COMMONWEALTH OF AUSTRALIA

Patents Act 1952 5963

CONVENTION APPLICATION FOR A STANDARD PATENT

I/WE, SUMITOMO ELECTRIC INDUSTRIES, LTD. of 15, Kitahama 5-chome, Higashi-Ku, Osaka, 541, Japan
a Japanese company

hereby apply for the grant of a Standard Patent for an invention entitled:

PROCESS FOR DEPOSITING A SUPERCONDUCTING THIN FILM

which is described in the accompanying complete specification.

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 27-3-90

This application is made under the provision of Part XVI of the Patents Act 1952 and is based on an application for a patent or similar protection made

in JAPAN	on 14 MARCH 1987	No. 59214/1987
JAPAN	on 16 MARCH 1987	No. 60317/1987
JAPAN	on 18 MARCH 1987	No. 63203/1987
JAPAN	on 18 MARCH 1987	No. 63204/1987
JAPAN	on 18 MARCH 1987	No. 63205/1987
JAPAN	on 18 MARCH 1987	No. 63206/1987

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LODGED AT SUB-OFFICE
14 MAR 1988
Sydney

Dated this 14th day of March 1988

By: Christopher Rice

Registered Patent Attorney

To: The Commissioner of Patents
COMMONWEALTH OF AUSTRALIA

オーストラリア用

Commonwealth of Australia
The Patents Act 1952
DECLARATION IN SUPPORT

In support of the (Convention) Application made by: SUMITOMO ELECTRIC INDUSTRIES, LTD., 15, Kitahama 5-chome, Higashi-ku, Osaka, 541 JAPAN

for a patent for an invention entitled: PROCESS FOR DEPOSITING A SUPERCONDUCTING THIN FILM

I (We) Tsuneo Nakahara, Representative Director,
of and care of the applicant company do solemnly and sincerely declare as follows:

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a) I am (We are) the applicant(s) for the patent

b) I am (We are) authorised by the applicant(s) for the patent to make this declaration on its behalf.

Delete the following if not a Convention Application.

The basic application(s) as defined by section 141 (142) of the Act was (were) made

in Japan on March 14, 1987 No. Showa 62-59214
in Japan on March 16, 1987 No. Showa 62-60317
in Japan on March 18, 1987 No. Showa 62-63203
in Japan on March 18, 1987 No. Showa 62-63204
in Japan on March 18, 1987 No. Showa 62-63205
in Japan on March 18, 1987 No. Showa 62-63206

by SUMITOMO ELECTRIC INDUSTRIES, LTD.

The basic application(s) referred to in this paragraph is (are) the first application(s) made in a Convention country in respect of the invention the subject of the application.

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a) I am (We are) the actual inventor(s) of the invention

b) Nobuhiko FUJITA, Naoji FUJIMORI, Hideo ITOZAKI, Saburo TANAKA Keizo HARADA and Tetsuji JODAI all care of Itami Works of Sumitomo Electric, Industries, Ltd., 1-1, Koyakita 1-chome, Itami-shi, Hyogo, Japan

is (are) the actual inventor(s) of the invention and the facts upon which SUMITOMO ELECTRIC INDUSTRIES, LTD.
is (are) entitled to make the application are as follows:

The above inventors assigned the invention to the applicant.

Declared at Osaka, JAPAN this 8th day of April 1988

Signed X Tsuneo Nakahara Status

TSUNEO NAKAHARA

(12) PATENT ABRIDGMENT (11) Document No. AU-B-13093/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 598113

(54) Title
PROCESS FOR DEPOSITING A SUPERCONDUCTING THIN FILM

International Patent Classification(s)
(51)[4] C23C 014/08 H01L 039/24 C03C 017/245

(21) Application No. : 13093/88 (22) Application Date : 14.03.88

(30) Priority Data

(31) Number	(32) Date	(33) Country
62-59214	14.03.87	JP JAPAN
62-60317	16.03.87	JP JAPAN
62-63203	18.03.87	JP JAPAN
62-63204	18.03.87	JP JAPAN
62-63205	18.03.87	JP JAPAN
62-63206	18.03.87	JP JAPAN

(43) Publication Date : 15.09.88

(44) Publication Date of Accepted Application : 14.06.90

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(56) Prior Art Documents
AU 27099/88 H01L 39/24
AU 24867/88 H01L 39/24
AU 591836 14357/88 H01L 39/24

(57) Claim

1. A process for preparing a superconducting thin film on a substrate, characterized in that a target made of a compound oxide containing Ba; one element M selected from the group consisting of Y, La, Gd, Ho Er and Yb; and Cu is used for carrying out physical vapour deposition under the presence of oxygen to produce a thin film of perovskite type or quasi-perovskite type oxide on said substrate.

4. A process claimed in claim 1 or 2, characterized in that said target is a finally sintered mass which is obtained by final sintering of a preliminary sintered material which is obtained by preliminary sintering a power mixture of an oxide, carbonate, nitrate or sulfate

.../2

of Ba; an oxide, carbonate, nitrate or sulfate of one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb; and an oxide, carbonate, nitrate or sulfate of Cu, said final sintering being carried out at a temperature ranging from 700° to 1,500°C, preferably from 700° to 1,300°C.

5. A process claimed in any one of claims 1 to 4, characterized in that said target is in a form of sintered powder material obtained from said preliminary sintered mass or said finally sintered mass.

COMMONWEALTH OF AUSTRALIA 598113

Patent Act 1952

COMPLETE SPECIFICATION

(ORIGINAL)

Class Int. Class

Application Number :

Lodged :

Complete Specification Lodged :

Accepted :

Published :

This document contains the amendments made under Section 49.

and is correct for printing.

Priority : 14 March 1987; 16 March 1987; 18 March 1987; 18 March 1987;

Related Art : 18 March 1987; 18 March 1987

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Complete Specification for the invention entitled:

PROCESS FOR DEPOSITING A SUPERCONDUCTING THIN FILM

The following statement is a full description of this invention including the best method of performing it known to us/me:-

S P E C I F I C A T I O N

Title of the Invention

PROCESS FOR PREPARING A SUPERCONDUCTING THIN FILM

Background of the Invention

Field of the invention

The present invention relates to a process for preparing a thin film of superconductor. More particularly, it relates to a process for depositing on a substrate a superconducting thin film of a compound oxide which is uniform in composition and has a higher transition temperature of superconductivity.

Description of the related art

The superconductivity is a phenomenon which is understood as a phenomenon of phase change under which the electrical resistance become zero and the perfect diamagnetism is observed. Thus, under the superconducting condition, electric current of a very high current density can be delivered without any loss of power.

Therefore, If the superconducting power cable is realized, the power loss of the order of 7 % which is inevitable in the conventional power cables can be reduced greatly. Realization of superconducting coils for generating a very high magnetic field is expected to accelerate development in the field of fusion power generation in which the electric power is consumed beyond its output under the present technology, as well as in the field of MHD power

generation or motor-generators. The development of superconductivity are demanded also in the other industrial fields such as in the field or electric power reservation; in the field of transportation for example magnetic levitation trains, or magnetically propelling ships; in the medical field such as high-energy beam radiation unit; or in the field of science such as NMR or high-energy physics.

In addition to the abovementioned power electric applications, the superconducting materials can be used in the field of electronics, for example, as a device using the Josephson effect in which quantum efficiency is observed macroscopically when an electric current is passed through a weak junction arranged between two superconducting bodies. Tunnel junction type Josephson device which is a typical application of the Josephson effect is expected to be a high-speed and low-power consuming switching device owing to smaller energy gap of the superconducting material. It is also expected to utilize the Josephson device as a high sensitive sensors or detectors for sensing very weak magnetic field, microwave, radiant ray or the like since variation of electromagnetic wave or magnetic field is reflected in variation of Josephson effect and can be observed as a quantum phenomenon precisely. Development of the superconducting devices is also demanded in the field of high-speed computers in which the power consumption per unit area is reaching to the upper limit of the cooling capacity with increment of the integration density in order to reduce energy consumption.

However, their actual usage have been restricted because the phenomenon of superconductivity can be observed only at very low cryogenic temperatures. Among known superconducting materials, a group of materials having so-called A-15 structure show rather higher Tc (critical temperature of superconductivity) than others, but even the top record of Tc in the case of Nb_3Ge which showed the highest Tc could not exceed 23.2 K at most. This means that liquidized helium (boiling point of 4.2 K) is only one cryogen which can realize such very low temperature of Tc. However, helium is not only a limited costly resource but also require a large-scaled system for liquefaction. Therefore, there had been a strong desire for another superconducting materials having higher Tc. But no material which exceeded the abovementioned Tc had been found for all studies for the past ten years.

Possibility of existence of a new type of superconducting materials having much higher Tc was revealed by Bednorz and Muller who discovered a new oxide type superconductor in 1986 [Z. Phys. B64 (1986) 189]

This new oxide type superconducting material is $[La, Ba]_2CuO_4$ or $[La, Sr]_2CuO_4$ which are called as the K_2NiF_4-type oxide. The K_2NiF_4-type oxides show such higher Tc as 30 to 50 K which are extremely higher than the known superconducting materials and hence it becomes possible to use liquidized hydrogen (b.p. = 20.4 K) or liquidized neon (b.p. = 27.3 K) as a cryogen which bring them to exhibit the superconductivity.

However, the above mentioned new type superconducting materials which was just born have been studied and developed only in a form of sintered bodies or as a bulk produced from powders. The superconducting sintered bodies having a form of a bulk inevitably contains non-reacted particles and hence is not uniform in composition and in structure, so that they can not be used for manufacturing electronics devices.

When the superconducting material is applied to a variety of electronics devices, it is indispensable to prepare a thin film of superconducting material. The superconducting thin film, however, can not be obtained if composition and structure of the thin film is not controlled precisely.

It is also expected to utilize the superconducting material to produce a superconducting elongated article comprising a supporting member made of metal or the like in a form of wire, stand, band, tape or the like and a superconducting thin film vacuum-deposited on the supporting member. In this case also, it is necessary to establish technology how to deposit the superconducting thin film in vacuum.

The vapour deposition technique has been used for producing a thin film of superconducting material such as Nb_3Ge and $BaPb_{1-x}Bi_xO_3$. In case of a thin film of Nb_3Ge, particles of Nb and Ge are sputtered out of several targets each consisting of Nb and Ge respectively and are deposited onto a substrate to form a film composed of Nb_3Ge. Japanese patent laid-open No. 56-109,824 discloses a process for

producing a thin film of $BaPb_{1-x}Bi_xO_3$. by means of sputtering technique. But, no prior art have disclosed detailed conditions of physical deposition of the new type compound oxides. The present invention was completed after a variety of experiments and examination which were done for overcome the abovementioned problem.

Therefore, an object of the present invention is to provide a process for producing a superconducting thin film which is uniform in composition and structure and has the higher critical temperature.

Summary of the Invention

The present invention provide a process for producing a superconducting thin film, characterized in that a target used for carrying out physical vapor deposition is made of a compound oxide containing Ba; one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb; and Cu to produce a thin film of perovskite type oxide or quasi-perovskite type oxide.

The physical vapor deposition include sputtering, ion plating, vacuum deposition, ion beam deposition and molecular beam deposition, but sputtering is most preferable.

The target preferably contains perovskite type oxide or quasi-perovskite type oxide. The term of quasi-perovskite type oxide means a structure which can be considered to have such a crystal structure that is similar to Perovskite-type oxides and includes an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

According to one preferred embodiment of the present invention, the target may be a preliminary sintered mass which is obtained by sintering a power mixture of an oxide, carbonate, nitrate or sulfate of Ba; an oxide, carbonate, nitrate or sulfate of one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb; and an oxide, carbonate, nitrate or sulfate of Cu, at a temperature raging from 250 to 1,200 °C, preferably 250 to 1,100 °C. It is more preferable that the target is made of a finally sintered mass which is obtained by further sintering the abovementioned preliminary sintered material or mass at a temperature raging from 700 to 1,500 °C, preferably from 700 to 1,300 °C.

The term of preliminary sintering means that powder material is subjected to heat-treatment or calicinated or sintered to produce a compound oxide.

The target can be in a form of power as well as in a form of block or mass

The target may be composed of a plurality of target segments, for example, three target segments consisting of oxide of Ba, oxide of M, and oxide of Cu. Hereinafter, "M" stands for one element selected from a group consisting of Y, La, Gd, Ho Er and Yb. It is also possible to use two target segments, for example, consisting of $(Ba, M)O_x$ and CuO, wherein "x" represents a number of $1 \leqq x$.

According to another aspect of the present invention, an atom ratio of Cu/(Ba+M) in the target is selected in a range of from 0.5 to 0.7 and an atom ratio of Ba/(Ba+M) in the target is preferably within a range of from 0.04 to 0.97,

preferably from 0.1 to 0.7. The atom ratio of Ba, M and Cu is determined on the basis of the atom ratio of Ba, M and Cu in an objective thin film to be produced. For example, the atom ratio can be adjusted in the function of evaporation rates of Ba, M and Cu on the basis of the atom ratio of Ba, M and Cu in the thin film to be produced. More precisely, the atom ratio of Ba/(Ba+M) in the target is preferably selected from the following ranges for respective elements M:

Atom ratio

Element "M"	General range	Preferable range
Ba/(Ba+Y)	0.05 - 0.95	0.2 - 0.6
Ba/(Ba+La)	0.04 - 0.96	0.1 - 0.4
Ba/(Ba+Gd)	0.04 - 0.97	0.5 - 0.7
Ba/(Ba+Ho)	0.05 - 0.96	0.5 - 0.6
Ba/(Ba+Er)	0.04 - 0.95	0.3 - 0.5
Ba/(Ba+Yb)	0.05 - 0.96	0.5 - 0.6

When the abovementioned atom ratios Ba/(Ba+M) are not higher than 0.04 and exceed 0.97, the resulting films deposited do not exhibit desired critical temperatures of superconductivity. The atom ratio of Ba, M and Cu in the target is preferably determined on the basis of the atom ratio of Ba, M and Cu in a thin film to be produced in consideration of evaporation rates of Ba, M and Cu, because the evaporation rates of Ba, M and Cu are not identical with each other and because melting points of respective oxides of

Ba, M and Cu which are constituents of the thin film are not identical. In other words, if the atom ratio Ba, M and Cu in the target is not selected properly, the thin film obtained does not have a desired composition which exhibits superconductivity. In case of sputtering technique, the atom ratio in the target may be determined on the basis of sputtering coefficients of oxides of respective elements.

According to another preferred embodiment of the present invention, a substrate on which the thin film is deposited is preferably heated by a heater at a temperature ranging from 184 °C to 1,520 °C, preferably 184 °C to 1,000 °C during the sputtering operation. The temperature at which the substrate is heated is preferably selected from the following ranges for respective systems:

Temperature of a substrate

Element "M"	General range	Preferable range
Y type	184 - 1,450	184 - 975
La type	285 - 1,480	285 - 980
Gd type	230 - 1,500	230 - 990
Ho type	260 - 1,500	260 - 1,000
Er type	280 - 1,520	280 - 980
Yb type	270 - 1,480	270 - 970

The substarate may be made of one of materials selected from a group consisting of glass, quartz, silicon, stainless

steel and ceramics such as MgO, $BaTiO_3$, sapphire, YSZ or the like.

According to another preferred embodiment of the present invention, an atmosphere of vaporization contain Ar and O_2. The partial pressure of Ar is preferably adjusted to a range of from 1.0×10^{-3} to 1×10^{-1} Torr, preferably 5.0×10^{-3} to 1×10^{-1} Torr, while the partial pressure of O_2 is preferably adjusted to a range of from 0.5×10^{-3} to 1×10^{-1} Torr, preferably 1.0×10^{-3} to 1×10^{-1} Torr. When the partial pressure of Ar is not higher than 1.0×10^{-3}, the deposition rate become too slow to produce the thin film in industrial scale. When the partial pressure of Ar exceeds 1×10^{-1} Torr, glow discharge occur, so that deposition of oxide which exhibit a desired superconducting property can not be obtained. If the partial pressure of O_2 is not higher than 0.5×10^{-3}, the resulting thin film does not contain satisfactory amount of perovskite type oxide or quasi-perovskite type oxide because of poor crystal structure. When the partial pressure of O_2 exceeds 1×10^{-1} Torr, the deposition rate become too slow to produce the thin film in industrial scale. The partial pressure of Ar and O_2 are preferably selected from the following ranges for respective systems:

The partial pressure of Ar (Torr)

Element "M"	General range	Preferable range
Y type	1.0×10^{-3} - 1×10^{-1}	5.0×10^{-3} - 1×10^{-1}
La type	2.0×10^{-3} - 9×10^{-2}	6.0×10^{-3} - 9×10^{-2}
Gd type	1.0×10^{-3} - 2×10^{-1}	5.0×10^{-3} - 2×10^{-1}
Ho type	1.0×10^{-3} - 3×10^{-1}	5.0×10^{-3} - 3×10^{-1}
Er type	1.2×10^{-3} - 1×10^{-1}	5.4×10^{-3} - 1×10^{-1}
Yb type	1.2×10^{-3} - 1×10^{-1}	5.4×10^{-3} - 1×10^{-1}

The partial pressure of O_2 (Torr)

Element "M"	General range	Preferable range
Y type	0.7×10^{-3} - 8×10^{-2}	1.0×10^{-3} - 8×10^{-2}
La type	1.0×10^{-3} - 9×10^{-2}	1.1×10^{-3} - 9×10^{-2}
Gd type	0.9×10^{-3} - 3×10^{-1}	1.1×10^{-3} - 3×10^{-1}
Ho type	0.8×10^{-3} - 2×10^{-1}	1.0×10^{-3} - 2×10^{-1}
Er type	0.5×10^{-3} - 1×10^{-1}	1.3×10^{-3} - 1×10^{-1}
Yb type	0.6×10^{-3} - 2×10^{-1}	1.1×10^{-3} - 2×10^{-1}

According to another preferred embodiment, the physical vapor deposition is performed by high-frequency sputtering technique (RF sputtering). The high-frequency power is less than 115 W/cm^{-2}, preferably less than 15 W/cm^{-2}. In case of RF sputtering, the speed or rate of deposition increase with increase of the high-frequency power. However, if the high-frequency power exceed 115 W/cm^{-2}, arc discharge or abnormal

discharge is apt to occur. Therefore, the high-frequency power which is less than 115 W/cm^{-2}, preferably less than 15 W/cm^{-2} was used in the present invention.

According to further preferred embodiment, the distance between the substrate and the target is adjusted at a value selected from a rage of 3 to 300 mm, preferably 15 to 300 mm. When the distance is too small, it is difficult to produce plasma between the substrate and the target. Particularly, in case of the high-frequency magnetron sputtering technique, the plasma is converged or concentrated in the neighborhood of a magnet positioned behind the target, uniform deposition of the thin film can not be produced if the distance between the substrate and the target is too small. Therefore, the distance must be larger than the predetermined minimum value. To the contrary, when the distance between the substrate and the target is too large, the deposition rate become too slow to effect practical deposition. Therefore, the distance is preferably adjusted from 3 mm to 300 mm, preferably from 15 mm to 300 mm.

The high-frequency power and the distance between the substrate and the target can be selected from the following ranges for respective systems:

The high-frequency power and
the distance between the substrate and the target

Element "M"	High-frequency power (W/cm2)	Distance (mm)	
		General range	Preferable range
Y type	≦ 95	4 - 230	15 - 230
La type	≦ 100	3 - 300	15 - 300
Gd type	≦ 103	3 - 225	16 - 225
Ho type	≦ 104	5 - 215	15 - 215
Er type	≦ 103	4 - 210	16 - 210
Yb type	≦ 98	4 - 221	16 - 220

According to a preferred embodiment, the thin film obtained by the abovementioned physical vapor deposition may be heat-treated or annealed additionally in order to reduce the difference between the onset temperature where superconductivity start to be observed and the critical temperature where resistance become zero. This heat-treatment can be carried out at a temperature ranging from 250 °C to 1,700 °C, preferably from 250 °C to 1,200 °C for 0.2 to 7 hours. Through this heat-treatment of the substrate, the thin film is subjected to the same effect as sintering, so that the film is changed to the proper perovskite type oxide or quasi-perovskite type oxide. However, if the temperature of this heat-treatment is too high, it is difficult to control the composition of the

deposited film and hence objective the proper perovskite type oxide or quasi-perovskite type oxide can not be obtained.

The heat-treatment permit to improve the critical temperature (Tc) of the superconducting thin film prepared according to the present invention and also to reduce the difference between the onset temperature where superconductivity start to be observed and the critical temperature where resistance become zero. Thus, atom ratio of oxygen in the deposited thin film can be controlled or adjusted by this heat-treatment in order to improve the superconducting property of the deposited film.

As described above, an object of the heat-treatment is to homogenize the composition of the deposited thin film and to obtain the proper perovskite type oxide or quasi-perovskite type oxide. If the temperature of the heat-treatment is not higher than 250 °C, it is difficult to obtain the objective perovskite type oxide or quasi-perovskite type oxide which possess the desired critical temperature of superconductivity or it takes extremely longer time to complete the heat-treatment. To the contrary, if the temperature of the heat-treatment exceed 1,700 °C, the objective perovskite type oxide or quasi-perovskite type oxide is too much exhausted or disappeared, resulting in lowering of the critical temperature. In practice, the temperature of the heat-treatment is preferably selected in the following ranges for respective types of "M":

Temperature of heat-treatment (°C)

Element "M"	General range	Preferable range
Y type	270 - 1,450	270 - 1,090
La type	280 - 1,480	280 - 1,100
Gd type	380 - 1,700	380 - 1,200
Ho type	250 - 1,650	250 - 1,150
Er type	260 - 1,700	260 - 1,200
Yb type	250 - 1,650	250 - 1,100

The thin film obtained according to the present invention has the formula:

$Ba_pM_qCu_rO_x$

wherein "M" represents one element selected from a group consisting of Y, La, Gd, Ho Er and Yb and "p", "q", "r" and "x" represent numbers which correspond to atom ratio of the elements of Ba ,M, Cu and O.

Particularly, the thin film is considered one of the following compound oxides or their mixture:

$(Ba, M)_2CuO_{4-x}$ ("x" is a number of $1 \leqq x$)

$(Ba, M)CuO_{3-x}$ ("x" is a number of $1 \leqq x$) or

$(Ba, M)_3Cu_2O_{7-*}$ ("*" is a number of $1 \leqq *$)

The thin film obtained according to the present invention can be also considered to have the following compositions or their mixture:

Y type $Ba_{0.6}Y_{0.4}CuO_3$ or

$BaY_{0.3}Cu_{0.7}O_3$

La type $Ba_{0.6}La_{0.4}CuO_3$ or

$BaLa_{0.3}Cu_{0.7}O_3$

Gd type $Ba_{0.6}Gd_{0.4}CuO_3$ or

$BaGd_{0.3}Cu_{0.7}O_3$

Ho type $Ho_{0.6}Ba_{0.4}CuO_3$ or

$HoBa_{0.3}Cu_{0.7}O_3$

Er type $Er_{0.6}Ba_{0.4}CuO_3$ or

$ErBa_{0.3}Cu_{0.7}O_3$

Yb type $Yb_{0.6}Ba_{0.4}CuO_3$ or

$YbBa_{0.3}Cu_{0.7}O_3$

As mentioned above, the target used in the present invention may be a preliminary sintered mass which is obtained by sintering a power mixture of an oxide, carbonate, nitrate or sulfate of Ba; an oxide, carbonate, nitrate or sulfate of one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb; and an oxide, carbcnate, nitrate or sulfate of Cu, or a finally sintered mass which is obtained by further sintering the abovementioned preliminary sintered material or mass. It is also possible to use, as the target, a powder which is obtained by pulverizing the abovementioned preliminary sintered mass or finally sintered mass and a sintered block which is prepared by press-molding the abovementioned powder.

When the abovementioned powder of the sintered mass is used as the target, the efficiency of evaporation can be improved and hence higher deposition rate is achieved. The particle size of the powder is preferably selected in a range of from 0.02 to 3 mm, more particularly, can be selected from

the following ranges for respective systems or types of element "M":

Particle size of sintered powder

Element "M"	Particle size (mm)
Y type	0.06 - 3
La type	0.06 - 3
Gd type	0.02 - 2
Ho type	0.03 - 2
Er type	0.03 - 2
Yb type	0.04 - 2

The target according to the present invention can be also used in the ion plating technique in which an ion beam from an electron gun is directed onto the target.

In fact, adjustment of components which is indispensable to obtain the proper superconducting thin film is facilitated because material of the target is made of sintered mass or powder, and hence it is not scattered by sputtering gas or the ion beam.

It is apparent from the description abovementioned that the process according to the present invention permit to produce a superconducting thin film made of compound oxide having higher Tc than conventional superconducting thin film and hence the superconducting thin film obtained according to the present invention can be utilized advantageously in a

applications of thin film devices, such as Matisoo switching elements or Josephson device, Anacker memory device or SQUID (Superconducting Quantum Interference Device).

Now, apparatus which can be used to realize the abovementioned process according to the present invention will be described with reference to attached drawings which are not limitative of the present invention.

Brief description of the drawings

Figure 1 illustrates an example of an sputtering machine which can be used to carry out the process of the present invention.

Figure 2 shows an illustrative cross section of an embodiment of an ion plating machine which can be used in the process according to the present invention.

An apparatus illustrated in Figure 1 shows a sputtering machine which is used for carrying out the process according to the present invention and includes a vacuum chamber or bell jar 1, a material target 2 placed in the vacuum chamber 1, a high-frequency power source 3 connected to the target 2, and a substrate 4 on which the thin film is deposited and being faced to the target 2. A vacuum pump (not shown) connected through a port 7 to the interior of the chamber 1 functions to create vacuum therein.

Bias voltage is impressed on the substrate 4 from a source of high-voltage 5. The substrate 4 is heated by a heater 6 so that the temperature of the substrate is

adjustable. The bell jar 1 has a gas inlet 8 for introducing argon gas.

An apparatus illustrated in Figure 2 shows an ion plating machine which can be used for carrying out the process according to the present invention and includes a vacuum chamber or bell jar 11, a material target 12 placed in the vacuum chamber 11, an electron gun 13 placed in the neighborhood of the target 12 for melting and evaporating material of the target 12, and a substrate 14 on which the thin film is deposited and being faced to the target 12. A vacuum pump (not shown) connected to the interior of the chamber 11 functions to create vacuum therein.

Bias voltage is impressed on the substrate 14 from a source of high-voltage 15. The substrate 14 is heated by a heater 16 so that the temperature of the substrate is adjustable. A high-frequency coil 17 is arranged in the bell jar 11 between the target 12 and the substrate 14 in such manner that evaporated particles are enclosed by the coil. The bell jar 11 has a gas inlet 18 for introducing oxygen gas.

Now, embodiments of the process according to the present invention will be described with reference to illustrative Examples, but the scope of the present invention should not be limited thereto.

Example 1

A superconducting thin film was produced in a sputtering machine illustrated in Fig. 1.

At first, powders of $BaCO_3$, $Y_2(CO_3)_3$, and CuO are mixed uniformly in such proportions that the atom ratio of Ba/(Ba+Y) is 0.4 and the atom ration of Ba/Cu is 2/3 and then compacted. Then, the resulting compacted powder mixture is subjected to a preliminary sintering at 820 °C for 12 hours. The resulting preliminary sintered mass is pulverized and then compacted again. The resulting compacted mass is further sintered finally at 1,080 °C to obtain a target of a sintered body. Sputtering is carried out on a substrate of silicon crystal under the following conditions:

Partial pressure of oxygen	4×10^{-2} Torr
Partial pressure of argon	3×10^{-2} Torr
Temperature of the substrate	700 °C
Bias voltage imposed on the substrate	- 60 V
High-frequency power	25 W/cm^{-2}
Distance between substrate and target	40 mm

A film of about 1 micron thick is obtained at a deposition rate of 3 Angstrom/sec. For comparison, the same operation as above is repeated but no oxygen is introduced in the chamber.

To determine electric resistance of the resulting thin film, a pair of electrodes of aluminum are vacuum-deposited on a surface of the thin film at opposite ends of the surface and a pair of lead wires are soldered to the deposited aluminum electrodes.

The result was that the thin film prepared under the partial pressure of oxygen of 4×10^{-2} Torr according to the present invention showed the onset temperature (from which

superconducting phenomenon started to be appeared) of 98 K and the critical temperature (at which the complete superconductor is obtained) of 94 K. On the other hand, in the comparative example in which a thin film is prepared without introducing oxygen, although the resulting thin film showed almost same onset temperature, the electric resistance dropped rather gradually before it became zero at about 9 K. This fact revealed that introduction of oxygen into the chamber for controlling oxygen contents in the thin film during the film formation was critical to obtain a desired superconducting thin film.

Example 2

In this Example, a powder prepared from the finally sintered body is used as a target. Namely, the finally sintered body obtained in Example 1 is pulverized to prepare the powder having a average particle size of 0.3 mm and sputtering is repeated under the same operation conditions as Example 1 to obtain a superconducting thin film.

In this Example, higher deposition rate of 14 Angstrom/sec. than Example 1 is achieved.

The thin film prepared in this Example 2 in which a target composed of a sintered power showed the onset temperature (from which superconducting phenomenon started to be appeared) of about 97 K and the critical temperature (at which the complete superconductor is obtained) of 92 K.

This fact revealed that the efficiency of film formation

can be improved without spoiling the properties of a superconducting thin film substantially.

Example 3

The same operation as Example 1 is repeated except that proportions of material powders are changed and a preliminary sintered mass is used as a target. Namely, powders of $BaCO_3$, $Y_2(CO_3)_3$, and CuO are mixed in such proportions that the atom ratio of Ba:Y:Cu becomes 0.9:0.25:1 and then, the mixture is compacted and sintered preliminary at 400 °C for 12 hours.

A thin film obtained by using a target of the abovementioned preliminary sintered mass showed the onset temperature of about 95 K.

This fact revealed that a superconducting thin film can be produced when a preliminary sintered oxide is used as a target.

Example 4

The thin film obtained in Example 1 is annealed at 550 °C for 20 minutes under oxygen atmosphere of the partial oxygen pressure of 0.9×10^{-1} Torr.

The superconducting transition temperatures of the resulting annealed thin film were measured by the same method as Example 1. The result showed that electric resistance dropped much sharply than the case of Example 1 and the difference between the onset temperature and the critical temperature was 2 K.

Example 5

The same operation as Example 1 is repeated except that the final sintering temperature is changed to 920 °C, the high-frequency power is changed to 2.0 W/cm^{-2} and a substarate of magnesia (MgO) is used.

The onset temperature and the critical temperature of the resulting thin film measured by the same method as Example 1 were 98 K and 95 K respectively.

Example 6

A superconducting thin film was produced in a sputtering machine illustrated in Fig. 1.

At first, powders of $BaCO_3$, $La_2(CO_3)_3$, and CuO are mixed uniformly in such proportions that the atom ratio of Ba/(Ba+La) is 0.2 and the atom ration of Ba/Cu is 2/3 and then compacted. Then, the resulting compacted powder mixture is subjected to a preliminary sintering at 810 °C for 12 hours . The resulting preliminary sintered mass is pulverized and then compacted again. The resulting compacted mass is further sintered finally at 1,070 °C to obtain a target of a sintered body. Sputtering is carried out on a substrate of silicon crystal under the following conditions:

Partial pressure of oxygen	1×10^{-2} Torr
Partial pressure of argon	1×10^{-2} Torr
Temperature of the substrate	690 °C
Bias voltage imposed on the substrate	- 150 V
High-frequency power	20 W/cm^{-2}
Distance between substrate and target	50 mm

A film of about 1 micron thick is obtained at a deposition rate of 5 Angstrom/sec. For comparison, the same operation as above is repeated but no oxygen is introduced in the chamber.

To determine electric resistance of the resulting thin film, a pair of electrodes of aluminum are vacuum-deposited on a surface of the thin film at opposite ends of the surface and a pair of lead wires are soldered to the deposited aluminum electrodes.

The result was that the thin film prepared under the partial pressure of oxygen of 1×10^{-2} Torr according to the present invention showed the onset temperature (from which superconducting phenomenon started to be appeared) of about 60 K and the critical temperature (at which the complete superconductor is obtained) of 51 K. On the other hand, in the comparative example in which a thin film is prepared without introducing oxygen, although the resulting thin film showed almost same onset temperature, the electric resistance dropped rather gradually before it became zero at about 4 K. This fact revealed that introduction of oxygen into the chamber for controlling oxygen contents in the thin film during the film formation was critical to obtain a desired superconducting thin film.

Example 7

In this Example, a powder prepared from the finally sintered body is used as a target. Namely, the finally sintered body obtained in Example 6 is pulverized to prepare

the powder having a average particle size of 0.2 mm and sputtering is repeated under the same operation conditions as Example 1 to obtain a superconducting thin film.

In this Example, higher deposition rate of 9 Angstrom/sec. than Example 6 is achieved.

The thin film prepared in this Example 7 in which a target composed of a sintered power showed the onset temperature (from which superconducting phenomenon started to be appeared) of about 55 K and the critical temperature (at which the complete superconductor is obtained) of 49 K.

This fact revealed that the efficiency of film formation can be improved without spoiling the properties of a superconducting thin film substantially.

Example 8

The same operation as Example 6 is repeated except that proportions of material powders are changed and a preliminary sintered mass is used as a target. Namely, powders of $BaCO_3$, $La_2(CO_3)_3$, and CuO are mixed in such proportions that the atom ratio of Ba:La:Cu becomes 0.7:0.85:1 and then, the mixture is compacted and sintered preliminary at 400 °C for 12 hours.

A thin film obtained by using a target of the abovementioned preliminary sintered mass showed the onset temperature of about 58 K.

This fact revealed that a superconducting thin film can be produced when a preliminary sintered oxide is used as a target.

Example 9

The thin film obtained in Example 6 is annealed at 610 °C for 20 minutes under oxygen atmosphere of the partial oxygen pressure of 1.3×10^{-1} Torr.

The superconducting transition temperatures of the resulting annealed thin film were measured by the same method as Example 6. The result showed that electric resistance dropped much sharply than the case of Example 6 and the difference between the onset temperature and the critical temperature was 1 K.

Example 10

The same operation as Example 6 is repeated except that the final sintering temperature is changed to 930 °C, the high-frequency power is changed to 1.8 W/cm^{-2} and a substarate of magnesia (MgO) is used.

The onset temperature and the critical temperature of the resulting thin film measured by the same method as Example 1 were 62 K and 53 K respectively.

Example 11

A superconducting thin film was produced in a sputtering machine illustrated in Fig. 1.

At first, powders of $BaCO_3$, $Ho_2(CO_3)_3$, and CuO are mixed uniformly in such proportions that the atom ratio of Ba/(Ba+Ho) is 0.55 and the atom ration of Ba/Cu is 2/3 and then compacted. Then, the resulting compacted powder mixture is subjected to a preliminary sintering at 830 °C for 12

hours . The resulting preliminary sintered mass is pulverized and then compacted again. The resulting compacted mass is further sintered finally at 1,000 °C to obtain a target of a sintered body. Sputtering is carried out on a substrate of silicon crystal under the following conditions:

Partial pressure of oxygen	1×10^{-2} Torr
Partial pressure of argon	2×10^{-2} Torr
Temperature of the substrate	890 °C
Bias voltage imposed on the substrate	- 35 V
High-frequency power	8 W/cm^{-2}
Distance between substrate and target	20 mm

A film of about 1 micron thick is obtained at a deposition rate of 2 Angstrom/sec. For comparison, the same operation as above is repeated but no oxygen is introduced in the chamber.

To determine electric resistance of the resulting thin film, a pair of electrodes of aluminum are vacuum-deposited on a surface of the thin film at opposite ends of the surface and a pair of lead wires are soldered to the deposited aluminum electrodes.

The result was that the thin film prepared under the partial pressure of oxygen of 1×10^{-2} Torr according to the present invention showed the onset temperature (from which superconducting phenomenon started to be appeared) of 106 K and the critical temperature (at which the complete superconductor is obtained) of 100 K. On the other hand, in the comparative example in which a thin film is prepared without introducing oxygen, although the resulting thin film

showed almost same onset temperature, the electric resistance dropped rather gradually before it became zero at about 8 K. This fact revealed that introduction of oxygen into the chamber for controlling oxygen contents in the thin film during the film formation was critical to obtain a desired superconducting thin film.

Example 12

In this Example, a powder prepared from the finally sintered body is used as a target. Namely, the finally sintered body obtained in Example 11 is pulverized to prepare the powder having a average particle size of 0.2 mm and sputtering is repeated under the same operation conditions as Example 11 to obtain a superconducting thin film.

In this Example, higher deposition rate of 4 Angstrom/sec. than Example 11 is achieved.

The thin film prepared in this Example 12 in which a target composed of a sintered power showed the onset temperature (from which superconducting phenomenon started to be appeared) of about 105 K and the critical temperature (at which the complete superconductor is obtained) of 98 K.

This fact revealed that the efficiency of film formation can be improved without spoiling the properties of a superconducting thin film substantially.

Example 13

The same operation as Example 11 is repeated except that proportions of material powders are changed and a preliminary

sintered mass is used as a target. Namely, powders of $BaCO_3$, $Ho_2(CO_3)_3$, and CuO are mixed in such proportions that the atom ratio of Ba:Ho:Cu becomes 0.9:0.85:1 and then, the mixture is compacted and sintered preliminary at 400 °C for 12 hours.

A thin film obtained by using a target of the abovementioned preliminary sintered mass showed the onset temperature of about 103 K.

This fact revealed that a superconducting thin film can be produced when a preliminary sintered oxide is used as a target.

Example 14

The thin film obtained in Example 11 is annealed at 780 °C for 20 minutes under oxygen atmosphere of the partial oxygen pressure of 1.1×10^{-1} Torr.

The superconducting transition temperatures of the resulting annealed thin film were measured by the same method as Example 11. The result showed that electric resistance dropped much sharply than the case of Example 1 and the difference between the onset temperature and the critical temperature was 3 K.

Example 15

The same operation as Example 11 is repeated except that the final sintering temperature is changed to 940 °C, the high-frequency power is changed to 3.3 W/cm^{-2} and a substarate of magnesia (MgO) is used.

The onset temperature and the critical temperature of the resulting thin film measured by the same method as Example 1 were 107 K and 102 K respectively.

Example 16 to 18

The same operation as Example 1 is repeated except that $Y_2(CO_3)_3$ in the material powder is changed to $Gd_2(CO_3)_3$ (Example 16), $Er_2(CO_3)_3$ (Example 17), and $Yb_2(CO_3)_3$ (Example 18) respectively and that the conditions of sputtering operation are changed or modified to the values shown in Table 1.

The onset temperature (Tci) (from which superconducting phenomenon started to be appeared) and the critical temperature (Tcf) (at which the complete superconductor is obtained) of the resulting thin film measured by the same method as Example 1 are also summarized in Table 1.

Table 1

	Example 16	17	18
Element "M"	Gd	Er	Yb
Atom ratio Ba/(Ba+M)	0.6	0.4	0.55
Atom ratio Ba/Cu	2/3	2/3	2/3
Preliminary sintering Temperature (°C)	810	840	850
Duration of Preliminary sintering (hr)	12	12	12
Final sintering Temperature (°C)	1,000	1,040	1,050
Substrate	Si	Si	Si
Partial pressure of oxygen (10^{-2} Torr)	1	1	1
Partial pressure of argon (10^{-2} Torr)	1	3	3
Temperature of the substrate (°C)	880	910	890
Bias voltage imposed on the substrate (V)	-90	-50	-70
High-frequency power (W/cm^{-2})	5	12	30
Distance between substrate and target (mm)	70	50	40
Deposition rate (Angstrom/sec.)	4	3	3
Film thickness (micron)	1	1	1
Onset temperature (Tci) (K)	108	98	95
Critical temp. (Tcf) (K)	101	92	85

Example 19 to 21

In these Examples 19 to 21, powders prepared from the finally sintered body are used as respective target. Namely, the finally sintered bodies obtained in Example 16 to 18 are pulverized to prepare powders having average particle sizes shown in Table 2 and sputtering operations are repeated under the same operation conditions as Example 16 to 18 except deposition rates are improved as are shown in Table 2.

The onset temperature (Tc) and the critical temperature (Tcf) at which the complete superconductor is obtained of the resulting thin films measured by the same method as Example 1 are also summarized in Table 2.

Table 2

	Example		
	19	20	21
Element "M"	Gd	Er	Yb
Average particle size (mm)	0.2	0.3	0.3
Deposition rate (Angstrom/sec.)	9	5	10
Onset temperature (Tci) (K)	106	96	94
Critical temp. (Tcf) (K)	99	91	85

Example 22 to 24

The same operations as Example 16 to 18 are repeated respectively except that proportions of material powders are changed and targets are changed to preliminary sintered

masses. Namely, powders of $BaCO_3$; $Gd_2(CO_3)_3$, $Er_2(CO_3)_3$ or $Yb_2(CO_3)_3$; and CuO are mixed in such proportions that the atom ratio of Ba : [Gd, Er or Yb] : Cu becomes respective values shown in the Table 3 and then, the resulting each mixture is compacted and sintered preliminary at 400 °C for 12 hours.

The onset temperature (Tci) of the resulting thin films measured by the same method as Example 1 are also summarized in Table 3.

Table 3

	Example 22	23	24
Element " M "	Gd	Er	Yb
Composition of target (atom ratio)			
Ba	0.7	0.9	0.85
Gd	0.85		
Er		0.85	
Yb			0.75
Cu	1.0	1.0	1.0
Onset temperature (Tci) (K)	105	95	92

Example 25 to 27

Each of the thin films obtained in Example 16 to 18 is annealed at a temperature shown in Table 4 for 20 minutes

under an oxygen atmosphere of the partial oxygen pressure shown in the Table 4.

The superconducting transition temperatures of the resulting annealed thin films were measured by the same method as Example 16. The result showed that electric resistance dropped much sharply than the case of Example 16 to 18 and the difference between the onset temperature and the critical temperature of respective thin films were improved as are shown in Table 4.

Table 4

	Example 25	26	27
Element " M " in targets	Gd	Er	Yb
Partial pressure of oxygen (x 10^{-1} Torr)	1.2	0.9	1.1
Annealing Temperature (°C)	770	710	680
Duration of annealing (hr)	20	20	20
(Tci) - (Tcf) (K)	4	4	83

Example 28 to 30

The same operations as Examples 16 to 18 are repeated except that the final sintering temperature, the high-frequency power are changed to values shown in Table 5 and a substarate of magnesia (MgO) is used for all Examples 28 to 30.

The onset temperatures of the resulting thin films measured by the same method as Example 1 are also shown in Table 5.

Table 5

	Example		
	28	29	30
Element "M" in targets	Gd	Er	Yb
Final sintering temperature (°C)	960	980	990
High-frequency power (W/cm^{-2})	5	3	10
(Tci) (K)	109	99	96

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for preparing a superconducting thin film on a substrate, characterized in that a target made of a compound oxide containing Ba; one element M selected from the group consisting of Y, La, Gd, Ho Er and Yb; and Cu is used for carrying out physical vapour deposition under the presence of oxygen to produce a thin film of perovskite type or quasi-perovskite type oxide on said substrate.

2. A process claimed in claim 1, characterized in that said target contains perovskite type oxide or quasi-perovskite type oxide.

3. A process claimed in claim 1 or 2, characterized in that said target is a preliminary sintered mass which is obtained by sintering a power mixture of an oxide, carbonate, nitrate or sulfate of Ba; and oxide, carbonate, nitrate or sulfate of one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb; and an oxide, carbonate, nitrate or sulfate of Cu, at a temperature ranging from 250° to 1,200°C.

4. A process claimed in claim 1 or 2, characterized in that said target is a finally sintered mass which is obtained by final sintering of a preliminary sintered material which is obtained by preliminary sintering a power mixture of an oxide, carbonate, nitrate or sulfate of Ba; an oxide, carbonate, nitrate or sulfate of one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb; and an oxide, carbonate, nitrate or sulfate of Cu, said final sintering being carried out at a temperature ranging from 700° to 1,500°C, preferably from 700° to 1,300°C.

5. A process claimed in any one of claims 1 to 4, characterized in that said target is in a form of sintered powder material obtained from said preliminary sintered mass or said finally sintered mass.

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6. A process claimed in any one of claims 1 to 4, characterized in that said target is in a form of sintered block obtained from said preliminary sintered mass or said finally sintered mass.

7. A process claimed in any one of claims 1 to 6, characterized in that said target is composed of a plurality of target segments.

8. A process claimed in claim 7, characterized in that each of said target segments is composed of an oxide of Ba, an oxide of one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb or an oxide of Cu.

9. A process claimed in claim 7, characterized in that said target is composed of two target segments each consisting of $(Ba, M)O_x$ and CuO, wherein M stands for one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb and x represents a number of $1 \leqq x$.

10. A process claimed in any one of claims 1 to 9, characterized in that an atom ratio of Ba/(Ba+M) is within a range of from 0.04 to 0.97, wherein M stands for one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb.

11. A process claimed in any one of claims 1 to 9, characterized in that an atom ratio of Ba/(Ba+M) is within a range of from 0.1 to 0.7, wherein M stands for one element M selected from a group consisting of Y, La, Gd, Ho Er and Yb.

12. A process claimed in any one of claims 1 to 11, characterized in that an atom ratio of Ba, M and Cu in said target is adjusted in the function of evaporation rates of Ba, M and Cu on the basis of the atom ratio of Ba, M and Cu in a thin film to be produced.

13. A process claimed in any one of claims 1 to 12, characterized in that Ar and O_2 are contained in an atmosphere of vaporization, the partial pressure of Ar ranging from 1.0×10^{-3} to 1×10^{-1} Torr.

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14. A process claimed in any one of claims 1 to 13, characterized in that the O_2 in the atmosphere of vaporization have the partial pressure ranging from 0.5×10^{-3} to 1×10^{-1} Torr.

15. A process claimed in any one of claims 1 to 14, characterized in that said physical vapor deposition is performed by high-frequency sputtering technique, the power of the high-frequency being less than 115 W/cm^{-2}.

16. A process claimed in claim 15, characterized in that said physical vapor deposition is performed by magnetron sputtering.

17. A process claimed in any one of claims 1 to 16, characterized in that the obtained thin film is further heat-treated.

18. A process claimed in 17, characterized in that said heat-treatment is carried out at a temperature ranging from 250°C to 1,700°C.

19. A process claimed in 17 or 18, characterized in that said heat-treatment is carried out under a partial pressure of O_2 which is not higher than 0.5×10^{-1} Torr.

20. A process claimed in any one of claims 1 to 19, characterized in that a substrate is heated by a heater during the sputtering operation.

21. A process claimed in 20, characterized in that said substrate is heated at a temperature ranging from 184°C to 1,520°C during the sputtering operation.

22. A process claimed in any one of claims 1 to 21, characterized in that said substrate is made of one of materials selected from a group consisting of glass, quartz, silicon, stainless steel and ceramics.

23. A process claimed in any one of claims 1 to 22, characterized in that the distance between said substrate and said target is adjusted at a value of from 3 to 300mm.

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24. A process claimed in any one of claims 1 to 14, characterized in that said physical vapor deposition is performed by ion plating technique.

25. A process claimed in any one of claims 1 to 14, characterized in that said physical vapor deposition is performed by one of vacuum deposition, ion beam deposition or molecular beam deposition.

26. The process of claim 13 wherein the partial pressure of Ar ranges from 5.0×10^{-3} to 1×10^{-1} Torr.

27. The process of claim 15 wherein the power of the high frequency is less than 15 W/cm^{-2}.

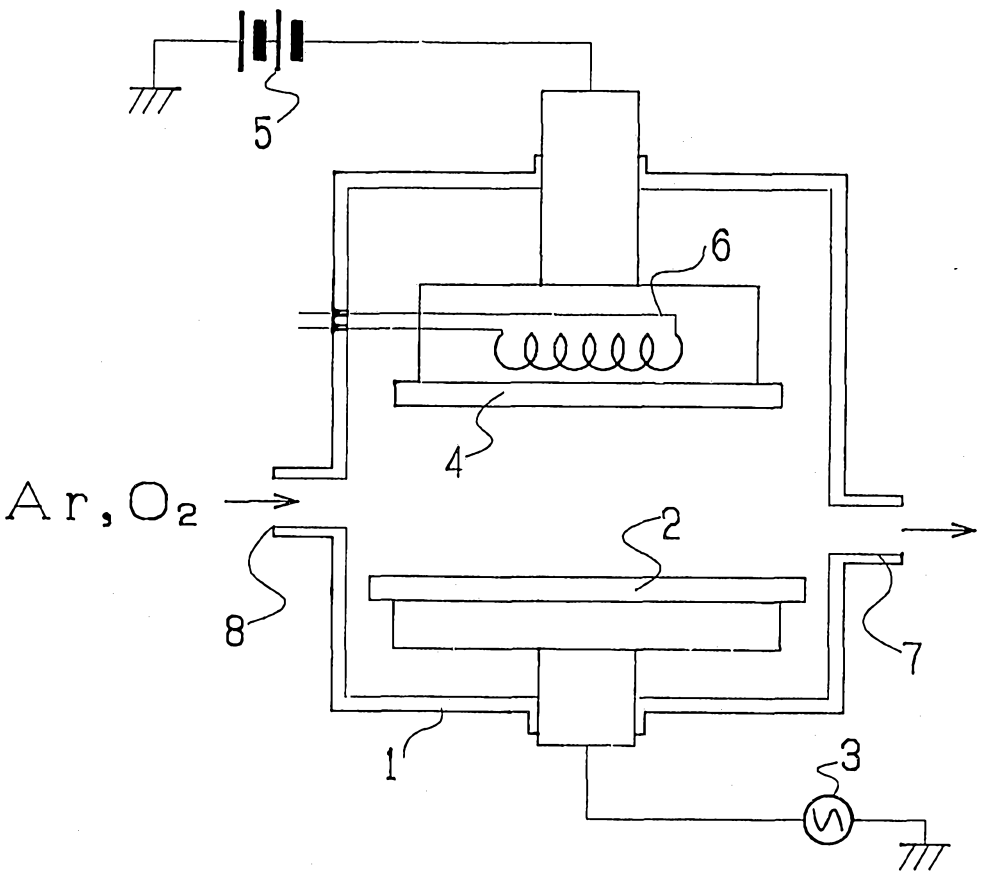
DATED this 20 day of March 1990

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FIGURE 1



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FIGURE 2

