7	A	1200	Y ₂ O ₃ : 1.0	TiN: 1.0	1800	5
8	A	---	Y ₂ O ₃ : 1.0	TiN: 1.0	1800	5
9	A	---	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 1.0	1800	5
10	A	700	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 1.0	1800	5
11	A	1500	Y ₂ O ₃ : 1.0	Ti ₃ O ₃ N ₂ : 1.0	1800	5

Table 5

Comparative Example	Content of Ti as Solid Solute (ppm)	Break Down Voltage (kV/mm)	Density (g/cm ³)	Mechanical Strength (kg/mm ²)	Unpaired Electron Concentration (/g)	Thermal Conductivity (W/m·K)
1	< 10	15	3.27	32	4.0 × 10 ¹²	137
2	< 10	18	3.26	35	9.1 × 10 ¹²	140
3	< 10	15	3.27	30	9.6 × 10 ¹²	149
4	< 30	17	3.28	36	6.0 × 10 ¹²	139
5	< 30	18	3.28	34	7.5 × 10 ¹²	142
6	< 30	14	3.28	38	9.5 × 10 ¹²	138
7	< 30	15	3.27	33	8.1 × 10 ¹²	141
8	< 30	18	3.27	31	7.6 × 10 ¹²	142
9	< 30	15	3.27	34	6.5 × 10 ¹²	140
10	< 30	12	3.27	31	5.9 × 10 ¹²	137
11	< 30	14	3.27	36	4.1 × 10 ¹²	139

From the results of Examples and comparative examples, it is understood that an aluminum nitride sintered body which has an amount of Ti as solid solute within a range of 50 to 1000 ppm in a weight ratio or unpaired electron concentration of at least $1 \times 10^{13}/g$ and contains an oxy-nitride of titanium and aluminum within a range of 0.1 to 5.0 percent by weight in terms of TiO₂ has a breakdown voltage of at least 20 kV/mm.

Fig. 4 is a graph showing relations between breakdown voltages and unpaired electron concentration values obtained from the aforementioned results of Examples and comparative examples, in addition to the general relation

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between the breakdown voltage and the unpaired electron concentration shown in Fig. 1. It is understood from this figure that the values of the unpaired electron concentrations and the breakdown voltages of the inventive aluminum nitride sintered bodies are remarkably improved as compared with the conventional aluminum nitride sintered bodies. When the relations between the unpaired electron concentration values and the breakdown voltages are shown on a straight line to measure inclination of this straight line, it is understood that the prior art exhibits inclination of 1.0×10^{-14} while the inventive sintered body exhibits inclination of 1.3×10^{-13} , i.e., 13 times as compared with the prior art. In other words, it is possible to increase the unpaired electron concentration by one digit as well as to increase the breakdown voltage to twice at the maximum according to the present invention.

From the linear relations between the unpaired electron concentration values and the breakdown voltages, it is also recognized possible to confirm the breakdown voltage of the sintered body by a nondestructive test through measurement of unpaired electron concentration.

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Claims

1. An aluminum nitride sintered body comprising aluminum nitride crystal grains, titanium being included as solid solute in said aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm, the unpaired electron concentration in said sintered body obtained from an absorption spectrum of electron spin resonance being at least $1 \times 10^{13}/\text{g}$.
2. An aluminum nitride sintered body in accordance with claim 1, containing an oxy-nitride of titanium and aluminum therein in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 .
3. An aluminum nitride sintered body in accordance with claim 2, wherein said oxy-nitride exists in said aluminum nitride sintered body in the form of grains, said grains being not more than 800 nm in diameter.
4. An aluminum nitride sintered body in accordance with claim 3, having thermal conductivity of at least 150 W/mK.
5. A method of preparing an aluminum nitride sintered body as defined in claim 1, comprising:
 - a step of preparing aluminum nitride powder;
 - a step of nitriding said aluminum nitride powder in an atmosphere containing nitrogen at a temperature of at least 800°C and not more than 1400°C;
 - a step of adding a sintering assistant, and an oxy-nitride of titanium, being in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , to said nitrided aluminum nitride powder, thereby obtaining mixed powder;
 - a step of preparing a compact from said mixed powder; and
 - a step of firing said compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.
6. A method of preparing an aluminum nitride sintered body as defined in claim 1, comprising:
 - a step of preparing aluminum nitride powder;
 - a step of ion-implanting titanium into said aluminum nitride powder for making titanium exist in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm;
 - a step of adding a sintering assistant to said aluminum nitride powder containing titanium for obtaining mixed powder;
 - a step of preparing a compact from said mixed powder; and
 - a step of firing said compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.



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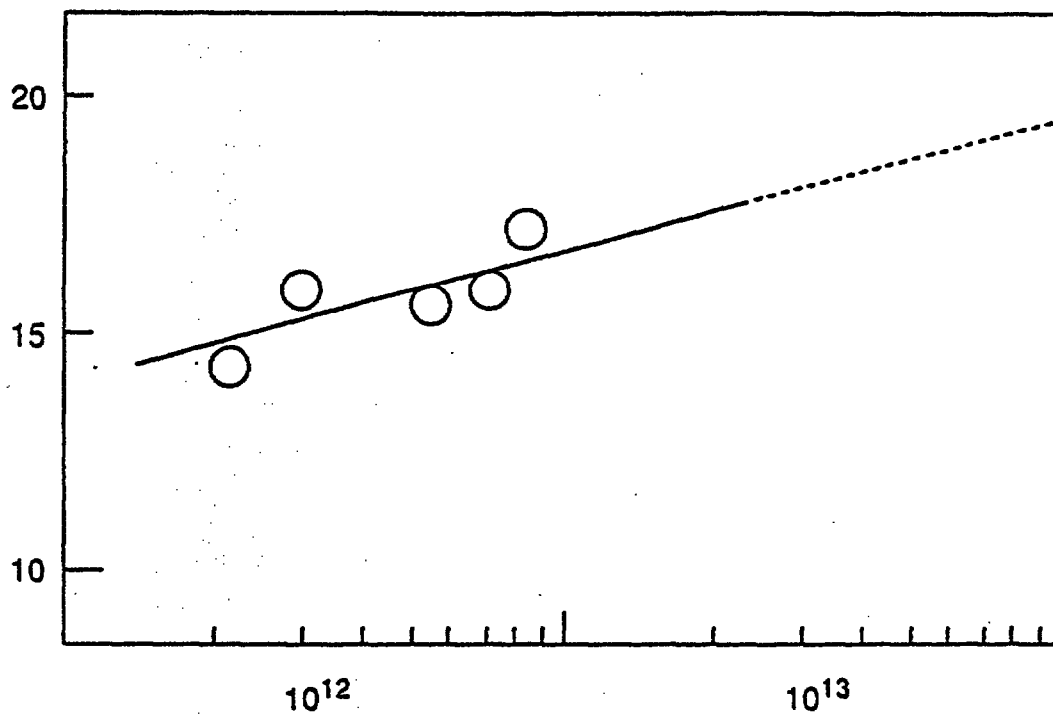


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FIG.1

BREAKDOWN VOLTAGE
(KV/mm)



UNPAIRED ELECTRON CONCENTRATION (1/g)

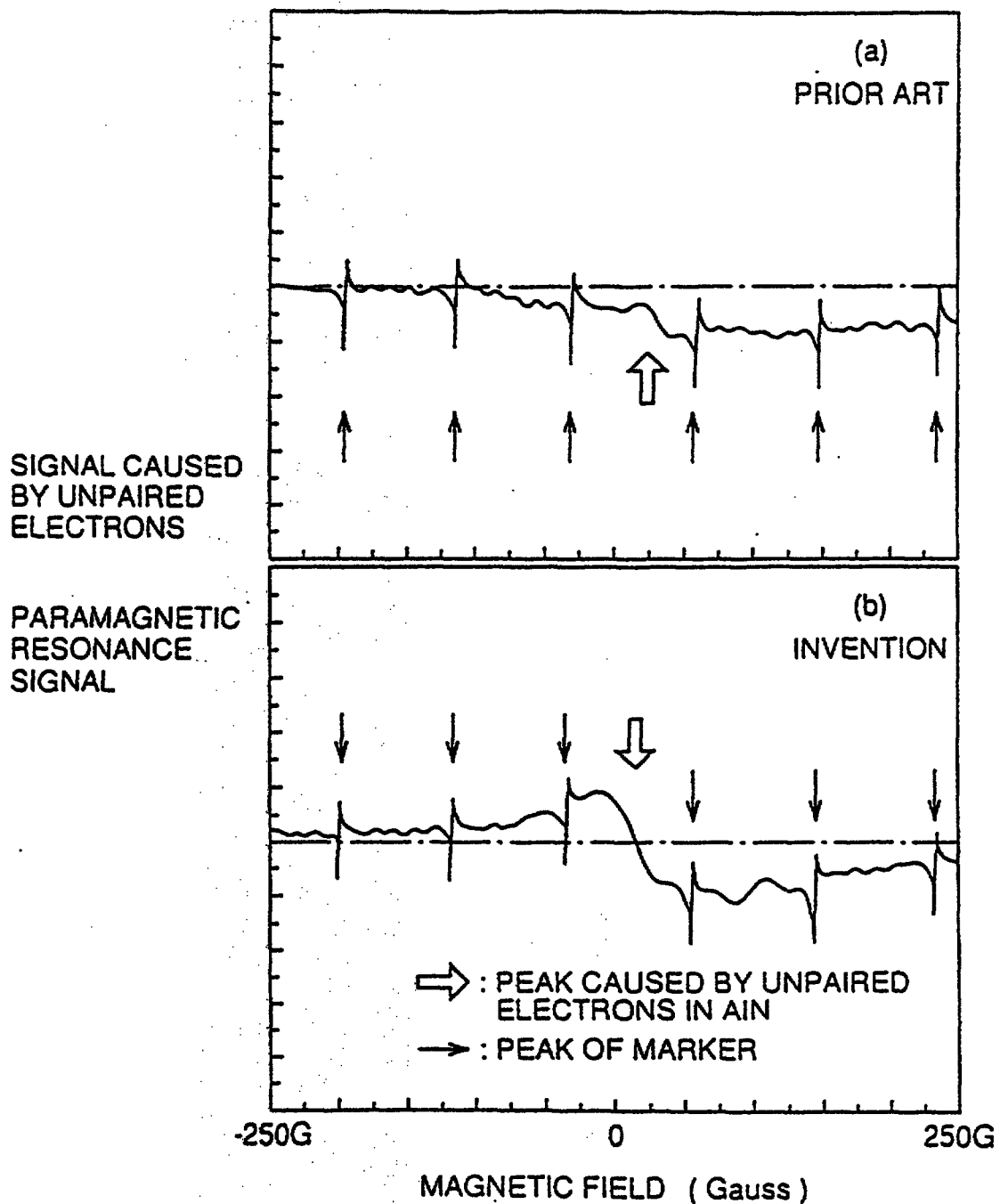
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FIG.2



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FIG.3A

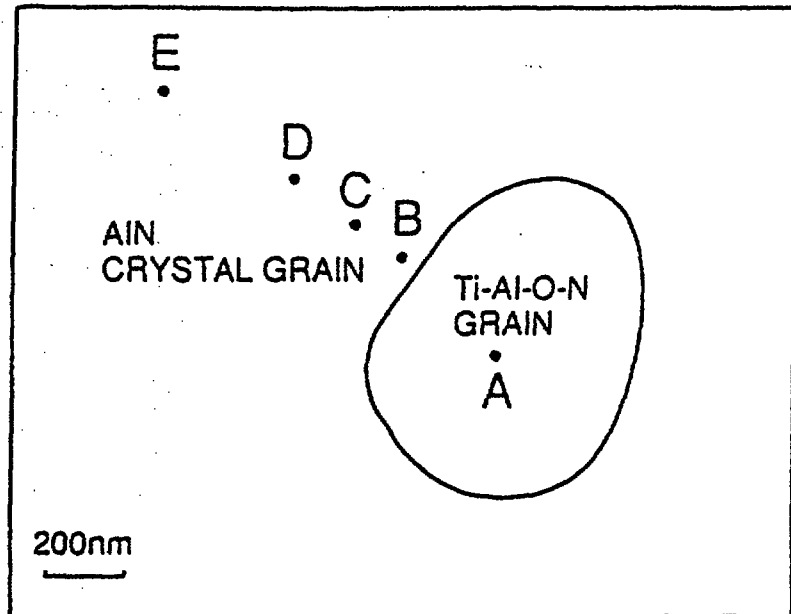
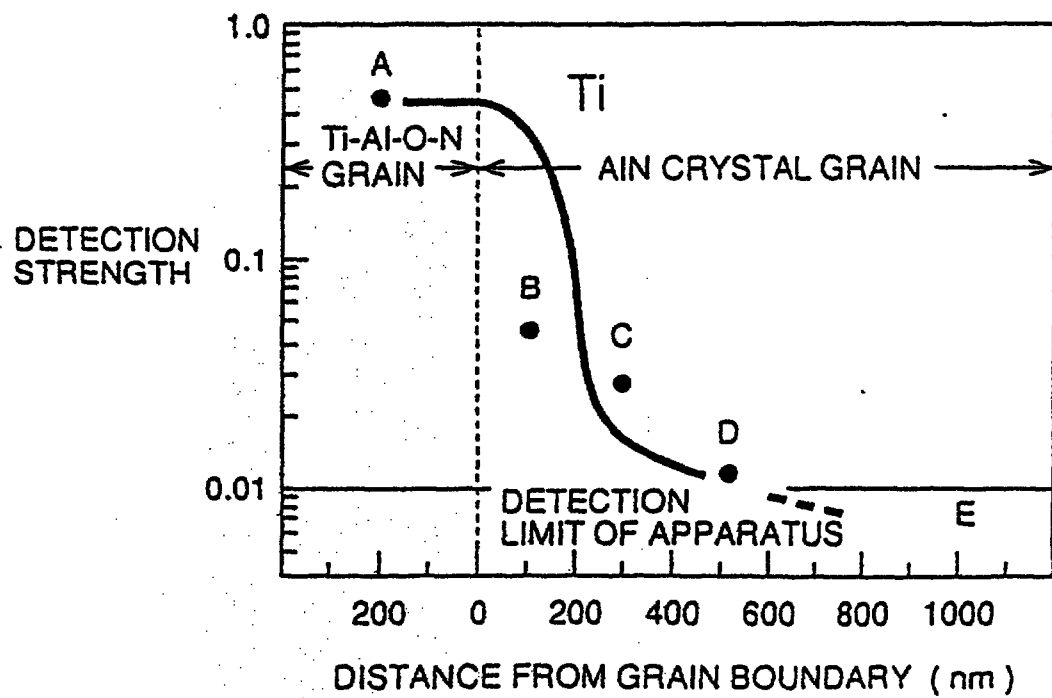


FIG.3B



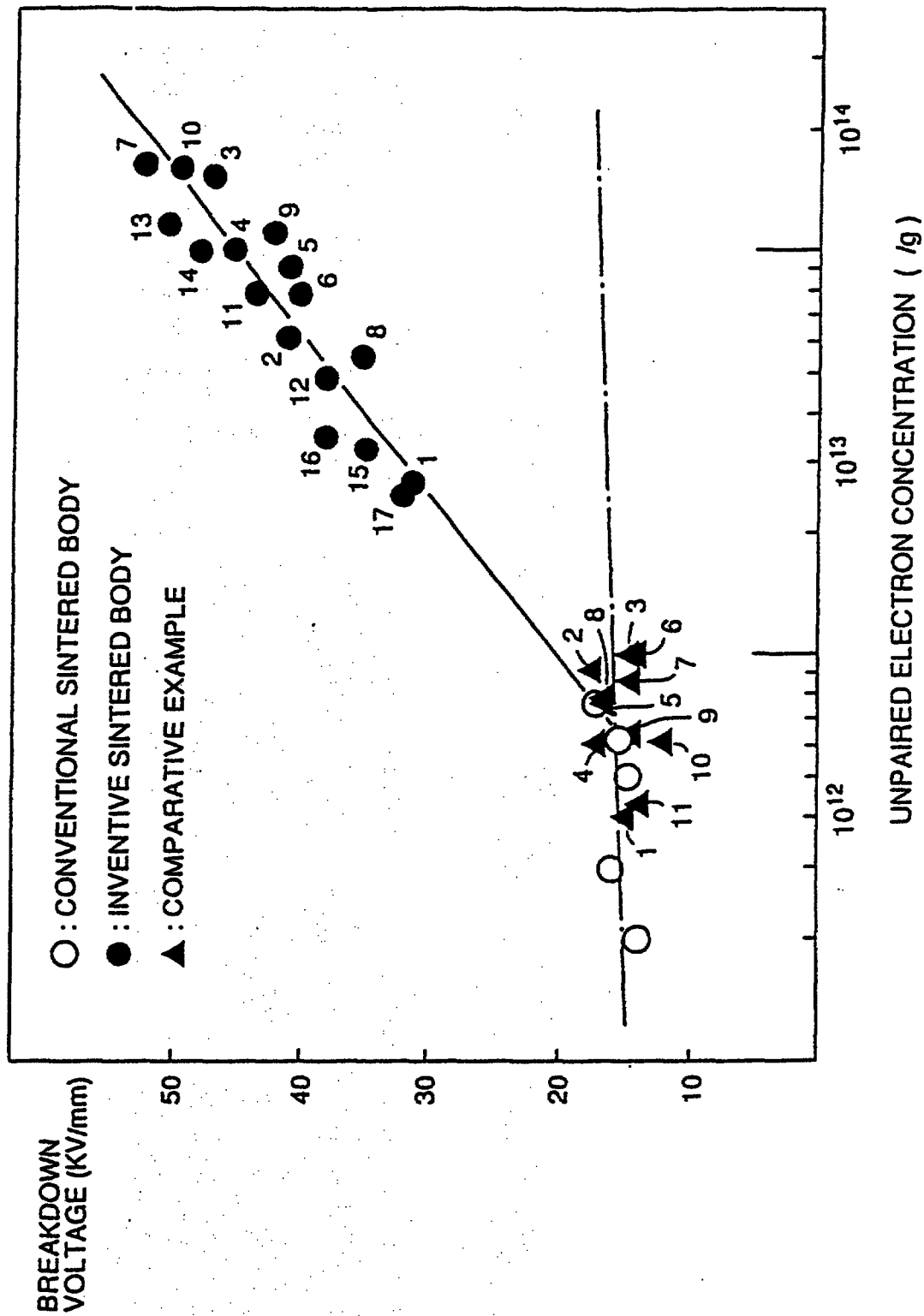
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FIG.4



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REPLACEMENT SHEETS		SG
☒ Description	: paged 1 to paged 24	
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☒ Drawing(s)	: paged 1 to paged 4	
☒ Abstract	: paged 28 to paged 29	
DATE OF RECEIPT		21 APR 1999

TITLE OF THE INVENTION

Aluminum Nitride Sintered Body and Method of
Preparing the Same

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an aluminum nitride sintered body having a high breakdown voltage in response to high integration of a circuit board, and a method of preparing the same.

Description of the Background Art

An aluminum nitride sintered body having high thermal conductivity is applied to a radiating material such as a substrate for a semiconductor device or a circuit board, for example. At present, high integration of a circuit board is developed in order to cope with high speed processing of mass data and miniaturization of information processing equipment. A material for such a highly integrated circuit board must have an excellent radiating property in order to cope with heat generated by high integration, as well as a high breakdown voltage in order to cope with narrow spaces between circuit wires.

An aluminum nitride sintered body is watched with interest as an excellent radiating substrate material, due to high thermal conductivity. A conventional aluminum nitride sintered body has a breakdown voltage of about 10

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to 20 kV/mm. Thus, awaited is an aluminum nitride sintered body, which is applicable to a highly integrated circuit board with a high breakdown voltage of at least 20 kV/mm. EP-A-507 961 discloses an aluminum sintered body containing a titanium compound.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an aluminum nitride sintered body having a high breakdown voltage as a substrate material which is responsive to high integration of a circuit, and a method of preparing the same.

In order to solve the aforementioned problem, the inventors have found that it is possible to remarkably improve the value of a breakdown voltage of an aluminum sintered body by forming and dispersing an oxy-nitride of titanium, for example, in a sintered body of aluminum nitride and partially including titanium as solid solute in aluminum nitride crystal grains. The present invention has been proposed on the basis of the following recognition by the inventors:

The inventors have found that there is a relation shown in Fig. 1 between a breakdown voltage of an aluminum nitride sintered body and unpaired electron concentration measured from an electron spin resonance absorption spectrum. It is understood from Fig. 1 that the value of

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the breakdown voltage is slightly increased with increase of the unpaired electron concentration in the aluminum nitride sintered body. However, there has been obtained no aluminum nitride sintered body having a breakdown voltage exceeding 20 kV/mm as a material for a circuit board which is responsive to high integration.

The inventors have energetically made deep study, to succeed in increasing unpaired electron concentration by preparing an aluminum nitride sintered body through the following steps: In a first step, aluminum nitride raw material powder is nitrified in a nitrogen atmosphere at a temperature of 800 to 1400°C, to convert a surface composition of the raw material powder from aluminum oxide (Al_2O_3) to aluminum oxy-nitride ($\text{Al}_x\text{O}_y\text{N}_z$: $0 < X < 1$, $0 < Y < 1$, $0 < Z < 1$). In a second step, an oxy-nitride of titanium (or titanium oxide covered with aluminum salt of fatty acid such as aluminum stearate or aluminum laurate) is added to the as-nitrified aluminum nitride raw material powder with a sintering assistant such as a rare earth oxide such as Y_2O_3 or an alkaline earth oxide such as CaO , and the mixture is sintered. Through such two steps, the inventors have succeeded in extremely increasing unpaired electron concentration of the aluminum nitride sintered body, improving thermal conductivity and remarkably improving the value of its breakdown voltage as compared

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compared with the prior art.

The aluminum nitride sintered body according to the present invention comprises aluminum nitride crystal grains, in which titanium element is included as solid solute in a weight ratio of at least 50 ppm and not more than 1000 ppm.

Further, the aluminum nitride sintered body according to the present invention contains an oxy-nitride of titanium and aluminum compound in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , with unpaired electron concentration, being obtained from an absorption spectrum of electron spin resonance, of at least $1 \times 10^{13}/\text{g}$. More preferably, the oxy-nitride of titanium and aluminum compound exists in the aluminum nitride sintered body in the form of grains, which are not more than 800 nm in diameter. The aluminum nitride sintered body has thermal conductivity of at least 150 W/mK.

On the other hand, a method of preparing an aluminum nitride sintered body according to the present invention comprises the following steps:

- a) a step of preparing aluminum nitride powder;
- b) a step of nitriding the aluminum nitride powder in an atmosphere containing nitrogen at a temperature of at least 800°C and not more than 1400°C;

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c) a step of adding a sintering assistant, and an oxy-nitride of titanium, being in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , to the as-nitrided aluminum nitride powder, thereby obtaining mixed powder;

d) a step of preparing a compact from the mixed powder; and

e) a step of firing the compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.

A method of preparing an aluminum nitride sintered body according to another aspect of the present invention comprises the following steps:

a) a step of preparing aluminum nitride powder;

b) a step of ion-implanting titanium into the aluminum nitride powder, thereby making titanium exist in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm;

c) a step of adding a sintering assistant to the aluminum nitride powder containing titanium for obtaining mixed powder;

d) a step of preparing a compact from the mixed powder; and

e) a step of firing the compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride

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sintered body.

Fig. 2 illustrates absorption spectra of electron spin resonance obtained from a conventional aluminum nitride sintered body and an aluminum nitride sintered body according to the present invention. It is understood from Fig. 2 that intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is remarkably increased as compared with that of the prior art. Referring to Fig. 2, the term "marker" indicates a standard material which exhibits a peak in a certain constant magnetic field. This standard material is measured with an unknown sample, in order to prevent a measurement error caused by an apparatus.

The reason why the intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is increased, which has not yet been clarified, can be considered as follows: First, aluminum oxy-nitride which is formed on the surface of the aluminum nitride raw material powder by surface treatment (for example, Reaction Formula: I) reacts with the oxy-nitride of titanium added thereto, to form an oxy-nitride (Ti-Al-O-N) of titanium and aluminum (for example, Reaction Formula: II). Since such an oxy-nitride of titanium and aluminum is instable under a high

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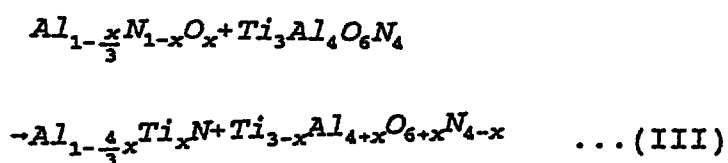
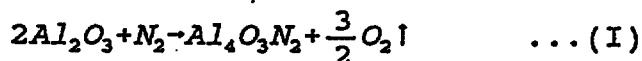
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temperature exceeding 1000°C as compared with an oxide (Ti-Al-O) of titanium and aluminum, a replacement reaction takes place between oxygen (-bivalent) contained in the aluminum nitride crystal grains as an impurity and nitrogen (-trivalent) in the aluminate nitride of titanium (oxy-nitride of titanium and aluminum) (for example, Reaction Formula: III). Thus, the oxy-nitride of titanium and aluminum may conceivably be stabilized due to approach to the composition of Ti-Al-O. At this time, a minus valence number is increased in the aluminum nitride crystal while a plus valence number is increased in the oxy-nitride of titanium and aluminum, and hence the material enters an electrically unbalanced state. In order to compensate for such a state, however, replacement takes place between aluminum (+trivalent) in the aluminum nitride crystal and titanium (+tetravalent) in the aluminate nitride of titanium, to recover electrically neutral conditions. As the result, titanium is conceivably included as solid solute in the aluminum nitride crystal to increase unpaired electron concentration. Thus, the intensity of the absorption spectrum of electron spin resonance obtained from the inventive aluminum nitride sintered body is remarkably increased.

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Reaction Formula



The aluminum nitride sintered body preferably contains at least 0.1 percent by weight and not more than 5.0 percent by weight of the oxy-nitride of titanium and aluminum compound in terms of TiO_2 , including titanium which is contained as solid solute in the aluminum nitride crystal lattice. If the content of the oxy-nitride of titanium and aluminum compound is less than 0.1 percent by weight, unpaired electron concentration is not much increased and the value of the breakdown voltage of the as-obtained aluminum nitride sintered body remains substantially similar to that of the prior art. If the content of the oxy-nitride of titanium and aluminum compound exceeds 5.0 percent by weight, on the other hand, grains of this oxy-nitride of titanium and aluminum compound formed in the aluminum nitride sintered body disadvantageously exceed 800 nm in diameter, to inhibit

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original high thermal conductivity of the aluminum nitride sintered body and reduce a heat radiation property of the sintered body for serving as a circuit board material.

Further, no titanium is included as solid solute in the aluminum nitride crystal grains if no surface treatment is carried out on the aluminum nitride raw material powder or a compound of titanium is not added in the form of an oxy-nitride. Thus, no increase can be expected in the breakdown voltage of the aluminum nitride sintered body.

In the inventive aluminum nitride sintered body, titanium must be included as solid solute in the aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm. If the amount of the as-dissolved titanium is less than 50 ppm, unpaired electron concentration decreases and thus breakdown voltage is not enough. If the amount of the solidly dissolved titanium exceeds 1000 ppm, on the other hand, the thermal conductivity deteriorates and thus the radiating property is not enough.

In the inventive aluminum nitride sintered body, further, the unpaired electron concentration obtained from an absorption spectrum of electron spin resonance is preferably at least $1 \times 10^{13}/\text{g}$, since it is possible to ensure a breakdown voltage of at least 20 kV/mm in this

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case.

The aluminum nitride sintered body, which is obtained by forming and dispersing an oxy-nitride of titanium and aluminum compound in an aluminum nitride sintered body and partially including titanium as solid solute in aluminum crystal grains can be prepared by the following method:

Commercially available aluminum nitride raw material powder is nitrided in an atmosphere containing nitrogen within a temperature range of 800 to 1400°C. The temperature range is set at 800 to 1400°C since no nitriding reaction progresses on the surface of the aluminum nitride raw material powder if the temperature is less than 800°C, while the grain size of the powder is increased due to a solid phase reaction between aluminum nitride grains to suppress dispersion of an oxy-nitride of titanium which is added in a later step if the temperature exceeds 1400°C.

Then, 0.3 to 3.0 percent by weight of a sintering assistant such as Y_2O_3 or $CaCO_3$ in terms of CaO is added to the aluminum nitride raw material powder which is surface-treated in the aforementioned manner, with addition of 0.1 to 5.0 percent by weight of an oxy-nitride of titanium in terms of TiO_2 . At this time, the oxy-nitride of titanium as added preferably has a particle size of not more than 1 μm , more preferably not more than 0.1 μm , so that the same

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is formed and dispersed in the aluminum nitride sintered body as an oxy-nitride of titanium and aluminum, and titanium is easily solidly dissolved in the aluminum nitride crystal grains. Then, about 1.0 to 3.0 percent by weight of a binder such as polyvinyl butyral is added to this aluminum nitride mixed powder, and mixed with the same in a ball mill for about 12 to 72 hours. Thereafter the powder is dried and granulated, so that the as-obtained powder is compacted under a pressure of 1.5 ton/cm², to obtain a pressed compact. At this time, the pressed compact is preferably 1.8 to 2.0 g/cm³ in density. Thereafter the pressed compact is debindered in a nitrogen atmosphere at a temperature of 600 to 800°C for about 2 to 3 hours. The as-treated pressed compact is fired in an atmosphere containing nitrogen at a temperature of 1500 to 1900°C for about 2 to 5 hours, to obtain an aluminum nitride sintered body.

In relation to the aforementioned method, it is also possible to obtain an aluminum nitride sintered body having a high breakdown voltage by ion-implanting titanium into the aluminum nitride raw material powder for making titanium exist in aluminum nitride crystal grains, and thereafter adding a sintering agent and a binder and carrying out mixing, granulation, press molding, debinding and firing under the same conditions as the

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above.

The inventors have observed an aluminum nitride sintered body having unpaired electron concentration of at least $1 \times 10^{13}/\text{g}$ obtained from an absorption spectrum of electron spin resonance with an SEM (scanning electron microscope) or a TEM (transmission electron microscope). Consequently, it has been proved that crystal grains other than aluminum nitride crystal grains existed in the aluminum nitride sintered body. These grains were subjected to elementary analysis through an EDX (energy dispersive X-ray analysis) or AES (Auger electron spectroscopy) or SIMS (Secondary Ion Mass Spectroscopy), to prove that the grains formed in the aluminum nitride crystal grains included Ti, Al, N, O, Ca, Mg, Si and C, and were mainly composed of Ti, Al, O and N. Further, grains of a titanium compound formed in the aluminum nitride sintered body existed as dispersed grains of not more than $0.8 \mu\text{m}$ (800 nm) in mean grain size.

Fig. 3A typically shows TEM images of Ti-Al-O-N grain contained in the aluminum nitride crystal grain, and Fig. 3B shows results of EDX analysis of Ti in respective points A to E in Fig. 3A. As the results of the EDX analysis of the inside of the aluminum nitride crystal grain around titanium compound grain, it has been clarified that Ti was diffused from the titanium compound

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grain of Ti-Al-O-N existing in AlN grains into aluminum nitride crystal grain, as shown in Fig. 3B. It has also been proved that the amount of Ti as solid solute in the aluminum nitride crystal lattice, which was varied with sintering conditions, was within a range of 50 to 1000 ppm.

According to the present invention, as hereinabove described, titanium is included as solid solute in the aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm, whereby unpaired electron concentration of the aluminum nitride sintered body can be extremely increased thereby remarkably improving the breakdown voltage as compared with the prior art. Further, the inventive aluminum nitride sintered body, which has unpaired electron concentration obtained from an electron spin resonance absorption spectrum of at least $1 \times 10^{13}/\text{g}$ and contains at least 0.1 percent by weight and not more than 5.0 percent by weight of an oxynitride of titanium and aluminum in terms of TiO_2 , is provided with a high breakdown voltage of at least 20 kV/mm. The inventive aluminum nitride sintered body having an excellent heat radiation property is sufficiently applicable to a circuit board material which is responsive to integration of the circuit.

According to the present invention, it is possible to

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obtain an aluminum nitride sintered body which has a higher breakdown voltage as compared with the prior art, whereby highly integrated circuit design is enabled when the inventive sintered body is applied to a circuit board material. Thus, it is possible to contribute to high-speed processing of information following high integration of the circuit, as well as to miniaturization of information processing equipment.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a relation between unpaired electron concentration and a breakdown voltage in an aluminum nitride sintered body;

Fig. 2 is a graph showing absorption spectra of electron spin resonance obtained from a conventional aluminum nitride sintered body and an aluminum nitride sintered body according to the present invention;

Fig. 3A typically illustrates TEM images of Ti-Al-O-N grain contained in an aluminum nitride crystal grain;

Fig. 3B is a graph showing results of EDX analysis of Ti distribution in aluminum nitride crystal grain and Ti-

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Al-O-N grain; and

Fig. 4 is a graph showing relations between unpaired electron concentration values and breakdown voltages in aluminum nitride sintered bodies according to comparative examples and Example of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

Aluminum nitride raw material powder shown at A in Table 1 was surface-treated in a nitrogen atmosphere at a temperature of 800°C, and thereafter 0.5 percent by weight of Y_2O_3 , serving as a sintering assistant was added to this material with addition of 0.2 percent by weight of an oxynitride of titanium ($Ti_3O_3N_2$) in terms of TiO_2 , so that the as-obtained powder was mixed in alcohol with a tumbling ball mill for 12 hours, as shown in Table 2. Thereafter 2 percent by weight of polyvinyl butyral was added as a binder to this mixed powder, which in turn was further sufficiently mixed and dried. The as-obtained powder was press-compacted under a pressure of at least 1.5 ton/cm². The as-obtained pressed compact was debindered at a temperature of 600°C for 2 hours, and then fired in a nitrogen atmosphere under a sintering temperature of 1800°C for 3 hours. The as-obtained aluminum nitride sintered body was subjected to measurement of density, a breakdown voltage, thermal conductivity, unpaired electron

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concentration, mechanical strength and an amount of titanium as solid solute in aluminum nitride crystal grains. The sintered body density was measured by an Archimedes' method, the thermal conductivity was measured by a laser flash method, the unpaired electron concentration was measured with an electron spin resonator, the mechanical strength was measured through JIS three-point bending strength, and the amount of titanium as solid solute was measured with EDX of TEM or AES, SIMS. Table 3 shows the results.

Examples 2 to 16

The aluminum nitride raw powder materials shown in Table 1 were treated at surface treatment temperatures shown in Table 2, and thereafter subjected to mixing with sintering assistants and press compacting, similarly to Example 1. The as-obtained pressed compacts were fired under sintering conditions shown in Table 2 by a method similar to that in Example 1, to prepare 15 types of aluminum nitride sintered bodies. Table 3 shows measurement values obtained as to these samples.

Example 17

Ti ions were implanted into the aluminum nitride raw material powder shown at A in Table 1, with energy of .4 MeV at about 10^{18} ions/cm². 0.5 percent by weight of Y₂O₃ was added to this powder and mixed in alcohol with a

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tumbling ball mill for 12 hours. Thereafter an aluminum nitride sintered body was obtained in a similar manner to Example 1. Table 3 also shows measurement values obtained as to this sample.

Table 1

Raw Material Powder	A	B	C
Total Oxygen Content (wt.%)	1.3	0.9	1.2
Carbon Content in Raw Material Powder (ppm)	300	230	500
Fe Content in Raw Material Powder (ppm)	<10	<10	<10
Si Content in Raw Material Powder (ppm)	9	50	82
Specific Surface Area of Raw Material Powder (m ² /g)	3.5	2.8	2.7
Mean Particle Size of Raw Material Powder (μm)	1.3	1.1	1.0

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Table 2

Example	Employed Raw Material Powder	Surface Treatment Temperature (°C)	Sintering Assistant (wt.%)	Ti Compound (wt.%, in terms of TiO_2)	Sintering Temperature (°C)	Sintering Time (hr.)
1	A	800	Y_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.2	1800	3
2	A	1000	Yb_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.5	1800	5
3	A	1200	CaO : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.5	1800	5
4	B	1200	Nd_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.5	1800	5
5	B	1300	Sm_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 0.5	1800	5
6	B	1000	Y_2O_3 : 0.5 CaO : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	3
7	B	1000	Yb_2O_3 : 0.5 CaO : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	5
8	C	1000	Y_2O_3 : 0.5 Nd_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	5
9	C	800	Yb_2O_3 : 0.5 Nd_2O_3 : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	5
10	C	1200	Nd_2O_3 : 0.5 CaO : 0.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.0	1650	3
11	C	1200	Y_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.5	1800	5
12	C	1400	Yb_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.5	1800	5
13	A	1300	Y_2O_3 : 1.5 Yb_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 1.5	1800	5
14	A	1200	Y_2O_3 : 1.5 Nd_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 2.0	1800	3
15	B	1200	Yb_2O_3 : 1.5 CaO : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 5.0	1500	5
16	B	1200	Yb_2O_3 : 1.5 Nd_2O_3 : 1.5	$\text{Ti}_3\text{O}_3\text{N}_2$: 3.0	1800	5
17	A		Y_2O_3 : 0.5	Ti Ion Implantation (10^{18} ions/cm ²)	1800	3

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Table 3

Example	Content of Ti as Solid Solute (ppm)	Break Down Voltage (kV/mm)	Density (g/cm ³)	Mechanical Strength (kg/mm ²)	Unpaired Electron Concentration (/g)	Thermal Conductivity (W/m·K)
1	60	31	3.27	48	2.7×10^{13}	170
2	100	41	3.27	45	6.0×10^{13}	169
3	780	47	3.26	48	1.5×10^{14}	160
4	480	46	3.27	42	1.0×10^{14}	152
5	220	41	3.27	47	9.0×10^{13}	150
6	440	40	3.27	41	7.9×10^{13}	190
7	650	52	3.28	43	1.6×10^{14}	170
8	170	35	3.28	45	5.5×10^{13}	165
9	440	44	3.27	42	1.1×10^{14}	155
10	920	50	3.28	45	1.6×10^{14}	155
11	320	44	3.27	48	7.8×10^{13}	230
12	110	39	3.27	43	4.9×10^{13}	200
13	800	52	3.28	41	1.1×10^{14}	234
14	650	48	3.28	46	1.0×10^{14}	178
15	50	35	3.12	40	3.2×10^{13}	150
16	80	39	3.28	45	3.5×10^{13}	217
17	80	32	3.27	40	2.1×10^{13}	165

It is clearly understood from Table 3 that unpaired electron concentration obtained from an electron spin resonance absorption spectrum exceeds $1 \times 10^{13}/g$ when the amount of Ti as solid solute is at least 50 ppm and not more than 1000 ppm in a weight ratio, and the aluminum nitride sintered body exhibits a high breakdown voltage. It is also understood that an aluminum nitride sintered body which has unpaired electron concentration of at least $1 \times 10^{13}/g$ and contains a compound of titanium within a

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range of 0.1 to 5.0 percent by weight in terms of TiO_2 has a high breakdown voltage.

As to the aluminum nitride sintered bodies obtained according to Examples 1, 2, 4 and 5, titanium compounds contained in the aluminum nitride crystal particles were examined through XRD (X-ray diffraction) or EDX. As the result, it was proved that the titanium compounds contained in the aluminum nitride sintered bodies were composed of Ti, Al, O and N, or Ti, Al, N, O, Ca, Mg and Si.

Comparative Example 1

Powder which was obtained by adding 1.0 percent by weight of Y_2O_3 , being in the form of fine particles for serving as a sintering assistant, to the aluminum nitride raw material powder shown at A in Table 1 was mixed in alcohol with a tumbling ball mill for 12 hours. Thereafter 2 percent by weight of polyvinyl butyral was added as a binder to this mixed powder, which in turn was further sufficiently mixed and dried. The as-obtained powder was press-compacted under a pressure of at least 1.5 ton/cm^2 . Thereafter the as-obtained pressed compact was debindered at a temperature of 600°C for 2 hours, and fired in a nitrogen atmosphere under a sintering temperature of 1800°C for 5 hours. The as-obtained aluminum nitride sintered body was subjected to

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measurement of density, a breakdown voltage, thermal conductivity, unpaired electron concentration, mechanical strength, and an amount of titanium as solid solute in aluminum nitride crystal grains. The sintered body density was measured by an Archimedes' method, the thermal conductivity was measured by a laser flash method, the unpaired electron concentration was measured with an electron spin resonator, the mechanical strength was measured through JIS three-point bending strength, and the amount of titanium was measured with EDX of TEM or AES, SIMS. Table 5 shows the results.

Comparative Examples 2 to 11

The aluminum nitride raw powder materials shown in Table 1 were surface-treated under conditions shown in Table 4, thereafter subjected to mixing, compacting and debinding in a method similar to that in comparative example 1, and then sintered under sintering conditions shown in Table 4. Table 5 shows measurement values obtained as to these samples of the aluminum nitride sintered bodies.

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Table 4

Comparative Example	Employed Raw Material Powder	Surface Treatment Temperature (°C)	Sintering Assistant (wt.%)	Ti Compound (wt.%, in terms of TiO_2)	Sintering Temperature (°C)	Sintering Time (hr.)
1	A	—	Y_2O_3 : 1.0	—	1800	5
2	A	1200	Y_2O_3 : 1.0	—	1800	5
3	A	1200	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 0.05	1800	5
4	A	1200	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 5.5	1800	5
5	A	1200	Y_2O_3 : 1.0	TiO_2 : 1.0	1800	5
6	A	—	Y_2O_3 : 1.0	TiO_2 : 1.0	1800	5
7	A	1200	Y_2O_3 : 1.0	TiN: 1.0	1800	5
8	A	—	Y_2O_3 : 1.0	TiN: 1.0	1800	5
9	A	—	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 1.0	1800	5
10	A	700	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 1.0	1800	5
11	A	1500	Y_2O_3 : 1.0	$\text{Ti}_3\text{O}_5\text{N}_2$: 1.0	1800	5

Table 5

Comparative Example	Content of Ti as Solid Solute (ppm)	Break Down Voltage (kV/mm)	Density (g/cm^3)	Mechanical Strength (kg/mm^2)	Unpaired Electron Concentration (/g)	Thermal Conductivity ($\text{W/m}^\circ\text{K}$)
1	< 10	15	3.27	32	4.0×10^{12}	137
2	< 10	18	3.26	35	9.1×10^{12}	140
3	< 10	15	3.27	30	9.6×10^{12}	149
4	< 30	17	3.28	36	6.0×10^{12}	139
5	< 30	18	3.28	34	7.5×10^{12}	142
6	< 30	14	3.28	38	9.5×10^{12}	138
7	< 30	15	3.27	33	8.1×10^{12}	141
8	< 30	18	3.27	31	7.6×10^{12}	142
9	< 30	15	3.27	34	6.5×10^{12}	140
10	< 30	12	3.27	31	5.9×10^{12}	137
11	< 30	14	3.27	36	4.1×10^{12}	139

From the results of Examples and comparative

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examples, it is understood that an aluminum nitride sintered body which has an amount of Ti as solid solute within a range of 50 to 1000 ppm in a weight ratio or unpaired electron concentration of at least $1 \times 10^{13}/\text{g}$ and contains an oxy-nitride of titanium and aluminum within a range of 0.1 to 5.0 percent by weight in terms of TiO_2 , has a breakdown voltage of at least 20 kV/mm.

Fig. 4 is a graph showing relations between breakdown voltages and unpaired electron concentration values obtained from the aforementioned results of Examples and comparative examples, in addition to the general relation between the breakdown voltage and the unpaired electron concentration shown in Fig. 1. It is understood from this figure that the values of the unpaired electron concentrations and the breakdown voltages of the inventive aluminum nitride sintered bodies are remarkably improved as compared with the conventional aluminum nitride sintered bodies. When the relations between the unpaired electron concentration values and the breakdown voltages are shown on a straight line to measure inclination of this straight line, it is understood that the prior art exhibits inclination of 1.0×10^{-14} while the inventive sintered body exhibits inclination of 1.3×10^{-13} , i.e., 13 times as compared with the prior art. In other words, it is possible to increase the unpaired electron

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concentration by one digit as well as to increase the breakdown voltage to twice at the maximum according to the present invention.

From the linear relations between the unpaired electron concentration values and the breakdown voltages, it is also recognized possible to confirm the breakdown voltage of the sintered body by a nondestructive test through measurement of unpaired electron concentration.

Although the present invention has been described and illustrated in detail, it is clearly 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 the present invention being limited only by the terms of the appended claims.

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CLAIMS

1. An aluminum nitride sintered body comprising aluminum nitride crystal grains, titanium being included as solid solute in said aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm, the unpaired electron concentration in said sintered body obtained from an absorption spectrum of electron spin resonance being at least $1 \times 10^{13}/g$.
- 2 An aluminum nitride sintered body in accordance with claim 1, containing an oxy-nitride of titanium and aluminum therein in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 .
3. An aluminum nitride sintered body in accordance with claim 2, wherein said oxy-nitride exists in said aluminum nitride sintered body in the form of grains, said grains being not more than 800 nm in diameter.
4. An aluminum nitride sintered body in accordance with claim 3, having thermal conductivity of at least 150 W/mK.
5. A method of preparing an aluminum nitride sintered body as defined in claim 1, comprising:
a step of preparing aluminum nitride powder;



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a step of nitriding said aluminum nitride powder in an atmosphere containing nitrogen at a temperature of at least 800°C and not more than 1400°C;

a step of adding a sintering assistant, and an oxy-nitride of titanium, being in a weight ratio of at least 0.1 % and not more than 5.0 % in terms of TiO_2 , to said nitrided aluminum nitride powder, thereby obtaining mixed powder;

a step of preparing a compact from said mixed powder; and

a step of firing said compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.

6. A method of preparing an aluminum nitride sintered body as defined in claim 1, comprising:

a step of preparing aluminum nitride powder;

a step of ion-implanting titanium into said aluminum nitride powder for making titanium exist in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm;

a step of adding a sintering assistant to said aluminum nitride powder containing titanium for obtaining mixed powder;

a step of preparing a compact from said mixed powder; and



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a step of firing said compact in an atmosphere containing nitrogen, thereby preparing an aluminum nitride sintered body.



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ALUMINUM NITRIDE SINTERED BODY AND METHOD
OF PREPARING THE SAME

ABSTRACT OF THE DISCLOSURE

Disclosed herein are an aluminum nitride sintered body having a high breakdown voltage for serving as a substrate material which is responsive to high integration of a circuit, and a method of preparing the same. The aluminum nitride sintered body contains titanium, which is included as solid solute in aluminum nitride crystal lattice in a weight ratio of at least 50 ppm and not more than 1000 ppm. Unpaired electron concentration in the sintered body obtained from an absorption spectrum of electron spin resonance is at least $1 \times 10^{13}/\text{g}$. At least 0.1 percent by weight and not more than 5.0 percent by weight of an oxy-nitride of titanium and aluminum exists in the aluminum nitride sintered body in terms of TiO_2 . The aluminum nitride sintered body has a breakdown voltage of 20 kV/mm. This aluminum nitride sintered body is obtained by nitriding aluminum nitride raw material powder in a nitrogen atmosphere at a temperature of 800 to 1400°C, adding an oxy-nitride of titanium thereto with a sintering assistant, and sintering the mixture.

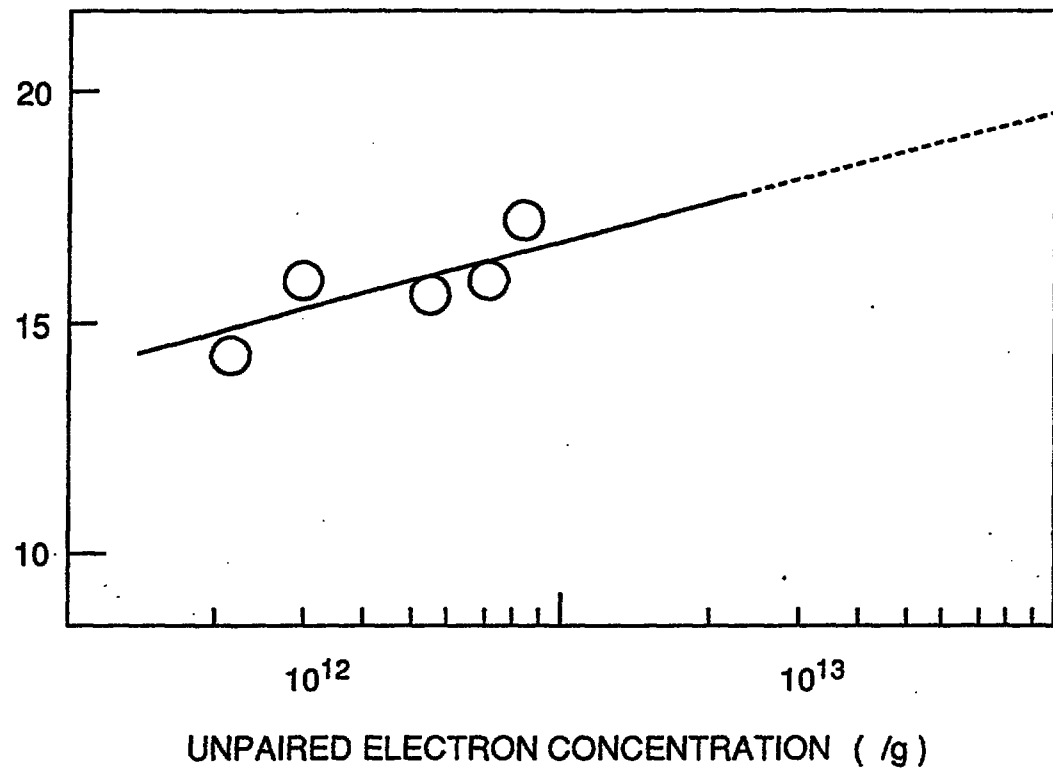
FIGURE 3A.

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FIG.1

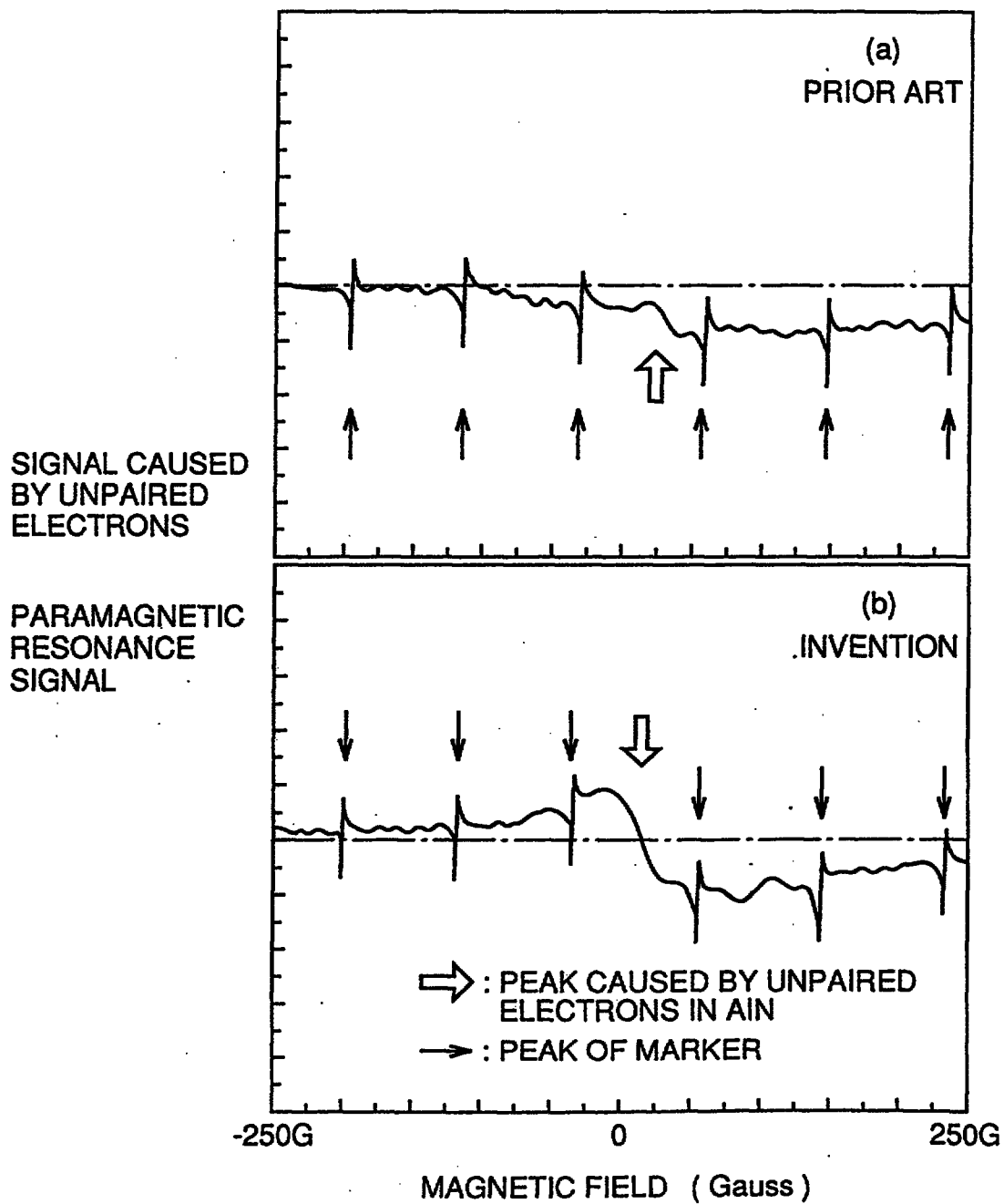
BREAKDOWN VOLTAGE
(KV/mm)



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FIG.2



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FIG.3A

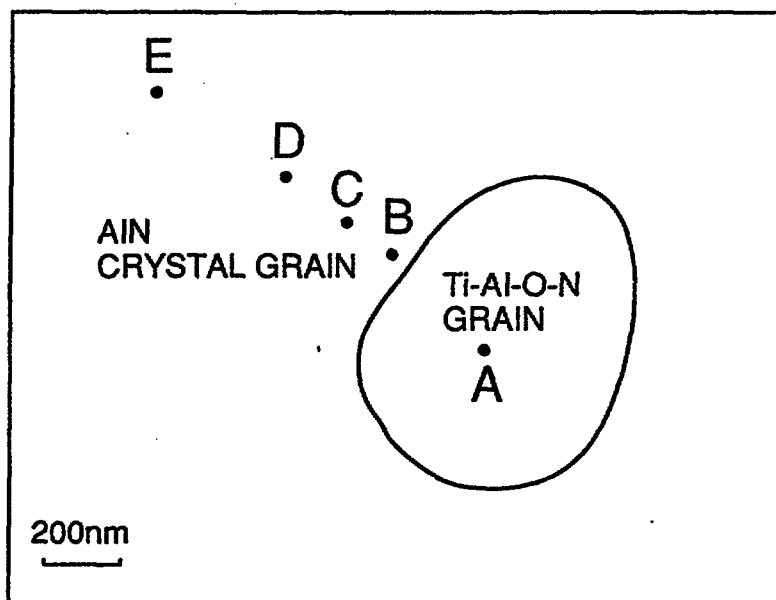
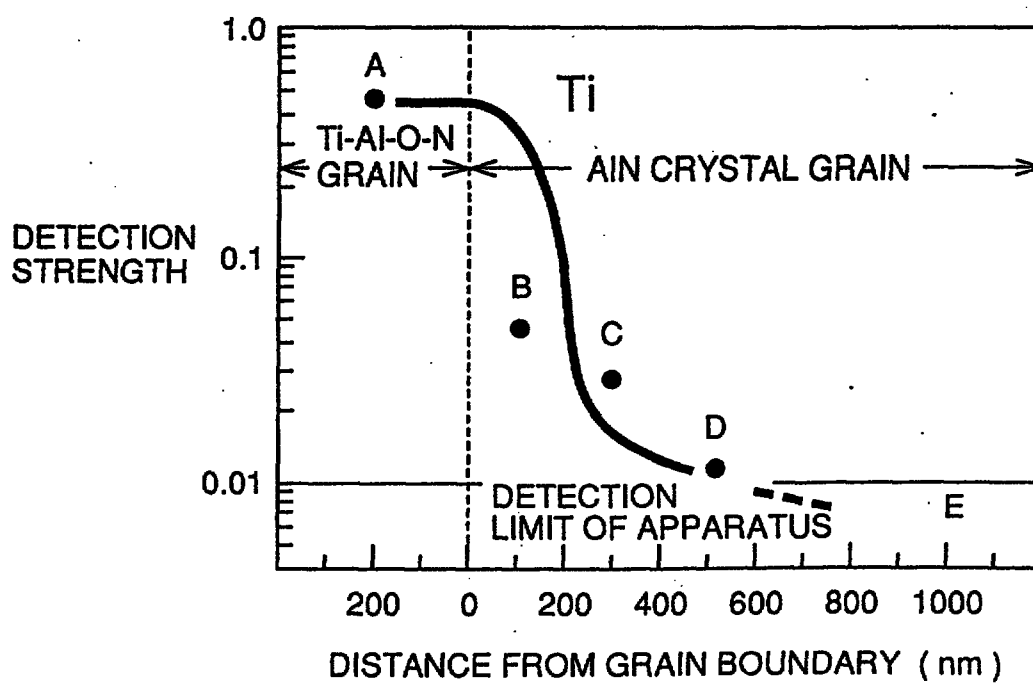


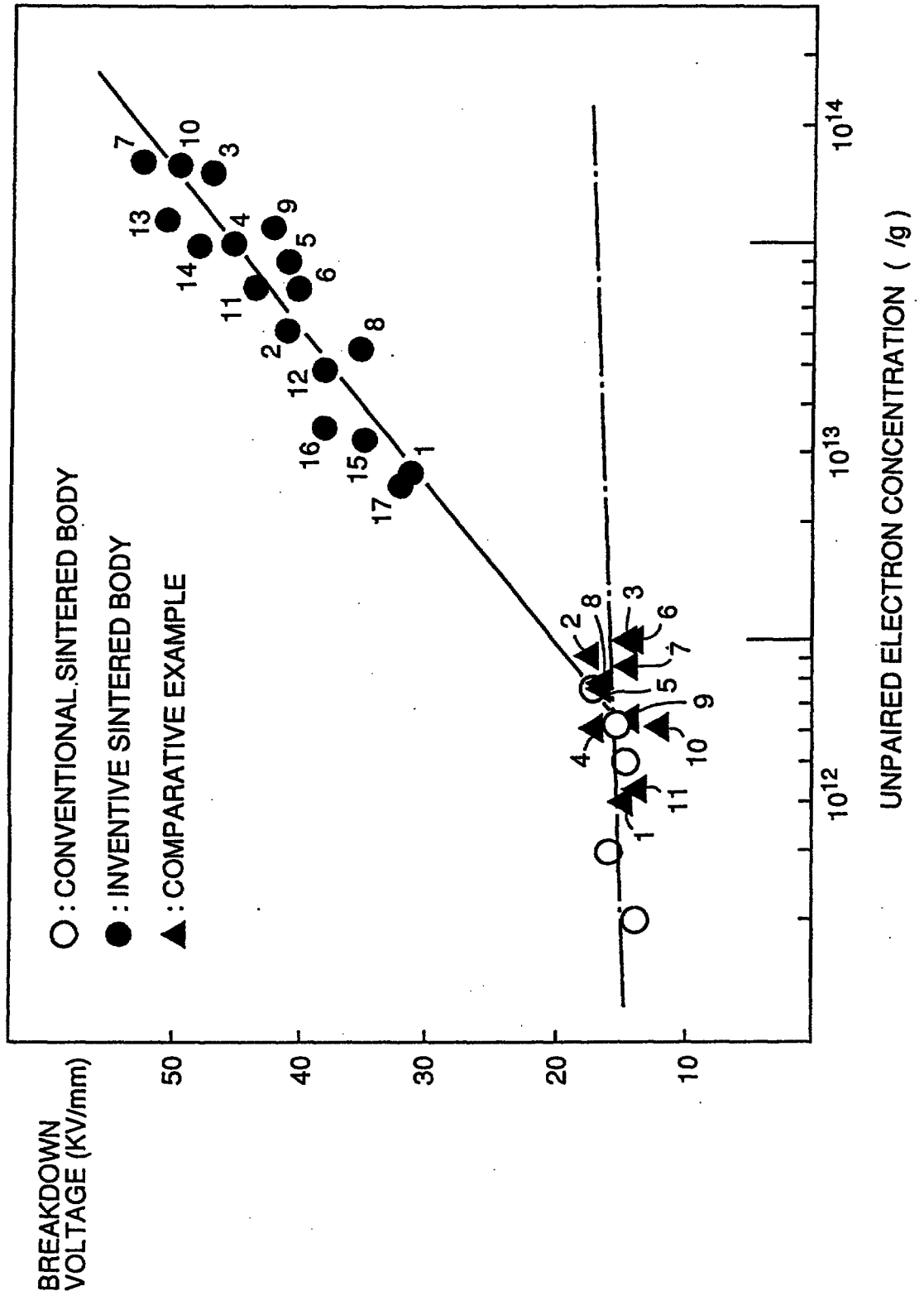
FIG.3B



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FIG.4



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