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(54) **Method for preparing metal oxide film**

(57) A method for preparing a metal oxide film using a sol-gel method including the steps of: forming a solution containing a complex including a metal oxide oligomer and an organic solvent; depositing the solution on a substrate; removing at least part of the organic solvent from the solution on the substrate; and thermally treating the substrate for converting the metal oxide ol-

igomer into the corresponding metal oxide film. In this method, since at least part of the solvent in the oligomer-solvent complex is removed before converting the metal oxide oligomer into the metal oxide film by the thermal treatment, the mutual diffusion between the substrate metal and in the metal oxide oligomer is prevented to provide a crack-free homogeneous metal oxide film on the substrate.

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Description

BACKGROUND OF THE INVENTION

(a) Field of the Invention

[0001] The present invention relates to a method for preparing a metal oxide film on a substrate by using a sol-gel method, which is appropriate for use as an optical material, a photoelectric converter material, an electronic material, a surface protection film, a capacitor, a piezoelectric element, an SAW filter, a ferroelectric material and a ferroelectric memory.

(b) Description of the Related Art

[0002] A metal oxide film is generally formed by employing a chemical vapor deposition (CVD) method, a physical vapor deposition (PVD) method or a sol-gel method.

[0003] A metal oxide film having a larger surface area is hardly prepared by using the CVD or the PVD, and the need for a vacuum system in these methods provides an increase in costs, thereby arising an economical problem. The sol-gel method free from the economical problem offers excellent feasibility, and is regarded as a low-cost preparation method for metal oxide films.

[0004] The conventional sol-gel method may be used for preparing a metal oxide film made by fine particles. The method is conducted by dissolving a metal salt in an alcoholic solvent, adding an acidic or an alkaline catalyst in the alcoholic solvent, and depositing the solvent on a substrate by brushing or dipping followed by drying and heating. The bonding strength among the particles of the metal oxide film prepared in this manner is weak at the time the metal oxide film is formed because the particles are fine. Accordingly, when a thick metal oxide film is formed in a single process, a crack is likely generated.

[0005] In order to form a crack-free homogeneous and thick metal oxide film by using the sol-gel method, it is necessary to make the thickness of the metal oxide film formed in one step as thin as possible and to repeat the step plural times.

[0006] Further, a dry inert gas is introduced to remove moisture in air during the sol preparation or the metal oxide film formation, and the dispersion stability of metal oxide particles in the sol continues only for about 1 to 3 months.

[0007] Examples of the sol-gel method using an alcoholic solvent and a hydrochloric acid or a nitric acid catalyst are described in T. Yoko, K. Kamiya and S. Sakka, *Yogyo Kyokaishi*, 95, 150 (1987) and K. Kato, *New Ceramics*, 9, No. 8, 28 (1996). The thickness of the metal oxide film obtained in a single formation process is reported to be 0.07 to 0.09 μm .

[0008] As an improvement of the conventional sol-gel method, a process of forming a mixed diffused layer on

a titanium substrate employed for an electrode for electrolysis is proposed (JP-A-11(1999)-222690).

[0009] In this conventional process, a solution containing polymerized titanium dioxide or a complex containing a metal oxide oligomer and an aromatic compound solvent is applied onto a titanium substrate by dipping and thermal treatment to form the mixed diffused layer. The dipping and the thermal treatment allow the titanium component in the titanium substrate and the metal component in the surface layer to diffuse toward each other to form an intermediate layer for strongly bonding the substrate and the surface metal oxide layer.

[0010] Although this process is appropriate for making a stacked structure consisting of two or more layers in which at least part of adjacent layers are mixed with each other, the process is inappropriate for making a crack-free homogeneous layer or film used as an optical material, a photoelectric converter material, an electronic material, a surface protection film, a piezoelectric element, an, a ferroelectric material and a ferroelectric memory.

SUMMARY OF THE INVENTION

[0011] In view of the foregoing, an object of the present invention is to provide a method for preparing a metal oxide film on a substrate by using the metal oxide oligomer and the organic solvent.

[0012] The present invention provides, in a first aspect thereof, a method for preparing a metal oxide film including the steps of: forming a solution containing a complex including a metal oxide oligomer and an organic solvent; depositing the solution on a substrate; removing at least part of the organic solvent from the solution on the substrate; and thermally treating the substrate for converting the metal oxide oligomer into the corresponding metal oxide film.

[0013] The present invention provides, in a second aspect thereof, a method for preparing a metal oxide film including the steps of: dissolving a metal salt into an organic solvent; adding a water-alcohol solution to the organic solvent to form a solution containing a complex including a metal oxide oligomer and the organic solvent; depositing the solution on a substrate; removing at least part of the organic solvent from the solution on the substrate; and thermally treating the substrate for converting the metal oxide oligomer into the corresponding metal oxide film.

[0014] In accordance with the present invention, at least part of the solvent in the complex containing the metal oxide oligomer and the organic solvent (hereinafter referred to as "oligomer-solvent complex") is removed before converting the metal oxide oligomer into the metal oxide film by means of the thermal treatment. Thereby, the diffusion of component between the substrate and in the metal oxide oligomer is prevented to provide a crack-free homogeneous metal oxide film on the substrate.

[0015] The above and other objects, features and advantages of the present invention will be more apparent from the following description.

BRIEF DESCRIPTION OF DRAWINGS

[0016]

Fig.1 is a surface photograph of a metal oxide film prepared in Example 1, taken with a scan electron microscope.

Fig.2 is an X-ray diffraction pattern of a metal oxide film prepared in Example 13.

Fig.3 is an X-ray diffraction pattern of a metal oxide film prepared in Example 14.

Fig.4 is a surface photograph of a metal oxide film prepared in Comparative Example 1, taken with a scan electron microscope.

PREFERRED EMBODIMENTS OF THE INVENTION

[0017] Based on the fact that the immediate heating of the substrate on which the oligomer-solvent complex is formed induces the diffusion of component between the metals in the substrate and in the metal oxide oligomer, the present inventors have investigated a technique for holding the metal oxide oligomer on the surface of the substrate while maintaining the structure of the metal oligomer as much as possible, which is once prepared in the oligomer-solvent complex and is homogeneous and substantially crack-free, to reach to the present invention.

[0018] In the present invention, an organic solvent is used as a solvent for forming, together with the metal oxide oligomer, the oligomer-solvent complex. The organic solvent includes an unsaturated organic solvent and a saturated organic solvent.

[0019] The unsaturated organic compound in the solvent includes an aromatic compound having one or more 6-membered rings consisting of carbons, a heterocyclic aromatic compound, an aliphatic or an alicyclic hydrocarbon compound having a carbon-carbon double bond or a carbon-carbon triple bond, a heterocyclic compound having a carbon-carbon double bond or a carbon-hetero atom double bond and an alcohol compound having not less than three carbon atoms and a carbon-carbon double bond.

[0020] More concretely, the unsaturated organic compound includes benzene, ethylbenzene, ethoxybenzene, nitrobenzene, toluene, xylene, aniline, dimethylaniline, acetophenone, methylbenzoate, ethylbenzoate, pyridine, picoline, furan, thiophene, oxazole, thiazole, 2-methylpyridine, hexene, 1-butene, 2-methyl-1,3-pentadiene, cyclopentene, pyran, 1-buten-3-ol and ethyl acetate.

[0021] The saturated organic compound includes an aliphatic hydrocarbon compound, an alicyclic hydrocarbon compound, a heterocyclic compound, and an alco-

hol compound having not less than three carbon atoms, a carbon-carbon double bond and a halogenated aliphatic hydrocarbon compound.

[0022] More concretely, the saturated organic compound includes hexane, cyclohexane, petroleum ether, n-butanol, diethyl ether, dioxane, tetrahydrofuran, diethylmercaptane, carbon tetrachloride, chloroform and carbon tetrafluoride.

[0023] Although the solvent employable in the present invention is not restricted thereto, the solvent is desirably liquid at room temperature and easily removable in a solvent removing step described later.

[0024] The form of a metal salt includes an alkoxide, an organic salt and an inorganic salt. The alkoxide includes ethoxide, n-propoxide, iso-propoxide, n-butoxide, iso-butoxide, sec-butoxide, and tert-butoxide. The organic salt includes a phenolate, a carboxylate, and a 1, 3-diketone-type salt. The inorganic salt includes a chloride, a sulfate and a nitrate.

[0025] When the chloride is used as the metal salt, hydrogen chloride may be produced in one or more of the subsequent steps. The hydrogen chloride may deteriorate the metal oxide film. The use of a basic aromatic solvent such as aniline, pyridine and nitrobenzene excludes the hydrogen chloride or chloride ion by means of the coordination with its nitrogen atom. Accordingly, the basic aromatic solvent is preferably used when the metal chloride is used as the metal salt.

[0026] The metal in the metal salt includes Mg, Al, Si, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Cr, Sr, Y, Zr, Nb, Mo, In, Sn, Sb, Cs, Ba, Ta, W, Ru, Os, Ir, Pb, Bi, La, Ce and Gd.

[0027] At first, the oligomer-solvent complex is prepared by using the unsaturated or the saturated organic solvent.

[0028] The metal salt is dissolved into or suspended in the organic solvent such that the metal ion concentration in the solvent is adjusted to be between 0.01 and 3 mol/liter. If the metal ion concentration is below 0.01 mol/liter, the distance between the adjacent metals is so large that the metal oxide oligomer cannot be smoothly formed in a step mentioned below. On the other hand, if the metal ion concentration exceeds 3 mol/liter, the distance between the adjacent metals is so small that the three-dimensional growth of the metal oxide oligomer cannot be suppressed in the step mentioned below, thereby hardly providing the planar metal oxide oligomer.

[0029] Then, a water-alcohol mixed solution (aqueous alcohol) is desirably added to the solution including the organic solvent and the metal salt dissolved or suspended therein, thereby subjecting the metal salt to hydrolysis and dehydration condensation to prepare the metal oxide oligomer formed by a plurality of units "Me-O (metal-oxygen)". The addition is preferably conducted at a temperature between 0 and 100 °C followed by heating at a temperature between 0 and 200 °C for effecting the hydrolysis and the dehydration condensa-

tion. The reactions proceed insufficiently at a temperature below 0 °C, and the control of the formation of the oligomer-solvent complex is hardly achieved at a temperature exceeding 200 °C because the reactions proceed too rapidly. The reactions may be conducted under pressure.

[0030] In this manner, the oligomer-solvent complex is prepared. However, the oligomer-solvent complex may be prepared by an alternative process.

[0031] The alcohol used in the water-alcohol mixed solution is not especially restricted, and includes ethyl alcohol, propyl alcohol, butyl alcohol, amyl alcohol, hexyl alcohol, heptyl alcohol, octyl alcohol, nonyl alcohol, decyl alcohol and glycerin.

[0032] The exemplified alcohols have a role of controlling the activity of the water for decreasing the hydrolysis reaction rate, thereby gradually growing the metal oxide oligomer. Accordingly, the ratio of the water in the water-alcohol mixed solution significantly affects the hydrolysis reaction rate. When the reaction rate is too rapid, the metal oxide oligomer produced by the hydrolysis has a disturbed arrangement. Conversely, when the reaction rate is too slow, a longer period of time is required to complete the reaction thereby reducing the efficiency though the arrangement is not disturbed.

[0033] Accordingly, the ratio of the water in the water-alcohol mixed solution is preferably between 0.1 and 20 % in weight. When the ratio of the water is below 0.1 % in weight, the hydrolysis proceeds so slowly that the economical operations cannot be attained. On the other hand, when the ratio exceeds 20 % in weight, the hydrolysis proceeds so abruptly that the hydrous metal oxide particles may be agglomerated.

[0034] The water-alcohol mixed solution is desirably added to the metal salt such that 0.1 to 3 mol/liter of the water is present per 1 mol/liter of the metal salt. When the volume of the water is below 0.1 mol/liter, the hydrolysis proceeds so slowly that the economical operations cannot be attained. On the other hand, when the volume of the water exceeds 3 mol/liter, the hydrolysis proceeds so rapidly that the three-dimensional growth of the metal oxide oligomer cannot be suppressed in the step mentioned below, thereby hardly providing the planar metal oxide oligomer.

[0035] In view of the performance of the alcohol, optimum liquid mixed with the water in the mixed solution is an alcohol. However, another solvent may be used with or in place of the alcohol.

[0036] When the unsaturated organic solvent is used, the double bond of the solvent coordinates to the metal ion of the metal salt and metal oxide oligomer during the hydrolysis and the dehydration condensation. Especially, when the solvent is the aromatic compound or the heterocyclic aromatic compound, the dehydration condensation of the metal hydroxide proceeds along the aromatic ring to form the complex having a planar structure formed by the metal oxide oligomer and the aromat-

ic compound solvent.

[0037] In the metal oxide oligomer prepared in this manner, it is assumed that the unsaturated organic solvent makes a bond to the metal oxide oligomer by coordinating the π -electron to the metal oxide oligomer, thereby forming the three-layered sandwich structure essentially consisting of (the unsaturated organic solvent) - (the metal oxide oligomer) - (the unsaturated organic solvent).

[0038] In the present invention, the saturated organic solvent having no π -electron may be used with or in place of the unsaturated organic solvent. Since the saturated organic solvent is also highly hydrophobic and the water is hardly dissolved in the saturated organic solvent, the attack of the water to the metal salt is suppressed to decrease the hydrolysis reaction rate, thereby forming a metal oxide oligomer having a homogeneous network.

[0039] The solution containing the oligomer-solvent complex was stable even after the solution was stored for one year in a cold dark place.

[0040] Then, after the solution containing the oligomer-solvent complex is concentrated depending on necessity, the solution is applied on a substrate, on which the metal oxide film is to be formed, by means of brush painting, spray coating, spin coating, and dip coating. Since the existence of the excess water is not preferable in the subsequent steps, the solvent containing the complex in which the water may remain can be replaced with a non-aqueous solvent.

[0041] The substrate employable in the present invention is not especially restricted, and may be appropriately selected depending on a purpose and a usage. The material of the substrate includes a single crystal such as silicon wafer, polycrystal glass, a metal, a polymer and ceramic, and the shape may be a thick plate, a small fragment, a bead, a ring, a cylinder, a fiber or a chain.

[0042] The concentration of the oligomer-solvent complex applied to the substrate is desirably between 0.01 and 5 mol/liter. When the concentration is out of the range, the solution is concentrated or diluted before the complex is applied on the substrate.

[0043] The applying procedure can be conducted preferably in a solvent atmosphere including hydrophobic solvent vapor. The solvent may be the same as or different from that used for forming the complex. When different, any organic compound other than the solvent in the oligomer-solvent complex can be used, including an unsaturated organic compound and a saturated organic compound, for example, aliphatic hydrocarbon, heterocyclic hydrocarbon, alicyclic hydrocarbon containing a hetero atom and an alcohol having a relatively longer carbon chain the number of which is three or more.

[0044] The thickness of the metal oxide film prepared in this manner on the substrate in a single film forming process is generally between 0.01 and 5 μm . The film

thickness is mainly controlled by the concentration and volume of the metal oxide oligomer in the solution containing the oligomer-solvent complex prepared in the previous step.

[0045] The above procedure may be repeated for obtaining a thicker metal oxide film.

[0046] Then, the oligomer-solvent complex thus prepared is thermally treated to form the metal oxide film on the substrate. In the film forming step different from the prior art, the heating is performed after at least part of the solvent containing the oligomer-solvent complex on the substrate is removed. The partial removal of the solvent prevents the diffusion and mixing between the substrate and the metal oxide oligomer, thereby forming the homogeneous and substantially crack-free metal oxide film on the substrate. A preferable removal rate is between 20 and 80 %.

[0047] The solvent removal can be conducted by any process in which the diffusion and the mixing between the substrate and the metal oxide oligomer do not occur, for example, by heating the substrate to a temperature at which the diffusion does not take place in an inert gas atmosphere, in the air, or by placing the substrate under a reduced pressure without heating, or by indirectly irradiating, on the surface of the substrate, infrared ray from an infrared lamp or ultraviolet ray from an ultraviolet lamp after the substrate is placed in a vessel saturated with organic solvent vapor.

[0048] The infrared ray provides the thermal effect on the solvent at least part of which is removed from the substrate by means of vaporization. On the other hand, when the ultraviolet ray having no or little thermal effect is applied to the solvent on the substrate, the ultraviolet ray decomposes at least part of the solvent.

[0049] The solvent fragments having a smaller molecular size formed by the solvent decomposition easily leave the substrate without heating.

[0050] The solvent used for the irradiation may be the same as or different from that used for the complex formation or the application to the substrate.

[0051] Then, the substrate having the metal oxide oligomer and the organic solvent at least part of which is removed is thermally treated to form the metal oxide film on the surface of the substrate.

[0052] The thermal treatment is preferably conducted at a temperature between 100 and 1300 °C to form the metal oxide film. The heating out of the temperature range may invite unfavorable results. The heating below 100 °C sometimes makes it difficult to crystallize the metal oxide film, and the heating exceeding 1300 °C sometimes precipitates unwanted crystals in addition to the desired ones.

[0053] The metal oxide film prepared in this manner is homogenous and substantially crack-free because the metal oxide oligomer is thermally treated after at least part of the solvent is removed.

[0054] The substrate having the homogeneous and crack-free metal oxide film thereon is useful as an opti-

cal material, a photoelectric converter material, an electronic material and a surface protection film, and more concretely, these include a capacitor, a piezoelectric element, an SAW filter, a ferroelectric material and a ferroelectric memory.

[0055] The present invention includes, other than the metal oxide film formation on the substrate, formation of an oligomer-solvent complex solution containing a metal oxide oligomer and an organic solvent, and formation of metal oxide powders.

[0056] The oligomer-solvent complex solution employable for the application to the substrate is also used in other usage.

[0057] The metal oxide powders having the desired homogeneous structure may be prepared by removing at least part of the organic solvent from the metal oxide oligomer-solvent complex solution followed by the thermal treatment.

[0058] Although Examples of the preparation of the metal oxide film by using metal oxide oligomer in accordance with the present invention will be described, the present invention shall not be restricted thereto.

Example 1

[0059] After titanium-n-butoxide acting as a metal salt was dissolved in benzene acting as an unsaturated organic solvent at a concentration of 1 mol/liter and stirred in an ice bath, aqueous butanol (water-butanol mixed solution) having 4.0 molar concentration was added dropwise to the titanium-n-butoxide solution such that 1.6 moles of the butanol per 1 mole of the titanium ion existed in the solution. After the solution was stirred for additional 1 hour in the ice bath, the bath temperature was elevated to 80 to 90 °C. The solution was concentrated by using an evaporator and then diluted such that the titanium ion concentration was adjusted to be 1 mol/liter.

[0060] After a titanium substrate polished with alumina having an average particle diameter of about 1 μm was washed with a neutral detergent, the detergent was rinsed out with ion exchange water. After the ultrasonic cleansing was conducted to the substrate in a mixed solution containing pure water, acetone and butanol for five minutes, the substrate was dipped in the titanium oxide oligomer-solvent complex solution in an atmosphere saturated with benzene vapor.

[0061] After the substrate was pulled up from the solution at a rate of 0.15 mm/sec. by using a stepping motor and place in a glass vessel, infrared ray from an infrared lamp was indirectly irradiated through the wall of the glass vessel to the substrate in the benzene atmosphere separated from the lamp by about 20 cm for 15 minutes for drying followed by the further drying at 120 °C for 30 minutes.

[0062] After the substrate was thermally treated at 580 °C for 1 hour, the substrate was allowed to stand for cooling until the temperature thereof reached to room

temperature, thereby forming a metal oxide film on the substrate. The thickness of the metal oxide film thus obtained was measured by using EPMA (electron probe microanalysis) to be about 0.6 μm .

[0063] A microphotograph taken with a scanning electron microscope (SEM) showing the surface of the metal oxide film thus obtained is shown in Fig.1. The microphotograph shows the formation of a substantially crack-free metal oxide film.

Example 2

[0064] A metal oxide film was prepared using the same procedures as those of Example 1 except that titanium-n-butoxide was dissolved in benzene at a concentration of 0.5 mol/liter and stirred at 5 °C, and a water-butanol mixed solution containing 1.5 mol/liter of water was added dropwise to the titanium-n-butoxide solution such that 0.2 mole of the water per 1 mole of the titanium-n-butoxide existed in the solution followed by the stirring for 1 hour at 5 °C, thereby adjusting the final concentration of the titanium ion to be 0.5 mol/liter. The thickness of the metal oxide film thus obtained was about 0.1 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 3

[0065] A metal oxide film was prepared using the same procedures as those of Example 1 except that, in place of the indirect irradiation of the infrared ray, the substrate was heated at a temperature range between 40 and 60 °C under a reduced pressure (133 h Pa). The thickness of the metal oxide film thus obtained was about 0.6 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 4

[0066] A metal oxide film was prepared using the same procedures as those of Example 1 except that acetophenone was employed as the unsaturated organic solvent in place of the benzene. The thickness of the metal oxide film thus obtained was about 0.4 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 5

[0067] A metal oxide film was prepared using the same procedures as those of Example 1 except that pyridine was employed in place of the benzene. The thickness of the metal oxide film was about 0.5 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 6

[0068] A metal oxide film was prepared using the same procedures as those of Example 1 except that α -picoline was employed in place of the benzene. The thickness of the metal oxide film was about 0.5 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 7

[0069] A metal oxide film was prepared using the same procedures as those of Example 1 except that cyclohexene was employed in place of the benzene. The thickness of the metal oxide film was about 0.4 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 8

[0070] A metal oxide film was prepared using the same procedures as those of Example 1 except that 1-buten-3-ol was employed in place of the benzene. The thickness of the metal oxide film was about 0.6 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 9

[0071] A metal oxide film was prepared using the same procedures as those of Example 1 except that n-hexane was employed in place of the benzene. The thickness of the metal oxide film was about 0.6 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 10

[0072] A metal oxide film was prepared using the same procedures as those of Example 1 except that tetrahydrofuran was employed in place of the benzene. The thickness of the metal oxide film was about 0.5 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 11

[0073] A metal oxide film was prepared using the same procedures as those of Example 1 except that n-butanol was employed in place of the benzene. The thickness of the metal oxide film was about 0.4 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

free.

Example 12

[0074] A metal oxide film was prepared using the same procedures as those of Example 1 except that zirconium-n-butoxide was employed as a metal salt in place of the titanium-n-butoxide. The thickness of the metal oxide film thus obtained was about 0.3 μm . The observation of the surface state of the substrate revealed that the substrate was homogeneous and crack-free.

Example 13

[0075] Barium acetate was added to the solution containing the titanium ion of 1 mol/liter prepared in Example 1 such that the equimolar barium ion to the titanium ion was present. After the bath temperature was raised to 80 to 90 °C and the reaction was allowed to proceed for 8 hours, the solution was concentrated by using an evaporator and diluted such that the barium titanate concentration was adjusted to be 1 mol/liter.

[0076] The diluted solution was coated on a quartz glass plate which had been degreased and cleaned by using a spin-coater. After the quartz glass plate subjected to drying was sintered for 1 hour at 700 °C by using an electric furnace in the atmosphere, the glass plate was spontaneously cooled to room temperature to form a metal oxide film.

[0077] The metal oxide film thus obtained was analyzed by using an X-ray diffraction apparatus, and an X-ray diffraction pattern obtained by the analysis is shown in Fig.2. The formation of barium titanate is confirmed by the X-ray diffraction pattern.

Example 14

[0078] The solution prepared in Example 1 containing 0.96 mole of the titanium ion, and the solution prepared in Example 12 containing 1.04 moles of the zirconium ion were mixed. After the bath temperature was raised to 80 to 90 °C and the reaction was allowed to proceed for 4 hours, equimolar lead acetate to the total of the titanium ion and the zirconium ion was added to the mixed solution. After the reaction was allowed to proceed for 8 hours at the bath temperature of 80 to 90 °C, the solution was concentrated by using an evaporator and diluted such that the composite metal oxide concentration was adjusted to be 1 mol/liter.

[0079] The diluted solution was coated on a quartz glass plate which had been degreased and cleaned by using a spin-coater. After the quartz glass plate subjected to drying was sintered for 1 hour at 700 °C by using an electric furnace in the atmosphere, the glass plate was spontaneously cooled to room temperature to form a metal oxide film.

[0080] The metal oxide film thus obtained was ana-

lyzed by using an X-ray diffraction apparatus, and an X-ray diffraction pattern obtained by the analysis is shown in Fig.3. The formation of PZT is confirmed by the X-ray diffraction pattern.

Example 15

[0081] After 1 mole of titanium tetrachloride acting as a metal salt, 6 moles of n-butanol and 5 moles of aniline acting as a basic aromatic solvent were mixed, the resulting solution was heated at about 100 °C for 10 hours for effecting a titanium alkoxide forming reaction, thereby preparing a solution containing a titanium alkoxide-coordinated complex.

[0082] After the complex containing solution was added to benzene acting as an aromatic solvent such that 0.5 mole of the titanium existed in 1 liter of the benzene and heated at about 80 °C for 6 hours, aqueous butanol having a water concentration of 1.84 mol/liter was added dropwise to the complex containing solution such that 0.4 mole of the water was added per 1 mole of the titanium ion. After the solution was heated at about 80 °C for 12 hours for affecting hydrolysis of the titanium alkoxide to convert the titanium alkoxide into titanium hydroxide and subsequent dehydration condensation of the titanium hydroxide to produce polymeric titanium oxide which was then coordinated to the solvent, thereby forming a complex containing the polymeric titanium oxide.

[0083] The resulting solution containing the complex was concentrated by using an evaporator until the titanium ion concentration became to 1.5 mol/liter to obtain a titanium oxide-containing solution.

[0084] After a glass substrate which had been degreased and cleansed was dipped in the titanium oxide-containing solution, the substrate was pulled up from the solution at a rate of 0.15 mm/sec. by using a stepping motor and spontaneously dried in air at about 25 °C for 1 hour. After a thermal treatment at 500 °C for 1 hour in an electric furnace including air, the substrate was spontaneously cooled down to room temperature.

[0085] The thickness of the metal oxide film measured with a film thickness measuring apparatus (tradename: F20, available from Filmetrics Corporation) was about 1.2 μm . The surface SEM microphotograph revealed that the film had no cracks and was homogeneous, flat and tight, and the adhesion with the glass substrate was excellent.

Comparative Example 1

[0086] A metal oxide film was prepared by using a conventional sol-gel method based on the method described in Yogyo Kyokaishi 95, 150 (1987).

[0087] After 0.1 mole of titanium isopropoxide and 0.4 mole of dehydrated ethanol were mixed at room temperature, stirred and cooled down to 0°C, a mixed solution containing 0.4 mole of dehydrated ethanol, 0.1 mole

of water and 0.008 mole of hydrochloric acid was added dropwise to the titanium isopropoxide solution under stirring to prepare oxide sol by means of hydrolysis at room temperature. The oxide sol was stored in a cold dark place for examining stability thereof. The oxide particles agglomerated in the sol after a lapse of two months, and was not used.

[0088] After a titanium substrate polished with alumina having an average particle diameter of about 1 μm was dipped into the oxide sol to which the concentration adjustment had been conducted, the substrate was pulled up from the solution at a rate of 0.15 mm/sec. by using a stepping motor and air-dried. After a thermal treatment at 580 °C for 1 hour for forming a metal oxide film, the substrate was spontaneously cooled down to room temperature. The thickness of the metal oxide film obtained was about 0.07 μm .

[0089] A microphotograph taken with a scanning electron microscope (SEM) showing the surface of the metal oxide film thus obtained is shown in Fig.2. The microphotograph shows the formation of distinctive fine cracks scattered in the metal oxide film formed by the sol in which the metal oxide particles were dispersed.

Comparative Example 2

[0090] After a titanium substrate pretreated by the same procedures as those of Example 12 was dipped for 5 minutes in the solution of which a concentration was adjusted similarly to Example 12, the substrate was pulled up from the solution at a rate of 0.15 mm/sec. by using a stepping motor and was immediately heat-treated at 580 °C for 1 hour. After the heat treatment, the substrate was spontaneously cooled down to room temperature. The observation of the surface state of the substrate thus obtained revealed that the titanium metal in the substrate and the zirconium oxide in the metal oxide film were mutually diffused to each other to form a mixed layer at an interface thereof.

[0091] Since the above embodiments are described only for examples, the present invention is not limited to the above embodiments and various modifications or alternations can be easily made therefrom by those skilled in the art without departing from the scope of the present invention.

Claims

1. A method for preparing a metal oxide film comprising the steps of:

forming a solution containing a complex including a metal oxide oligomer and an organic solvent;
depositing the solution on a substrate; and
thermally treating the substrate for converting the metal oxide oligomer into the corresponding

metal oxide film.

characterized by removing at least part of the organic solvent from the solution on the substrate between the solution deposition step and the thermal treating step.

2. The method as defined in claim 1, wherein the metal of the metal oxide oligomer is one or more metals selected from the group consisting of Mg, Al, Si, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Cr, Sr, Y, Zr, Nb, Mo, In, Sn, Sb, Cs, Ba, Ta, W, Ru, Os, Ir, Pb, Bi, La, Ce and Gd.
3. The method as defined in claim 1, wherein at least part of the organic solvent is removed by irradiating infrared ray and/or ultraviolet ray on the substrate.
4. The method as defined in claim 1, wherein at least part of the organic solvent is removed by heating the substrate at a temperature below that at which diffusion of component between the substrate and the metal oxide oligomer starts.
5. The method as defined in claim 1, wherein at least part of the organic solvent is removed under a reduced pressure.
6. The method as defined in claim 1, wherein at least part of the organic solvent is removed by irradiating infrared ray or ultraviolet ray.
7. The method as defined in claim 1, wherein the organic compound is an unsaturated organic compound.
8. The method as defined in claim 7, wherein the unsaturated organic compound is one or more compounds selected from the group consisting of an aromatic compound having one or more 6-membered rings consisting of carbons, a heterocyclic aromatic compound, an aliphatic or an alicyclic hydrocarbon compound having a carbon-carbon double bond or a carbon-carbon triple bond, a heterocyclic compound having a carbon-carbon double bond or a carbon-hetero atom double bond or an alcohol compound having not less than three carbon atoms and a carbon-carbon double bond.
9. The method as defined in claim 7, wherein the unsaturated organic compound is one or more compounds selected from the group consisting of benzene, ethylbenzene, ethoxybenzene, nitrobenzene, toluene, xylene, aniline, dimethylaniline, acetophenone, methylbenzoate, ethylbenzoate, pyridine, picoline, furan, thiophene oxazole, thiazole, 2-methylpyridine, hexene, 1-butene, 2-methyl-1,3-pentadiene, cyclopentene, pyran and 1-buten-

3-ol.

10. The method as defined in claim 1, wherein the organic compound is a saturated organic compound.

11. The method as defined in claim 10, wherein the saturated organic compound is one or more compounds selected from the group consisting of an aliphatic hydrocarbon compound, an alicyclic hydrocarbon compound, a heterocyclic compound, and an alcohol compound having not less than three carbon atoms and a carbon-carbon double bond.

12. The method as defined in claim 10, wherein the saturated organic compound is one or more compounds selected from the group consisting of hexane, cyclohexane, petroleum ether, n-butanol, diethyl ether, dibutyl ether, dioxane and tetrahydrofuran.

13. The method as defined in claim 1, wherein the thermal treatment is conducted in a temperature range between 100 and 1300°C.

14. A metal oxide film prepared in accordance with the method of claim 1.

15. The metal oxide film as defined in claim 14, wherein the metal oxide in the metal oxide film is one or more composite metal oxides selected from the group consisting of Mg, Al, Si, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Cr, Sr, Y, Zr, Nb, Mo, In, Sn, Sb, Cs, Ba, Ta, W, Ru, Os, Ir, Pb Bi, La, Ce and Gd.

16. A method for preparing a metal oxide film comprising the steps of:

dissolving a metal salt into an organic solvent;
adding a water-alcohol solution to the organic solvent to form a solution containing a complex including a metal oxide oligomer and the organic solvent;
depositing the solution on a substrate; and
thermally treating the substrate for converting the metal oxide oligomer into the corresponding metal oxide film;

characterized by removing at least part of the organic solvent from the solution on the substrate between the solution deposition step and the thermal treating step.

17. The method as defined in claim 16, wherein the metal of the metal salt is one or more metals selected from the group consisting of Mg, Al, Si, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Cr, Sr, Y, Zr, Nb, Mo, In, Sn, Sb, Cs, Ba, Ta, W, Ru, Os, Ir, Pb Bi,

La, Ce and Gd.

18. The method as defined in claim 16, wherein the metal salt is one or more salt selected from the group consisting of an alkoxide, an organic salt and an inorganic salt.

19. The method as defined in claim 16, wherein the water-alcohol solution contains 0.23 to 9.2 mol/liter of the water and the alcohol has 1 to 10 carbon atoms.

20. The method as defined in claim 16, wherein the concentration of the metal salt in the organic solvent is between 0.01 and 3 mol/liter, and the water-alcohol solution is added to the organic solvent such that 0.1 to 3 moles of the water is added per 1 mole of the metal salt.

21. The method as defined in claim 16, wherein the complex formation is conducted by adding the water-alcohol solution to the organic solvent dissolving the metal salt at a temperature between 0 and 100°C followed by heating at a temperature between 0 and 200°C for effecting hydrolysis and dehydration condensation to form the complex.

22. A metal oxide oligomer-containing solution prepared by adding a water-alcohol mixed solution to an organic solvent dissolving a metal salt to form a solution dissolving a complex containing a metal oxide oligomer and the organic solvent.

23. The metal oxide oligomer-containing solution as defined in claim 22, wherein the metal of the metal salt is one or more metals selected from the group consisting of Mg, Al, Si, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Cr, Sr, Y, Zr, Nb, Mo, In, Sn, Sb, Cs, Ba, Ta, W, Ru, Os, Ir, Pb Bi, La, Ce and Gd.

24. The metal oxide oligomer-containing solution as defined in claim 22, wherein the metal salt is one or more salt selected from the group consisting of an alkoxide, an organic salt and an inorganic salt.

25. The metal oxide oligomer-containing solution as defined in claim 22, wherein the water-alcohol solution contains 0.5 to 20 % in weight of the water and the alcohol has 1 to 10 carbon atoms.

26. The metal oxide oligomer-containing solution as defined in claim 22, wherein the concentration of the metal salt in the organic solvent is between 0.01 and 3 mol/liter, and the water-alcohol solution is added to the organic solvent such that 0.1 to 3 moles of the water is added per 1 mole of the metal salt.

27. The metal oxide oligomer-containing solution as defined in claim 22, wherein the complex formation is

conducted by adding the water-alcohol solution to the organic solvent dissolving the metal salt at a temperature between 0 and 100°C followed by heating at a temperature between 0 and 200°C for effecting hydrolysis and dehydration to form the complex. 5

28. Metal oxide powders prepared by removing at least part of an organic solvent from a metal oxide oligomer—solvent complex solution and by converting the metal oxide oligomer into metal oxide by thermal treatment. 10

29. A metal oxide-containing solution prepared by heating a solution containing a metal salt, an alcohol and a basic aromatic solvent to form a solution containing a complex having a coordinated metal alkoxide and by heating the complex-containing solution for converting the metal alkoxide into the metal oxide. 15

30. The metal oxide-containing solution as defined in claim 29, wherein the metal salt is a metal chloride. 20

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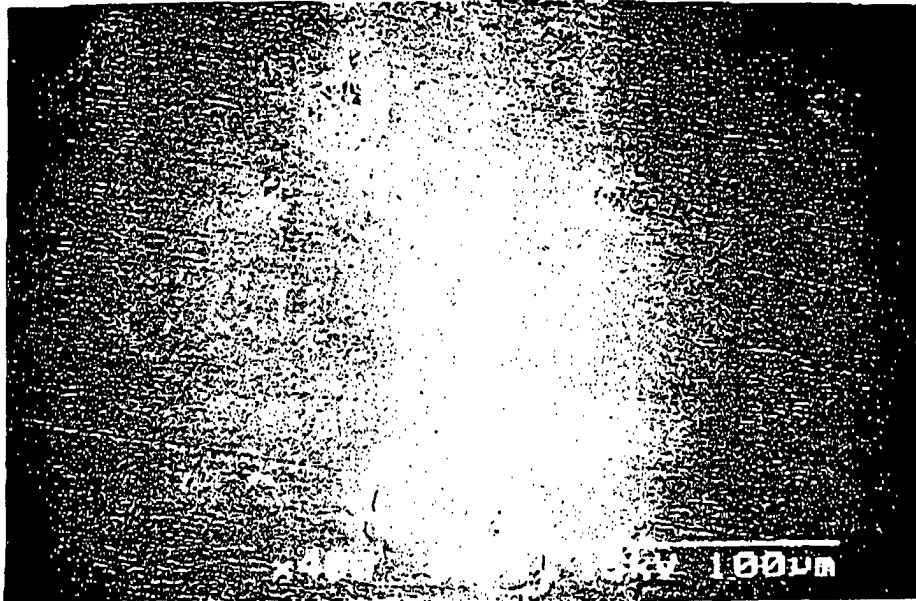
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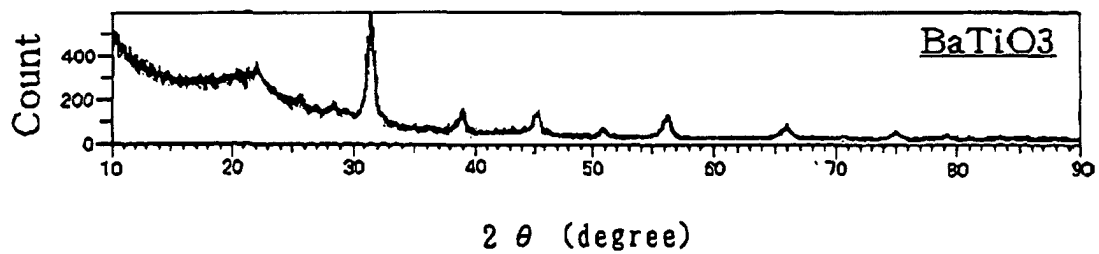
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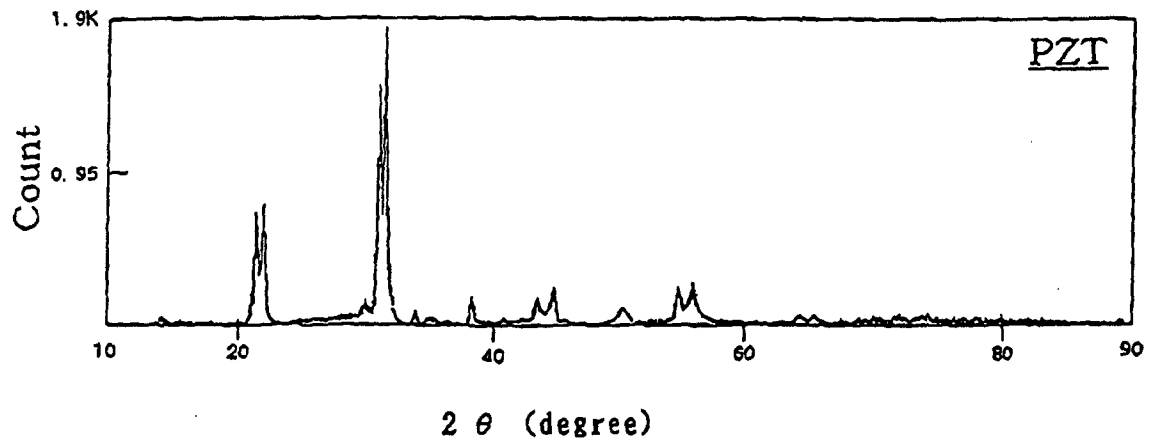
F i g . 1



F i g . 2



F i g . 3



F i g . 4
prior art

