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(54) DIELECTRIC COMPOSITES, AND MULTI-LAYERED CAPACITORS AND ELECTRONIC DEVICES COMPRISING THEREOF

DIELEKTRISCHE VERBUNDWERKSTOFFE, MEHRSCHICHTIGE KONDENSATOREN UND ELEKTRONISCHE VORRICHTUNGEN, DIE DIESE ENTHALTEN

COMPOSITES DIÉLECTRIQUES ET CONDENSATEURS MULTICOUCHES ET DISPOSITIFS ÉLECTRONIQUES LES COMPRENANT

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Description

FIELD OF THE INVENTION

[0001] A dielectric composite and a multi-layered capacitor and an electronic device including the same are disclosed.

BACKGROUND OF THE INVENTION

[0002] A multi-layer ceramic condenser (MLCC), which is a small-size condenser having a large capacity, is an electronic device obtained by alternately laminating a dielectric ceramic composition and an internal electrode and firing the same simultaneously. However, according to the ongoing requirements for electronic devices to provide a small size, a thin film, and a higher capacity, there remains an increasing need to develop a condenser having further smaller size and greater thinness, and higher capacity than the conventional multi-layered ceramic condenser structure.

[0003] In addition, an intergranular insulation type capacitor of dielectric materials exhibiting good dielectric characteristics may form a grain boundary insulation layer between crystal grains having conductivity or semi-conductivity, e.g., conductive or semiconductive crystal grains, so the intergranular insulation type capacitor may have a high apparent relative permittivity, and down-sizing and higher capacity may be possible.

[0004] An apparent relative permittivity of the intergranular insulation type capacitor tends to be generally proportional to a particle size and inversely proportional to a thickness of the grain boundary insulation layer. However, a relative permittivity of the grain boundary insulation layer is also decreased with a decreased thickness of the grain boundary insulation layer, and the grain boundary insulation layer may have problems in that the thickness of the grain boundary insulation layer may be maintained in a predetermined level taking into account or considering the relative permittivity of the intergranular insulation type capacitor.

[0005] EP 0634756A discloses a metal oxide resistor for use in a power circuit breaker. It discloses as prior art a sintered composite including a plurality of metal oxide grains and clay binding those grains. Carbon particles are included grain boundaries. It also discloses a modification in which carbon particles exist in an amorphous or glass state at some of the triple points of the grain boundaries and are converted into graphite, a two-dimensional structure, near the grain boundaries.

[0006] US 6292355 discloses a strontium titanate based grain boundary barrier layer capacitor, the layers comprising an oxide melt infiltrated into the grain boundaries of the strontium titanate grained matrix, the melt containing CaO and BaO in a particular molar ratio.

[0007] US 2013/286541 discloses strontium titanate dielectric composites with a donor in the crystal grains and acceptor elements in a grain boundary layer.

SUMMARY OF THE INVENTION

[0008] The invention is defined by the claims.

[0009] An embodiment provides a dielectric composite having a high capacity characteristic and also being capable of to be down-sized and having a thickness of a film therein being decreased, by including a material exhibiting a high relative permittivity even in a region having a thickness of several to several tens of nanometers.

[0010] An embodiment provides a multi-layered capacitor and an electronic device including the dielectric composite.

[0011] According to an embodiment, a dielectric composite is defined in claim 1.

[0012] The two-dimensional layered material may include a single layer.

[0013] The two-dimensional layered material may include two or more laminated layers.

[0014] The two-dimensional layered material may directly contact the surface of at least one of the crystal grains.

[0015] The two-dimensional layered material may cover an entirety of the surface of at least one of the crystal grains.

[0016] The two-dimensional layered material may have a thickness of less than or equal to about 120 nanometers (nm).

[0017] The two-dimensional layered material may have a relative permittivity of greater than or equal to about 50 and less than or equal to about 1000.

[0018] The grain boundary insulation layer may further include a three-dimensional bulk material mixed with the two-dimensional layered material.

[0019] The two-dimensional layered material may be present in a range of about 10 volume% to about 100 volume% based on 100 volume% of the grain boundary insulation layer.

[0020] The two-dimensional layered material may be one delaminated from a material including an aurivillius phase, a material including a Ruddlesden-Popper phase, a material including a Dion-Jacobson phase, and titano-niobate, or a combination thereof.

[0021] The two-dimensional layered material may be represented by Chemical Formula 1.

[Chemical Formula 1] $X_m(A_{(n-1)}B'_nO_{(3n+1)})$

[0022] In Chemical Formula 1, X may include H, an alkali metal, a cationic compound, or a combination thereof, A may include Ca, Na, Ta, Bi, Ba, Sr, or a combination thereof, B' may include W, Mo, Cr, Ta, Nb, V, Zr, Hf, Pb, Sn, La, Ti, or a combination thereof, $0 \leq m \leq 2$, and $n \geq 1$.
[0023] The cationic compound X may include a tetramethylammonium compound, a tetraethylammonium compound, a tetrapropylammonium compound, a tetrabutylammonium compound, a methylamine compound, an ethylamine compound, a propylamine compound, a butylamine compound, a polyethylenimine compound, or a combination thereof.
[0024] The two-dimensional layered material represented by Chemical Formula 1 is electrically neutral.
[0025] The crystal grains may include a material including barium titanate, strontium titanate, lead titanate, lead zirconate, lead zirconate titanate, or a combination thereof.
[0026] The crystal grains may have an average particle diameter in a range of about 50 nm to about 2 micrometers (μm).
[0027] The dielectric composite may have a relative permittivity of greater than or equal to about 1,000 and less than or equal to about 20,000.
[0028] An embodiment provides a multi-layered capacitor including laminated alternate layers including an internal electrode, and a dielectric layer, wherein the dielectric layer includes the dielectric composite.
[0029] The internal electrode and the dielectric layer may include three or more laminated layers.
[0030] The dielectric layer may have a thickness of less than about 500 nanometers.
[0031] The dielectric layer may have a thickness of less than about 500 nm and may have a relative permittivity of greater than or equal to about 4,000 and less than or equal to about 40,000.
[0032] Further, an embodiment provides an electronic device including the dielectric composite according to the embodiment.
[0033] The electronic device may include a varistor, a thermistor, or a capacitor for storing energy.
[0034] The dielectric composite according to an embodiment includes a two-dimensional layer device in which a relative permittivity is not decreased even if a thickness of the grain boundary insulation layer is decreased, so the grain boundary insulation layer may be formed in, e.g., include, an ultra-thin film, thereby it may overcome limits of the conventional intergranular insulation type capacitor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035]

FIG. 1 is a schematic view showing a fine structure of a dielectric composite according to an embodiment,
FIGS. 2 and 3 are schematic views showing various fine structures of dielectric composites according to embodiments, and
FIG. 4 is a schematic view showing a multi-layered capacitor according to an embodiment.

DETAILED DESCRIPTION

[0036] Advantages and characteristics of this disclosure, and a method for achieving the same, will become evident referring to the following example embodiments together with the drawings attached hereto. However, the embodiments should not be construed as being limited to the embodiments set forth herein. If not defined otherwise, all terms (including technical and scientific terms) in the specification may be defined as commonly understood by one skilled in the art. The terms defined in a generally-used dictionary may not be interpreted ideally or exaggeratedly unless clearly defined. In addition, unless explicitly described to the contrary, the word "comprise" and variations such as "comprises" or "comprising", will be understood to imply the inclusion of stated elements but not the exclusion of any other elements.
[0037] Further, the singular includes the plural unless otherwise defined.
[0038] In the drawings, the thickness of layers, films, panels, regions, etc., are exaggerated for clarity. Like reference numerals designate like elements throughout the specification.
[0039] It will be understood that when a first element such as a layer, film, region, or substrate is referred to as being "on" second element, it can be directly on the other element or intervening elements may also be present. In contrast, when an element is referred to as being "directly on" another element, there are no intervening elements present.
[0040] As used herein, relative permittivity refers to a dielectric constant of a material or the absolute permittivity of a material expressed as a ratio relative to the permittivity of vacuum.
[0041] As used herein, "particle diameter" refers to a maximum size that a particle may have. For example, particle diameter refers a longitudinal length when the crystal grain has a shape of oval or a uniaxially elongated shape similar to the oval such as a sheet, a plate, or a needle, a diameter length in a case of a circle/spherical shape, or a farthest distance of the line connecting any two points in the crystal grain boundary in a case of polygonal or amorphous shape.

[0042] In addition, the particle diameter of the crystal grain in the present specification may be quantified by a metrology to show an average size of a groups of crystal grains, but the generally-used way may include a mode diameter showing the maximum value of the distribution, a median diameter corresponding to the median of the integrated distribution curved-line, and various average diameter (numeric average, length average, area average, mass average, volume average, etc.). Unless otherwise defined, the phrase "average particle diameter" refers to a numeral average diameter which is measured as D50 (particle diameter at which the distribution is 50%).

[0043] Hereinafter, a composition of a dielectric composite according to an embodiment is described with references to FIGS. 1 to 3.

[0044] FIG. 1 is a schematic view showing a fine structure of a dielectric composite according to an embodiment.

[0045] A dielectric composite according to an embodiment includes a plurality of crystal grains including a material having semi-conductivity or conductivity and a grain boundary insulation layer between the crystals grains, e.g., surrounding the crystal grains or a boundary of the crystal grains.

[0046] Additionally, the plurality of crystal grains and grain boundaries are connected to each other directly and/or in parallel, so the crystal grains and grain boundaries may carry out a function of a capacitor having a predetermined capacitance as the whole. In other words, the dielectric composite according to an embodiment is an intergranular insulation type capacitor providing a capacitance to the grain boundary insulation layer formed between two crystal grains when applying a predetermined voltage to two adjacent crystal grains.

[0047] An embodiment is not necessarily limited thereto, but may be formed in a multi-layered capacitor by laminating the dielectric layers including dielectric composites in two or more layers as will be described in further detail.

[0048] Referring to FIG. 1, a plurality of crystal grains is disposed in plural. A plurality of crystal grains may include a material having semi-conductivity or conductivity, i.e., the material may be a semiconductor or conductive material. A material constituting the crystal grain may be a metal oxide including, for example, barium titanate, strontium titanate, lead titanate, lead zirconate, lead zirconate titanate, or a combination thereof.

[0049] According to an embodiment, the material constituting the crystal grain may further include a donor element. In other words, the metal oxide constituting the crystal grain may have oxygen vacancy, and the donor element may be incorporated, e.g., solid-dissolved, in the crystal grain. Thereby, the crystal grain may become a semiconductor. Examples of the donor element may include La, Sm, Dy, Ho, Y, Nd, Ce, Nb, Ta, W, or the like.

[0050] In addition, an average particle diameter of the crystal grains according to an embodiment may be varied or variously determined taking into account or considering an apparent relative permittivity of the dielectric composite which will be described in further detail below, but the average particle diameter of the crystal grains may be adjusted within an appropriate range so that the dielectric composite may be down-sized and a thickness of a thin film decreased.

[0051] An average particle diameter of the crystal grain may be for example less than or equal to about 2.0μm, less than or equal to about 1.9μm, less than or equal to about 1.8 μm, less than or equal to about 1.7μm, less than or equal to about 1.6μm, less than or equal to about 1.5μm, less than or equal to about 1.4μm, less than or equal to about 1.3μm, less than or equal to about 1.2μm, less than or equal to about 1.1μm, less than or equal to about 1.0μm, less than or equal to about 900nm, less than or equal to about 800nm, less than or equal to about 700nm, less than or equal to about 600nm, less than or equal to about 500nm, and for example greater than or equal to about 50nm, greater than or equal to about 60nm, greater than or equal to about 70nm, greater than or equal to about 80nm, greater than or equal to about 90nm, or greater than or equal to about 100nm.

[0052] The grain boundary insulation layer includes a two-dimensional layered material covering at least a portion of the crystal grain surface.

[0053] As used herein, unless otherwise defined, a "two-dimensional layered material" refers to a material having a two-dimensional crystal structure which is a material, e.g., a sheet or film including one or more layered structures, specifically including 1 to 9 atomic layers.

[0054] That is, the two-dimensional layered material may be formed in a single layer or in a multi-layered structure in which each single layer is stacked to form a multi-layer. In an embodiment, nine or fewer layers are stacked to form the multi-layered structure.

[0055] In addition, when the two-dimensional layered material has the multi-layered structure, each of the layers may be physically and/or chemically bound with each other. In this case, a portion of the layers may have a crystalline structure different from the two-dimensional crystal structure.

[0056] According to an embodiment, the grain boundary insulation layer may include a two-dimensional layered material as shown in FIG. 1. However, an embodiment is not necessarily limited thereto, in that the grain boundary insulation layer may include the two-dimensional layered material together with a three-dimensional bulk material having a different crystal structure from the two-dimensional layered material, as shown in FIGS. 2 and 3.

[0057] FIGS. 2 and 3 are schematic views showing various fine structures of dielectric composites according to some embodiments.

[0058] Referring to FIGS. 2 and 3, the three-dimensional bulk material may be combined, e.g., mixed, with the two-dimensional layered material to form the grain boundary insulation layer. The three-dimensional bulk material may have a multi-crystalline structure including three-dimensional crystal particles, but the multi-crystalline structure may not have a two-dimensional crystal structure since the multi-crystalline structure may not include a two-dimensional layered material.

[0059] Further according to an embodiment, the three-dimensional bulk material may be a material in which an acceptor element is included in the material for the crystal grain. Examples of the acceptor element may include Mn, Co, Ni, Cr, and the like.

[0060] In other words, the three-dimensional bulk material may be formed contacting two adjacent crystal grains, e.g., indirectly physically connecting the adjacent crystal grains to each other. However, the three-dimensional bulk material includes an acceptor element aiding, e.g., accelerating, formation of a Schottky barrier, which improves a resistivity, so that the three-dimensional bulk material may have or provide excellent insulation unlike the crystal grain.

[0061] Still further according to an embodiment, an amount of the two-dimensional layered material, e.g., a ratio of the two-dimensional layered material to the three-dimensional bulk material, in the grain boundary insulation layer is not particularly limited, but may be varied or variously determined taking into account or considering the each relative permittivity of the two-dimensional layered material and the three-dimensional bulk material, a raw material, an estimated thickness of the grain boundary insulation layer, and the like, but the amount of the two-dimensional layered material may be adjusted such that two-dimensional layered material exhibits excellent relative permittivity even if the grain boundary insulation layer is formed in a size of several to several tens of nanometers.

[0062] An amount of the two-dimensional layered material in the grain boundary insulation layer may be for example greater than or equal to about 10 volume%, greater than or equal to about 15 volume%, greater than or equal to about 20 volume%, greater than or equal to about 25 volume%, greater than or equal to about 30 volume%, greater than or equal to about 35 volume%, greater than or equal to about 40 volume%, greater than or equal to about 45 volume%, greater than or equal to about 50 volume%, greater than or equal to about 55 volume%, greater than or equal to about 60 volume%, greater than or equal to about 65 volume%, greater than or equal to about 70 volume%, greater than or equal to about 75 volume%, greater than or equal to about 80 volume%, greater than or equal to about 85 volume%, greater than or equal to about 90 volume%, greater than or equal to about 95 volume%, or about 100 volume% based on 100 volume% of the grain boundary insulation layer.

[0063] Meanwhile, the two-dimensional layered material may directly contact, e.g., be directly contacted with, the crystal grain surface as shown in FIGS. 1 and 2; and at least a portion thereof may be disposed leaving in a predetermined interval space from the crystal grain surface as shown in FIG. 3.

[0064] In addition, the two-dimensional layered material may be formed to cover only a partial region of the crystal grain surface to cover a portion of the crystal grain surface as shown in FIG. 2, or may be formed to cover the whole surface of the crystal grain as shown in FIG. 1 or FIG. 3.

[0065] In an embodiment, the two-dimensional layered material may be a compound represented by Chemical Formula 1.

[Chemical Formula 1] $X_m(A_{(n-1)}B'_nO_{(3n+1)})$

[0066] In Chemical Formula 1, X includes H, an alkali metal, a cationic compound, or a combination thereof, A includes Ca, Na, Ta, Bi, Ba, Sr, or a combination thereof, B' includes W, Mo, Cr, Ta, Nb, V, Zr, Hf, Pb, Sn, La, Ti, or a combination thereof, $0 \leq m \leq 2$, and $n \geq 1$.

[0067] The cationic compound as used herein includes polymers, and may be positively charged or capable of being positively charged under the conditions of use. The cationic compound may include a (C1 to C16 alkyl)ammonium compound, a (C1 to C16 alkyl) phosphonium compound, a (C1 to C16 alkyl)amine compound, an amine polymer, or a combination thereof. The alkylamine compound may be a primary, secondary, or tertiary amine.

[0068] The cationic compound may include a tetramethylammonium compound, a tetraethylammonium compound, a tetrapropylammonium compound, a tetrabutylammonium compound, a methylamine compound, an ethylamine compound, a propylamine compound, a butylamine compound, a polyethylenimine compound, or a combination thereof.

[0069] In Chemical Formula 1, a stoichiometric ratio of X, A, B' and O may be adjusted to provide electrical neutrality for the whole of the two-dimensional layered material. That is, the material represented by Chemical Formula 1 may be electrically neutral.

[0070] According to an embodiment, a thickness of the two-dimensional layered material is not particularly limited, but may be varied or variously determined taking into account or considering a material of the crystal grain, an average particle diameter of the crystal grains, a material of the two-dimensional layered material, an amount of the two-dimensional layered material in the grain boundary insulation layer, and the like, but a thickness of the two-dimensional layered material may be adjusted enough to improve an appearance dielectric constant of a dielectric composite which will be described in further detail by reducing the thickness of the grain boundary insulation layer.

[0071] A thickness of the two-dimensional layered material may be for example less than or equal to about 120 nm, less than or equal to about 110 nm, less than or equal to about 100 nm, less than or equal to about 50 nm, less than or equal to about 40 nm, less than or equal to about 30 nm, less than or equal to about 20 nm, or less than or equal to about 10 nm or may have for example a thickness of several nanometers to several tens of nanometers, for example, in a range of about 2 nm to about 80 nm, in a range of about 3 nm to about 70 nm in a range of about 4 nm to about 60 nm, or in a range of about 5 nm to about 50 nm.

[0072] A thickness of the two-dimensional layered material may be calculated by analyzing an image taken with an AFM (Atomic Force Microscope).

[0073] The two-dimensional layered material may exhibit a relative permittivity caused by the two-dimensional crystal structure. The relative permittivity of the two-dimensional layered material is not particularly limited, but may be varied or variously determined taking into account or considering a raw material of the two-dimensional layered material, a kind of the two-dimensional crystal structure, the number of the laminated layers, an average particle diameter of the crystal grains, a material for the crystal grain, and the like, but the relative permittivity of the two-dimensional layered material is determined to provide the grain boundary insulation layer with a capacitance as much at least to operate as a capacitor when applying a predetermined voltage to crystal grains.

[0074] A relative permittivity of the two-dimensional layered material may be for example greater than or equal to about 10, greater than or equal to about 20, greater than or equal to about 30, greater than or equal to about 40, greater than or equal to about 50, greater than or equal to about 60, greater than or equal to about 70, greater than or equal to about 80, greater than or equal to about 90, or greater than or equal to about 100. In an embodiment, A relative permittivity of the two-dimensional layered material may be for example less than or equal to about 1000.

[0075] A relative permittivity of the two-dimensional layered material may be calculated by using a method that disposing the two-dimensional layered material between a pair of probes contained in an AFM (Atomic Force Microscope) and thereafter applying a predetermined voltage to the pair of probes.

[0076] According to an embodiment, the two-dimensional layered material may be a metal oxide nano sheet delaminated from a material having aurivillius phase, a material having a Ruddlesden-Popper phase, a material having a Dion-Jacobson phase, titano-niobate, or a combination thereof.

[0077] For example, at least one of the material having aurivillius phase, the material having Ruddlesden-Popper phase, the material having Dion-Jacobson phase, titano-niobate, or a combination thereof as a raw material is treated in an acid solution to be protonated, and reacted with an alkylammonium or an alkylamine compound to widen a gap between layers of the layered structure existing in the raw material, and then agitated with a solvent including water, alcohol, acetonitrile, dimethylsulfoxide, dimethyl formamide, propylene carbonate, or a combination thereof to form delaminated metal oxide nano sheets.

[0078] A process of delaminating $Ca_2Na_2Nb_5O_{16}$ as an example of the two-dimensional layered material according to an embodiment is described as follows: $KCa_2Na_2Nb_5O_{16}$ and an acid compound, for example, HNO_3 are reacted to substitute K+ with H+, so a protonated layered material of $HCa_2Na_2Nb_5O_{16}$ is obtained. The obtained $HCa_2Na_2Nb_5O_{16}$ is reacted with, for example, an alkylammonium compound such as tetraalkylammonium hydroxide to substitute the H+ with, for example, tetrabutylammonium salt (TBA+).

[0079] The alkylammonium compound may be a C1 to C16 alkylammonium compound. As the alkylammonium molecule has a large size, the alkylammonium molecule widens a gap between $Ca_2Na_2Nb_5O_{16}$ layers by entering between $Ca_2Na_2Nb_5O_{16}$ layers, causing an interlayer separation. Thereby the $Ca_2Na_2Nb_5O_{16}$ is delaminated to provide $Ca_2Na_2Nb_5O_{16}$ nano sheets when the $Ca_2Na_2Nb_5O_{16}$ is added into a solvent and agitated.

[0080] Meanwhile, the intergranular insulation type capacitor generally satisfies Equation 1 related with an apparent relative permittivity.

[Equation 1]

$$\varepsilon_r APP \propto \varepsilon_r \cdot d/t$$

[0081] In Equation 1, ε_rAPP refers to an apparent relative permittivity of the dielectric composite, ε_r refers to a relative permittivity caused by a material for the grain boundary insulation layer, d refers to an average particle diameter of the crystal grains, and t refers to a thickness of the grain boundary insulation layer.

[0082] Among the conventional intergranular insulation type capacitors, the grain boundary insulation layer includes only three-dimensional bulk material, and the relative permittivity of the three-dimensional bulk material tends to depend upon the amount of the three-dimensional bulk material.

[0083] Accordingly, when the thickness (t) of grain boundary insulation layer is reduced, the amount of the material for the grain boundary insulation layer may be decreased, thereby the apparent relative permittivity of the intergranular insulation type capacitor will be also decreased. Thus the conventional, i.e., comparative intergranular insulation type capacitor may have difficulty providing the grain boundary insulation layer with an ultrathin film with a thickness less than or equal to the predetermined thickness.

[0084] On the other hand, in the dielectric composite according to an embodiment, the grain boundary insulation layer at least includes a two-dimensional layered material, so the dielectric composite may exhibit a relative permittivity greater than or equal to a predetermined level caused by the two-dimensional layer material as the intergranular insulation type capacitor even if the grain boundary insulation layer is formed in an ultrathin film having a thickness t of several to several tens of nanometers. That is, by using the two-dimensional layered material, the thickness and the relative permittivity of the grain boundary insulation layer may be independently controlled, e.g., controlled independent of one another, unlike the conventional comparative intergranular insulation type capacitor.

[0085] The relative permittivity of the dielectric composite according to an embodiment may be varied or variously determined taking into account or depending upon the average particle diameter of the crystal grains and the thickness of the grain boundary insulation layer, but the dielectric composite may have a relative permittivity that allows for the dielectric composite to be used as a capacitor even if the dielectric composite is formed in an ultra-small size and an ultra-thin film.

[0086] A relative permittivity of the dielectric composite may be for example greater than or equal to about 1,000, greater than or equal to about 2,000, greater than or equal to about 3,000, greater than or equal to about 4,000, greater than or equal to about 5,000, greater than or equal to about 6,000, greater than or equal to about 7,000, greater than or equal to about 8,000, greater than or equal to about 9,000, or greater than or equal to about 10,000. In an embodiment, a relative permittivity of the dielectric composite may be for example less than or equal to about 20,000.

[0087] Accordingly, the dielectric composite according to an embodiment may exhibit a relative permittivity greater than or equal to a predetermined level caused by the two-dimensional layered material positioned in the grain boundary insulation layer even if the grain boundary insulation layer is formed in an ultrathin film of several to several tens of nanometers.

[0088] As described above, as the dielectric composite according to an embodiment includes the two-dimensional layered material having a high relative permittivity even in a region having a thickness of several to several tens of nanometers, the dielectric composite may be formed in a small size and a thin film and also have a high capacity characteristics.

[0089] Hereinafter, a structure of the multi-layered capacitor including the dielectric composite according to an embodiment is described with reference to FIG. 4.

[0090] FIG. 4 schematically shows a multi-layered capacitor according to an embodiment.

[0091] The multi-layered capacitor 1 according to an embodiment may have a structure in which an internal electrode 12 and a dielectric layer 11 are alternated and laminated, wherein the dielectric layer 11 includes the dielectric composite shown in FIGS. 1 to 3.

[0092] In the multi-layered capacitor 1 according to an embodiment, the internal electrode 12 and the dielectric layer 11 are alternated and laminated two or more times, e.g., the internal electrode 12 and the dielectric layer 11 include three or more laminated layers. Thereby the adjacent internal electrodes and the dielectric layer disposed therebetween may function as a unit capacitor.

[0093] In addition, in the multi-layered capacitor 1 according to an embodiment, the internal electrode 12 and the dielectric layer 11 may be alternated and laminated greater than or equal to about two times, for example, greater than or equal to about three times, for example, greater than or equal to about four times, for example, greater than or equal to about five times, so the multi-layered capacitor 1 may exhibit a capacitance caused by the structure in which the internal unit capacitors are disposed in parallel.

[0094] The internal electrode 12 may be formed to have a smaller area than the area of the dielectric layer 11. Meanwhile, the internal electrodes 12 may have the same area as each other but, adjacent internal electrodes may not be completely covered and may be laminated in a zig-zag pattern as shown in FIG. 4.

[0095] The dielectric layer 11 may be formed in a larger area than the area of the internal electrode 12, and adjacent dielectric layers may be connected to each other, so the cross-sectional surface thereof may be a serpentine shape on the whole as shown in FIG. 4.

[0096] Meanwhile, according to an embodiment, the multi-layered capacitor 1 may further include a pair of external electrodes 13 contacting or surrounding both lateral sides of the stacked structure including the dielectric layer 11 and the internal electrode 12 as shown in FIG. 4. However, an embodiment is not necessarily limited thereto, but the multi-layered capacitor 1 may have a structure in which the external electrode is omitted, and the internal electrodes may extend longitudinally on or in both sides of the stacked structure of the dielectric layer and the internal electrode, or the internal electrode may be directly connected to the power source without the external electrode.

[0097] The multi-layered capacitor may include a plurality of dielectric layers and internal electrodes, and the total thickness of the dielectric layer is important factor to provide the multi-layered capacitor with down-size and thin-film. However, the dielectric layer of a comparative multi-layered capacitor includes $BaTiO_3$, $PbTiO_3$, or the like as the dielectric material, so the relative permittivity is also decreased according to the thickness decrease as described above.

[0098] Thereby, when the total thickness of the dielectric layer is decreased to provide a thin film in a comparative multi-layered capacitor, a thickness of each layer of the dielectric layer may be limited up to about 550 nm to about 600 nm, in this case, a comparative dielectric layer may have a relative permittivity ranging from about 3,000 to about 3,500. In addition, when the thickness of a comparative dielectric layer is formed in a ultra-thin film of less than or equal to the predetermined or limit range, e.g., in the range limit, the relative permittivity with respect to the thickness may be sharply decreased, and a deteriorated property that may not be used as a dielectric layer for a multi-layered capacitor may be exhibited.

[0099] However, in the multi-layered capacitor 1 according to an embodiment, the dielectric layer 11 includes the dielectric composite, and thus, a thickness of one layer of the dielectric layer 11 may be less than or equal to about 3,000 nm, less than or equal to about 2,500 nm, less than or equal to about 2,000 nm, less than or equal to about 1,500 nm, less than or equal to about 1,000 nm, or less than or equal to about 500 nm, and for example 480 nm, less than or equal to about 460 nm, less than or equal to about 440 nm, less than or equal to about 420 nm, less than or equal to about 400 nm, less than or equal to about 380 nm, less than or equal to about 360 nm, less than or equal to about 340 nm, less than or equal to about 320 nm, less than or equal to about 300 nm, or even about 200 nm to about 300 nm, which provides a thin film.

[0100] Thereby, the multi-layered capacitor 1 according to an embodiment may exhibit a relative permittivity greater than or equal to a predetermined level caused by the two-dimensional layered material for the grain boundary insulation layer in the dielectric layer 11. The other words, even if the thickness per one layer of the dielectric layer 11 is reduced within the range, a relative permittivity of, for example, greater than or equal to about 1,000, greater than or equal to about 1,500, greater than or equal to about 2,000, greater than or equal to about 2,500, greater than or equal to about 3,000, greater than or equal to about 4,000, greater than or equal to about 4,200, greater than or equal to about 4,400, greater than or equal to about 4,600, greater than or equal to about 4,800, greater than or equal to about 4,900, greater than or equal to about 5,000, greater than or equal to about 7,000, greater than or equal to about 8,000, greater than or equal to about 9,000, greater than or equal to about 10,000, greater than or equal to about 12,000, greater than or equal to about 14,000, greater than or equal to about 16,000, greater than or equal to about 18,000, or greater than or equal to about 20,000 per one layer of the dielectric layer 11 may be exhibited. In an embodiment, a relative permittivity of the dielectric layer may be for example less than or equal to about 40,000.

[0101] The multi-layered capacitor 1 may a relative permittivity caused by the dielectric layer 11. The multi-layered capacitor 1 according to an embodiment may have for example a relative permittivity of greater than or equal to about 1,000, greater than or equal to about 1,500, greater than or equal to about 2,000, greater than or equal to about 2,500, greater than or equal to about 3,000, greater than or equal to about 4,000, greater than or equal to about 4,200, greater than or equal to about 4,400, greater than or equal to about 4,600, greater than or equal to about 4,800, greater than or equal to about 4,900, greater than or equal to about 5,000, greater than or equal to about 7,000, greater than or equal to about 8,000, greater than or equal to about 9,000, greater than or equal to about 10,000, greater than or equal to about 12,000, for example 14,000, greater than or equal to about 16,000, greater than or equal to about 18,000, or greater than or equal to about 20,000. In an embodiment, a relative permittivity of the multi-layered capacitor may be for example less than or equal to about 40,000

[0102] That is, the multi-layered capacitor 1 according to an embodiment may significantly reduce a thickness per one layer of the dielectric layer 11 compared to a comparative capacitor, so a laminated number of the inner dielectric layer in the multi-layered capacitor 1 and the capacitance may be remarkably improved under the same conditions as the comparative capacitor.

[0103] In addition, an embodiment provides a multi-layered capacitor 1 which is capable of being formed with an ultra-thin film and down-sized and simultaneously to have improved capacitance and relative permittivity.

[0104] Meanwhile, an embodiment may provide an electronic device including the dielectric composite. The electronic device may be formed in a single layer of the dielectric composite, or may be formed in a multi-layer as in the multi-layered capacitor 1. The electronic device according to an embodiment may be a kind of a device performing a function of a variable resistor such as a varistor and a thermistor or may be a capacitor for storing energy.

[0105] Hereinafter, specific examples are illustrated. However, these examples are exemplary and the scope of the present disclosure is not limited thereto.

Example 1

[0106] Starting materials of TiO_2 and $SrCO_3$ and a donor element of dysprosium (Dy) are mixed, and the mixture is treated with a ball milling to provide a mixture. The obtained mixture is evaporated and then fired to provide a strontium titanate ($SrTiO_3$) core material having oxygen vacancy. The obtained strontium titanate ($SrTiO_3$) core material has an average particle diameter of about 200 nm.

[0107] Separately, K_2CO_3, $CaCO_3$, Nb_2O_5, $NaNbO_3$ are mixed as a starting material, and the mixture is formed in a pellet. The obtained pellet is heated to provide $KCa_2Na_2Nb_5O_{16}$ powder. The obtained $KCa_2Na_2Nb_5O_{16}$ powder is added into an HCl solution or an HNO_3 solution and agitated, and then filtered to provide $HCa_2Na_2Nb_5O_{16}$ powder.

[0108] The obtained $HCa_2Na_2Nb_5O_{16}$ powder is added into a tetrabutylammonium hydroxide (TBAOH) aqueous solution and agitated and centrifuged to provide two-dimensional nano sheets. A composition of the two-dimensional nano sheet is $Ca_2Na_2Nb_5O_{16}$. The obtained two-dimensional nano sheet has an average thickness of 2.5 nm and an average particle diameter of 500 nm.

[0109] The thickness of the two-dimensional nano sheet may be calculated by analyzing an image taken with an AFM (Atomic Force Microscope).

[0110] The average particle of the two-dimensional nano sheet may be calculated by analyzing an image taken with an AFM (Atomic Force Microscope).

[0111] Then the obtained two-dimensional nano sheet is coated on a grain boundary of the core material of strontium titanate ($SrTiO_3$) using polyethylenimine as a cationic compound, so as to provide a grain boundary insulation layer including the two-dimensional nano sheet. Thereby, the intermediate product has a structure of a grain boundary insulation layer including a core including a strontium titanate ($SrTiO_3$) core material and a two-dimensional nano sheet surrounding the core.

[0112] Then the crystal grain core-grain boundary insulation layer is reduced and fired at 1250 °C under H_2 atmosphere in 1% humidity to provide oxygen vacancy to strontium titanate ($SrTiO_{3-\delta}$) in the grain boundary, and it is re-oxidized under humid N_2 atmosphere at 1,000 °C to provide dielectric composite. Then a pair of electrodes consists of In-Ga are formed on the both side of the obtained dielectric composite to provide an intergranular insulation type capacitor according to Example 1. The dielectric composite of the intergranular insulation type capacitor according to Example 1 has a structure corresponded to FIG. 1, and the grain boundary insulation layer has a thickness of about 5 nm.

[0113] The thickness of the grain boundary insulation layer may be obtained by a method that distinguishing crystal grains and grain boundaries by using AFM (Atomic Force Microscope) and/or SEM (Scanning Electron Microscope) and thereafter calculating the thickness of the distinguished grain boundaries.

Example 2

[0114] An intergranular insulation type capacitor according to Example 2 is prepared in accordance with the same procedure as in Example 1, except that an accepter element of manganese (Mn) is added to the strontium titanate grain boundary during preparing the strontium titanate ($SrTiO_3$) core material. The intergranular insulation type capacitor according to Example 2 has a structure corresponding to FIG. 2, and a rate of the two-dimensional nanosheet in the grain boundary insulation layer is 50 volume%.

[0115] In other words, the grain boundary insulation layer according to Example 2 has a structure in which a three-dimensional bulk material including strontium titanate ($SrTiO_3$) having no oxygen vacancy and the accepter element and the two-dimensional nano sheets are combined.

Example 3

[0116] An intergranular insulation type capacitor according to Example 3 is prepared in accordance with the same procedure as in Example 2, except that the amount of the two-dimensional nanosheet in the grain boundary insulation layer is adjusted to 70 volume%. The dielectric composite of the intergranular insulation type capacitor according to Example 3 has a structure corresponding to FIG. 2, but an amount of the two-dimensional nanosheet is slightly increased with respect to Example 2.

Example 4

[0117] The intergranular insulation type capacitor according to Example 3 is prepared in accordance with the same procedure as in Example 2, except that the amount of the two-dimensional nanosheet in the grain boundary is adjusted to be 90 volume%. The dielectric composite of the intergranular insulation type capacitor according to Example 4 has a structure corresponding to FIG. 2, but the amount of the two-dimensional nanosheet is increased with respect to Examples 2 and 3.

Example 5

[0118] The intergranular insulation type capacitor according to Example 5 is prepared in accordance with the same procedure as in Example 1, except that the average particle diameter of the crystal grains is adjusted to be about 100 nm during preparing strontium titanate ($SrTiO_3$). The dielectric composite of the intergranular insulation type capacitor according to Example 5 has a structure corresponding to FIG. 1.

Example 6

[0119] The intergranular insulation type capacitor according to Example 6 is prepared in accordance with the same procedure as in Example 1, except that the average particle diameter of the crystal grains is adjusted to be about 300 nm during preparing strontium titanate ($SrTiO_3$). The dielectric composite of the intergranular insulation type capacitor according to Example 6 has a structure corresponding to FIG. 1.

Example 7

[0120] The intergranular insulation type capacitor according to Example 7 is prepared in accordance with the same procedure as in Example 1, except that the strontium titanate ($SrTiO_3$) grain boundary is coated with a two-dimensional nano sheet having a composition of $Ca_2Nb_3O_{10}$ during preparing the grain boundary insulation layer. The dielectric composite of the intergranular insulation type capacitor according to Example 7 has the structure corresponding to FIG. 1.

Example 8

[0121] The intergranular insulation type capacitor according to Example 8 is prepared in accordance with the same procedure as in Example 1, except that the crystal grain is prepared with a barium titanate ($BaTiO_3$) instead of strontium titanate ($SrTiO_3$). The dielectric composite of the intergranular insulation type capacitor according to Example 8 has the structure corresponding to FIG. 1.

Comparative Example 1

[0122] Starting materials of TiO_2 and $SrCO_3$ and a donor element of dysprosium (Dy) are mixed, and the mixture is treated with a ball milling to provide a mixture. The obtained mixture is evaporated and fired to provide a strontium titanate ($SrTiO_3$) having oxygen vacancy. The obtained strontium titanate ($SrTiO_3$) crystal grain has an average particle diameter of about 200 nm.

[0123] Then the strontium titanate ($SrTiO_3$) grain boundary is added with an acceptor element of manganese (Mn) and fired under the reduction condition and baked again under the air atmosphere to be re-oxidized to provide a dielectric composite. Then a pair of electrodes consists of In-Ga are formed on the both side of the obtained dielectric composite to provide an intergranular insulation type capacitor according to Comparative Example 1 is obtained.

[0124] In the intergranular insulation type capacitor according to Comparative Example 1, the grain boundary insulation layer does not include the two-dimensional nanosheet unlike in FIG. 1, and includes strontium titanate ($SrTiO_3$) with no oxygen vacancy and an acceptor element of manganese (Mn).

[0125] Hereinafter, compositions and all properties of intergranular insulation type capacitors according to Examples 1 to 8 and Comparative Example 1 are shown in Table 1.

(Table 1)

	Crystal grain		Grain boundary insulation layer			Apparent relative permittivity of intergranular insulation type capacitor (ε_rAPP)
	Composition	Average particle diameter (nm)	Composition	Two-dimensional nanosheet amount (volume %)	Thickness (nm)	
Ex.1	$SrTiO_{3-\delta}$	200	$Ca_2Na_2Nb_5O_{16}$	100	5	9,600
Ex.2	$SrTiO_{3-\delta}$	200	$Ca_2Na_2Nb_5O_{16}$ + $SrTiO_3$	50	5	5,400
Ex.3	$SrTiO_{3-\delta}$	200	$Ca_2Na_2Nb_5O_{16}$ + $SrTiO_3$	70	5	7,080
Ex.4	$SrTiO_{3-\delta}$	200	$Ca_2Na_2Nb_5O_{16}$ + $SrTiO_3$	90	5	8,760
Ex.5	$SrTiO_{3-\delta}$	100	$Ca_2Na_2Nb_5O_{16}$	100	5	4,800
Ex.6	$SrTiO_{3-\delta}$	300	$Ca_2Na_2Nb_5O_{16}$	100	5	14,,400

(continued)

	Crystal grain		Grain boundary insulation layer			Apparent relative permittivity of intergranular insulation type capacitor (ε_rAPP)
	Composition	Average particle diameter (nm)	Composition	Two-dimensional nanosheet amount (volume %)	Thickness (nm)	
Ex.7	$SrTiO_{3-\delta}$	200	$Ca_2Nb_3O_{10}$	100	5	4800
Ex. 8	$BaTiO_{3-\delta}$	200	$Ca_2Na_2Nb_5O_{16}$	100	5	9,600
Comparative Ex. 1	$SrTiO_{3-\delta}$	200	$SrTiO_3$	0	5	1,200

[0126] Referring to Table 1, it is confirmed that the intergranular insulation type capacitor according to an embodiment has an aspect that an apparent relative permittivity is proportional to an average particle diameter of the crystal grains and a two-dimensional nanosheet amount, which is changed depending upon the composition of the two-dimensional nanosheet.

[0127] Meanwhile, the condition of Example 1 is changed as follows, so each intergranular insulation type capacitor according to Examples 9 and 10 and Comparative Examples 2 and 3 is prepared.

Example 9

[0128] An intergranular insulation type capacitor according to Example 9 is prepared in accordance with the same procedure as in Example 1, except that the strontium titanate ($SrTiO_3$) core material is formed to provide an average particle diameter with about 1,300 nm, and manganese (Mn) is added as an acceptor element to the strontium titanate grain boundary during preparing the strontium titanate ($SrTiO_3$) core material. The dielectric composite of the intergranular insulation type capacitor according to Example 9, the grain boundary insulation layer is formed to have a thickness of several tens of nanometers. In addition, The dielectric composite of the intergranular insulation type capacitor according to Example 9 has a structure corresponding to FIG. 2, and the amount of the two-dimensional nanosheet in the grain boundary insulation layer is 80 volume%.

Example 10

[0129] A strontium titanate ($SrTiO_3$) core material is prepared in accordance with the same procedure as in Example 1, except that the strontium titanate ($SrTiO_3$) core material is formed to have an average particle diameter of about 1000 nm, and manganese (Mn) is added as an acceptor element to the strontium titanate grain boundary during preparing the strontium titanate ($SrTiO_3$) core material.

[0130] Separately, start elements of K_2CO_3, $SrCO_3$, Nb_2O_5 are mixed, and the mixture is formed in a pellet. The obtained pellet is heated to provide a $KSr_2Nb_3O_{10}$ powder. The obtained $KSr_2Nb_3O_{10}$ powder is added into a HCl solution or an HNO_3 solution and agitated and then filtered to provide $HSr_2Nb_3O_{10}$ powder.

[0131] The obtained $HSr_2Nb_3O_{10}$ powder is added into a TBAOH aqueous solution and agitated and centrifuged to provide two-dimensional nano sheets. The two-dimensional nano sheet has a composition of $Sr_2Nb_3O_{10}$. The obtained two-dimensional nano sheet has an average thickness of 1.5 nm and an average particle diameter of 500 nm.

[0132] Then the obtained two-dimensional nano sheet is coated on the grain boundary of strontium titanate ($SrTiO_3$) core material using a cationic compound of polyethylenimine, so a grain boundary insulation layer including two-dimensional nano sheets is obtained. Thereby, an intermediate product has a grain boundary insulation layer structure including a core of a strontium titanate ($SrTiO_3$) core material and a two-dimensional nano sheet surrounding the core.

[0133] Then the crystal grain core-grain boundary insulation layer is reduced and fired at 1250 °C under H_2 atmosphere in 1% humidity to provide strontium titanate with oxygen vacancy ($SrTiO_{3-\delta}$) in the grain boundary, and it is re-oxidized at 900 °C under the air atmosphere to provide a dielectric composite. Then a pair of electrodes consists of In-Ga are formed on the both side of the obtained dielectric composite to provide an intergranular insulation type capacitor according to Example 10. A grain boundary insulation layer is formed in a thickness of several tens of nanometers in the dielectric composite of the intergranular insulation type capacitor according to Example 10. In addition, the dielectric composite of the intergranular insulation type capacitor according to Example 10 has the structure corresponding to FIG. 2, and an amount of the two-dimensional nanosheet in the grain boundary insulation layer is 80 volume%.

Comparative Example 2

[0134] A strontium titanate ($SrTiO_3$) core material is prepared in accordance with the same procedure as in Example 1, except that the strontium titanate ($SrTiO_3$) core material is formed to have an average particle diameter of about 1,300 nm.

[0135] Then the obtained strontium titanate ($SrTiO_3$) grain boundary is added with manganese (Mn) as an acceptor element, and then fired under a reduction condition and baked again under the air atmosphere to be re-oxidized, so that an intergranular insulation type capacitor according to Comparative Example 2 is obtained. The dielectric composite of the intergranular insulation type capacitor according to Comparative Example 2, the grain boundary insulation layer is formed in a thickness of several tens of nanometers.

[0136] In the intergranular insulation type capacitor according to Comparative Example 2, the grain boundary insulation layer does not include two-dimensional nanosheets unlike FIG. 1 and includes strontium titanate ($SrTiO_3$) having no oxygen vacancy and an acceptor element of manganese (Mn).

Comparative Example 3

[0137] An intergranular insulation type capacitor according to Comparative Example 3 is prepared in accordance with the same procedure as in Comparative Example 2, except that the strontium titanate ($SrTiO_3$) core material is formed to have an average particle diameter of about 1,000 nm. In the intergranular insulation type capacitor according to Comparative Example 3, the grain boundary insulation layer is formed in a thickness of several tens of nanometers.

[0138] In the intergranular insulation type capacitor according to Comparative Example 3, the grain boundary insulation layer does not include the two-dimensional nanosheet as in Comparative Example 2 and includes strontium titanate ($SrTiO_3$) having no oxygen vacancy and an acceptor element of manganese (Mn).

[0139] Hereinafter, the compositions and all properties of intergranular insulation type capacitors according to Examples 9 and 10 and Comparative Examples 2 and 3 are shown in Table 2.

(Table 2)

	Crystal grain		Grain boundary insulation layer			Apparent relative permittivity of Intergranular insulation type capacitor (ε_rAPP)
	Compos-ition	Average particle diameter (nm)	Composi tion	Two-dimensio nal nanoshe et amount (volume %)	Thickne ss	
Ex.9	$SrTiO_{3-\delta}$	1,300	$Ca_2Na_2Nb_5O_{16}$ + $SrTiO_3$	80	several tens of nanom eters	4,420
Ex.10	$SrTiO_{3-\delta}$	1,000	$Sr_2Nb_3O_{10}$ + $SrTiO_3$	80	several tens of nanom eters	7,950
Comp arative Ex.2	$SrTiO_{3-\delta}$	1,300	$SrTiO_3$	0	several tens of nanom eters	2,600
Comp arative Ex.3	$SrTiO_{3-\delta}$	1,000	$SrTiO_3$	0	several tens of nanom eters	2,300

[0140] Referring to Tables 1 and 2, it is confirmed that the intergranular insulation type capacitors according to Examples 9 and 10 have larger average particle diameters of the crystal grain than those of Examples 1 to 8, and the thicknesses of the grain boundary insulation layers are also increased in about 5 nm to several tens of nanometers.

[0141] Meanwhile, referring to Table 2, it is confirmed that Examples 9 and 10 that the grain boundary insulation layer includes the two-dimensional nanosheet exhibit a superior apparent relative permittivity to those of Comparative Examples 2 and 3 including no two-dimensional nanosheet, with the average particle diameter of the same crystal grain as a reference.

[0142] In addition, it is confirmed that referring to Examples 9 and 10, the apparent relative permittivity may be changed in the case that the material of the two-dimensional nanosheet is different even if using the crystal grain core material of the same material including almost similar average particle diameter because ε_rAPP in Equation 1 is changed depending upon the change of the nanosheet material.

[0143] While this disclosure has been described in connection with what is presently considered to be practical example embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

Claims

1. A dielectric composite, comprising

   a plurality of crystal grains comprising a semiconductor or conductive material, and
   a grain boundary layer between the crystal grains,
   characterized in that the grain boundary layer is an insulation layer comprising a two-dimensional layered dielectric material covering at least a portion of a surface of at least one of the crystal grains.

2. The dielectric composite of claim 1, wherein the two-dimensional layered material comprises a single layer.

3. The dielectric composite of claim 1 or 2, wherein the two-dimensional layered dielectric material comprises two or more laminated layers.

4. The dielectric composite of any preceding claim, wherein the two-dimensional layered dielectric material directly contacts the surface of at least one of the crystal grains.

5. The dielectric composite of claim 1, wherein the two-dimensional layered dielectric material covers an entirety of the surface of at least one of the crystal grains.

6. The dielectric composite of any preceding claim, wherein the two-dimensional layered dielectric material has a thickness of less than or equal to 120 nanometers.

7. The dielectric composite of any preceding claim, wherein the two-dimensional layered dielectric material has a relative permittivity of greater than or equal to 50 and less than or equal to 1000.

8. The dielectric composite of any preceding claim, wherein the grain boundary insulation layer further comprises a three-dimensional bulk material combined with the two-dimensional layered dielectric material.

9. The dielectric composite of any preceding claim, wherein the two-dimensional layered dielectric material is present in a range of 10 volume% to 100 volume%, based on 100 volume% of the grain boundary insulation layer.

10. The dielectric composite of any preceding claim, wherein the two-dimensional layered dielectric material is delaminated from a material comprising an aurivillius phase, a material comprising a Ruddlesden-Popper phase, a material comprising a Dion-Jacobson phase, titano-niobate, or a combination thereof.

11. The dielectric composite of any preceding claim, wherein the two-dimensional layered dielectric material is represented by Chemical Formula 1:

    [Chemical Formula 1] $X_m(A_{(n-1)}B'_nO_{(3n+1)})$

    wherein, in Chemical Formula 1, X comprises H, an alkali metal, a cationic compound, or a combination thereof, A comprises Ca, Na, Ta, Bi, Ba, Sr, or a combination thereof, B' comprises W, Mo, Cr, Ta, Nb, V, Zr, Hf, Pb, Sn, La, Ti, or a combination thereof, $0 \leq m \leq 2$, and $n \geq 1$, and optionally X comprises the cationic compound, and the cationic compound comprises a tetramethylammonium compound, a tetraethylammonium compound, a tetrapropylammonium compound, a tetrabutylammonium compound, a methylamine compound, an ethylamine compound, a propylamine compound, a butylamine compound, a polyethylenimine compound, or a combination thereof, and further optionally wherein the two-dimensional layered material represented by Chemical Formula 1 is electrically neutral.

12. The dielectric composite of any preceding claim, wherein the crystal grains comprise barium titanate, strontium titanate, lead titanate, lead zirconate, lead titanate zirconate, or a combination thereof; or has an average particle diameter in a range of 50 nanometers to 2 micrometers.

13. The dielectric composite of any preceding claim, wherein the dielectric composite has a relative permittivity of greater than or equal to 1000, and optionally greater than or equal to 4000, and less than or equal to about 20000.

14. A multi-layered capacitor (1) comprising:

laminated alternate layers comprising an internal electrode (12) and
a dielectric layer (11),
wherein the dielectric layer comprises the dielectric composite of any preceding claim, and optionally wherein the internal electrode and the dielectric layer comprise three or more laminated layers.

15. An electronic device comprising the dielectric composite of any of claims 1 to 13, and optionally wherein the electronic device is a varistor, a thermistor, or a capacitor for storing energy.

Patentansprüche

1. Dielektrischer Verbundstoff, umfassend

eine Vielzahl von Kristallkörnern, umfassend ein Halbleiter- oder leitendes Material; und
eine Korngrenzschicht zwischen den Kristallkörnern;
dadurch gekennzeichnet, dass die Korngrenzschicht eine Isolationsschicht ist, die ein zweidimensionales geschichtetes dielektrisches Material umfasst, das zumindest einen Abschnitt einer Oberfläche von zumindest einem der Kristallkörner bedeckt.

2. Dielektrischer Verbundstoff nach Anspruch 1, wobei das zweidimensionale geschichtete Material eine einzelne Schicht umfasst.

3. Dielektrischer Verbundstoff nach Anspruch 1 oder 2, wobei das zweidimensionale geschichtete dielektrische Material zwei oder mehr laminierte Schichten umfasst.

4. Dielektrischer Verbundstoff nach einem vorhergehenden Anspruch, wobei das zweidimensionale geschichtete dielektrische Material die Oberfläche von zumindest einem der Kristallkörner direkt kontaktiert.

5. Dielektrischer Verbundstoff nach Anspruch 1, wobei das zweidimensionale geschichtete dielektrische Material eine Gesamtheit der Oberfläche von zumindest einem der Kristallkörner bedeckt.

6. Dielektrischer Verbundstoff nach einem vorhergehenden Anspruch, wobei das zweidimensionale geschichtete dielektrische Material eine Dicke von weniger als oder gleich 120 Nanometern aufweist.

7. Dielektrischer Verbundstoff nach einem vorhergehenden Anspruch, wobei das zweidimensionale geschichtete dielektrische Material eine relative Permittivität von mehr als oder gleich 50 und weniger als oder gleich 1000 aufweist.

8. Dielektrischer Verbundstoff nach einem vorhergehenden Anspruch, wobei die Korngrenzenisolationsschicht ferner ein dreidimensionales Volumenmaterial kombiniert mit dem zweidimensionalen geschichteten dielektrischen Material umfasst.

9. Dielektrischer Verbundstoff nach einem vorhergehenden Anspruch, wobei das zweidimensionale geschichtete dielektrische Material in einem Bereich von 10 Volumen-% bis 100 Volumen-% basierend auf 100 Volumen-% der Korngrenzenisolationsschicht vorhanden ist.

10. Dielektrischer Verbundstoff nach einem vorhergehenden Anspruch, wobei das zweidimensionale geschichtete dielektrische Material von einem Material, das eine Aurivilius-Phase umfasst, einem Material, das eine Ruddlesden-

Popper-Phase umfasst, einem Material, das eine Dion-Jacobson-Phase umfasst, Titano-Niobat oder einer Kombination davon delaminiert ist.

11. Dielektrischer Verbundstoff nach einem vorhergehenden Anspruch, wobei das zweidimensionale geschichtete dielektrische Material durch die chemische Formel 1 dargestellt wird:

[Chemische Formel 1] $X_m(A_{(n-1)}B'_nO_{(3n+1)})$

wobei in der chemischen Formel 1 X H, ein Alkalimetall, eine kationische Verbindung oder eine Kombination davon umfasst, A Ca, Na, Ta, Bi, Ba, Sr oder eine Kombination davon umfasst, B' W, Mo, Cr, Ta, Nb, V, Zr, Hf, Pb, Sn, La, Ti oder eine Kombination davon umfasst, $0 \leq m \leq 2$, und $n \geq 1$, und optional X die kationische Verbindung umfasst und die kationische Verbindung eine Tetramethylammoniumverbindung, eine Tetraethylammoniumverbindung, eine Tetrapropylammoniumverbindung, eine Tetrabutylammoniumverbindung, eine Methylaminverbindung, eine Ethylaminverbindung, eine Propylaminverbindung, eine Butylaminverbindung, eine Polyethyleniminverbindung oder eine Kombination davon umfasst, und wobei ferner optional das zweidimensionale geschichtete Material, das durch die chemische Formel 1 dargestellt ist, elektrisch neutral ist.

12. Dielektrischer Verbundstoff nach einem vorhergehenden Anspruch, wobei die Kristallkörner Bariumtitanat, Strontiumtitanat, Bleititanat, Bleizirkonat, Bleititanatzirkonat oder eine Kombination davon umfassen; oder einen durchschnittlichen Partikeldurchmesser in einem Bereich von 50 Nanometern bis 2 Mikrometern aufweisen.

13. Dielektrischer Verbundstoff nach einem vorhergehenden Anspruch, wobei der dielektrische Verbundstoff eine relative Permittivität von mehr als oder gleich 1000 und optional mehr als oder gleich 4000 und weniger als oder gleich etwa 20000 aufweist.

14. Mehrschichtiger Kondensator (1), umfassend:

laminierte abwechselnde Schichten, die eine Innenelektrode (12) und eine dielektrische Schicht (11) umfassen, wobei die dielektrische Schicht den dielektrischen Verbundstoff nach einem vorhergehenden Anspruch umfasst und wobei optional die Innenelektrode und die dielektrische Schicht drei oder mehr laminierte Schichten umfassen.

15. Elektronische Vorrichtung, umfassend den dielektrischen Verbundstoff nach einem der Ansprüche 1 bis 13, und wobei optional die elektronische Vorrichtung ein Varistor, ein Thermistor oder ein Kondensator zum Speichern von Energie ist.

Revendications

1. Composite diélectrique comprenant :

une pluralité de grains cristallins comprenant un matériau conducteur ou semi-conducteur, et
une couche limite de grain entre les grains cristallins,
caractérisé en ce que la couche limite de grain est une couche isolante comprenant un matériau diélectrique bidimensionnel en couches recouvrant au moins une partie d'une surface d'au moins l'un des grains cristallins.

2. Composite diélectrique selon la revendication 1, ledit matériau bidimensionnel en couches comprenant une seule couche.

3. Composite diélectrique selon la revendication 1 ou 2, ledit matériau diélectrique bidimensionnel en couches comprenant deux couches stratifiées ou plus.

4. Composite diélectrique selon l'une quelconque des revendications précédentes, ledit matériau diélectrique bidimensionnel en couches étant en contact direct avec la surface d'au moins l'un des grains cristallins.

5. Composite diélectrique selon la revendication 1, ledit matériau diélectrique bidimensionnel en couches recouvrant l'intégralité de la surface d'au moins l'un des grains cristallins.

6. Composite diélectrique selon l'une quelconque des revendications précédentes, ledit matériau diélectrique bidimensionnel en couches ayant une épaisseur inférieure ou égale à 120 nanomètres.

7. Composite diélectrique selon l'une quelconque des revendications précédentes, ledit matériau diélectrique bidimensionnel en couches ayant une permittivité relative supérieure ou égale à 50 et inférieure ou égale à 1000.

8. Composite diélectrique selon l'une quelconque des revendications précédentes, ladite couche isolante limite de grain comprenant en outre un matériau brut tridimensionnel combiné au matériau diélectrique bidimensionnel en couches.

9. Composite diélectrique selon l'une quelconque des revendications précédentes, ledit matériau diélectrique bidimensionnel en couches étant présent dans la plage de 10 % en volume à 100 % en volume, sur la base de 100 % en volume de la couche isolante limite de grain.

10. Composite diélectrique selon l'une quelconque des revendications précédentes, ledit matériau diélectrique bidimensionnel en couches étant délaminé à partir d'un matériau comprenant une phase Aurivillius, d'un matériau comprenant une phase Ruddlesden-Popper, d'un matériau comprenant une phase Dion-Jacobson, de titano-niobate ou d'une combinaison de ceux-ci.

11. Composite diélectrique selon l'une quelconque des revendications précédentes, ledit matériau diélectrique bidimensionnel en couches étant représenté par la formule chimique 1 :

[Formule chimique 1] $X_m(A_{(n-1)}B'_nO_{(3n+1)})$

dans laquelle, dans la formule chimique 1, X représente un atome H, un métal alcalin, un composé cationique ou une combinaison de ceux-ci, A représente un atome Ca, Na, Ta, Bi, Ba, Sr ou une combinaison de ceux-ci, B' représente un atome W, Mo, Cr, Ta, Nb, V, Zr, Hf, Pb, Sn, La, Ti ou une combinaison de ceux-ci, $0 \leq m \leq 2$ et $n \geq 1$, et éventuellement X comprend le composé cationique, et le composé cationique comprend un composé tétraméthylammonium, un composé tétraéthylammonium, un composé tétrapropylammonium, un composé tétrabutylammonium, un composé méthylamine, un composé éthylamine, un composé propylamine, un composé butylamine, un composé polyéthylénimine ou une combinaison de ceux-ci, et éventuellement en outre ledit matériau bidimensionnel en couches représenté par la formule chimique 1 étant électriquement neutre.

12. Composite diélectrique selon l'une quelconque des revendications précédentes, lesdits grains cristallins comprenant du titanate de baryum, du titanate de strontium, du titanate de plomb, du titanate-zirconate de plomb ou une combinaison de ceux-ci ; ou ayant un diamètre moyen de particule dans la plage de 50 nanomètres à 2 micromètres.

13. Composite diélectrique selon l'une quelconque des revendications précédentes, ledit composite diélectrique ayant une permittivité relative supérieure ou égale à 1000, et éventuellement supérieure ou égale à 4000, et inférieure ou égale à environ 20000.

14. Condensateur à plusieurs couches (1) comprenant :

des couches alternées stratifiées comprenant une électrode interne (12) et
une couche diélectrique (11),
ladite couche diélectrique comprenant le composite diélectrique selon l'une quelconque des revendications précédentes, et éventuellement ladite électrode interne et ladite couche diélectrique comprenant trois couches stratifiées ou plus.

15. Dispositif électronique comprenant le composite diélectrique selon l'une quelconque des revendications 1 à 13, et éventuellement ledit dispositif électronique étant une varistance, une thermistance ou un condensateur pour stocker de l'énergie.

FIG. 1

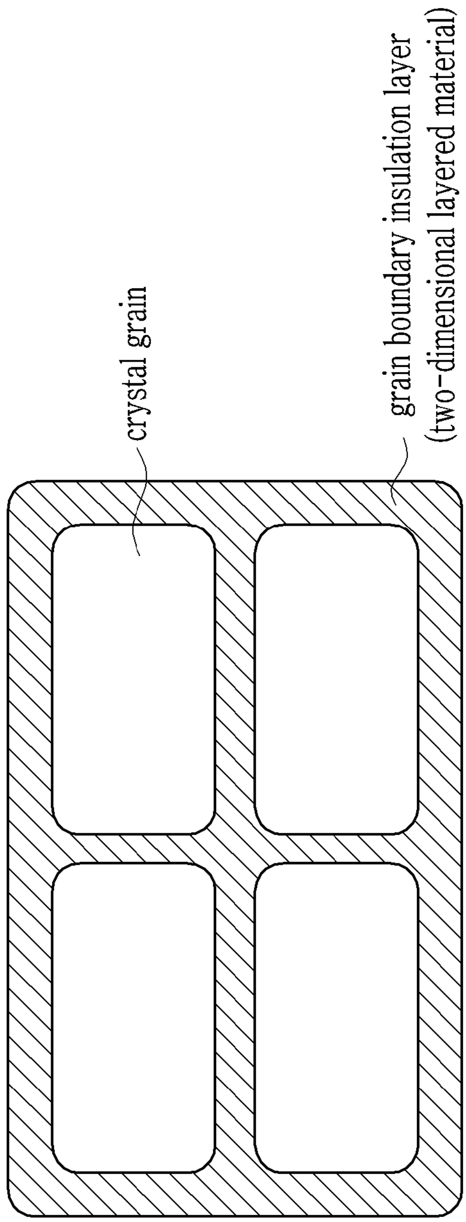

crystal grain
grain boundary insulation layer
(two-dimensional layered material)

FIG. 2

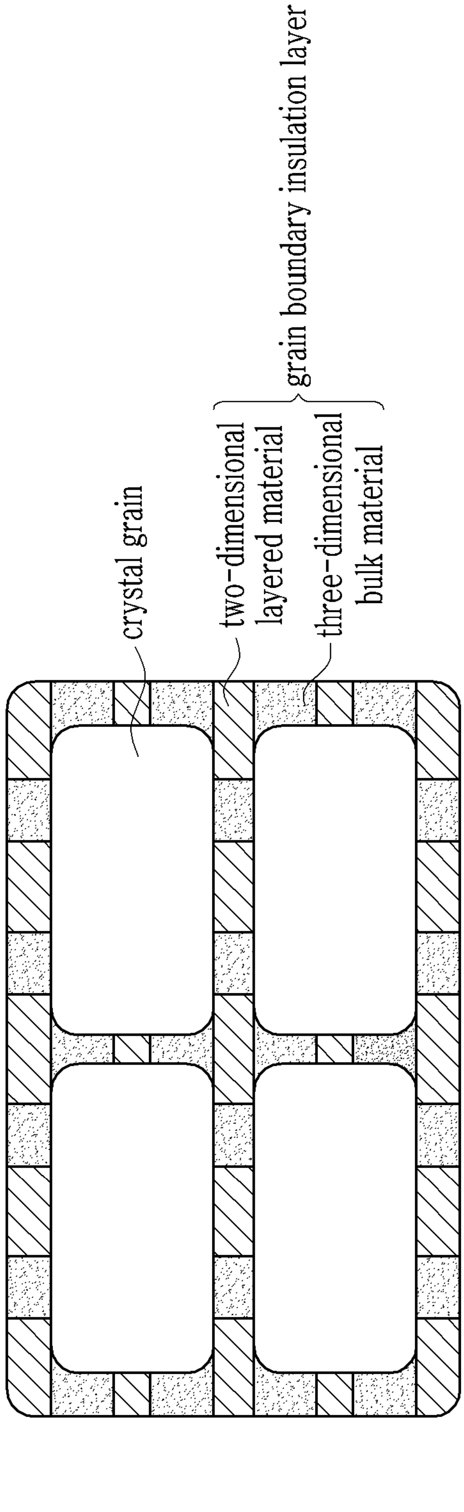

crystal grain
two-dimensional layered material
three-dimensional bulk material
grain boundary insulation layer

FIG. 3

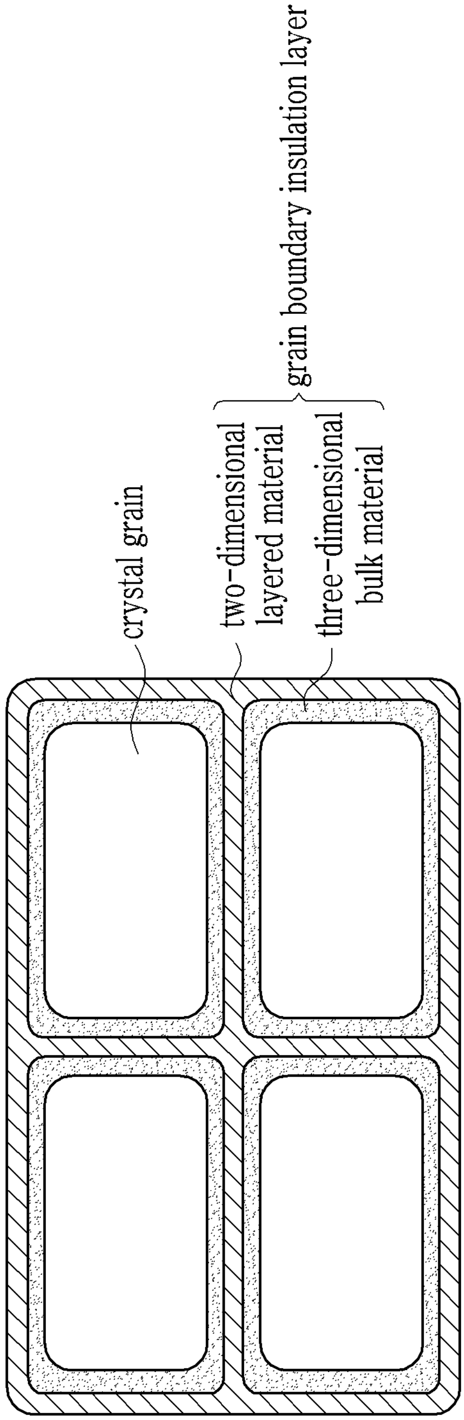
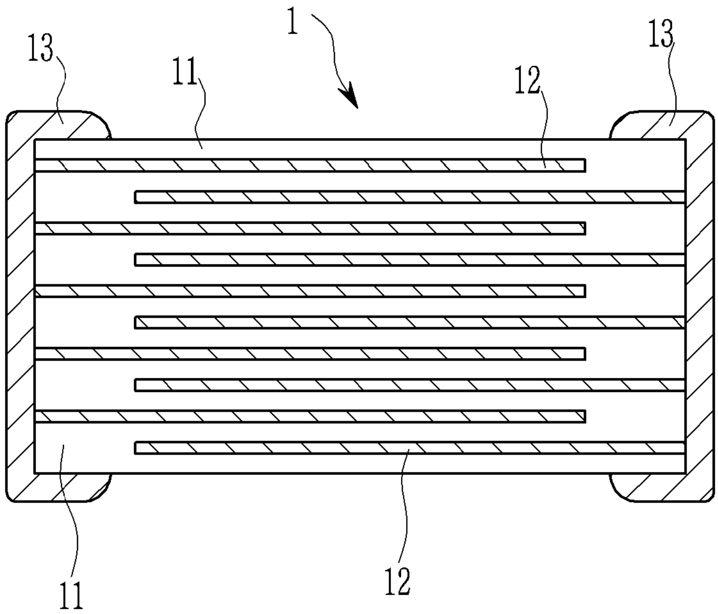

crystal grain
two-dimensional layered material
three-dimensional bulk material
grain boundary insulation layer

FIG. 4



REFERENCES CITED IN THE DESCRIPTION

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