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(54) Controlled thallous oxide evaporation for thallium superconductor films and reactor design

Kontrollierte Thalliumoxyd-Verdampfung für Thallium-Supraleiter-Filme und Aufbau des Reaktors

Evaporation contrôlé d'oxyde de thallium pour films de thallium supraconducteurs et projet de réacteur

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(73) Proprietor: **SUPERCONDUCTOR TECHNOLOGIES INC.**
Santa Barbara California 93111-2310 (US)

(72) Inventors:
- **Eddy, Michael Martin**
  130 Goleta California 93117 (US)
- **Olson, William Levin**
  Buellton, California 93427 (US)
- **James, Timothy Walton**
  Goleta, California 93117 (US)

(74) Representative: **Sexton, Jane Helen et al**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

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EP-A- 0 358 545

- **JAPANESE JOURNAL OF APPLIED PHYSICS LETTERS, vol. 28, no. 1, January 1989, TOKYO, JP, pp. 85-87; R.J. LIN et al.: 'Forming Superconducting Tl-Ca-Ba-Cu-O Thin Films by the Diffusion Method'**

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Description

Technical Field

5 The field of this invention is the production of thallium high temperature superconductor films.

Background

After the initial excitement of being able to produce high temperature superconductors, namely materials which are superconducting above the vaporization temperature of nitrogen, the problems of producing these materials in useful form have become only too evident. Among the cuprate compositions which are particularly interesting because of their high superconducting transition temperature are the thallium compounds. These compounds are particularly difficult to prepare because of the nature of thallium oxides. Tl_2O_3 is unstable, so that at the elevated processing temperatures normally employed, it decomposes to Tl_2O and O_2. In order to maintain the thallium present in the oxide mixture used to form the superconductor, it is necessary to control the amount of thallium in the vapor phase and in the liquid phase of the oxide composition. Among the other difficulties with processing thallium is that thallium is highly reactive, so that reactors which are employed must take into account the reaction of the structural materials with thallium. One is therefore confronted with working with a highly reactive material which can exist in both the vapor and liquid phases simultaneously at elevated temperatures, while trying to control the distribution of the thallium between the liquid and vapor phases in order to obtain the appropriate composition for a high temperature superconductor.

For many applications, one wishes to have a thin high temperature superconducting film on a substrate. Among the substrates are magnesium oxide, lanthanum aluminate and sapphire. For microwave device development, sapphire has many advantages including extremely low loss tangent at low temperature, availability in large area substrates, low cost and general acceptance as a microwave substrate. In addition, for low loss films on sapphire, several orders of magnitude improvement in the Q of a microwave device can still be achieved as high temperature super-conducting films are improved. However, formation of thallium high temperature superconducting films on sapphire are subject to reaction and formation of barium or strontium aluminate compounds as second phases.

There is substantial interest in being able to produce thallium cuprate high temperature superconducting films and a wide variety of substrates for production of microwave and millimeter wave applications. It is therefore of interest to provide processes and reactors which will allow for the controlled and reproducible production of high temperature superconducting films on substrates of interest for the production of devices.

Literature

Ginley and co-workers at Sandia National Laboratories recently reported the preparation of superconducting thin films of the 2122 thallium compound (Tl_2,Ca,Ba_2,Cu_2,O_8). Jim Kwak at the same laboratory has reported polycrystalline thallium based films on yttria stabilised zirconia. Their films were prepared on ytrria stabilized zirconia substrates by sequential e-beam evaporation of the individual metals on the substrate, followed by a post deposition reaction step in a closed platinum crucible. The films that were obtained were unoriented and exhibited a transition temperature of 97K. IBM has reported preparing oriented thin films of the 2223 and 2122 compounds by rf diode sputtering.

A large number of articles have been published concerned with the thallium compounds. Illustrative of these articles are Sheng and Hermann, Nature, (1988) 332:55-58; Sheng and Hermann, Nature, (1988) 332:138-139; Ginley et al., Physica C, (1988) 152:217-222; Superconductor Week, Vol. 2, no. 18, May 9, 1988, reported that Sandia had prepared unoriented polycrystalline Tl thin films that have reached critical current densities of 110,000 A/cm^2 at 77K with a T_c at 97K. In the presence of a high magnetic field (6 Tesla), a critical current density of 1 x 10^6 A/cm^2 at 4K was observed.

Venkatesan et al., Appl. Phys. Lett. (1988) 52:1193-1195, and Wu et al., Proceedings of SPIE Symposium on high T_c Superconductors, Newport Beach, CA March 1988, report the use of pulsed laser deposition for preparation of high T_c superconducting thin films. Venkatesan et al., and Wu et al., supra claim to have achieved YBaCuO films that are superconducting after deposition at 650°C, followed by oxygen annealing at 450°C. Witanachchi et al., (Appl. Phys. Lett., in press) report that with the addition of DC bias plasma during laser ablation of high Tc superconducting YBaCuo thin films, in situ superconducting films can be achieved at substrate temperatures as low as 400°C.

EP-A-357509 describes a two step process for forming a thallium oxide superconductor. Firstly an intermediate compound oxide containing metal elements of the superconductor except thallium is placed in a vessel and secondly, thallium or thallium oxide is reacted with the intermediate compound oxide. There is no controlled venting of the reaction chamber whilst the superconductor is being formed.

EP-A-358545 also describes a two step process comprising depositing a thin film of thallium-containing compound oxide on a substrate by physical vapor deposition method or chemical vapor deposition method and then subjecting the resulting thin film to heat treatment at between 880°C and 920°C for a predetermined time under conditions such

that the partial pressure of thallium oxide becomes higher than the saturated vapor pressure of thallium oxide at that temperature. The substrate with the film thereon and a vapour source of thallium oxide are placed in a pipe having an opening at an extreme end. The pipe is set in a sintering furnace into which oxygen is supplied so that oxygen gas can penetrate into the pipe through its open end.

SUMMARY OF THE INVENTION

Methods and reactors are provided for the production of thallium cuprate high temperature superconducting films on a wide variety of substrates, by providing for a two-step process comprising the formation of a thallium-containing precursor film followed by post-deposition thermal processing. The post-deposition thermal processing is advantageously performed in a reactor vessel sized and adapted to receive the thallium-containing precursor film disposed on the substrate, the vessel including at least one aperture to permit controlled venting of the thallium. Such use of a controlled diffusion barrier for the reactor permits control of the thallous oxide evaporation rate from the confined space above the film. In the preferred embodiment, the vessel comprises a piece having at least one vent hole, and surrounding containment, such as a side piece and an adjacent bottom piece. In yet a further aspect of this embodiment, the hole or holes may in turn be covered by a relatively large, flat piece of material having a channel, which provides for a reproducible, well defined, diffusion leak for evaporative loss of thallous oxide from the melt during thermal processing.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagrammatic elevational side view of an embodiment of the reactor and
Figure 2 is a diagrammatic elevational side view of an alternate embodiment.

DESCRIPTION OF SPECIFIC EMBODIMENTS

Methods and apparatus are provided for the reproducible production of high temperature superconducting thallium-based cuprate films on a wide variety of substrates. Generally, a two step process is used; wherein, first, an oxide matrix is formed on the substrate, and second, thermal treatment of the substrate and matrix is performed in a reactor vessel.

Coating of the substrate may be achieved in a variety of ways. One technique is to use chemical precursors, which upon pyrolysis may provide the desired oxide as a coating. Another technique is to employ a liquid comprising a sol of the metal oxides having an appropriate stoichiometry for production of the superconductor. Other techniques have been indicated, which involve vapor phase deposition. The first technique to be considered will be employing metallo-organic precursors to produce the oxides.

The composition of the coating may vary as to the thallium, usually having at least about a "stoichiometric amount" of thallium. Thallium may be provided from a source of thallium in the reactor and be absorbed by the superconductor precursor composition or the additional source of thallium may reduce evaporative loss of thallium from the coating. With excesses of thallium in the coating the excess may be removed using a thallium sink, e.g., a calcium, barium, copper oxide composition, controlled leakage, or the like. Oxygen overpressures also serve to control the thallium evaporative loss.

Once the film has been formed, a relatively strict temperature regimen will be employed for the heating of the film to provide the proper composition for the high temperature superconductor film.

Generally, controlled, uniform heating will be employed to achieve a predetermined temperature in the range of about 750 to 900°C, more usually about 800 to 875°C.

The thickness of the film will generally be in the range of about 0.5 to 5 µm, while the film area will be in the range of about 0.5 to 5 mm. The volume of the cavity above the film will generally range from about 10^4-10^8µm^3. Desirably, the cavity will be in the range of about 200 to 500 mm^3. The height of the cavity will generally be from about 10 to 100 µm, preferably 15 to 60 µm. The surface opposite the film may serve as a thallium source or sink. That is, the opposite wall from the film may be comprised of thallium oxide, so as to contribute to a thallium overpressure in the cavity or may be a combination of two or more of calcium, barium and copper oxides, so as to absorb thallium released from the superconductor precursor film.

In addition, a conduit may be provided for connecting the cavity to a source of oxygen, thallium, or other gas or for changing, usually by reducing the pressure in the cavity and evacuating the cavity of volatile components in the cavity, such as thallium oxide and oxygen.

There are a number of parameters which can be varied in relation to the thallium and oxygen present in the film and the cavity. One can provide for excess thallium in the superconducting film precursor, as a film on the wall of the cavity, or by introduction of thallium oxide from an outside source. Alternatively, one may remove thallium oxide from the cavity by providing for a chemical thallium oxide sink on the walls of the cavity or by providing for a conduit into the

cavity which allows for removal of thallium oxide from the cavity. In addition, one may vary the oxygen over pressure in the cavity, which will affect the volatility of thallium oxide in the film or source. Thus, by varying the thallium oxide in the cavity which will be directly related to the amount of thallium oxide in the precursor film, one can control the formation and composition of the high temperature superconducting film.

One may also provide for pellets comprising all or some of thallium, calcium, barium and copper oxides, which may act as sources or sinks of thallium oxide, which may be placed in a manner which allows for communication between the cavity and the pellets but preventing contact between the pellets and the superconductor film precursor. The various configurations will be discussed in relation to the various devices or apparatuses employed for the development of the high temperature superconductor films. After the appropriate superconducting composition is prepared, it may then be subjected to a thermal anneal. The parameters for the thermal anneal will be different from the preparation of the superconducting film. For the anneal, the superconducting film is rapidly heated to a temperature in the range of about 500 to 850°C, generally over a period of about 10 to 30 sec. The temperature will then be maintained, ±15% for a period of about 5 to 60 min, preferably from about 15 to 45 min in an oxygen atmosphere while in the presence or absence of a thallium source. The temperature for the source, if present, will be higher by at least about 50°C, preferably from about 100 to 150°C higher than the superconducting film. The oxygen pressure can range between about 0.133 and 666610 Pa (0.001 torr and 5000 torr). The temperature of the source will be heated analogously to the superconducting film, so that the ultimate temperature for the source is reached at or shortly after the temperature for the film is reached. The temperature for the source will be maintained substantially constant during the period of annealing and will then be allowed to cool, at about the same time and rate as the superconducting film, back to room temperature. Desirably, cooling of the source will begin shortly before the cooling of the superconducting film, usually from about 0.5 to 5 min prior.

The devices of the subject invention will have means for controlling the temperature profile of the process, so that rapid heating/cooling can be achieved with short term maintenance at the predetermined elevated temperature. In addition, means are provided for controlling the thallium oxide overpressure, which means may include controlling the oxygen overpressure, as well as providing for a source or sink of thallium oxide within the reactor cavity. In addition, the volume of the reactor cavity is controlled, so as to be only a small multiple of the volume of the superconducting film precursor and access to the cavity can be provided with means for introducing or removing the volatile components present in the cavity.

Six principal methods may be used to control the rate of thallous oxide vaporization from the deposit which occurs during thermal processing. The first involves changing the amount of empty volume present in the cavity. This can be controlled by varying the thickness of the spacer or by placing inert spacers to take up excess volume in the reactor. A second method involves increasing the process temperature to increase thallium volatilization. A third method is to change the overall oxygen partial pressure during a particular time-temperature process sequence. Since oxygen actively suppresses volatilization of thallous oxide, lowering the total system pressure is an effective mechanism for increasing thallium volatilization at any given temperature. A fourth method is to vary the spacing between the individual substrate layers that make up the walls of the reactor. The greater the spacing between the substrates, the greater thallium evaporation rate from the film. For example, if the sapphire reactor wafers are fitted tightly together, either by use of inconel clips or heavy weights placed on the lever arm, loss of thallium from the film is extremely small, even when held at 860°C in one atm of oxygen for reaction times of 8 min or more. On the other hand, if the cap is omitted from the reactor, and the film heated in an open crucible, thallium completely evaporates in a few seconds. A fifth method for controlling thallium oxide vaporization is the rate of heating. The faster the rate of heating, the more liquid thallium oxide present and the greater the amount of vaporization. The sixth method involves the hold time and the elevated temperature. The greater the hold time, the more thallium oxide is vaporized and lost.

In the preferred design, the design is created with the purpose of fabricating a controlled diffusion barrier for the reactor that can be reproducibly constructed and readily modified to control the thallous oxide evaporation rate from the confined space above the film. This is accomplished by first drilling a hole into the top wafer. The hole in turn is covered with a large flat piece of sapphire into which has been carefully milled a channel of well defined width, length and depth. The trench in the sapphire cap is placed directly over the hole in the top wafer of the reactor and the entire assemblage tightly held together. Satisfactory results have been obtained using grooves that are approximately 500 µm deep and 200 µm wide. The groove provides a reproducible well defined diffusion leak for evaporative loss of thallous oxide from the melt during thermal processing.

The device is depicted in Figs. 1 and 2. The reactor 150 has base plate 152, top plate 154, with orifice 156 in top plate 154. Spacer 158 separates base plate 152 and 154 and defines the volume of the cavity 160. Substrate 162 sits on base plate 152 and is coated with the superconductor precursor film 164. Grooved cap 166, providing a diffusion leak channel, not shown, covers orifice 156 and is held in place by weight 168, although clips may also be used. The assembly of plates 152, 154 and spacer 158 are held together by clips 170.

Finally, in accordance with a preferred embodiment of this invention, the structure of Fig. 1 is modified in that the clips 170 are placed from the base plate 152 over the top blow off valve 166. This modified arrangement provides a

more reproducible seal than other arrangements.

As shown in Fig. 2 the reaction assembly 180 is located on a quartz transport plate 182 which is disposed within a quartz tube 184. The reaction assembly 180 is then disposed within the furnace 186. The system is flushed with pure oxygen to remove contaminants, and the temperature cycle commenced. With respect to these experiments, most runs have been performed at one atmosphere of oxygen and the thallium content of the amorphous deposit, loss rate as a function of temperature, and final weight are selected to give the best morthology and T_c in the finished film. To control the weight loss, these experiments have been performed with slow heating and cooling rates. Typically, 5° per minute has been the typical heating rate.

An example of a typical procedure using the above described equipment is given below. Using a laser ablation technique the following parameters and materials were used:

Substrate Material = $LaAl0_3$	Vendor = AT&T
Beam Energy = 2.2J/cm2	Chamber Pressure = 5mtorr (0.667 Pa)
Target composition = 8223	Deposition time = 42 min.
Substrate temp. = 25C	Atmosphere = O_2
Film thickness = 1.5µm	

The thermal process per file was as follows:

Ramp 1 = 50 deg/min	to 680C	
Ramp 2 = 25 deg/min	to 720C	
Ramp 3 = 5 deg /min	to 780C	hold for 5 min.
Ramp 4 = 5 deg/min	to 860C	hold for 2 min.

Cool by switching off power to furnace.

The leak dimensions of the groove were 500 µm x 500 µm. The pressure was 1.01×10^5 Pa (760 torr).

The film made from this experiment had a T_c = 101.7K, with a transition width of 1.6K. The R_s at 77K and 10GHz was 0.2 mohms. The Q factor at 14GHz was 11,000. The use of this film as a 2.5GHz resonator in a microstrip configuration gave a Q of 9500 at relatively low power (-65dBm) and 5500 at relatively high power (-10dBm).

It is evident from the above results, that superconducting films can be obtained for use in a variety of devices, where the films have high superconducting transition temperatures, good surface resistivity properties, equal or better than copper films, in their performance. Markedly improved epitaxial quality is obtained with various substrates, such as magnesium oxide and lanthanum aluminate. The films exhibit sharp XRD rocking curves and well defined electron channeling patterns were 1 cm^2 areas. The films show superior microwave performance at high power. Tl thin film resonators fashioned from thin films into strip line and microwave configurations have significantly higher "Q's" than cryogenically cooled silver resonators at power levels as high as 20 dBm. The resonators exhibited no power dependance over power ranges between -70 and -10 dBm. The power levels at -10 dBm is characteristic of the power levels present in practical passive microwave devices, representing approximately 1 mW of power. In passive microwave devices, employing a stripline or microstrip-configuration resonator, the devices can outperform cryogenic silver by as much as 30 times at 2 GHz and 77K.

The method is simple, film growth is driven by evaporation of thallous oxide at high temperature and therefore can be done rapidly. The process coupled with the characteristically rapid diffusion kinetics of liquid phase processes, minimizes substrate/film interdiffusion reactions by limiting the process time at high temperature to below about 10 min.

A secondary thallium source is not required, minimizing toxic waste disposal requirements. Compatibility problems of processing thallous oxide in an oxygen atmosphere at high temperature, i.e., corrosion chemical reactivity, are minimized by using sapphire as the reactor. The reactor design is simple and has a very low thermal mass, lending itself to controlled, uniform heating and cooling of the sample.

The use of extremely small reactor volumes guarantees rapid equilibrium between the film and vapor, thereby minimizing lateral composition/-morphological gradients in the film. The thermal process geometry appears to be both readily scalable and compatible with current available rapid thermal annealing furnace equipment. The thallous oxide vaporization rate from the film can be controlled by varying the oxygen partial pressure, temperature and the diffusion-limited (leak rate-gapped dimensions) loss rate from the reactor.

Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the scope of the appended claims.

Claims

1. A reactor vessel (150) for thermal processing of a deposited metal oxide film (164) including thallium on a substrate (162) to be crystallized into a superconductor, comprising a vessel including a chamber (160) large enough to receive the substrate and film, characterized in that the vessel includes at least one aperture (156) to permit controlled venting of the thallium.

2. The reactor vessel of claim 1 for thermal processing of a film and substrate to be crystallized into a thallium-containing superconductor, comprising:

   a top piece (154) with at least one vent hole for venting thallium during the thermal processing,
   a bottom piece (152), and
   a spacer (158) for defining a chamber with the top piece and bottom piece, the chamber being large enough to accommodate the film and substrate.

3. The reactor vessel of claim 2 wherein the top piece, bottom piece and spacer are formed of sapphire.

4. The reactor vessel of claim 2 or 3 further including reactor clips (170) to hold the top piece, bottom piece and spacer together.

5. The reactor vessel of claim 2 further including a cover (166) capable of covering over at least one vent hole.

6. The reactor vessel of claim 5 wherein the cover includes a channel.

7. The method of forming a thallium-containing oxide high temperature superconductor, comprising the steps of:

   forming a thallium-containing precursor film on a substrate,
   volatilizing thallium from the precursor film in a vessel having a vent for thallium, and
   controlling the rate of leakage from the vessel during volatilization.

8. The method of claim 7 wherein the precursor is thallium rich.

9. The method of claim 7 wherein the precursor comprises thallium, calcium, barium and copper in which the molar ratio of Tl:Ca:Ba:Cu is in the range of 0.5:2:2:3 to 8:2:2:3.

10. The method of any one of claims 7 to 9 wherein the thallium is volatilized from the precursor film in part by heating of the precursor film.

11. The method of any one of claims 7 to 10 wherein the thallium is volatilized from the precursor film in part by heating of the precursor film and controlling the oxygen pressure.

12. A method according to any one of claims 7 to 11 further including after the volatilization, cooling the resultant film.

13. A thallium based superconductor thin film resonator obtainable by a method according to any one of claims 7 to 12 exhibiting substantially no power dependence over power ranges between -70 and -10dBm.

Patentansprüche

1. Reaktionsgefäß (150) zur Wärmebehandlung eines abgelagerten Metalloxidfilms (164), umfassend Thallium, auf einem Substrat (162), die zu einem Supraleiter zu kristallisieren sind, umfassend ein Gefäß mit einer Kammer (160), die groß genug ist, um Substrat und Film aufzunehmen, dadurch gekennzeichnet, daß das Gefäß mindestens eine Öffnung (156) zur Ermöglichung einer kontrollierten Entlüftung des Thallium enthält.

2. Reaktionsgefäß nach Anspruch 1 zur Wärmebehandlung eines Films und Substrats, die zu einem Thallium-haltigen Supraleiter zu kristallisieren sind, umfassend:

   ein Kopfstück (154) mit mindestens einem Entlüftungsloch zur Entlüftung des Thalliums während der Wärme-

behandlung,

ein Bodenstück (152), und

5 ein Zwischenstück (158) zur Umgrenzung einer Kammer mit dem Kopfstück und dem Bodenstück, wobei die Kammer groß genug ist, um Film und Substrat aufzunehmen.

3. Reaktionsgefäß nach Anspruch 2, worin das Kopfstück, das Bodenstück und das Zwischenstück aus Saphir bestehen.

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4. Reaktionsgefäß nach Anspruch 2 oder 3, welches ferner Reaktorklemmen (170) zum Zusammenhalten des Kopfstücks, des Bodenstücks und des Zwischenstücks enthält.

5. Reaktionsgefäß nach Anspruch 2, welches ferner eine Abdeckung (166) enthält, die zur Abdeckung mindestens
15 eines Entlüftungslochs in der Lage ist.

6. Reaktionsgefäß nach Anspruch 5, worin die Abdeckung einen Kanal umfaßt.

7. Verfahren zur Herstellung eines Thallium-haltigen Oxid-Hochtemperatur-Supraleiters, umfassend die folgenden
20 Schritte:

Bilden eines Thallium-haltigen Vorläuferfilms auf einem Substrat,

Verdampfen des Thalliums aus dem Vorläuferfilm in einem Gefäß mit einer Entlüftung für Thallium, und

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Kontrollieren der Ausströmrate aus dem Gefäß während der Verdampfung.

8. Verfahren nach Anspruch 7, worin der Vorläufer Thalliumreich ist.

30 **9.** Verfahren nach Anspruch 7, worin der Vorläufer Thallium, Calcium, Barium und Kupfer umfaßt, wobei das Molverhältnis von Tl:Ca:Ba:Cu im Bereich von 0,5:2:2:3 bis 8:2:2:3 liegt.

10. Verfahren nach einem der Ansprüche 7 bis 9, worin das Thallium aus dem Vorläuferfilm teilweise durch Erhitzen des Vorläuferfilms verdampft wird.

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11. Verfahren nach einem der Ansprüche 7 bis 10, worin das Thallium aus dem Vorläuferfilm teilweise durch Erhitzen des Vorläuferfilms und Kontrollieren des Sauerstoffdrucks verdampft wird.

12. Verfahren nach einem der Ansprüche 7 bis 11, welches ferner nach der Verdampfung die Abkühlung des resultie-
40 renden Films umfaßt.

13. Auf Thallium basierender Supraleiter-Dünnfilm-Resonator, zu erhalten mittels eines Verfahrens nach einem der Ansprüche 7 bis 12, der im wesentlichen keine Energieabhängigkeit im Leistungsbereich von zwischen -70 und -10 dBm zeigt.

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Revendications

1. Récipient de réacteur (150) pour le traitement thermique d'un film d'oxyde métallique (164) incluant du thallium
50 déposé sur un substrat (162) à cristalliser en un supraconducteur, comprenant un récipient incluant une chambre (160) suffisamment grande pour recevoir le substrat et le film, caractérisé en ce que le récipient inclut au moins une ouverture (156) pour permettre un échappement contrôlé du thallium.

2. Récipient de réacteur selon la revendication 1 pour le traitement thermique d'un film et d'un substrat à cristalliser
55 en un supraconducteur contenant du thallium, comprenant :

une partie du dessus (154) avec au moins un trou d'évent pour l'échappement de thallium pendant le traitement thermique,

une partie du bas (152), et
un espaceur (158) pour définir une chambre avec la partie du dessus et la partie du bas, la chambre étant suffisamment grande pour loger le film et le substrat.

3. Récipient de réacteur selon la revendication 2, dans lequel la partie du dessus, la partie du bas et l'espaceur sont formés de saphir.

4. Récipient de réacteur selon la revendication 2 ou 3, incluant en outre des pinces de réacteur (170) pour maintenir la partie du dessus, la partie du bas et l'espaceur ensemble.

5. Récipient de réacteur selon la revendication 2, incluant en outre un couvercle (166) pouvant recouvrir au moins un trou d'évent.

6. Récipient de réacteur selon la revendication 5, dans lequel le couvercle inclut un canal.

7. Procédé de formation d'un supraconducteur haute température à base d'oxyde contenant du thallium, comprenant les étapes consistant à :

   former un film de précurseur contenant du thallium sur un substrat,
   volatiliser du thallium à partir du film de précurseur dans un récipient ayant un évent pour le thallium, et
   à contrôler le taux de fuite à partir du récipient pendant la volatilisation.

8. Procédé selon la revendication 7, dans lequel le précurseur est riche en thallium.

9. Procédé selon la revendication 7, dans lequel le précurseur comprend du thallium, du calcium, du baryum et du cuivre, le rapport molaire de Tl:Ca:Ba:Cu étant dans la gamme de 0,5:2:2:3 à 8:2:2:3.

10. Procédé selon l'une quelconque des revendications 7 à 9, dans lequel le thallium est volatilisé à partir du film de précurseur en partie par chauffage du film de précurseur.

11. Procédé selon l'une quelconque des revendications 7 à 10, dans lequel le thallium est volatilisé à partir du film de précurseur en partie par chauffage du film de précurseur et contrôle de la pression d'oxygène.

12. Procédé selon l'une quelconque des revendications 7 à 11, incluant en outre, après la volatilisation, le refroidissement du film résultant.

13. Résonateur à film mince supraconducteur à base de thallium pouvant être obtenu par un procédé selon l'une quelconque des revendications 7 à 12, ne présentant pratiquement pas de dépendance vis-à-vis de la puissance dans des gammes de puissance entre -70 et -10 dBm.

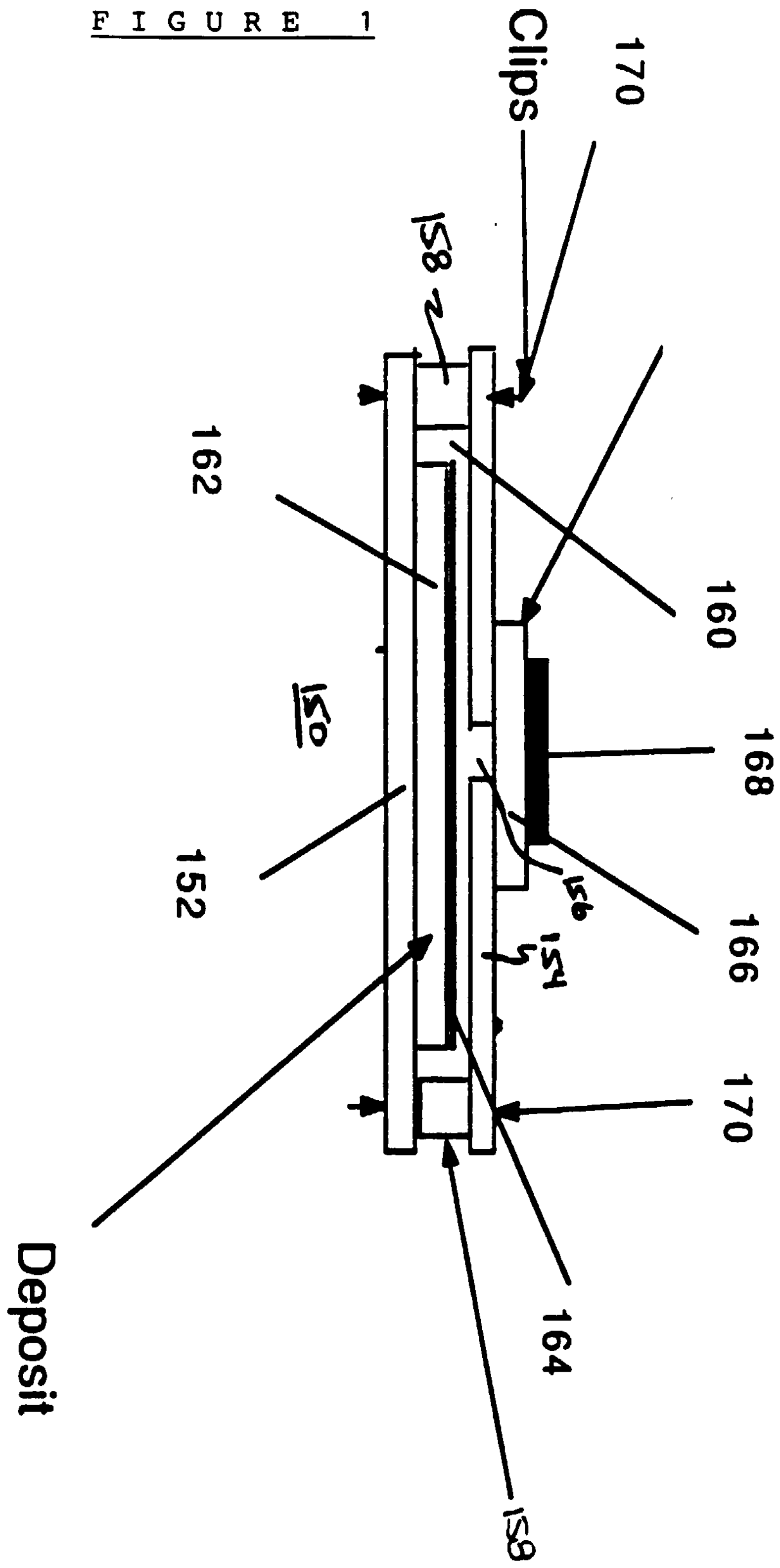
FIGURE 1
Clips
170
158
162
160
150
168
152
166
156
154
170
164
Deposit
159

FIGURE 2