



(11) **EP 3 113 188 B9**

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see
Description Paragraph(s) 66

(51) Int Cl.:
H01B 3/10 ^(2006.01) **H01G 4/10** ^(2006.01)
C04B 35/495 ^(2006.01)

(48) Corrigendum issued on:
21.03.2018 Bulletin 2018/12

(45) Date of publication and mention
of the grant of the patent:
01.11.2017 Bulletin 2017/44

(21) Application number: **16176678.7**

(22) Date of filing: **28.06.2016**

(54) **DIELECTRIC COMPOSITION AND ELECTRONIC COMPONENT**

DIELEKTRISCHE ZUSAMMENSETZUNG UND ELEKTRONISCHES BAUTEIL

COMPOSITION DIÉLECTRIQUE ET COMPOSANT ÉLECTRONIQUE

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR

(30) Priority: **29.06.2015 JP 2015129687**

(43) Date of publication of application:
04.01.2017 Bulletin 2017/01

(73) Proprietor: **TDK Corporation**
Tokyo 108-0023 (JP)

(72) Inventors:
• **MASAOKA, Raitarou**
Minato-ku, Tokyo 108-0023 (JP)
• **UCHIYAMA, Hiroki**
Minato-ku, Tokyo 108-0023 (JP)
• **FUJII, Shohei**
Minato-ku, Tokyo 108-0023 (JP)

• **SHIROKAWA, Maiko**
Minato-ku, Tokyo 108-0023 (JP)

(74) Representative: **Epping - Hermann - Fischer**
Patentanwaltsgesellschaft mbH
Schloßschmidstraße 5
80639 München (DE)

(56) References cited:
EP-A1- 0 782 976 CN-A- 103 794 441
JP-A- H09 183 656 JP-A- S62 170 102
JP-A- S63 200 407

• **FRANCIS GALASSO ET AL: "Ordering in**
Compounds of the A(B' 0.33 Ta 0.67)O 3 Type",
INORGANIC CHEMISTRY, vol. 2, no. 3, 1 June
1963 (1963-06-01), pages 482-484, XP055313325,
EASTON, US ISSN: 0020-1669, DOI:
10.1021/ic50007a013

EP 3 113 188 B9

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to a dielectric composition and an electronic component.

5 **BACKGROUND**

[0002] The MIMO (Multi-Input Multi-Output) technique which simultaneously utilizes a plurality of frequency bands has been put into use so as to provide a communication with a higher speed and a larger capacity in mobile communicating equipment which is represented by a smart phone or a tablet. Each frequency band needs a RF component. If the frequency bands for communication are increased in number, each component needs to be further downsized and provided with more functions to maintain the original size of the equipment where increased components are disposed.

[0003] Such an electronic component working at a high frequency can be, for example, a diplexer, a band-pass filter or the like. All of these components contain the combination of dielectric material(s) functioning as capacitor and magnetic material(s) functioning as inductor. In order to provide good high-frequency characteristics, each kinds of loss at a high-frequency region are required to be suppressed.

[0004] The requirements for the dielectric material are as follows. (1) According to the requirements for downsizing, the relative permittivity (ϵ_r) is required to be high in order to decrease the area of the capacitor. (2) The dielectric loss is required to be low, i.e., the Q value is required to be high in order to obtain a good selectivity in frequencies. (3) The breakdown voltage is required to be high.

[0005] For example, as the representative material having a low dielectric loss in the GHz band, the amorphous film of SiNx can be mentioned. However, its relative permittivity (ϵ_r) is as low as 6.5, so a large area is needed to provide the target functions. In this respect, it is hard to meet the downsizing requirements.

[0006] In Patent Document 1, a technique involving $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ which is a kind of material with a low dielectric loss (i.e., a high Q value) has been disclosed. This kind of material is a condensed sintered compact obtained by a thermal treatment at a temperature of 1500°C or higher, and its relative permittivity (ϵ_r) at 10 GHz is 24.7 and the Q value is 51000. Similar compounds are also disclosed in Patent Document 2.

[0007] In addition, it has been disclosed in Non-Patent Document 1 that $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ is subjected to depositing film by the PLD method (i.e., pulsed laser deposition method) and then crystallized via a thermal treatment at 600°C so as to provide a relative permittivity (ϵ_r) of 33.3 at 2.66 GHz and a $\tan\delta$ of 0.0158 (the value is 63.3 when calculated in terms of Q value).

Non-Patent Document

[0008] Non-Patent Document 1: Jpn. J. Appl. Phys. vol. 42(2003) pp. 7428-7431 "Properties of $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ Thin Films Prepared by Pulsed-Laser Deposition"

Patent Documents

[0009]

Patent Document 1: JP-A-H8-319162

Patent Document 2: EP 0 782 976 A

45 **SUMMARY**

[0010] However, the technique in Patent Document 1 is about a sintered compact. Besides, sufficient volume is required in order to achieve the dielectric properties, and thus it will be much too large in size if the material is to be used in the electronic component working at a high frequency. On the other hand, it can be known that if $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ in Patent Document 1 is prepared as a film to downsize the component, such a high Q value will be hardly obtained as that in the conventional sintered compact. Further, as for the technique in Non-Patent Document 1, although a relative permittivity (ϵ_r) of 33.3 and a Q value of 63.3 can be obtained when the material is formed as a film, a higher Q value is expected for the electronic component working at a high frequency.

[0011] In addition, anything about the breakdown voltage is not mentioned in Patent Documents 1 and 2 and Non-Patent Document 1.

[0012] The present invention has been completed in view of the actual conditions mentioned above. The present invention aims to provide a dielectric composition with a high relative permittivity, a low dielectric loss (i.e., a high Q value), and further a high breakdown voltage even when used in a downsized component and also an electronic com-

ponent using the dielectric composition.

[0013] In order to achieve the mentioned aim, the dielectric composition according to the present invention is characterized in that it comprises a complex oxide represented by the formula of $x\text{AO}-y\text{BO}-z\text{C}_2\text{O}_5$ (wherein A represents at least one element selected from the group consisting of Ba, Ca and Sr, B represents Mg, and C represents at least one element selected from the group consisting of Nb and Ta) as the main component, wherein x, y and z meet the following conditions, $x+y+z=1.000$, $0.000<x\leq 0.281$, $0.625\leq y<1.000$ and $0.000<z\leq 0.375$.

[0014] When x, y and z fall within the mentioned ranges, a dielectric composition can be obtained with a high relative permittivity, a high Q value and further a high breakdown voltage.

[0015] Further, compared to the use of a conventional dielectric composition in an electronic component working at a high frequency, the use of the dielectric composition of the present invention provides an electronic component such as a dielectric resonator or a dielectric filter with a sufficiently high relative permittivity, a high Q value (i.e., a high S/N ratio), and further a high breakdown voltage even when the component is downsized.

[0016] The present invention is capable of providing a dielectric composition having a high relative permittivity, a low dielectric loss (i.e., a high Q value), and further a high breakdown voltage even when it is downsized. Also, an electronic component using the dielectric composition can be provided in the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

Figure 1 is a cross-sectional view of a film capacitor in one embodiment of the present invention.

Figure 2 is a picture taken by an SEM (i.e., scanning electron microscope) showing the surface of the dielectric composition (in Example 1) according to one embodiment of the present invention where the dielectric composition is film-deposited by heating the substrate to 200°C.

DETAILED DESCRIPTION OF EMBODIMENTS

[0018] Hereinafter, the preferable embodiments of the present invention will be described with reference to the drawings based on different cases.

(Film capacitor 10)

[0019] Figure 1 is a cross-sectional view of film capacitor 10 as an example of the electronic component using the dielectric composition in one embodiment of the present invention. Film capacitor 10 is provided with lower electrode 3, upper electrode 4 and dielectric film 5 disposed between lower electrode 3 and upper electrode 4, which three are laminated on the surface of supporting substrate 1. Foundation layer 2 is provided between supporting substrate 1 and lower electrode 3 to enhance the adhesion between them. Supporting substrate 1 guarantees the whole mechanical strength of film capacitor 10.

[0020] The shape of the film capacitor is not particularly restricted and is usually cuboid. Further, its size is not particularly restricted. The thickness or the length can be appropriately set in accordance with specific uses.

(Supporting substrate 1)

[0021] There is no particular restriction on the material for forming supporting substrate 1 as shown in Figure 1. For example, single crystals such as single crystalline Si, single crystalline SiGe, single crystalline GaAs, single crystalline InP, single crystalline SrTiO₃, single crystalline MgO, single crystalline LaAlO₃, single crystalline ZrO₂, single crystalline MgAl₂O₄ and single crystalline NdGaO₃, or ceramic polycrystalline substrate such as polycrystalline Al₂O₃, polycrystalline ZnO and polycrystalline SiO₂, or substrate of metals such as Ni, Cu, Ti, W, Mo, Al, Pt or the like or the alloys thereof can form supporting substrate 1, but there is no particular restriction. Among these materials, the single crystalline Si is usually used as the substrate from the viewpoint of the low cost and good processabilities. The resistivity of supporting substrate 1 varies depending on the material of the substrate. When a material having a low resistivity is used as the substrate, the leakage of the current flowing towards the substrate side will affect the electric properties of film capacitor 10 if such a substrate is directly used. Thus, sometimes an insulating treatment can be performed on the surface of supporting substrate 1 so as to prevent the current in use from flowing to supporting substrate 1. For example, when the single crystalline Si is used as supporting substrate 1, the surface of supporting substrate 1 can be oxidized to form an insulating layer of SiO₂. Alternatively, insulating materials such as Al₂O₃, SiO₂, Si₃N_x or the like can be formed on the surface of supporting substrate 1. The material for the insulating layer or the film thickness is not restricted as long

as supporting substrate 1 can be kept to be insulated. However, the film thickness is preferred to be 0.01 μm or more. A thickness less than 0.01 μm cannot ensure the insulation and thus is not preferred as the thickness of the insulating layer. There is no particular restriction on the thickness of the supporting substrate 1 as long as the mechanical strength of the whole film capacitor can be ensured. For example, the thickness can be set to be 10 μm to 5000 μm . When the thickness is thinner than 10 μm , the mechanical strength may not be ensured. On the other hand, if the thickness is thicker than 5000 μm , a problem may be caused that it cannot contribute to the downsizing of the electronic component.

(Foundation layer 2)

[0022] In the present embodiment, film capacitor 10 shown in Figure 1 preferably has foundation layer 2 on the surface of supporting substrate 1 which has been provided with an insulating treatment. Foundation layer 2 is inserted to enhance the adhesion between supporting substrate 1 and lower electrode 3. As an example, Cr is usually inserted as foundation layer 2 when Cu is used in lower electrode 3 and Ti is usually inserted as foundation layer 2 when Pt is used as lower electrode 3.

[0023] Foundation layer 2 is not restricted to these materials because the purpose is to improve the adhesion. In addition, foundation layer 2 can be omitted if the adhesion between supporting substrate 1 and lower electrode 3 can be guaranteed.

(Lower electrode 3)

[0024] The material for forming lower electrode 3 is not particularly restricted as long as it is conductive. For instance, lower electrode 3 can be formed by metals such as Pt, Ru, Rh, Pd, Ir, Au, Ag, Cu, Ni and the like or the alloys thereof or the conductive oxides thereof. In this respect, a material can be selected in accordance with the cost or the atmosphere during the thermal treatment for dielectric layer 4. In addition to air, the thermal treatment for dielectric layer 4 can also be carried out in an inert gas such as N_2 or Ar or a mixed gas of an inert gas and an oxidative gas O_2 , or a mixed gas of an inert gas and a reductive gas H_2 . The film thickness of lower electrode 3 is not particularly restricted as long as lower electrode 3 can function as an electrode. Further, the thickness is preferred to be 0.01 μm or more. A thickness less than 0.01 μm is not preferable because the conductivity will deteriorate in that case. In addition, when a substrate composed of Cu, Ni, Pt or the like or a conductive oxide material is used as supporting substrate 1, foundation layer 2 and lower electrode 3 mentioned above can be omitted, wherein, Cu, Ni, Pt or the like or a conductive oxide material can be used as an electrode.

[0025] A thermal treatment can be provided after the formation of the lower electrode 3 so as to improve the adhesion between foundation layer 2 and lower electrode 3 and also to improve the stability of lower electrode 3. When the thermal treatment is performed, the heating rate is preferably $10^\circ\text{C}/\text{min}$ to $2000^\circ\text{C}/\text{min}$, and more preferably $100^\circ\text{C}/\text{min}$ to $1000^\circ\text{C}/\text{min}$. The holding temperature during the thermal treatment is preferably 400°C to 800°C , and the holding time is preferred to be 0.1 hour to 4.0 hours. If any parameter goes beyond the ranges mentioned above, the adhesion will not be good and the surface of lower electrode 3 will be uneven so that the dielectric properties of dielectric film 5 is likely to deteriorate.

(Dielectric film 5)

[0026] The dielectric composition for forming dielectric film 5 comprises a complex oxide represented by the formula of $x\text{AO}-y\text{BO}-z\text{C}_2\text{O}_5$ (A represents at least one element selected from the group consisting of Ba, Ca and Sr, B represents Mg, and C represents at least one element selected from the group consisting of Nb and Ta) as the main component.

[0027] Further, when the main component of the dielectric composition is represented as $x\text{AO}-y\text{BO}-z\text{C}_2\text{O}_5$, x, y and z will meet the following conditions. That is, $x+y+z=1.000$, $0.000<x\leq 0.281$, $0.625\leq y<1.000$ and $0.000<z\leq 0.375$.

[0028] The inventors of the present invention consider the main reason for achieving the effects of maintaining the high Q value together with improving the relative permittivity compared to the pure MgO is as follows. In general, it is known that MgO with good crystal symmetry has a high Q value, but sufficient dielectric polarization cannot be obtained due to the symmetry, and thus a high relative permittivity cannot be obtained. When the elements represented by the A and the C are added, a part of MgO will turn into perovskite type $\text{A}^{2+}(\text{B}^{2+}_{1/3}\text{B}^{5+}_{2/3})\text{O}_3$. Thus, A high Q value can be maintained and the relative permittivity can be improved compared to the pure MgO.

[0029] In addition, it is considered that the difference of the energy level between the outermost atomic orbital of 2p-orbital in O and that of 3s-orbital in Mg is large, so the excitation of the electron will be hard to arise by containing a lot of MgO. Thus, the effect of preventing electron avalanche (which is the representative breaking mode) from easily happening will be enhanced, and the breakdown voltage will be increased.

[0030] When x is more than 0.281, excessive BaO will react with H_2O or CO_2 in the air to produce $\text{Ba}(\text{OH})_2$ or BaCO_3 , and thus no sufficient Q value can be obtained. If y is less than 0.625, no sufficient Q value can be obtained. If z is higher

than 0.375, the excessive Ta_2O_5 will easily produce the oxygen vacancy and turn the composition semi-conductive. Also, the dielectric loss tends to increase, i.e., the Q value tends to decrease. If the range of x, y and z meet the following conditions, a high relative permittivity, a high Q value and a high breakdown voltage can be provided. In particular, the conditions are $x+y+z=1.000$, $0.000<x\leq 0.281$, $0.625\leq y<1.000$ and $0.000<z\leq 0.375$.

[0031] Further, in the formula mentioned above, x, y and z preferably meet the conditions, i.e., $x+y+z=1.000$, $0.000<x\leq 0.281$, $0.625\leq y<1.000$ and $0.000<z\leq 0.125$.

[0032] When x, y and z fall within the ranges mentioned above, a part of MgO turns into perovskite type $A^{2+}(B^{2+}_{1/3}B^{5+}_{2/3})O_3$. Besides, the effects of maintaining the high breakdown voltage and obtaining a higher Q value can be easily provided by containing more MgO which has high bandgap energy.

[0033] A represents at least one element selected from the group consisting of Ba, Ca and Sr. The same effect will be produced no matter only one element or several elements from Ba, Ca and Sr are used. In addition, B represents Mg, and C represents at least one element selected from the group consisting of Nb and Ta. With respect to C, the same effect will be produced no matter only one element from Nb and Ta or both elements are used.

[0034] The thickness of the dielectric film 5 is preferably 10 nm to 2000 nm, and more preferably 50 nm to 1000 nm. If the thickness is less than 10 nm, the dielectric breakdown is likely to happen. When the thickness exceeds 2000 nm, the area of the electrode needs to be broadened so as to enlarge the electrostatic capacity of the capacitor, and it may be hard to downsize depending on the designs of the electronic component. In the measurement of the thickness of the dielectric film, the dielectric film can be milled by a processing device involving FIB (focused ion beam), and then the obtained cross-section is observed by an SIM (scanning ion microscope) to measure the thickness.

[0035] Dielectric film 5 is preferably formed by various deposition methods such as vacuum evaporation, sputtering, PLD, MO-CVD (Metal-organic chemical vapor deposition), MOD (Metal organic decomposition) or Sol-Gel, CSD (Chemical solution deposition) or the like. At that time, a trace of impurities or subcomponents may be contained in the starting material in use (i.e., the deposition material, various target materials, organometallic material and etc.), but no particular problem will arise as long as they are not impurities which will significantly deteriorate the insulation properties.

[0036] Further, a trace of impurities or subcomponents may be contained in the dielectric composition as long as they are not matters which will significantly deteriorate the dielectric properties (i.e., the relative permittivity, the Q value, or the breakdown voltage). Thus, the amount of the main component as the balance is not particularly restricted. For example, the amount of the main component is 50mol% or more and 100mol% or less relative to the whole dielectric composition comprising the main component.

[0037] In addition, the dielectric film 5 is usually only composed of the dielectric composition of the present invention, but it can also be a laminated structure in combination with films made of other dielectric compositions. For example, by making into a laminated structure with the conventional amorphous dielectric films or the crystalline films such as Si_3N_x , SiO_x , Al_2O_x , ZrO_x , Ta_2O_x or the like, the impedance of the dielectric film 5 or the temperature dependence of relative permittivity can be adjusted.

(Upper electrode 4)

[0038] In one example of the present embodiment, film capacitor 10 is provided with upper electrode 4 on the surface of dielectric film 5, wherein upper electrode 4 functions as another electrode in film capacitor 10. The material for forming upper electrode 4 is not particularly restricted as long as it is conductive. Upper electrode 4 can be formed by the same material as that for lower electrode 3. Also, the film thickness of upper electrode 4 is not particularly restricted as long as the function as an electrode can be exerted, and the thickness is preferred to be 10 nm or more. A film thickness of 10 nm or less is not preferable for upper electrode 4 because the conductivity will deteriorate in that case.

[0039] In the embodiment mentioned above, a film capacitor is presented as an example of the electronic component using the dielectric composition according to one embodiment of the present invention. However, the electronic component using the dielectric composition of the present invention is not limited to the film capacitor and also can be any electronic component having a dielectric film such as a diplexer, a band-pass filter, a balun or a coupler.

Examples

[0040] Hereinafter, the present invention will be further described based on detailed examples, but the present invention is not limited to these examples.

(Example 1) (Comparative Example 1)

[0041] First of all, a Ti film as the foundation layer with a thickness of 20 nm was deposited by a sputtering method on the surface of a square supporting substrate of 10 mm × 10 mm with a thickness of 350 μm, wherein, the supporting substrate had a SiO_2 insulating film with a thickness of 6 μm on the surface of Si.

[0042] Next, a Pt film as the lower electrode with a thickness of 100 nm was deposited by sputtering method on the deposited Ti film mentioned above.

[0043] The formed Ti/Pt film was provided with a thermal treatment at the ordinary pressure under oxygen atmosphere with a heating rate of 400°C/min and a holding temperature of 700°C for 30 minutes.

[0044] The PLD method was used in the formation of the dielectric film. The targets necessary in the formation of the dielectric film were prepared as follow.

[0045] First, MgO and Ta₂O₅ were weighed to get the amounts of Mg and Ta in Sample No. 1 to Sample No. 9 and Sample No.11 to Sample No.14 as shown in Table 1. The weighed starting powders together with water and ZrO₂ beads of φ2 mm were put into a wide-mouth poly-pot of 1L and then subjected to wet mixing for 20 hours. Then, the slurry of the mixed powder was dried at 100°C for 20 hours. The obtained mixed powder was put into a crucible made of Al₂O₃ and the first calcination was performed in air at 1250°C for 5 hours to provide the MgO-Ta₂O₅ calcined powder.

[0046] Thereafter, the obtained MgO-Ta₂O₅ calcined powder and BaCO₃ were weighed to get the ratios of Sample No.1 to Sample No.14 as shown in Table 1. The weighed starting powders together with water and ZrO₂ beads of φ2 mm were put into a wide-mouth poly-pot of 1L and then subjected to wet mixing for 20 hours. Then, the slurry of the mixed powder was dried at 100°C for 20 hours. The obtained mixed powder was put into a crucible made of Al₂O₃ and the second calcination was performed in air at 1050°C for 5 hours to provide the BaO-MgO-Ta₂O₅ calcined powder.

[0047] The BaO-Ta₂O₅ based compound without Mg inhibited the generation of the target product of BaO-MgO-Ta₂O₅. However, with such calcination in two steps, BaO-Ta₂O₅ based compound was prevented from generating.

[0048] The resultant calcined powder was put into a mortar, and an aqueous solution of PVA (i.e., polyvinyl alcohol) with a concentration of 6 wt% was added as a binder in an amount of 4 wt% relative to the calcined powder. A pestle was used to prepare granulated powder, and then the granulated powder was added into a mold of φ20 mm to provide a thickness of about 5 mm. Then, a molded body was obtained by using a uniaxial pressing machine at room temperature under a pressure of 2.0×10⁸ Pa.

[0049] After that, a de-binder treatment was provided to the resultant molded body under atmospheric air with a heating rate of 100°C/hour and a holding temperature of 400°C for 4 hours. Then, a sintering process was performed under atmospheric air with a heating rate of 200°C/hour and a holding temperature of 1600°C to 1700°C for 12 hours.

[0050] Next, the obtained sintered compact was ground on both surfaces by using a cylindrical grinding machine until the thickness became 4 mm, so the target for PLD necessary in the deposition of the dielectric film was prepared.

[0051] Thus prepared target for PLD was used in the PLD method to form a dielectric film with a thickness of 400 nm on the lower electrode. During the film-depositing using the PLD method, the oxygen pressure was controlled to be 1×10⁻¹ Pa and the substrate was heated to 200°C. In addition, in order to expose part of the lower electrode, a metal mask was used to form an area where no dielectric film was deposited. The dielectric film was provided with an annealing treatment at 600°C in the O₂ atmosphere for 1 hour.

[0052] In the measurement of the thickness of the dielectric film, the dielectric film was milled by FIB and then the resultant cross-section was observed by SIM to measure the thickness.

[0053] After deposition, the composition of the dielectric film was analyzed in all samples by the following method. It had been confirmed that the composition was identical to that described in Table 1.

(Composition analysis)

[0054] The composition analysis was carried out by using a wavelength dispersive X-ray fluorescence spectrometry (ZSX-100e produced by Rigaku Corporation) at the room temperature.

[0055] Thereafter, a vapor deposition apparatus was used to deposit an Ag film as the upper electrode on the obtained dielectric film. The upper electrode was formed to have a diameter of 100 μm and a thickness of 100 nm with the use of a metal mask, providing Sample No.1 to Sample No.14 with the structure shown in Figure 1.

[0056] As for all the obtained film capacitor samples, the relative permittivity, the Q value and the breakdown voltage were respectively measured by the following methods.

(Relative permittivity (ε_r) and Q value)

[0057] The relative permittivity (ε_r) and the Q value (no unit for both) of the film capacitor samples were calculated based on the results from the measurement of the electrostatic capacity and film thickness under a frequency of 2GHz and an input signal level (measuring voltage) of 0.5 Vrms at a reference temperature of 25°C using an RF impedance/material analyzer (4991A produced by Agilent Technologies). It was preferred to have a higher relative permittivity. A relative permittivity of 10 or more was deemed as a good result. Further, the Q value was preferred to be higher and a value of 650 or more was deemed as a good result.

EP 3 113 188 B9

(Breakdown voltage (Vbd))

[0058] As for the film capacitor samples, a digital ultra-high resistance / micro current meters (ADVANTEST R8340) was connected with the exposed area of the lower electrode and also the upper electrode. A voltage was applied in a step of 5V/second to perform the measurement, and the voltage value was read when the resistance value dropped by double digits from the initial resistance value. The value was regarded as the breakdown voltage value (the unit was V) of the sample. The value obtained by dividing the breakdown voltage value (the unit was V) by the thickness of the dielectric film was deemed as the breakdown voltage (kV/ μm) and was shown in Table 1. The breakdown voltage was preferred to be higher and a value of 0.5 kV/ μm or more was deemed as a good result.

5

10

15

20

25

30

35

40

45

50

55

5
10
15
20
25
30
35
40
45
50
55

[Table 1]

Sample No.	AO			BO		C ₂ O ₅			Relative permittivity (-)	Q value (-)	Breakdown voltage (kV/μm)
	Ba	Ca	Sr	Mg	Y	Nb	Ta	Z			
	x			y			z				
Example 1	1	0.281	0.000	0.000	0.714	0.000	0.005	0.005	19	851	0.7
	2	0.281	0.000	0.000	0.625	0.000	0.094	0.094	20	870	0.6
	3	0.198	0.000	0.000	0.625	0.000	0.177	0.177	21	748	0.6
	4	0.100	0.000	0.000	0.625	0.000	0.275	0.275	21	689	0.5
	5	0.005	0.000	0.000	0.625	0.000	0.370	0.370	22	659	0.5
	6	0.198	0.000	0.000	0.807	0.000	0.005	0.005	14	983	0.8
	7	0.005	0.000	0.000	0.807	0.000	0.188	0.188	16	703	0.8
	8	0.005	0.000	0.000	0.990	0.000	0.005	0.005	15	1527	0.9
	9	0.125	0.000	0.000	0.750	0.000	0.125	0.125	17	1249	1.1
	10	0.375	0.000	0.000	0.625	0.000	0.000	0.000		Immeasurable	
	11	0.333	0.000	0.000	0.556	0.000	0.111	0.111	20	868	0.3
	12	0.222	0.000	0.000	0.556	0.000	0.222	0.222	21	653	0.3
	13	0.111	0.000	0.000	0.556	0.000	0.333	0.333	23	639	0.2
	14	0.000	0.000	0.000	0.556	0.000	0.444	0.444	27	612	0.1
Comparative Example 1											

Sample No.1 to Sample No. 9

[0059] Similar to the sample shown in Figure 2, no defect such as crack was found on the surface in Sample No. 1 to Sample No. 9. According to Table 1, it was confirmed that Sample No. 1 to Sample No. 9 were dielectric compositions with BaO-MgO-Ta₂O₅ as the main component where the main component of the dielectric composition was represented by xBaO-yMgO-zTa₂O₅ and x, y and z met the conditions of x+y+z=1.000, 0.000<x≤0.281, 0.625≤y<1.000 and 0.000<z≤0.375, and the samples had a relative permittivity of 10 or more, a Q value of 650 or more and a breakdown voltage of 0.5 kV/μm or more.

Sample No.1, Sample No. 2, Sample No.6, Sample No.8 and Sample No.9

[0060] According to Table 1, it was confirmed that Sample No. 1, Sample No. 2, Sample No.6, Sample No.8 and Sample No.9 where the main component of the dielectric film was represented by xBaO-yMgO-zTa₂O₅ and x, y and z met the conditions (i.e., x+y+z=1.000, 0.000<x≤0.281, 0.625≤y<1.000 and 0.000<z≤0.125) had a relative permittivity of 10 or more and a Q value of 850 or more and a breakdown voltage of 0.5 kV/μm or more. Thus, it could be confirmed that the relative permittivity and the breakdown voltage could be maintained and the Q value could be further increased by defining the range of z.

Sample No.10 to Sample No.14

[0061] The dielectric properties of Sample No. 10 with x>0.281 could not be evaluated due to crack. In Sample No. 11 to Sample No. 14, no defect such as crack was found on the surface as similar as the sample shown in Figure 2. It was confirmed that Sample No. 11 to Sample No. 14 with y<0.625 had a breakdown voltage of less than 0.5 KV/μm.

(Example 2)

[0062] BaCO₃, CaCO₃, SrCO₃, MgO and Ta₂O₅ were weighed to get the amounts of Ba, Ca, Sr, Mg and Ta listed in Table 2. A calcined powder of MgO-Ta₂O₅ was obtained in the first calcination. Calcined powders of CaO-MgO-Ta₂O₅ (in Sample No.15), SrO-MgO-Ta₂O₅ (in Sample No.16), (Ba-Ca)O-MgO-Ta₂O₅ (in Sample No.17), (Ca-Sr)O-MgO-Ta₂O₅ (in Sample No.18), (Sr-Ba)O-MgO-Ta₂O₅ (in Sample No.19) and (Ba-Ca-Sr)O-MgO-Ta₂O₅ (in Sample No.20) were respectively obtained in the second calcination. Targets were prepared in the same way as in Example 1 except the compositions were different, and film capacitors of Sample No.15 to Sample No.20 were respectively prepared. The results from the same evaluations as in Example 1 were shown in Table 2.

5
10
15
20
25
30
35
40
45
50
55

[Table 2]

	Sample No.	AO			BO		C ₂ O ₅			Relative permittivity (-)	Q value (-)	Breakdown voltage (kV/ μ m)
		Ba	Ca	Sr	Mg	Nb	Ta	Z				
		x			Y							
Example 1	9	0.125	0.000	0.000	0.750	0.000	0.125	17	1249	1.1		
Example 2	15	0.000	0.125	0.000	0.750	0.000	0.125	14	1267	1.2		
	16	0.000	0.000	0.125	0.750	0.000	0.125	11	1321	1.1		
	17	0.063	0.063	0.000	0.750	0.000	0.125	16	1258	1.2		
	18	0.000	0.063	0.063	0.750	0.000	0.125	13	1294	1.2		
	19	0.063	0.000	0.063	0.750	0.000	0.125	14	1285	1.1		
	20	0.042	0.042	0.042	0.750	0.000	0.125	14	1279	1.2		

Sample No.9, Sample No.15 to Sample No.20

5 **[0063]** Similar to the sample shown in Figure 2, no defect such as crack was found on the surface in Sample No.15 to Sample No.20. According to Table 2, Sample No.9 and Sample No.15 to Sample No.20 exhibited almost the same properties, wherein, in these samples AO-MgO-Ta₂O₅ was contained in the dielectric composition as the main component and A contained at least one selected from the group consisting of Ba, Ca and Sr. Besides, it was confirmed that Sample No.9 and Sample No.15 to Sample No.20 had a relative permittivity of 10 or more, a Q value of 650 or more and a breakdown voltage of 0.5 kV/μm or more.

10 (Example 3)

15 **[0064]** BaCO₃, MgO, Ta₂O₅ and Nb₂O₅ were weighed to get the amounts of Ba, Mg, Ta and Nb listed in Table 3. Calcined powders of MgO-Nb₂O₅ (in Sample No.21), and MgO-(Ta-Nb)₂O₅ (in Sample No.22) were obtained in the first calcination respectively. And calcined powders of BaO-MgO-Nb₂O₅ (in Sample No.21), and BaO-MgO-(Ta-Nb)₂O₅ (in Sample No.22) were obtained in the second calcination respectively. Targets were prepared in the same way as in Example 1 except the compositions were different, and film capacitor samples of Sample No.21 and Sample No.22 were respectively prepared. The results from the same evaluations as in Example 1 were shown in Table 3.

20

25

30

35

40

45

50

55

5
10
15
20
25
30
35
40
45
50
55

(Table 3)

	Sample No.	AO			BO		C ₂ O ₅			Relative permittivity (-)	Q value (-)	Breakdown voltage (kV/ μ m)
		Ba	Ca	Sr	Mg	Nb	Ta	Z				
		x			Y							
Example 1	9	0.125	0.000	0.000	0.750	0.000	0.125	17	1249	1.1		
Example 3	21	0.125	0.000	0.000	0.750	0.125	0.000	18	1192	1.0		
	22	0.125	0.000	0.000	0.750	0.063	0.063	18	1221	1.1		

Sample No.9, Sample No.21 and Sample No.22

5 **[0065]** Similar to the sample shown in Figure 2, no defect such as crack was found on the surface in Sample No.21 and Sample No.22. According to Table 3, it was confirmed that Sample No.9, Sample No.21 and Sample No.22 exhibited almost the same properties, wherein, in these samples, the dielectric composition contained BaO-MgO-C₂O₅ as the main component and C contained at least one selected from the group consisting of Nb and Ta. Besides, it was confirmed that Sample No.9, Sample No.21 and Sample No.22 had a relative permittivity of 10 or more, a Q value of 650 or more and a breakdown voltage of 0.5 kV/ μ m or more,.

10 (Example 4)

15 **[0066]** BaCO₃, CaCO₃, SrCO₃, MgO, Ta₂O₅ and Nb₂O₅ were weighed to get the amounts of Ba, Ca, Sr, Mg, Ta and Nb listed in Table 4. Calcined powders of MgO-(Ta-Nb)₂O₅ (in Sample No.23 to Sample No.26) were obtained in the first calcination. Calcined powders of (Ba-Ca)O-(Mg)O-(Ta-Nb)₂O₅ (in Sample No.23), (Ca-Sr)O-(Mg)O-(Ta-Nb)₂O₅ (in Sample No.24), (Sr-Ba)O-(Mg)O-(Ta-Nb)₂O₅ (in Sample No.25) and (Ba-Ca-Sr)O-(Mg)O-(Ta-Nb)₂O₅ (in Sample No.26) were obtained in the second calcination respectively. Targets were prepared in the same way as in Example 1 except the compositions were different, and film capacitors of Sample No.23 to Sample No.26 were respectively prepared. The results from the same evaluations as in Example 1 were shown in Table 4.

20

25

30

35

40

45

50

55

5
10
15
20
25
30
35
40
45
50
55

(Table 4)

	Sample No.	A			B		C			Relative permittivity (-)	Q value (-)	Breakdown voltage (kV/ μ m)
		Ba	Ca	Sr	Mg	Nb	Ta	Z				
		x			Y							
Example 1	9	0.125	0.000	0.000	0.750	0.000	0.125	17	1249	1.1		
Example 4	23	0.063	0.063	0.000	0.750	0.063	0.063	16	1122	1.0		
	24	0.000	0.063	0.063	0.750	0.063	0.063	15	1001	1.0		
	25	0.063	0.000	0.063	0.750	0.063	0.063	16	1126	1.0		
	26	0.042	0.042	0.042	0.750	0.063	0.063	16	1182	1.1		

Sample No.23 to Sample No.26

5 **[0067]** Similar to the sample shown in Figure 2, no defect such as crack was found on the surface in Sample No.23 to Sample No.26. According to Table 4, it was confirmed that Sample No.23 to Sample No.26 exhibited almost the same properties, wherein, the dielectric composition in these samples contained AO-BO-C₂O₅ as the main component and A contained at least one element selected from the group consisting of Ba, Ca and Sr, B was Mg, and C contained at least one element selected from the group consisting of Nb and Ta. Besides, it was confirmed that Sample No.23 to Sample No.26 had a relative permittivity of 10 or more, a Q value of 650 or more and a breakdown voltage of 0.5 kV/ μ m or more,

10 (Example 5)

[0068] The sample was prepared by the same method as that of Sample No.9 in Example 1 except that the dielectric film was deposited by the sputtering method. Besides, the evaluations were performed in the same way as in Example 1. The obtained results were shown in Table 5.

15 (Example 6)

[0069] The sample was prepared by the same method as that of Sample No.9 in Example 1 except that the dielectric film had a thickness of 800 nm. Besides, the evaluations were performed in the same way as in Example 1. The obtained results were shown in Table 5.

25

30

35

40

45

50

55

5
10
15
20
25
30
35
40
45
50
55

[Table 5]

	Sample No.	AO				BO		C ₂ O ₅			Relative permittivity (-)	Q value (-)	Breakdown voltage (kV/μm)	
		Ba	Ca	Sr		Mg		Nb	Ta	Z				
		x		y										
Example 1	9	0.125	0.000	0.000	0.750	0.000	0.000	0.125	17	1249	1.1	PLD/400nm		
Example 5	27	0.125	0.000	0.000	0.750	0.000	0.125	16	1333	1.0	Sputtering/400nm			
Example 6	28	0.125	0.000	0.000	0.750	0.000	0.125	17	1374	1.2	PLD/800nm			

Sample No.27 and Sample No.28

[0070] Similar to the sample shown in Figure 2, no defect such as crack was found on the surface in Sample No.27 and Sample No.28. According to Table 5, it was confirmed that the relative permittivity was 10 or more, the Q value was 650 or more and the breakdown voltage was 0.5 kV/ μm or more when the dielectric film of the present embodiment was used even if the dielectric films were prepared by a different method (Sample No.27) or the dielectric films had a different thickness (Sample No.28).

[0071] As described above, the present invention relates to a dielectric composition and an electronic component. In particular, the present invention provides a dielectric composition and an electronic component using this dielectric composition, in which the dielectric composition and the electronic component have a high relative permittivity, a low dielectric loss (i.e., a high Q value), and further a high breakdown voltage even when they are downsized. In this respect, the electronic component using the dielectric composition can be downsized and provided with excellent functions. The present invention widely provides novel technologies to a film component working at a high frequency which uses dielectric films such as a diplexer or a band-pass filter.

DESCRIPTION OF REFERENCE NUMERALS

[0072]

- 1 Supporting substrate
- 2 Foundation layer
- 3 Lower electrode
- 4 Upper electrode
- 5 Dielectric film
- 10 Film capacitor

Claims

1. A dielectric composition **characterized in** comprising a complex oxide represented by a formula of $x\text{AO}-y\text{BO}-z\text{C}_2\text{O}_5$ as the main component, wherein,

A represents at least one element selected from the group consisting of Ba, Ca and Sr,

B represents Mg,

C represents at least one element selected from the group consisting of Nb and Ta, and

x, y and z meet the following conditions,

$$x+y+z=1.000,$$

$$0.000 < x \leq 0.281,$$

$$0.625 \leq y < 1.000,$$

and

$$0.000 < z \leq 0.375.$$

2. The dielectric composition of claim 1 **characterized in** comprising a complex oxide represented by the formula in which x, y and z meet the following conditions as the main component,

$$x+y+z=1.000,$$

$$0.000 < x \leq 0.281,$$

5

$$0.625 \leq y < 1.000,$$

and

10

$$0.000 < z \leq 0.125.$$

3. An electronic component comprising the dielectric composition of claim 1 or 2.

15

Patentansprüche

1. Dielektrische Zusammensetzung, **dadurch gekennzeichnet, dass** sie ein komplexes Oxid aufweist, das durch eine Formel $x\text{AO}-y\text{BO}-z\text{C}_2\text{O}_5$ als Hauptbestandteil dargestellt wird, wobei

20

A zumindest ein Element ausgewählt aus der Gruppe bestehend aus Ba, Ca und Sr darstellt, B Mg darstellt, C zumindest ein Element ausgewählt aus der Gruppe bestehend aus Nb und Ta darstellt, und x, y und z die folgenden Bedingungen erfüllen,

25

$$x + y + z = 1,000,$$

$$0,000 < x \leq 0,281,$$

30

$$0,625 \leq y < 1,000,$$

und

35

$$0,000 < z \leq 0,375.$$

40

2. Dielektrische Zusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** sie aufweist ein komplexes Oxid, das durch die Formel dargestellt wird, bei der x, y und z die folgenden Bedingungen als Hauptbestandteil erfüllen,

45

$$x + y + z = 1,000,$$

$$0,000 < x \leq 0,281,$$

50

$$0,625 \leq y < 1,000,$$

und

55

$$0,000 < z \leq 0,125.$$

3. Elektronisches Bauteil aufweisend die dielektrische Zusammensetzung nach Anspruch 1 oder 2.

Revendications

1. Composition diélectrique, **caractérisée en ce qu'**elle comprend un oxyde complexe, représenté par une formule de $x\text{AO}-y\text{BO}-z\text{C}_2\text{O}_5$, comme composant principal, où :

A représente au moins un élément sélectionné parmi le groupe consistant en Ba, Ca et Sr;

B représente du Mg ;

C représente au moins un élément sélectionné parmi le groupe consistant en Nb et Ta, et

x, y et z satisfont les conditions suivantes :

$$x + y + z = 1,000 ;$$

$$0,000 < x \leq 0,281 ;$$

$$0,625 \leq y < 1,000,$$

et

$$0,000 < z \leq 0,375.$$

2. Composition diélectrique selon la revendication 1, **caractérisée en ce qu'**elle comprend un oxyde complexe, représenté par la formule suivant laquelle x, y et z satisfont les conditions suivantes, comme composant principal :

$$x + y + z = 1,000 ;$$

$$0,000 < x \leq 0,281 ;$$

$$0,625 \leq y < 1,000,$$

et

$$0,000 < z \leq 0,125.$$

3. Composant électronique comprenant la composition diélectrique selon la revendication 1 ou 2.

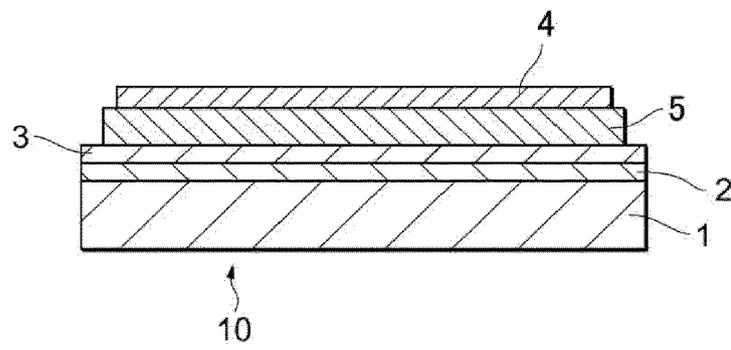


Fig. 1

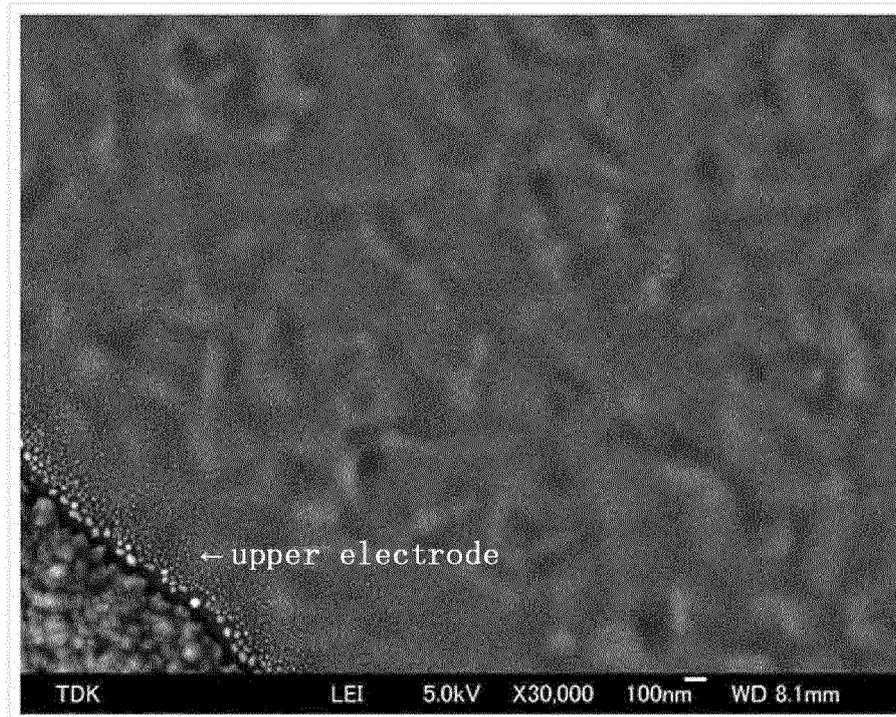


Fig. 2

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP H8319162 A [0009]
- EP 0782976 A [0009]

Non-patent literature cited in the description

- Properties of Ba(Mg_{1/3}Ta_{2/3})O₃Thin Films Prepared by Pulsed-Laser Deposition. *Jpn. J. Appl. Phys.*, 2003, vol. 42, 7428-7431 [0008]