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(54) **OXIDE HIGH-TEMPERATURE SUPERCONDUCTOR AND ITS PRODUCTION METHOD**

HOCHTEMPERATURSUPRALEITER UND HERSTELLUNGSVERFAHREN DAFÜR

OXYDE SUPRACONDUCTEUR HAUTE TEMPERATURE ET SON PROCEDE DE PRODUCTION

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(73) Proprietor: **Japan Science and Technology Agency**  
**Kawaguchi-shi**  
**Saitama 332-0012 (JP)**

(72) Inventors:  
• **ATHINARAYANAN, Sundaresan**  
**Tsukuba-shi,**  
**Ibaraki 305-0046 (JP)**  
• **IHARA, Hideo DI**  
  
**(JP)**

(74) Representative: **Sparing Röhl Henseler**  
**Patentanwälte**  
**European Patent Attorneys**  
**Postfach 14 04 43**  
**40074 Düsseldorf (DE)**

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- **O'CONNOR J.D. ET AL.: 'Low-temperature processing of superconducting Ti2Ba2Ca1Cu2Ox films on CeO2 buffered sapphire' APPLIED PHYSICS LETTERS vol. 69, no. 1, 01 July 1996, pages 115 - 117, XP002966813**
- **KHAN NAWAZISH A. ET AL.: 'Superconducting properties of Cu1-xTlxBa2Ca3Cu4O12-y thin films' SUPERCONDUCTOR SCIENCE AND TECHNOLOGY vol. 14, no. 8, August 2001, pages 603 - 606, XP002966814**

**EP 1 443 131 B1**

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**Description**Technical Field

5 **[0001]** The present invention relates to an oxide high temperature superconductor that excels in high-frequency properties and a method of making such an oxide high temperature superconductor.

Background Art

10 **[0002]** Of oxide high temperature superconductors, a Cu family superconductor thin film (see Kotai Butsuri (Solid State Physics), Vol. 35, No. 5, 2000) excels in superconducting properties, and research and development efforts have diversely been devoted to putting it to practical use. The excellent superconducting characteristics which a Cu family superconductor thin film possesses include the feature that it excels in high-frequency properties as mentioned in the literature referred to above. In order to fabricate a superconductor thin film that can be applied to a high-frequency device  
15 such as a microwave device, of importance is not only the high-frequency properties of the superconductor thin film itself but also those of a substrate on which the superconductor thin film is to be epitaxially grown.

**[0003]** Fabricating a Cu family oxide high temperature superconductor that excels in superconducting properties requires the superconductor thin film to be excellent in both crystallographic integrity and crystallographic orientation.

20 **[0004]** For a conventional Cu family superconductor thin film, use has been made of a SrTiO<sub>3</sub> substrate that is small in lattice mismatch with such a superconductor thin film and as a result is capable of growing thereon such a superconductor thin film that is high in crystallographic integrity and excellent in crystallographic orientation. However, since it is large in dielectric constant (specific dielectric constant = about 300), SrTiO<sub>3</sub> is unsuitable to form a substrate for growing a superconductor thin film thereon for particular use in a high frequency device.

25 **[0005]** Thus, in order to be applicable to a high frequency device, there has been sought an oxide high temperature superconductor in which an oxide high temperature superconductor thin film that is high in crystallographic integrity and excellent in crystallographic orientation is formed on a substrate that is low in dielectric constant, and a method whereby such an oxide high temperature superconductor thin film can be simply epitaxially grown on such a substrate. O'Connor et al (Appl. Phys. Lett 69(1) pages 115-117, 1996) teaches using a CeO<sub>2</sub> buffer layer on sapphire and low temperatures for the deposition of high temperature superconducting oxides.  
30

Disclosure of the Invention

35 **[0006]** It is accordingly a first object of the present invention to provide an oxide high temperature superconductor in which an oxide high temperature superconductor thin film that is high in crystallographic integrity and excellent in crystallographic orientation is formed on a substrate that is low in dielectric constant.

**[0007]** A second object of the present invention is to provide a method of making an oxide high temperature superconductor thin film that is high in crystallographic integrity and excellent in crystallographic orientation is formed on a substrate that is low in dielectric constant.

**[0008]** The present invention provides an oxide high temperature superconductor according to the features of claim 1.

40 **[0009]** According to this makeup, an oxide high temperature superconductor composed as specified above which excels in both crystallographic integrity and crystallographic orientation is allowed to form on a substrate of low dielectric constant. It should be noted here that such oxide superconductors of composition as mentioned above include so-called YBCO type, Y(Ln)-[123] type and Hg type oxide high temperature superconductors.

**[0010]** The said crystalline substrate is preferably a sapphire substrate having a sapphire R face (1, -1, 0, 2).

45 **[0011]** In an oxide high temperature superconductor as set forth in claim 1, the said oxide high temperature superconductor thin film containing Ba as a constituent element may be epitaxially grown whereby an amorphous phase composed to form this oxide high temperature superconductor is deposited on the said second buffer layer and the deposited amorphous phase is heat-treated in an oxygen atmosphere at a pressure of 1.0 to 10 atm in the presence of Ag<sub>2</sub>O or AgO, or alternatively in the presence of Tl.

50 **[0012]** In order to achieve the second object mentioned above there is also provided in accordance with the present invention as set forth in claim 6, a method of making a thin film of an oxide high temperature superconductor.

**[0013]** According to this makeup, an oxide high temperature superconductor composed as specified above which excels in both crystallographic integrity and crystallographic orientation is allowed to epitaxially grow on a substrate of low dielectric constant. It should be noted here that such oxide superconductors of composition as mentioned above  
55 include so-called YBCO type, Y(Ln)-[123] type and Hg type oxide high temperature superconductors.

**[0014]** According to this method makeup, the buffer layer can be obtained easily, that is well lattice-matched with the said oxide high temperature superconductor and at the same time acts as a barrier to the diffusion of Ba of the said oxide high temperature superconductor thin film being epitaxially grown, therefore, an oxide high temperature super-

conductor thin film that excels in both crystallographic integrity and crystallographic orientation can be easily epitaxially grown.

**[0015]** The said crystalline substrate is preferably a sapphire substrate having a sapphire R face (1, -1, 0, 2).

**[0016]** In a method as set forth in claim 6, the said oxide high temperature superconductor thin film containing Ba as a constituent element thereof, may be epitaxially grown whereby an amorphous phase composed to form this oxide high temperature superconductor is deposited on the said buffer layer and the deposited amorphous phase is heat-treated in an oxygen atmosphere at a pressure of 1.0 to 10 atm in the presence of Ag<sub>2</sub>O or AgO, or alternatively in the presence of Tl.

#### Brief Description of the Drawings

**[0017]** The present invention will better be understood from the following detailed description and the drawings attached hereto showing certain illustrative forms of implementation of the present invention. In this connection, it should be noted that such forms of implementation illustrated in the accompanying drawings hereof are intended in no way to limit the present invention but to facilitate an explanation and understanding thereof. In the drawings:

Fig. 1 shows an AFM (Atomic Force Microscopic) image of a surface of a CeO<sub>2</sub> (100) layer grown on a sapphire R (1, -1, 0, 2) face substrate;

Fig. 2 is a diagram showing a diffraction pattern by XRD (X-ray diffractometer) of an oxide high temperature superconductor fabricated in accordance with the present invention;

Fig. 3 is a diagram showing results of measurement by XRD of an in-plane orientation of the oxide high temperature superconductor fabricated in accordance with the present invention; and

Fig. 4 is a diagram showing a diffraction pattern by XRD indicating that Sr in a second buffer layer does not react with Ce in a first buffer layer, which layers are made in accordance with the present invention.

#### Best Modes for Carrying Out the Invention

**[0018]** Hereinafter, the present invention will be described in detail with reference to certain suitable forms of implementation thereof illustrated in the drawing figures.

**[0019]** At the outset, mention is made of an oxide high temperature superconductor fabricating method of the present invention as regards a specific form of implementation thereof.

**[0020]** Of superconductors having a superconducting transition temperature of not less than 77 K, a Cu family oxide high temperature superconductor such as CuTi-[12231 or CuTi-[1234] (see Kotai Butsuri [Solid State Physics], Vol. 35, No.5, 2000), namely having a composition expressed by

composition formula: Cu<sub>1-x</sub>Tl<sub>x</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8-w</sub>, or

composition formula: Cu<sub>1-x</sub>Tl<sub>x</sub>Ba<sub>2</sub>Ca<sub>3</sub>Cu<sub>4</sub>O<sub>10-w</sub>

where  $0 \leq x \leq 1$  and  $0 \leq w \leq 4$  is a material having a lowest microwave surface resistance. Realizing an excellent microwave device makes it necessary to select a substrate having a low dielectric constant and at the same time to make a good lattice match between a superconductor thin film and the substrate.

**[0021]** While a single crystal sapphire R (1, -1, 0, 2) face substrate is optimum as it is of low cost, large in surface area and low in dielectric constant, it cannot be used as it is because of its too-large lattice mismatch with a Cu family oxide high temperature superconductor thin film.

**[0022]** In order to solve this problem, it is known to be effective to use a CeO<sub>2</sub> (100) buffer layer on the sapphire R(1, -1, 0, 2) face substrate.

**[0023]** A specific example of the CeO<sub>2</sub> layer grown on the sapphire substrate is given below.

**[0024]** Fig. 1 shows an AFM (Atomic Force Microscopic) image of a surface of a CeO<sub>2</sub> (100) layer grown on a sapphire R (1, -1, 0, 2) face substrate. A specimen was formed from a sapphire R (1, -1, 2, 2) face substrate held at a temperature of 525°C which had a CeO<sub>2</sub> layer built up thereon to a thickness of 200 nm by magnetron RF sputtering in a mixed gas of Ar at 5 mTorr and N<sub>2</sub>O at 10 mTorr whereafter it was heat-treated at a temperature of 1100°C.

**[0025]** As is apparent from Fig. 1, it is seen that CeO<sub>2</sub> grains are rectangular and at the same time are aligned in the directions of (-1, 1, 0, 1) and (1, 1, -2, 0). Thus, CeO<sub>2</sub> is an optimum material to devise a lattice match between the sapphire substrate and the oxide high temperature superconductor thin film.

**[0026]** However, if it is attempted to grow an oxide high temperature superconductor thin film epitaxially on a sapphire substrate having CeO<sub>2</sub> formed thereon as a buffer layer, the problem arises that the epitaxial growth temperature of the oxide high temperature superconductor thin film causes Ba in the oxide high temperature superconductor thin film to react with Ce, forming BaCeO<sub>3</sub>, thus preventing the oxide high temperature superconductor thin film from being satisfactory in both crystallographic integrity and crystallographic orientation.

**[0027]** The present inventors have discovered that this problem is solved if there is built up on the CeO<sub>2</sub> layer as a

first buffer layer a thin film as a second buffer layer of an oxide high temperature superconductor in which Ba as a constituent element thereof is substituted with Sr that does not readily react with Ce and then a Ba containing oxide high temperature superconductor thin film is allowed to grow epitaxially on the second buffer layer, and have thus arrived at the present invention. To wit, the thin film in which Sr is substituted for Ba in the oxide high temperature superconductor thin film is akin in crystallographic structure and lattice constant to the oxide high temperature superconductor thin film to be epitaxially grown thereon and extremely high in lattice matching with the latter, and functions as an optimum buffer layer in which Sr does not readily reacts with Ce; hence it gives the oxide high temperature superconductor thin film excellent crystallographic integrity and orientation.

**[0028]** Thus formed in accordance with the present invention, an oxide high temperature superconductor in which an oxide high temperature superconductor thin film containing Ba as a constituent element thereof is formed on a crystalline substrate is **characterized in that** it comprises a first buffer layer for alleviating or reducing a lattice mismatch between the crystalline substrate and the oxide high temperature superconductor thin film, and a second buffer layer of a Sr oxide formed on the first buffer layer in order to act as a barrier to Ba diffusion from the high temperature superconductor thin film, interposed between the crystalline substrate and the oxide high temperature superconductor thin film. As a result, an oxide high temperature superconductor is obtained that excels in both crystallographic integrity and crystallographic orientation by virtue of the fact that even if the first buffer layer for reducing the lattice mismatch of the substrate with the oxide high temperature superconductor thin film is made of a material that readily brings about a surface reaction with Ba in the oxide high temperature superconductor thin film, the second buffer layer prevents the occurrence of such a surface or interfacial reaction.

**[0029]** Next, a first specific example of the present invention is shown below.

**[0030]** First, mention is made of how a specimen was prepared. A sapphire R (1, -1, 2, 0) face substrate was heat-treated at a temperature of 1100°C for a period of 2 hours, and then its surface was smoothened and made clean. The resulting sapphire substrate was held at a temperature of 600°C and had a CeO<sub>2</sub> layer built up thereon to a thickness of 15 nm by magnetron RF sputtering in a mixed gas atmosphere of Ar at 5 mTorr and N<sub>2</sub>O at 10 mTorr.

**[0031]** Subsequently, the substrate with its temperature lowered to 50 °C had formed thereon, as the thin film in which Ba in the composition: Cu<sub>1-x</sub>Tl<sub>x</sub>Ba<sub>2</sub>CaCu<sub>2</sub>O<sub>8-w</sub> is substituted with Sr, an amorphous film of Cu<sub>1-x</sub>Tl<sub>x</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8-w</sub> to a film thickness of 200 nm by magnetron RF sputtering.

**[0032]** Next, this amorphous film had built up thereon an amorphous film having the composition of an oxide high temperature superconductor of CuTlBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10-w</sub> as to a film thickness of 700 nm by magnetron RF sputtering.

**[0033]** Thereafter, the specimen was taken out of the magnetron RF sputtering apparatus and was charged, together with a thallium containing high temperature superconductor disk (composed of CuTl-Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> and of 17.5 mm in radius, 4 mm thick and 10g in weight) and 50 mg of Tl<sub>2</sub>O<sub>3</sub> powder particles dispersed thereon, in a hermetically sealed container made of silver (a board shaped container of 18 mm in radius and 10 mm in height) and was then heat-treated at a temperature of 860 °C for a time period of 30 minutes.

**[0034]** Fig. 2 is a diagram showing a diffraction pattern by XRD (X-ray diffractometer) of the oxide high temperature superconductor fabricated in accordance with the present invention. In the diagram, the numerals affixed to the peaks of the diffraction pattern indicate their corresponding Miller face indices, the numerals in the parentheses indicate their corresponding oxide high temperature superconductors, and the lettering Al<sub>2</sub>O<sub>3</sub> affixed to some peaks indicates that they are diffraction peaks for the sapphire substrate. As is apparent from the diagram, it is seen that a CuTlBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10-w</sub> oxide type high temperature superconductor fabricated in accordance with a method of the present invention, namely CuTl-[1223] is epitaxially grown oriented along the crystallographic c-axis.

**[0035]** Fig. 3 is a diagram showing results of measurement by XRD indicating an in-plane orientation of the oxide high temperature superconductor fabricated in accordance with the present invention. It is a diagram showing results of the measurement by XRD in which with the angle of diffraction 2θ held at the angle of diffraction for the (107) Miller index face, the specimen is rotated at an angle of rotation φ about an axis perpendicular to the plane of incidence. As is apparent from the diagram, it is seen that an oxide high temperature superconductor fabricated in accordance with a method of the present invention is excellent in its in-plane orientation, too.

**[0036]** Shown next are results of experiment confirming that Sr in the second buffer layer does not react with Ce in the first buffer layer. A specimen used was identical to that used in the first specific example except that it did not have the amorphous film built up thereon, which has the composition of an oxide high temperature superconductor of CuTlBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10-w</sub>, and that it was heat-treated at a temperature of 890 °C higher than that in the first specific example. Fig. 4 is a diagram showing a diffraction pattern by XRD indicating that Sr in the second buffer layer does not react with Ce in the first buffer layer. In the diagram, the numerals affixed to the peaks of the diffraction pattern indicate their corresponding Miller face indices, the numerals in the parentheses indicate their corresponding oxide high temperature superconductor's type, and the letterings CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the parentheses affixed to some peaks indicate that they are diffraction peaks for the CeO<sub>2</sub> and the sapphire substrate. As is apparent from the diagram, no diffraction peak by SrCeO<sub>3</sub> is observed. It is also shown that the diffraction strength for CeO<sub>2</sub> remains substantially unchanged compared with that before the heat-treatment. From these, it has been confirmed that no reaction takes place between Sr in the

second buffer layer substituted for Ba in the oxide high temperature superconductor and Ce in the first buffer layer composed of CeO<sub>2</sub>.

**[0037]** Next, a second specific example of the present invention is given.

**[0038]** The second specific example is identical to the first specific example except that an Ag<sub>2</sub>O powder is used instead of the Ti<sub>2</sub>O<sub>3</sub> powder.

**[0039]** Using this method, a CuTiBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10-w</sub> oxide type high temperature superconductor, namely CuTI-[1223], was fabricated. Its results of measurement by XRD indicated the same characteristics as in Figs. 2 and 3, and its superconducting transition temperature T<sub>c</sub> and critical current density J<sub>c</sub> were found to be 100 K and 4x10<sup>4</sup>A/cm<sup>2</sup>, respectively. These superconducting properties are found to be somewhat inferior to those with a CuTI-[1223] oxide type high temperature superconductor fabricated on a SrTiO<sub>3</sub> substrate, but this is apparently due to cracking and hence can obviously be improved if a preventive measure for the cracking is taken.

**[0040]** While the present invention has been shown in the above specific examples as applied to a CuTI-[1223] oxide type high temperature superconductor, it is obvious that the invention is applicable to any oxide high temperature superconductor containing Ba as a constituent element and having a composition expressed by composition formula:

$Cu_{1-x}M_x(Ba_{1-y}Sr_y)_2(Ca_{1-z}L_z)_{n-1}(Cu_{1-q}Q_q)_nO_{2n+4-w}$  or composition formula:  $(Cu_{1-x}M_x)_2(Ba_{1-y}Sr_y)_2(Ca_{1-z}L_z)_{n-1}(Cu_{1-q}Q_q)_nO_{2n+4-w}$  where:

M represents Ti, Hg, Bi, Pb, In, Ga, Al, B, C, Si, Sn, Ag, Au, S, N, P, Mo, Re, Os, Cr, Ti, V, Fe, one element in the lanthanide series, or one or more alkali metal elements,

L represents Mg, Y, or one or more elements in the lanthanide series. Q represents either or both of Mg and Zn, and  $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq z \leq 1$ ,  $0 \leq q < 0.1$ ,  $0 \leq w \leq 4$ , and  $2 \leq n \leq 5$ .

**[0041]** While the second buffer layer is shown in the above specific examples as composed of an oxide high temperature superconductor identical to a target oxide high temperature superconductor to be epitaxially grown except that Ba therein is substituted with Sr, it is obvious that it may be composed of an oxide high temperature superconductor that is not identical but similar to the target oxide high temperature superconductor and which has its Ba constituent substituted with Sr.

**[0042]** While the second buffer layer is shown in the above specific examples as composed of an oxide high temperature superconductor identical to a target oxide high temperature superconductor except that Ba therein is substituted with Sr, it is obvious that it may be a Sr oxide film that is well lattice-matched with the target oxide high temperature superconductor.

**[0043]** Accordingly, as a second form of implementation of the present invention, there is provided an oxide high temperature superconductor made by an oxide high temperature superconductor thin film containing Ba as a constituent element and formed on a crystalline substrate, **characterized in that** it comprises a buffer layer composed of a Sr oxide and interposed between the crystalline substrate and the oxide high temperature superconducting film for reducing a lattice mismatch between them and also for serving as a barrier to the diffusion of Ba from the oxide high temperature superconductor thin film. An oxide high temperature superconductor that excels in both crystallographic integrity and orientation can here again be obtained by virtue of the fact that a Sr oxide alleviates or reduces lattice mismatch between the crystalline substrate and an oxide high temperature superconducting film and at the same time prevents the interfacial reaction between the crystalline substrate and Ba in the oxide high temperature superconducting film which will otherwise occur if the substrate is made of a material that contains a substance liable to interfacially reacting with Ba from the oxide high temperature superconductor thin film.

**[0044]** While the present invention has been shown in the above specific examples as regards a Ba containing oxide high temperature superconductor grown epitaxially on a sapphire substrate, it is obvious that the invention is not limited to such an oxide high temperature superconductor but is applicable to any one of oxide magnetic material, an oxide dielectric and an oxide conductor, which contains Ba and is epitaxially grown on a sapphire substrate.

#### Industrial Applicability

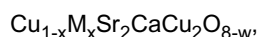
**[0045]** The present invention thus permits fabricating on a substrate of low dielectric constant an oxide high temperature superconductor that is high in crystallographic integrity and at the same time excels in crystallographic orientation.

#### **Claims**

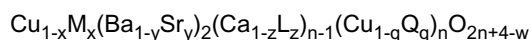
1. An oxide high temperature superconductor comprising a crystalline substrate, a first buffer layer formed on said crystalline substrate, and an oxide high temperature superconductor thin film, wherein said first buffer layer is made of CeO<sub>2</sub>,

**characterized in that**

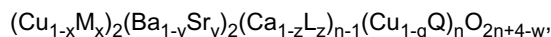
a second buffer layer is formed on said first buffer layer, and said oxide high temperature superconductor thin film is formed on said second buffer layer, wherein said second buffer layer has a composition formula:



said oxide high temperature superconductor thin film has a composition formula:



or



M represents Tl, Hg, Bi, Pb, In, Ga, Al, B, C, Si, Sn, Ag, Au, S, N, P, Mo, Re, Os, Cr, Ti, V, Fe, one element in the lanthanide series, or one or more alkali metal elements,

L represents Mg, Y, or one or more elements in the lanthanide series,

Q represents either or both of Mg and Zn, and

$0 \leq x \leq 1$ ,  $0 \leq y < 1$ ,  $0 \leq z \leq 1$ ,  $0 \leq q < 0.1$ ,  $0 \leq w \leq 4$ , and  $2 \leq n \leq 5$ .

2. The oxide high temperature superconductor as set forth in claim 1, wherein said crystalline substrate is a sapphire substrate.
3. The oxide high temperature superconductor as set forth in claim 2, wherein said sapphire substrate has a sapphire R face (1, -1, 0, 2).
4. The oxide high temperature superconductor as set forth in claim 1, **characterized in that** said oxide high temperature superconductor thin film is epitaxially grown whereby an amorphous phase composed to form this oxide high temperature superconductor is deposited on said second buffer layer and the deposited amorphous phase is heat-treated in an oxygen atmosphere at a pressure of 1.0 to 10 atm in the presence of Ag<sub>2</sub>O or AgO.
5. The oxide high temperature superconductor as set forth in claim 1, **characterized in that** said oxide high temperature superconductor thin film is epitaxially grown whereby an amorphous phase composed to form this oxide high temperature superconductor is deposited on said second buffer layer and the deposited amorphous phase is heat-treated in an oxygen atmosphere at a pressure of 1.0 to 10 atm in the presence of Tl.
6. A method of making a oxide high temperature superconductor comprising the steps of:

providing a crystalline substrate,

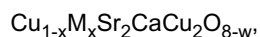
forming on said crystalline substrate a first buffer layer, and

forming an oxide high temperature superconductor thin film, wherein using CeO<sub>2</sub> as material for said first buffer layer,

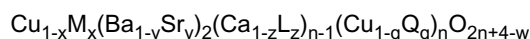
**characterized by**

forming on said first buffer layer a second buffer layer, and

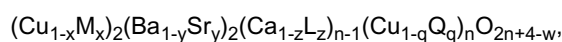
epitaxially growing said oxide high temperature superconductor thin film on said second buffer layer, wherein using a composition formula for said second buffer layer as follows:



using a composition formula for said oxide high temperature superconductor thin film as follows:



or



## EP 1 443 131 B1

M represents Tl, Hg, Bi, Pb, In, Ga, Al, B, C, Si, Sn, Ag, Au, S, N, P, Mo, Re, Os, Cr, Ti, V, Fe, one element in the lanthanide series, or one or more alkali metal elements,

L represents Mg, Y, or one or more elements in the lanthanide series,

Q represents either or both of Mg and Zn, and

$0 \leq x \leq 1$ ,  $0 \leq y < 1$ ,  $0 \leq z \leq 1$ ,  $0 \leq q < 0.1$ ,  $0 \leq w \leq 4$ , and  $2 \leq n \leq 5$ .

7. The method as set forth in claim 6, wherein using a sapphire substrate for said crystalline substrate.

8. The method as set forth in claim 7, wherein using a sapphire R face (1, -1, 0, 2) with said sapphire substrate.

9. The method as set forth in claim 6, **characterized in that** said oxide high temperature superconductor thin film is epitaxially grown whereby an amorphous phase composed to form this oxide high temperature superconductor is deposited on said second buffer layer and the deposited amorphous phase is heat-treated in an oxygen atmosphere at a pressure of 1.0 to 10 atm in the presence of  $\text{Ag}_2\text{O}$  or  $\text{AgO}$ .

10. The method as set forth in claim 6, **characterized in that** said oxide high temperature superconductor thin film is epitaxially grown whereby an amorphous phase composed to form this oxide high temperature superconductor is deposited on said second buffer layer and the deposited amorphous phase is heat-treated in an oxygen atmosphere at a pressure of 1.0 to 10 atm in the presence of Tl.

### Patentansprüche

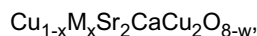
1. Oxid-Hochtemperatursupraleiter, der ein kristallines Substrat, eine auf dem kristallinen Substrat gebildete erste Pufferschicht und eine Oxid-Hochtemperatursupraleiter-Dünnschicht umfasst, wobei die erste Pufferschicht aus  $\text{CeO}_2$  hergestellt ist,

**dadurch gekennzeichnet, dass**

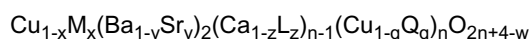
auf der ersten Pufferschicht eine zweite Pufferschicht gebildet ist und

die Oxid-Hochtemperatursupraleiter-Dünnschicht auf der zweiten Pufferschicht gebildet ist, wobei

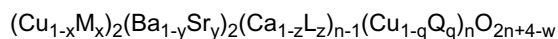
die zweite Pufferschicht die folgende Zusammensetzungsformel besitzt:



wobei die Oxid-Hochtemperatursupraleiter-Dünnschicht die folgende Zusammensetzungsformel besitzt:



oder



wobei M repräsentiert: Tl, Hg, Bi, Pb, In, Ga, Al, B, C, Si, Sn, Ag, Au, S, N, P, Mo, Re, Os, Cr, Ti, V, Fe, ein Element der Lanthanide oder ein oder mehrere Alkalimetallelemente,

wobei L repräsentiert: Mg, Y oder eines oder mehrere Elemente der Lanthanide,

wobei Q repräsentiert: Mg und/oder Zn und

wobei:  $0 \leq x \leq 1$ ,  $0 \leq y < 1$ ,  $0 \leq z \leq 1$ ,  $0 \leq q < 0,1$ ,  $0 \leq w \leq 4$  und  $2 \leq n \leq 5$ .

2. Oxid-Hochtemperatursupraleiter nach Anspruch 1, wobei das kristalline Substrat ein Saphirsubstrat ist.

3. Oxid-Hochtemperatursupraleiter nach Anspruch 2, wobei das Saphirsubstrat eine Saphir-R-Fläche (1, -1, 0, 2) besitzt.

4. Oxid-Hochtemperatursupraleiter nach Anspruch 1, **dadurch gekennzeichnet, dass** die Oxid-Hochtemperatursupraleiter-Dünnschicht epitaktisch aufgewachsen ist, wobei eine amorphe Phase, die gebildet ist, um diesen Oxid-Hochtemperatursupraleiter zu bilden, auf der zweiten Pufferschicht abgelagert ist und die abgelagerte amorphe Phase in einer Sauerstoffatmosphäre bei einem Druck von 1,0 bis 10 atm in Gegenwart von  $\text{Ag}_2\text{O}$  oder  $\text{AgO}$  wärmebehandelt ist.

## EP 1 443 131 B1

5. Oxid-Hochtemperatursupraleiter nach Anspruch 1, **dadurch gekennzeichnet, dass** die Oxid-Hochtemperatursupraleiter-Dünnschicht epitaktisch aufgewachsen ist, wobei eine amorphe Phase, die gebildet ist, um diesen Oxid-Hochtemperatursupraleiter zu bilden, auf der zweiten Pufferschicht abgelagert ist und die abgelagerte amorphe Phase in einer Sauerstoffatmosphäre bei einem Druck von 1,0 bis 10 atm in Gegenwart von TI wärmebehandelt ist.

6. Verfahren zum Herstellen eines Oxid-Hochtemperatursupraleiters, das die folgenden Schritte umfasst:

Vorsehen eines kristallinen Substrats,

Bilden einer ersten Pufferschicht auf dem kristallinen Substrat und

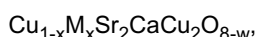
Bilden einer Oxid-Hochtemperatursupraleiter-Dünnschicht, wobei als Material für die erste Pufferschicht  $\text{CeO}_2$  verwendet wird,

**gekennzeichnet durch**

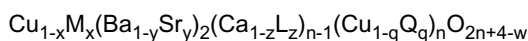
Bilden einer zweiten Pufferschicht auf der ersten Pufferschicht und

epitaktisches Aufwachsen der Oxid-Hochtemperatursupraleiter-Dünnschicht auf der zweiten Pufferschicht, wobei

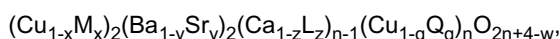
Verwenden der folgenden Zusammensetzungsformel für die zweite Pufferschicht:



Verwenden der folgenden Zusammensetzungsformel für die Oxid-Hochtemperatursupraleiter-Dünnschicht:



oder



wobei M repräsentiert: Tl, Hg, Bi, Pb, In, Ga, Al, B, C, Si, Sn, Ag, Au, S, N, P, Mo, Re, Os, Cr, Ti, V, Fe, ein Element der Lanthanide oder ein oder mehrere Alkalimetallelemente,

wobei L repräsentiert: Mg, Y oder eines oder mehrere Elemente der Lanthanide,

wobei Q repräsentiert: Mg und/oder Zn und

wobei:  $0 \leq x \leq 1$ ,  $0 \leq y < 1$ ,  $0 \leq z \leq 1$ ,  $0 \leq q < 0,1$ ,  $0 \leq w \leq 4$  und  $2 \leq n \leq 5$ .

7. Verfahren nach Anspruch 6, wobei für das kristalline Substrat ein Saphirsubstrat verwendet wird.

8. Verfahren nach Anspruch 7, wobei mit dem Saphirsubstrat eine Saphir-R-Fläche (1, -1, 0, 2) verwendet wird.

9. Verfahren nach Anspruch 6, **dadurch gekennzeichnet, dass** die Oxid-Hochtemperatursupraleiter-Dünnschicht epitaktisch aufgewachsen ist, wobei eine amorphe Phase, die gebildet ist, um diesen Oxid-Hochtemperatursupraleiter zu bilden, auf der zweiten Pufferschicht abgelagert ist und die abgelagerte amorphe Phase in einer Sauerstoffatmosphäre bei einem Druck von 1,0 bis 10 atm in Gegenwart von  $\text{Ag}_2\text{O}$  oder  $\text{AgO}$  wärmebehandelt ist.

10. Verfahren nach Anspruch 6, **dadurch gekennzeichnet, dass** die Oxid-Hochtemperatursupraleiter-Dünnschicht epitaktisch aufgewachsen ist, wobei eine amorphe Phase, die gebildet ist, um diesen Oxid-Hochtemperatursupraleiter zu bilden, auf der zweiten Pufferschicht abgelagert ist und die abgelagerte amorphe Phase in einer Sauerstoffatmosphäre bei einem Druck von 1,0 bis 10 atm in Gegenwart von TI wärmebehandelt ist.

### Revendications

1. Un oxyde supraconducteur à haute température, qui comprend un substrat cristallin, une première couche tampon formée sur ledit substrat cristallin, et un film mince d'oxyde supraconducteur à haute température, pour lequel ladite première couche tampon est faite de  $\text{CeO}_2$ ,

**caractérisé en ce que**

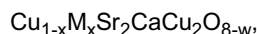
une seconde couche tampon est formée sur ladite première couche tampon, et

ledit film mince d'oxyde supraconducteur à haute température est formé sur ladite seconde couche tampon,

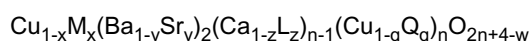
**en ce que** ladite seconde couche tampon a une formule de composition :



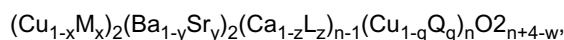
## EP 1 443 131 B1



en ce que ledit film mince d'oxyde supraconducteur à haute température a une formule de composition :



ou



M représentant Tl, Hg, Bi, Pb, In, Ga, Al, B, C, Si, Sn, Ag, Au, S, N, P, Mo, Re, Os, Cr, Ti, V, Fe, un élément de la série des lanthanides, ou un ou plusieurs éléments de métal alcalin,

L représentant Mg, Y, ou un ou plusieurs éléments de la série des lanthanides,

Q représentant Mg ou Zn ou les deux, et

$0 \leq x \leq 1$ ,  $0 \leq y < 1$ ,  $0 \leq z \leq 1$ ,  $0 \leq q < 0.1$ ,  $0 \leq w \leq 4$  et  $2 \leq n \leq 5$ .

2. L'oxyde supraconducteur à haute température selon la revendication 1, pour lequel ledit substrat cristallin est un substrat en saphir.
3. L'oxyde supraconducteur à haute température selon la revendication 2, pour lequel le substrat en saphir a une face R du saphir (1, -1, 0, 2).
4. L'oxyde supraconducteur à haute température selon la revendication 1, **caractérisé en ce que** ledit film mince d'oxyde supraconducteur à haute température est obtenu par croissance épitaxiale, pour laquelle une phase amorphe composée pour former cet oxyde supraconducteur à haute température, est déposée sur ladite seconde couche tampon et la phase amorphe déposée est traitée à chaud dans une atmosphère d'oxygène à une pression de 1.0 à 10 atm en présence d'Ag<sub>2</sub>O ou AgO.
5. L'oxyde supraconducteur à haute température selon la revendication 1, **caractérisé en ce que** ledit film mince d'oxyde supraconducteur à haute température est obtenu par croissance épitaxiale, pour laquelle une phase amorphe composée pour former cet oxyde supraconducteur à haute température, est déposée sur ladite seconde couche tampon et la phase amorphe déposée est traitée à chaud dans une atmosphère d'oxygène à une pression de 1.0 à 10 atm en présence de Tl.
6. Un procédé pour fabriquer un oxyde supraconducteur à haute température, qui comprend les étapes de :

fournir un substrat cristallin,

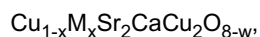
former sur ledit substrat cristallin, une première couche tampon, et

former un film mince d'oxyde supraconducteur à haute température, en utilisant du CeO<sub>2</sub> comme matériau de ladite première couche tampon,

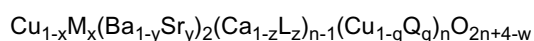
**caractérisé par**

former sur ladite première couche tampon, une seconde couche tampon, et faire croître de manière épitaxiale ledit film mince d'oxyde supraconducteur à haute température sur ladite seconde couche tampon,

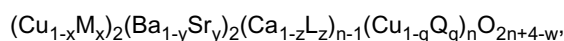
en utilisant une formule de composition pour ladite seconde couche tampon comme suit :



en utilisant une formule de composition pour ledit film mince d'oxyde supraconducteur à haute température comme suit :



ou



M représentant Tl, Hg, Bi, Pb, In, Ga, Al, B, C, Si, Sn, Ag, Au, S, N, P, Mo, Re, Os, Cr, Ti, V, Fe, un élément

## EP 1 443 131 B1

de la série des lanthanides, ou un ou plusieurs éléments de métal alcalin,  
L représentant Mg, Y, ou un ou plusieurs éléments de la série des lanthanides,  
Q représentant Mg ou Zn ou les deux, et  
 $0 \leq x \leq 1$ ,  $0 \leq y < 1$ ,  $0 \leq z \leq 1$ ,  $0 \leq q < 0.1$ ,  $0 \leq w \leq 4$  et  $2 \leq n \leq 5$ .

- 5
7. Le procédé selon la revendication 6, pour lequel il est utilisé un substrat en saphir pour ledit substrat cristallin.
8. Le procédé selon la revendication 7, pour lequel il est utilisé une face R du saphir (1, -1, 0, 2) avec ledit substrat en saphir.
- 10
9. Le procédé selon la revendication 6, **caractérisé en ce que** ledit film mince d'oxyde supraconducteur à haute température est obtenu par croissance épitaxiale, pour laquelle une phase amorphe composée pour former cet oxyde supraconducteur à haute température, est déposée sur ladite seconde couche tampon et la phase amorphe déposée est traitée à chaud dans une atmosphère d'oxygène à une pression de 1.0 à 10 atm en présence d'Ag<sub>2</sub>O ou AgO.
- 15
10. Le procédé selon la revendication 6, **caractérisé en ce que** ledit film mince d'oxyde supraconducteur à haute température est obtenu par croissance épitaxiale, pour laquelle une phase amorphe composée pour former cet oxyde supraconducteur à haute température, est déposée sur ladite seconde couche tampon et la phase amorphe déposée est traitée à chaud dans une atmosphère d'oxygène à une pression de 1.0 à 10 atm en présence de Tl.
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FIG. 1

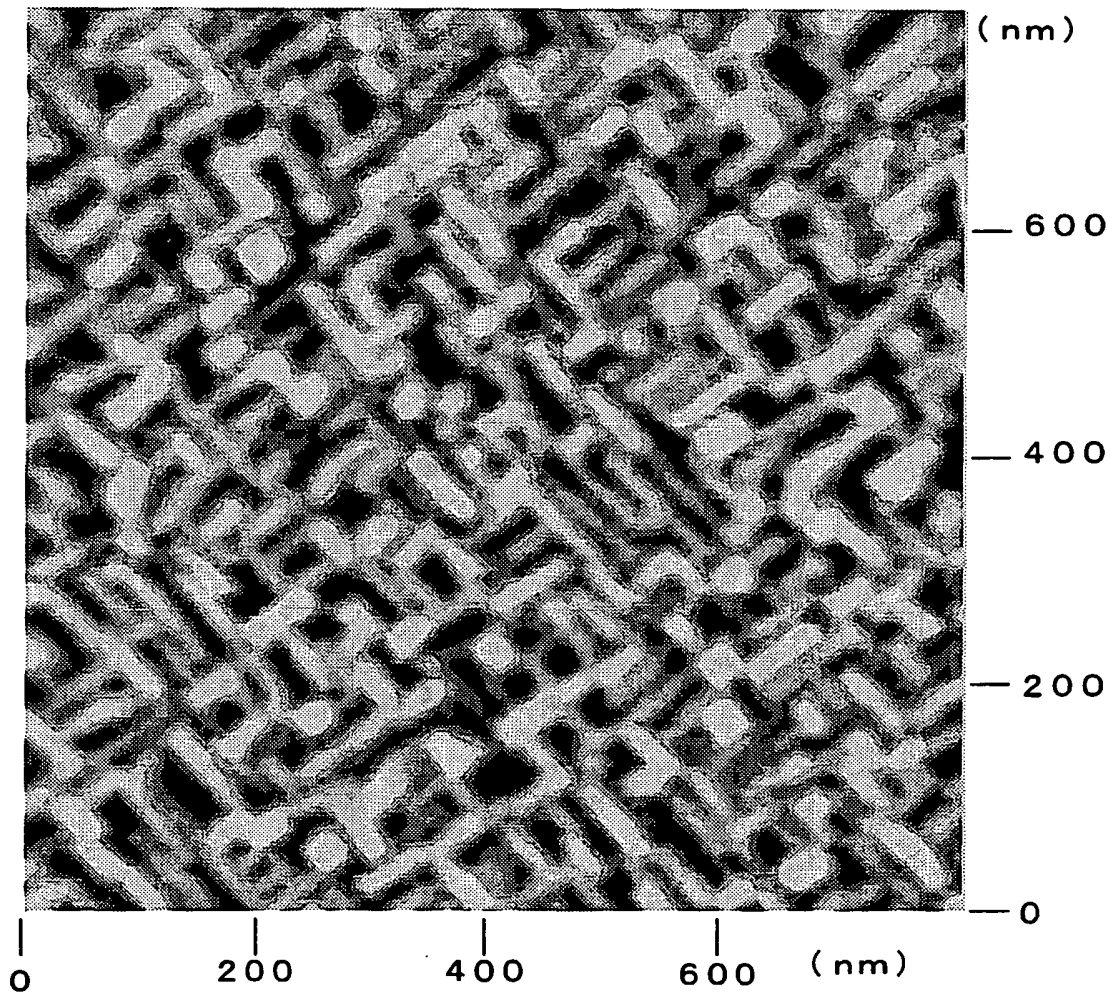
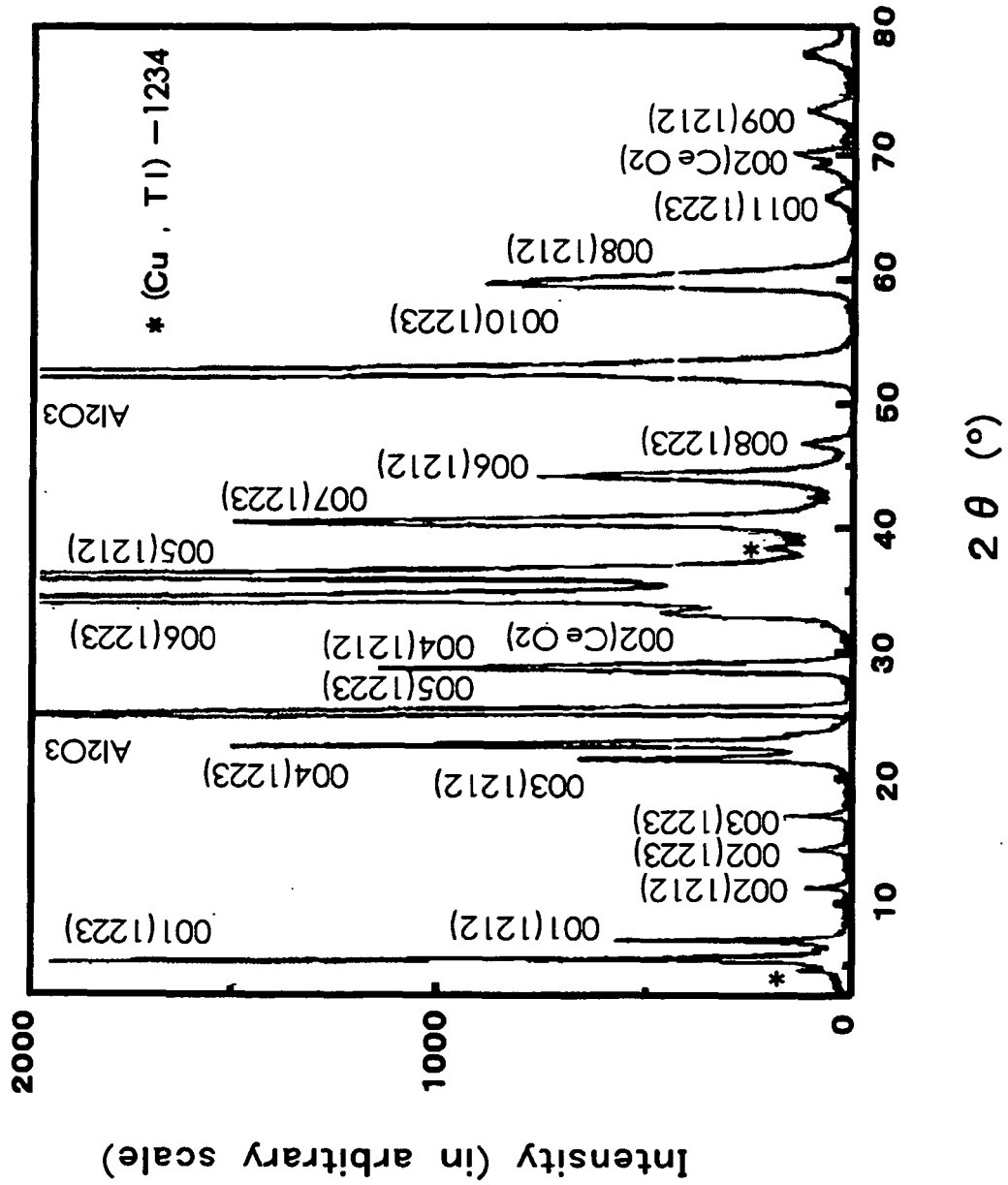


FIG. 2



F I G . 3

CuTI-1223/TISr-1212/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

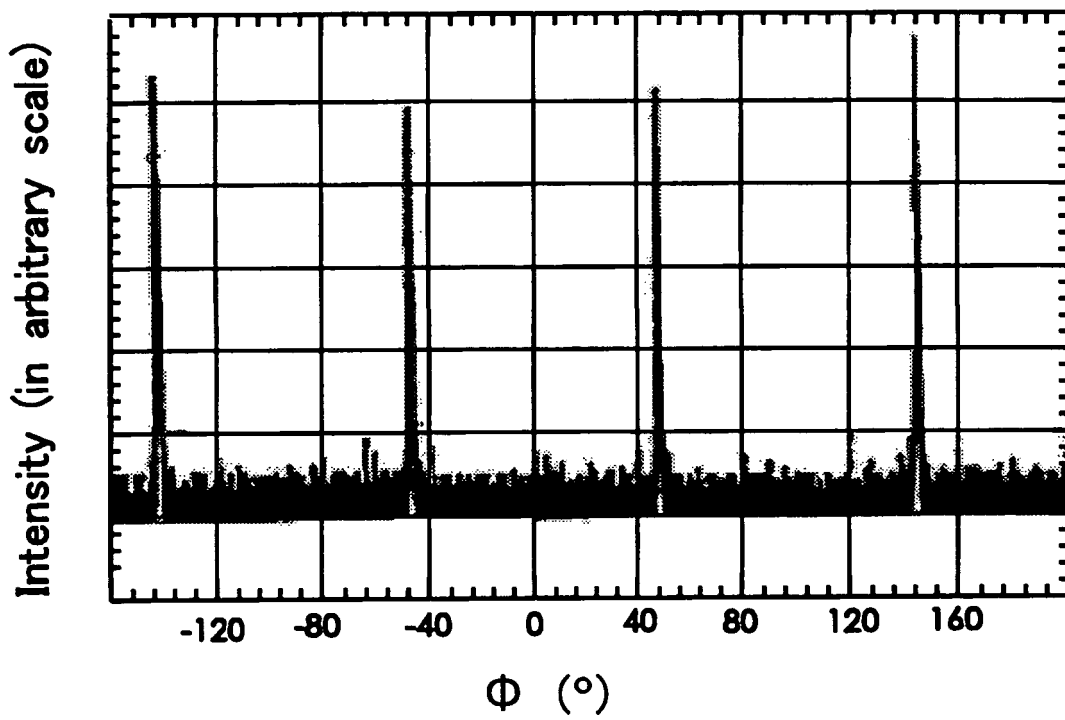
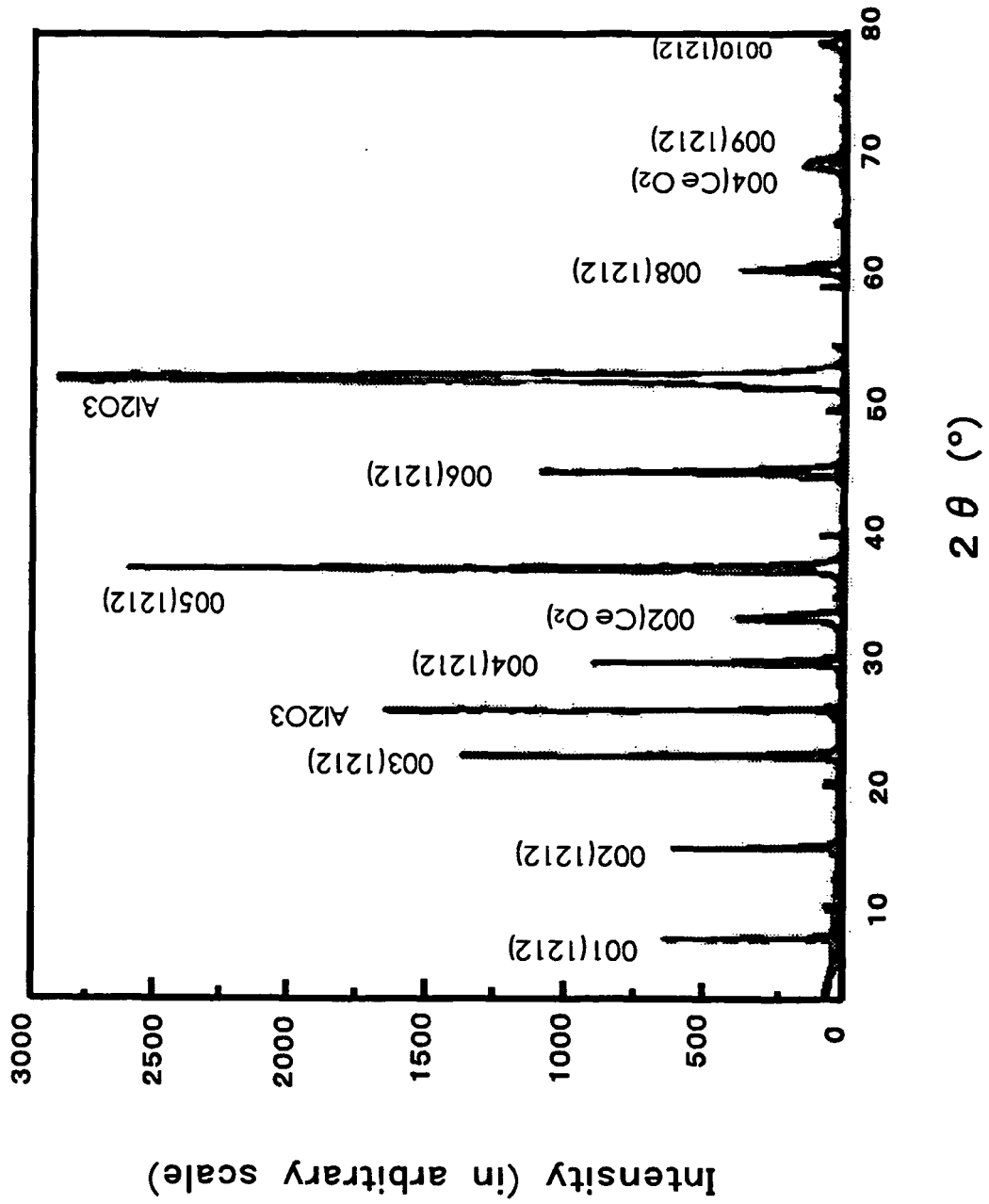


FIG. 4



**REFERENCES CITED IN THE DESCRIPTION**

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**Non-patent literature cited in the description**

- *Kotai Butsuri*, 2000, vol. 35 (5 [0002] [0020])
- **O'Connor et al.** *Appl. Phys. Lett.*, 1996, vol. 69 (1), 115-117 [0005]