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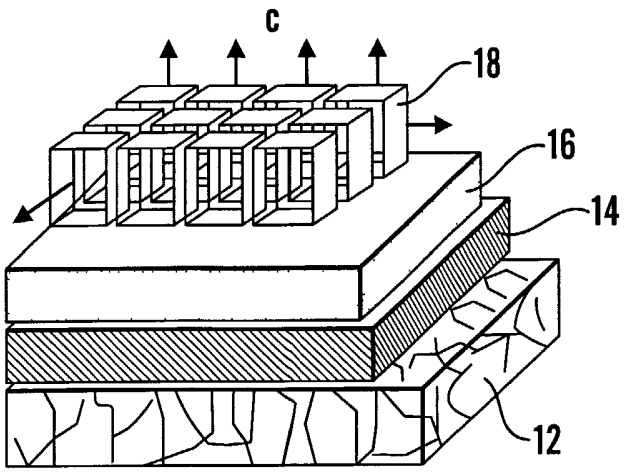
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(54) Title: LONG SUPERCONDUCTOR FABRICATION



(57) Abstract: A long length superconductor comprising a metallic substrate (12) such as nickel/nickel alloy, a metal oxide layer (14) forming the basis of a buffer layer, and a further layer of metal oxide (16) grown on the surface of the seed layer which may be a rare earth transition metal oxide. The further layer may be grown by liquid phase epitaxy, in a continuous process in which molten material is fed onto a horizontally moving substrate under temperature controlled conditions. A rare earth barium cuprate superconductor layer (18) is formed on top. Alternatively a superconductor layer may be grown directly on a suitable substrate, by applying it as a printed layer in an organic binder, then heating it to reach a single liquid state and cooling at controlled rate so as to promote nucleation.

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"Long Superconductor Fabrication"

This invention relates to the fabrication of long superconductors, particularly on metallic tape substrates such as nickel, including methods of growing suitable buffer layers.

Long length superconducting cables have many potential industrial applications, notably power cables and magnet windings for magnetic resonance imaging, high field research magnets, motors and transformers. Bi-based superconducting materials are beginning to be commercialised through demonstrator applications in the transmission industry. However, owing to their poor current carrying performance in the presence of magnetic fields, it is unlikely that the Bi-based superconductors will achieve the property requirements for magnetic winding applications.

Rare earth barium cuprate superconductors of the formula: $REBa_2Cu_3O_{7-x}$ (or REBCO), on the other hand, do have adequate intrinsic properties for such applications. What is currently limiting the performance of these materials is the difficulty in the processing of them because it is necessary to achieve very highly aligned crystallites to allow the superconducting current to be transferred across the crystallites. Another issue is achieving highly aligned metallic substrates and highly aligned buffer layers onto which the superconductor can be grown. There are currently two main methods to achieve the required texture. The first is a method called IBAD (ion beam assisted deposition) which gives a highly textured buffer layer on a polycrystalline, randomly oriented Ni-based substrate, and the second is called RABITs (rolling assisted biaxial texturing of substrates) which produces a highly textured Ni-based substrate by mechanical working.

Typically, the requirements for balancing various different properties of the materials used in the fabrication of such super conductors lead to a multilayer structure, of the kind illustrated in Figure 1. This comprises a metallic/ceramic substrate tape 2, having a protective layer 4 on its reverse surface, whilst the front surface carries a buffer

layer 6 formed by one of the above methods, having a "ReBCO" layer 8 formed on the buffer layer 6. On top of this are a further "shunt" layer 10, and one or more further insulator and stress relief layers 12.

For the IBAD route, the superconducting layer needs to be deposited on the IBAD buffer. For the RABiTs route, the buffer layer and superconducting layer need to be deposited on the RABiTs substrate. There are a variety of ceramic processing techniques available to deposit these layers. There are advantages and disadvantages to each. The present invention provides improved processing routes and new buffer layer compositions for RaBiTs substrates, including processing methods and compositions having advantages over existing methods for fabrication of both the buffer layer and superconducting layer on a RABiTs substrate.

Accordingly, a first aspect of the present invention provides a method of forming a buffer layer in an elongate superconductor, comprising first forming a nickel oxide seed layer, on a nickel substrate, by surface oxidation epitaxy (SOE), and then growing a further layer of nickel oxide, on the surface of the SOE seed layer, by liquid phase epitaxy.

The use of liquid phase epitaxy to grow the NiO on the surface of the SOE seed layer leads to a much improved NiO buffer layer, which is smoother, more highly textured and has improved grain connectivity.

A further aspect of the invention provides a method of fabricating a superconducting layer or a buffer layer in an elongate superconductor structure comprising (a) feeding a rod of superconductor or buffer layer material plus flux into the focus of a heat source to produce a molten zone at a predetermined higher temperature; and (b) moving an elongate textured substrate in a horizontal plane beneath the molten zone at a suitable rate, the substrate being maintained at a suitable lower temperature to promote epitaxial growth; whereby the liquid from the molten zone falls onto the moving substrate and epitaxial growth is thereby promoted on the substrate.

Preferably, the substrate is a RABiTs Ni-based substrate. The NiO layer has around a 9% lattice mismatch with REBCO and so it is just about possible to grow an epitaxial REBCO film on the surface of the NiO. However, NiO alone is not an ideal buffer layer since there is still some poisoning of the REBCO by Ni in the NiO. On the other hand, NiO so readily forms on the surface of the Ni substrate that it is preferable to fabricate a high quality NiO layer first, and then develop subsequent buffers, rather than trying to develop other buffers on the Ni and then find that a poor quality NiO layer forms during the fabrication of these oxides: the poor quality oxide may lead to spalling or increased surface roughness in those other buffers. The drawback of the SOE approach on its own is that the NiO layer surface roughness is quite high and the grain connectivity is not ideal.

In practice, at least one further oxide buffer layer is required on the surface of the NiO to allow the growth of Ni free REBCO, and according to a further feature of the invention, a rare earth transition metal oxide buffer layer such as Nd_2CuO_4 may be grown by liquid phase epitaxy on the surface of NiO.

Another aspect of the invention therefore provides a superconductor structure comprising a metallic substrate, a buffer layer structure including (a) a metal oxide seed layer formed on the substrate by surface oxidation epitaxy (SOE) and (b) a further layer of metal oxide such as a rare earth transition metal oxide grown on the surface of the seed layer; and a superconducting layer formed on the buffer layer or layers. Preferably the further layer of metal oxide is grown by liquid phase epitaxy (LPE).

A further aspect of the invention provides a superconductor structure comprising a metallic substrate of a first metal, and also including a thin metallic buffer layer of a second metal formed by physical vapour deposition (PVD) and a superconducting layer formed on the metallic buffer layer by liquid phase epitaxy (LPE).

The present invention also provides methods which enable $Nd_{2-x}Ce_xCuO_4$ (x=0-0.15) thick films to be grown directly on $LaAlO_3$ substrates and surface oxidised Ni tapes by fast liquid-phase processing methods.

It provides films with a smooth surface and a very good biaxial texture, typically with FWHM=0.8° and 5° on $LaAlO_3$ substrates and surface oxidised Ni tapes, respectively. Films of thickness of 5-15 μm have been grown at rates in excess of 2 μm/min. $Nd_{2-x}Ce_xCuO_4$ has a good lattice and thermal-expansion match to REBCO, minimum reaction with the high-temperature CuO:BaO solutions, and is non-poisoning to superconductivity. It is an ideal buffer for liquid phase expitaxy (LPE) processing of $REBa_2Cu_3O_{7-\delta}$ (RE=rare earth, REBCO) thick films.

Since the discovery of high T_c superconductors in 1986, there has been an enormous effort worldwide to establish a scaleable method for the fabrication of coated conductors on metallic tapes. Although short length samples with J_c over 1 MA/cm^3 have been prepared by a number of vapour deposition methods, e.g. pulsed laser deposition (PLD),[1] they have so far failed to produce long-length conductors at reasonable economic cost. An alternative route to vapour deposition methods is LPE, which has been widely used for the growth of semiconductor and garnet thin films during the 1970s and 1980s.[2] LPE does not require a high vacuum system, so the system is much cheaper to build. The advantages of LPE compared to vapour methods are the very fast growth rate, typically 1-10 μm/min, and the capability of growing thick films without degrading the structural perfection. LPE growth of REBCO thick films on single crystal substrates has so far produced very encouraging results. In-plane texture of the films is generally excellent, with a FWHM less than 3° from XRD pole figures.[3] Typical growth rates of 1 μm/min are achievable and films of thickness up to 10 μm with 100% density can be obtained in minutes. T_c's achieved are above 90 K. In a self-field at 77 K, transport J_c's over 1 MA/cm^2 have been achieved and this value does not degrade severely with increasing film thickness up to ~10 μm.[4]

However, LPE growth of REBCO thick films on metallic substrates is much more difficult. There are special problems associated with LPE. The high growth temperature largely increases the risk of reaction between the substrate and the film. The solubility of RE's in the BaO:CuO solution is very low, therefore nucleation and growth is more difficult than the traditional LPE of semiconductors and garnets. Compared to PLD and other vapor deposition methods, LPE has a much lower available supersaturation and hence a much smaller driving force for growth. As a consequence, a close lattice matched substrate is required. At present, most of the buffer layers have been developed for the use in vapor deposition methods and are therefore not suitable for LPE growth. There is an urgent need to find a suitable metallic substrate and its buffer layers, which can meet the special conditions of LPE. Nd_2CuO_4, a tetragonal crystal with $a=b\approx0.394$ nm, is a good potential buffer for LPE. Since its composition falls under the RE-Ba-Cu-O system, Nd_2CuO_4 neither poisons superconductivity nor reacts strongly with the barium cuprate solution at high temperature. It has a fairly close lattice match and thermal expansion match to REBCO. In this letter, we show that it is possible to grow Nd_2CuO_4 thick films on metallic substrates by a scaleable method.

Accordingly a further aspect of the present invention provides a method of growing layers of Nd_2CuO_4 or Nd_2CuO_4 doped with Ce, directly on an $LaAlO_3$ substrate or a Ni or Ni alloy substrate, comprising applying a precursor composition of approximately 25% Nd_2O_3 : 75% CuO in an organic binder onto the substrate by screen printing, heating to a suitable temperature to reach a single liquid state and then cooling at a controlled rate so as to promote the nucleation and growth of Nd_2CuO_4.

In a preferred method according to this latter aspect of the invention, the composition is heated to 1150°C and held at that temperature for about 15 minutes before cooling to room temperature at 300°C/hr.

According to another aspect of the present invention, a hydraulically pressed and sintered source rod composed of approximately 40% Nd_2O_3 : 60% CuO is heated to

produce a molten zone at one end so that the liquid material drops onto a $LaAlO_3$ substrate or a textured Ni or NiO substrate located beneath it whilst the substrate is maintained at a suitable temperature to induce epitaxial growth.

This latter method in particular allows the formation of a highly in-plane aligned NiO layer on textured Ni or Ni alloy tapes, so that the Nd_2CuO_4/NiO/Ni architecture can be fabricated using a one-step process, without separate pre-oxidation step. In addition, when doped with Ce^{4+}, $Nd_{2-x}Ce_x$ CuO4/NiO/Ni is itself a superconductor at about 25°K, and consequently provides a coated conductor with potential magnetic applications.

The substrates used in the experiments were (001) $LaAlO_3$ single crystals (Epi-polish, size:10×5×0.5 mm^3) and (002)-textured Ni foils (FWHM=8-10°, size:10×5×0.1 mm^3). Before being used in the film growth, the (002) textured Ni foils were oxidised in flowing oxygen at 1240-1250 °C for two hours. The NiO layers were formed pseudomorphically on the (002) Ni foils with a biaxial texture around 10° and a thickness of 20 μm.[5-7]

Some embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings in which:

Figure 1 is a cross-section through a known type of elongate superconductor;

Figure 2 is a diagrammatic perspective view of the structure of a first type of superconductor in accordance with the present invention;

Figure 3 is a diagrammatic perspective view of the construction of a second type of superconductor;

Figure 4 is a schematic view of a horizontal LPE process in operation;

Figure 5 is a typical XRD Θ-2Θ scan of Nd_2Cu0_4 thick films grown from liquid phase;

Figure 6 is a XRD pole Figure measurement of an Nd_2Cu_4 film grown on an (001) $LaAl0_3$;

Figure 7a is a photomicrograph of a pure Nd_2CuO_4 film grown on $LaAlO_3$;

Figure 7b is a photomicrograph of a pure $Nd_{1.85}Cl_{0.15}CuO_4$ film grown on $LaAlO_3$;

Figure 8a is an XRD pole Figure of an Nd_2CuO_4 grown on an NiO/Ni substrate;

Figure 8b is a photomicrograph of a Nd_2CuO_4 film grown on surface oxidised Ni; and

Figure 8c is an SEM image of a growth island boundary in the film of Figure 8b.

Referring to Figure 2 of the drawings, the process begins with a substrate 12 of Ni alloy, corresponding to the layer 2 in Figure 1, which is formed by RABiTS. This has a lattice constant of 3.52 to 3.6 Å, and a NiO seed layer 14 is then formed on the surface by surface oxidation epitaxy. This layer has a lattice constant of 4.172 Å.

In order to improve the quality of the NiO layer, liquid phase epitaxy may be utilised and leads to a much improved NiO buffer. It is smoother, more highly textured and has improved grain connectivity. The LPE NiO is grown on a textured piece of Ni foil which has had a short surface oxidation treatment to give a thin SOE NiO layer which is textured but whose surface is not evenly covered and is rough. The growth of the LPE NiO layer occurs by dipping and spinning the foil in a crucible of a LiBO2-NiO flux at around 900-1000°C (the composition of the flux is in the primary crystallisation phase field of NiO- for example, a composition 85% {Li2O-B2O3}+15% NiO).

A further buffer layer 16 comprising a transition metal oxide such as Nd_2CuO_4 is then formed on top of the nickel oxide layer, by liquid phase epitaxy. This layer has a lattice constant of 3.92Å, as against 3.86Å for REBCO, and is consequently a good lattice match. It also has the advantage that it contains only the significant elements present in REBCO, namely RE and CU.

This is important for the LPE process since elements different to those in the flux used to grow the REBCO layer 18 will dissolve rapidly in that flux during growth of the REBCO layer. It is also a potential buffer layer for deposition using other routes. It

should be noted that other RE elements could be substituted for Nd in Nd_2CuO_4 to be compatible with the RE in REBCO.

Nd_2CuO_4 melts incongruently but has a high Nd solubility in the self flux of CuO and so is easily grown by LPE. For example it can be grown on $LaAlO_3$ substrate at 1100°C. The approximate growth rate obtained is 5μm/mm, providing films which are highly textured.

An alternative construction is illustrated in Figure 3, in which a thin metallic buffer layer 20 is provided instead of an oxide layer. Once again, the process starts with a RABiTs Ni alloy substrate 12, whose lattice constant is in the range 3.5 to 3.6Å.

Ideally, it would be preferable to grow REBCO straight onto Ni without buffer layers. In general this cannot be done due to poisoning effects, so that a buffer layer is required. Oxide buffers are generally used since they are well lattice matched to the REBCO layer and they are generally inert. However, it is beneficial to use a thin metallic buffer layer instead of oxide layer since it is quicker and easier to grow. Pd buffer layers have been tried for growth on RABiTS substrates using physical vapour deposition (PVD) but Pd alone is not, in practice suitable for PVD.

In Figure 3 the buffer layer is Pt or a Pt alloy grown by a PVD technique. Pt is quite closely lattice matched to REBCO and with a small Cu or Ni concentration, is even better lattice matched. It can be grown cold by sputtering in a cube orientation and need only be very thin. Also, the surface roughness is not critical for subsequent growth of a high quality REBCO layer (22) by LPE. As shown in the Figure, the Pt alloy buffer layer 20 has a lattice constant approaching 3.92Å which, again, is well matched to the REBCO (22) lattice constant of 3.855Å.

It will of course be appreciated that the buffer layer of Figure 3. i.e. Pt grown by a PVD technique could be used in addition to the buffer layer of Figure 2 in certain circumstances.

Conventional methods of liquid phase epitaxy suffer from the drawback that they are difficult to implement on a continuous basis, and Figure 4 illustrates a novel horizontal LPE process which provides fast growth of a REBCO buffer layer. This employs a traditional zone refining furnace with an infra red heating source, as illustrated in the Figure.

A hydraulically pressed and sintered source rod (24) of RE_2CuO_4 + flux (CuO) is fed into the focus of an IR/laser beam (26) to produce a molten zone at $\simeq$1200°C.

When the increasing size of the molten zone (28) exceeds the limit of the surface tension, the liquid (30) falls down onto the moving substrate (32) below, which is maintained at a suitable temperature (~900C) for the epitaxial growth induced from the highly textured substrate. (Nio/Ni etc).

Advantage of this novel LPE process are that it provides a faster growth rate, and allows lower growth temperature at the substrate, which greatly reduces the risk of reaction between the substrate and the growing film. It is also practical for long lengths.

Nd_2CuO_4 thick films can also be grown from the liquid phase using a number of other techniques. One method that has been used is top dipping LPE growth. For example a high temperature solution of 25%Nd_2O_3:75%CuO is prepared at 1180 °C and then quickly cooled to about 1100 °C, at which temperature the substrates are dipped into the liquid and rotated at 60 rpm. After growing in liquid for 2 to10 minutes, the substrates are pulled clear and brought to room temperature in about 30 minutes. In this way it is possible to grow films between 5 and 15 μm thick, corresponding to an averaged growth rate of 2 μm/min.

In another method according to the present invention, a precursor with composition around 25%Nd_2O_3:75%CuO was screen-printed on the substrates using an organic binder (Johnson Matthey 63/2 binder) and then heated up to 1150 °C to reach a single liquid state. This temperature was kept for about 15 minutes and then cooled

down to room temperature at 300 °C/hr. Because of the large surface area to volume ratio and the faster evaporation of CuO than Nd_2O_3, the liquid became supersaturated rapidly, leading to the nucleation and growth of Nd_2CuO_4 on the substrates. In order to obtain a smooth surface, it was essential to make sure that the film growth had finished and the extra CuO liquid had been evaporated completely before the fast cooling to room temperature started. This was done by proper control of the precursor composition and the dwell temperature and time. There was a large difference in the evaporation rates between the CuO and Nd_2O_3 (or CeO_2) in air or low pO_2. This was often reported as a problem in the bulk single crystal growth of $Nd_{2-x}Ce_xCuO_4$ and higher oxygen pressure (pO_2=1-2 atm) was used in order to prevent the evaporation of CuO from the liquid.[8,9] Therefore, there was a fairly large temperature and composition window for processing by evaporation.

In a further method according to the invention, a growth system similar to the traditional zone-refining furnace was used. A hydraulically pressed and sintered source rod of 40%Nd_2O_3:60%CuO was fed into the focus of an infrared beam to produce a molten zone at one end. When the increasing size of the molten zone exceeded the limit of the surface tension, the liquid dropped down onto the substrate below, which was maintained at a suitable temperature (~900 °C) for the epitaxial growth induced from the highly textured substrate. Because of the extremely good wetting property of the high-temperature cuprate solution, the liquid drops quickly spread out on the substrates.

The top-dipping method LPE has the advantage of simplicity and easy control. The main problem for this method is the low available supersaturation and hence low driving force for dense nucleation in large lattice mismatch substrates such as NiO/Ni. Therefore, it was hard to achieve 100% coverage. The problem may actually limit its actual application as a scaleable process. This led to the development of the methods of the present invention. Films grown by the screen-printing method generally have a better coverage as well as an excellent texture, although it requires a precise control and a

relatively high growth temperature. The "molten rod" method has the important combined benefit of high supersaturation and largely reduced growth temperature at substrates, although a more sophisticated growth system was used. Both of these methods are actually suitable as a scaleable process for rapid growth of $Nd_{2-x}Ce_xCuO_4$ buffers.

Among these latter three methods, the screen-printing method has so far been studied in most detail and the results presented below (Figs. 5-8) were measured from the samples made by this method. A typical XRD θ-2θ scan of Nd_2CuO_4 thick films grown from liquid phase is shown in Fig.5, where the main recorded reflections were (00*l*) (*l*=2, 4, 6, ..., 12), indicating the film was dominantly *c*-oriented. The XRD pole figure measurement revealed that the Nd_2CuO_4 films grown on (001) $LaAlO_3$ substrates had a nearly single crystal quality with the FWHM=0.8°, as shown in Fig.6. There was a 18° rotation of the film orientation from the *a*-axis of substrates, indicating the epitaxial relation was Nd_2CuO_4{001}<100> // $LaAlO_3${001}<130>. The <100>//<100> epitaxy did not occurred because the <130> directions of $LaAlO_3$ (*a*=0.378nm) had a better lattice match. Three unit cells of Nd_2CuO_4 (*a*=0.394nm) could grow along the <130> axis of $LaAlO_3$ with a relative lattice mismatch of about 1%, i.e. $\frac{1}{3}|<130>|_{LAO} = \frac{1}{3}\sqrt{(3a_{LAO})^2 + a_{LAO}^2} = 0.398nm$.

By doping 15% smaller ion of Ce^{4+} into Nd_2CuO_4, the epitaxial relation was switched to <100>//<100>, as shown in Fig.7. In the pure Nd_2CuO_4 film in Fig.7(a), the boundaries of squared growth islands were found tilted an angle of about 18° to the substrate edge (*a*-axis), while in the $Nd_{1.85}Ce_{0.15}CuO_4$ films in Fig.7(b), the growth boundaries were parallel to the substrate edges. Thus the Ce doping gives a better oriented Nd_2CuO_4 as well as having its own superconducting characteristics.

Although the texture of surface oxidised Ni foils was only about 10°, the Nd_2CuO_4 films grown on such NiO/Ni substrates showed an improved biaxial texture over substrates, as shown in the XRD pole figure in Fig.8(a). The typical FWHM of Nd_2CuO_4

was about 5°. Such an improvement in film texture has often been observed in the films grown by LPE,[10] which is another advantage of liquid assisted growth. Under the right growth conditions, very smooth surfaces of Nd_2CuO_4 films were achieved despite the rough surface of NiO/Ni substrates. The surface roughness of Nd_2CuO_4 films was measured to be 5-10nm by an optical interferometer, compared to 200nm for the NiO/Ni substrates. Such a surface is of high quality for subsequent REBCO growth. Shown in Fig.8(b) is a typical optical micrograph of the surface of Nd_2CuO_4 films grown on surface oxidised Ni. A couple of lines on the surface in Fig.8(b) are not macroscopic cracks, instead they are faceted boundaries of growth islands, as revealed in the SEM image in Fig.8(c), which shows the contrast due to the different heights of the edges of the boundaries.

Similar results were obtained for the Ce^{4+} doped films on the surface oxidised Ni. We note that $Nd_{2-x}Ce_xCuO_4$ is an electron-doped superconductor with a T_c of above 24 K.[11] Hence, the single layer of $Nd_{2-x}Ce_xCuO_4$ itself may have potential low temperature magnetic applications without any additional REBCO layer.

In conclusion, $Nd_{2-x}Ce_xCuO_4$ thick films have been grown on $LaAlO_3$ substrates and surface oxidised, textured Ni tapes using scaleable, liquid phase processing methods. The films had excellent biaxial texture and a good surface smoothness suitable for subsequent REBCO growth by LPE and other processing routes.

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CLAIMS

1. A superconductor structure comprising a metallic substrate, a buffer layer structure including (a) a metal oxide seed layer formed on the substrate by surface oxidation epitaxy (SOE) and (b) a further layer of metal oxide grown on the surface of the seed layer;

and a superconducting layer formed on the buffer layer or layers.

2. A superconductor structure according to claim 1 in which the further layer of metal oxide is grown by liquid phase epitaxy (LPE).

3. A superconductor structure according to claim 1 or claim 2 in which the metal is nickel and the metal oxide seed layer is nickel oxide.

4. A superconductor structure according to any preceding claim in which the further layer of metal oxide is nickel oxide grown by LPE using a composition in the primary crystallisation phase field of NiO.

5. A superconductor structure according to any preceding claim in which the further layer of metal oxide is a rare earth transition metal oxide such as Nd_2CuO_4.

6. A superconductor structure according to any preceding claim in which the substrate is formed by rolling assisted biaxial texturing of substrate (RABITS).

7. A superconductor structure according to any preceding claim in which the superconducting layer comprises a rare earth barium cuprate superconductor of the formula $REBa_2Cu_30_{7-x}$ (REBCO).

8. A superconductor structure comprising a metallic substrate of a first metal, and also including a thin metallic buffer layer of a second metal formed by physical vapour deposition (PVD) and a superconducting layer formed on the metallic buffer layer by liquid phase epitaxy (LPE).

9. A superconductor structure according to claim 8 in which the metallic substrate is nickel or a nickel alloy, the buffer layer is platinum or platinum alloy, and the superconducting layer is $REBa_2Cu_3O_{7-x}$ (REBCO).

10. A superconductor structure according to any one of claims 1 to 7 and also including a further thin metallic buffer layer of a different metal formed by physical vapour deposition.

11. A superconductor structure according to claim 10 in which the thin metallic buffer layer is platinum or a platinum alloy.

12. A method of forming a buffer layer in an elongate superconductor, comprising first forming a nickel oxide seed layer, on a nickel substrate, by surface oxidation epitaxy (SOE), and then growing a further layer of nickel oxide, on the surface of the SOE seed layer, by liquid phase epitaxy.

13. A method of fabricating a superconducting layer or a buffer layer in an elongate superconductor structure comprising (a) feeding a rod of superconductor or buffer layer material plus flux into the focus of a heat source to produce a molten zone at a predetermined higher temperature; and (b) moving an elongate textured substrate in a horizontal plane beneath the molten zone at a suitable rate, the substrate being maintained at a suitable lower temperature to promote epitaxial growth; whereby the liquid from the molten zone falls onto the moving substrate and epitaxial growth is thereby promoted on the substrate.

14. A method according to claim 13 in which the layer being formed comprises the superconductor material $REBa_2Cu_3O_{7-x}$ (REBCO) which is fed in the form of a rod including CuO flux, the higher temperature being ~ 1200°C, and the lower temperature being ~ 900°C.

15. A method according to claim 12 in which the layer being formed comprises a nickel oxide buffer layer, which is fed in the form of a rod including $LiBO_2$-NiO flux.

16. A method according to claim 12 wherein the substrate is nickel or nickel alloy with a suitable buffer layer.

17. A method of growing layers of Nd_2CuO_4 or Nd_2CuO_4 doped with Ce, directly on an $LaAlO_3$ substrate or a Ni or Ni alloy substrate, comprising applying a precursor composition of approximately 25% Nd_2O_3 : 75% CuO in an organic binder onto the substrate by screen printing, heating to a suitable temperature to reach a single liquid state and then cooling at a controlled rate so as to promote the nucleation and growth of Nd_2CuO_4.

18. A method according to claim 17 in which the composition is heated to approximately 1150°C and held at that temperature for about 15 minutes before cooling to room temperature.

19. A method of forming a highly in-plane aligned NiO layer on textured Ni or NiO alloy tapes, comprising the steps of preparing a hydraulically pressed and sintered source rod composed of approximately 40% Nd_2O_3 and 60% CuO, heating the rod to produce a molten zone at one end and allowing the liquid material to drop onto a $LaAlO_3$ substrate or a textured Ni or NiO subtrate located beneath it while the substrate is maintained at a suitable temperature to induce epitaxial growth.

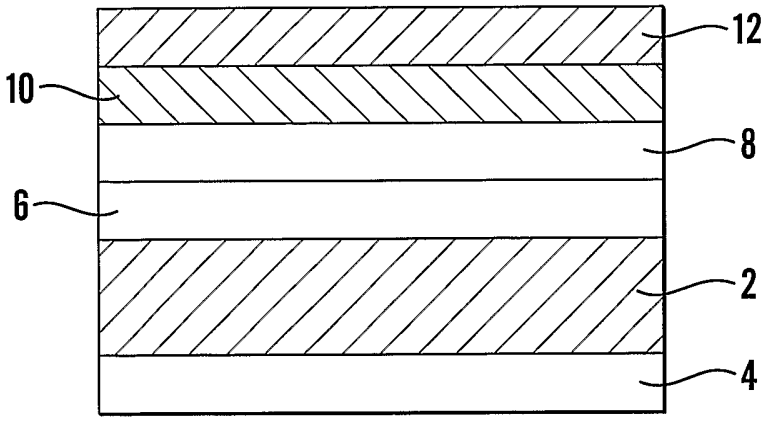


Fig.1

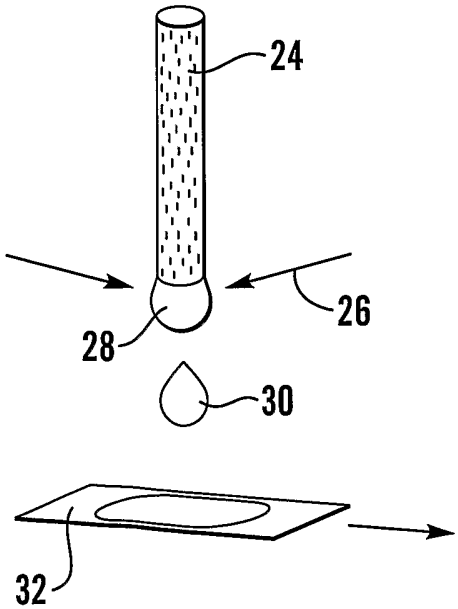


Fig.4

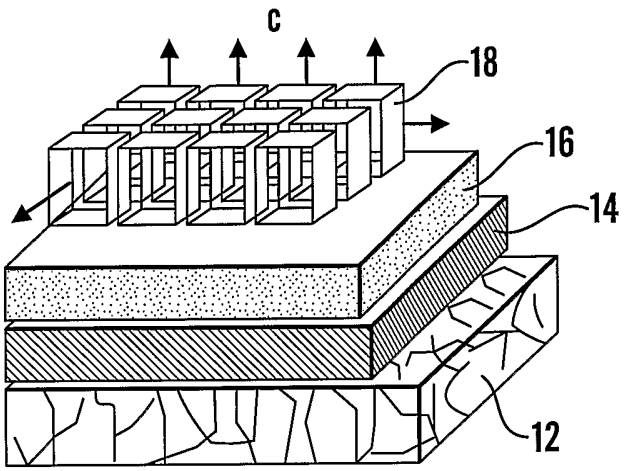


Fig.2

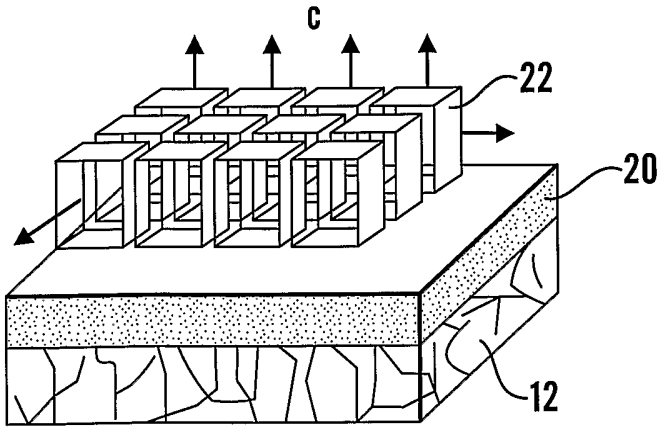


Fig.3

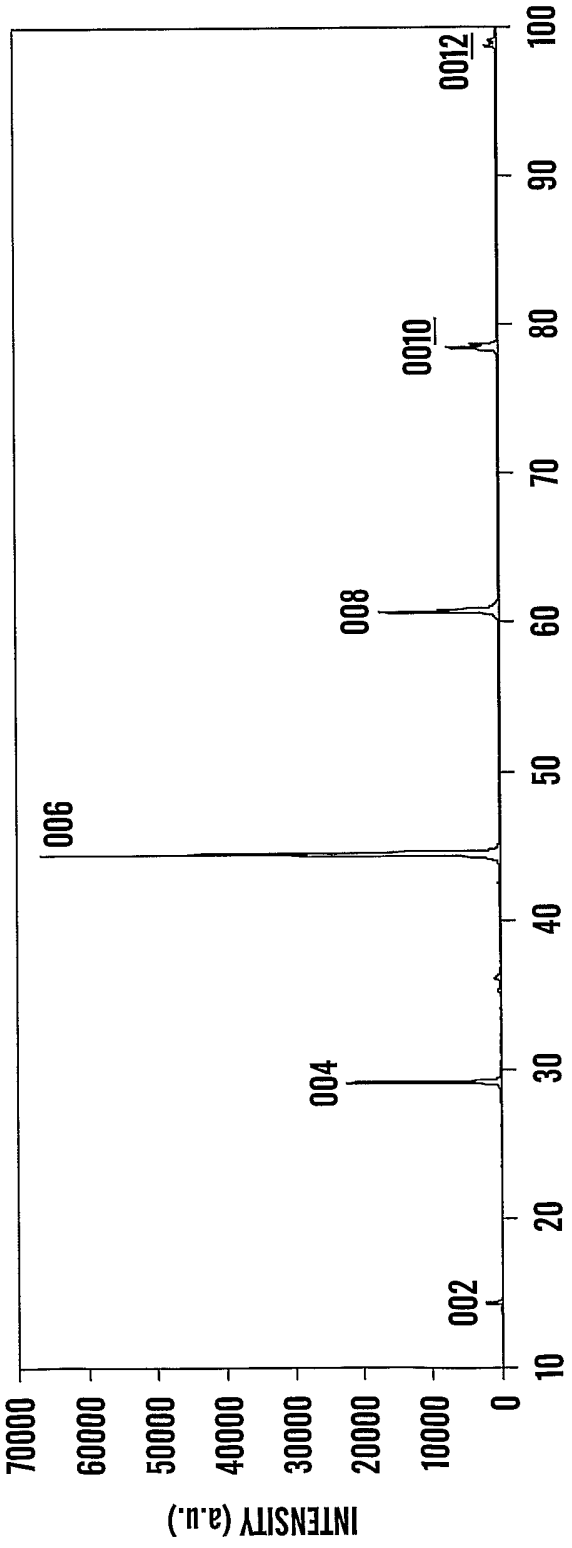

INTENSITY (a.u.)
70000
60000
50000
40000
30000
20000
10000
0
10
20
30
40
50
60
70
80
90
100
2θ (°)
002
004
006
008
0010
0012

Fig.5

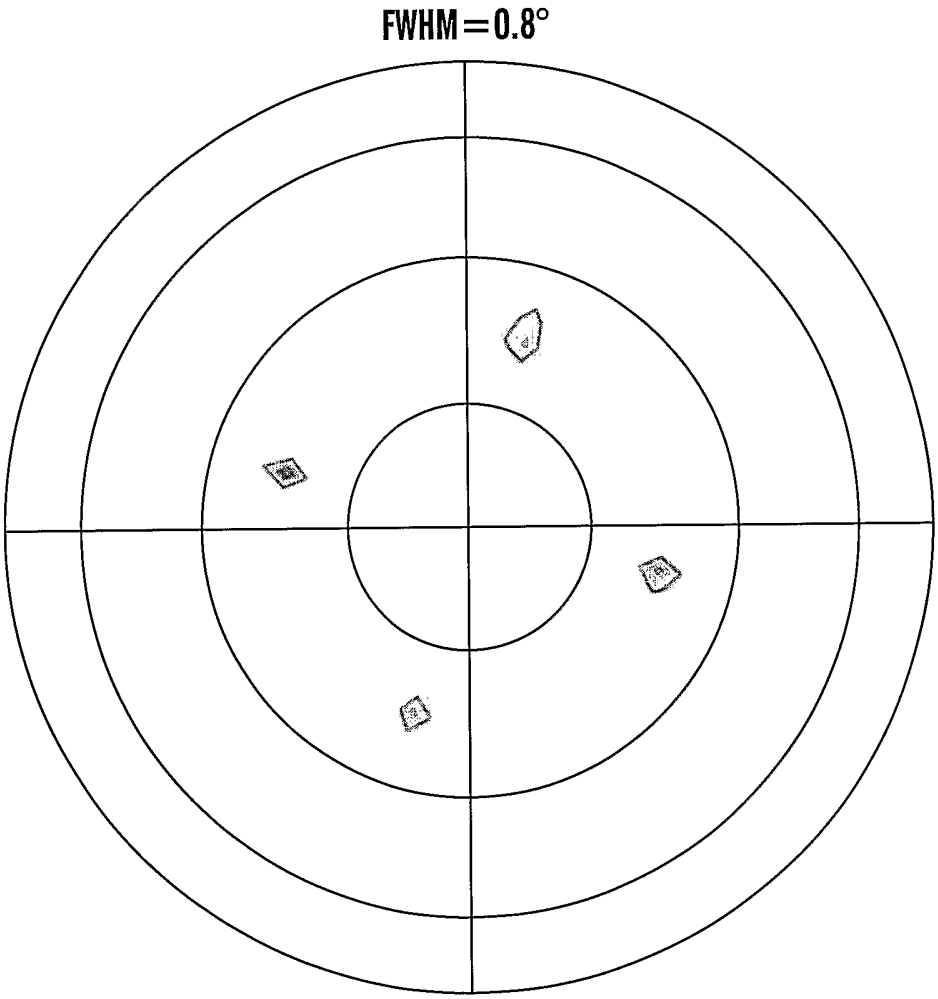


Fig.6

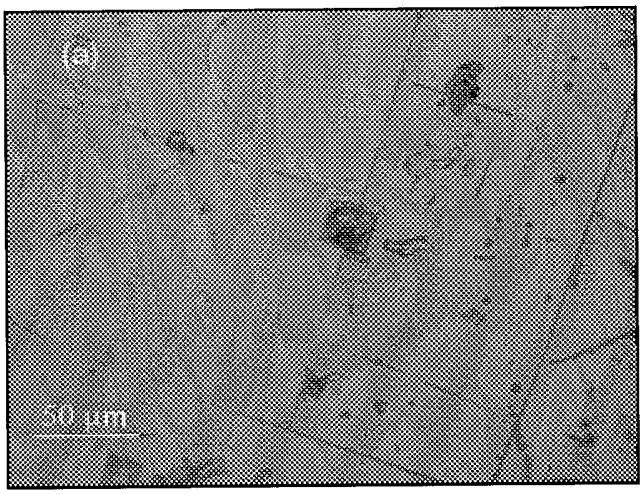


Fig.7a

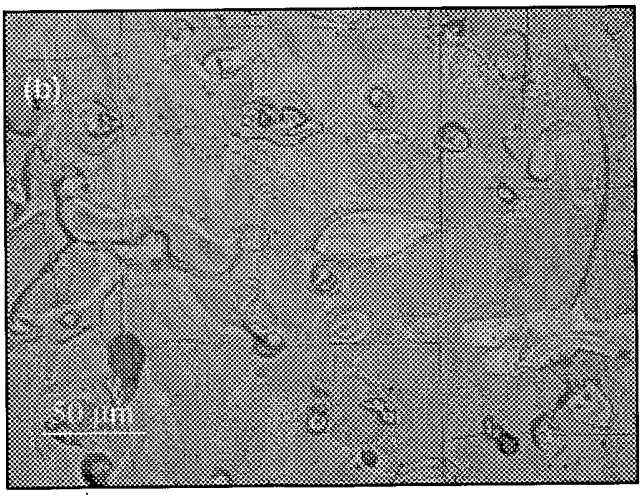


Fig.7b

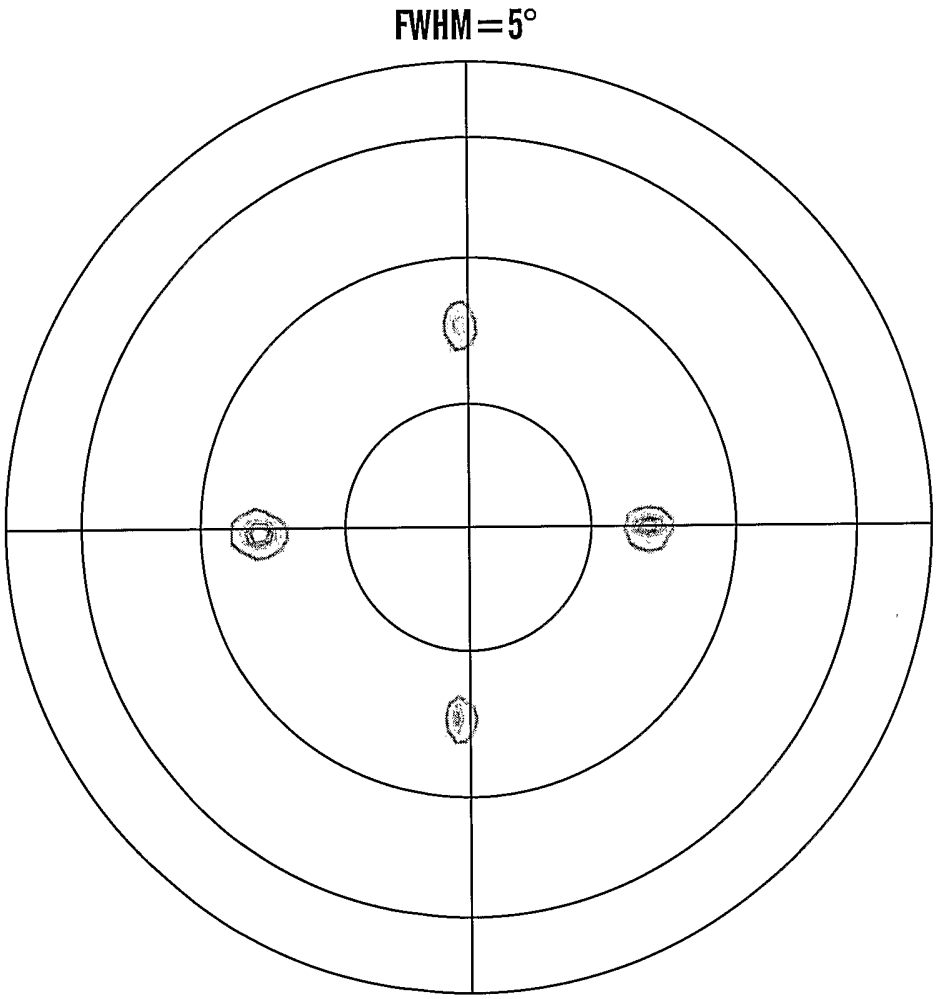


Fig.8a

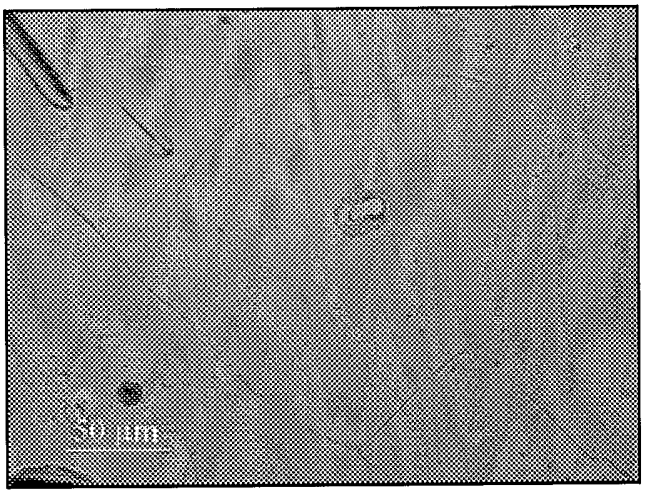


Fig.8b

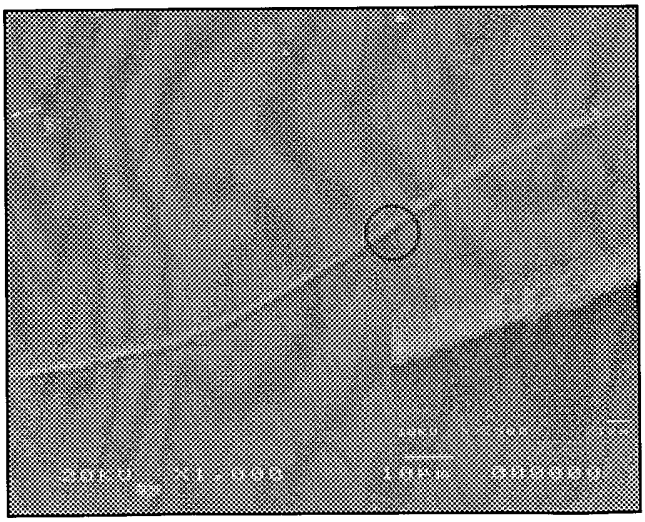


Fig.8c

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 02/01814

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L39/14 H01L39/24 C30B19/00 C23C20/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	IZUMI T ET AL: "LPE growth of RE123 crystals from NiO saturated solution" IEEE TRANSACTIONS ON APPLIED SUPERCONDUCTIVITY, vol. 11, no. 1, pt.3, March 2001 (2001-03), pages 3481-3484, XP002229576 ISSN: 1051-8223	1-3,5-7
A	section I. "Introduction" page 3483, left-hand column, paragraph 2 -page 3484	12,16

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 February 2003	13.05.03

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Köpf, C

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 02/01814

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KUROSAKI H ET AL: "Fabrication of buffer layers and seed layers on biaxially textured Ni tapes for YBCO superconducting wire" 13TH INTERNATIONAL SYMPOSIUM ON SUPERCONDUCTIVITY (ISS 2000), TOKYO, JAPAN, 14-16 OCTOBER 2000, vol. 357-360, pt.2, 2001, pages 938-941, XP004274356 Physica C ISSN: 0921-4534	1,3,5-7
A	the whole document	12,16

X	EP 0 884 787 A (FURUKAWA ELECTRIC CO LTD; INTERN. SUPERCONDUCTIVITY TECHNOLOGY CENTER) 16 December 1998 (1998-12-16)	1,3,5-7
A	page 4, line 11 -page 6, line 8; figure 3; example 2	12,16

X	HE Q ET AL: "Deposition of biaxially-oriented metal and oxide buffer-layer films on textured Ni tapes: new substrates for high-current, high-temperature superconductors" PHYSICA C, vol. 275, no. 1-2, 10 February 1997 (1997-02-10), pages 155-161, XP004114521 ISSN: 0921-4534 the whole document	1,5-7, 10,11

A	WO 00 63926 A (FUJIKURA LTD ET AL) 26 October 2000 (2000-10-26) -& EP 1 178 494 A (FUJIKURA LTD ET AL) 6 February 2002 (2002-02-06) paragraph [0032] - paragraph [0056]; figures 1-5	1,3,4,7, 12,16

P,X	QI X ET AL: "Rapid growth of Nd2-xCexCuO4 thick films as a buffer for the growth of rare-earth barium cuprate-coated conductors" JOURNAL OF MATERIALS RESEARCH, vol. 17, no. 1, January 2002 (2002-01), pages 1-4, XP009005118 ISSN: 0884-2914 the whole document	1-3,5-7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 02/01814

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-7, 10-12, 15, 16

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-7,10-12,15,16

   Superconductor structure comprising a metallic substrate, a buffer comprising a metal oxide seed layer and a further metal oxide layer, and a superconductor layer; and a method of forming the buffer layer by surface oxidation epitaxy of Ni substrate and liquid phase epitaxy of a nickel oxide layer

2. Claims: 8-9

   Superconductor structure comprising a substrate of a first metal, a buffer layer comprising a second metal, and a superconductor layer

3. Claims: 13-14, 19

   Method of forming a layer comprising feeding a source material rod into a heating zone to produce a molten zone and allow liquid to drop onto a substrate

4. Claims: 17-18

   Method of growing Nd2Cu04 layers comprising screen printing a precursor composition of Nd203 + CuO + organic binder onto a substrate, heating and cooling

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 02/01814

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0884787 A	16-12-1998	JP 11003620 A	06-01-1999
		US 6226858 B	08-05-2001
WO 0063926 A	26-10-2000	JP 2000299026 A	24-10-2000
		JP 2000302596 A	31-10-2000
		EP 1178494 A	06-02-2002