

[DESCRIPTION]

[Title of Invention]

SURFACE LAYER SUPERCONDUCTOR AND FABRICATION METHOD OF THE
SAME

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[Technical Field]

[0001]

The present invention relates to a method of fabricating a surface layer
superconductor in which a surface layer superconducting transition temperature is made
10 to be higher than an internal superconducting transition temperature, and a surface layer
superconductor. For example, the invention relates to a technology in which a surface
layer is processed to form a superconducting circuit and which is capable of being used
for superconducting devices such as Josephson elements, voltage standards,
high-frequency elements, computing elements, high-sensitivity magnetic sensors,
15 high-sensitivity electromagnetic wave sensors, and superconducting band pass filters, and
superconducting electronics.

[Background Art]

[0002]

20 A superconducting device has functions (quantum coherence, high sensitivity,
and high precision) superior to those of other devices, and thus the superconducting
device is known as a device highly expected for practical use. A method of realizing
superconducting devices and superconducting electronics by preparing a superconducting
thin film on a substrate (refer to PTL 1) and processing the thin film and the substrate has
25 been explored. However, generally, a superconductor has a complex chemical

composition compared to a semiconductor, and has a problem of mismatch in a lattice constant with the substrate. Therefore, it is difficult to manufacture a thin film in which a composition is accurate, and thus orientation and crystallinity are satisfactory.

Furthermore, there is a problem of reproducibility and stability in the device

5 characteristics. Moreover, the manufacturing process is very complex and thin film deposition apparatus is very expensive and handling thereof is difficult. In addition, the substrate is also costly. Accordingly, spreading of the superconducting device has been hindered. Also, a method of manufacturing a surface layer superconductor using a chemical reaction has been suggested (refer to PTL 2 and PTL 3).

10 However, it is difficult to make the superconducting device stably operate with good reproducibility by diffusing a metal element or oxygen atoms with good controllability. In addition to this technology, a surface processing method of a superconductor has been investigated (refer to PTL 4 and PTL 5).

15 However, a surface layer superconductor was not observed in the surface processing technology in the literature.

[0003]

PTL 1 discloses a method of manufacturing an oxide superconducting thin film using laser ablation. In addition to the technology of PTL 1, various thin-film manufacturing methods such as sputtering, MBE (Molecular Beam Epitaxy), and CVD
20 (Chemical Vapor Deposition) have been suggested in various patents.

PTL 2 discloses a method of forming a superconducting thin film (surface layer superconductor) using a chemical reaction by depositing Bi_2O_3 thin film, which supplies deficient Bi, on a BiSrCaCu-based oxide thin film that exhibits a semiconductor state in a Bi deficient state, and by performing a heat treatment.

25 PTL 3 discloses a method in which with respect to a high-temperature

superconducting single crystal that becomes an insulating material by a reduction treatment, superconductivity of a surface layer alone is restored by a chemical reaction called partial oxidation treatment to make the surface layer into a superconductor layer.

PTL 4 discloses a method capable of cleaning a surface of an oxide
5 superconductor while maintaining superconducting characteristics. However, this method is not a technology causing superconductivity only at a surface layer.

PTL 5 discloses a technology of grinding a surface of a superconductor.
However, the technology is aimed to greatly reduce alternating current loss of the superconductor itself, and the technology is not a technology of causing
10 superconductivity only at a surface layer.

[Citation List]

[Patent Literature]

[0004]

15 [PTL 1] Japanese Patent No. 3188912

[PTL 2] Japanese Patent No. 3015408

[PTL 3] Japanese Patent No. 5207271

[PTL 4] Japanese Unexamined Patent Application, First Publication No.

H07-14900

20 [PTL 5] Japanese Unexamined Patent Application, First Publication No.

S52-133586

[Summary of Invention]

[Technical Problem]

25 [0005]

An aspect of the invention is to provide a surface layer superconductor without a variation in characteristics and a method of stably fabricating the surface layer superconductor, and with good reproducibility. Furthermore, an aspect of the invention is to provide a surface layer superconductor in which a fabricating process is simple, the cost is low, mass production is possible and the process is conveniently realized. We also outline the method of fabricating the surface layer superconductor.

[Solution to Problem]

[0006]

10 According to an aspect of the invention, there is provided a method of fabricating a surface layer superconductor. The method includes performing a treatment for removing a surface and exposing a new processed surface for a superconducting crystal in which superconductivity is suppressed in order to fabricate a surface layer superconductor in which a surface layer superconducting transition temperature of the new processed surface is higher than a superconducting transition temperature of the inside of the crystal.

According to another aspect of the invention, there is provided a method of fabricating a surface layer superconductor. The method includes forming a processed surface by performing a treatment for a crystal of a perovskite-type copper oxide-based high-temperature superconductor within a composition range in which a stripe order (which is the segregation of charge carriers (holes) into hole-rich unidirectional charge stripes, forming antiphase boundaries between hole-poor antiferromagnetically ordered spin domains) that suppresses superconductivity is present. This method expose a surface that intersects the c-axis of the crystal and fabricate a surface layer superconductor in which a surface layer superconducting transition temperature of the

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processed surface is higher than a superconducting transition temperature of the inside of the crystal.

[0007]

In the method of manufacturing the surface layer superconductor, it is preferable
5 that the processed surface intersecting the c-axis of the crystal is a processed surface that has an intersection angle of 60° to 120° with the c-axis.

In the method of manufacturing the surface layer superconductor, it is preferable that at least a part of the processed surface constitutes of a two-dimensional copper-oxygen plane.

10 In the method of manufacturing the surface layer superconductor, it is preferable to use a copper oxide-based high-temperature superconductor expressed by the compositional formula of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0.10 \leq x \leq 0.15$) as the copper oxide-based high-temperature superconductor within the composition range in which the stripe order that suppresses superconductivity is present.

15 In the method of manufacturing the surface layer superconductor, it is preferable that a method of forming the processed surface is any one of grinding, cleavage, division, cutting, and etching.

In the method of manufacturing the surface layer superconductor, it is preferable that the processed surface is a surface that is exposed by removing a deteriorated portion
20 of the surface of the crystal.

[0008]

According to still another aspect of the invention, we introduce a surface layer superconductor. The superconductor is formed from a crystal of a perovskite-type copper oxide-based high-temperature superconductor within a composition range in
25 which a stripe order that suppresses superconductivity is present. The superconductor

includes a processed surface, which is generated by a treatment for exposing a surface that intersects a c-axis of the crystal. A surface layer superconducting transition temperature of the processed surface is higher than a superconducting transition temperature of the inside of the crystal other than the processed surface.

5 [0009]

In the surface layer superconductor, it is preferable that the processed surface that intersects the c-axis of the crystal is a processed surface that has an intersection angle of 60° to 120° with the c-axis.

10 In the surface layer superconductor, it is preferable that at least a part of the processed surface constitutes of a two-dimensional copper-oxygen plane.

In the surface layer superconductor, it is preferable that the copper oxide-based high-temperature superconductor within the composition range in which the stripe order that suppresses superconductivity is present is a copper oxide-based high-temperature superconductor expressed by a compositional formula of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0.10 \leq x \leq 0.15$).

15 In the surface layer superconductor, it is preferable that the processed surface is any one of a surface processed by grinding, a surface processed by cleavage, a surface processed by division, a surface processed by cutting, and a surface processed by etching.

In the surface layer superconductor, it is preferable that the processed surface is a surface that is exposed by removing a deteriorated portion of the surface of the crystal.

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[Advantageous Effects of Invention]

[0010]

When one aspect of the invention is used, it is possible to avoid a problem of mismatch in a lattice constant with a substrate, and it is possible to stably fabricate a surface layer superconductor in which a composition is accurate, and orientation and

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crystallinity are satisfactory, and in which a variation in characteristics is not present with good reproducibility without using an expensive film growth apparatus, or a substrate. Furthermore, since the surface layer superconductor may be obtained by only the treatment for removing a deteriorated surface and newly exposing a processed surface
5 without using a chemical reaction, a film forming process is simplified, and thus a manufacturing process becomes very simple.

This surface treatment is the same as a surface treatment that is performed during manufacturing of a common substrate, and a new complicated process is not necessary. Accordingly, the cost decreases, mass production is possible and thus a
10 high-quality surface layer superconductor may be conveniently obtained.

[Brief Description of Drawings]

[0011]

FIG. 1A is a perspective diagram illustrating a state in which voltage terminals
15 for the measurement of a surface layer electric resistance are set up at a surface layer superconductor related to a first embodiment.

FIG. 1B is a perspective diagram illustrating a state in which voltage terminals for the measurement of an internal electric resistance are set up at the surface layer superconductor related to the first embodiment.

20 FIG. 1C is a perspective diagram illustrating a state in which terminals for the measurement of a surface layer thermoelectromotive force are set up at the surface layer superconductor related to the first embodiment.

FIG. 1D is a perspective diagram illustrating a state in which terminals for the measurement of an internal thermoelectromotive force are set up at the surface layer
25 superconductor related to the first embodiment.

FIG. 2 is a graph illustrating the temperature dependence of the electrical resistivity of a processed surface, and the inside of a surface layer superconductor having a composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.115$).

FIG. 3 is a graph illustrating the temperature dependence of the electrical resistivity of the processed surface, and the inside of a surface layer superconductor having a composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$).

FIG. 4 is a graph illustrating the temperature dependence of the thermoelectromotive force of the processed surface, and the inside of the surface layer superconductor having the composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$).

FIG. 5 is a graph illustrating the temperature dependence of the electrical resistivity of the processed surface, and the inside of a surface layer superconductor having a composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.139$).

FIG. 6 is a graph illustrating the temperature dependence of the electrical resistivity of the processed surface, and the inside of a superconductor having a composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.076$).

FIG. 7 is a graph illustrating the temperature dependence of the electrical resistivity of the processed surface, and the inside of a superconductor having a composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.092$).

FIG. 8 is a graph illustrating Ba concentration (x) dependence of a superconducting transition temperature, which is determined from the electrical resistivity of the processed surface, and the inside of the surface layer superconductor having the composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$.

FIG. 9 is a graph illustrating the temperature dependence of the electrical resistivity of a surface layer (having an inclination of 30° from a copper-oxygen plane), and the inside of the surface layer superconductor having the composition ratio of

$\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$).

FIG. 10 is a graph illustrating the temperature dependence of the electrical resistivity of the processed surface (processed surface from cleavage), and the inside of the surface layer superconductor having the composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x =$
5 0.120).

FIG. 11 is a graph illustrating the temperature dependence of the electrical resistivity of the processed surface (cut surface), and the inside of the surface layer superconductor having the composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$).

FIG. 12 is a graph illustrating the temperature dependence of the electrical
10 resistivity of the processed surface (P800 abrasive paper-processed surface), and the inside of the surface layer superconductor having the composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$).

FIG. 13 is a graph illustrating the temperature dependence of the electrical resistivity of the processed surface (alumina abrasive powder-ground surface), and the
15 inside of the surface layer superconductor having the composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$).

FIG. 14 is a graph illustrating the temperature dependence of the electrical resistivity of the processed surface (plasma-etched surface), and the inside of the surface layer superconductor having the composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$).

20 FIG. 15 is a graph illustrating the temperature dependence of the electrical resistivity of the processed surface, and the inside of the surface layer superconductor having a composition ratio of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.105$).

[Description of Embodiments]

[0012]

25 (First Embodiment)

Hereinafter, an embodiment of the invention will be described with reference to drawings. In addition, the invention is not limited to the embodiment to be described below.

The surface layer superconductor of the embodiment may be obtained by
5 performing a treatment for removing a deteriorated surface and newly exposing a new processed surface for a superconductor in which superconductivity is suppressed so as to increase a surface layer superconducting transition temperature of the newly exposed processed surface with respect to a superconducting transition temperature of the inside.

As a superconductor in which superconductivity is suppressed, various kinds of
10 superconductors including a metal-based superconductor, an oxide superconductor, an iron-based superconductor, and other superconductors to which impurities, defects, and electron correlation are introduced may be used. However, a superconductor in which a stripe order that suppresses superconductivity is present may be suitably used.

[0013]

15 FIG. 1A shows a perspective diagram of a surface layer superconductor related to the first embodiment.

A surface layer superconductor A of this embodiment is constituted by a crystal
1 of perovskite-type copper oxide-based high-temperature superconductor within a composition range in which a stripe order is present, and includes a processed surface 1a
20 that is generated by a treatment for exposing a plane that intersects a c-axis of the crystal 1. A surface layer superconducting transition temperature of the processed surface 1a is higher than a superconducting transition temperature inside the crystal other than the processed surface.

As shown in FIG. 1A, the crystal 1 of this embodiment is a rectangular chip type,
25 and a processed surface 1a is formed on the top surface thereof by the above-described

treatment. In this embodiment, the processed surface 1a is a processed surface that is formed along a plane orthogonal to a c-axis of the crystal 1 by a processing method such as grinding, cutting, and cleavage to be described later in detail after manufacturing the crystal 1.

5 In addition, side surfaces 1b and 1c and a bottom surface 1d of the crystal 1 are not formed as a processed surface by a particularly intended treatment. In this embodiment, “surface not formed as a processed surface” represents a surface for which the above-described processing to form the processed surface is not performed, or which is left as is in the air after the processing even when being processed, and thus impurities
10 in the air are attached thereto, a surface having a reaction layer that reacts with moisture or chemical materials such as carbon dioxide in the air, or a surface in which a strain occurs and thus a transition temperature does not become higher than a transition temperature inside the crystal 1. In addition, the “surface not formed as a processed surface” represents a surface at which a transition temperature does not become higher
15 than a transition temperature inside the crystal 1 due to an arbitrary reason such as a difference in a crystal orientation even when a treatment for forming the processed surface is performed.

The relationship between the crystal orientation of the crystal 1 and the processed surface, and the relevance about whether or not a superconducting transition
20 temperature increases with respect to a superconducting transition temperature inside the crystal 1 will be described later.

[0014]

Hereinafter, the crystal 1 will be described.

As the crystal 1 of the superconductor in which a stripe order that suppresses
25 superconductivity is present, various kinds of superconductors expressed by

compositional formulae such as $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{La}_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Nd})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Sm})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Eu})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Gd})_{2-x}\text{Sr}_x\text{CuO}_4$, or $(\text{La}, \text{Tb})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Nd})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Sm})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Eu})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Gd})_{2-x}\text{Ba}_x\text{CuO}_4$, or $(\text{La}, \text{Tb})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Nd})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Sm})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Eu})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Gd})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, or $(\text{La}, \text{Tb})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ may be used. However, a superconductor expressed by a compositional formula of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ may be appropriately used. It is known that in a perovskite-type copper oxide-based high-temperature superconductor expressed by the compositional formula of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, the stripe order that suppresses

superconductivity within a range of $0.10 \leq x \leq 0.15$ is present.

[0015]

The crystal 1 of the superconductor in this embodiment may be a superconductor manufactured by an arbitrary method. However, for example, the crystal 1 may be manufactured by methods such as a sintering method, a flux method, a pulling-up method, and a film fabricating method. A floating zone method by laser heating or lamp heating may be appropriately used.

In this embodiment, the crystal 1 of the superconductor in which superconductivity is suppressed may have an arbitrary shape. In addition, the cross-section of the crystal 1 may have an arbitrary shape such as a square, a rectangle, a circle, an ellipse (oval), and a hexagon in addition to the chip type shown in FIG. 1A. In addition, the crystal 1 may be a thin film fabricated on a substrate by a film fabricating method.

[0016]

In the case of the perovskite-type copper oxide-based superconductor, it is preferable that a plane that is wholly or partially constituted by a two-dimensional

copper-oxygen plane is the processed surface 1a. It is preferable that a surface itself, which is parallel to the two-dimensional copper-oxygen plane having a tendency to exhibit a surface layer superconducting effect, is the processed surface 1a. In addition, the processed surface 1a may be slightly inclined with respect to the two-dimensional copper-oxygen plane. For example, the processed surface 1a may be a plane that is inclined by about 60° to 120° with respect to a c-axis of the crystal of the perovskite-type copper oxide-based high-temperature superconductor. The processed surface may be a bottom surface 1d instead of the top surface 1a.

As shown in FIG. 1A, when defining the a-axis, b-axis, and c-axis of the crystal 1 of the perovskite-type copper oxide-based high-temperature superconductor, an ab-plane orthogonal to the c-axis is preferably the processed surface 1a. The directions of the a-axis and b-axis illustrated in FIG. 1A are for descriptive purposes. Since the a-axis and b-axis are equivalent in the stripe order, the effect is not changed if the crystal 1 in which the a-axis and b-axis are rotated around the c-axis is used.

In addition, even in a processed surface that is inclined by 60° to 120° with respect to the c-axis (in other words, since the ab-plane intersects with the c-axis at 90° , the processed surface is inclined by the range within $\pm 30^\circ$ with respect to the ab-plane), a proximity effect is exhibited between microcrystals having exposed the ab-plane close to each other along the processed surface, and thus the processed surface may exhibit a higher superconducting transition temperature than that of a portion that shows the stripe order inside the crystal 1.

[0017]

In the treatment for removing a deteriorated surface and newly exposing a new processed surface 1a according to the invention, as is the case with cleavage or cutting, a

completely new surface may be exposed, or a new surface may be exposed by removing the vicinity of the surface. Although not particularly limited, examples of the treatment and processing for removing the vicinity of the surface and newly exposing a new processed surface 1a include grinding such as filing and lapping, etching, ion milling, plasma etching, electrolytic grinding, and the like. From the viewpoints of easiness of treatment and processing operation and an effect thereof, it is preferable to adopt a processed surface obtained by grinding or plasma etching.

[0018]

The treatments for removing the deteriorated surface and newly exposing a processed surface as a new surface may be performed by each kind of processing alone, but the treatment may be performed in combination of plural kinds of processing to reliably obtain an effect of improving the superconducting transition temperature of the surface layer.

In the case of grinding, for example, abrasive paper within a range of P240 to P2500 may be used. In the case of plasma etching, for example, conditions within a range of 10 W to 1 kW may be adapted. In addition, the processed surface 1a may be prepared with combination of these treatments.

[0019]

Next, the stripe order in the copper oxide high-temperature superconductor will be described. In the copper oxide superconductor which has a structure in which two-dimensional copper-oxygen planes are laminated and which exhibits a high superconducting transition temperature, it is known that the copper oxide superconductor shows an anomaly in which superconductivity is specifically suppressed when a hole concentration is in the vicinity of $1/8 = 0.125$, and the anomaly is referred to as $1/8$ anomaly. As a cause of the anomaly, the following theory is regarded as to be strongly

likely. Holes are arranged in a strip shape in a two-dimensional copper-oxygen plane, and thus movement of the holes is restricted and superconductivity is suppressed. An ordered state in which the holes are arranged in this manner is referred to as the stripe order.

5 [0020]

According to recent research, the present inventors have discovered that even when stripe order is formed in the whole crystal and thus superconductivity is suppressed, when a deteriorated surface is removed to form a processed surface, the superconducting transition temperature of the processed surface may be made to be higher than that of
10 other portions (the inside of the crystal). That is, they have found that with respect to the crystal, when performing a treatment for newly exposing a fresh surface (a processed surface) in such a manner that a two-dimensional copper-oxygen plane is wholly or partially included, it is possible to obtain a surface layer superconductor in which the superconducting transition temperature of the new processed surface is higher than the
15 superconducting transition temperature inside the crystal.

When using this technology, the same function as a superconducting thin film may be realized on the surface of the crystal, and with good reproducibility, by preparing a processed surface using a simple treatment, without the need of advanced technology.

[0021]

20 In a surface layer superconductor A having a structure shown in FIG. 1A, the top surface of the crystal 1 is the processed surface 1a. Here a pair of voltage terminals, (electrodes) 2 and 3 are mounted and spaced from each other on the processed surface 1a. A voltmeter 5 is then connected to these terminals and a current source 6 is connected to the side surfaces 1c and 1c. Under these experimental set up conditions, the surface
25 layer superconducting transition temperature of the processed surface 1a may be

measured based on a 4-terminal method.

In addition, as shown in FIG. 1B, when a pair of voltage terminals (electrodes) 7 and 8 are mounted on a side surface 1b of the crystal 1, a voltmeter 9 is connected to these terminals, and the current source 6 is connected to the side surfaces 1c and 1c, an
5 internal superconducting transition temperature (superconducting transition temperature along the side surface 1b) of the crystal 1 may be measured. In addition, the side surfaces 1b and 1c are surfaces that are not subjected to the above-described processing.

When the crystal 1 in a state shown in FIG. 1A is cooled by a freezing machine and the like, and the temperature is lowered, the resistance at an arbitrary temperature
10 becomes zero and thus a superconducting current starts to flow. Accordingly, the superconducting transition temperature of the processed surface 1a may be measured. In addition, similarly when the temperature of the crystal 1 in a state shown in FIG. 1B is lowered, the superconducting transition temperature of the side surface 1b may be measured.

15 [0022]

In the surface layer superconductor A of this embodiment, the superconducting transition temperature of the processed surface 1a becomes higher than the superconducting transition temperature of the side surface 1b. This difference occurs due to a variation in a surface state of the crystal 1 by the treatment for forming the
20 processed surface 1a.

After a crystal is manufactured by the above-described method - including the floating zone method, the sintering method, the flux method, or the pulling-up method - when the crystal is left in air the surface becomes varied.

For example, a cause of this variation is as follows. After manufacturing,
25 foreign matter in the air is attached to the surface of the crystal and thus the surface

becomes contaminated. In addition, reaction products are generated on the surface of the crystal due to reaction with reactive chemical materials such as moisture or carbon dioxide in the air. Furthermore, the variation occurs due to an influence of strain.

Even when the crystal after being manufactured is examined, rising of superconducting transition temperature only in a specific surface does not occur.

[0023]

Conversely, when a new processed surface is newly exposed with respect to the crystal of the perovskite-type copper oxide-based high-temperature superconductor having the stripe order in such a manner that a two-dimensional copper-oxygen plane is included, the above-described foreign matter, reaction products, strain, and the like may be removed. As a result, it may be assumed that a phenomenon in which the superconducting transition temperature is raised only in a specific surface may be caused. It is known that the stripe order occurs due to a phase transition of a crystal structure, and thus it is considered that some correlation is present between the stripe order and strain.

Accordingly, the following mechanism is assumed to occur: Stripe order is suppressed in a plane from which the strain is removed due to some reason. As described above, a plane from which the stripe order is suppressed may be obtained by removing or changing an effect of contamination or attached materials, or an effect of strain along a specific crystal plane using arbitrary means. Accordingly, it may be assumed that the superconducting transition temperature may be raised at the processed surface 1a. In addition, this mechanism was not reported in the past, and is discovered for the first time by the present inventors.

[0024]

As described above, the surface layer superconductor A shown in FIG. 1 is used after being cooled to a temperature which is lower than the superconducting transition

temperature shown at the processed surface 1a and which is higher than the superconducting transition temperature shown at the side surface 1b of the crystal 1, that is, the superconducting transition temperature shown at the inside of the crystal 1.

Under the cooling conditions, the crystal 1 may obtain superconducting characteristics only at a surface layer along the processed surface 1a. Accordingly, when a necessary circuit is formed at a surface layer portion including the processed surface 1a, the crystal 1 may be used for electronic devices such as a Josephson element, a voltage standard, a high-frequency element, a computing element, a high-sensitivity magnetic sensor, a high-sensitivity electromagnetic wave sensor, and a superconducting band pass filter.

In addition, after this circuit or element is formed on the surface layer portion of the processed surface 1a, it is preferable that the circuit or element is covered with a protective layer so as not to be modified due to contact with air.

[0025]

The surface layer superconductor A that is obtained as described above may be obtained by a simple treatment to form the processed surface 1a as a surface along the ab-plane orthogonal to the c-axis of the crystal 1, or inclined by about 60° to 120° with respect to the c-axis. Accordingly, the surface layer superconductor A may be manufactured in a very easy manner. In addition, the treatment that is performed to form the processed surface 1a is a processing method such as grinding (including grinding using an abrasive powder, filing, lapping, and the like), etching, ion milling, plasma etching, and electrolytic grinding. These are not special methods but processing methods that are known in the related fields. Accordingly, the manufacturing of the surface layer superconductor A may be easily performed.

Examples

[0026]

Hereinafter, a specific method of realizing the surface layer superconductor will be described in detail, but the invention is not limited to the following examples.

Implementation was performed using $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ in which the stripe order that suppresses superconductivity was present mainly at a Ba concentration x within a range of 0.10 to 0.15. A single crystal of an oxide superconductor expressed by a composition ratio of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ was prepared by a floating zone method using laser heating which is disclosed in Japanese Patent No. 5046101, and Japanese Patent No. 5181396.

[0027]

The single crystal of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ was grown by a floating zone method using lamp heating. A treatment and processing for exposing a new surface by grinding, etching and the like was performed for the single crystal.

Electrical resistivity was measured with an electrode arrangement (four-terminal method) shown in FIGS. 1A and 1B using commercially available PPMS (physical property measuring system) manufactured by Quantum Design, Inc. Measurement of a thermoelectromotive force (Seebeck coefficient) was performed with an arrangement configuration shown in FIGS. 1C and 1D. In the configuration shown in FIGS. 1C and 1D, the same electrode terminals and voltmeter as the case of FIGS. 1A and 1B were provided to the processed surface 1a and the side surface 1b of the crystal 1, respectively. In addition, in FIGS. 1C and 1D, a member indicated by a reference numeral 10 is a thermal reservoir that comes into contact with one side surface 1c of the crystal 1, a member indicated by reference numeral 11 is a heater that comes into contact with other side surface 1c, and a member indicated by reference numeral 12 is a current source.

Voltage terminals were mounted sufficiently inward on each surface so as not to

be affected by an adjacent surface, that is, the voltage terminals were mounted in such a manner that the voltage terminals 2 and 3 mounted on the processed surface 1a did not come into contact with the side surfaces 1b and 1c. Superconducting transition temperatures at a surface parallel to a two-dimensional copper-oxygen plane (ab-plane) (orthogonal to the c-axis) or slightly inclined with respect to the two-dimensional copper-oxygen plane, and at a surface orthogonal to the two-dimensional copper-oxygen plane (parallel to the c-axis) were obtained.

The superconducting transition temperatures correspond to a surface layer superconducting transition temperature and an internal superconducting transition temperature, T_{cs} and T_c , respectively. Specifically, a surface voltage (V_s) or an internal voltage (V_{ab}) was measured by allowing a current or heat to flow uniformly.

Hereinafter, a surface electrical resistivity is written as ρ_s , an internal electrical resistivity is written as ρ_{ab} , a surface thermoelectromotive force is written as S_s , and an internal thermoelectromotive force is written as S_{ab} .

In addition, the thermoelectromotive force may be obtained by measuring a temperature difference (ΔT) between the positions of the two voltage terminals 2 and 3 illustrated in FIG. 1C, or between the positions of the two voltage terminals 7 and 8 illustrated in FIG. 1D using a differential thermocouple, and calculating the thermoelectromotive force (Seebeck coefficient S) as " $S = \Delta V / \Delta T$ ". Steady method was used in which an electromotive force (ΔV) is measured under steady temperature gradient (steady thermal flow).

[Example 1]

[0028]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.115$) was prepared in the following order, and electrical resistivity was measured.

(1) Preparation of raw material rod: Dried La_2O_3 , BaCO_3 , and CuO (all of these had a purity of 99.9%) were used as raw materials, and these were weighed in a ratio of $\text{La} : \text{Ba} : \text{Cu} = 1.88 : 0.12 : 1.05$ in terms of molar ratio to obtain a total amount of 10 g. Then, these raw materials were mixed, and were allowed to react with each other at 950°C for 12 hours. The reaction material obtained was pulverized, and was closely packed into a rubber tube having a diameter of 7 mm. Then, hydrostatic pressing was applied and the cylindrical rod obtained was sintered while raising the temperature from 950°C to 1,100°C for 12 hours. A sintered rod obtained was used as a raw material rod, and was attached to an upper shaft of a crystal growth furnace.

10 [0029]

(2) Preparation of seed crystal: A sintered rod was prepared in the same sequence as (1), and the sintered rod was used as a seed crystal, and was attached to a lower shaft of the crystal growth furnace.

(3) Preparation of solvent: Dried La_2O_3 , BaCO_3 , and CuO (all of these had a purity of 99.9%) were used as raw materials, and these were weighed in a ratio of $\text{La} : \text{Ba} : \text{Cu} = 1 : 1 : 5$ in terms of molar ratio to obtain a total amount of 10 g. Then, these raw materials were mixed, and were allowed to react with each other at 850°C for 12 hours. The reaction material obtained was pulverized, and was closely packed into a rubber tube having a diameter of 7 mm. Then, hydrostatic pressing was performed, and a cylindrical rod obtained was sintered at 850°C for 12 hours. A disk-shaped body of 0.26 g was cut from the sintered rod obtained, and was used as a solvent. The solvent was attached to an upper end of the seed crystal.

(4) Crystal growth: The solvent was melted with laser heating by applying three atmospheres of oxygen to connect the raw material rod to the seed crystal. Then, crystal

growth according to a floating zone method was performed at 0.5 mm/h while rotating the upper shaft and the lower shaft at 30 rpm in directions opposite to each other. Laser power during the growth was 13.0 W. A polycrystalline state appeared at an initial stage of the growth, but crystal orientations were gradually aligned in one orientation, and thus
5 a single crystal was ultimately obtained.

[0030]

(5) Processing of crystal: The crystal orientation was determined by a Laue photograph, the crystal was cut into the chip shape of FIG. 1 using a diamond saw (blade thickness: 0.3 mm, and a rotation speed: 5 rpm) at a cutting speed of 2 $\mu\text{m}/\text{sec}$, and the
10 entire surface was manually ground for 1 minute using P1200 abrasive paper and ethanol (lubricant) to newly expose a new surface (processed surface), whereby a surface layer superconductor was obtained.

Silver paste (DuPont 6838) was applied with the electrode arrangement shown in FIG. 1, and was heated in an oxygen flow at 450°C for 10 minutes.

15 (6) Measurement of electrical resistivity: As shown in FIG. 2, temperature dependence of electrical resistivity of the surface (processed surface) and the inside was measured. A superconducting transition temperature determined from a temperature at which a resistance becomes zero was 33 K at the surface (T_{cs}), and was 26 K in the inside (T_c). In a region between the two transition temperatures (temperature difference was 7
20 K) a surface layer superconductor was formed. In the inside, superconductivity is suppressed due to presence of the stripe order, and thus the transition temperature is lowered. At the surface layer, since a treatment and processing for removing a deteriorated surface and newly exposing a new surface is performed, the surface layer superconducting transition temperature of the newly exposed surface is higher than the
25 superconducting transition temperature of the inside.

[Example 2]

[0031]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$) was prepared in the following manner and order, and the electrical resistivity was measured.

5 (1) Preparation of raw material rod: The raw material rod was prepared in the same sequence as Example 1 except that a mixing molar ratio was a ratio of La : Ba : Cu = 1.87 : 0.13 : 1.05.

(2) Preparation of seed crystal: A sintered rod was prepared in the same sequence as (1), and the sintered rod was used as a seed crystal, and was attached to a
10 lower shaft of the crystal growth furnace.

(3) Preparation of solvent: A disk-shaped body of 0.26 g was cut from the sintered solvent rod that was obtained in Example 1, and was used as a solvent. The solvent was attached to an upper end of the seed crystal.

(4) Crystal growth: Crystal growth was performed in the same sequence as
15 Example 1 except that the laser power was set to 13.6 W. A polycrystalline state appeared at an initial stage of the growth, but crystal orientations were gradually aligned in one orientation, and thus a single crystal was ultimately obtained.

(5) Processing of crystal: The crystal was processed in the same sequence as Example 1, and attaching of the electrodes was performed.

20 (6) Measurement of electrical resistivity: As shown in FIG. 3, temperature dependence of electrical resistivity of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which a resistance becomes zero was 36 K at the surface (T_{cs}), and was 22 K in the inside (T_c). In a region between the two transition temperatures (temperature difference was 14 K) a
25 surface layer superconductor was formed. In the inside, superconductivity is suppressed

due to presence of the stripe order, and thus the transition temperature is lowered. At the surface layer, since a treatment and processing for removing a deteriorated surface and newly exposing a new surface is performed, the surface layer superconducting transition temperature of the newly exposed surface is higher than the superconducting transition temperature of the inside.

[Example 3]

[0032]

A thermoelectromotive force was measured in the following sequence using a single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$).

(1) to (5): The same as Example 2.

(6) Measurement of thermoelectromotive force: As shown in FIG. 4, temperature dependence of a thermoelectromotive force of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which the electromotive force becomes zero was 36 K at the surface (T_{cs}), and was 22 K in the inside (T_c). This is the same as the result of the electrical resistivity in Example 2. In a region between the two transition temperatures (temperature difference was 14 K) a surface layer superconductor was formed. In the inside, superconductivity is suppressed due to presence of the stripe order, and thus the transition temperature is lowered. At the surface, since a treatment and processing for removing a deteriorated surface and newly exposing a new surface is performed, the surface layer superconducting transition temperature of the newly exposed surface (processed surface) is higher than the superconducting transition temperature of the inside.

[Example 4]

[0033]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.139$) was prepared in the following

manner and order, and the electrical resistivity was measured.

(1) Preparation of raw material rod: The raw material rod was prepared in the same sequence as Example 1, except that a mixing molar ratio was a ratio of La : Ba : Cu = 1.85 : 0.15 : 1.05.

5 (2) Preparation of seed crystal: A sintered rod was prepared in the same sequence as (1), and the sintered rod was used as a seed crystal, and was attached to a lower shaft of the crystal growth furnace.

(3) Preparation of solvent: A disk-shaped body of 0.26 g was cut from the sintered solvent rod that was obtained in Example 1, and was used as a solvent. The
10 solvent was attached to an upper end of the seed crystal.

(4) Crystal growth: Crystal growth was performed in the same sequence as Example 1 except that the laser power was set to 15.0 W. A polycrystalline state appeared at an initial stage of the growth, but crystal orientations were gradually aligned in one orientation, and thus a single crystal was ultimately obtained.

15 (5) Processing of crystal: The crystal was processed in the same sequence as Example 1, and attaching of the electrodes was performed.

(6) Measurement of electrical resistivity: As shown in FIG. 5, temperature dependence of electrical resistivity of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which a
20 resistance becomes zero was 34 K at the surface (T_{cs}), and was 21 K in the inside (T_c). In a region between the two transition temperatures (temperature difference was 13 K) a surface layer superconductor was formed. In the inside, superconductivity is suppressed due to presence of the stripe order and thus the transition temperature is lowered. At the surface, since a treatment and processing for removing a deteriorated surface and newly
25 exposing a new surface is performed, the surface layer superconducting transition

temperature of the newly exposed surface (processed surface) is higher than the superconducting transition temperature of the inside.

(Comparative Example 1)

[0034]

5 A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.076$) was prepared in the following manner and order, and the electrical resistivity was measured.

(1) Preparation of raw material rod: The raw material rod was prepared in the same sequence as Example 1 except that a mixing molar ratio was a ratio of La : Ba : Cu = 1.82 : 0.08 : 1.05.

10 (2) Preparation of seed crystal: A sintered rod was prepared in the same
sequence as (1), and the sintered rod was used as a seed crystal, and was attached to a lower shaft of the crystal growth furnace.

(3) Preparation of solvent: A disk-shaped body of 0.31 g was cut from the sintered solvent rod that was obtained in Example 1, and was used as a solvent. The
15 solvent was attached to an upper end of the seed crystal.

(4) Crystal growth: Crystal growth was performed in the same sequence as Example 1 except that the laser power was set to 13.0 W. A polycrystalline state appeared at an initial stage of the growth, but crystal orientations were gradually aligned in one orientation, and thus a single crystal was ultimately obtained.

20 (5) Processing of crystal: The crystal was processed in the same sequence as Example 1, and attaching of the electrodes was performed.

(6) Measurement of electrical resistivity: As shown in FIG. 6, temperature dependence of electrical resistivity of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which a
25 resistance becomes zero was equally 22 K at the surface (T_{cs}) and in the inside (T_c).

The surface layer superconductor was not formed. Since stripe order is not present, superconductivity in the inside is not suppressed, and thus a difference in superconductivity between the surface and the inside is not present.

(Comparative Example 2)

5 [0035]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.092$) was prepared in the following manner and order, and the electrical resistivity was measured.

(1) Preparation of raw material rod: The raw material rod was prepared in the same sequence as Example 1 except that a mixing molar ratio was a ratio of La : Ba : Cu
10 = 1.90 : 0.10 : 1.05.

(2) Preparation of seed crystal: A sintered rod was prepared in the same sequence as (1), and the sintered rod was used as a seed crystal, and was attached to a lower shaft of the crystal growth furnace.

(3) Preparation of solvent: A disk-shaped body of 0.36 g was cut from the
15 sintered solvent rod that was obtained in Example 1, and was used as a solvent. The solvent was attached to an upper end of the seed crystal.

(4) Crystal growth: Crystal growth was performed in the same sequence as Example 1 except that the laser power was set to 13.2 W. A polycrystalline state
20 appeared at an initial stage of the growth, but crystal orientations were gradually aligned in one orientation, and thus a single crystal was ultimately obtained.

(5) Processing of crystal: The crystal was processed in the same sequence as Example 1, and attaching of the electrodes was performed.

(6) Measurement of electrical resistivity: As shown in FIG. 7, temperature
25 dependence of electrical resistivity of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which a

resistance becomes zero was equally 30 K at the surface (T_{cs}) and in the inside (T_c).

The surface layer superconductor was not formed. Since stripe order is not present, superconductivity in the inside is not suppressed, and thus a difference in superconductivity between the surface and the inside is not present.

5 [0036]

The superconducting transition temperatures of the surface and the inside in Examples 1 to 4, and Comparative Examples 1 and 2 are collectively shown in FIG. 8 as a function of the composition x . In a region of higher temperature than the superconducting transition temperature of the surface, superconductivity is not present at
10 any of the surface and the inside. In a region of lower temperature than the superconducting transition temperature of the inside, superconductivity occurs at both of the surface and the inside, and thus this is the same as a common superconductor.

In an intermediate temperature region between the two kinds of transition temperatures, superconductivity occurs only at the surface, and thus usage as a
15 superconducting thin film (surface layer superconductor) is possible. In respective temperature regions of FIG. 8, a normal state portion having a finite resistance in the chip-shaped crystal is schematically shown by a gray color, and a superconducting portion having a zero resistance is schematically shown by a white color.

At the intermediate temperature region, superconductivity in the inside is
20 suppressed due to presence of the stripe order, and thus the transition temperature is lowered. At the surface, the treatment and processing for exposing a new surface is performed, and thus the superconducting transition temperature is increased only at the surface, and is higher than that of the inside. Particularly, in the vicinity of $x = 0.125$ where stripe order is the strongest, a difference between both transition temperatures is
25 large, and a temperature at which the surface layer superconductivity starts to appear is

high, and thus this is advantageous in usage as the surface layer superconductor.

Hereinbefore, the surface layer superconductivity associated with a surface parallel to the two-dimensional copper-oxygen plane (ab-plane) has been described.

However, even in a case where the surface is inclined from the ab-plane, the surface layer
5 superconductor may be used.

[Example 5]

[0037]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$) was prepared in the following manner and order, and a surface inclined by 30° from the two-dimensional

10 copper-oxygen plane was exposed, and then the electrical resistivity was measured.

(1) to (4): The same as Example 2.

(5) Processing of crystal: The crystal was processed in the same sequence as Example 2, and attaching of the electrodes was performed. However, the crystal was cut using a diamond saw (blade thickness: 0.1 mm, and rotation speed: 3600 rpm) at a
15 cutting speed of 50 $\mu\text{m}/\text{second}$ in such a manner that a surface inclined by 30° from the two-dimensional copper-oxygen plane was partially exposed. P800 abrasive paper was used for surface grinding, and the surface grinding was manually performed for 1 minute without using a lubricant. An alumina abrasive powder having a particle size of 1 μm and ethanol (lubricant) were used for grinding of other surfaces, and the grinding was
20 manually performed for 30 minutes. With regard to the electrodes, gold paste (TR-1301, manufactured by Tanaka Kikinzo) was applied, and was heated in an oxygen flow at 900°C for 10 minutes.

(6) Measurement of electrical resistivity: As shown in FIG. 9, temperature dependence of electrical resistivity of the surface and the inside was measured. A

superconducting transition temperature determined from a temperature at which a resistance becomes zero was 26 K at the surface (T_{cs}), and was 16 K in the inside (T_c).

In a region between the two transition temperatures (temperature difference was 10 K), a surface layer superconductor was formed. In the inside, superconductivity is suppressed

5 due to presence of stripe order, and thus the transition temperature is lowered. At the surface, since a treatment and processing for removing a deteriorated surface and newly exposing a new surface is performed, the surface layer superconducting transition temperature of the newly exposed surface is higher than the superconducting transition temperature of the inside.

10 [0038]

Even at the inclined surface, the ab-plane appears in a terraced (stepped) shape in an atomic scale, and respective fragments of the ab-plane are coupled to each other due to a proximity effect, and thus the entirety of a surface layer becomes a superconductor. It is not necessary for the surface to be a plane, and the surface may be

15 a curved surface. However, in a case of a plane with good smoothness in which a surface is orthogonal to the ab-plane, the ab-plane does not appear even partially, and thus the surface layer superconductivity does not appear. The superconducting transition temperature (T_c) of the inside may be determined using this property.

[0039]

20 In the surface treatment of most of the examples as described above, grinding using the P1200 abrasive paper was used, but the treatment and processing for exposing a new surface is not limited to this method. Other treatment and processing method for exposing surfaces will be described below in detail.

[Example 6]

25 [0040]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$) was prepared in the following manner and order, and a surface parallel to the two-dimensional copper-oxygen plane was exposed by cleavage, and then the electrical resistivity was measured.

(1) to (4): The same as Example 2.

5 (5) Processing of crystal: The crystal was processed in the same sequence as Example 2, and attaching of the electrodes was performed. However, a surface parallel to the two-dimensional copper-oxygen plane was exposed by cleavage. In this example, a surface which was accidentally cleaved was used, but the cleavage may be intentionally performed using a sharp metal object such as a flat-blade watch screwdriver. A surface
10 orthogonal to the two-dimensional copper-oxygen plane was cut using a diamond saw (blade thickness: 0.1 mm, and rotation speed: 3600 rpm) at a cutting speed of 50 $\mu\text{m}/\text{second}$, and was manually ground using an alumina abrasive powder having a particle size of 1 μm and ethanol (lubricant) for 30 minutes. With regard to the electrodes, gold paste (TR-1301, manufactured by Tanaka Kikinzoku) was applied, and
15 was heated in an oxygen flow at 900°C for 10 minutes.

(6) Measurement of electrical resistivity: As shown in FIG. 10, temperature dependence of electrical resistivity of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which a resistance becomes zero was 32 K at the surface (T_{cs}), and was 16 K in the inside (T_c).

20 In a region between the two transition temperatures (temperature difference was 16 K), a surface layer superconductor was formed. In the inside, superconductivity is suppressed due to presence of stripe order, and thus the transition temperature is lowered. At the surface, since a treatment and processing for removing a deteriorated surface and newly exposing a new surface is performed, the surface layer superconducting transition
25 temperature of the newly exposed surface is higher than the superconducting transition

temperature of the inside.

[Example 7]

[0041]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$) was prepared in the following
5 manner and order, and a surface was exposed by cutting, and then the electrical resistivity
was measured.

(1) to (4): The same as Example 2.

(5) Processing of crystal: The crystal was processed in the same sequence as
Example 2, and attachment of the electrodes was performed. However, a surface was
10 obtained by performing the cutting using a diamond saw (blade thickness: 0.1 mm, and
rotation speed: 3600 rpm) at a cutting speed of 50 $\mu\text{m}/\text{second}$. With regard to the
electrodes, gold paste (TR-1301, manufactured by Tanaka Kikinzo) was applied, and
was heated in an oxygen flow at 900°C for 10 minutes.

(6) Measurement of electrical resistivity: As shown in FIG. 11, temperature
15 dependence of electrical resistivity of the surface and the inside was measured. A
superconducting transition temperature determined from a temperature at which a
resistance becomes zero was 31 K at the surface (T_{cs}), and was 19 K in the inside (T_c).
In a region between the two transition temperatures (temperature difference was 12 K), a
surface layer superconductor was formed. In the inside, superconductivity is suppressed
20 due to presence of stripe order, and thus the transition temperature is lowered. At the
surface, since a treatment and processing for removing a deteriorated surface and newly
exposing a new surface is performed, the surface layer superconducting transition
temperature of the newly exposed surface is higher than the superconducting transition
temperature of the inside.

25 [Example 8]

[0042]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$) was prepared in the following order, and a surface was ground with P800 abrasive paper, and then electrical resistivity was measured.

5 (1) to (4): The same as Example 2.

(5) Processing of crystal: The crystal was processed in the same sequence as Example 2, and attaching of the electrodes was performed. However, the P800 abrasive paper was used for grinding of a surface parallel to the two-dimensional copper-oxygen plane, and the grinding was manually performed for 1 minute without using a lubricant.

10 An alumina abrasive powder having a particle size of 1 μm and ethanol (lubricant) were used for grinding of a surface orthogonal to the two-dimensional copper-oxygen plane, and the grinding was manually performed for 30 minutes. With regard to the electrodes, gold paste (TR-1301, manufactured by Tanaka Kikinokoku) was applied, and was heated in an oxygen flow at 900°C for 10 minutes.

15 (6) Measurement of electrical resistivity: As shown in FIG. 12, temperature dependence of electrical resistivity of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which a resistance becomes zero was 35 K at the surface (T_{cs}), and was 16 K in the inside (T_c). In a region between the two transition temperatures (temperature difference was 19 K) a
20 surface layer superconductor was formed. In the inside, superconductivity is suppressed due to presence of the stripe order, and thus the transition temperature is lowered. At the surface, since a treatment and processing for removing a deteriorated surface and newly exposing a new surface is performed, the surface layer superconducting transition temperature of the newly exposed surface is higher than the superconducting transition
25 temperature of the inside.

[Example 9]

[0043]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$) was prepared in the following manner and order, and a surface was ground with an alumina abrasive powder having a particle size of 1 μm , and then the electrical resistivity was measured.

(1) to (4): The same as Example 2.

(5) Processing of crystal: The crystal was processed in the same sequence as Example 2, and attaching of the electrodes was performed. However, an alumina abrasive powder having a particle size of 1 μm and ethanol (lubricant) were used for grinding of the entire surfaces, and the grinding was manually performed for 30 minutes. With regard to the electrodes, gold paste (TR-1301, manufactured by Tanaka Kikinzoku) was applied, and was heated in an oxygen flow at 900°C for 10 minutes.

(6) Measurement of electrical resistivity: As shown in FIG. 13, temperature dependence of electrical resistivity of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which a resistance becomes zero was 37 K at the surface (T_{cs}), and was 16 K in the inside (T_c). In a region between the two transition temperatures (temperature difference was 21 K) a surface layer superconductor was formed. In the inside, superconductivity is suppressed due to presence of the stripe order, and thus the transition temperature is lowered. At the surface, since a treatment and processing for removing a deteriorated surface and newly exposing a new surface is performed, the surface layer superconducting transition temperature of the newly exposed surface is higher than the superconducting transition temperature of the inside.

[Example 10]

[0044]

A single crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.120$) was prepared in the following manner and order, and a surface was etched with plasma, and then the electrical resistivity was measured.

(1) to (4): The same as Example 2.

5 (5) Processing of crystal: The crystal was processed in the same sequence as Example 2, and attaching of the electrodes was performed. However, etching with plasma (argon flow rate of 6.4 sccm, 1 mTorr, 400 W, ion current of 1.4 mA, and for 30 seconds) was used for treatment of a surface parallel to the two-dimensional copper-oxygen plane, and an alumina abrasive powder having a particle size of 1 μm and
10 ethanol (lubricant) were used for grinding of a surface orthogonal to the two-dimensional copper-oxygen plane, and the grinding was manually performed for 30 minutes. With regard to the electrodes, gold paste (TR-1301, manufactured by Tanaka Kikinzoku) was applied, and was heated in an oxygen flow at 900°C for 10 minutes.

(6) Measurement of electrical resistivity: As shown in FIG. 14, temperature
15 dependence of electrical resistivity of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which a resistance becomes zero was 27 K at the surface (T_{cs}), and was 19 K in the inside (T_c). In a region between the two transition temperatures (temperature difference was 8 K), a surface layer superconductor was formed. In the inside, superconductivity is suppressed
20 due to presence of the stripe order, and thus the transition temperature is lowered. At the surface, since a treatment and processing for removing a deteriorated surface and newly exposing a new surface is performed, the surface layer superconducting transition temperature of the newly exposed surface is higher than the superconducting transition temperature of the inside.

As the treatment and processing for removing a deteriorated surface and exposing a new surface in Examples 1 to 10 described above, an arbitrary method such as grinding and etching may be possible as long as the new surface may be exposed.

[0046]

5 It is known that the stripe order, which suppresses superconductivity, is also present in $\text{La}_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Nd})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Sm})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Eu})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Gd})_{2-x}\text{Sr}_x\text{CuO}_4$ or $(\text{La}, \text{Tb})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Nd})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Sm})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Eu})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Gd})_{2-x}\text{Ba}_x\text{CuO}_4$, or $(\text{La}, \text{Tb})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Nd})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Sm})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Eu})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Gd})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, or $(\text{La}, \text{Tb})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$ in addition to $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, and a weak stripe order may be seen in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. In these material groups, the surface layer superconductivity caused by the stripe order that suppresses superconductivity also appears. Among these, with respect to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, a specific method of realizing the surface layer superconductivity will be described in detail.

[Example 11]

[0047]

A single crystal of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.105$) was prepared in the following manner and order, and the electrical resistivity was measured.

20 (1) Preparation of a raw material rod: Dried La_2O_3 , SrCO_3 , and CuO (all of these had a purity of 99.9%) were used as raw materials, and these were weighed in a ratio of $\text{La} : \text{Sr} : \text{Cu} = 1.895 : 0.105 : 1.05$ in terms of molar ratio to obtain a total amount of 10 g. Then, these raw materials were mixed, and were allowed to react with each other at 950°C for 12 hours. The reaction material obtained was pulverized, and was closely packed into a rubber tube having a diameter of 7 mm. Then, hydrostatic pressing was

25

performed, and a cylindrical rod obtained was sintered at 1,180°C for 12 hours. A sintered rod obtained was used as a raw material rod, and was attached to an upper shaft of a crystal growth furnace.

(2) Preparation of seed crystal: A sintered rod was prepared in the same sequence as (1), and the sintered rod was used as a seed crystal, and was attached to a lower shaft of the crystal growth furnace.

[0048]

(3) Preparation of solvent: Dried La_2O_3 , SrCO_3 , and CuO (all of these had a purity of 99.9%) were used as raw materials, and these were weighed in a ratio of La : Sr : Cu = 71 : 13 : 116 in terms of molar ratio to obtain a total amount of 10 g. Then, these raw materials were mixed, and were allowed to react with each other at 950°C for 12 hours. The reaction material obtained was pulverized, and was closely packed into a rubber tube having a diameter of 7 mm. Then, hydrostatic pressing was performed, and a cylindrical rod obtained was sintered at 950°C for 12 hours. A disk-shaped body of 0.12 g was cut from the sintered rod obtained, and was used as a solvent. The solvent was attached to an upper end of the seed crystal.

(4) Crystal growth: The solvent was melted with lamp heating by applying two atmospheres of oxygen to connect the raw material rod to the seed crystal. Then, crystal growth according to a floating zone method was performed at 0.5 mm/h while rotating the upper shaft and the lower shaft at 20 rpm in directions opposite to each other. Lamp power during the growth was 557 W. A polycrystalline state appeared at an initial stage of the growth, but crystal orientations were gradually aligned in one orientation, and thus a single crystal was ultimately obtained.

(5) Processing of crystal: The crystal orientation was determined by a Laue photograph, the crystal was cut into the chip shape of FIG. 1 using a diamond saw (blade

thickness: 0.3 mm, and a rotation speed: 5 rpm) at a cutting speed of 2 $\mu\text{m/sec}$, and the entire surface was manually ground for 1 minute using P1200 abrasive paper and ethanol (lubricant) to newly expose a new processed surface. Silver paste (DuPont 6838) was applied with the electrode arrangement shown in FIG. 1, and was heated in an oxygen
 5 flow at 450°C for 10 minutes.

(6) Measurement of electrical resistivity: As shown in FIG. 15, temperature dependence of electrical resistivity of the surface and the inside was measured. A superconducting transition temperature determined from a temperature at which a resistance becomes zero was 32 K at the surface (T_{cs}), and was 27 K in the inside (T_c).

10 In a region between the two transition temperatures (temperature difference was 5 K), a surface layer superconductor was formed. In the inside, superconductivity is suppressed due to presence of the stripe order, and thus the transition temperature is lowered. At the surface layer, since a treatment and processing for removing a deteriorated surface and newly exposing a new surface is performed, the surface layer superconducting
 15 transition temperature of the newly exposed surface is higher than the superconducting transition temperature of the inside.

[0049]

$\text{La}_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Nd})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Sm})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Eu})_{2-x}\text{Sr}_x\text{CuO}_4$, $(\text{La}, \text{Gd})_{2-x}\text{Sr}_x\text{CuO}_4$, or $(\text{La}, \text{Tb})_{2-x}\text{Sr}_x\text{CuO}_4$ are materials in which stripe
 20 order is stabilized by adding Ba, Nd, Sm, Eu, Gd, or Tb as an additive to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in which a weak stripe order may be seen. In addition, $(\text{La}, \text{Nd})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Sm})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Eu})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Gd})_{2-x}\text{Ba}_x\text{CuO}_4$, or $(\text{La}, \text{Tb})_{2-x}\text{Ba}_x\text{CuO}_4$, $(\text{La}, \text{Nd})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Sm})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Eu})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, $(\text{La}, \text{Gd})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, or $(\text{La}, \text{Tb})_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$ are materials in which stripe order is further
 25 stabilized by adding Nd, Sm, Eu, Gd, or Tb as an additive to $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ or $\text{La}_{2-x}(\text{Sr},$

$\text{Ba})_x\text{CuO}_4$ in which a stripe order is already seen. Accordingly, even in the copper oxide high-temperature superconductors, the surface layer superconductivity caused by the stripe order that suppresses superconductivity is further stabilized. Even in a stripe order of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, and the like, the surface layer superconductivity is naturally stabilized. Furthermore, in a case where a cause of suppressing superconductivity is present in addition to the stripe order, the treatment and processing for removing a deteriorated surface allows the exposure of a new surface with a consequently increased surface layer superconducting transition temperature, with respect to the superconducting transition temperature of the inside.

10 [Reference Signs List]

[0050]

A: Surface layer superconductor

1: Crystal

1a: Processed surface

15 1b, 1c: Side surface

1d: Bottom surface

2, 3: Voltage terminal (Electrode)

5: Voltmeter

6: Current source

20 7, 8: Voltage terminal (Electrode)

9: Voltmeter

10: Thermal reservoir

11: Heater

12: Current source

[CLAIMS]

[Claim 1]

A method of fabricating a surface layer superconductor, the method comprising:
performing a treatment and processing for removing a surface and forming a
5 new processed surface for a superconducting crystal in which superconductivity is
suppressed so as to fabricate a surface layer superconductor in which a surface layer
superconducting transition temperature of the new processed surface is higher than a
superconducting transition temperature of the inside of the crystal.

[Claim 2]

10 A method of fabricating a surface layer superconductor, the method comprising:
forming a processed surface by performing a treatment or processing for a
crystal of a perovskite-type copper oxide-based high-temperature superconductor within
a composition range in which a stripe order that suppresses superconductivity is present
to expose a surface that intersects a c-axis of the crystal so as to fabricate a surface layer
15 superconductor in which a surface layer superconducting transition temperature of the
processed surface is higher than a superconducting transition temperature of the inside of
the crystal other than the processed surface.

[Claim 3] The method of fabricating the surface layer superconductor according
to claim 1 or 2,

20 wherein the processed surface that intersects the c-axis of the crystal is a
processed surface that has an intersection angle of 60° to 120° with the c-axis.

[Claim 4]

The method of fabricating the surface layer superconductor according to any one
of claims 1 to 3,

25 wherein at least a part of the processed surface is constituted by a

two-dimensional copper-oxygen plane.

[Claim 5] The method of fabricating the surface layer superconductor according to any one of claims 1 to 4,

wherein as the copper oxide-based high-temperature superconductor within the composition range in which the stripe order that suppresses superconductivity is present, a copper oxide-based high-temperature superconductor expressed by a compositional formula of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0.10 \leq x \leq 0.15$) is used.

[Claim 6]

The method of fabricating the surface layer superconductor according to any one of claims 1 to 5,

wherein a method of forming the processed surface is any one of grinding, cleavage, division, cutting, and etching.

[Claim 7]

The method of fabricating the surface layer superconductor according to any one of claims 1 to 5,

wherein the processed surface is a surface that is exposed by removing a deteriorated portion of the surface of the crystal.

[Claim 8]

A surface layer superconductor formed from a crystal of a perovskite-type copper oxide-based high-temperature superconductor within a composition range in which a stripe order that suppresses superconductivity is present, comprising:

a processed surface which is generated by a treatment or processing for exposing a surface that intersects a c-axis of the crystal,

wherein a surface layer superconducting transition temperature of the processed surface is higher than a superconducting transition temperature of the inside of the crystal

other than the processed surface.

[Claim 9]

The surface layer superconductor according to claim 8,
wherein the processed surface that intersects the c-axis of the crystal is a
5 processed surface that has an intersection angle of 60° to 120° with the c-axis.

[Claim 10]

The surface layer superconductor according to claim 8 or 9,
wherein at least a part of the processed surface is constituted by a
two-dimensional copper-oxygen plane.

10 [Claim 11]

The surface layer superconductor according to any one of claims 8 to 10,
wherein the copper oxide-based high-temperature superconductor within the
composition range in which the stripe order that suppresses superconductivity is present
is a copper oxide-based high-temperature superconductor expressed by a compositional
15 formula of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0.10 \leq x \leq 0.15$).

[Claim 12]

The surface layer superconductor according to any one of claims 8 to 11,
wherein the processed surface is any one of a surface processed by grinding, a
surface processed by cleavage, a surface processed by division, a surface processed by
20 cutting, and a surface processed by etching.

[Claim 13]

The surface layer superconductor according to any one of claims 8 to 11,
wherein the processed surface is a surface that is exposed by removing a
deteriorated portion of the surface of the crystal.