Description

The present invention relates to a method for preparing a compound oxide superconductor thin film, and more particularly, it relates to a method for preparing a compound oxide superconducting thin film of homogeneous composition having a high critical temperature of superconduction

Superconduction, which is explained as phase transition of electrons, is a phenomenon by which a conductor loses all resistance to electric current under specific conditions to present complete diamagnetism.

Various types of superconducting devices have been proposed and developed in the field of electronics, to which the superconducting phenomenon is typically applied. A typical example of such superconducting devices is that employing the Josephson effect, through which a quantum effect is macroscopically developed by applied current when superconductive materials are weakly joined with each other. A tunnel junction type Josephson device, which has a small energy gap between superconductive materials, is expected as a switching device of an extremely high speed with low power consumption. Further, application of the Josephson device to a supersensitive sensor for magnetic fields, microwaves, radioactive rays or the like is also expected since the Josephson effect for electromagnetic waves or magnetic fields is developed as a real (correct) quantum phenomenon.

Development of a superconducting device for a very high speed computer is demanded since power consumption per unit area has approached the limit of cooling ability, while application of a superconductive material having no current loss to an interconnection member is demanded with improvement in degree of integration of an electronic circuit.

In spite of various efforts, superconduction critical temperatures T_c of conventional superconductive materials remained below 23 K, that of Nb_3Ge, for many years. However, it was discovered in 1986 than sintered bodies of $[La,Ba]_2CuO_4$, $[La,Sr]_2CuO_4$ and the like superconduct at higher critical temperatures, to open the possibility of non-cryogenic superconduction. It has been observed that these substances superconduct at critical temperatures of 30 to 50 K, which are extremely higher than those of the conventional materials. Some of the substances have superconducted at temperatures exceeding 70 K.

It has been announced that a compound oxide called YBCO, which is expressed as $Y_1Ba_2Cu_3O_{7-x}$, is a 90 K level superconductor. Further, compound oxides of Bi-Sr-Ca-Cu and Tl-Ba-Ca-Cu, which superconduct at temperatures exceeding 100 K, are so chemically stable that the same are not deteriorated in superconductivity with time, dissimilarly to YBCO or the like.

Superconductivity of a superconductor prepared by any such compound oxide is greatly influenced by oxygen deficiency in crystal. If oxygen deficiency in crystal is improper, the critical temperature is reduced to increase difference between an onset temperature and a temperature at which electrical resistance is completely zeroized.

In general, a superconductor thin film of the aforementioned compound oxide has been provided by forming a film by physical deposition such as sputtering with a deposition source of an oxide generated by sintering or the like and thereafter performing heat treatment in an oxygen atmosphere or exposing the film to oxygen plasma.

Such a compound oxide superconductor material is easily deteriorated in superconductivity particularly when the same is provided in the form of a thin film. This is conceivable because oxygen deficiency in crystal of the compound oxide superconductor is made inadequate in formation of the thin film, to cause a significant problem in use of the compound oxide superconductor material.

EP-A-0 282 839, a document according to Art. 54(3) EPC, discloses the use of an oxygen ion beam during deposition of a thin film oxide superconductor.

Furthermore, EP-A-0 285 132, being also a document according to Art. 54(3) EPC, however, according to Art. 54(4) EPC only for the Designated Contracting States DE, FR and GB, discloses a method for producing thin films of oxide superconductors, which comprises: independently vaporizing at least one material selected from the group consisting of the elements of Ia, IIa and IIIa groups of the periodic table and their compounds and at least one material selected from the group consisting of the elements of Ib, IIb and IIIb groups of the periodic table and their compounds in the presence of molecular oxygen or oxygen ions and depositing the vaporized material together with oxygen on a substrate to form a thin film of the oxide superconductor.

EP-A-0 292 387 falling within the terms of Art. 54(3) EPC discloses a process for manufacturing a superconductor, wherein a material composed of compound oxide is irradiated by an oxygen ion beam to convert this material into a superconductor.

An object of the present invention is to solve the aforementioned problem of the prior art and provide a method for preparing a thin film of a compound oxide superconductive material having a high critical

temperature T_C, which is homogeneous in composition and structure.

The present invention as claimed in claim 1 provides a method for preparing a thin film of superconductor composed of compound oxide the superconductivity of which is influenced by oxygen deficiency, on a substrate by physical vapor deposition technique, wherein evaporated particles are deposited on said substrate by use of a deposition source of a corresponding compound oxide, and an oxygen concentration gradient is formed in a corresponding deposition film by irradiating said substrate with an oxygen ion beam whose intensity is varied in time while the evaporated particles deposit on said substrate to form said deposition film.

The superconducting thin film produced by the method according to the present invention may be a compound oxide superconductor having pseudo-perovskite crystal structure of composition expressed in, for example, a general formula $(\alpha_{1-x}\beta_x)\gamma_y O_z$, in which α stands for an element selected from IIa group of the periodic table, an element β stands for an element selected from IIIa group of the periodic table and an element γ stands for an element selected from a group comprising Ib, IIb, IIIb, IVa and VIIIa group of the periodic table, x is an atomic ratio of β with respect to $(\alpha + \beta)$ and satisfies a range of $0.1 \leq x \leq 0.9$, and y and z are respective atomic ratios with respect to the atomic ratio of $(\alpha_{1-x}\beta_x)$ which is considered to be equal to 1 and each satisfy ranges of $0.4 \leq y \leq 3.0$ and $1 \leq z \leq 5$ respectively, such as $(Sr,La)_2CuO_4$ and $(Ba,La)_2CuO_4$.

The element α belonging to the group IIa of the periodic table is preferably selected from Ba, Sr, Ca, Mg and Be, more preferably from Ba and Sr, for example. 10 to 80 % of this element α may be replaced by one or two elements selected from Mg, Ca and Sr. The element β belonging to the group IIIa of the periodic table is preferably selected from Y and lanthanoids such as La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm or Yb, and more preferably from Y, La and Ho, for example. 10 to 80 % of a lanthanoid element may be replaced by one or two elements selected from the other lanthanoids. The element γ is generally Cu, which may be partially displaced by another element selected from those belonging to the groups Ib, IIb, IIIb, IVa and VIIIa of the periodic table such as Ti or V. In more concrete terms, the inventive superconductor is preferably prepared by a compound oxide expressed in any of the following formulas:

$Y_1Ba_2Cu_3O_{7-x}$, $La_1Ba_2Cu_3O_{7-x}$, $Ho_1Ba_2Cu_3O_{7-x}$, $Nd_1Ba_2Cu_3O_{7-x}$, $Sm_1Ba_2Cu_3O_{7-x}$, $Eu_1Ba_2Cu_3O_{7-x}$, $Gd_1Ba_2Cu_3O_{7-x}$, $Dy_1Ba_2Cu_3O_{7-x}$, $Er_1Ba_2Cu_3O_{7-x}$, $Yb_1Ba_2Cu_3O_{7-x}$ where x represents a number satisfying $0 < x < 1$.

The thin film which can be produced by the present invention, it is preferable to include a superconductor thin film which is conceivable in a mixed phase mainly formed of a compound oxide being in composition expressed as $\Theta_4(\Phi_{1-q},Ca_q)_mCu_nO_{p+r}$ in which Θ stands for Bi or Tl, Φ stands for Sr when Θ is Bi and stands for Ba when Θ is Tl, m and n are numbers each satisfying ranges of $6 \leq m \leq 10$ and $4 \leq n \leq 8$ respectively, $p = (6+m+n)$, q is a number which satisfies a range of $0 < q < 1$, and r is a number which satisfies a range of $-2 \leq r \leq 2$, such as that of:

$Bi_4Sr_4Ca_4Cu_6O_{20+r}$, where r represents a number satisfying $-2 \leq r \leq +2$,

$Bi_2Sr_2Ca_2Cu_3O_{10+r}$, where r represents a number satisfying $-2 \leq r \leq +2$,

$Tl_4Ba_4Ca_4Cu_6O_{20+r}$, where r represents a number satisfying $-2 \leq r \leq +2$, or

$Tl_2Ba_2Ca_2Cu_3O_{10+r}$, where r represents a number satisfying $-2 \leq r \leq +2$,

while the superconductor may be in a single phase expressed in any of the above formulas.

According to a preferred embodiment of the present invention, the deposition source is preferably prepared by mixed powder of oxides or carbonates of constituents for the compound oxide superconductor temporarily sintered at a temperature of 250 to 1200 °C or regularly sintered at a temperature within a range of 700 to 1500 °C. The deposition source may be provided in the form of sintered powder or a sintered block. The term "temporary sintering" herein used indicates treatment of temporarily firing a powder material to obtain a compound oxide.

According to another embodiment of the present invention, a plurality of deposition sources may be employed to perform physical deposition. When Ba is selected as α, Y is selected as β and Cu is selected as γ, for example, three deposition sources may be prepared by oxides of Ba, Y and Cu respectively. Alternatively, the method according to the present invention may be carried out by employing two deposition sources of $Ba_{1-x}Y_xO_z$, where x and z represent the numbers defined above, and an oxide of Cu.

The deposition source employed in the present invention is preferably in atomic ratios Y/(Y + Ba) of 0.06 to 0.94, more preferably of 0.1 to 0.4, Ba/(La + Ba) of 0.04 to 0.96, more preferably of 0.08 to 0.45 and Sr/(La + Sr) of 0.03 to 0.95, more preferably of 0.05 to 0.1. The atomic ratios of constituents for the compound oxide superconductor in the aforementioned deposition source are determined in accordance with those of constituents for the compound oxide superconductor forming a target thin film. For example, the atomic ratios between Ba, Y and Cu in the deposition sources are adjusted on the basis of those between Ba, Y and Cu in the thin film to bed formed, in response to deposition efficiency value, reaction

factors etc. of Ba, Y and Cu.

According to the present invention, an O and/or O_2 ion beam is applied to a substrate during deposition. The ion source is preferably of a separately exhaustible cold cathode type. O_2 gas being within a range of 2.27×10^{-3} to 1.11 Pa (1.7×10^{-5} to 8.3×10^{-3} Torr), preferably flows in the ion source, discharge voltage of which is preferably in a range of 0.5 to 10 kV. Acceleration voltage of the ion source is preferably within a range of 50 V to 40 kV.

According to still another embodiment of the present invention, a deposition atmosphere preferably contains O_2 with O_2 partial pressure being within a range of 1.33×10^{-6} to 1.33 Pa (1.0×10^{-8} to 1.0×10^{-2} Torr).

According to a further embodiment of the present invention, the substrate is heated by a heater to a temperature within a range of 230 to 1410 °C. The substrate is preferably prepared by MgO monocrystal or $SrTiO_3$ monocrystal, while the same may be prepared by glass, quartz, Si, stainless steel or ceramics.

The present invention is characterized in that physical deposition is performed by applying an O or O_2 ion beam while changing beam intensity, by use of a deposition source of a compound oxide, thereby to form a thin film of a compound oxide superconductor.

The thin film formed according to the method of the present invention is conceivable in a mixed phase of composition expressed in a general formula $(\alpha_{1-x}\beta_x)\gamma_xO_z$, where α, β and γ represent the elements defined above, x represents the atomic ratio of β to $\alpha + \beta$ such that $0.1 \leq x \leq 0.9$, and y and z represent atomic ratios satisfying $0.4 \leq y \leq 3.0$ and $1 \leq z \leq 5$ respectively when$(\alpha_{1-x}\beta_x)$ has the atomic ratio 1, mainly composed of $Y_1Ba_2Cu_3O_{7-x}$, for example.

An oxide employed as the deposition source in the present invention is a sintered member provided by sintering powder materials of oxides or carbonates of Ba, Y and Cu when Ba is selected as α, Y is selected as β and Cu is selected as γ, for example, as hereinabove described. The deposition source may be prepared by that temporarily or regularly sintered. Further, the deposition source may be in the form of powder obtained by pulverizing a sintered body, or a sintered block. In the case of the sintered powder, the particle size is preferably within a range of 0.01 to 1 mm. When such a deposition source of powder is employed, the film-forming rate is advantageously increased.

According to a further embodiment of the present invention, the deposition source is preferably in atomic ratios Y/(Y + Ba) of 0.06 to 0.94, more preferably of 0.1 to 0.4, Ba/(La + Ba) of 0.04 to 0.96, more preferably of 0.03 to 0.45 and Sr/(La + Sr) of 0.03 to 0.95, more preferably of 0.05 to 0.1. If the atomic ratios of the deposition source are out of the above ranges, a desired critical temperature of superconduction cannot be obtained since composition or crystal structure of a deposition film is made different from a desired pseudo-perovskite type one.

When Ba is selected as α, Y is selected as β and Cu is selected as γ, for example, the atomic ratios between Ba, Y and Cu in the deposition source are preferably determined on the basis of those between Ba, Y and Cu in the thin film in consideration of deposition efficiency, reaction factors and the like of Ba, Y and Cu. This is because the oxides of Ba, Y and Cu, being constituents for the inventive thin film, are different in melting point, vapor pressure etc. from each other, to be dissimilar in deposition efficiency, reaction factor etc. to each other. Namely, the thin film cannot be in desired atomic ratios unless those in the deposition source are properly selected. In case of sputtering, atomic ratios in the deposition source can be determined through calculation from sputtering coefficients of respective metal oxides and vapor pressure etc. on the substrate.

According to the present invention as claimed in claim 1, the O or O_2 ion beam is applied to the substrate during deposition while changing beam intensity. Superconductivity of an oxide superconductor is greatly influenced by oxygen deficiency in crystal. However, there has been established no technique of controlling oxygen deficiency, and hence superconductivity of an oxide superconductor is instable. In order to solve such a problem, the present invention supplies an oxygen concentration gradient to a deposition film by applying an oxygen ion beam during film formation while changing beam intensity. Through such oxygen ion beam application, a part of the deposition film is necessarily provided with proper oxygen concentration, to be excellent in superconductivity. A superconductor being at least partially excellent in superconductivity is regarded as highly superconductive as a whole.

Only the O_2 ion beam is preferably employed in the present invention, and hence the ion source is preferably prepared by a cold cathode type one. Further, O_2 gas within a range of 2.27×10^{-3} to 1.11 Pa (1.7×10^{-5} to 8.3×10^{-3} Torr). preferably flows in the ion source. The O_2 ion beam is deficient when the flow rate of the O_2 gas is below 2.27×10^{-3} to 1.11 Pa (1.7×10^{-5} Torr. while the same is excessive when the flow rate is above 8.3×10^{-3} Torr). whereby the target thin film may not be reformed. The ion source is preferably separately exhaustible, since this ion source is different in pressure from a chamber.

Discharge voltage of the ion source is preferably within a range of 0.5 to 10 kV. If the discharge voltage is less than 0.5 kV, ions are insufficiently generated while the excited state of the ions is instabilized when the discharge voltage exceeds 10 kV. Further, acceleration voltage of the ions is preferably within a range of 50 V to 40 kV. If the acceleration voltage is less than 50 V, oxygen cannot be sufficiently introduced into the thin film, while the cost for the apparatus is increased when the acceleration voltage exceeds 40 kV.

According to the present invention, the physical deposition is preferably performed through evaporation in low-pressure gas in a deposition atmosphere containing O_2 gas with O_2 partial pressure in a range of 1.33×10^{-6} to 1.33 Pa (1.0×10^{-8} to 1.0×10^{-2} Torr). When the O_2 partial pressure is less than 1.33×10^{-6} Pa (1.0×10^{-8} Torr)., the deposition film is inferior in crystallinity and it is difficult to obtain a perovskite or pseudo-perovskite oxide. Crystallinity is improved as the O_2 partial pressure is increased, while the deposition rate is extremely reduced when the O_2 partial pressure exceeds 1.33 Pa (1.0×10^{-2} Torr).

According to a further embodiment of the present invention, the substrate is preferably prepared by MgO monocrystal or $SrTiO_3$ monocrystal with its (001) or (110) plane being employed as a film forming surface. This is because the compound oxide superconductor employed in the inventive method has crystal anisotropy in its superconduction critical current density, and it is possible to make current easily flow in the horizontal or depth direction of the thin film by employing the film forming surface of the aforementioned substrate.

According to a further embodiment of the present invention, the substrate is heated by a heater to a temperature within a range of 230 to 1410°C. Such heating of the substrate acts on the thin film similarly to sintering, thereby to provide a proper perovskite or pseudo-perovskite oxide. However, it is difficult to control composition of the deposition film if the substrate temperature is too high, whereby a target perovskite or pseudo-perovskite oxide cannot be obtained.

According to the present invention as hereinabove described, it is possible to provide a thin film of a superconducting oxide which is higher in stability of superconductivity and critical temperature than the conventional superconductor. Thus, the present invention is effectively applied to the field of employing a superconductor as a thin film device such as a Matisoo switching device called a Josephson device, an Anacker memory device or a superconducting quantum interferometer (SQUID).

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

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 schematically illustrates a deposition apparatus employed for providing a superconducting thin film in an embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Fig. 1 schematically illustrates a deposition apparatus, which is employed for providing a superconducting oxide thin film in an embodiment of the present invention.

The apparatus as shown in Fig. 1 mainly comprises a chamber 1, a deposition source 2 and an electron gun 3 for heating the deposition source 2, both of which are arranged in the chamber 1, and a substrate 5 opposed to the deposition source 2 to be provided with a thin film on its surface. The chamber 1 is connected with a vacuum pump (not shown) through an exhaust hole 8, so that its interior can be evacuated.

A separately exhaustible ion source 10 is mounted on the chamber 1 toward the substrate 5. This ion source 10 is formed by an introduction hole 19 for introducing O_2 gas, an exhaust hole 18, a cold cathode type ion generating electrode 11 and an ion extracting electrode 12.

A heater 6 is mounted on the substrate 5 to adjust its temperature. Further, an introduction hole 9 for atmosphere gas is mounted on the chamber 1.

Description is now made on the procedure for carrying out the method according to the present invention by utilizing the apparatus as shown in Fig. 1.

The deposition source 2 and the substrate 5 are mounted in the chamber 1, which is then evacuated to introduce O_2 gas to a prescribed pressure level. O_2 gas is also introduced into the ion source 10 to a prescribed level. The substrate 5 is heated by the heater 6 to an appropriate temperature, and the electron gun 3 is started and high-frequency power is applied to the ion generating electrode 11, thereby to start deposition. The amounts of supply and exhaust are so adjusted that O_2 gas partial pressure in the chamber

1 is not changed during deposition. The O_2 ion beam is adjusted by voltage applied to the ion generating electrode 11 and that voltage of the ion extracting electrode 12.

Description is now made on Examples of the present invention, while the scope of the present invention is not limited by these Examples, as a matter of course.

In each Example, a compound oxide superconducting thin film was provided by utilizing the deposition apparatus as shown in Fig. 1.

For the purpose of comparison, two types of thin films were formed for each Example under the same conditions, with application and without application of the oxygen ion beam. Film-forming conditions of respective Examples are listed in Tables.

Example 1

The substrate 3 and the deposition source 2 were mounted in the chamber 1, which was then evacuated to 2.67×10^{-8} Pa (2×10^{-10} Torr). to introduce O_2 gas of 6.67×10^{-4} Pa (5.0×10^{-6} Torr). The ion source 10 was also evacuated to 4.0×10^{-5} Pa (3×10^{-8} Torr). to introduce O_2 gas of 6.67×10^{-2} Pa (5×10^{-4} Torr). The substrate 3 was heated up to 600 °C, to start deposition. The deposition source 2 was heated by the electron gun 3, and discharge voltage of 1.1 kV and acceleration voltage of 1.0 kV were first applied to the ion source 10. The deposition source 2 was prepared by a $YBa_2Cu_3O_7$ sintered block, which was obtained by mixing Y_2O_3 and $BaCO_3$ in the mole ratio Y/Ba of 1:2, mixing CuO by 10 wt.% in excess of an amount for attaining the mole ratio 1:2:3 between Y, Ba and Cu and sintering the mixed substance at 950 °C. The substrate 5 was prepared by an MgO monocrystal substrate, the (001) plane of which was employed as a film forming surface.

A film was formed at a film forming rate of about 5nm/S (0.50 Å/sec) to be in thickness of 1 µm by continuously changing the discharge voltage and acceleration voltage of the ion source 10 from 0.8 to 1.3 kV and from 0.5 to 2 kV respectively while changing intensity of the oxygen ion beam. Then, a sample was prepared to measure resistance of the thin film thus obtained, by forming a pair of Al electrodes on both end portions of the thin film formed on the substrate 5 by vacuum deposition and soldering lead wires to the Al electrodes.

The sample was dipped in liquid helium in a cryostat and temporarily cooled to 8 K to confirm transition to a superconducting state. Then the sample was gradually heated by a heater, thereby to measure a temperature T_{CI} at which the sample started to lose superconductivity and present electric resistance, and a temperature T_C at which the sample completely lost superconductivity to present electric resistance similarly to a normal state.

Table 1 shows principal film forming conditions and the temperatures T_C and T_{CI} of Example 1.

Example 2

The deposition source 2 was prepared by an $LaBa_2Cu_3O_7$ sintered block obtained by mixing La_2O_3 and $BaCO_3$ in the mole ratio La/Ba of 1:2, mixing CuO by 10 wt.% in excess of an amount for attaining the mole ratio 1:2:3 between La, Ba and Cu and sintering the mixed substance at 970 °C. The substrate 5 was prepared by an MgO monocrystal substrate, the (001) plane of which was employed as a film forming surface.

A thin film was formed in procedure identical to that of Example 1, to measure temperatures T_C and T_{CI} in a similar manner. Table 1 also shows principal film forming conditions and the temperatures T_C and T_{CI} of Example 2.

Example 3

As a deposition source a sintered block of $(La_{0.925}Sr_{0.075})_2CuO_4$ sintered block obtained by mixing La_2O_3 and $SrCO_3$ in the mole ratio La/Sr of 0.925/0.075, mixing CuO by 10 wt.% in excess of an amount for attaining an atomic ratio 1.85:0.15:1 between La, Sr and Cu and sintering the mixed substance at 925 °C. The substrate 5 was prepared by an $SrTiO_3$ monocrystal substrate, the (001) plane of which was employed as a film forming surface.

A thin film was formed by procedure identical to that of Example 1, to similarly measure temperatures T_C and T_{CI}. Table 1 also shows principal film forming conditions and the temperatures T_C and T_{CI} of Example 3.

Example 4

The deposition source 2 was prepared by a $Bi_4Sr_4Ca_4Cu_6O_{20+r}$ ($-2 \leq r \leq 2$) block obtained by mixing Bi_2O_3, $SrCO_3$, CaO and CuO powder to be in composition after sintering, of $Bi_4Sr_4Ca_4Cu_6O_{20+r}$, and sintering the mixture at 820°C. The substrate 5 was prepared by an $SrTiO_3$ monocrystal substrate, the (110) plane of which was employed as a film forming surface.

A thin film was formed in procedure identical to that of Example 1, to similarly measure temperatures T_C and T_{CI}. Table 2 shows principal film forming conditions and the temperatures T_C and T_{CI} of Example 4.

Example 5

The deposition source 2 was prepared by a $Tl_4Ba_4Ca_4Cu_6O_{20+r}$ ($-2 \leq r \leq 2$) block obtained by mixing Tl_2O_3, $BaCO_3$, CaO and CuO powder to be in composition, after sintering, of $Tl_4Ba_4Ca_4Cu_6O_{20+r}$, and sintering the mixture at 910°C. The substrate 5 was prepared by an $SrTiO_3$ monocrystal substrate, the (110) plane of which was employed as a film forming surface.

A thin film was formed in procedure similar to that of Example 1, to similarly measure temperatures T_C and T_{CI}. Table 2 also shows principal film forming conditions and the temperatures T_C and T_{CI} of Example 5.

Table 1

	O_2 Partial Pressure (Torr) Pa	Substrate Temperature (°C)	Ion Source			Film Forming Rate (Å/sec.)	T_C (K)	T_{Ci} (K)
			O_2 Pressure (Torr) Pa	Discharge Voltage (kV)	Acceleration Voltage (kV)			
1	(5.0×10^{-5}) 6.67×10^{-3}	600	(5×10^{-4}) 6.67×10^{-2}	0.8 ~ 1.3	0.5 ~ 2.0	(0.5) 5	98	72
			——	——	——	(0.5) 5	66	13
			——	——	——	(1.0) 10	77	59
2	(2.0×10^{-5}) 2.67×10^{-3}	700	(5×10^{-4}) 6.67×10^{-2}	0.8 ~ 1.3	0.7 ~ 1.5	(1.0) 10	21	—
			——	——	——	(1.0) 10	73	55
3	(1.0×10^{-5}) 1.33×10^{-3}	750	(5×10^{-4}) 6.67×10^{-2}	0.8 ~ 1.3	0.5 ~ 3.0	(1.0) 10	34	—
			——	——	——	(1.0) 10		

Table 2

	O_2 Partial Pressure (Torr) Pa	Substrate Temperature (°C)	Ion Source: O_2 Pressure (Torr) Pa	Ion Source: Discharge Voltage (kV)	Ion Source: Acceleration Voltage (kV)	Film Forming Rate (Å/sec.) nm/s	T_c (K)	T_{ci} (K)
4	(8.0×10^{-8}) 1.07×10^{-5}	650	(5×10^{-4}) 6.67×10^{-2}	0.8 ~ 1.3	0.6 ~ 2.5	(1.5) 15	90	95
				——	——	(1.5) 15	88	64
5	(1.0×10^{-5}) 1.33×10^{-3}	680	(5×10^{-4}) 6.67×10^{-2}	1.0 ~ 3.0	1.0 ~ 3.0	(2.0) 20	85	70
				——	——	(2.0) 20	81	57

It has been proved by these Examples that crystal structure and oxygen concentration of a thin film can be properly controlled by application of the O_2 ion beam, to form an oxide superconducting thin film of excellent properties.

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

* C L M S *

Claims

1. A method of preparing a thin film of superconductor composed of compound oxide the superconductivity of which is influenced by oxygen deficiency, on a substrate (5) by physical vapor deposition technique, wherein evaporated particles are deposited on said substrate (5) by use of a deposition source (2) of a corresponding compound oxide, and an oxygen concentration gradient is formed in a corresponding deposition film by irradiating said substrate (5) with an oxygen ion beam whose intensity is varied in time while the evaporated particles deposit on said substrate (5) to form said deposition film.

2. A method in accordance with claim 1, wherein said oxygen ion beam is composed by O and/or O_2 ions.

3. A method in accordance with claim 1, wherein said ion beam is produced by an ion source provided with separately exhaustible evacuation means.

4. A method in accordance with claim 1, wherein said ion beam is produced by a cold cathode type ion source.

5. A method in accordance with claim 1, wherein oxygen gas flows through an ion source at a pressure ranging from 2.27×10^{-3} to 1.11 Pa (1.7×10^{-5} to 8.3×10^{-3} Torr).

6. A method in accordance with claim 1, wherein said ion beam is produced by an ion source which is actuated at a discharge voltage ranging from 0.5 kV to 10kV.

7. A method in accordance with claim 1, wherein said ion beam is accelerated under an acceleration potential ranging from 50 V to 40 kV.

8. A method in accordance with claim 1, wherein said substrate is heated to a temperature ranging from 230 to 1,410 °C during the deposition of evaporated particles thereon.

9. A method in accordance with claim 1, wherein the physical vapor deposition is carried out in an atmosphere containing oxygen gas having a partial pressure ranging from 1.33×10^{-6} to 1.33 Pa (1.0×10^{-8} to 1.0×10^{-2} Torr).

10. A method in accordance with claim 1, wherein said substrate is a monocrystal of MgO or $SrTiO_3$.

11. A method in accordance with claim 10, wherein the evaporated particles are deposited on a (001) plane of said monocrystal.

12. A method in accordance with claim 10, wherein the evaporated particles are deposited on a (110) plane of said monocrystal.

13. A method in accordance with claim 1, wherein said thin film obtained is composed of a compound oxide having a composition represented by the general formula:

$$(\alpha_{1-x}\beta_x)\gamma_y O_z$$

in which α stands for an element selected from IIa group of the periodic table, an element β stands for an element selected from IIIa group of the periodic table and an element γ stands for an element selected from a group comprising Ib, IIb, IIIb, IVa and VIIIa group of the periodic table, x is an atomic ratio of β with respect to (α + β) and satisfies a range of $0.1 \leq x \leq 0.9$, and y and z are respective atomic ratios with respect to the atomic ratio of $(\alpha_{1-x}\beta_x)$ which is considered to be equal to 1 and satisfy ranges of $0.4 \leq y \leq 3.0$ and $1 \leq z \leq 5$ respectively.

14. A method in accordance with claim 13, wherein said thin film obtained is composed of a compound oxide having a composition represented by the general formula:

$LnBa_2Cu_3O_{7-x}$

in which Ln stands for at least one elements selected from a group comprising Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb, and x is a number satisfying a range of $0 < x < 1$.

15. A method in accordance with claim 13, wherein said thin film obtained is composed of a compound oxide having a composition represented by the general formula:

$(La_{1-x}M_x)_2CuO_4$

in which M stands for Ba or Sr, and x is a number satisfying a range of $0 < x < 1$.

16. A method in accordance with claim 1, wherein said thin film obtained is composed of a compound oxide having a composition represented by the general formula:

$\Theta_4(\Phi_{1-q}Ca_q)_mCu_nO_{p+r}$

in which Θ stands for Bi or Tl, Φ stands for Sr when Θ is Bi and stands for Ba when Θ is Tl, m and n are numbers each satisfying ranges of $6 \leq m \leq 10$ and $4 \leq n \leq 8$ respectively, $p = (6+m+n)$, q is a number which satisfies a range of $0 < q < 1$, and r is a number which satisfies a range of $-2 \leq r \leq +2$.

17. A method in accordance with claim 16, wherein said thin film obtained is composed of a compound oxide having a composition:

$Bi_4Sr_4Ca_4Cu_6O_{20+r}$

in which r is a number satisfying a range of $-2 \leq r \leq +2$.

18. A method in accordance with claim 16, wherein said thin film obtained is composed of a compound oxide having a composition:

$Tl_4Ba_4Ca_4Cu_6O_{20+r}$

in which r is a number satisfying a range of $-2 \leq r \leq +2$.

Patentansprüche

1. Verfahren zum Herstellen eines dünnen Supraleiterfilms, zusammengesetzt aus zusammengesetztem Oxid, dessen Supraleitung durch Sauerstoffmangel beeinflußt wird, auf einem Substrat (5) durch physikalische Dampfabscheidungstechnik, wobei verdampfte Teilchen auf dem Substrat (5) durch Verwendung einer Abscheidungsquelle (2) aus einem entsprechenden zusammengesetzten Oxid abgeschieden werden, und ein Sauerstoffkonzentrationsgradient in einem entsprechenden Abscheidungsfilm ausgebildet wird durch das Bestrahlen des Substrats (5) mit einem Sauerstoffionenstrahl, dessen Intensität mit der Zeit variiert wird während die verdampften Teilchen sich auf dem Substrat (5) abscheiden, um den Abscheidungsfilm auszubilden.

2. Verfahren nach Anspruch 1, wobei der Sauerstoffionenstrahl aus O- und/oder O_2-Ionen zusammengesetzt ist.

3. Verfahren nach Anspruch 1, wobei der Ionenstrahl durch eine Ionenquelle erzeugt wird, die mit getrennt entleerbaren Evakuiermitteln versehen ist.

4. Verfahren nach Anspruch 1, wobei der Ionenstrahl durch eine Ionenquelle vom Kaltkathodentyp erzeugt wird.

5. Verfahren nach Anspruch 1, wobei Sauerstoffgas durch eine Ionenquelle mit einem Druck von $2{,}27 \times 10^{-3}$ bis 1,11 Pa ($1{,}7 \times 10^{-5}$ bis $8{,}3 \times 10^{-3}$ Torr) fließt.

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6. Verfahren nach Anspruch 1, wobei der Ionenstrahl durch eine Ionenquelle erzeugt wird, die mit einer Entladungsspannung von 0,5 kV bis 10 kV betrieben wird.

7. Verfahren nach Anspruch 1, wobei der Ionenstrahl durch ein Beschleunigungspotential von 50 V bis 40 kV beschleunigt wird.

8. Verfahren nach Anspruch 1, wobei das Substrat auf eine Temperatur von 230 bis 1410 °C während der Abscheidung der verdampften Teilchen darauf erwärmt wird.

9. Verfahren nach Anspruch 1, wobei die physikalische Dampfabscheidung in einer Atmosphäre durchgeführt wird, die Sauerstoffgas mit einem Partialdruck von $1{,}33 \times 10^{-6}$ bis 1,33 Pa ($1{,}0 \times 10^{-8}$ bis $1{,}0 \times 10^{-2}$ Torr) enthält.

10. Verfahren nach Anspruch 1, wobei das Substrat ein Einkristall aus MgO oder $SrTiO_3$ ist.

11. Verfahren nach Anspruch 10, wobei die verdampften Teilchen auf einer (001)-Ebene des Einkristalls abgeschieden werden.

12. Verfahren nach Anspruch 10, wobei die verdampften Teilchen auf einer (110)-Ebene des Einkristalls abgeschieden werden.

13. Verfahren nach Anspruch 1, wobei der erhaltene dünne Film aus einem zusammengesetzten Oxid zusammengesetzt ist, das eine Zusammensetzung aufweist, die durch die allgemeine Formel

$$(\alpha_{1-x}\beta_x)\gamma_y O_z$$

repräsentiert wird, in der α für ein Element steht, daß aus der Gruppe IIa des Periodensystems ausgewählt ist, ein Element β für ein Element steht, das aus der Gruppe IIIa des Periodensystems ausgewählt ist und ein Element γ für ein Element steht, das aus einer Gruppe ausgewählt ist, die die Ib-, IIb-, IIIb-, IVa- und VIIIa-Gruppe des Periodensystems enthält, x ein Atomverhältnis von β in Bezug auf (α + β) ist und den Bereich von $0{,}1 \leq x \leq 0{,}9$ erfüllt, und y und z entsprechende Atomverhältnisse in Bezug auf das Atomverhältnis von $(\alpha_{1-x}\beta_x)$ sind, von dem angenommen wird, daß es 1 ist und die die Bereiche von $0{,}4 \leq y \leq 3{,}0$ und $1 \leq z \leq 5$ erfüllen.

14. Verfahren nach Anspruch 13, wobei der erhaltene dünne Film aus einem zusammengesetzten Oxid zusammengesetzt ist, das eine Zusammensetzung aufweist, die durch die allgemeine Formel

$$LnBa_2Cu_3O_{7-x}$$

repräsentiert wird, in der Ln für wenigstens ein Element steht, das aus einer Gruppe ausgewählt ist, die Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm und Yb enthält und x eine Zahl ist, die den Bereich von $0 < x < 1$ erfüllt.

15. Verfahren nach Anspruch 13, wobei der erhaltene dünne Film aus einem zusammengesetzten Oxid zusammengesetzt ist, das eine Zusammensetzung aufweist, die durch die allgemeine Formel

$$(La_{1-x}M_x)_2CuO_4$$

repräsentiert wird, in der M für Ba oder Sr steht und x eine Zahl ist, die den Bereich von $0 < x < 1$ erfüllt.

16. Verfahren nach Anspruch 1, wobei der erhaltene dünne Film aus einem zusammengesetzten Oxid zusammengesetzt ist, das eine Zusammensetzung aufweist, die durch die allgemeine Formel

$$\theta_4(\Phi_{1-q}Ca_q)_mCu_nO_{p+r}$$

repräsentiert wird, in der θ für Bi oder Tl steht, Φ für Sr steht, wenn θ Bi ist und Φ für Ba steht, wenn θTl ist, m und n Zahlen sind, die jeweils die Bereiche von $6 \leq m \leq 10$ und $4 \leq n \leq 8$ erfüllen, p =-

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(6+m+n), q eine Zahl ist, die den Bereich von $0 < q < 1$ erfüllt und r eine Zahl ist, die den Bereich von $-2 \leq r \leq +2$ erfüllt.

17. Verfahren nach Anspruch 16, wobei der erhaltene dünne Film aus einem zusammengesetzten Oxid zusammengesetzt ist, das eine Zusammensetzung von

$Bi_4Sr_4Ca_4Cu_6O_{20+r}$

aufweist, in der r eine Zahl ist, die den Bereich von $-2 \leq r \leq +2$ erfüllt.

18. Verfahren nach Anspruch 16, wobei der erhaltene dünne Film aus einem zusammengesetzten Oxid zusammengesetzt ist, das eine Zusammensetzung von

$Tl_4Ba_4Ca_4Cu_6O_{20+r}$

aufweist, in der r eine Zahl ist, die den Bereich von $-2 \leq r \leq +2$ erfüllt.

Revendications

1. Méthode de préparation d'une couche mince de supraconducteur composé d'un oxyde composite ou mixte dont la supraconductivité est influencée par le manque d'oxygène, sur un substrat (5) par une technique physique de dépôt de vapeur, méthode dans laquelle les particules évaporées sont déposées sur ledit substrat(5) par utilisation d'une source (2) de dépôt d'un oxyde composite correspondant, et formation d'un gradient de la concentration en oxygène dans une couche de dépôt correspondant, par irradiation dudit substrat (5) avec un faisceau d'ions oxygène dont on fait varier l'intensité dans le temps, cependant que les particules évaporées se déposent sur ledit substrat (5) pour former ladite couche de dépôt.

2. Méthode selon la revendication 1, dans laquelle ledit faisceau d'ions oxygène est composé d'ions O et/ou O_2.

3. Méthode selon la revendication 1, dans laquelle ledit faisceau d'ions est produit par une source d'ions munie d'un moyen ou dispositif de mise sous vide pouvant être soumis à évacuation séparée.

4. Méthode selon la revendication 1, dans laquelle ledit faisceau d'ions est produit par une source d'ions du type cathode froide.

5. Méthode selon la revendication 1, dans laquelle l'oxygène gazeux circule en passant par une source d'ions à une pression comprise entre $2,27 \times 10^{-3}$ et 1,11 Pa ($1,7 \times 10^{-5}$ à $8,3 \times 10^{-3}$ Torr (mm de Hg)-).

6. Méthode selon la revendication 1, dans laquelle ledit faisceau d'ions est produit par une source d'ions qui est mise en service à une tension électrique de décharge comprise entre 0,5 kV et 10 kV.

7. Méthode selon la revendication 1, dans laquelle ledit faisceau d'ions est accéléré sous un potentiel d'accélération compris entre 50 volts et 40 kV.

8. Méthode selon la revendication 1, dans laquelle ledit substrat est chauffé jusqu'à une température comprise entre 230 et 1410 °C pendant le dépôt, sur ce substrat, des particules évaporées.

9. Méthode selon la revendication 1, dans laquelle le dépôt physique en phase vapeur est effectué dans une atmosphère contenant de l'oxygène gazeux ayant une pression partielle comprise entre $1,33 \times 10^{-6}$ et 1,33 Pa ($1,0 \times 10^{-8}$ à $1,0 \times 10^{-2}$ Torr).

10. Méthode selon la revendication 1, dans laquelle ledit substrat est un monocristal de MgO ou de $SrTiO_3$.

11. Méthode selon la revendication 10, dans laquelle les particules évaporées sont déposées sur un plan (001) dudit monocristal.

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12. Méthode selon la revendication 10, dans laquelle les particules évaporées sont déposées sur un plan (110) dudit monocristal.

13. Méthode selon la revendication 1, dans laquelle ladite couche mince obtenue se compose d'un oxyde composite ayant une composition représentée par la formule générale :

$$(\alpha_{1-x}\beta_x)\gamma_y O_z$$

dans laquelle α représente un élément choisi dans le groupe IIa du tableau périodique, β représente un élément choisi dans le groupe IIIa du tableau périodique et γ représente un élément choisi dans un ensemble comprenant des éléments de groupe Ib, IIb, IIIb, IVa et VIIIa du tableau périodique; x représente un rapport atomique entre β et (α + β) et se situe dans une gamme répondant à la relation $0,1 \leq x \leq$ à 0,9, et y et z représentent des rapports atomiques respectifs par rapport au rapport atomique de $(\alpha_{1-x}\beta_x)$, que l'on considère comme égal à 1 et ces nombres satisfont les relations $0,4 \leq y \leq 3,0$ et $1 \leq z \leq 5$, respectivement.

14. Méthode selon la revendication 13, dans laquelle ladite couche mince obtenue se compose d'un oxyde composite ayant une composition représentée par la formule générale :

$$LnBa_2Cu_3O_{7-x}$$

dans laquelle Ln représente au moins un élément choisi dans un groupe comprenant Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm et Yb, et x est un nombre satisfaisant la relation $0 < x < 1$.

15. Méthode selon la revendication 13, dans laquelle ladite couche mince obtenue se compose d'un oxyde composite dont la composition est représentée par la formule générale :

$$(La_{1-x}M_x)_2CuO_4$$

dans laquelle M représente Ba ou Sr, et x est un nombre satisfaisant la relation $0 < x < 1$.

16. Méthode selon la revendication 1, dans laquelle ladite couche mince obtenue se compose d'un oxyde composite dont la composition est représentée par la formule générale :

$$\theta_4(\phi_{1-q}Ca_q)_mCu_nO_{p+r}$$

dans laquelle θ représente Bi ou Tl; ϕ représente Sr quand θ représente Bi et représente Ba quand θ représente Tl; n et m sont des nombres satisfaisant chacun à la relation $6 \leq m \leq 10$ et $4 \leq n \leq$ à θ, respectivement, $p = (6 + m + n)$, q est un nombre satisfaisant la relation $0 < q < 1$, et r est un nombre satisfaisant la relation $-2 \leq r \leq +2$.

17. Méthode selon la revendication 16, dans laquelle ladite pellicule mince obtenue se compose d'un oxyde composite ayant pour composition :

$$Bi_4Sr_4Ca_4Cu_6O_{20+r}$$

formule dans laquelle r est un nombre satisfaisant la relation $-2 \leq r \leq +2$.

18. Méthode selon la revendication 16, dans laquelle ladite pellicule mince obtenue se compose d'un oxyde composite ayant pour composition :

$$Tl_4Ba_4Ca_4Cu_6O_{20+r}$$

dans laquelle r est un nombre satisfaisant la relation $-2 \leq r \leq +2$.